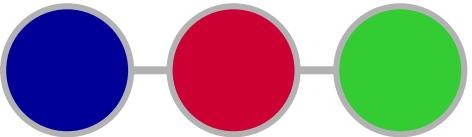
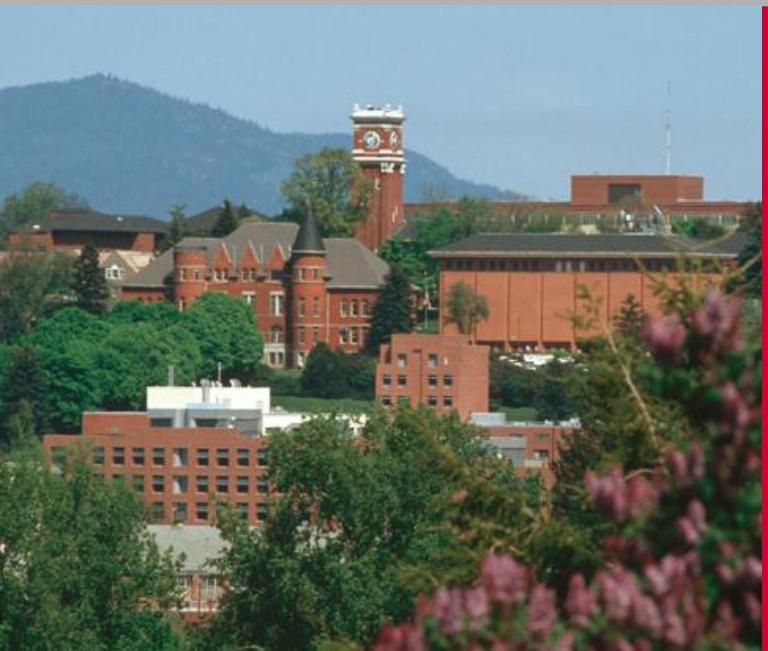




World Class. Face to Face.



Ultraviolet Photoelectron Spectroscopy (UPS)

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

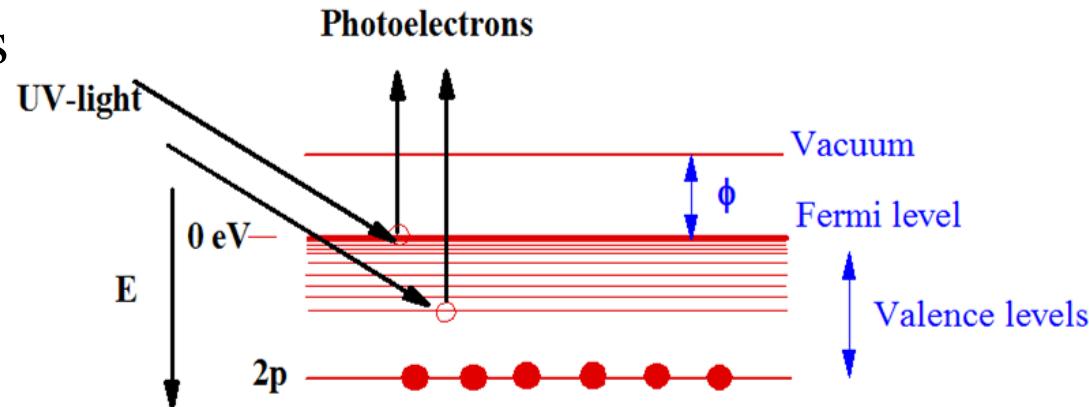
scudiero@wsu.edu

Photon energies for UPS range from 10-50 eV; greater than typical work function: 2-5 eV.

Vacuum Ultraviolet radiation is used to determine:

- ❖ work functions
- ❖ ionization energies
- ❖ examine valence levels

UPS Principle



$$\text{Photoelectron: } \text{BE} = h\nu - \text{KE}$$

Photoemission Process and Koopmans' Theorem

$$I_i = -\varepsilon_i$$

(the ion is represented by (N-1) frozen orbitals)

I_i : Ionization energy for the removal of electrons = $\Delta E = E_i - E_f$
 ε_i : orbital energy of that state

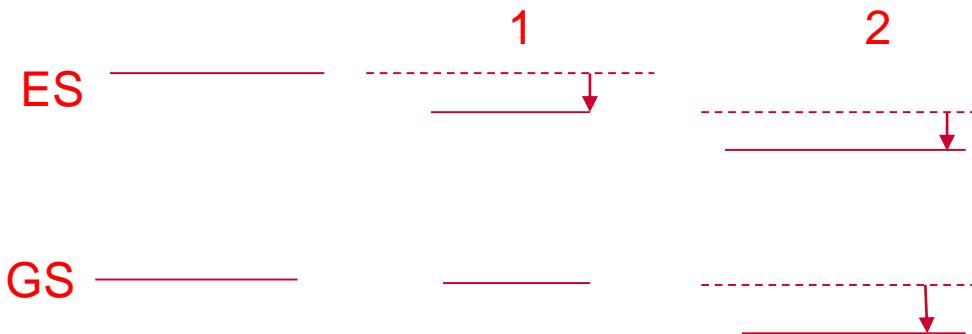
Ground state (GS) = initial state and excited state (ES) final state of the atom/molecule

Koopmans' theorem makes possible the identification of calculated orbital energies with ionization potentials.

Does not allow for electronic relaxation correction

Electronic Relaxation

- 1. Relaxation correlation:** (relaxation energy for ion state)
- 2. Correlation correction:** energy levels shift for neutral and ion state



Measured BE lower than the one calculated from Koopmans' theorem.

Example: O 1s in CO

$$BE \text{ (exp)} = 532.3 \text{ eV}$$

$$BE \text{ (Koopmans)} = 562.4 \text{ eV}$$

O 2s

$$BE \text{ (exp)} = 38.9 \text{ eV}$$

$$BE \text{ (Koopmans)} = 41.1 \text{ eV}$$

I_i always lower because of relaxation and correlation corrections.

Commonly Used Lines (16.6 to 40.8 eV)

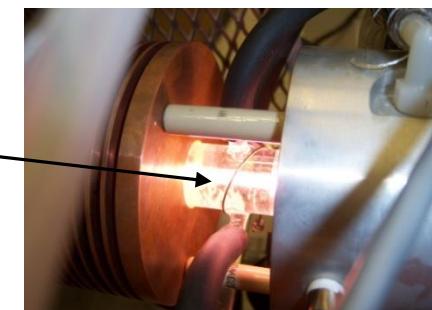
- Ne I (16.6 eV), Ne II (26.8 eV)
- He I (21.2 eV), He II (40.8 eV)

Produced by cold cathode capillary discharge. Resonance fluorescence produced when the gas is excited in the discharge and then decays back to its ground state.

I -- light emitted from neutral atoms

II -- light emitted by singly ionized atoms

Light (salmon color)
-He I

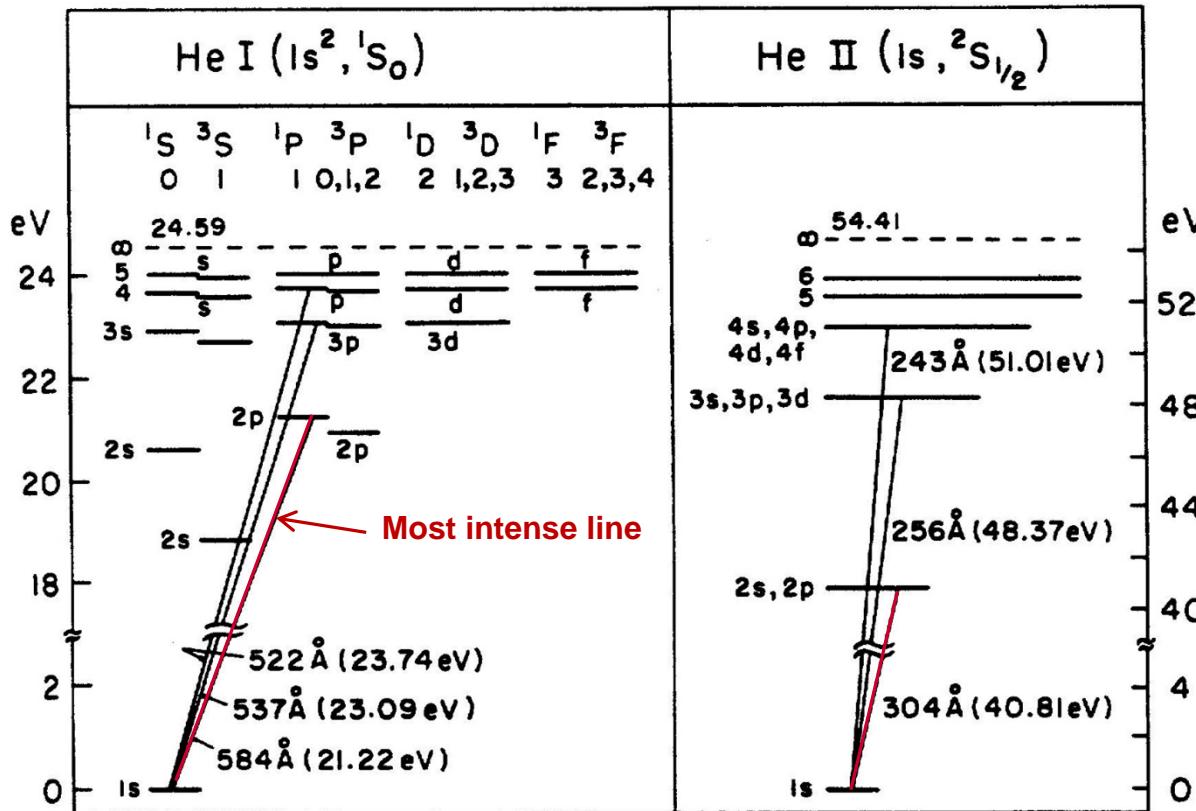


Transition from the first excited state to the G.S is usually the most intense (called resonance).

Turner and Jobory (*J. Chem. Phys.* 1962, 37, 3007) introduced the He I resonance line in 1962. He II line was first used by Price and co-workers in 1970 (*Potts, A.W. Lenpka, H.J. Streets D.G. and price, W.C. Phil. Trans Roy. Soc. London A*, 1970, 268, 59).



He I and He II (Grotian diagram)



Strongest resonance lines (584 \AA , 98% of the emission intensity).

Intensity of 537 \AA , 522 \AA and 304 \AA lines = 2 % of the 584 \AA .

Probing the Valence Bands

UPS: powerful and versatile technique to study

- ❖ *Electronic structure* of the valence bands
- ❖ *Work function* of a material.

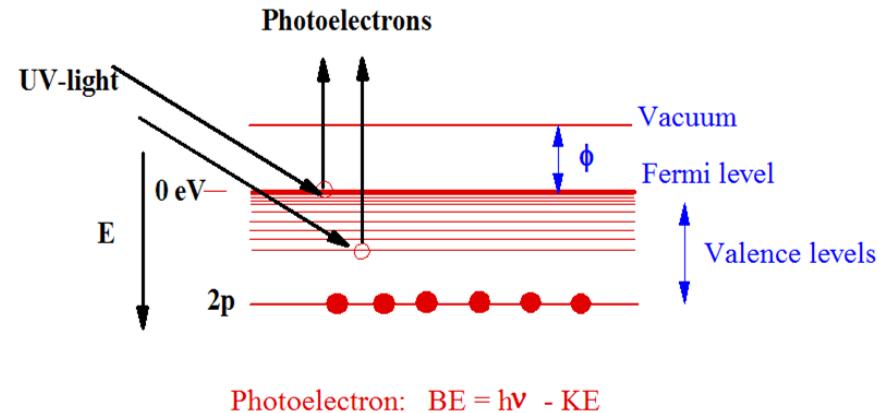
PE process depends on parameters such as:

Emitted electron parameters

- Kinetic energy
- Emission angles
- Spin polarization

Incident photon parameters

- Photon energy ($h\nu$)
- Angle of incidence
- Polarization

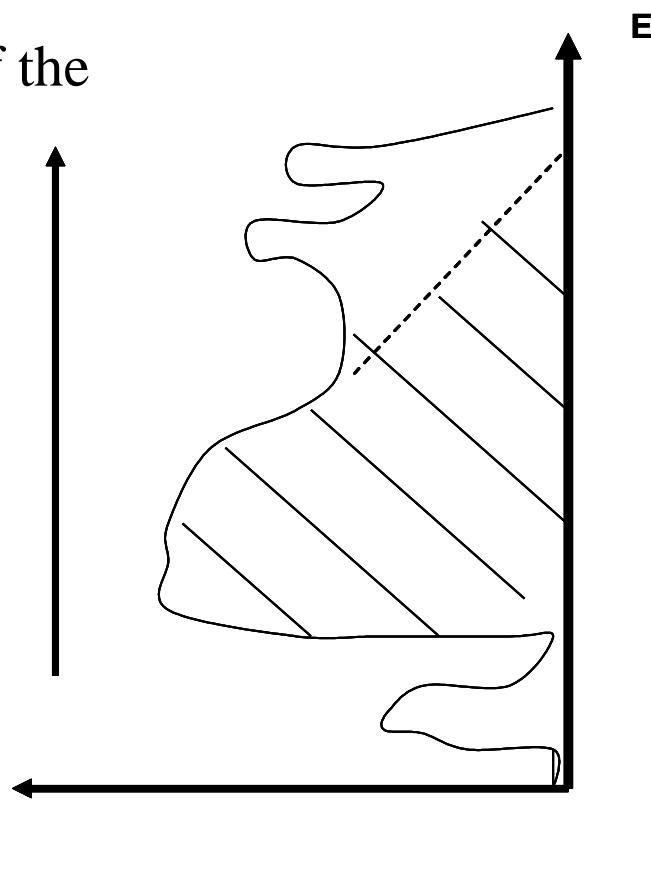




How does the electron **Density of States (DOS)** relate to the observed emission?

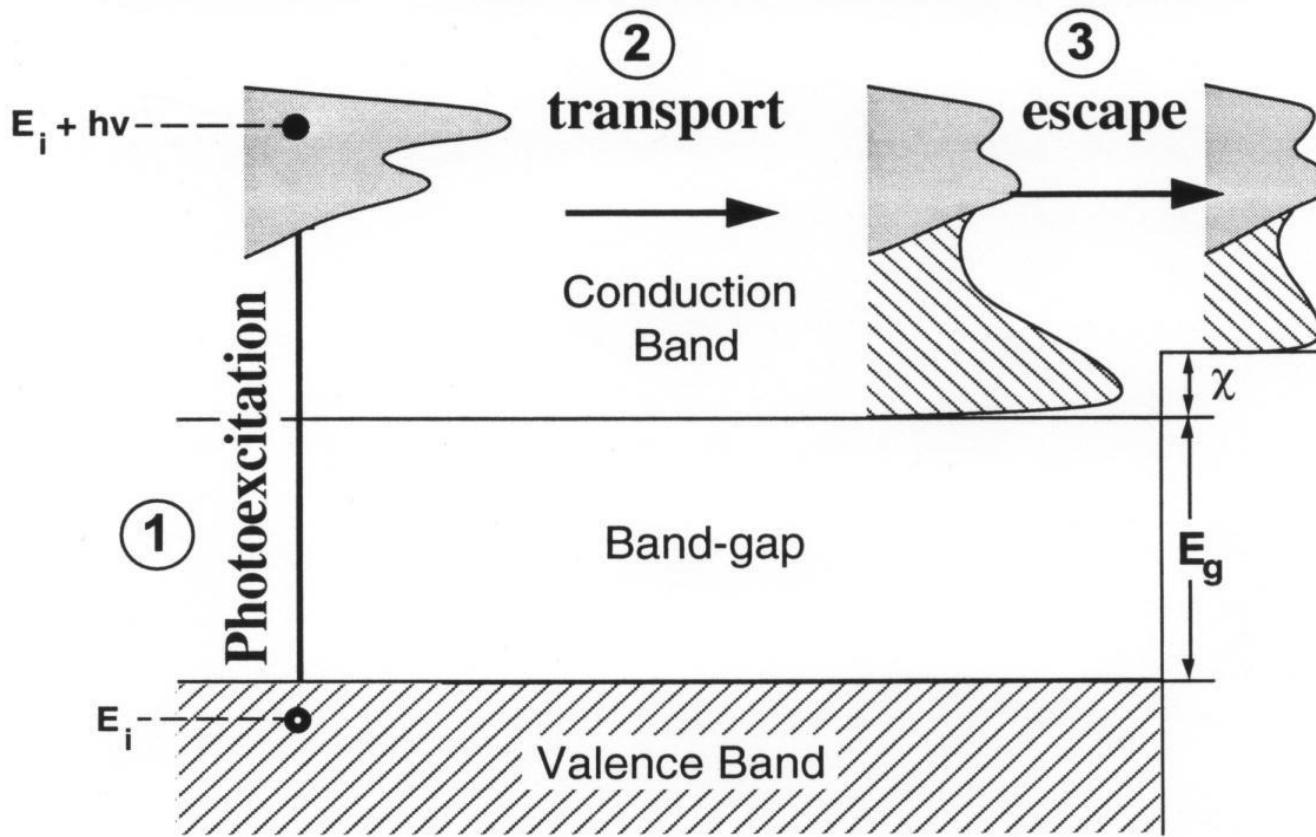
1. XPS VB ($h\nu > 1000$ eV): good reflection of the density of states (weighted by the transition rate across the VB).

2. UPS VB ($h\nu < 50$ eV): more complex but richer in information.





Three Step Model



The energy distribution curve is given by

$$N(E) = AN_0(E)L(E)T(E)$$

$$N(E) = A N_0(E) L(E) T(E)$$

$N_0(E)$: energy distribution of the electrons after photoexcitation.

$L(E)$: characteristic transport length of the excited electrons
(closely related to the electron mean free path).

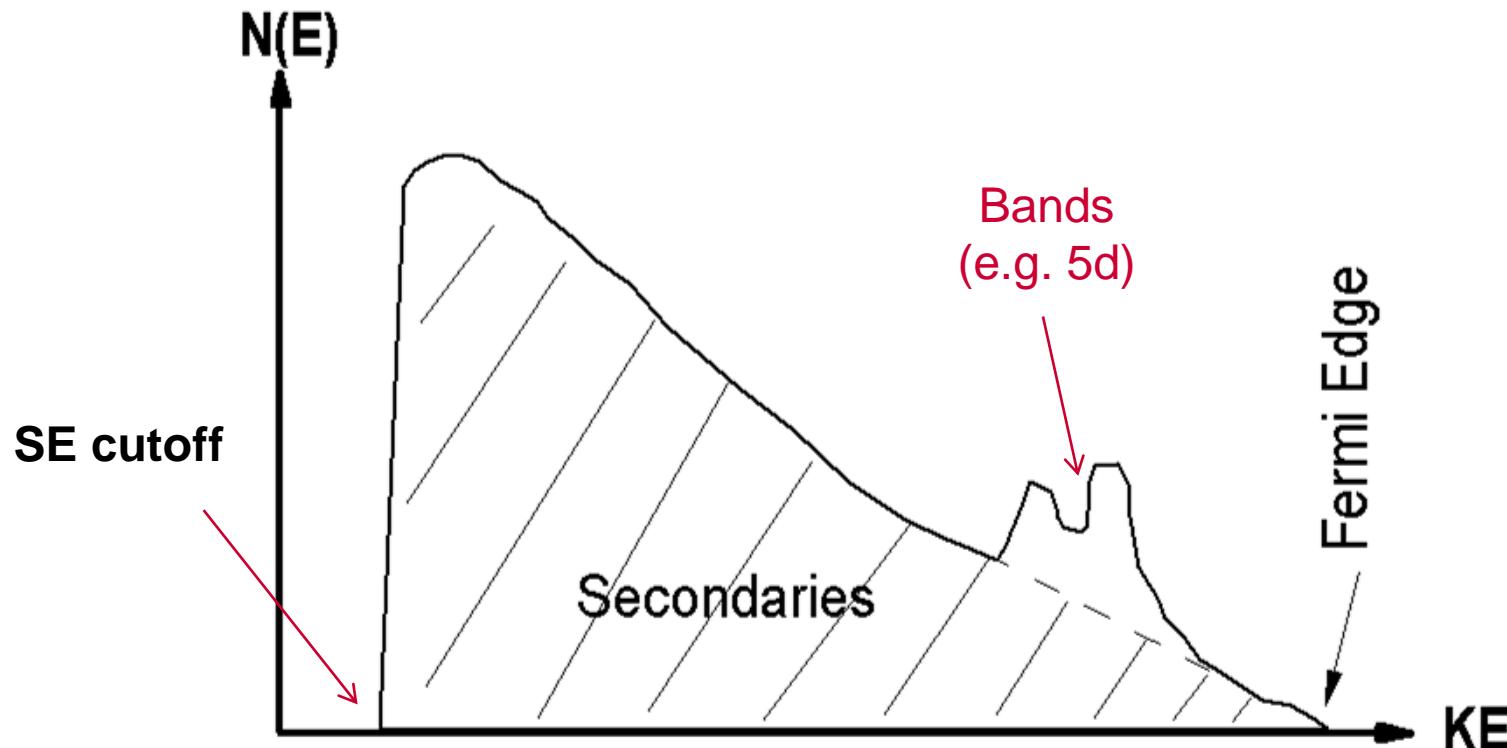
$L(E) \approx l(E) / \alpha(h\nu)$ (transport length of excited electron escaping
into the vacuum without scattering)

$\alpha(h\nu)$: absorption coefficient

$l(E)$: electron escape depth

$T(E)$: probability for emission into vacuum
(does not introduce any structure to the spectra)

Inelastically scattered electrons have enough energy to escape into vacuum to form the **background** (secondaries).



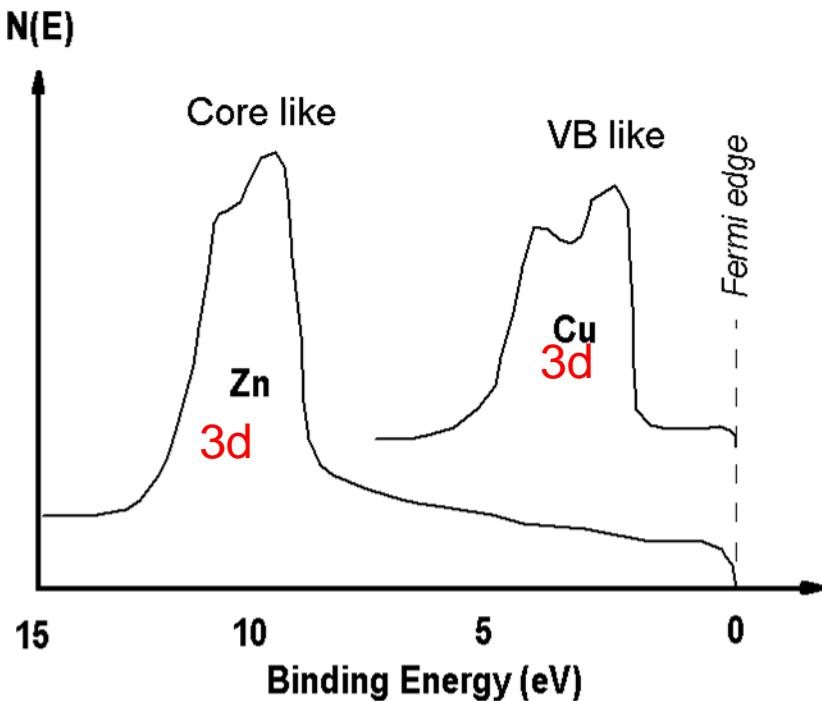
Valence states vs. core states: ***NO well-defined boundary*** between these levels.

Valence states extend to 10-15 eV and
Core levels can be as shallow as a few eV

In general, the boundary can be found around 10-15 eV (BE) levels.

High BE →→ core like

Low BE →→ valence band like

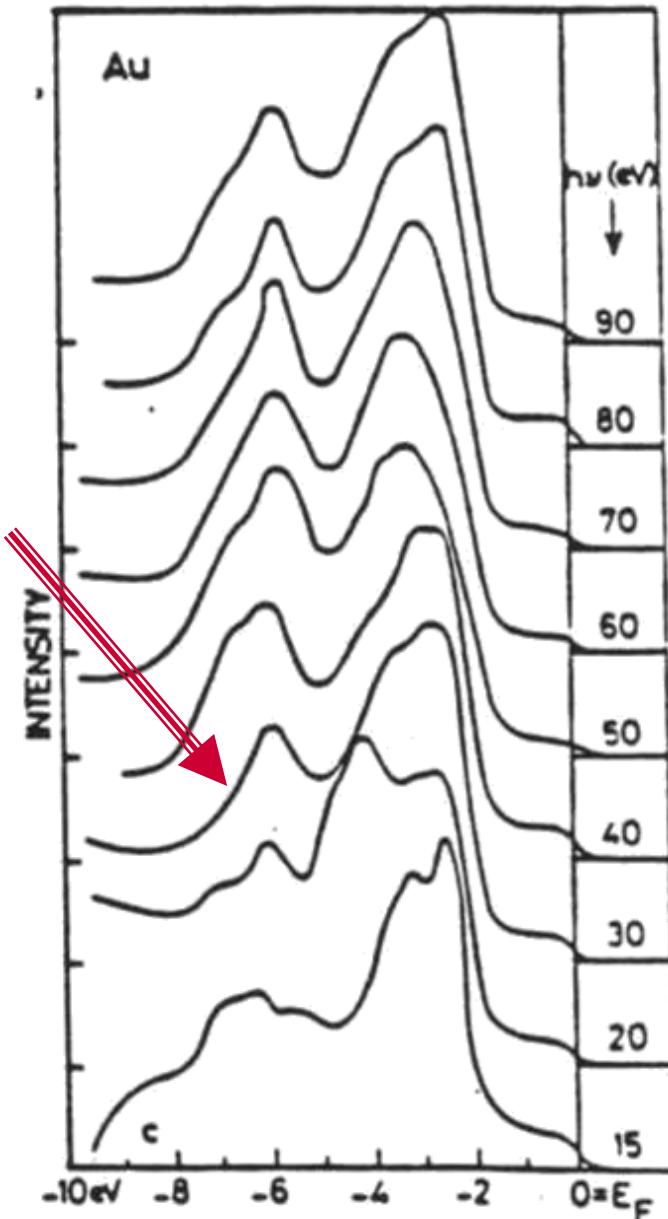


NO well-defined photon energy ($h\nu$) above which the excited valence band (VB) resembles the DOS.

However, for $h\nu > 40$ eV, the excited VB generally converges to a same spectrum as shown in this example for gold.

(DOS modulated by only the change in cross-section across the VB and no effect of empty states).

Drastic changes for 15 to 30 eV but looks very much the same from 40 eV to 90 eV



Photoionization Process

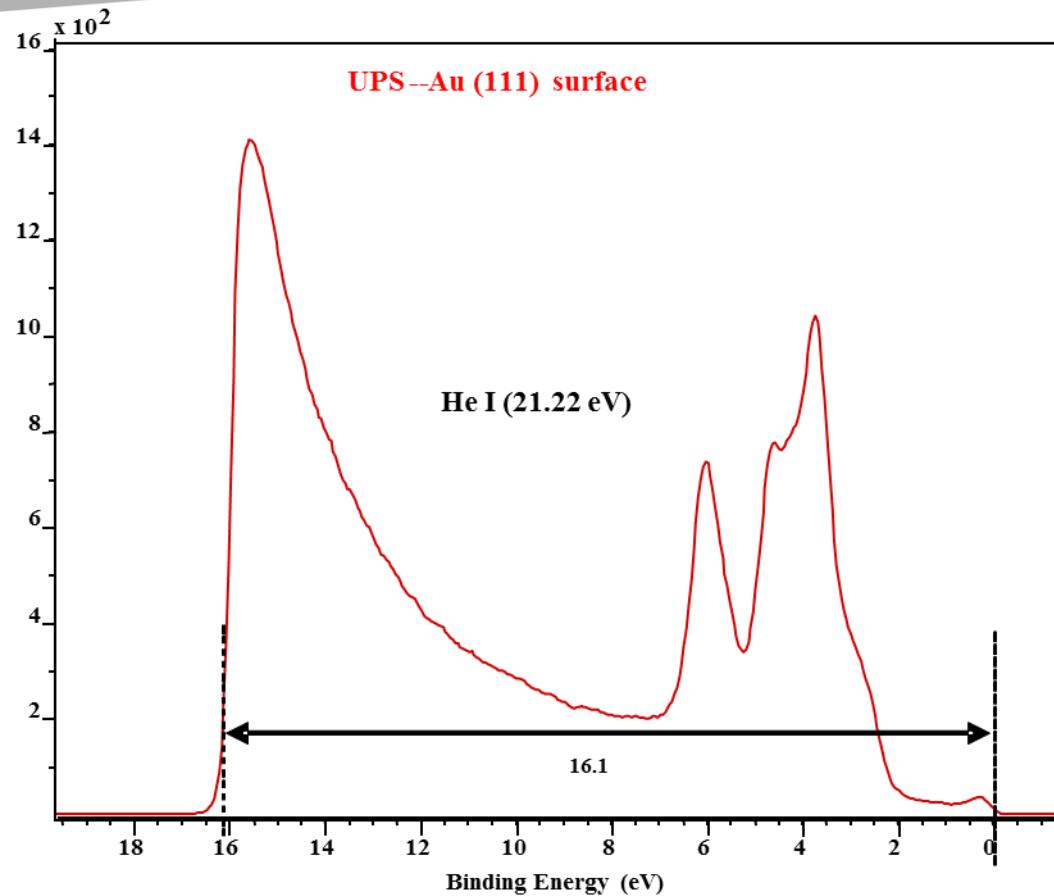
In general, however the photoionization process is described by the following expression:

$$I_i = h\nu + K_i \quad I \text{ is the ionization energy}$$

Case I: Metals

UPS could be used to determine the work function of metals. By measuring the width of the emitted electrons (W) from the onset of the secondary electrons up to the Fermi edge and subtracting W from the energy of the incident UV light $h\nu$, the work function ϕ_m is then given by

$$\phi_m = h\nu - W$$



Example: Au (111) single crystal

$W = 16.10 \text{ eV}$, Photon energy $h\nu = 21.22 \text{ eV}$

$\phi_m = 21.22 - 16.10 = 5.12 \text{ eV} \pm 0.15 \text{ eV}$ (resolution of the instrument)

Literature value 5.3 eV (CRC)

Case II: Molecular systems

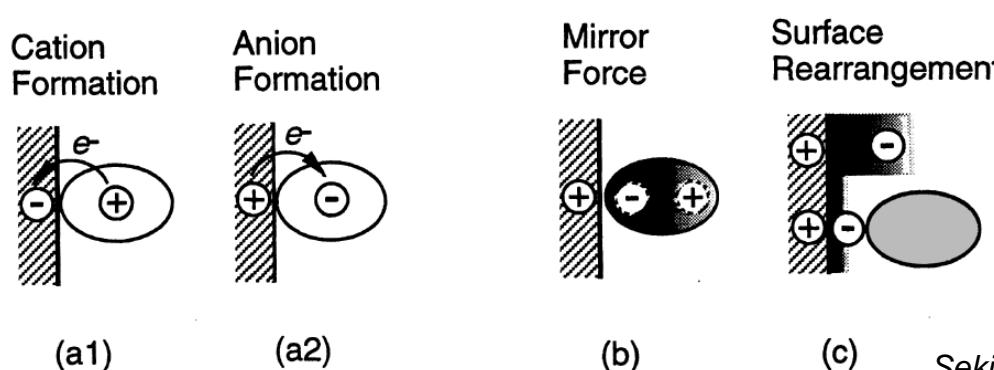
(molecular film adsorbed on metal)

Not so simple in case of molecules

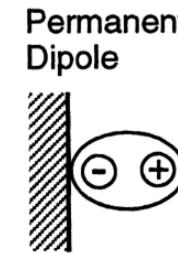
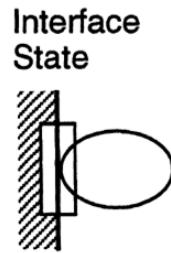
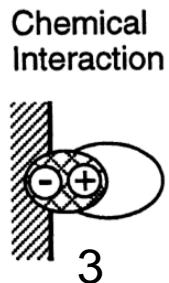
Why?

1. Charge transfer across the interface (combination of strong acceptor-low work function or strong donor-high work function).
2. Redistribution of electron cloud (polarization of the electron cloud attracted by the image charge formed in the metal).

Charge Transfer



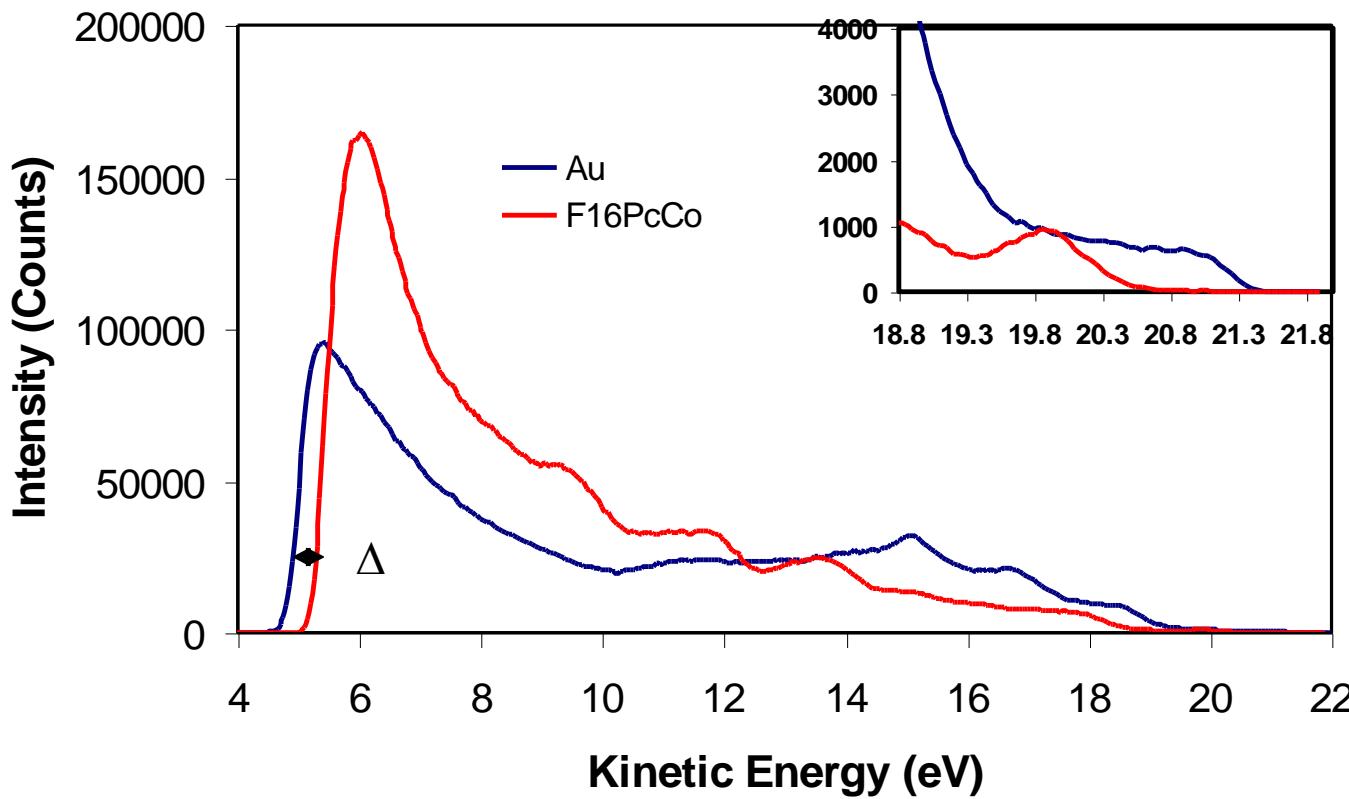
3. Interfacial chemical reactions (well known case for CO and benzene on clean metal surfaces).



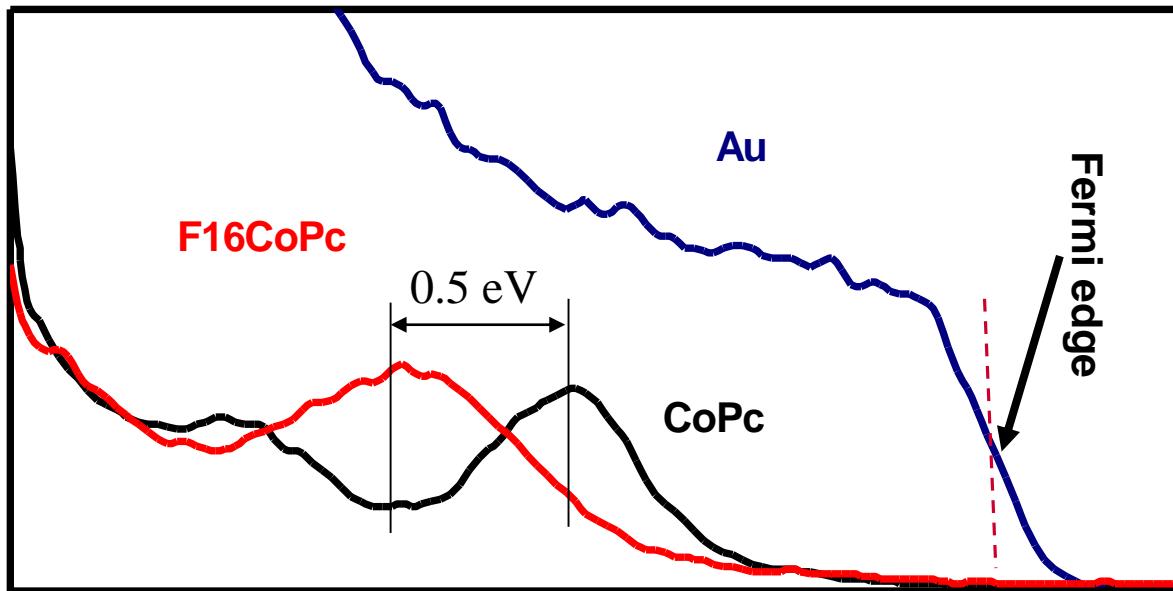
4. Strong chemical interaction between the surface and the adsorbate leading to the rearrangement of the electronic cloud and the molecular and surface geometries (both directions of dipoles possible),

Others

5. Existence of interface state serving as a buffer of charge carriers
6. Orientation of polar molecules or functional groups.



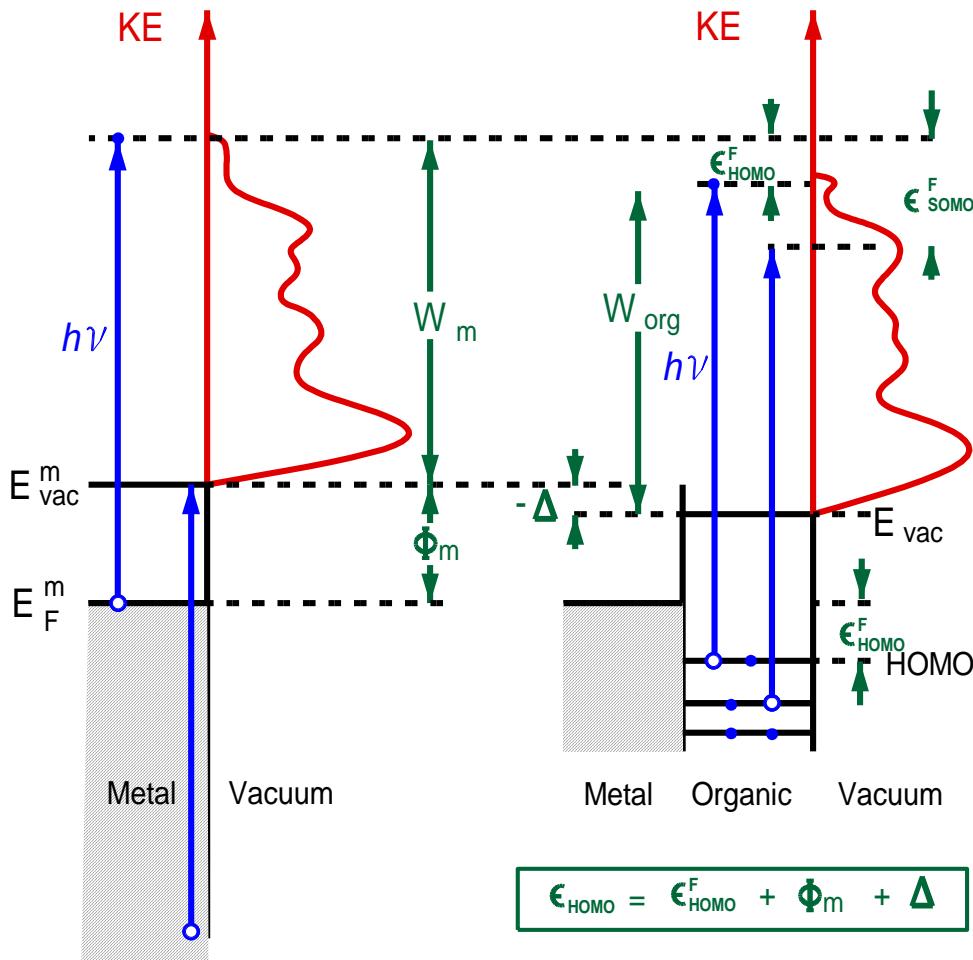
A vacuum shift $\Delta = 0.5$ eV at the lower KE side of the UPS spectrum.



First ionization energies for H_{16}CoPc and F_{16}CoPc (HOMO) adsorbed on Au surface.

Tightly bound electrons in $\text{F}_{16}\text{CoPc} \rightarrow$ need more energy (higher KE).

Energy relationships

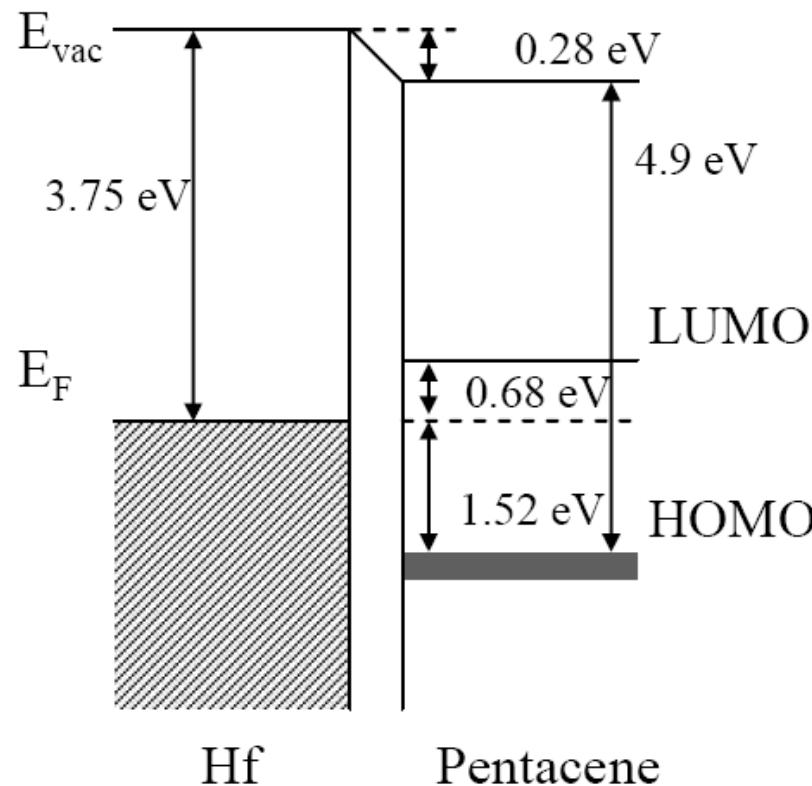
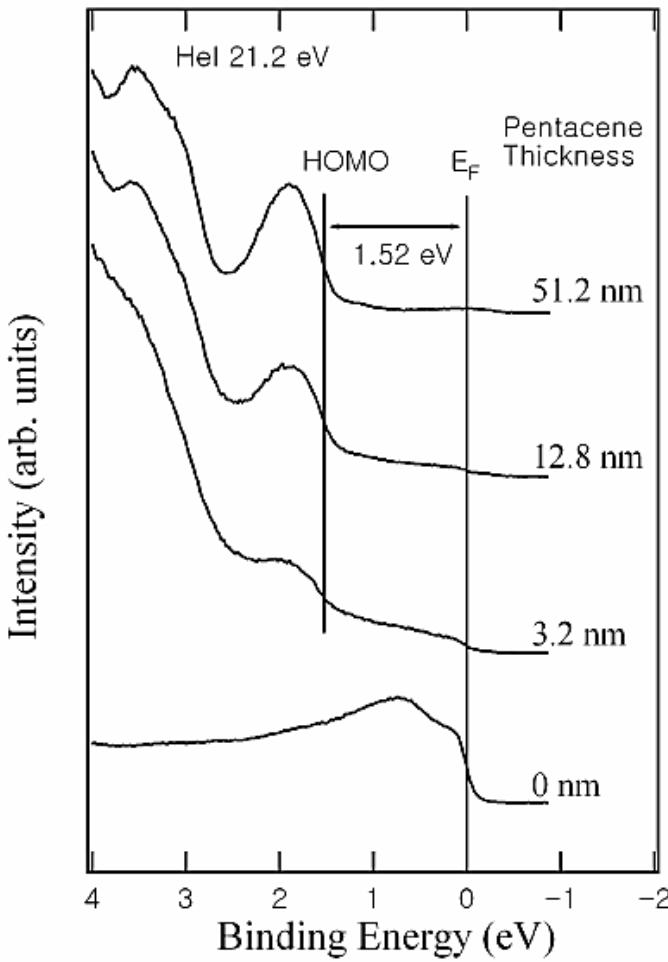


Left for Au, right for an organic layer deposited on Au substrate.

Δ : vacuum shift (presence of a dipole moment at the interface)

ϵ_{HOMO} : HOMO (molecules) or Valence band maximum (VBM) for semiconductors

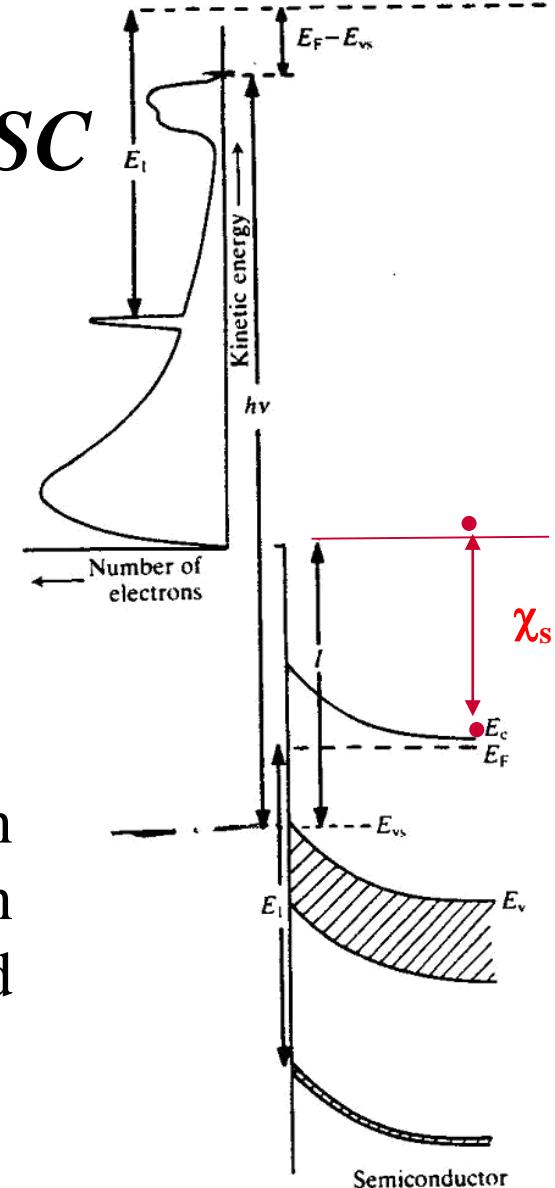
Organic thin-film transistors (OTFTs)



$\Delta = 0.28$ eV: interfacial dipole at the interface between pentacene and Hf.

Typical UPS spectrum for a n-type SC

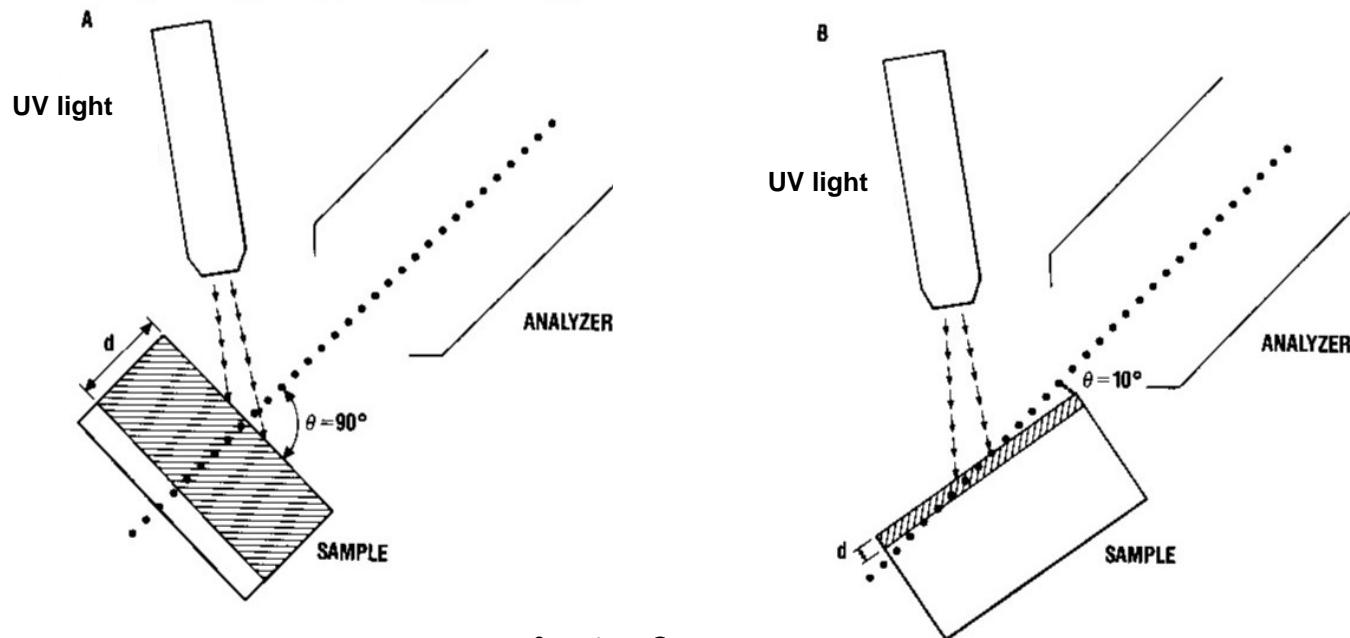
- The important surface parameter for semiconductor is the electron affinity χ_s .
- Knowing E_v and band gap $\Rightarrow E_c$ and then χ_s
- χ_s defined as the difference in energy between an electron at rest outside the surface and an electron at the bottom of the conduction band just inside the surface



Angle Resolved Photoemission

Changing (decreasing) the angle of electron emission relative to a solid surface UPS probes shallow depth.

Can be used to get the dispersion relation (E vs k: wavevector)



$$d = \lambda \sin \theta$$

Angle resolved PE

- Determine the energy, E, and the electron momentum, $\hbar k$, of the emitted photoelectron outside the solid
 - relate to the energy dispersion, E vs. k, inside the solid.
- Angle – resolved photoemission: most direct technique to determine this relation experimentally.
- For PE: simple conservation laws:

Energy conservation:

$$E_i = E_f - h\nu$$

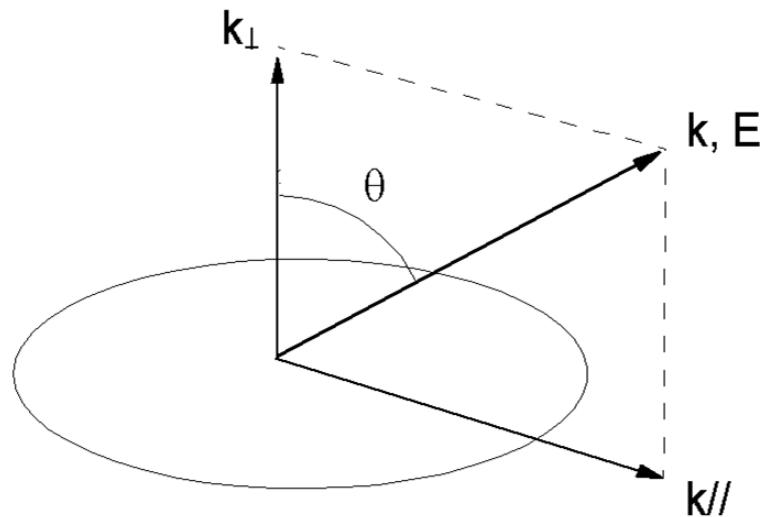
Momentum conservation:

$$\mathbf{k}_{i//} = \mathbf{k}_{f//}$$

E_{\perp} is not conserved (periodicity is broken).

For all practical purposes, we can ignore the momentum due to the photon

$$E = \frac{(\hbar k)^2}{2m}$$



Knowing E and then $|\mathbf{k}_i\rangle$ one get the band structure diagram $\mathbf{E} \rightarrow \mathbf{k}$

2D material where all interactions between the layers can be neglected and apply the conservation laws, we can write $k_{//}$ as follows:

$$\mathbf{p}^2 = p_{//}^2 + p_{\perp}^2$$

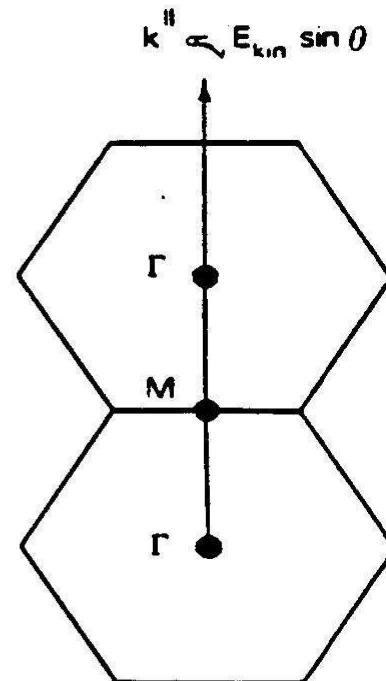
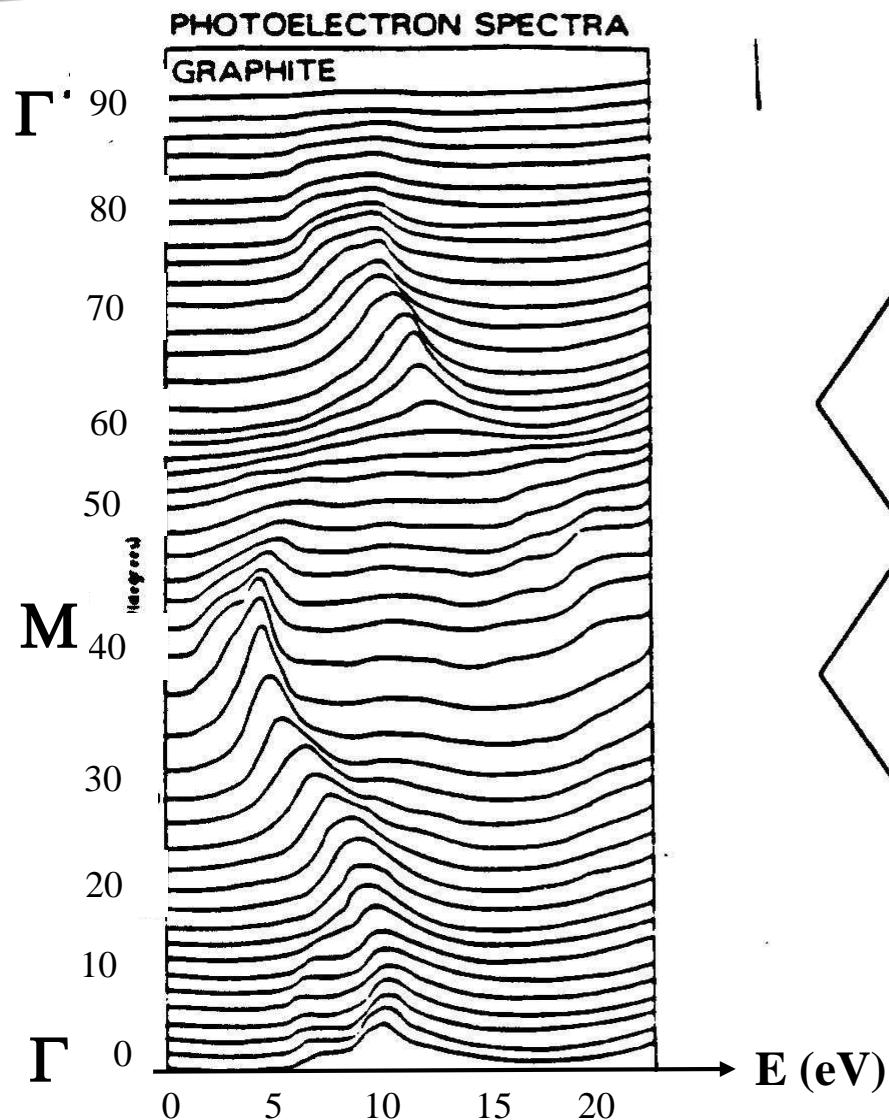
Knowing that $p_{//} = (k_f)_{//} = (k_i)_{//}$

$k_{//}$ can then be rewritten as

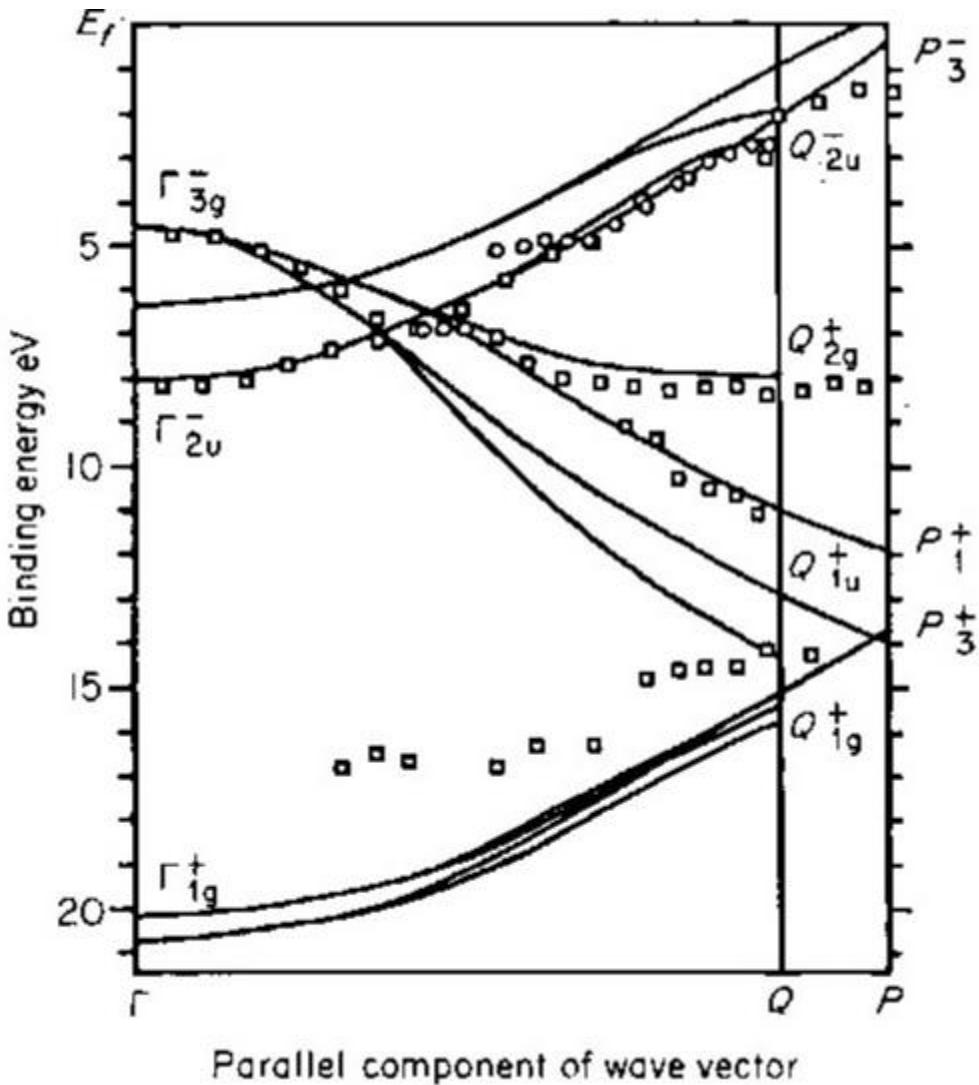
$$k_{//} = \frac{\sqrt{2mE}}{\hbar} \sin \theta$$

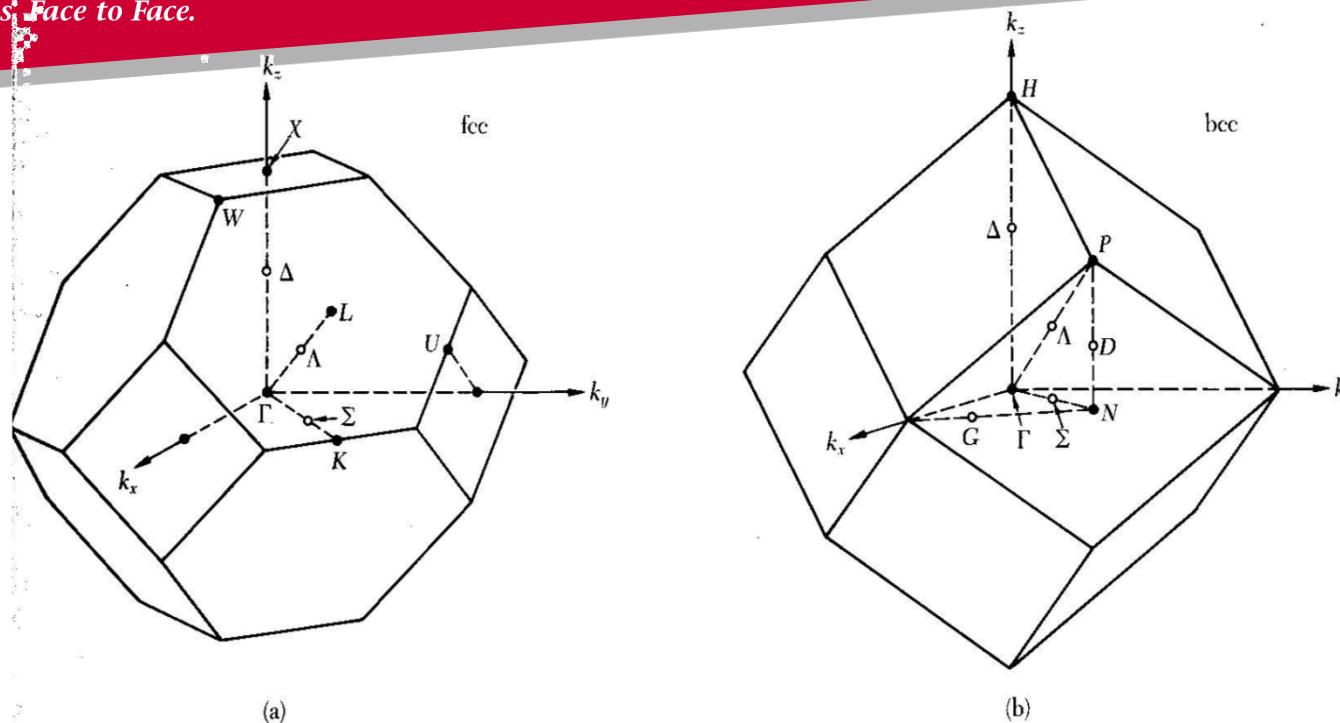
Measuring the E of a band as a function of angle and using the relation

$$E = \frac{(\hbar k)^2}{2m} \quad \rightarrow \quad k_{//} \text{ can be determined}$$



The experimental data BE vs. $k//$ (□) for the first Brillouin zone in agreement with the calculated bands (lines) of Painter and Ellis (*G.S. Painter and D. E. Ellis, Phys. Rev. B1, 4747, 1970*) shown here.





Symmetry points and axes of the Brillouin zones of the fcc (a) and bcc (b) lattices. The zone centers are Γ .

In (a) the boundary point at $2\pi/a$ (001) is X ; the boundary point at $2\pi/a$ ($1/2, 1/2, 1/2$) is L , the line Δ runs between Γ and X .

In (b) the corresponding symbols are H , P and Δ .

Problems associated with UPS

1. At the UV energies the background of degraded electrons severally *distorts the spectrum* near the work function cut-off.
2. The *cross-section* of rare earth 4f and actinide 5f states are *small*.
3. *The shape of the PE spectrum is modulated by the unoccupied density of states.*

Note that XPS has a *lower resolution* and *lower rates* of data acquisition but it is *insensitive* to the *empty density of states* providing a clear view of the disposition of the occupied electronic orbital.

4. *Behavior of an electronic orbital* in different chemical state

example is Au [Xe] 4f¹⁴ 5d¹⁰ 6s¹ in two different systems.



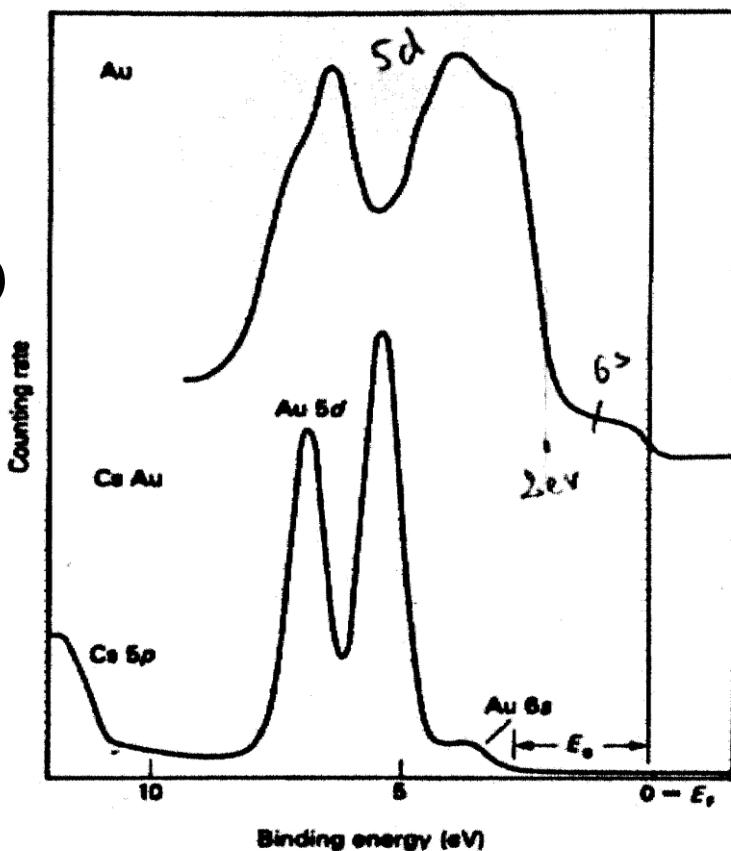
❖ Metal Au. The 5d electrons form a broad band between 2-8 eV and the 6s electron between 2eV and the E_F cut-off.

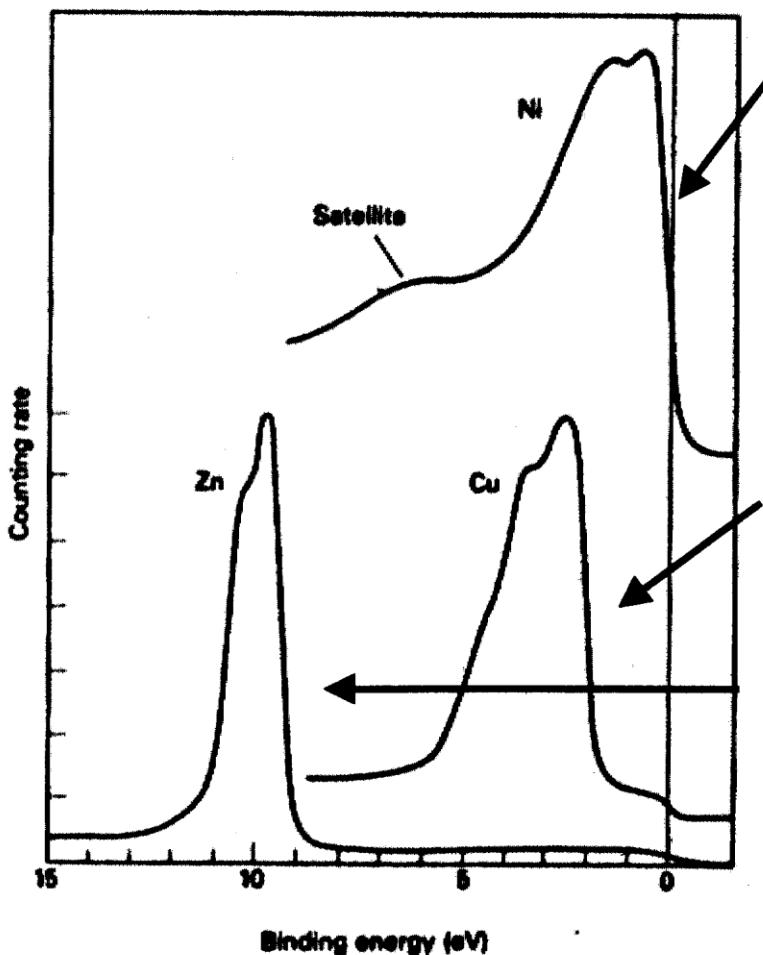
The 6s band extends to much greater BE,
strongly hybridized with the 5d band.

❖ CsAu, a red transparent SC ($E_g = 2.6$ eV)
Au becomes a negative ion with filled $6s^2$

5d¹⁰: core like spin-orbit doublet
(1.5 eV splitting)

6s: VB at 3eV below E_F





d band is partially filled, it intersects the E_F .

d^{10} shell → the d band falls well below the E_F and show a band like character.

d^{10} shell → the d band is 10 eV below E_F and therefore show core-like character.

UPS spectra of some d-group transition metals (Ni, Cu, Zn).

The transition from valence-like to core-like behavior with increasing atomic number is clearly seen

PE from UPS **NOT** exactly total one-electron density of states

- (1) Lifetime broadening,
- (2) Difference in cross-section
- (3) Multi-electron excitations.

Lifetime broadening

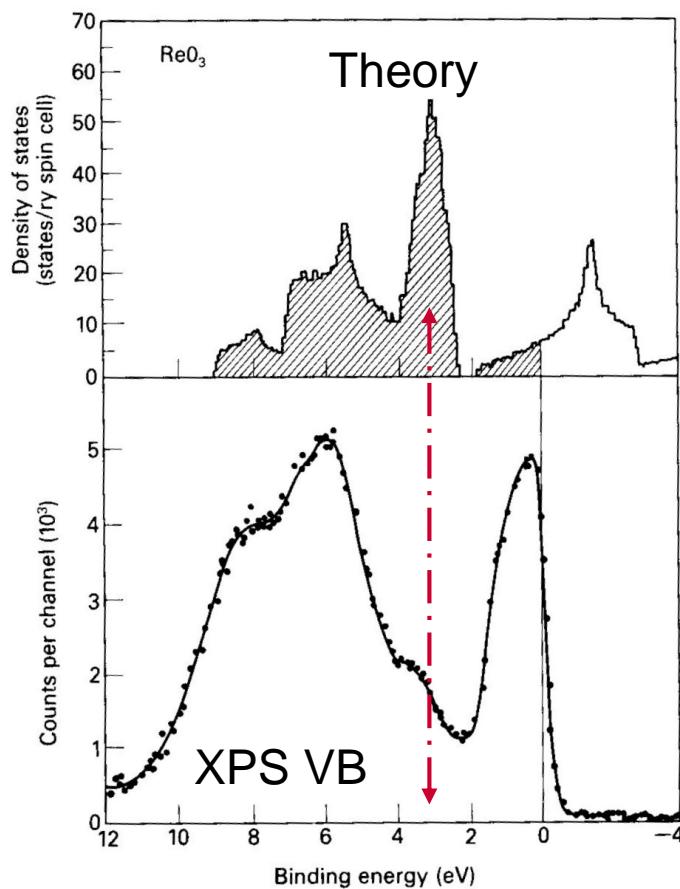
The VB spectrum is distorted by the hole-lifetime width which changes with BE →→ Lorentzian tailing of the band edge makes it difficult to define the bottom of the CB.

Example: the bottom of the Cu 4s band is not detectable (at 7.8 eV)

Difference in cross-section

Rhenium oxide (ReO_3), a copper-colored conductor with electronic configuration of $\text{Re}[\text{Xe}] 4\text{f}^{14} 5\text{d}^1$. Experiment + theory agree on the 5d CB below E_F well separated from the O 2p VB.

Experimental data not in good agreement with the calculated total DOS. This reflects the *d*-admixture into the VB and a disparity in the cross-section which favors Re 5d over O 2p by a factor 30



(*p*-derived features are generally suppressed in XPS and strong *d*-hybridized features enhanced).

VB peak at 3.5 eV largely O 2p character, is almost totally suppressed while the lower part of the VB and the CB at 1 eV are greatly enhanced.

In UPS the situation is generally reversed and the photoelectric cross-section is essential for the interpretation of VB spectra.

The cross-section for PE of a system in state i by a photon of energy $h\nu$ leaving the system in a final state f consisting of a photoelectron of energy ε plus an ion in state j is given by:

$$\sigma_{i,j}(\varepsilon) = \left(\frac{4\pi^2 \alpha a_0^2}{3g_i} \right) (\varepsilon + I_{i,j}) |M_{i,j}|^2$$

Where α is the fine structure constant $1/137$, a_0 is the Bohr radius, g is the number of degenerate sublevels of initial discrete state, $I_{i,j}$ the ionization energy (expressed in Rydberg). Using the dipole approximation which is good to 1% at $h\nu = 800$ eV and 5% at $h\nu = 2000$ eV. The dipole matrix element becomes

$$|M_{i,j}|^2 = \frac{4}{(\varepsilon + I_{i,j})^2} \sum_{i,j} \left| \langle f \left| \sum_{\mu} \nabla_{\mu} \right| i \rangle \right|^2 = \sum \left| \langle f \left| \sum_{\mu} r_{\mu} \right| i \rangle \right|^2$$

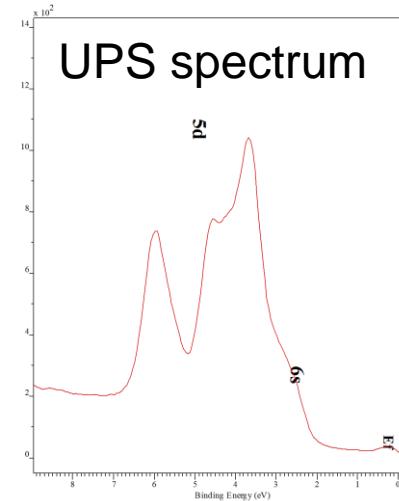
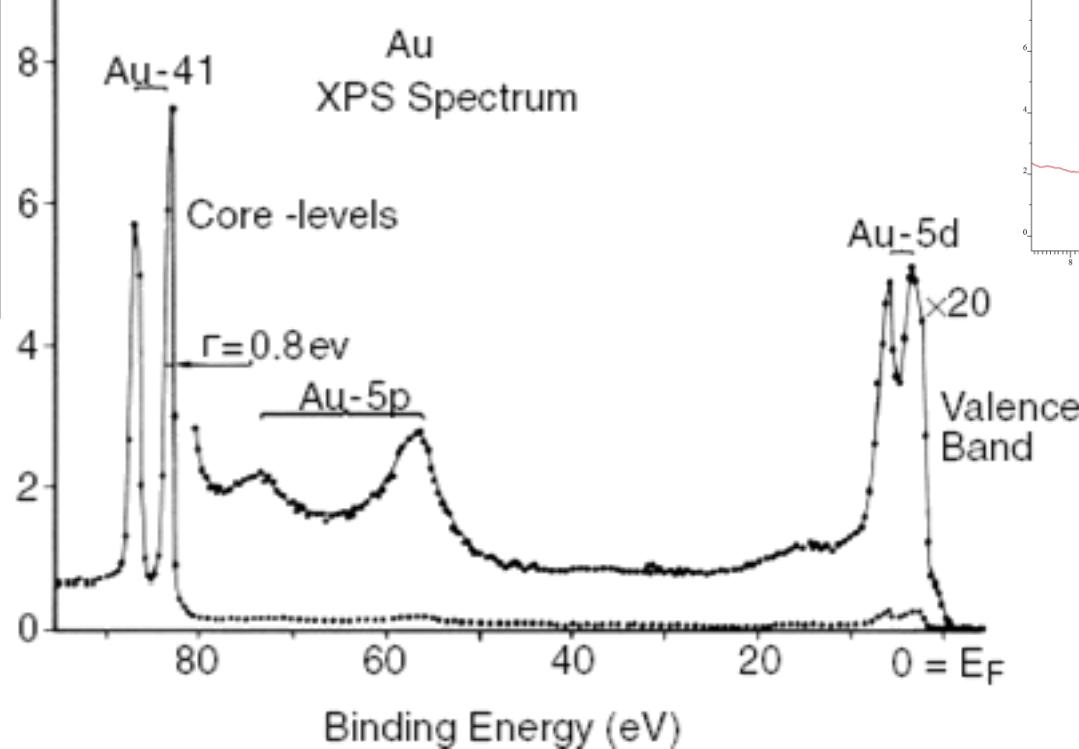
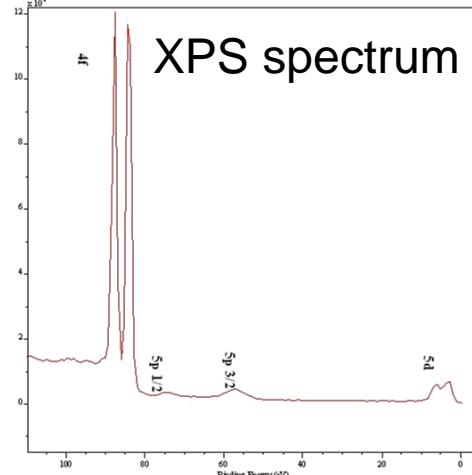
Photoionization cross-section reduces to one of finding initial and final state wave function.

In the case of Xe and gold studied by Manson (*Manson, S.T. Topics in Applied Physics V 26, p135*), the ε_F wave function for Xe has a very small amplitude in the core region so that the overlap with the

Au 4d is quite small making $|M_{i,j}|^2$ very small.

As the photon energy $h\nu$ increases, the ε_F wave function becomes more penetrating and the dipole matrix element $|M_{i,j}|^2$ and σ increase.

In the case of Au, the cross-section for the 5d- and 5p- states increase drastically for $h\nu < 100$ eV (UPS) and the cross-section for the 4f-state decreases. The situation is reversed at $h\nu > 200$ eV (XPS).

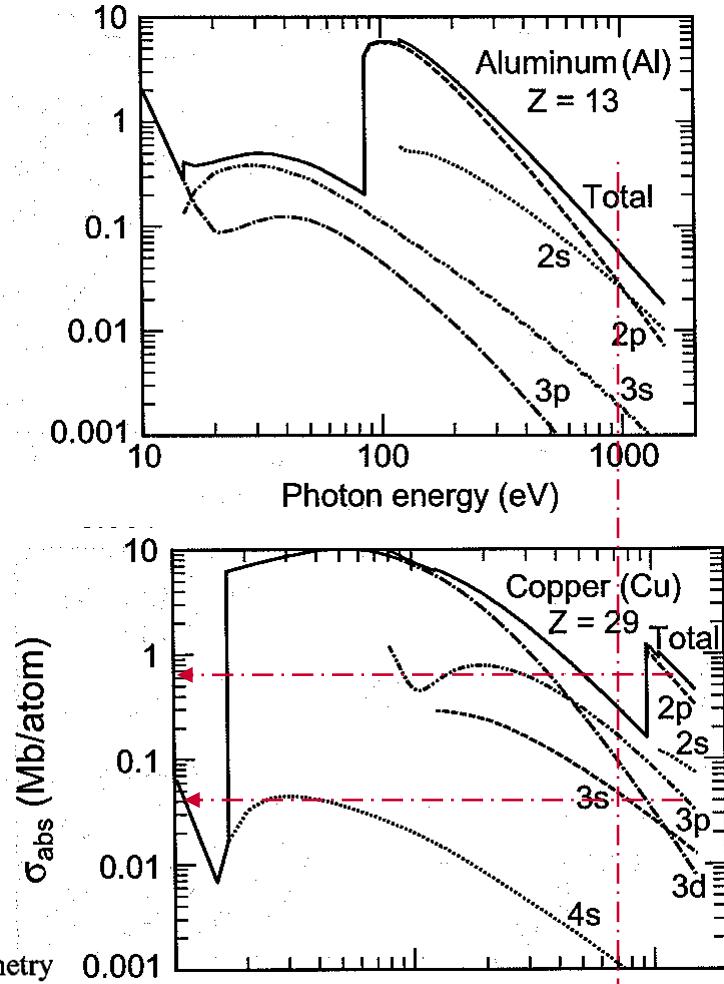
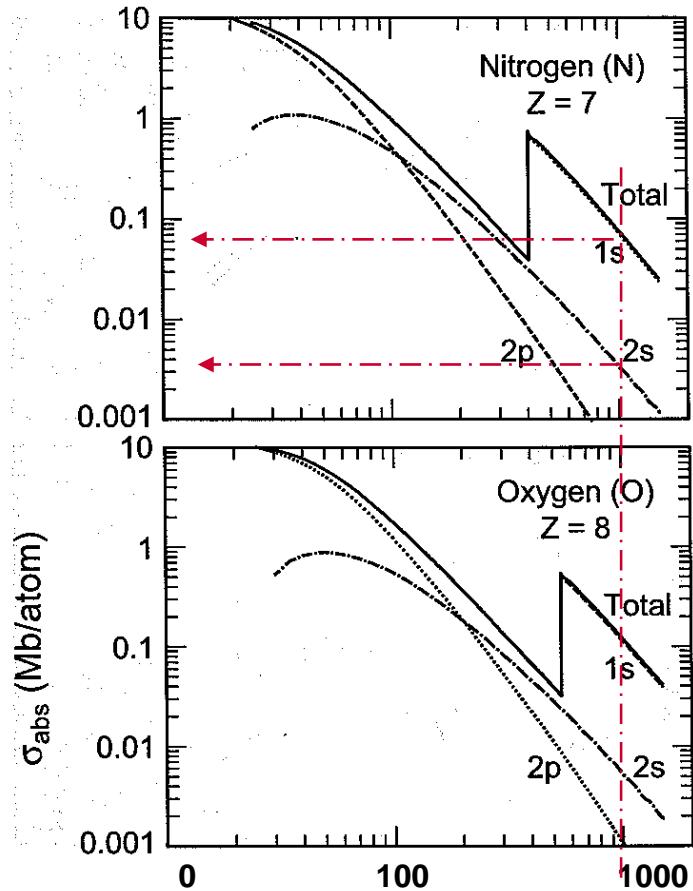


Energy dependence of the photoionization cross-section can be exploited to

1. Enhance features in UPS
2. Suppress Others.

The situation is reversed in XPS

Calculated subshell photoionization cross-sections by Lindau



Multi-electron excitation

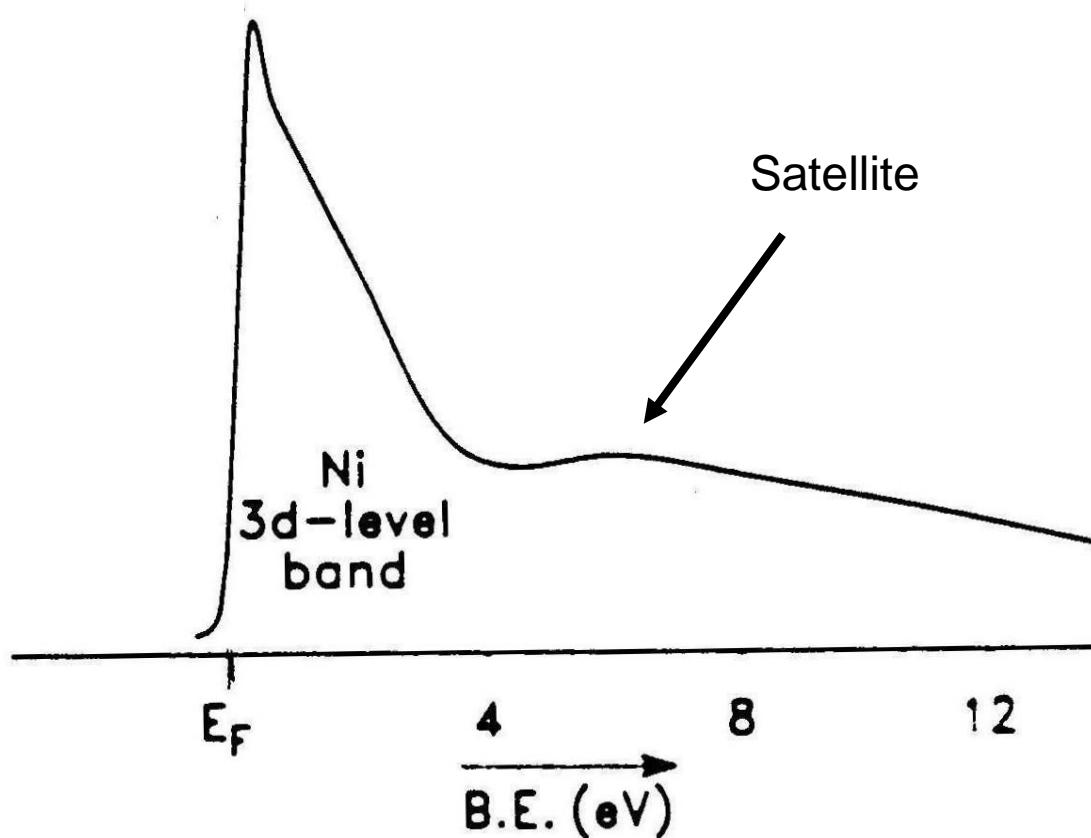
Introduces extra features in the DOS

No guarantee observed feature corresponds to a feature in the one-electron density of states.

Shake-up satellites are weak because the relaxation energy associated with the *outer shell* is much *smaller* than for a core level.

Strong coupling of electrons within a shell allows multiple hole states to be excited through configuration interaction or resonance process.

Example: a feature 6 eV below the E_F is the result of the multi-electron excitation (satellite) in Ni UPS VB.



Chemisorption Studies

Based upon a comparison between

1. Electronic levels of gas phase spectra
2. Chemisorbed spectra.

Information can be obtained on

1. Identification of species
2. Reaction products

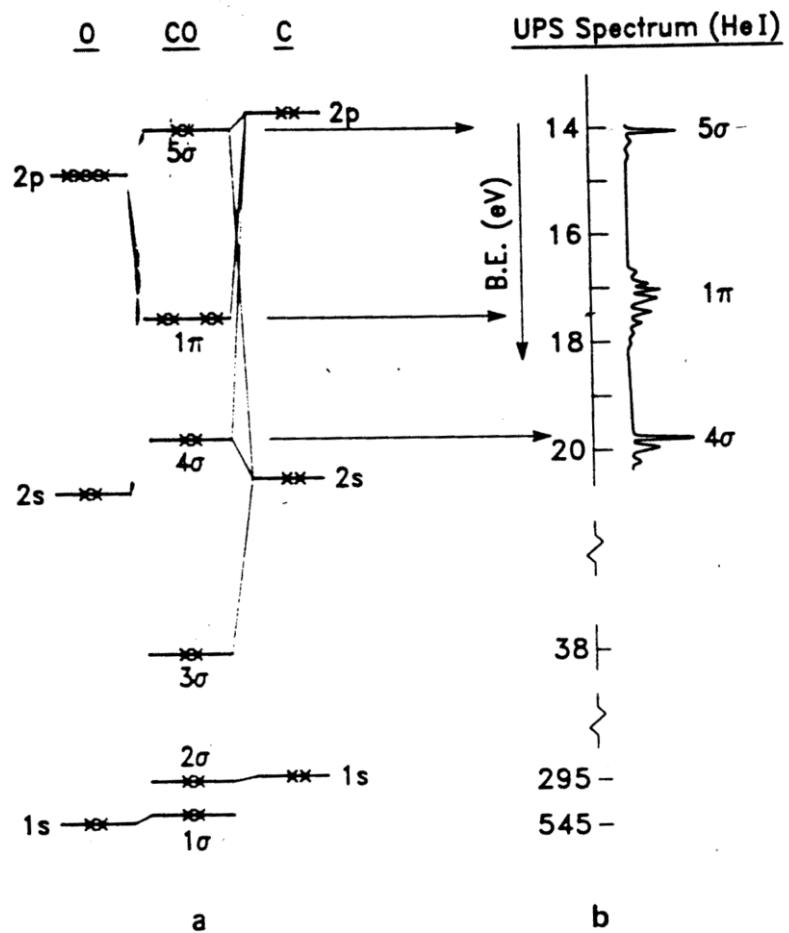
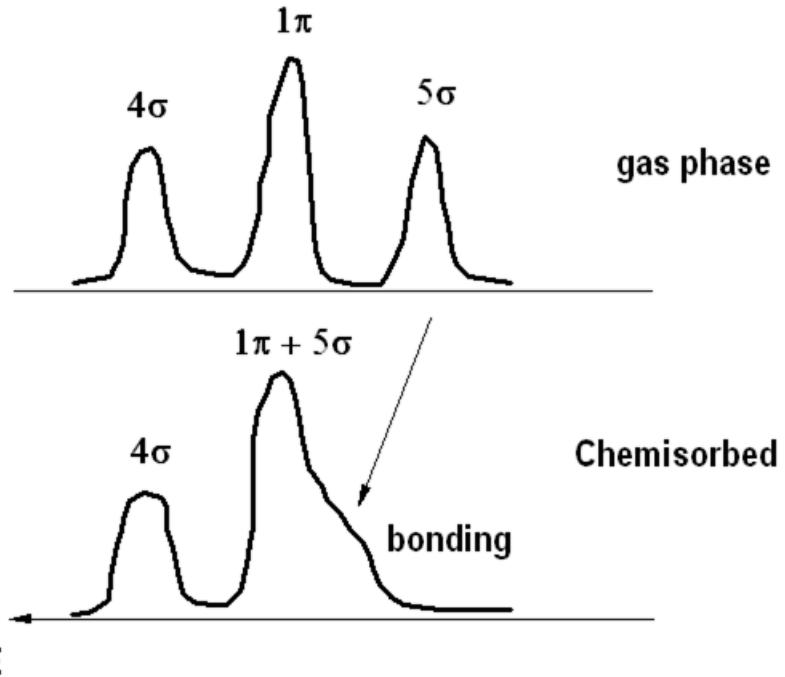
Energy level positions can identify orbitals participating in gas substrate bonding

Polarization and photon energy dependence can provide

1. Electron orbital identification
2. Orientation of the chemisorbed species
(structural information)

Example: CO molecule in the gas phase (orbitals and UPS spectrum)

Schematic orbital for CO



UPS spectra of CO on clean Ni (the 5σ orbital take part in the bonding to the surface) versus clean Ni.

