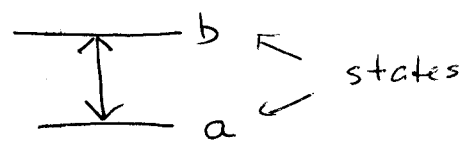


Photo-electron Spectroscopy

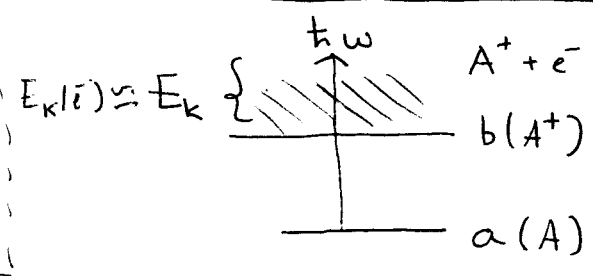
Let's first consider atoms & molecules:

Normal Spectroscopy



$$\Delta E = E_b - E_a = h\nu = \hbar\omega$$

Photo-electron Spectroscopy

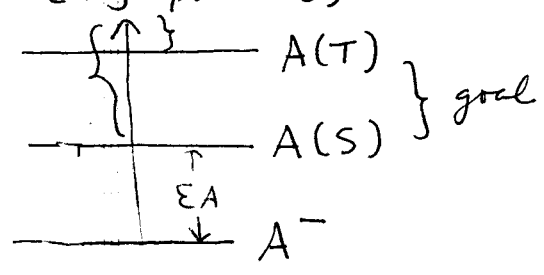


$$\hbar\omega = \epsilon_{ph} = E_b(A^+) - E_a(A) + E_k(e^-)$$

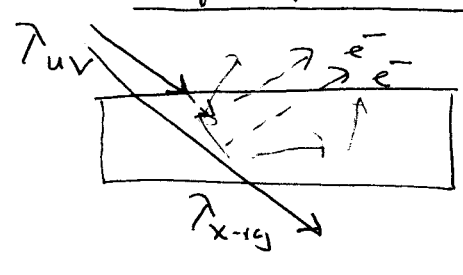
Measurement of $\hbar\omega + E_k \Rightarrow E_b - E_a$

reduced selection rules
but reduced resolution

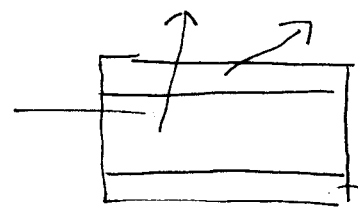
T-S Splitting (my postdoc)



Surface / Solid Applications



The penetration of emitted electrons back to the surface is not great, so most come from the surface region.



primary (still at original energy)
substrate & adsorbate

secondary:
some energy lost
hard to interpret

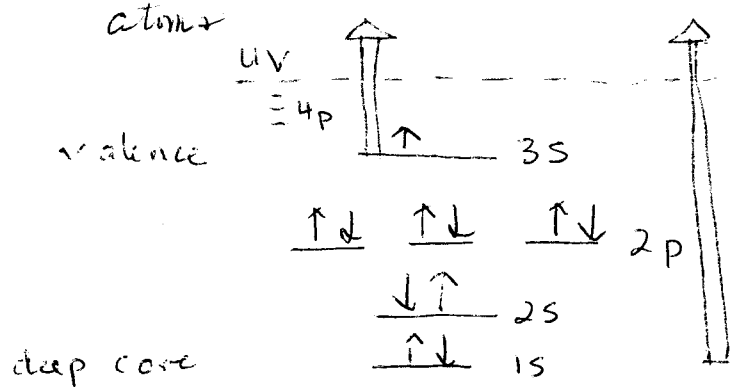
trapped

(orbital analysis)

X-Rays vs UV

It is assumed below that unoccupied orbitals remain the same (Koopman's Th)

Consider sodium Na ($1s^2 2s^2 2p^6 3s^1$)²S



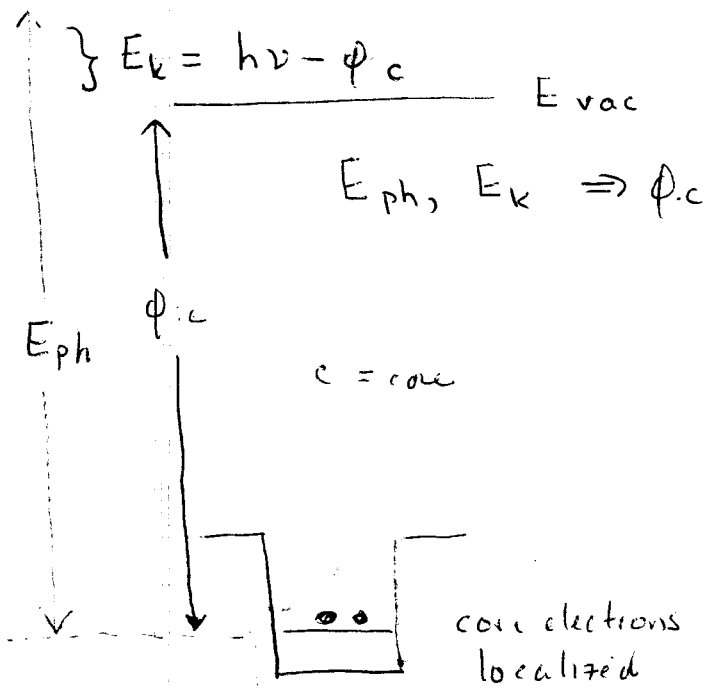
IP($3s^1$) = 5.12 eV ($\lambda < 242$ nm)

IP($2p^6$) = 47.06 eV ($\lambda < 26$ nm)

X-ray 0.01 - 10 nm

Now for surfaces:

X-ray Photoelectron Spectroscopy (XPS)



To a first approximation, core electrons do NOT participate in bonding and their energies are only characteristic of the type of atom (or molecule).

XPS useful for elemental analysis of a sample.
ESCA: electron spectroscopy for chemical analysis

Fine structure tells some details of environment "chemical shifts"

Final state relaxes to remove hole.
(fluorescence for example)
or Auger - see later

$E_{1s} \propto -Z^2$ without shielding

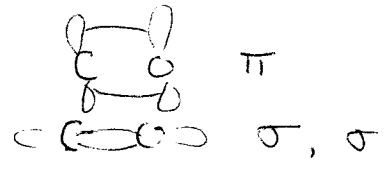
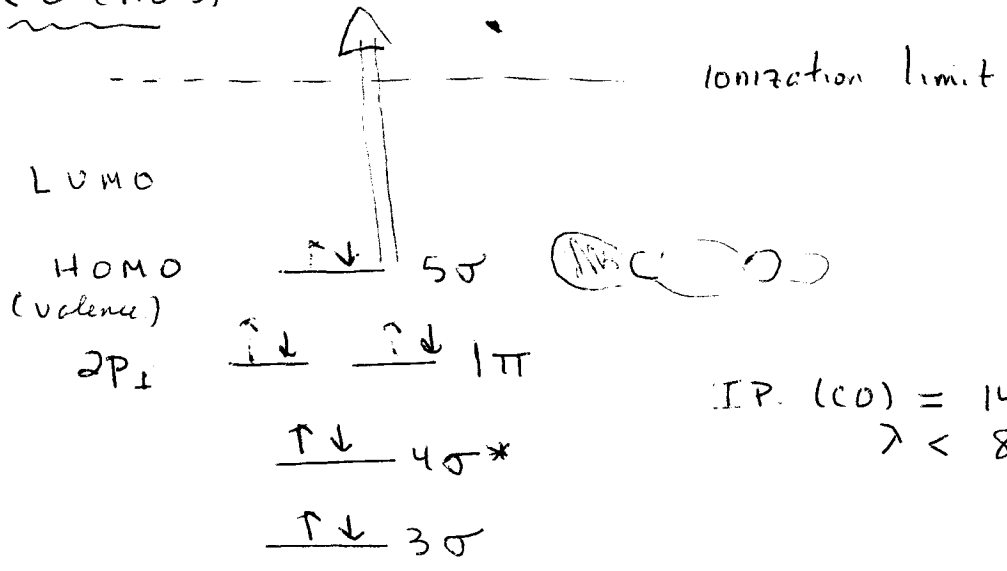
$E_{1s} (Z=1) = -13.6$ eV

$E_{1s} (Z=10) = -1360$ eV

Can also study higher electrons (2s, 2p, etc)

-16a⁺ = ...

CO (MO's)



14 electrons

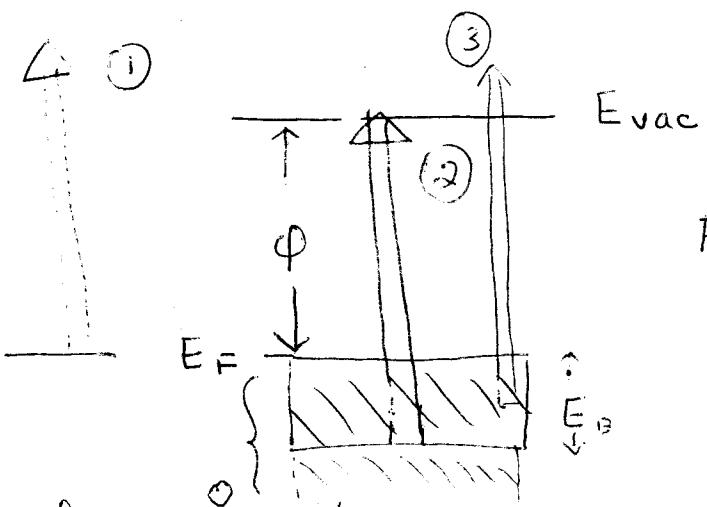
IP. (CO) = 14.1 eV
 $\lambda < 880 \text{ \AA}$ (88 nm)

one 1s { $\uparrow\downarrow$ 2 σ^* , $\uparrow\downarrow$ 1 σ } localized onto C + O $^1\Sigma$

vibrational substructure.

Should consider CO⁺ states ← CO states

UV Photoelectron Spectroscopy (UPS)



Emitted electrons come from the valence band.

Fixed ν : maximum kinetic energy stems from electrons at the Fermi level

① $\Rightarrow E_k^{\max}$

The result $E_k = 0$ defines the depth into the VB that can be probed.

ϕ : sensitive to surface because of dipole effect

Na: $\phi = 2.28 \text{ eV}$ minimum photon energy that kicks out electron
 $E_F = 3.24 \text{ eV}$

$E_k^{\max} = h\nu - \phi$ $E_k = h\nu - \phi - E_B$ ③ general case

Example

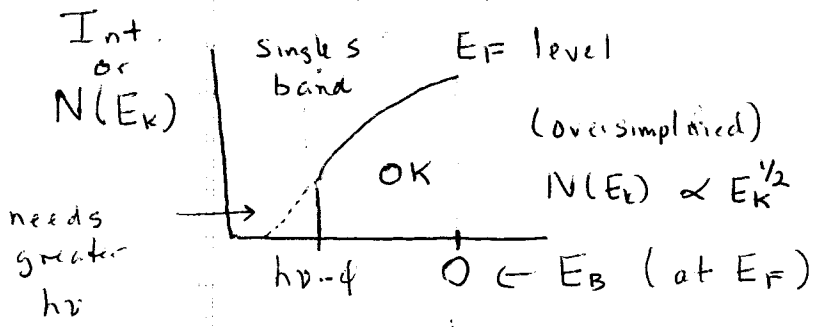
$\lambda = 250 \text{ nm}$ $h\nu = 4.96 \text{ eV}$

$E_k^{\max} = 4.96 \text{ eV} - 2.28 \text{ eV} = 2.68 \text{ eV}$

$E_k = 0 \Rightarrow E_B^{\max} = h\nu - \phi = 2.68 \text{ eV}$ below E_F .

energy of electron below E_B binding energy.

Spectrum: intensity of electrons emitted maps out density of electronic states.



From single band, can get E_F (total width of band) + ϕ (highest $N(E_k)$)

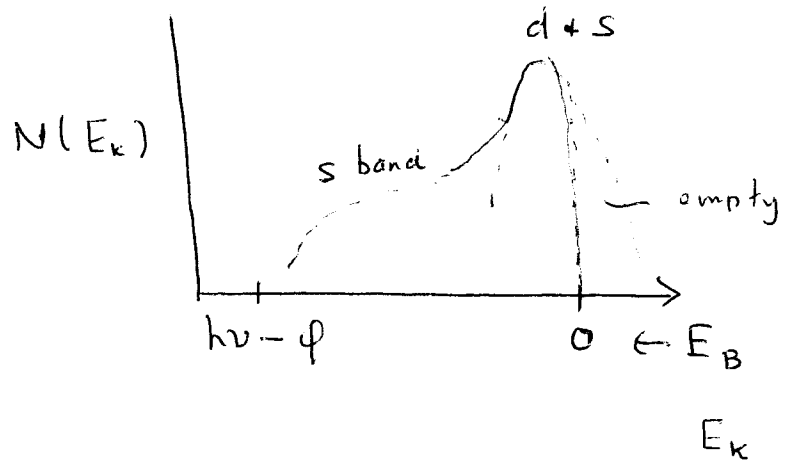
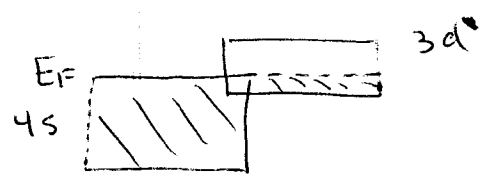
Transition Metals

d + s bands accessible
more complex

0 $h\nu - \phi$ $E_k \rightarrow$
 (secondaries subtracted out)

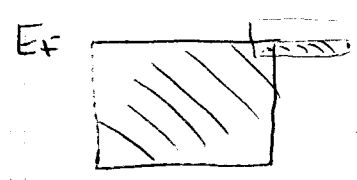
$E_k = h\nu - \phi - E_B$

$E_B = h\nu - \phi - E_k$



Adsorbates

studied by difference spectra
 Yields MO's of adsorbate and orbitals between adsorbate & substrate.



MO band \Rightarrow increased density of states

e.g. CO surface 5σ orbital important in chemisorption

Normal 5σ gas-phase spectrum replaced

(oversimplified) : "final" states important in which MO's change (CO^+ is not CO)

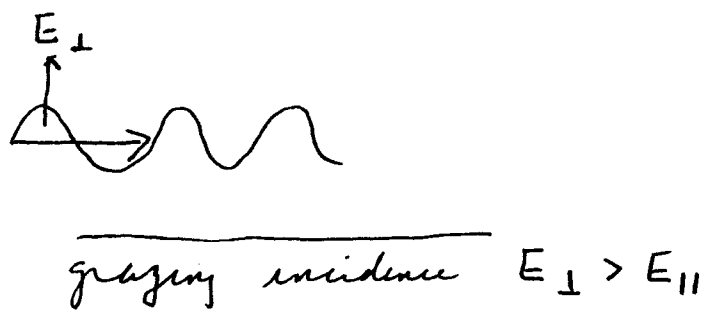
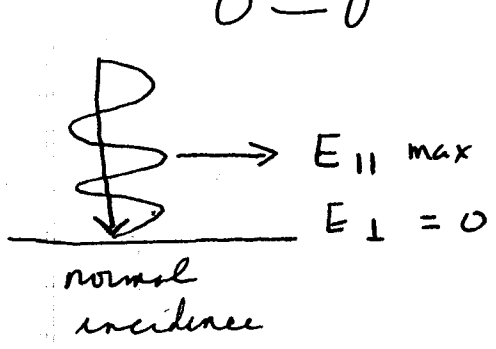
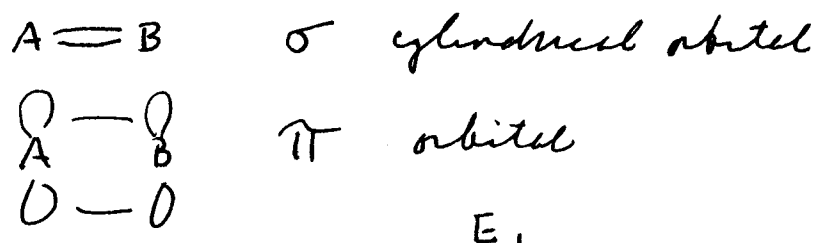
Other techniques:

- a) comparison of adsorbate spectrum with pure gas phase "fingerprint". Shows what molecular MO's are involved in binding with substrate. (substantial shifting)
- ↓
- b) molecular orientation probed by variation of of the orientation of electric vector of incident light with respect to intermolecular axis.

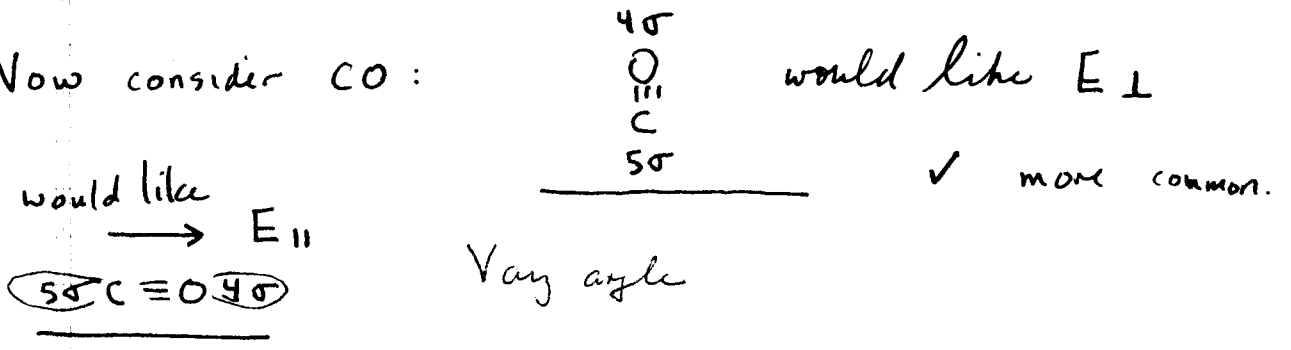
Selection Rules (Atkins + Barnes)

- (i) σ orbitals excited with maximum probability when \vec{E} aligned along molecular axis
- (ii) π orbitals excited with maximum probability when $\vec{E} \perp$ to bond axis.

"excited" means more photoelectrons emitted.



Now consider CO:



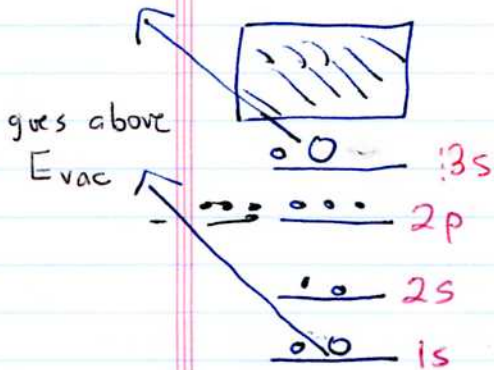
Auger Electron Spectroscopy (AES, like XPS)

- often used to determine elements near surface

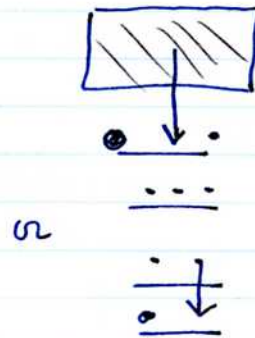
- can use X-rays, ions, or electrons

electrons: 3-5 keV (can use LEED apparatus)

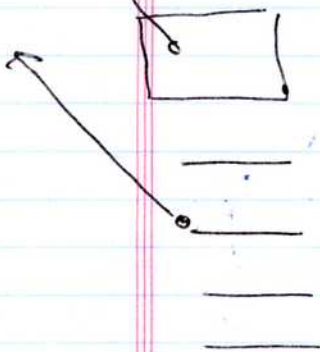
① Initial core ionization forms hole (or even valence electron)



② Radiantless Transition to fill hole



③ Extra energy from relaxation more than enough to kick out another electron



secondary electrons depend on element

Example: atomic Boron ($1s^2 2s^2 2p^1$)

