Lecture 11

Photoelectron Peak Intensities

Photoelectron Peak Intensities

The PE intensity N_k produced from a subshell k can be calculated by integrating the differential intensity dN_k from various volume elements.

dN_k = [X-ray flux at x, y, z]
[No. of atoms or molecules in x,y,z]
[Differential cross-section for k subshell]
[Acceptance solid angle of electron analyzer at x,y,z]
[Probability of escape from sample with negligible direction change]
[Instrumental detection efficiency]

ΩWill vary over specimen volume.
X ray flux is normally constant, I_0. Probability of no-loss escape can be given as $T(E_{kin}, k^f, x,y,z)$

The detection efficiency is the probability that an electron escaping from the sample in a direction acceptable to the spectrometer leads to a single final count.

This will vary with E_{kin}.

The atomic or molecular density can be given by $\rho(x,y,z)$

$$dN_k = I_0 \cdot \rho(x,y,z)\, dx\, dy\, dz \cdot d\sigma_k/d\Omega \cdot \Omega\, (E_{kin}, x,y,z) \cdot T(E_{kin}\; k^f,x,y,z) \cdot D_0(E_{kin})$$

$$dN_k = I_0 \cdot \rho(x,y,z)\, dx\, dy\, dz \cdot d\sigma_k/d\Omega \cdot \Omega(E_{kin}, x,y,z) \cdot \exp[-l/\Lambda_e(E_{kin})] \cdot D_0(E_{kin})$$

l is the path length of escape into vacuum.

Peak intensities from solids

a) Semi-infinite specimen, Atomically flat, Clean surface, peak k with kinetic energy $E_{kin} \equiv E_k$

$$N_k(\theta) = I_0\, \Omega_0\, (E_k)\, A_0(E_k)\, D_0(E_k)\, \rho\, d\sigma_k/d\Omega\, \Lambda_e\, (E_k)$$

b) Specimen thickness t, atomically clean

$$N_k(\theta) = I_0\, \Omega_0(E_k)\, A_0(E_k)\, D_0(E_k)\, \rho\, d\sigma_k/d\Omega\, \Lambda_e\, (E_k) \\ [1-\exp(-t\, /\Lambda_e(E_k)\, \sin\theta)]$$

c) Semi infinite substrate with uniform overlayer of thickness t

peak k, with $E_{kin} \equiv E_k$

$$N_k(\theta) = I_0\, \Omega_0(E_k)\, A_0(E_k)\, D_0(E_k)\, \rho\, d\sigma_k/d\Omega\, \Lambda_e(E_k)$$
$$[1\text{-}\exp(-t/\Lambda_e(E_k) \sin \theta)]$$

Peak l, with $E_{kin} \equiv E_l$ From the overlayer

$$N_l(\theta) = I_0\, \Omega_0(E_l)\, A_0(E_l)\, D_0(E_l)\, \rho'\, d\sigma_l/d\Omega\, \Lambda_e'(E_l)$$
$$[1\text{-}\exp\,(-t\Lambda_e'(E_l) \sin \theta]$$

$\Lambda_e(E_k)$ – attenuation length in substrate

$\Lambda_e'(E_k)$ – attenuation length in overlayer

overlayer/substrate ratio,

$$N_l(\theta)/N_k(\theta) = [\Omega_0(E_l)\, A_0(E_l)\, D_0(E_l)\, \rho'\, d\sigma_l/d\Omega)\, \Lambda_e'\,(E_l)\, /$$
$$\Omega_0(E_k) A_0(E_k)\, D_0(E_k)\, \rho\, d\sigma_k/d\Omega\, \Lambda_e(E_k)]$$
$$[l - \exp(-t\,/\,\Lambda_e'(E_l) \sin \theta][\exp(t\,/\,\Lambda_e(E_k) \sin \theta\,]$$

Substrate peaks are attenuated by the overlayer and this effect is enhanced at low θ. Overlayer /substrate ratio increases with decreasing θ.

d) Semi-infinite substrate with a non-attenuating overlayer at fractional coverage

Peak k from the substrate

$$N_k(\theta) = I_0\, \Omega_0(E_k)\, A_0(E_k)\, D_0(E_k)\, \rho\, (d\sigma_k/d\Omega)\;\; \Lambda_e(E_k)$$

Peak l from overlayer

$$N_l(\theta) = I_0\, \Omega_0(E_l)\, A_0(E_l)\, D_0(E_l)\, s'\, (d\sigma_l/d\Omega)\, (1/\sin\theta)$$

Overlayer/substrate ratio:

$$N_l(\theta)/N_k(\theta) = [\Omega_0(E_l)\, A_0(E_l)\, D_0(E_l)\, s'\, (d\sigma_l/d\Omega)\, / \\ \Omega_0(E_k)\, A_0(E_k)\, D_0(E_k)\, s\, (d\sigma_k/d\Omega)\, \Lambda_e(E_k)\, (\sin\theta\, /d)]$$

$$N_l(\theta)/N_k(\theta) = [s'/s] \cdot [D_0(E_l)\, \Omega_0(E_l)\, A_0(E_l)\, (d\sigma_l/d\Omega)\, d \,/\, D_0(E_k)\, \Omega_0(E_k)\, A_0(E_k)\, (d\sigma_k/d\Omega)\, \Lambda_e(E_k) \sin\theta\,]$$

s' = mean surface density of atoms in which peak l originates in cm^{-2}

s = mean surface density of substrate atoms in cm^{-2}.

s'/s = fractional surface coverage of the atomic species in which peak l originates.

d = mean separation of layers of density s in the substrate (calculated from s/ρ).

This expression can be used to get fractional surface coverage.

Core electron BE shifts

1. Lifetime of core hole
2. Final state energy values multiplet, vibrational broadening
3. Unresolved chemically shifted peaks.

Instrumental causes of width

a) x-ray width
b) Resolving power of analyser
c) Non-uniform surface charging.

A B.E shift within 0.1 eV is measurable.

For a gaseous sample, the B.E shift of k electron in two different chemical environments 1 and 2,

$$\Delta E_b^v(A, k, 1\text{-}2) = (E_b^v(k))_1 - (E_b^v(k))_2$$

$$= (E_{kin})_2 - (E_{kin})_1 \qquad \text{(for gases)}$$

For solids, Fermi level referenced B.E to be used.

$$\Delta E_b^F(A, k, 1\text{-}2) = (E_b^F(k))_1 - (E_b^F(k))_2$$
$$= (E_{kin})_2 - (E_{kin})_1 + (\phi_{spect})_2 - (\phi_{spect})_1 + (V_c)_2 - (V_c)_1$$

where ϕ_{spect} is spectrometer work function and V_c is charging potential. If ϕ_{spect} and V_c changes are negligible,

$$\Delta E_b^F(A, k, 1\text{-}2) = (E_b^F(k))_1 - (E_b^F(k))_2$$
$$= (E_{kin})_2 - (E_{kin})_1$$

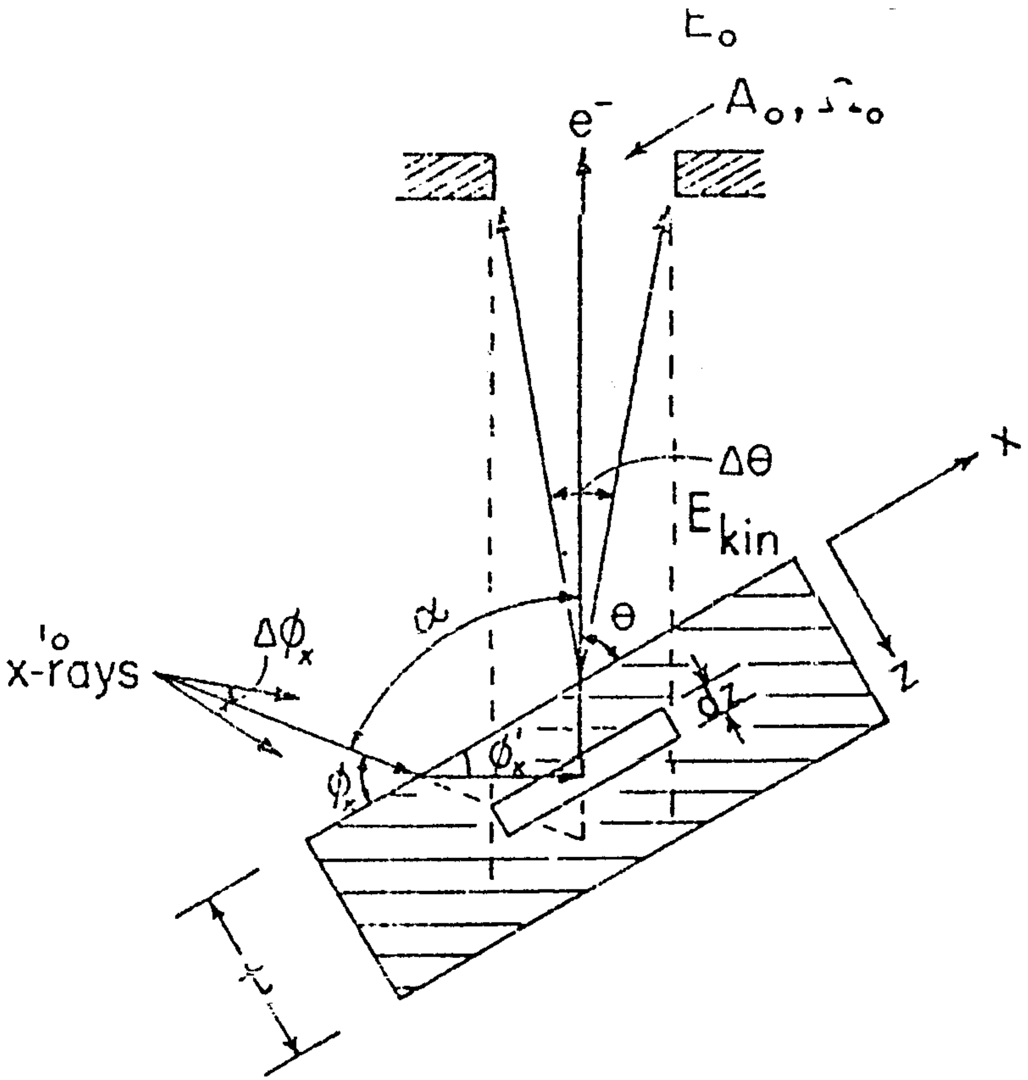
For vacuum level referenced BEs,

$$\Delta E_b^v(A, k, 1\text{-}2) = \Delta E_b^F(A, k, 1\text{-}2) + (\phi_s)_1 - (\phi_s)_2$$

Calculations

$$\Delta E_b^v(A, k, 1\text{-}2) = (E_b^v(k))_1 - (E_b^v(k))_2$$
$$= -(\in_k)_1 + (\in_k)_2 - (\delta E_{relax})_1 + (\delta E_{relax})_2$$
$$+ (\delta E_{relat})_1 - (\delta E_{relat})_2 + (\delta E_{corr})_1 - (\delta E_{corr})_2$$

Or $\Delta E_b^v(A, k, 1\text{-}2) = -\Delta \in_k - \Delta(\delta E_{relax}) + \Delta(\delta E_{relat}) + \Delta(\delta E_{corr})$



Idealized spectrometer geometry for calculating photoelectron peak intensities from solid specimens.

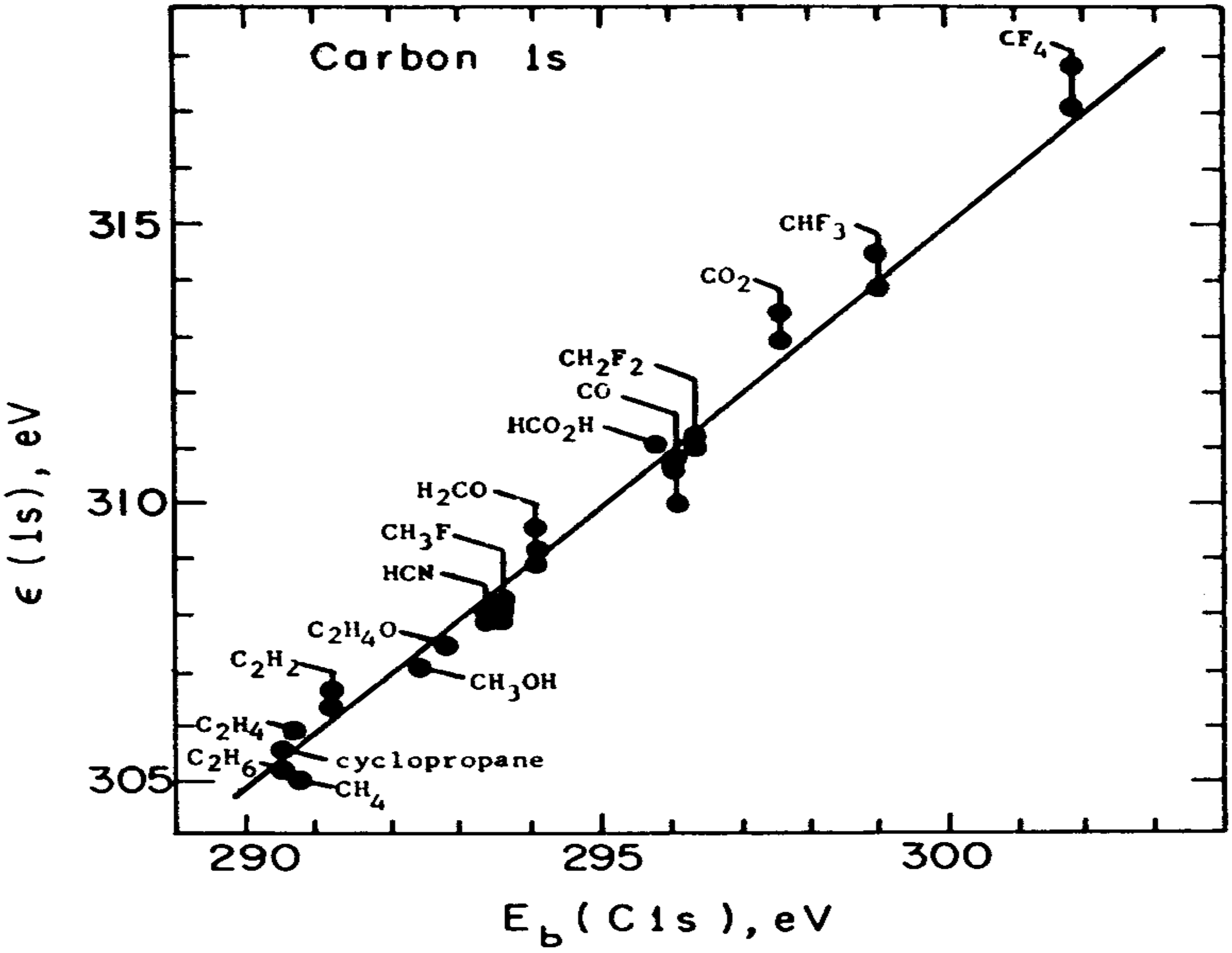


Fig. 18. Plot of carbon 1*s* binding energies calculated via Koopmans' Theorem against experimental binding energies for several carbon-containing gaseous molecules. For some molecules, more than one calculated value is presented. The slope of the straight line is unity. The two scales are shifted with respect to one another by 15 eV, largely due to relaxation effects. All of the theoretical calculations were of roughly double-zeta accuracy or better. (From Shirley, ref. 7.)

Models

a) $E_b^v(k) =$ $E_b^v(k, q_A)$ $+$ V

Compound	Free ion of charge q_A	Potential due to all other atoms

$V = e^2 \Sigma_{i \neq A}\, q_i / r_iA$

b) $\Delta E_b^v(A, k, 1\text{-}2) = c_A q_A + V + I$

c) $E_b^v(A,k, 1\text{-}2) = c_A' q_A + e^2 \Sigma_{i \neq A}\, q_i / rA_i$

d) $\Delta E_b(A, k, 1\text{-}2) = \Sigma_{groups}\, \Delta E_b\ (group)$

FINAL STATE EFFECTS

Relaxation, multiplet, shake-up, shake-off, other many electron effects

All of them are related, but it is better to treat them separately.

Relaxation effects

Relaxation is the primary cause of shift between vacuum referenced elemental BEs and the corresponding solid.

Examples: Noble gas atoms in a metal lattice.

On going from CH_4 to $C_{13}H_{28}$ the C1s BE shifts by 0.6eV, the relaxation shift is 2eV.

UPS spectra of valence levels of molecules chemisorbed on solids. BEs of levels not involved in bonding are lower than for free molecules.

ΔE_{relax} = difference between $-\varepsilon_k$ and the binding energy calculated by performing a Hatree Fock calculation on ion and neutral.

FINAL STATE EFFECTS: Some more introduction

Electron – Electron Interactions
Coulomb
Exchange

Main line

Extra (Satellite) lines

Also no-loss peak

Inelastic energy loss
Background structures

Intrinsic
Extrinsic

Theoretical treatment is difficult, but models are available.
Localised orbitals and cluster models.

Introduction to final state effects: Cu^{2+}

Cu-di halides:

Cu^{2+} state ← $3d^9L$ → ligand state F^-, Cl^-, Br^- np filled states

2P ionisation leads to → $3d^{10}L^{-1}$

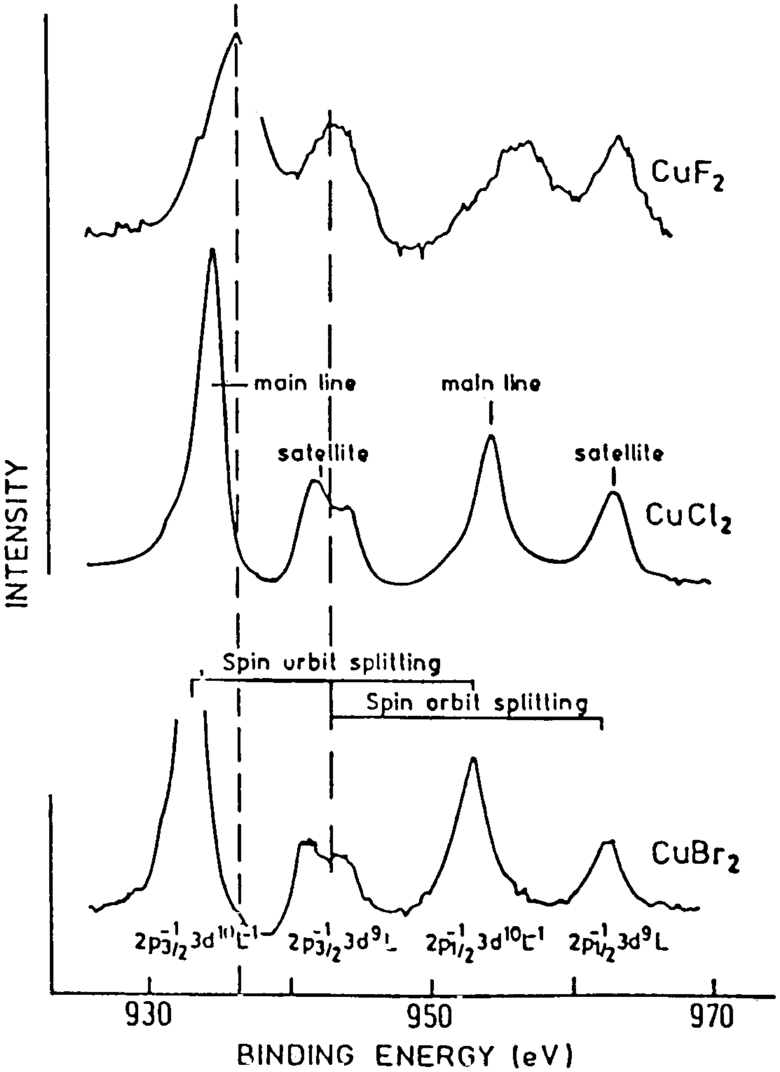
2P ionisation leads to → $3d^9L$

$3d^{10}L^{-1}$ → main line

$$E_{main} = E(c^{-1}d^{10}L^{-1}) \approx E(c^{-1}d^{10}) + E(L^{-1})$$

↓

Assuming weak hybridisation between metal ion and ligands



XPS spectra of the 2p core levels of CuF_2, $CuCl_2$ and $CuBr_2$. Cu^{2+} has a $3d^9$ initial-state configuration. The satellite-line energies roughly coincide in the three compounds while the main-line energies show large difference. This makes the assignment of $2p_{3/2,1/2}$ $3d^9$ to the satellite lines likely, Leaving the assignment $2p_{3/2,1/2}$ $3d^{10}$ L^{-1} for the main line; their energies differ because of the different ligand binding energies.

$E_{sat} = E(c^{-1}d^9L)$

This first order assumption suggests why satellite lines are ligand independent.

Satellite lines are generally those which cannot be explained by one electron picture.

In the case of Cu di halides, the situation is reverse. Satellite line leaves the system unaltered, but the main line is configurationally different, which occurs at a lower energy.

Situation can be described differently.

Ionization leads to core hole with extra charge. Lowering of 3d energy will bring it below valence shell and consequent charge transfer from valence levels leads to ground state (main line).