

Photoelectron Peak Intensities in Solids

Electronic structure of solids
Photoelectron emission through solid
Inelastic scattering
Other excitations
Intrinsic and extrinsic
Shake-up, shake-down and shake-off
Plasmon
Vibrations, phonons

Inelastic Scattering in Solids

If a mono energetic flux N_0 at energy E_{kin} is generated at a point, the no loss flux N_0 at length l can be given as,

$$N = N_0 \exp [-l/\Lambda_e(E_{kin})]$$

Λ_e is the electron attenuation length. This means that inelastic scattering occurs after photoemission, extrinsic. Photoelectron energy loss can also be intrinsic, occurring during excitation. The attenuation lengths are measured by XPS or Auger. The results fall in a universal curve.

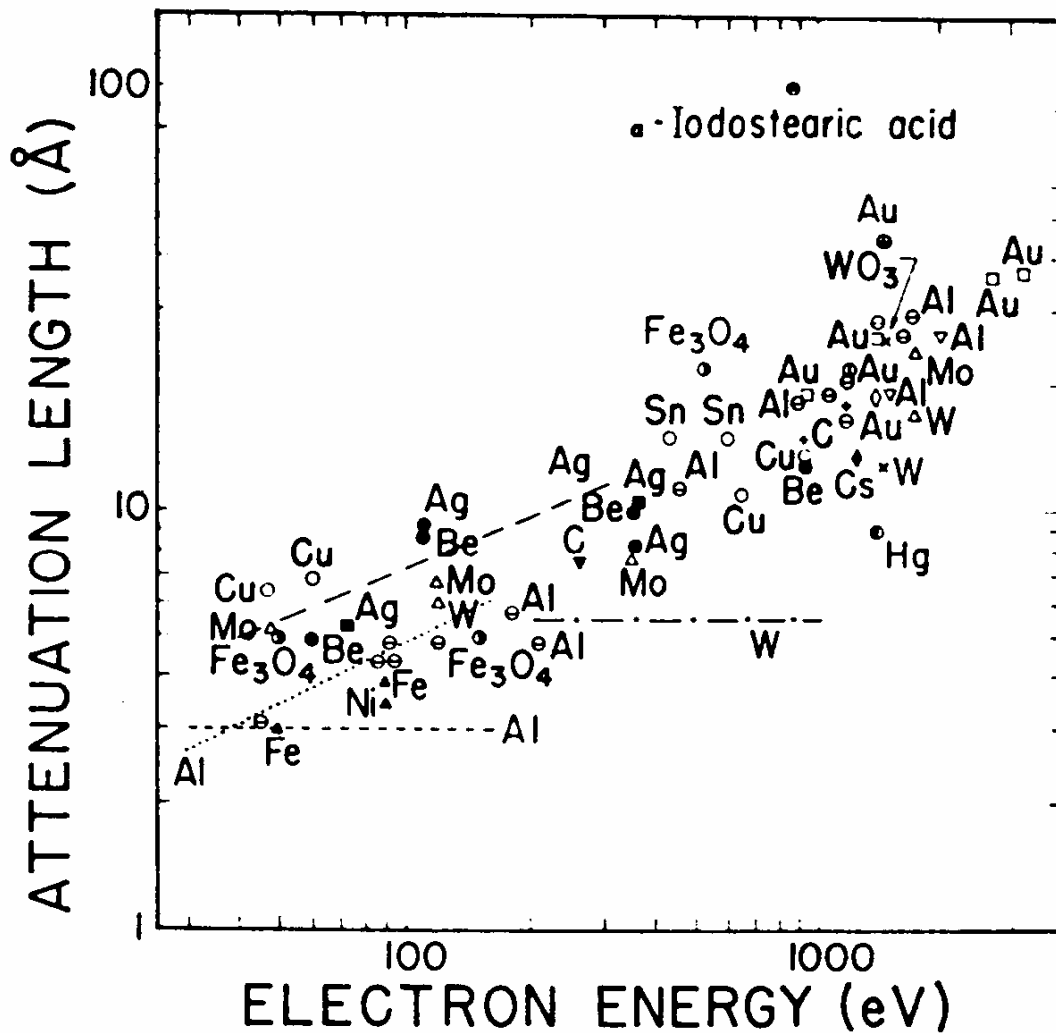


Fig. 16. Summary of experimental values for the electron inelastic attenuation length Λ_e for various solids. (From Powell, ref. 20.)

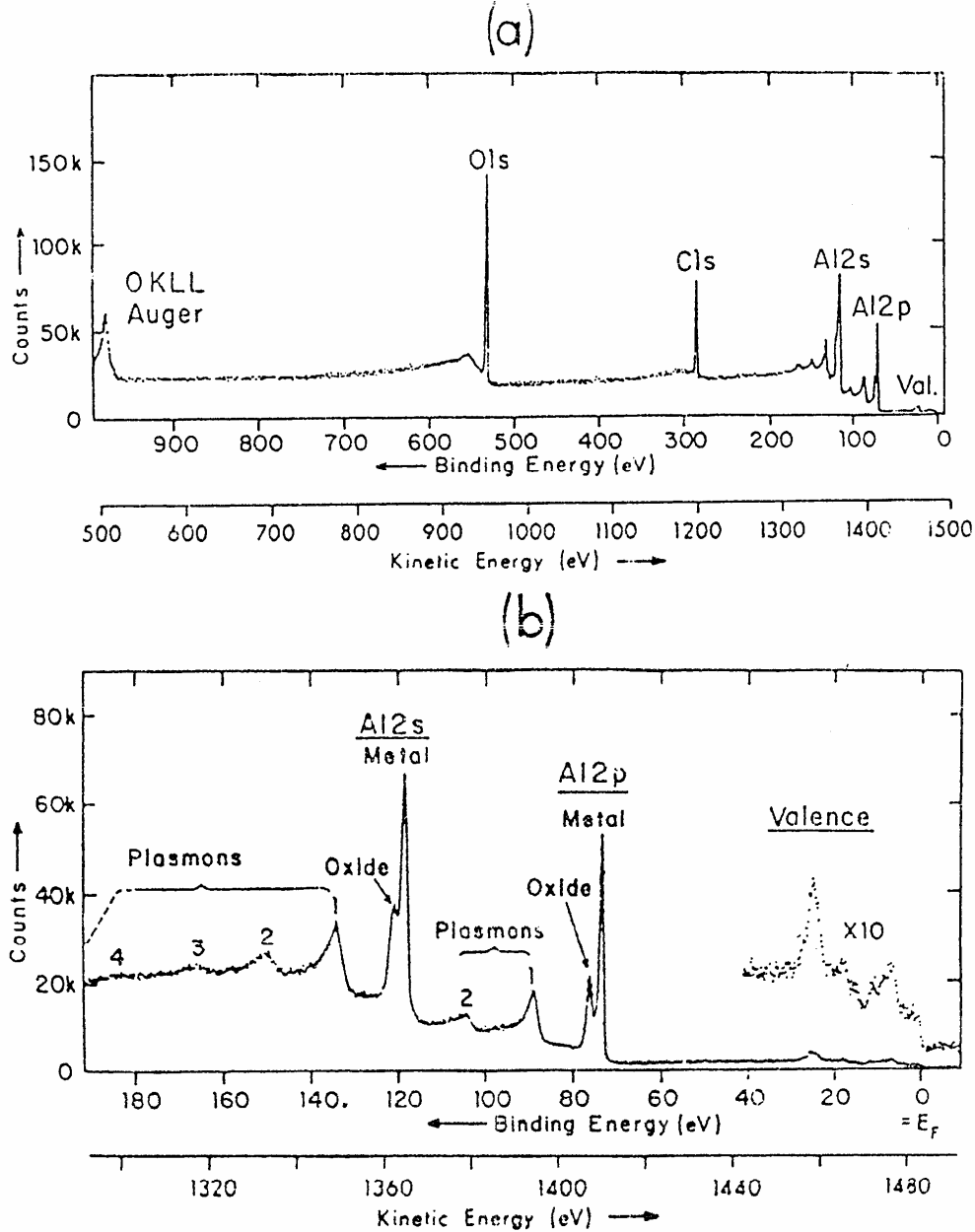
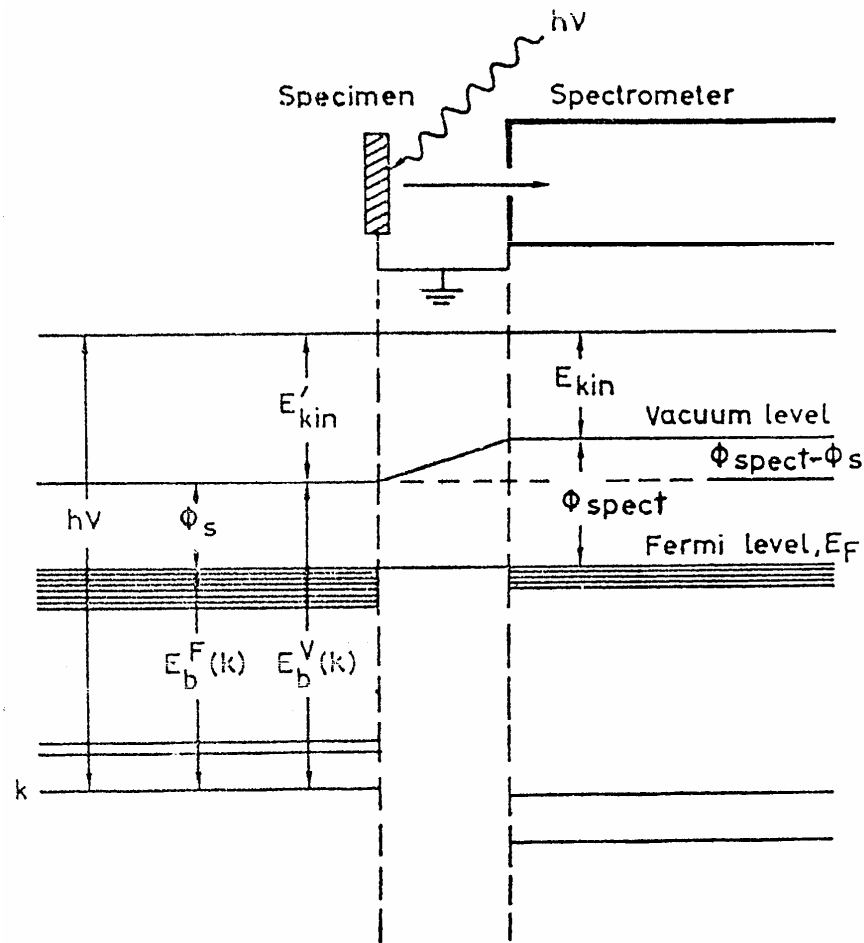


Fig. 1. Typical XPS spectra obtained from an oxidized aluminium specimen with carbonaceous contaminant overlayer. Monochromatized $AlK\alpha$ radiation was used for excitation. (a) Overall spectrum with all major no-loss features labelled. (b) Expanded-see spectrum of the $Al2s$, $Al2p$, and valence regions. Chemically-shifted oxide- and metal-co peaks are indicated, as well as inelastic loss peaks due to bulk plasmon creation.



Energy level diagram for a metallic specimen in electrical equilibrium with an electron spectrometer. The closely spaced levels near the Fermi level E_F represent the filled portions of the valence bands in specimen and spectrometer. The deeper levels are core levels. An analogous diagram also applies to semi-conducting or insulating specimens, with the only difference being that E_F lies somewhere between the filled valence bands and the empty conduction bands above.

minimum Λ_e occurs around 30-100 eV and below which it increases. Maximum surface sensitivity at 30-100eV. The high energy data can be fitted to,

$$\Lambda_e(E_{\text{kin}}) \propto (E_{\text{kin}})^{0.52}$$

Λ_e may not be a constant for a material. It may vary from bulk to surface as the dominant mode of extrinsic inelastic scattering may vary depending on whether it is bulk or surface. For a free electron metal, it may not deviate much.

Models and attenuation length measurements.

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.

$$dN_k = [\text{X-ray flux at } x, y, z]$$

[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]

Ω will vary over specimen volume.

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

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 $\rho(x,y,z)$

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

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

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 $E_{\text{kin}} \equiv E_k$

$$N_k(\theta) = I_0 \Omega_0(E_k) A_0(E_k) D_0(E_k) \rho \frac{d\sigma_k}{d\Omega} \Lambda_e(E_k)$$

- b) Specimen thickness t, atomically clean

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

c) Semi infinite substrate with uniform overlayer of thickness t

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

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

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

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

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

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

overlayer/substrate ratio,

$$N_l(\theta)/N_k(\theta) = [\Omega_0(E_l) A_0(E_l) D_0(E_l) \rho' \frac{d\sigma_l}{d\Omega} \Lambda_e'(E_l) / \Omega_0(E_k) A_0(E_k) D_0(E_k) \rho \frac{d\sigma_k}{d\Omega} \Lambda_e(E_k)] [1 - \exp(-t / \Lambda_e'(E_l) \sin \theta)] [\exp(t / \Lambda_e(E_k) \sin \theta)]$$

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:

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

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

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,

$$\begin{aligned}\Delta E_b^v(A, k, 1-2) &= (E_b^v(k))_1 - (E_b^v(k))_2 \\ &= (E_{\text{kin}})_2 - (E_{\text{kin}})_1 \quad (\text{for gases})\end{aligned}$$

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

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

where ϕ_{spect} is spectrometer work function and V_c is charging potential. If

ϕ_{spect} and V_c changes are negligible,

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

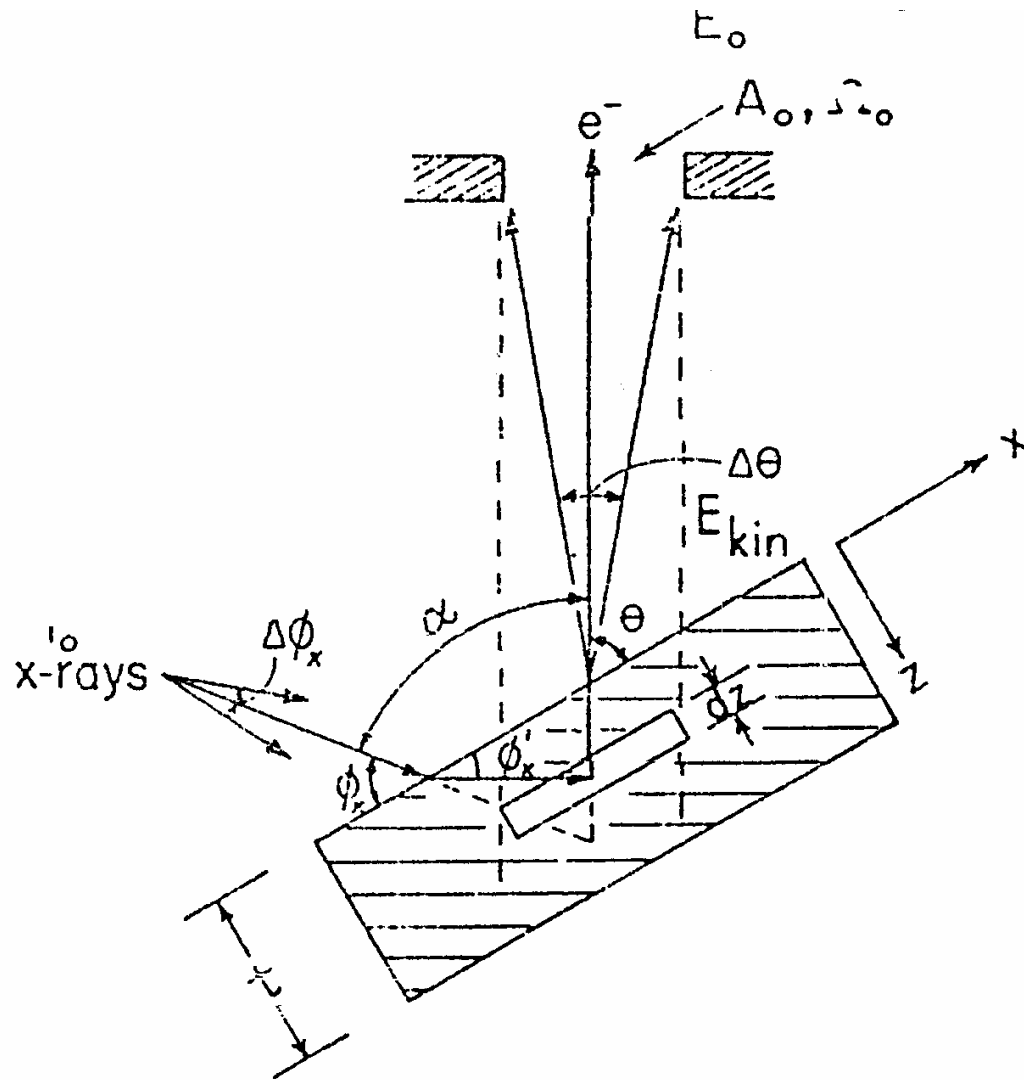
For vacuum level referenced BEs,

$$\Delta E_b^V(A, k, 1-2) = \Delta E_b^F(A, k, 1-2) + (\phi_s)_1 - (\phi_s)_2$$

Calculations

$$\begin{aligned}\Delta E_b^V(A, k, 1-2) &= (E_b^V(k))_1 - (E_b^V(k))_2 \\ &= -(\epsilon_k)_1 + (\epsilon_k)_2 - (\delta E_{\text{relax}})_1 + (\delta E_{\text{relax}})_2 \\ &\quad + (\delta E_{\text{relat}})_1 - (\delta E_{\text{relat}})_2 + (\delta E_{\text{corr}})_1 - (\delta E_{\text{corr}})_2\end{aligned}$$

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



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

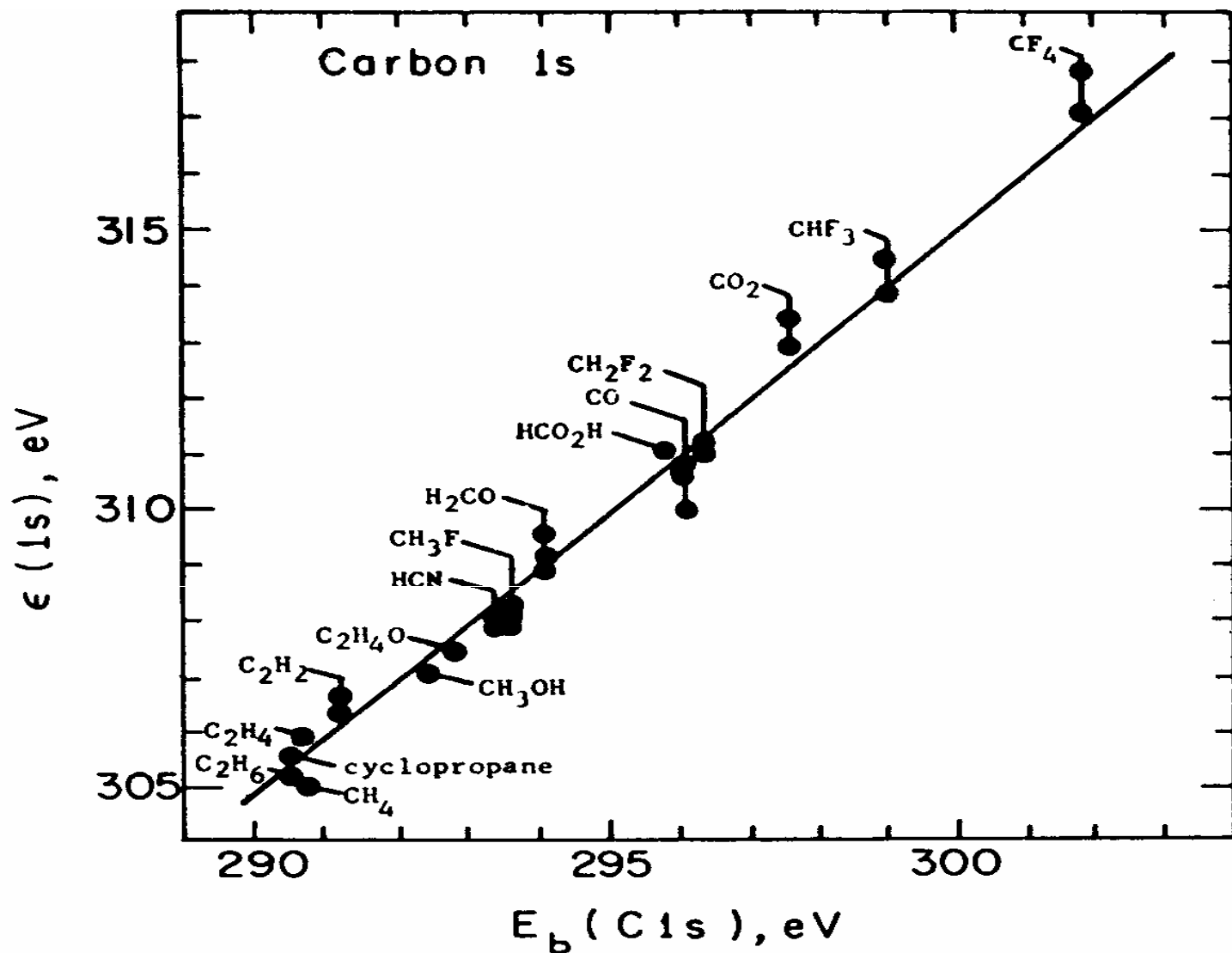


Fig. 18. Plot of carbon 1s binding energies calculated via Koopmans' Theorem against experimental binding energies for several carbon-containing gaseous molecules. For some molecules, more than one calculated value is presented. The slope of the straight line is unity. The two scales are shifted with 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

$$\begin{array}{lll} \text{a) } E_b^v(k) = & E_b^v(k, q_A) & + \quad V \\ \text{Compound} & \text{Free ion of} & \text{Potential due} \\ & \text{charge } q_A & \text{to all other atoms} \\ & V = e^2 \sum_{i \neq A} q_i / r_{iA} & \end{array}$$

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

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

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

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.

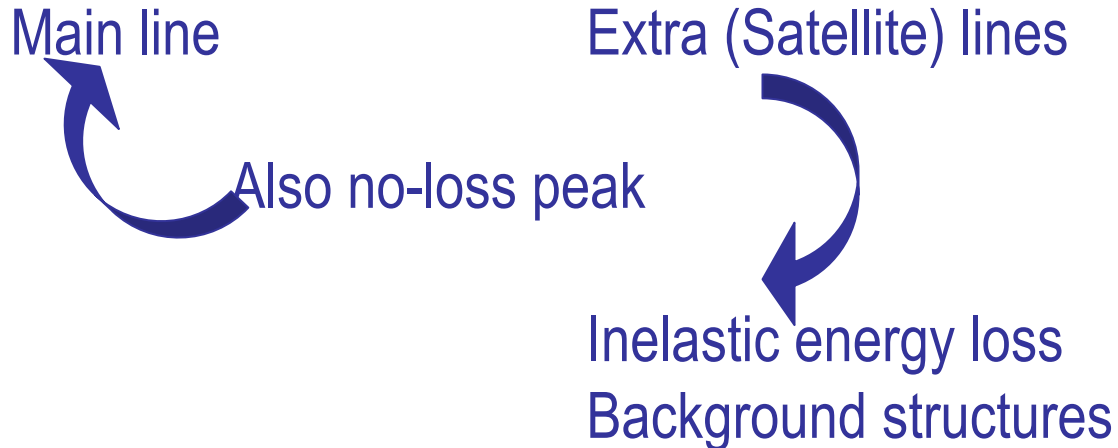
On going from CH_4 to $\text{C}_{13}\text{H}_{28}$ the C1s BE shifts by 0.6eV, the relaxation shift is 2eV.

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 Hartree Fock calculation on ion and neutral.

FINAL STATE EFFECTS: Some more introduction

Electron – Electron Interactions
Coulomb
Exchange



Intrinsic
Extrinsic

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

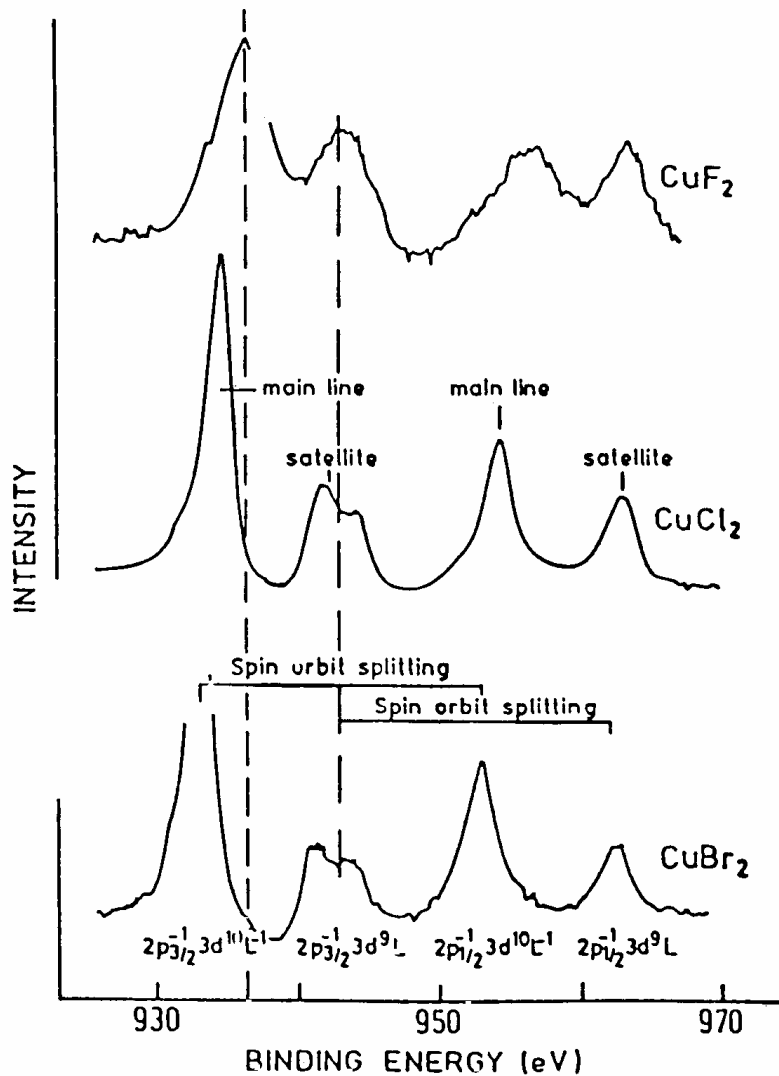
Introduction to final state effects: Cu^{2+}

Cu-di halides:



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

Assuming weak hybridisation between metal ion and ligands



XPS spectra of the 2p core levels of CuF₂, CuCl₂ and CuBr₂. Cu²⁺ has a 3d⁹ 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.

$$(2J_1+1)/(2J_2+2)$$

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

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).