

*Surface and Interface Science*  
*Physics 627; Chemistry 541*

*Lectures 5*  
*Sept 16 2010*

*Surface Chemical Characterization:*  
*X-ray Photoelectron Spectroscopy*

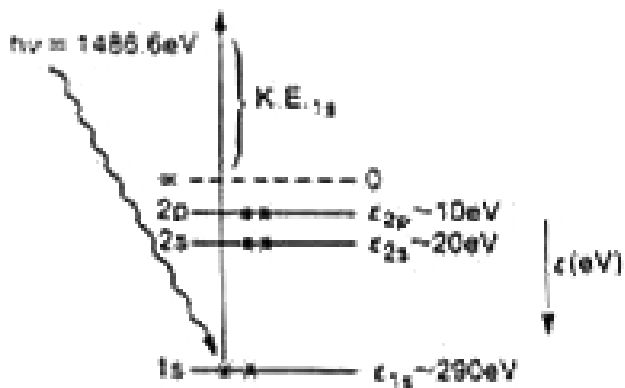
***References:***

- 1) Woodruff & Delchar, Pp. 127-171
- 2) Briggs and Seath, 2<sup>nd</sup> Edition, Vol. 1, Ch. 3, 4, 5
- 3) Ertl & Kupperts, 65 - 83
- 4) Powel and Jablonski, J. Phys. Chem Ref. Data **28**, Pp. 19 – 62 (1999)

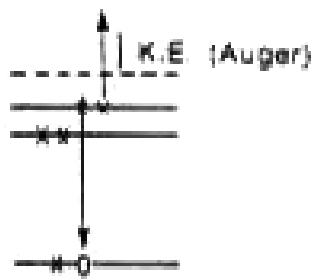
Electrons absorb X-ray photon and are ejected from atom

Energy balance: Photon Energy – Kinetic Energy = Binding Energy

$$h\nu - KE = BE$$

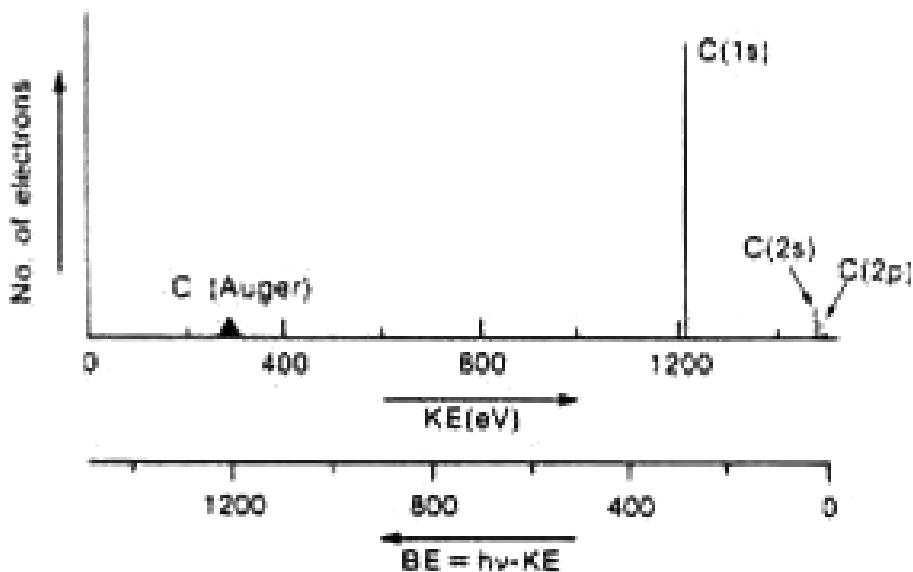


**Photoemission**



**Auger Decay**

- Spectrum = Kinetic energy distribution of photoemitted electrons
- Different orbitals give different peaks in spectrum
- Peak intensities depend on
  - photoionization cross section
  - (largest for C 1s)
- Extra peak: Auger emission

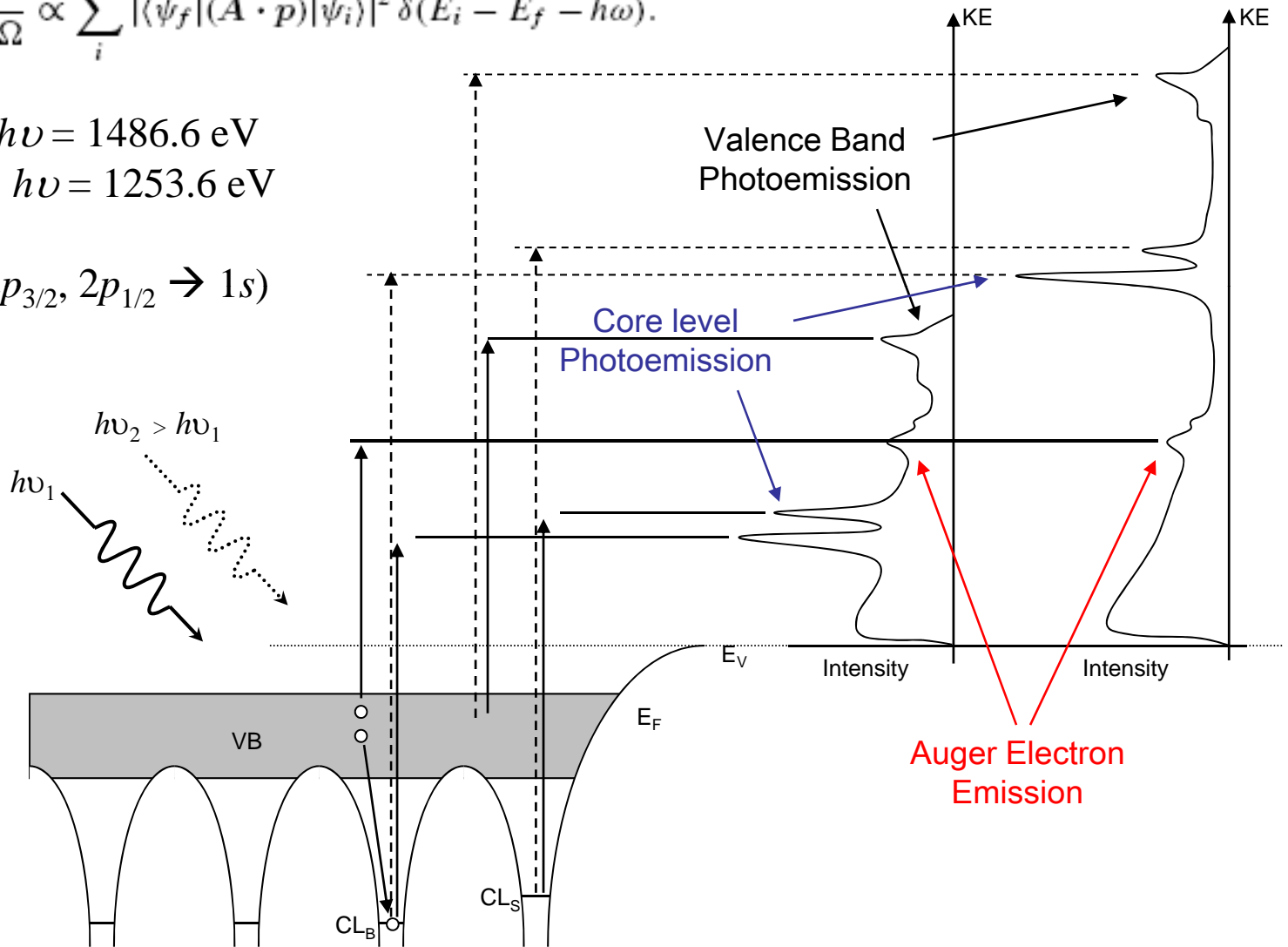


# Photoelectron Spectroscopy

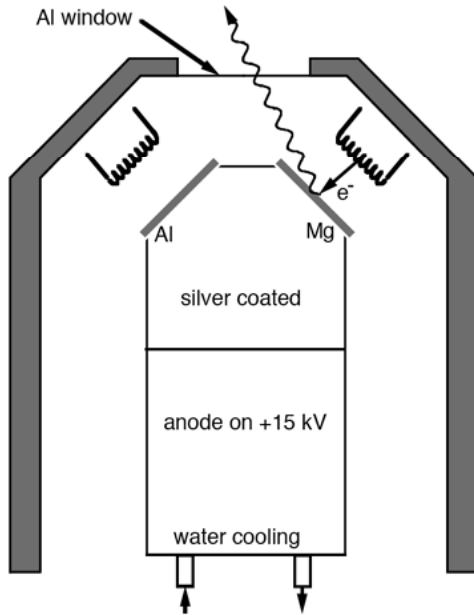
$$\frac{d\sigma}{d\Omega} \propto \sum_i |\langle \psi_f | (A \cdot p) | \psi_i \rangle|^2 \delta(E_i - E_f - \hbar\omega).$$

Al  $K_\alpha$ :  $h\nu = 1486.6 \text{ eV}$   
 Mg  $K_\alpha$ :  $h\nu = 1253.6 \text{ eV}$

( $K_\alpha = 2p_{3/2}, 2p_{1/2} \rightarrow 1s$ )

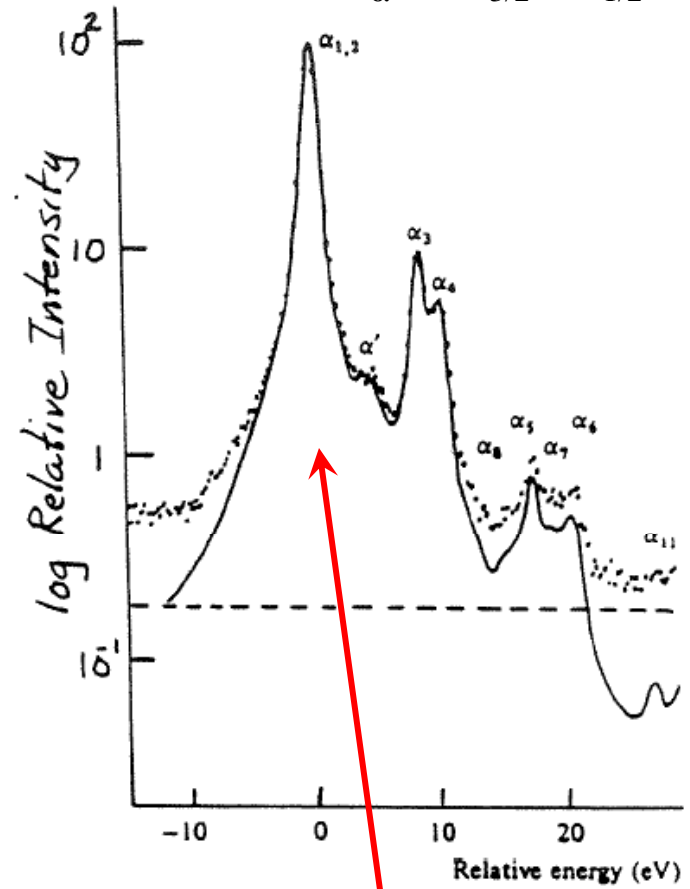


# X-ray Source



Al  $K_\alpha$ :  $h\nu = 1486.6 \text{ eV}$   
 Mg  $K_\alpha$ :  $h\nu = 1253.6 \text{ eV}$

( $K_\alpha = 2p_{3/2}, 2p_{1/2} \rightarrow 1s$ )



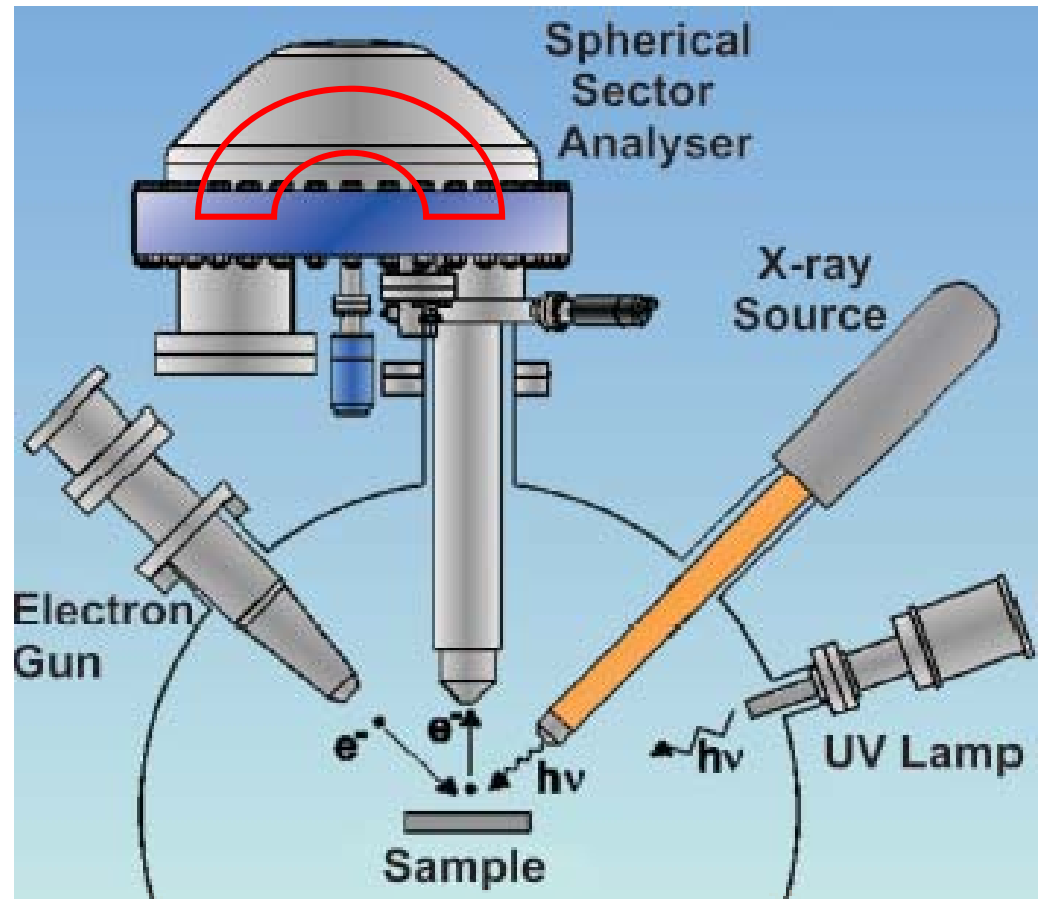
Mg  $K_\alpha$



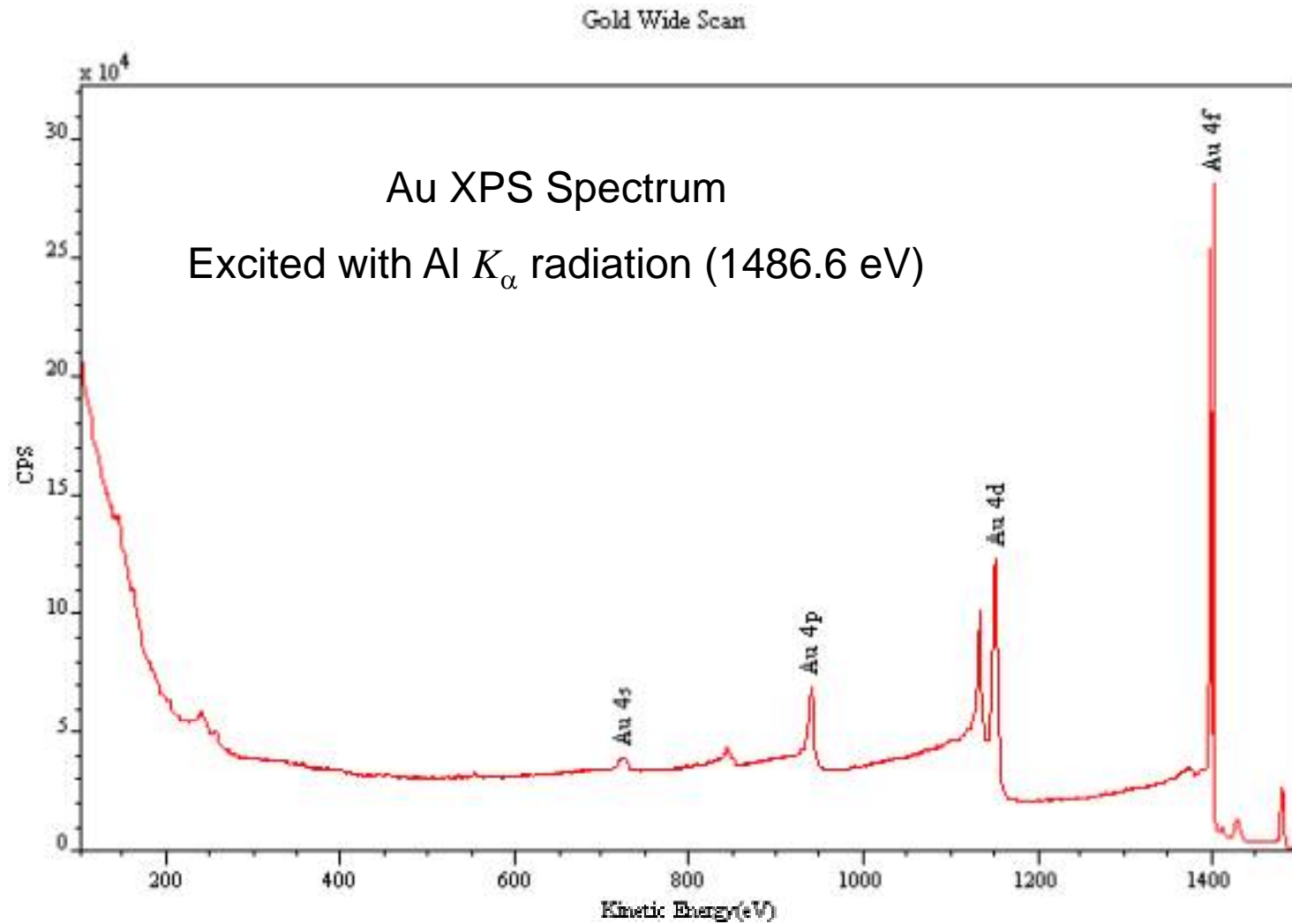
# Instrumentation: How are measurements made?

## Essential components:

- **Sample:** usually 1 cm<sup>2</sup>
- **X-ray source:** Al: 1486.6 eV;  
Mg 1256.6 eV
- **Electron Energy Analyzer:**  
100 mm radius concentric hemispherical analyzer; vary voltages to vary pass energy.
- Detector: electron multiplier (channeltron)
- Electronics, Computer
- Note: All in **ultrahigh vacuum** (<10<sup>-8</sup> Torr) (<10<sup>-11</sup> atm)
- State-of-the-art small spot ESCA: 10 μm spot size.



# Typical XPS spectrum



# X-ray and Spectroscopic Notation

Principal quantum number:

$$n = 1, 2, 3, \dots$$

Orbital quantum number:

$$l = 0, 1, 2, \dots, (n-1)$$

Spin quantum number:

$$s = \pm 1/2$$

Total angular momentum:

$$j = l + s = 1/2, 3/2, 5/2$$

## Spin-orbit split doublets

Table 3.1 X-ray and spectroscopic notation

Quantum numbers			X-ray suffix	X-ray level	Spectroscopic level
$n$	$l$	$j$			
1	0	1/2	1	K	1s <sub>1/2</sub>
2	0	1/2	1	L <sub>1</sub>	2s <sub>1/2</sub>
2	1	3/2	2	L <sub>2</sub>	2p <sub>1/2</sub>
2	1	1/2	3	L <sub>3</sub>	2p <sub>3/2</sub>
3	0	1/2	1	M <sub>1</sub>	3s <sub>1/2</sub>
3	1	3/2	2	M <sub>2</sub>	3p <sub>1/2</sub>
3	1	1/2	3	M <sub>3</sub>	3p <sub>3/2</sub>
3	2	5/2	4	M <sub>4</sub>	3d <sub>3/2</sub>
3	2	3/2	5	M <sub>5</sub>	3d <sub>5/2</sub>
	etc.		etc.	etc.	etc.

Table 3.5 Spin-orbit splitting parameters

Subshell	$j$ values	Area ratio
s	1/2	—
p	1/2, 3/2	1 : 2
d	3/2, 5/2	2 : 3
f	5/2, 7/2	3 : 4

## Peak width:

$\Delta E$  measured as FWHM; if assume Gaussian:

$$\Delta E = (\Delta E^2_{\text{natural}} + \Delta E^2_{\text{photons}} + \Delta E^2_{\text{analyzer}})^{1/2}$$

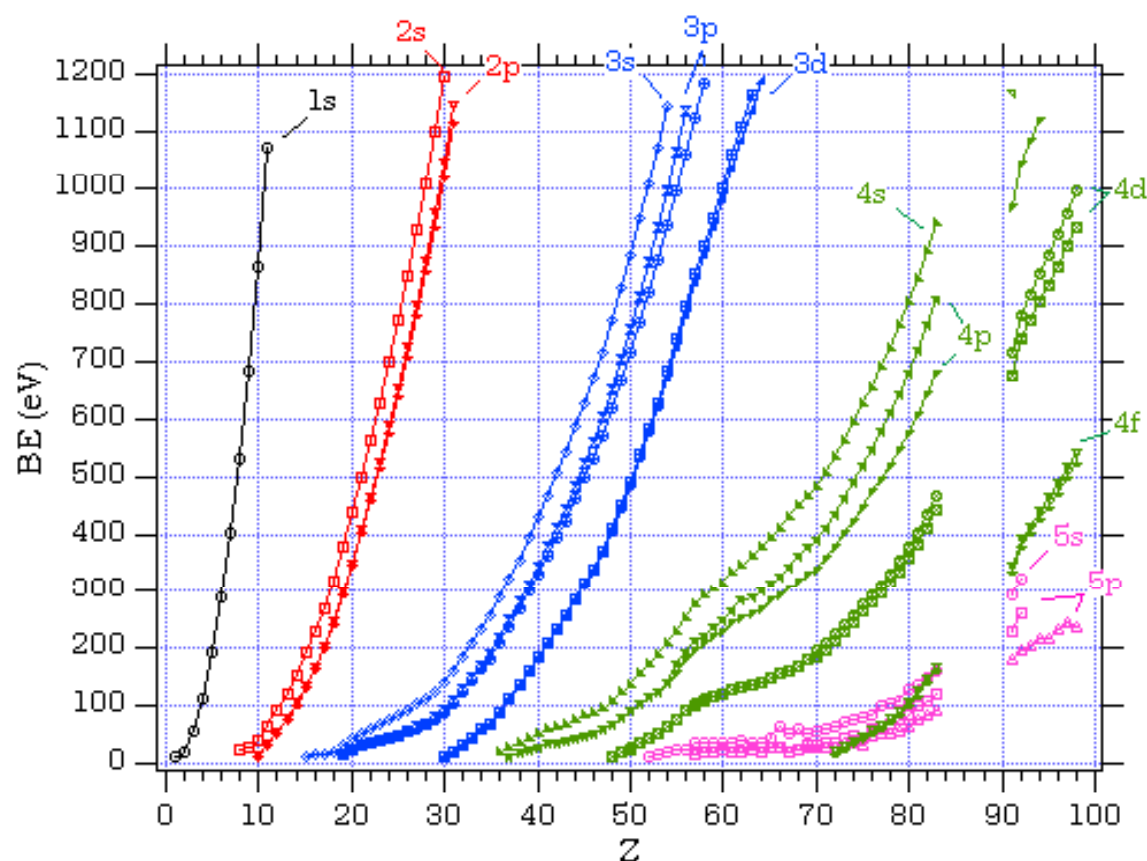
Lifetime width:  $\Gamma = \hbar/\tau$  for  $\Gamma \sim 1$  eV,  $\tau \sim 10^{-15}$  s

# Peak Identification: Core level Binding Energies

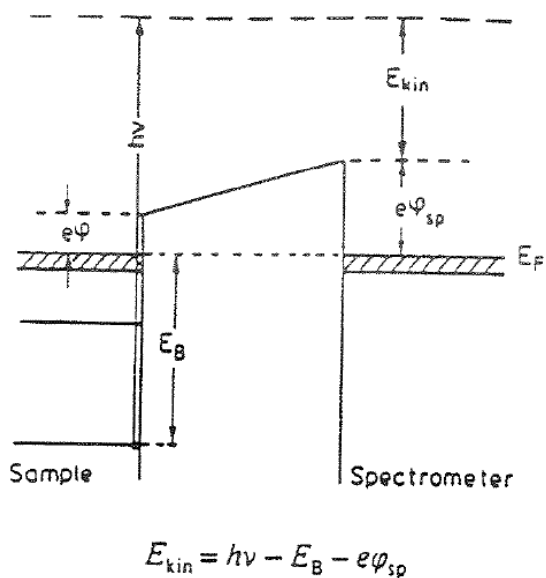
## XPS Photoelectron Binding Energies\* versus Atomic Number

Where the same BE is quoted for different spin-orbit split subshells, the individual subshells are either not resolved or have a complex structure. Spin-orbit coupling:  $2p_{1/2}$ ,  $2p_{3/2}$  etc.

Z	1s	2s	2p <sub>1</sub>	2p <sub>3</sub>	3s	3p <sub>1</sub>	3p <sub>3</sub>	3d <sub>3</sub>	3d <sub>5</sub>	4s	4p <sub>1</sub>	4p <sub>3</sub>	4d <sub>3</sub>	4d <sub>5</sub>	4f <sub>5</sub>	4f <sub>7</sub>	5s	5p <sub>1</sub>	5p <sub>3</sub>	
1	14																			
2	21																			
3	56																			
4	113																			
5	191																			
6	287																			
7	402																			
8	531	23																		
9	686	30																		
10	863	41	14	14																
11	1072	64	31	31																
12		90	51	51																
13		119	74	74																
14		153	103	102																
15		191	134	133	14															
16		229	166	165	17															
17		270	201	199	17															
18		319	243	241	22															
19		378	296	293	33	17	17													
20		439	350	347	44	25	25													
21		501	407	402	53	31	31													
22		565	464	458	62	37	37													
23		630	523	515	69	40	40													
24		698	586	577	77	46	45													
25		770	652	641	83	49	48													
26		847	723	710	93	56	55													



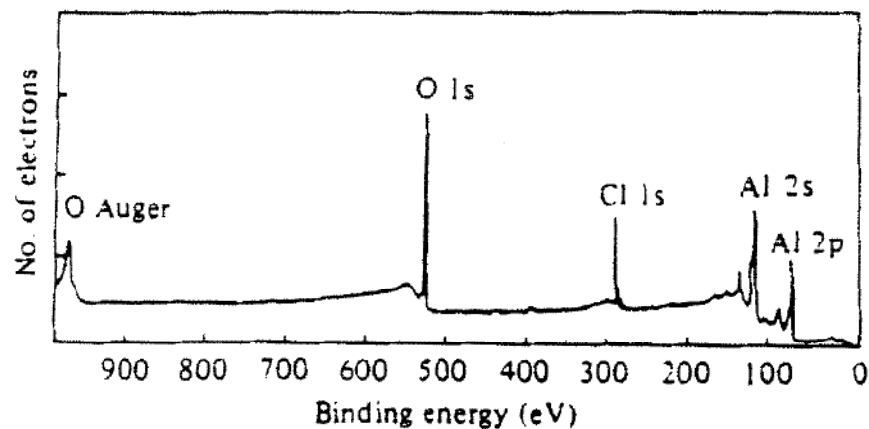
# Measuring Spectra: Typical spectral features



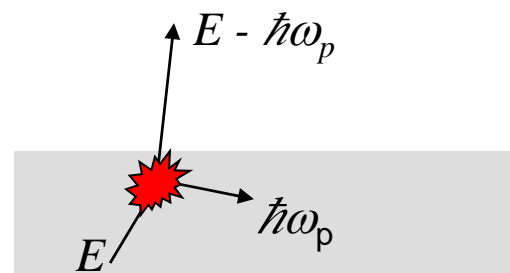
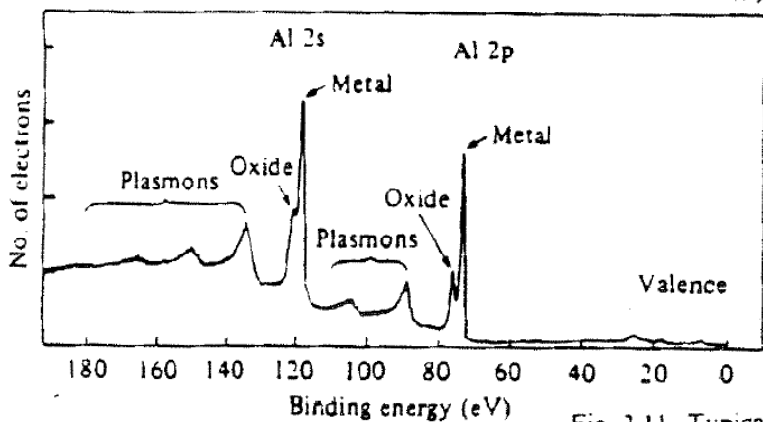
As sample and analyzer are in electrical contact, Fermi levels align.

$$KE_{PE} + e\phi_{analyzer} = h\nu$$

## The big picture: Elemental Identification



## Zoom in: Chemical shifts, plasmons



## Measuring Spectra: Typical spectral features

Associate binding energies with orbital energies, BUT USE CAUTION!!!,

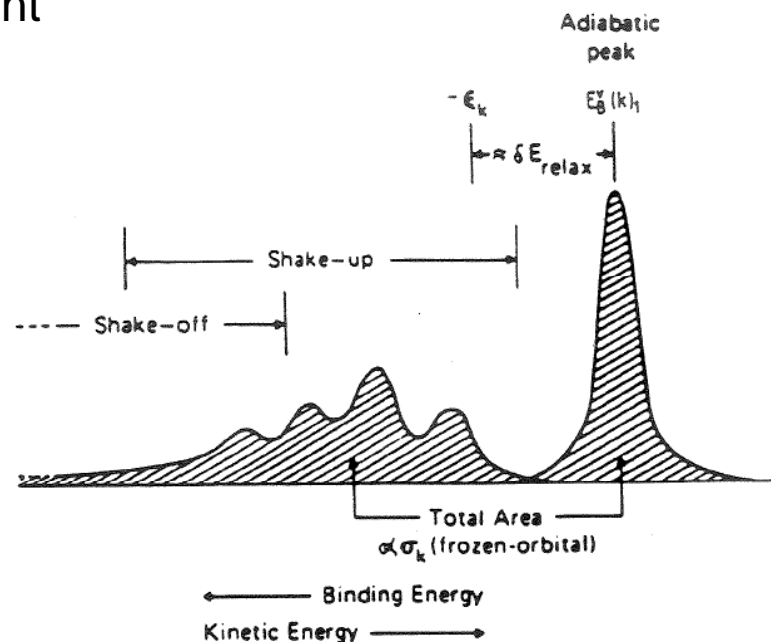
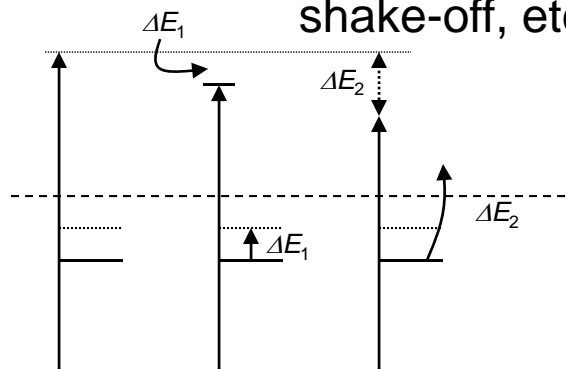
$$\begin{aligned} \text{Energy conservation: } E_i(N) + h\nu &= E_f(N-1) + \text{KE} \\ \rightarrow h\nu - \text{KE} &= E_f(N-1, k) - E_i(N) = E_B \end{aligned}$$

Binding energy is more properly associated with ionization energy.

In HF approach, Koopmans' Theorem:  $E_B = \epsilon_k$  (orbital energy of  $k^{\text{th}}$  level)  
Formally correct within HF. Wrong when correlation effects are included.

ALSO: Photoexcitation is rapid event  
 $\rightarrow$  sudden approximation

Gives rise to shake-up,  
shake-off, etc...



# Measuring Spectra: Qualitative results

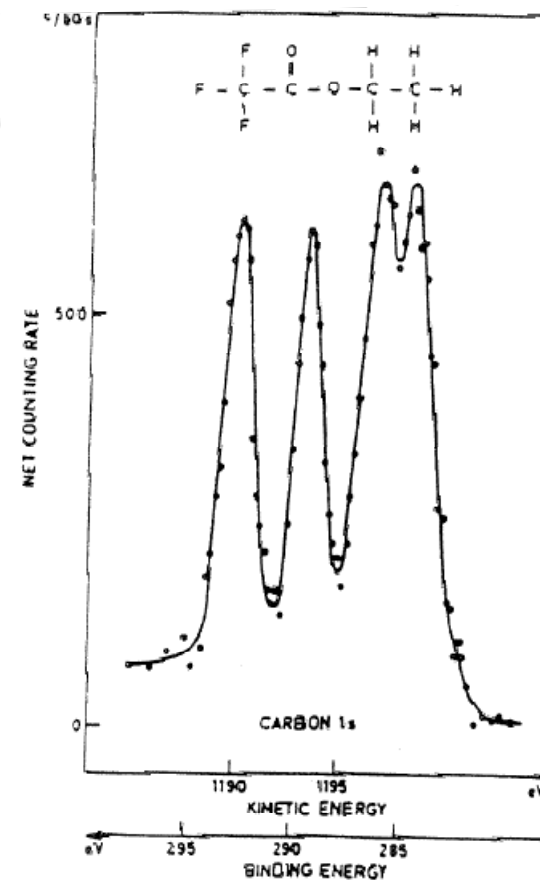
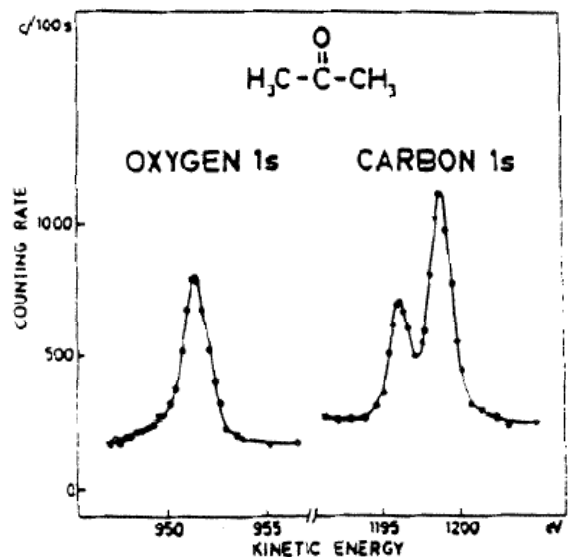
A: Identify Element

B: Chemical shifts of core levels:

Consider core levels of the same element in different chemical states:

$$\Delta E_B = E_B(2) - E_B(1) = E_K(2) - E_K(1)$$

Often correct to associate  $\Delta E_B$  with change in local electrostatic potential due to change in electron density associated with chemical bonding ("initial state effects"). **Caution:** Not always the case, so be careful!!!



## Measuring Spectra: Qualitative results

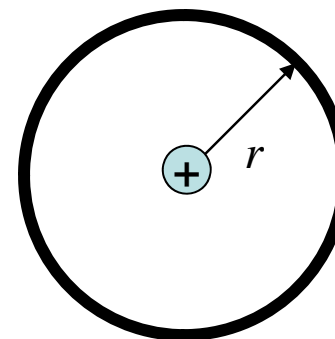
Estimate chemical shift:

If charge  $q$  is added to  
(or removed from) valence shell,  
then potential inside changed by:

$$\Delta E = q/r$$

Where  $\Delta E = E_i - E_i^0$

Here  $E_i^0$  = reference level;  $E_i$  = binding energy of core level



Plug in typical numbers:  $\Delta E \sim 5 - 10$  eV.

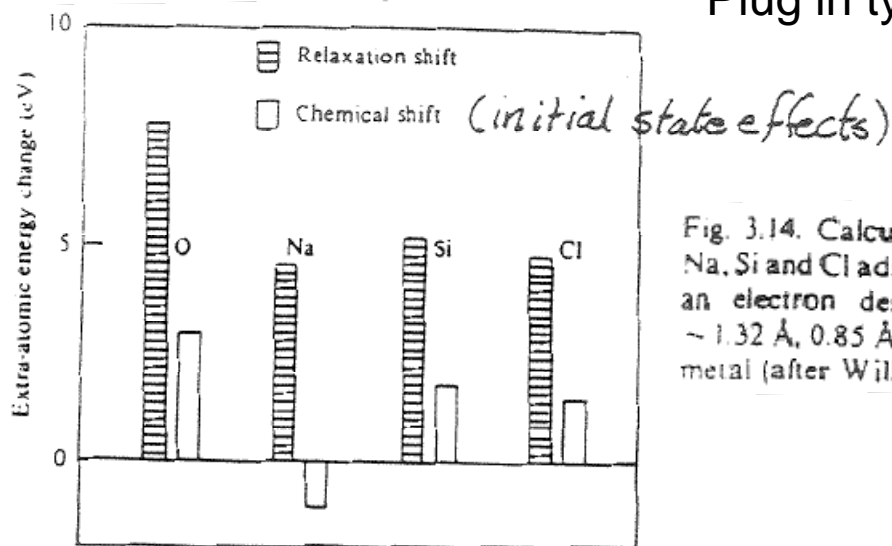
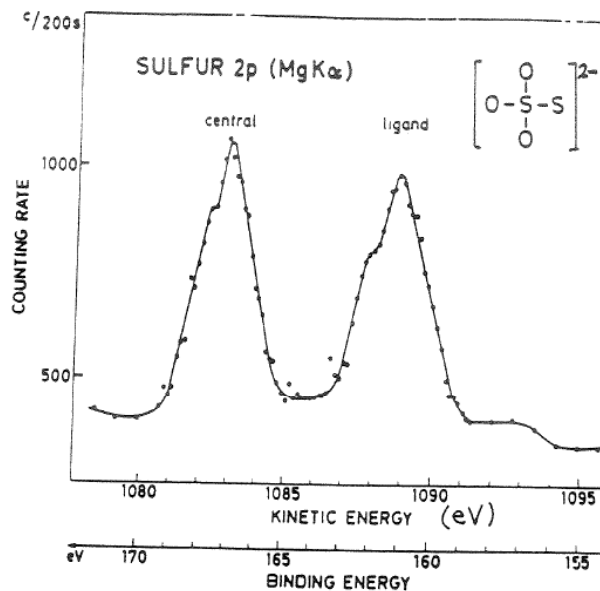


Fig. 3.14. Calculated extra-atomic relaxation shifts and chemical shifts for O, Na, Si and Cl adsorbed on jellium - an ideal smooth free electron surface having an electron density appropriate to Al. Metal-adsorbent separations were  $\sim 1.32$  Å,  $0.85$  Å and  $0.80$  Å for Na, Si and Cl while O was placed inside the metal (after Williams & Lang, 1977).

**BUT USE CAUTION!!!**

# Measuring Spectra: Qualitative results



Initial state shifts

Trends

Fingerprinting

Sometimes even agrees well with Koopmans' theorem

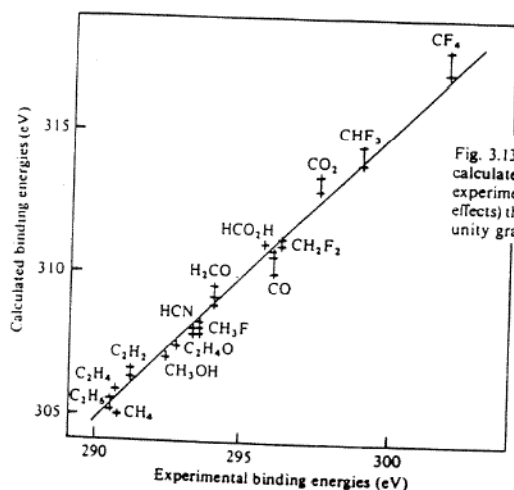


Fig. 3.13. Comparison of experimental XPS C 1s binding energies with those calculated via Koopman's theorem for C in a range of molecules. Although experimental and theoretical values differ by 15 eV (associated with relaxation effects) the systematic comparison is excellent as indicated by the straight line of unity gradient (after Shirley, 1973).

Chemical shift of C 1s varies systematically with initial state calculations.

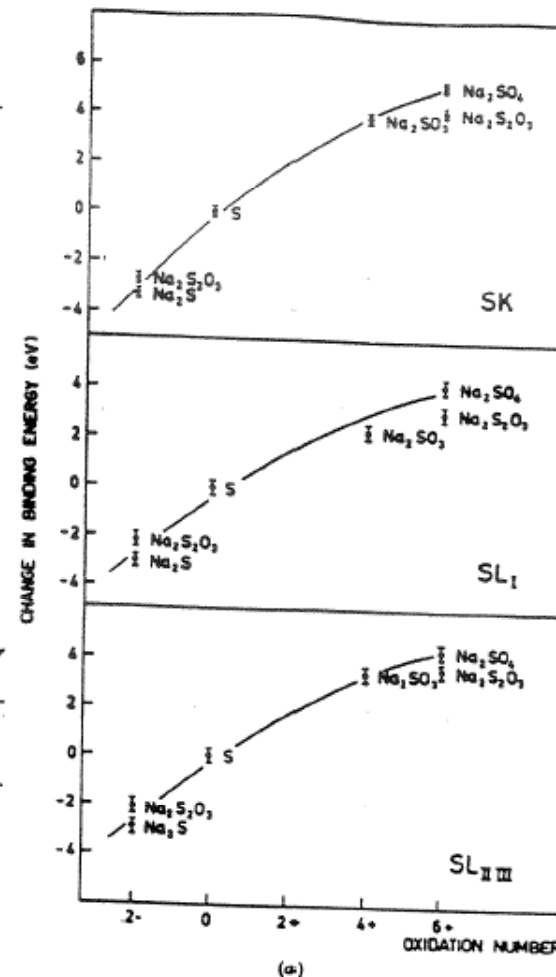


Fig. V:18. Chemical shifts in the K and L shells of sulfur versus oxidation number in a series of inorganic compounds with sodium (a) and potassium (b) as cations.<sup>66</sup>

## Measuring Spectra: Quantitative analysis

Estimate chemical concentration, chemical state, spatial distribution of surface species

Often assumed that sample is in single phase. May be very far from truth.

Current state-of-the-art small-spot XPS systems have spatial resolution in the nm range. Specializing in spectromicroscopy, but at the sacrifice of versatility.

More standard modern systems can operate in the  $\mu\text{m}$  range.

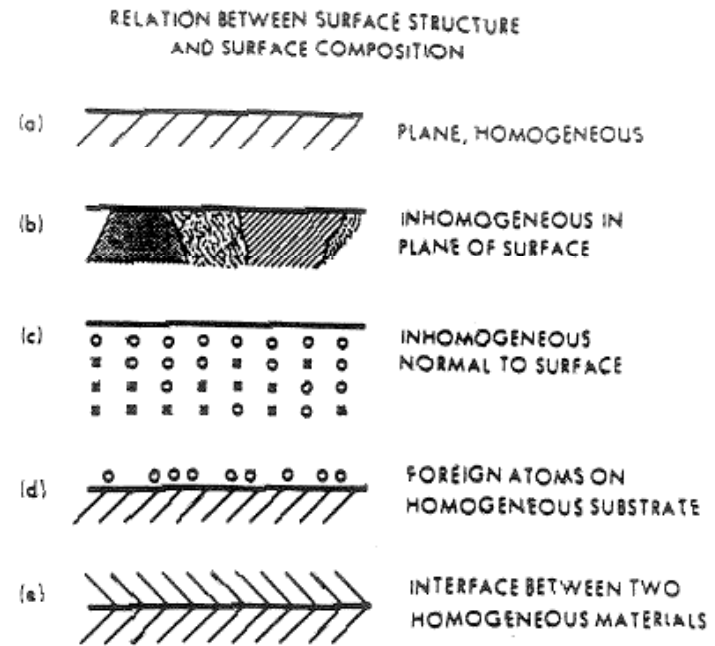
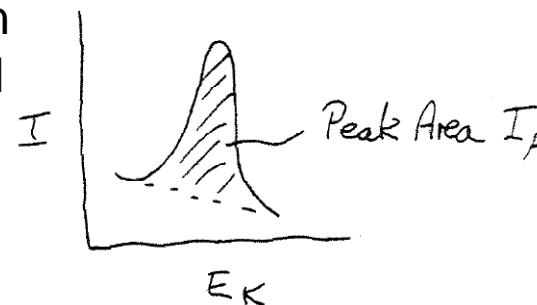


FIG. 1. Idealized surface structures: (a) plane homogeneous surface; (b) a surface with lateral inhomogeneities consisting of several different surface phases; (c) a surface with depth inhomogeneities (the circles and the crosses represent different types of atoms); (d) a surface phase consisting of a submonolayer of foreign atoms on an otherwise homogeneous surface; and (e) an interface between two homogeneous bulk phases (Ref. 1).

## Measuring Spectra: Quantitative analysis

Primary assumption for quantitative analysis: Ionization probability (photoemission cross section) of a core level is nearly independent of valence state for a given element.

→ Intensity  $\propto$  number of atoms in detection volume.



$$I_A = \sigma_A(\hbar\omega)D(E_A) \int_{\gamma=0}^{\pi} \int_{\varphi=0}^{2\pi} L_A(\gamma) \iint_{x,y} J_o(x,y) T(x,y,\gamma,\varphi,E_A) \int_z N_A(x,y,z) \exp\left[-\frac{z}{\lambda_M(E_A)\cos\theta}\right] dx dy dz d\gamma d\theta$$

Where:

$\sigma_A$  = photoionization cross section

$D(E_A)$  = detection efficiency of spectrometer at  $E_A$

$L_A(\gamma)$  = angular asymmetry of photoemission intensity

$\gamma$  = angle between incident X-rays and detection

$J_o(x,y)$  = flux of primary photons onto surface at point  $(x,y)$

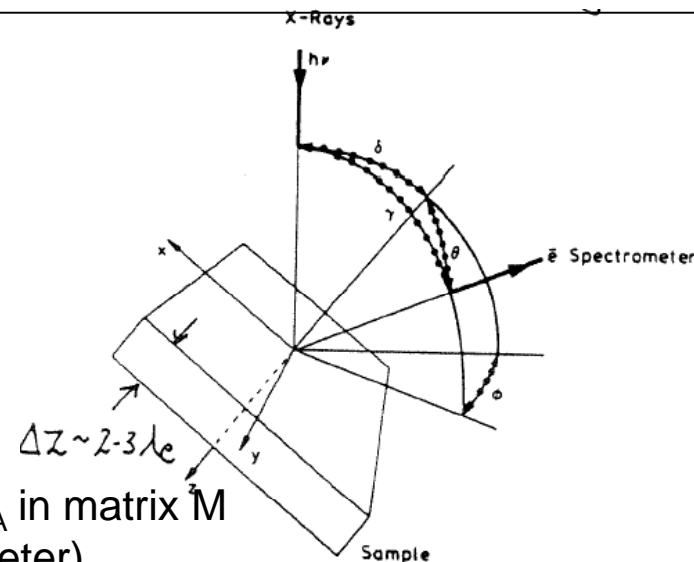
$T$  = Analyzer transmission

$\phi$  = Azimuthal angle

$N_A(x,y,z)$  = density of A atoms at  $(x,y,z)$

$\lambda_M$  = electron attenuation length of electrons with energy  $E_A$  in matrix M

$\theta$  = detection angle (between sample normal and spectrometer)



# Measuring Spectra: Quantitative analysis

For small entrance aperture (fixed  $\phi$ ,  $\gamma$ ) and uniformly illuminated sample :

$$I_A = \sigma_A(\hbar\omega)D(E_A)L_A(\gamma_i)J_oN_A\lambda_M(E_A)\cos\theta_iG(E_A)$$

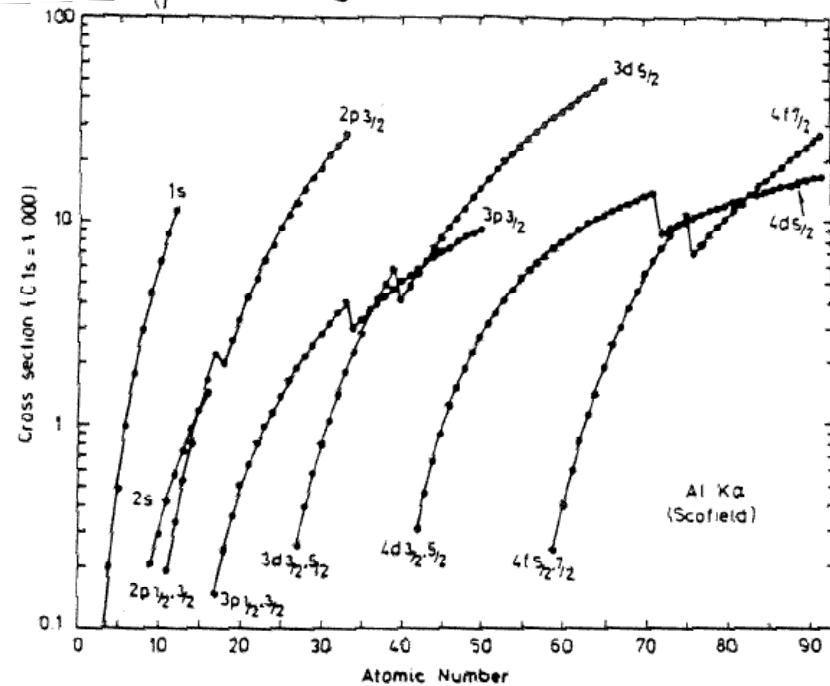
Angles  $\gamma_i$  and  $\theta_i$  are fixed by the sample geometry, and:

$$G(E_A) = \iint_{x,y} T(x, y, E_A) dx dy$$

$G(E_A)$  = product of area analyzed and analyzer transmission function (“étendue”)

Consider each factor in the equation above:

- $D(E_A)$  = constant for spectrometers operating at fixed pass energy
- $\sigma_A$  : well described by Scofield calculation of cross section:



5.14 Calculated values of the cross-section  $\sigma_A(h\nu)$  for Al  $K\alpha$  radiation in terms of the C 1s cross-section. (After Scofield<sup>26</sup>)

# Measuring Spectra: Quantitative analysis

- For photoelectrons ejected by unpolarized X-rays, angular asymmetry factor is:

$$L_A(\gamma) = 1 + \frac{1}{2} \beta_A \left( \frac{3}{2} \sin^2 \gamma - 1 \right)$$

Where  $-1 \leq \left( \frac{3}{2} \sin^2 \gamma - 1 \right) \leq +\frac{1}{2}$

[Know  $\beta$ , calculate  $L_A(\gamma_i)$ ]

- For spectrometers operating in retarding mode:  $G(E_A) \sim 1/E_A$

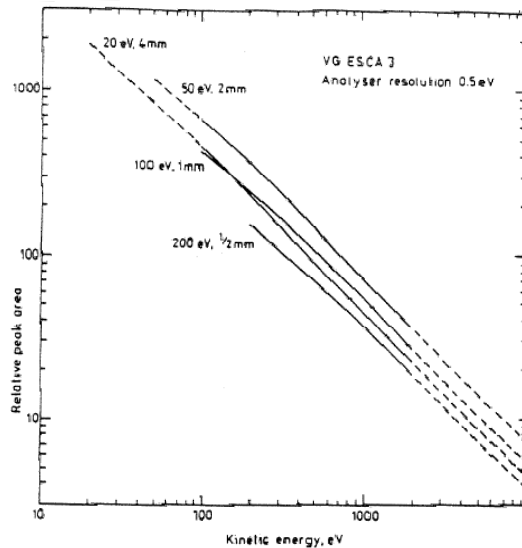


Figure 5.17 The transmitted peak area intensity as a function of kinetic energy for various slit widths and pass energies giving an analyser resolution of 0.5 eV in the VG Scientific ESCA 3. (After Seah<sup>27</sup>)

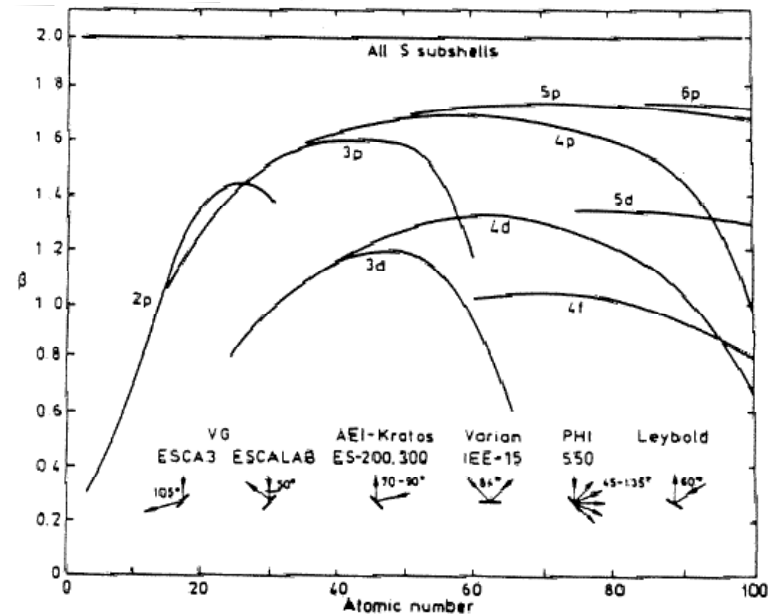


Figure 5.15 Calculated values of  $\beta$ . (After Reilman, Msezane and Manson. <sup>43</sup>) Typical commercial configurations are shown in the lower part of the diagram.

So, for pure element, this leads to

$$I_A^o = \frac{B \sigma_A L_A(\gamma_i) N_A^o \lambda_M(E_A)}{E_A}$$

B is proportionality constant that can be eliminated by setting a reference peak to have unit intensity.

## Measuring Spectra: Quantitative analysis

EXAMPLES: Assume two components, A and B, in the surface region

Case I: A and B form homogeneous solid solution:



Want relative concentration of A and B =  $\chi_A/\chi_B$  where  $\chi_A$  = atomic fraction of A .

Compare  $I_A$  for solid solution AB with  $I_A^o$  for pure element:

$$\text{For A have: } \frac{I_A}{I_A^o} = \frac{N_A \lambda_{AB}(E_A)}{N_A^o \lambda_A(E_A)} \quad \text{Similarly, for B: } \frac{I_B}{I_B^o} = \frac{N_B \lambda_{AB}(E_B)}{N_B^o \lambda_B(E_B)}$$

Now,  $\lambda_M$  is well approximated by:  $\lambda_M = c_M E_M^{0.5} \cong 0.41 a_M^{1.5} E_M^{0.5}$  [where  $a_M, \lambda_M$  in nm and  $E_M$  in eV]

Furthermore,  $N_A^o = a_A^{-3}$  and  $N_A = a_{AB}^{-3} \chi_A$  (atoms/nm<sup>3</sup>)

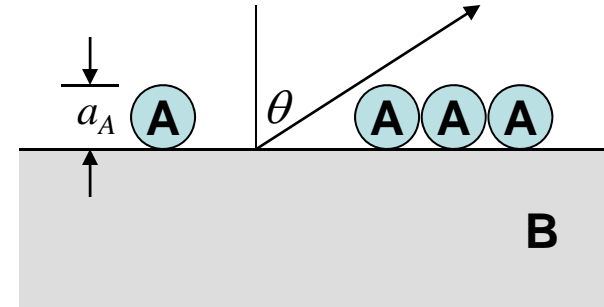
$$\text{Therefore: } \frac{N_A / N_A^o}{N_B / N_B^o} = \frac{\chi_A}{\chi_B} \left( \frac{a_A}{a_B} \right)^3 \quad \text{or, in terms of } I_A \text{ and } I_B \quad \frac{\chi_A}{\chi_B} = \left( \frac{a_B}{a_A} \right)^{1.5} \frac{I_A / I_A^o}{I_B / I_B^o} = \left( \frac{I_A}{I_B} \right) \left( \frac{a_B}{a_A} \right)^{1.5} \left( \frac{I_B^o}{I_A^o} \right)$$

[best to use ref. standards from own spectrometer]

## Measuring Spectra: Quantitative analysis

Case II: Fractional monolayer of A on B:

[Let  $\Theta_A$  = fractional coverage of A]



$I_B$  contribution:  $(1-\Theta_A)I_B^o$  contribution from exposed portion of surface

$\Theta_A I_B^o \exp\left[-\frac{a_A}{\lambda_A(E_B) \cos \theta}\right]$  contribution from beneath overlayer

$$\text{So: } I_B = I_B^o \left\{ 1 - \Theta_A + \Theta_A \exp\left[-\frac{a_A}{\lambda_A(E_B) \cos \theta}\right] \right\}$$

$$\text{Signal from overlayer: } I_A = \Theta_A I_A^o \left\{ 1 - \exp\left[-\frac{a_A}{\lambda_A(E_A) \cos \theta}\right] \right\}$$

$$\text{Which yields: } \frac{I_A}{I_B} = \frac{I_A^o}{I_B^o} \frac{\Theta_A \left\{ 1 - \exp\left[-\frac{a_A}{\lambda_A(E_A) \cos \theta}\right] \right\}}{1 - \Theta_A \left\{ 1 - \exp\left[-\frac{a_A}{\lambda_A(E_B) \cos \theta}\right] \right\}}$$

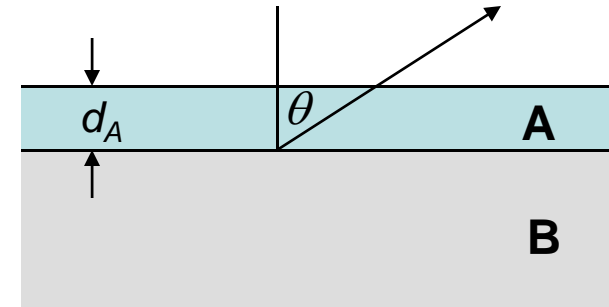
## Measuring Spectra: Quantitative analysis

Case III: Overlayer of thickness  $d_A$  of A on B:

Substrate:  $I_B = I_B^o \exp\left[-\frac{d_A}{\lambda_A(E_B) \cos \theta}\right]$

Overlayer:  $I_A = I_A^o \left\{1 - \exp\left[-\frac{d_A}{\lambda_A(E_A) \cos \theta}\right]\right\}$

So:  $\frac{I_A / I_A^o}{I_B / I_B^o} = \frac{\left\{1 - \exp\left[-\frac{d_A}{\lambda_A(E_A) \cos \theta}\right]\right\}}{\left\{\exp\left[-\frac{d_A}{\lambda_A(E_B) \cos \theta}\right]\right\}}$



If two core levels have similar binding energy, then:  $\lambda_A(E_A) \sim \lambda_B(E_B)$

Which yields:  $\frac{I_A / I_A^o}{I_B / I_B^o} \approx \left\{ \exp\left[\frac{d_A}{\lambda_A(E_A) \cos \theta}\right] - 1 \right\}$  and thus:  $d_A \approx \lambda_A(E_A) \cos \theta \ln \left[ 1 + \frac{I_A / I_A^o}{I_B / I_B^o} \right]$