

Lectures 12

Understanding surfaces



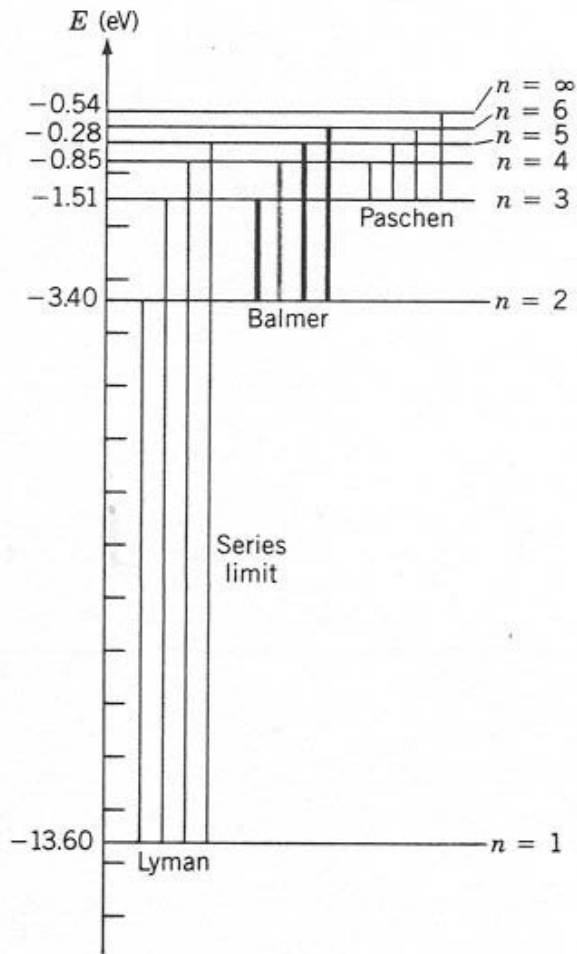
Surface science is an important component in physical sciences

Energy, chemicals, pharmaceuticals,....

Electron spectroscopy is the most important surface analysis tool

Kai M. Siegbahn (1918 - 2007)

Nobel Prize 1981 – High Resolution Electron Spectroscopy

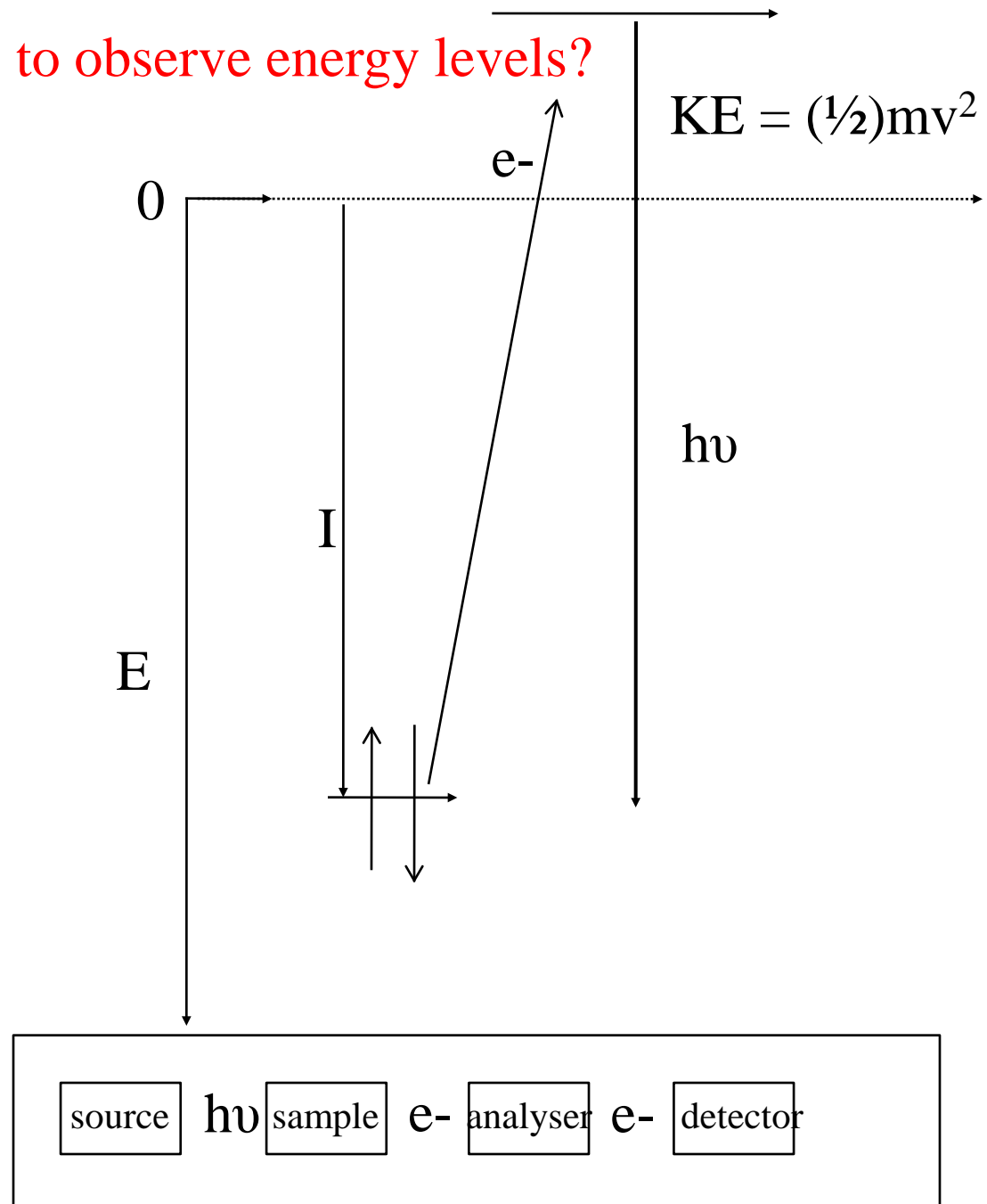


How to observe energy levels?

$$I = h\nu - \frac{1}{2}mv^2$$

Photoelectron equation

Koopmans' theorem



Structure and Properties of Matter

Spectroscopy

Scattering

Physical Properties

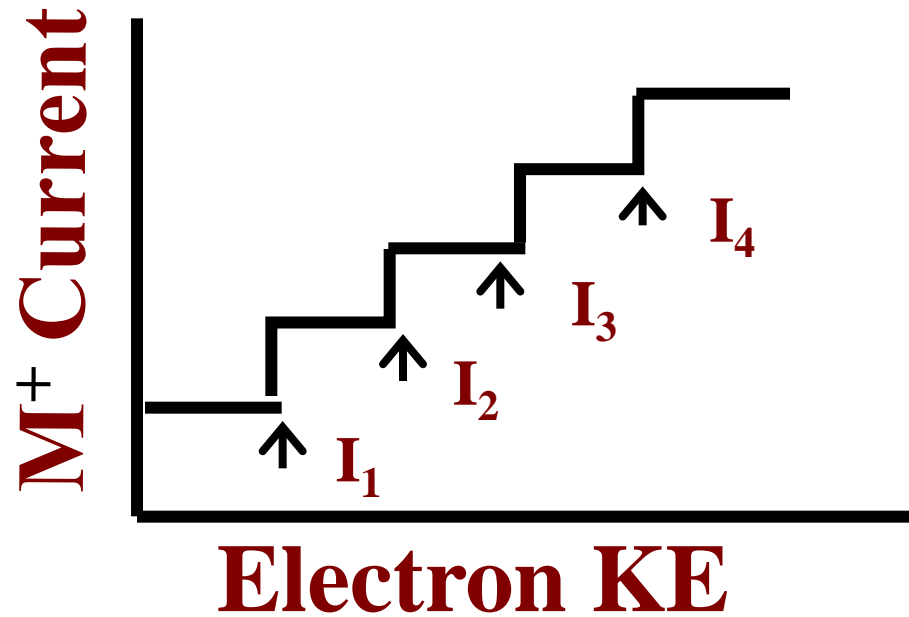
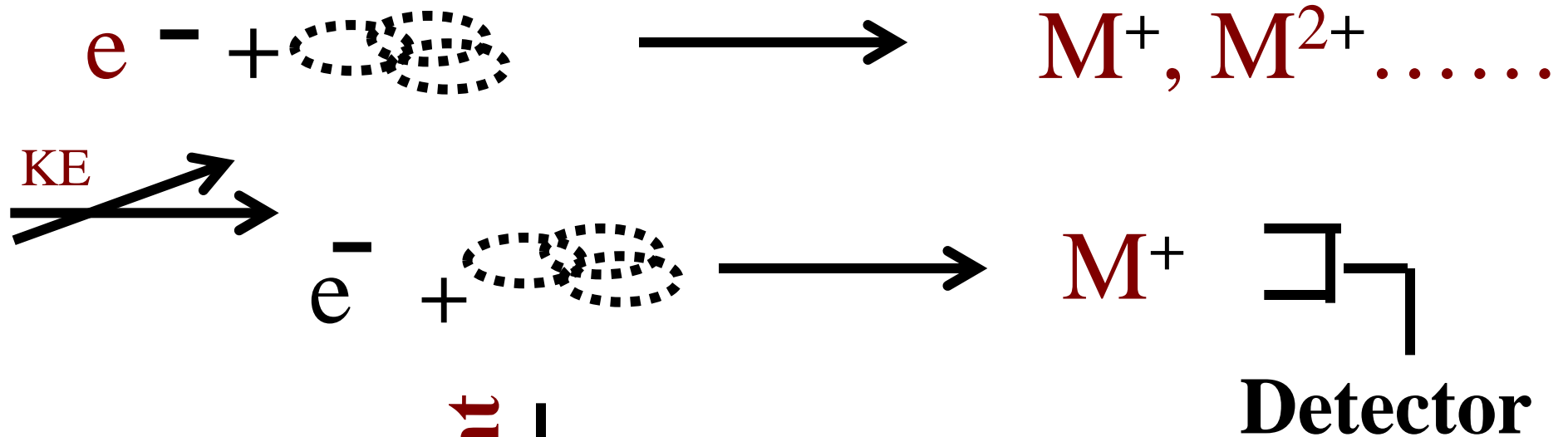
Spectroscopy (pre-1965)

Absorption

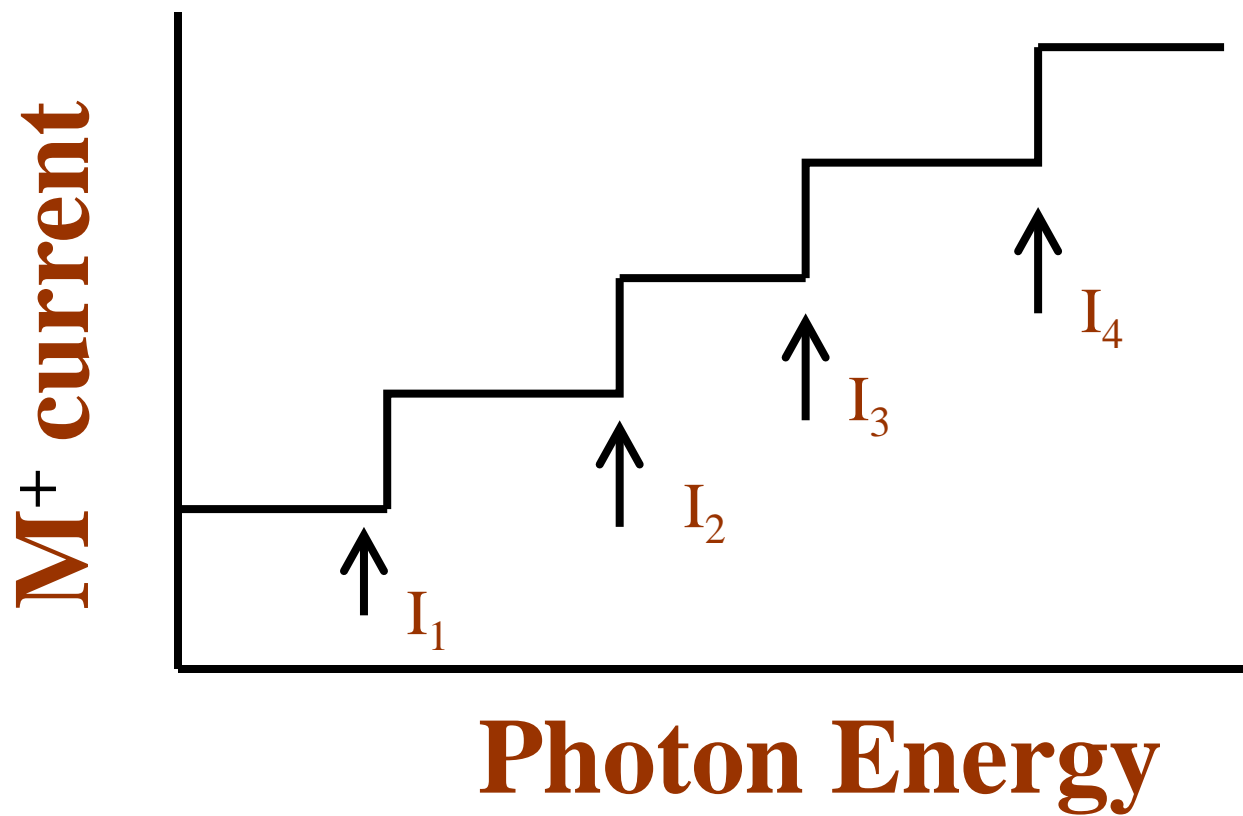
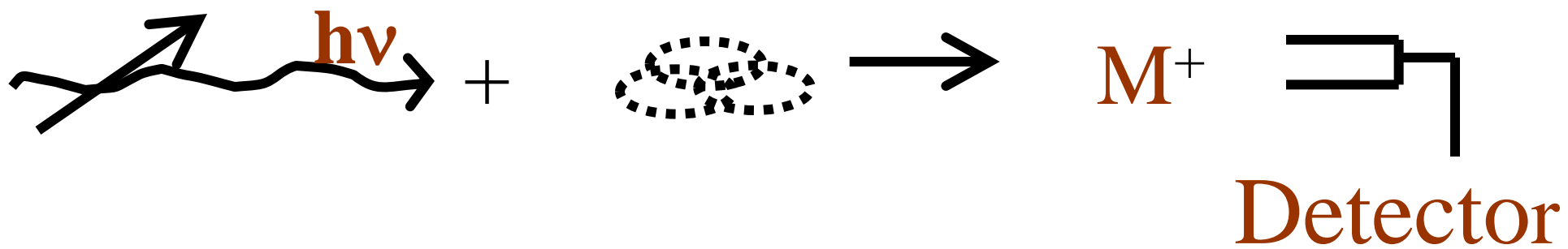
Magnetic

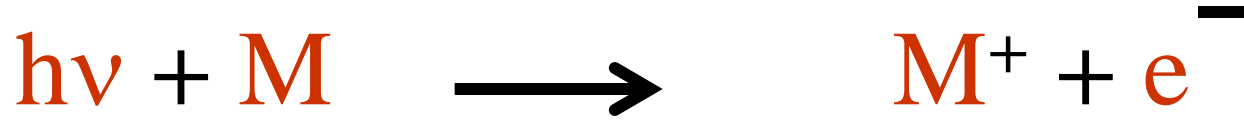
Mass

Spectroscopy using electrons

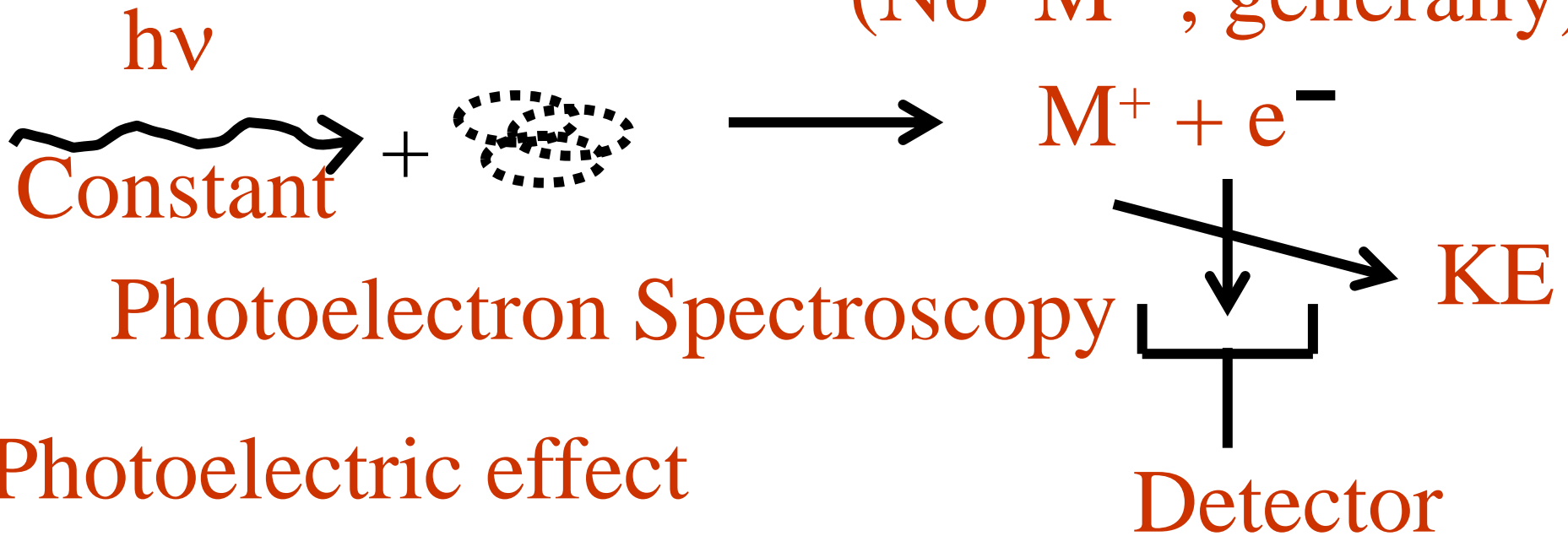


Ionization efficiency curves





(No M^{2+} , generally)



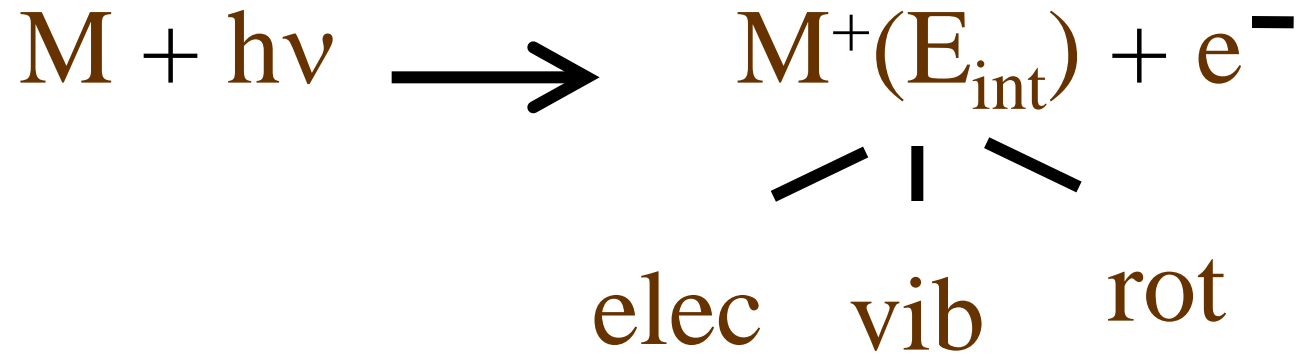
Photoelectron Spectroscopy

Photoelectric effect

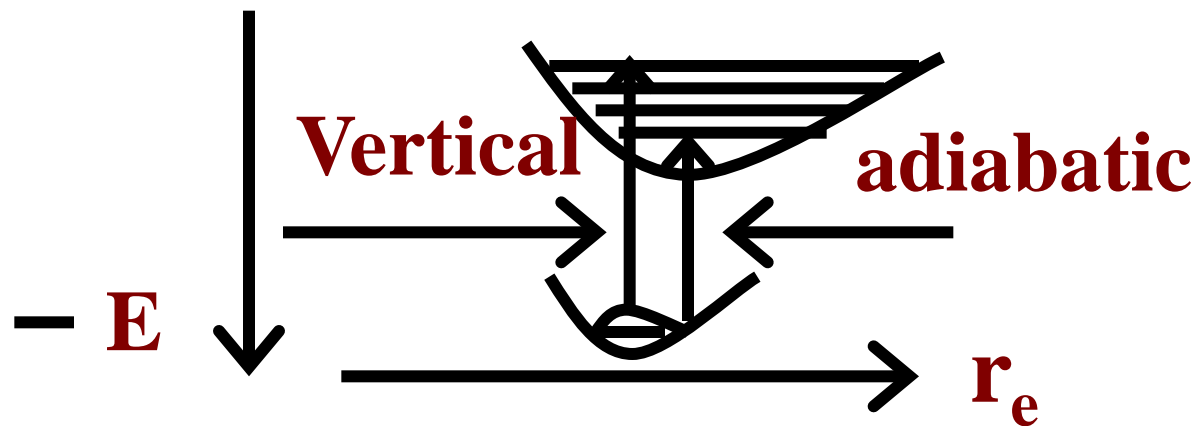
Early experiments in 1887

$$h\nu = KE + \phi \quad 1905$$

Photoion can be excited



$$h\nu - I - E_{\text{int}} = \text{KE of the electron}$$



$$h\nu - KE_1$$

$$h\nu - KE_2$$

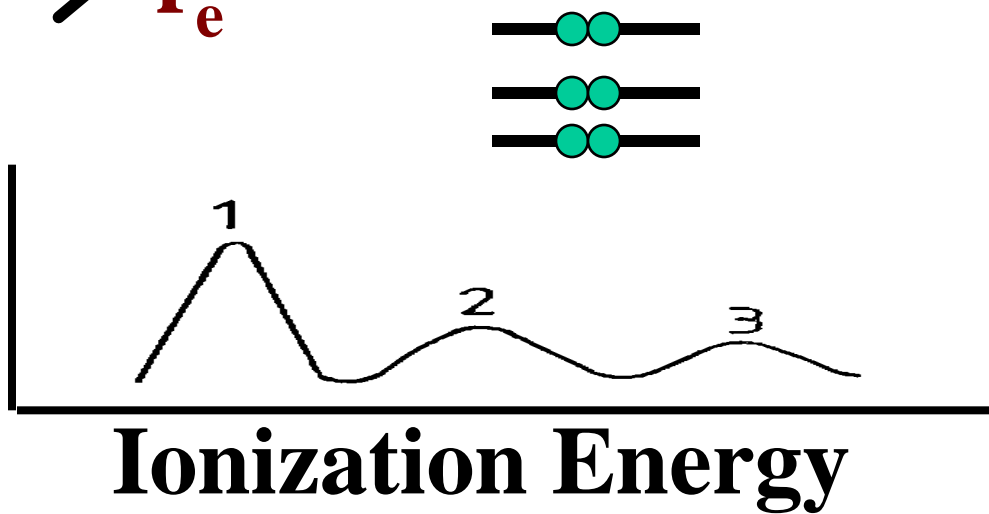
$$h\nu - KE_3$$

$$IP_1$$

$$IP_2$$

$$IP_3 \dots\dots$$

Counts / sec



Depth of analysis depends on photon energy

energy

He I 21.2 eV $2^1P \rightarrow 1^1S$

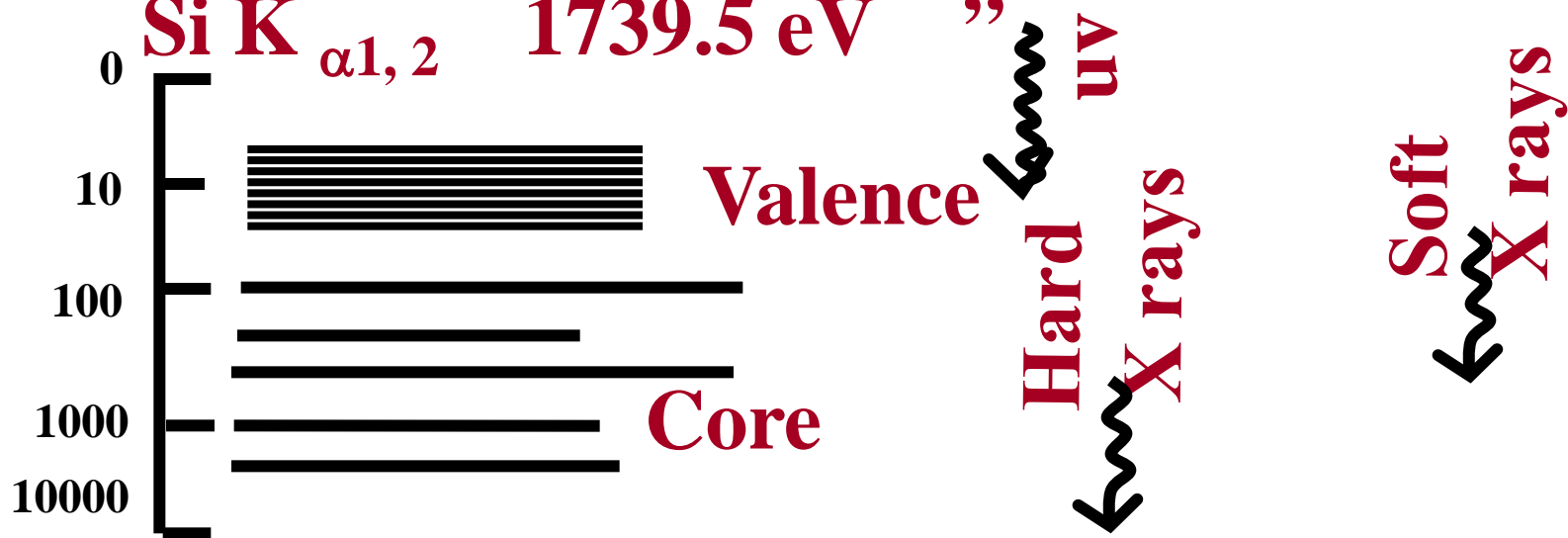
He II 40.8 eV $2P \rightarrow 1S$ of He^+

Al $K_{\alpha 1,2}$ 1486.6 eV $2P_{3/2,1/2} \rightarrow 1S$

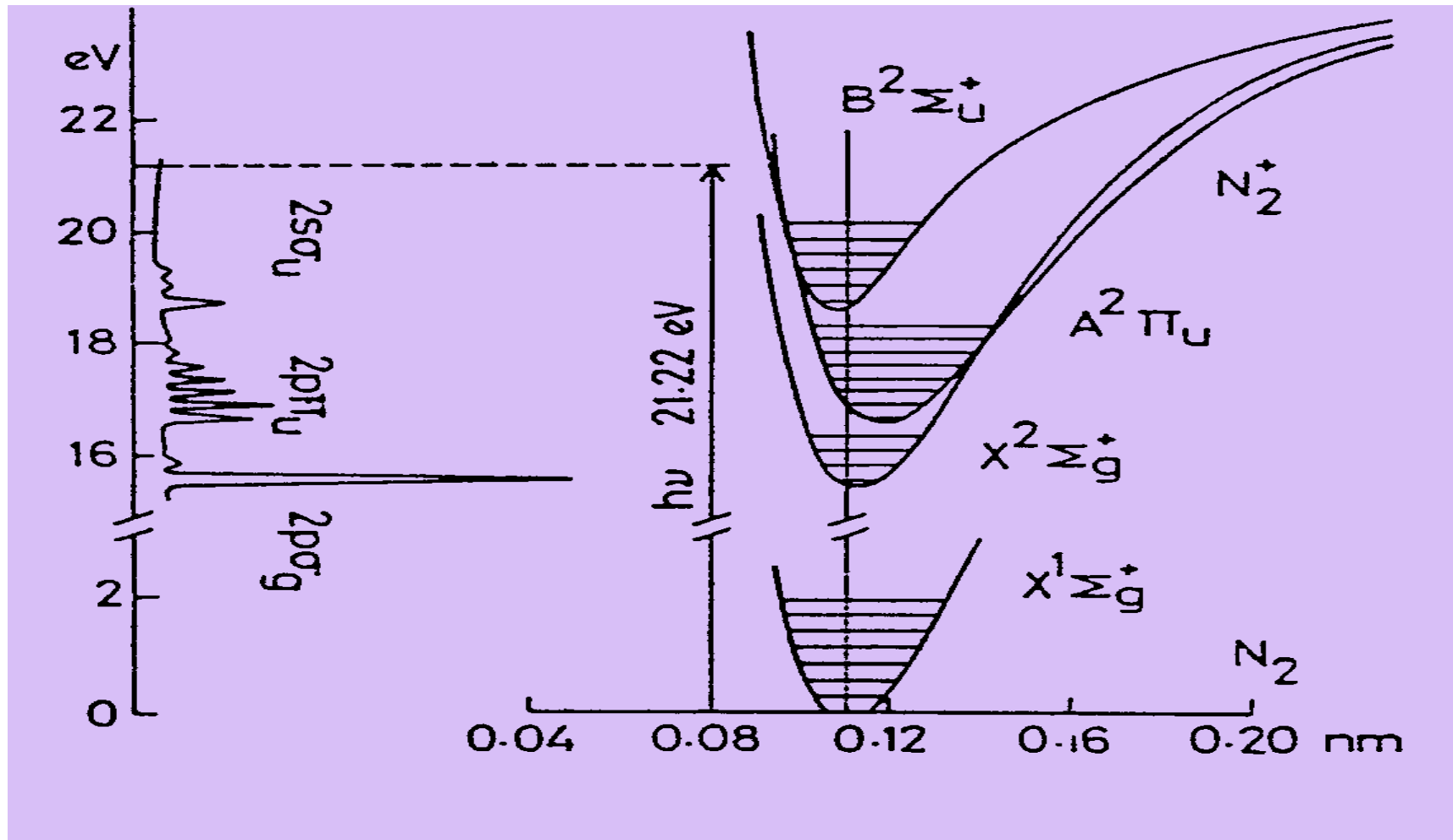
Mg $K_{\alpha 1,2}$ 1253.6 eV ”

Na $K_{\alpha 1,2}$ 1041.0 eV ”

Si $K_{\alpha 1,2}$ 1739.5 eV ”



Photoelectron spectrum is a reflection of the potential energy surfaces



INTERNUCLEAR DISTANCE

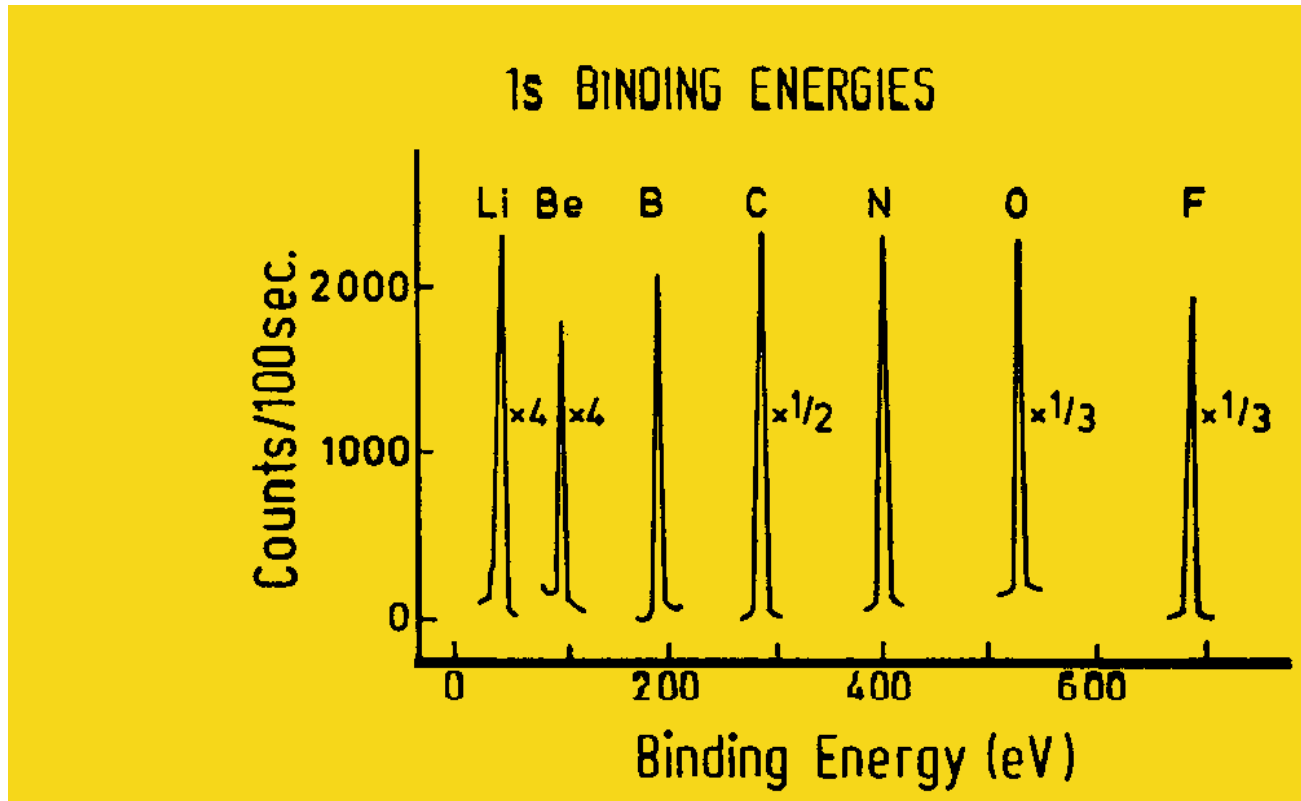
UPS

2 P σ_g \rightarrow non bonding 2345 to 2191 cm⁻¹

2 P π_u \rightarrow bonding 2345 to 1850 cm⁻¹

2 S σ_u \rightarrow weakly antibonding 2345 to 2397 cm⁻¹

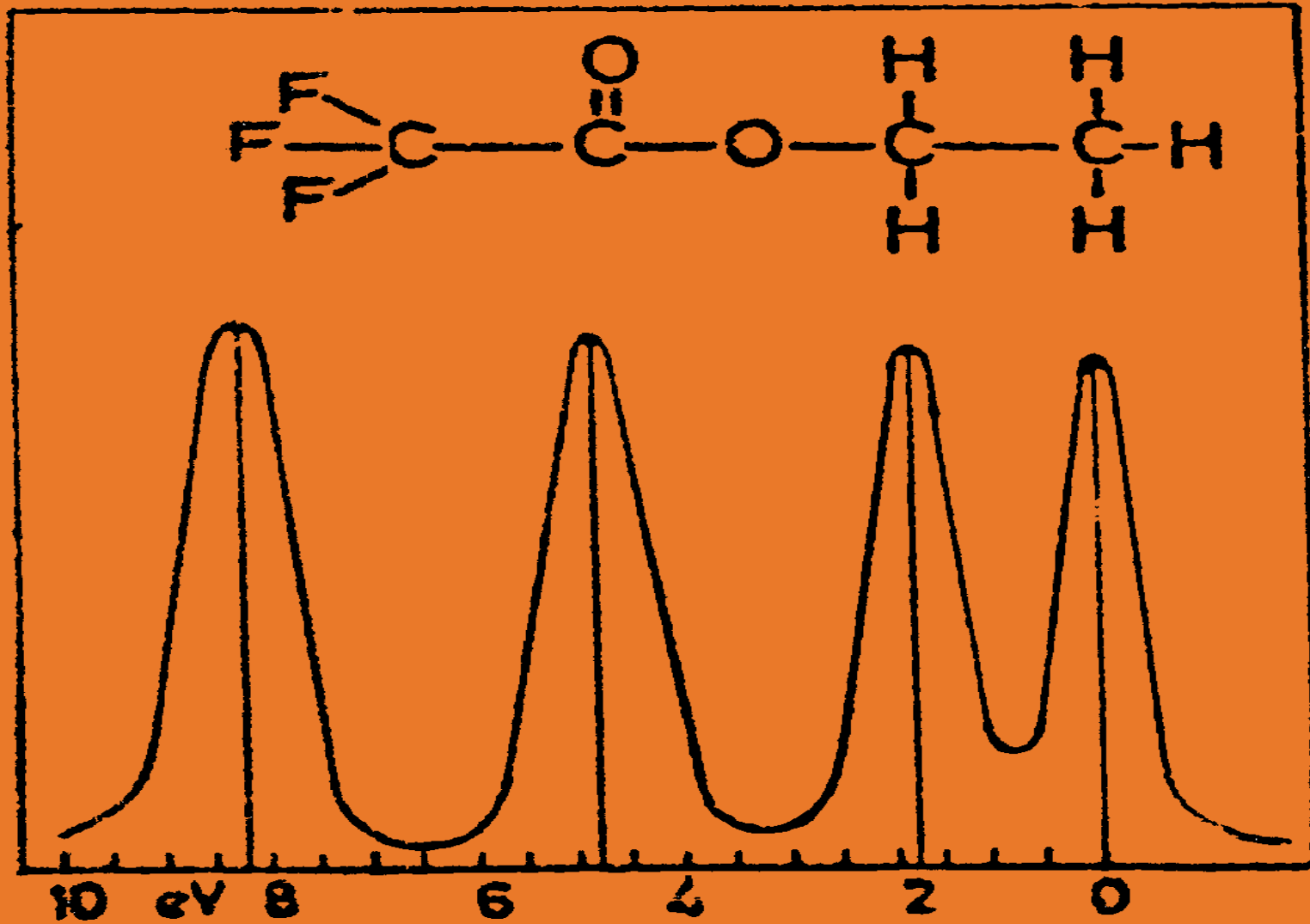
XPS



XPS-spectra of the 1s core levels of Li, Be, B, C, N, O, F.

Chemical analysis – ESCA (qualitative, quantitative)

Counting Rate

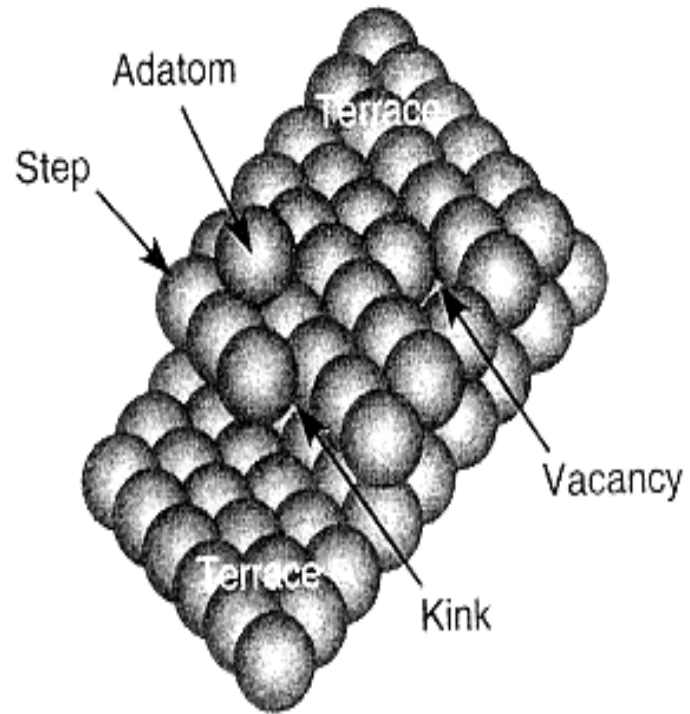


$E_B = 291.2 \text{ eV}$

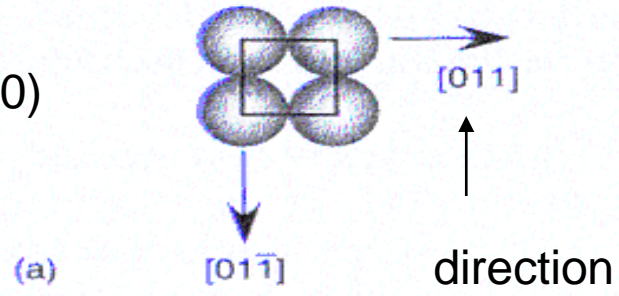
Chemical Shift

Surface sensitivity
Inelastic mean free path

Steps, kinks and defects

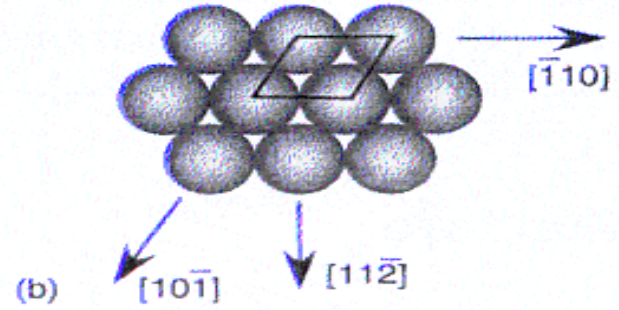


plane \longrightarrow (100)

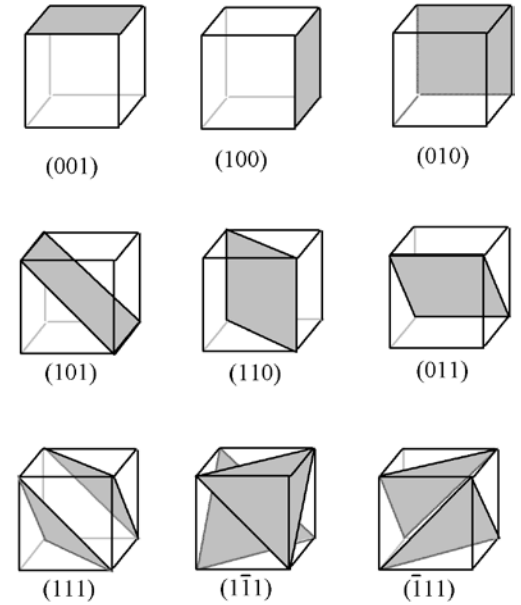


fcc unit cell

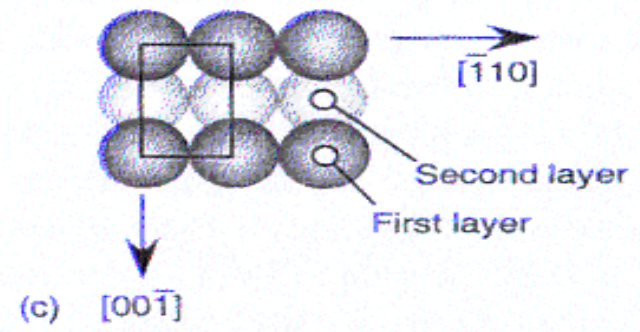
Direction and plane



(111)



(110)

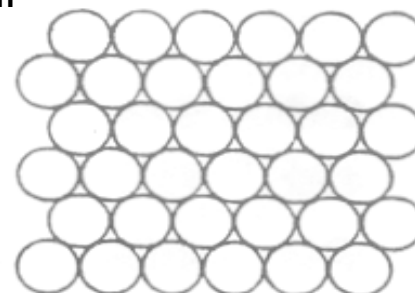
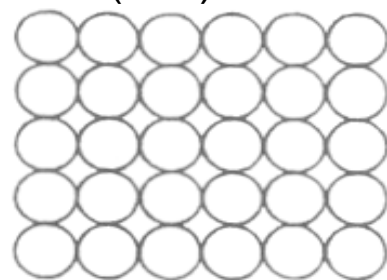


Reconstruction

(1x1) surface for all

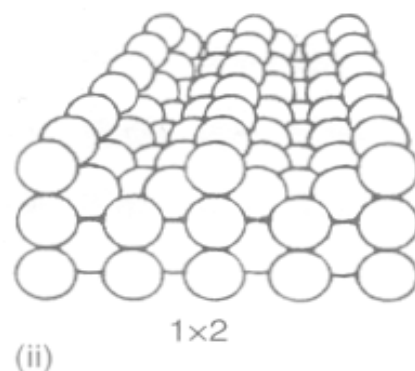
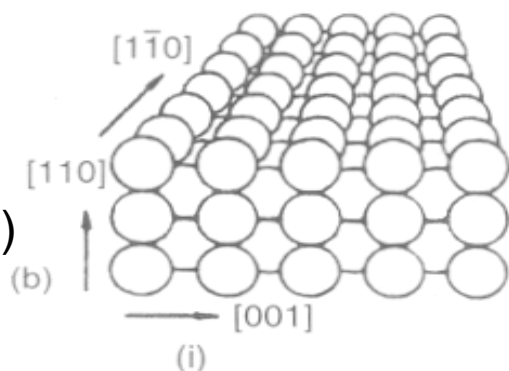
(100)

(a)



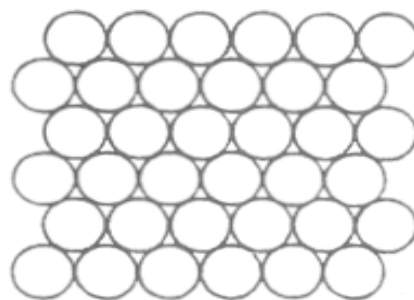
(110)

(b)

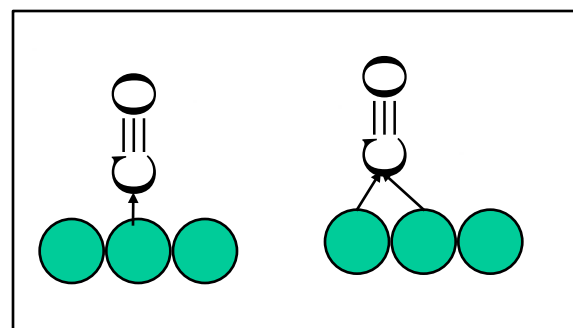


(111)

(c)



↑
planes



Adsorbate
structure

Determination of surface structure

AES

IR (RAIRS)

LEED

EELS and surface vibrations

SPM (STM, AFM)

SEXAFS