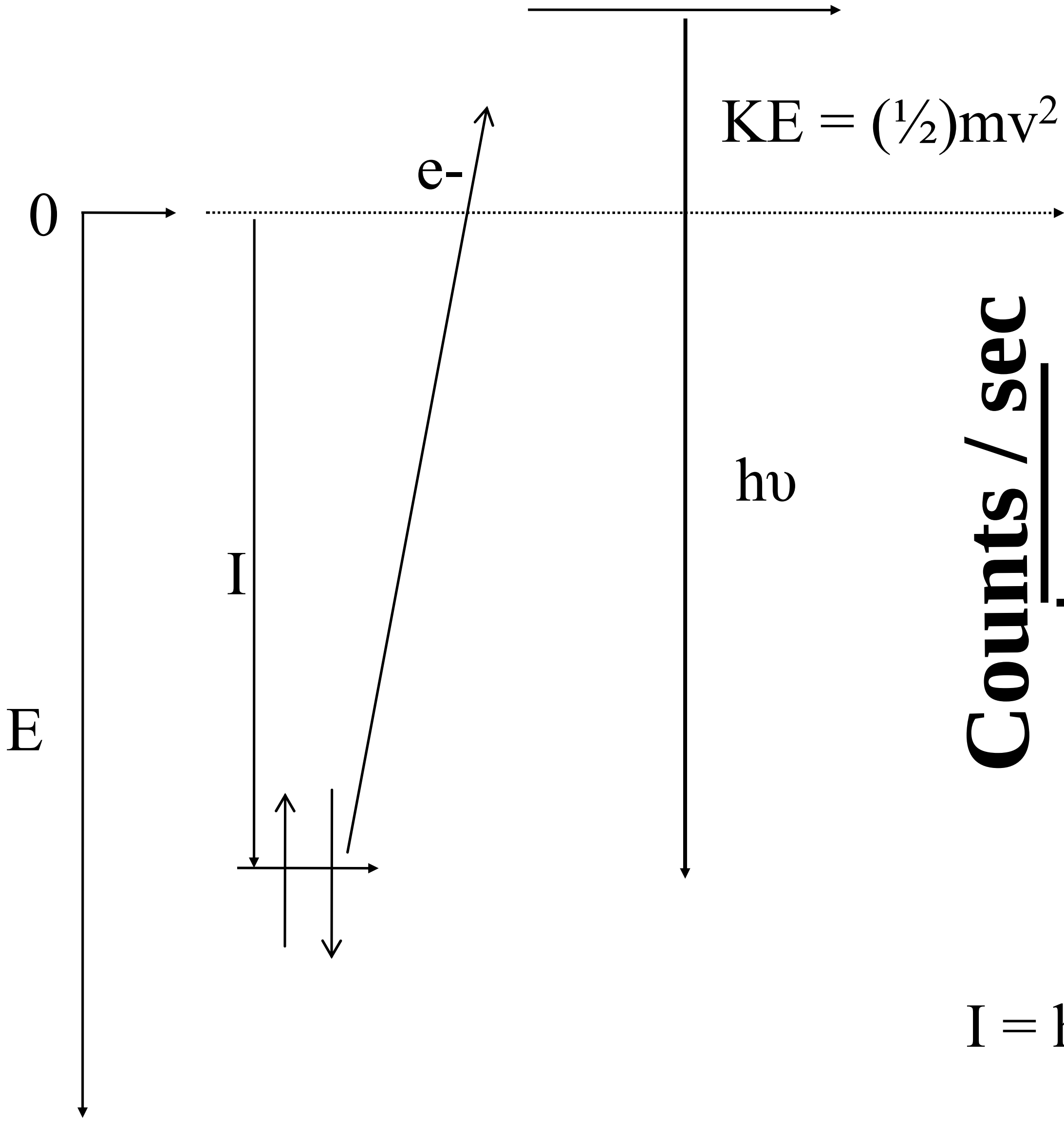
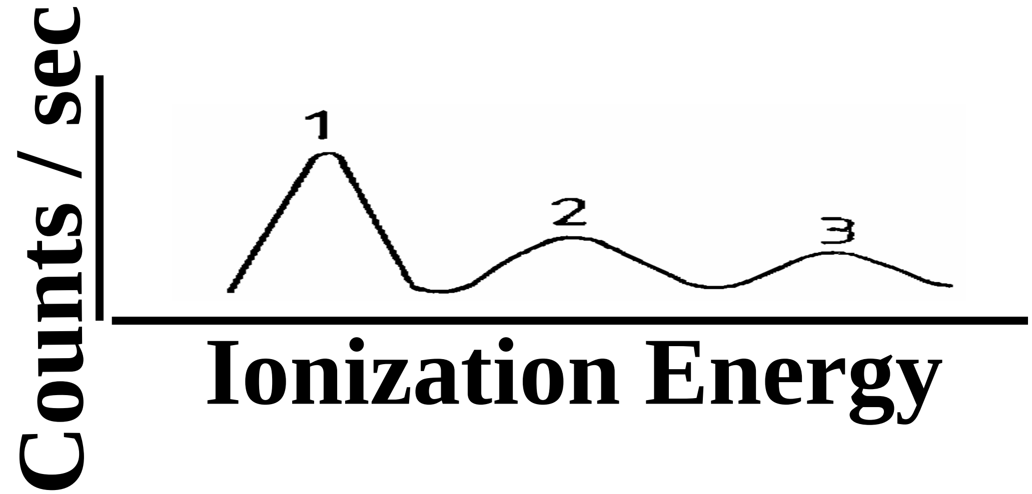
Lectures 1-2
Surfaces - spectroscopies

Almost all chemical science today has an important surface science component

Energy, chemicals, pharmaceuticals,….
Electron spectroscopy is the most important surface analysis tool

Kai M. Siegbahn (1918 - 2007)
Nobel Prize 1981 – High resolution Electron Spectroscopy





$I = h\upsilon - (\tfrac{1}{2})mv^2$

Photoelectron equation

Koopmans' theorem

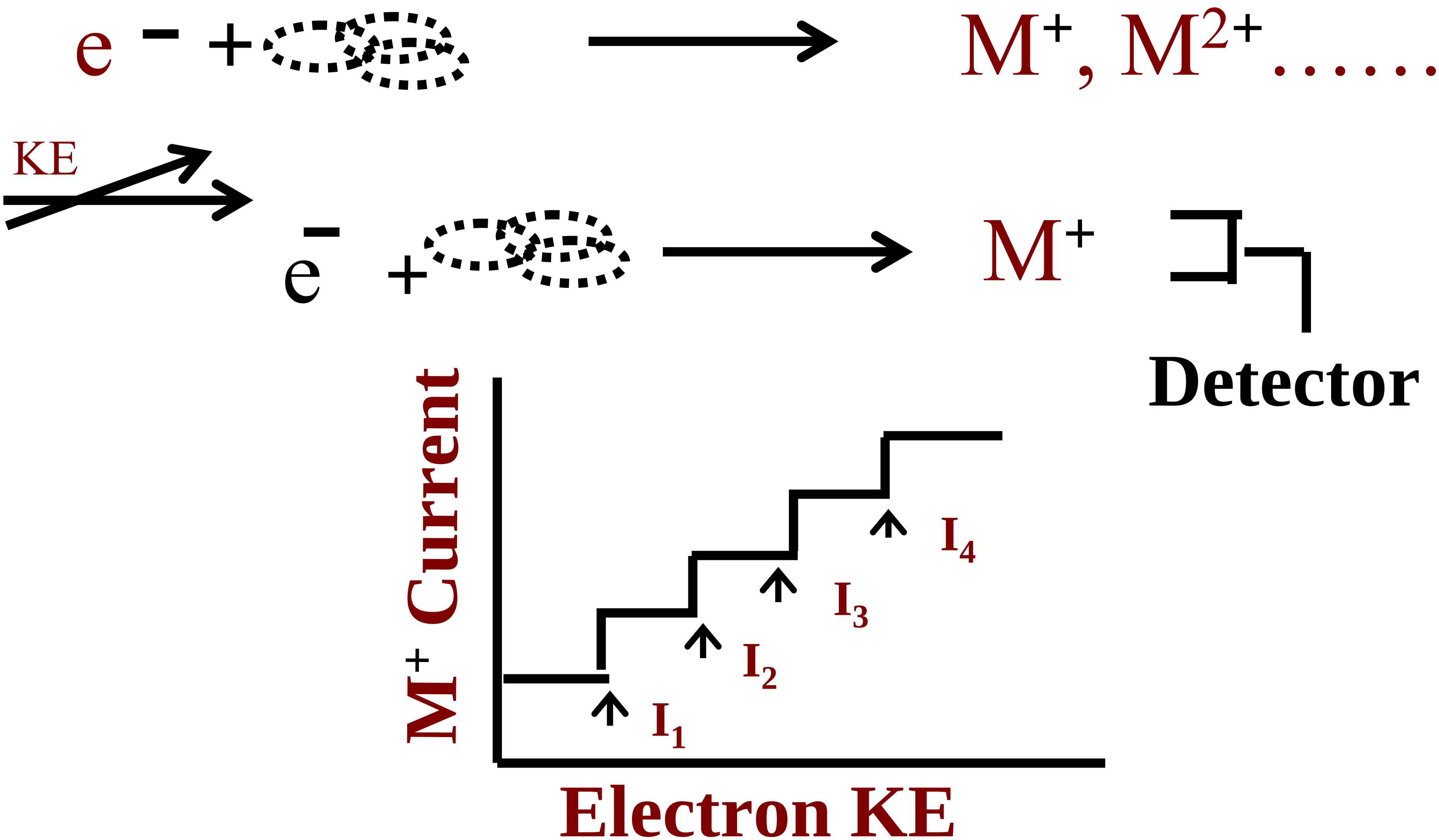
Structure and Properties of Matter

Spectroscopy
Scattering
Physical Properties

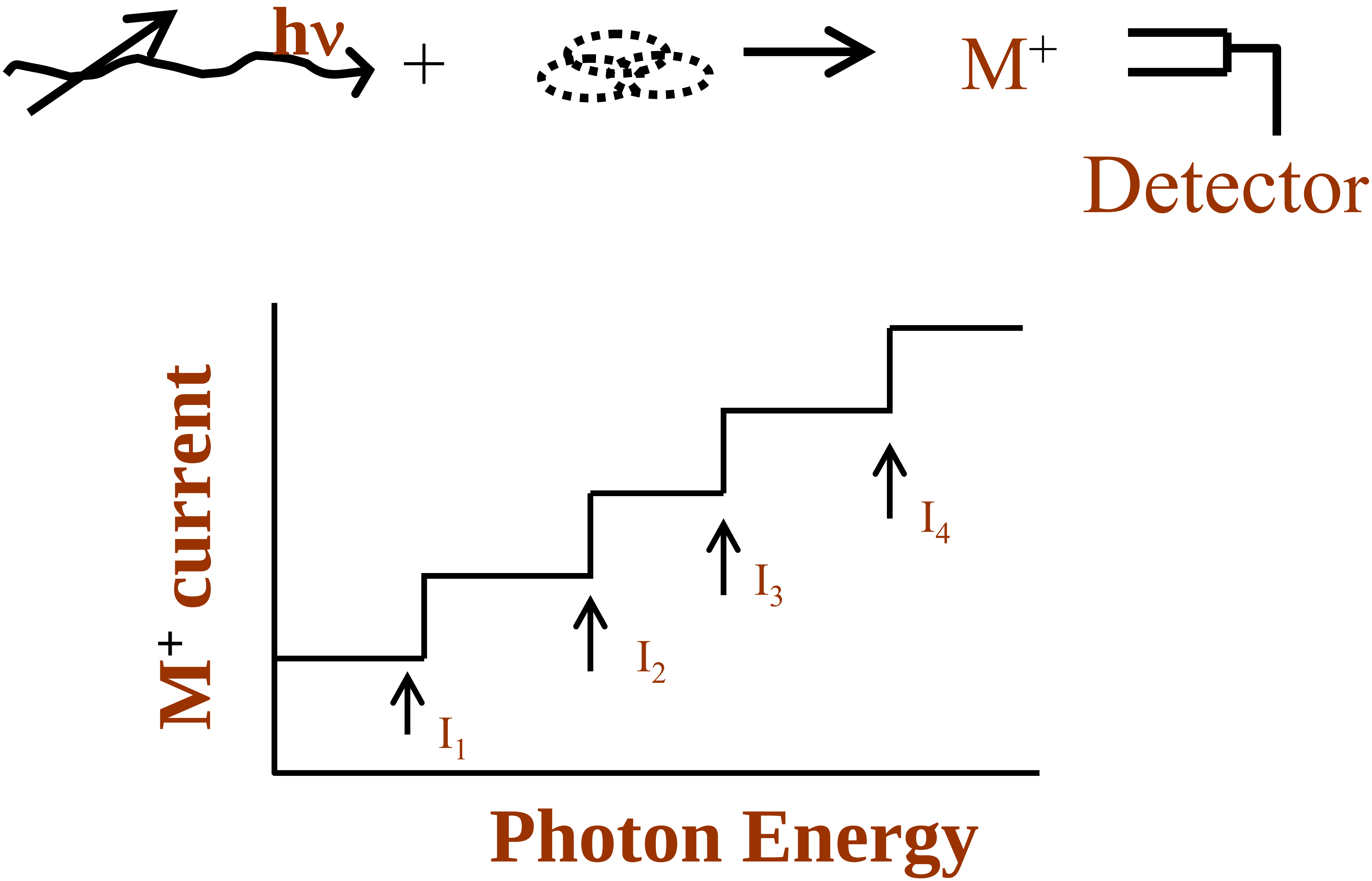
Spectroscopy (pre-1965)

Absorption
Magnetic
Mass

Spectroscopy using electrons



Ionization efficiency curves

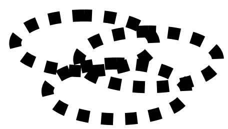


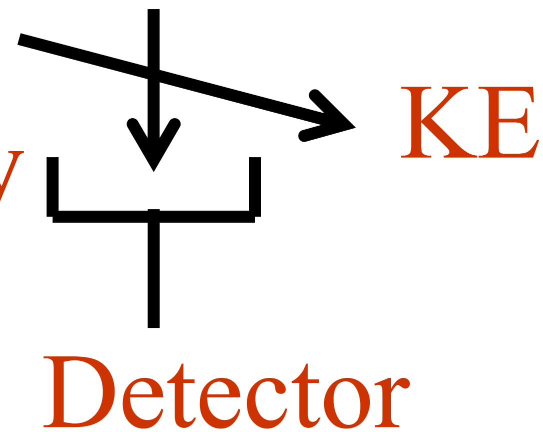
hν
+
M+
Detector
M+ current
I1
I2
I3
I4
Photon Energy

$h\nu + M \longrightarrow M^{+} + e^{-}$

(No M^{2+}, generally)

$h\nu$

Constant +  $\longrightarrow M^{+} + e^{-}$



Photoelectron Spectroscopy

Photoelectric effect

Early experiments in 1887

$h\nu = KE + \phi$ 1905

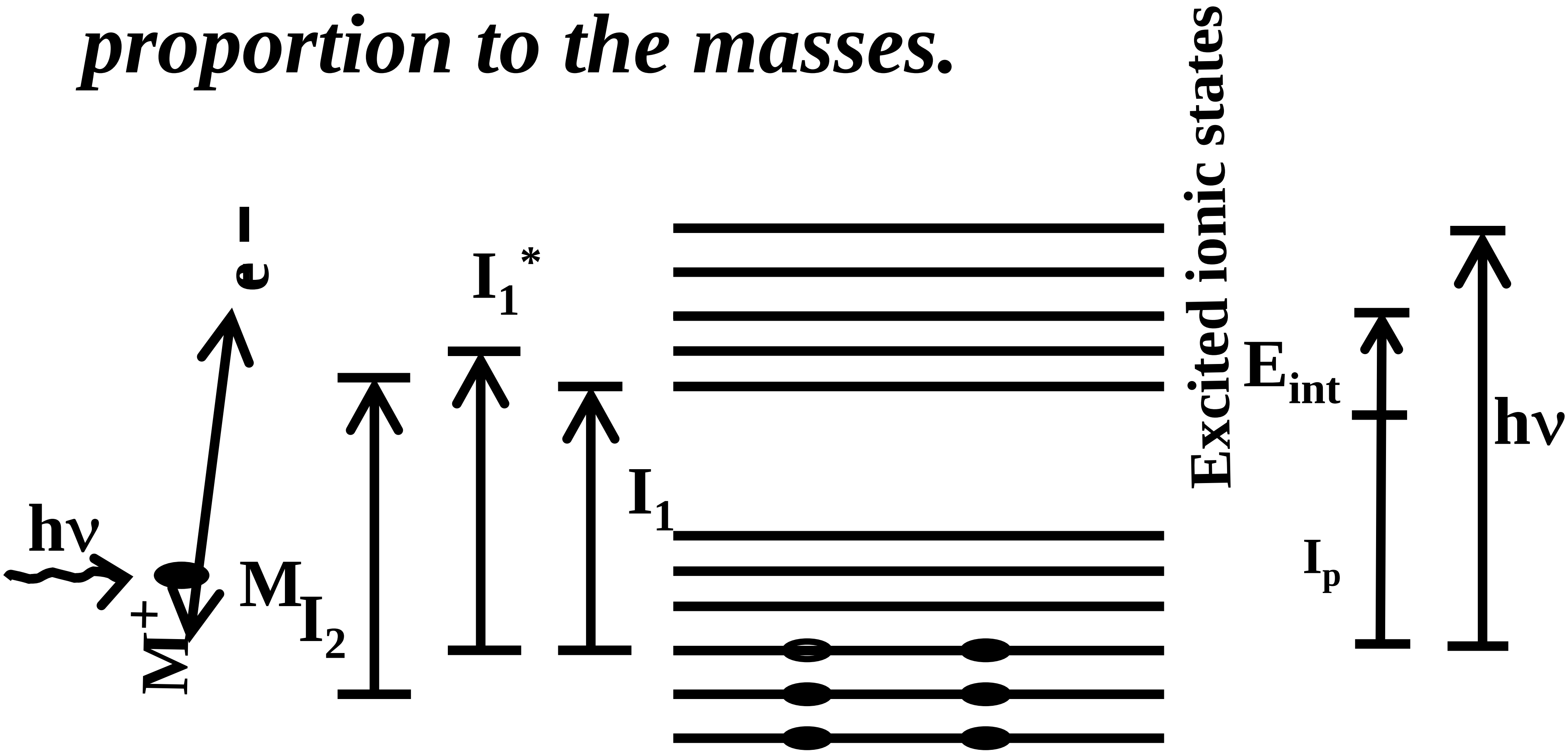
Photoion can be excited

$$M + h\nu \longrightarrow M^+(E_{int}) + e^-$$

elec vib rot

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

Conservation of momentum requires that excess energy is partitioned in inverse proportion to the masses.



Electron and ion separates with equal momenta.

$$mu = MU$$

The relative velocity,

$$V = u + U$$

$$= U\,(1 + M/m)$$

$$= u\,(1 + m/M)$$

The kinetic energies,

$$\tfrac{1}{2}\,MU^2 = \frac{1}{2M}\left(\frac{mMV}{m+M}\right)^2$$

$$\tfrac{1}{2}\,mu^2 = \frac{1}{2m}\left(\frac{mMV}{m+M}\right)^2$$

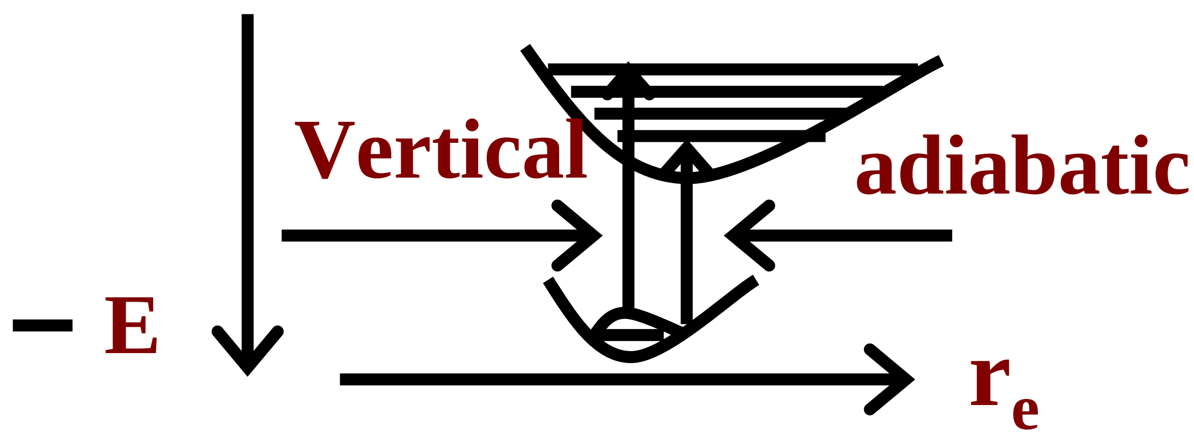
$$h\nu - (I_p + E_{int}) = KE$$

$$h\nu - KE = I_p + E_{int}$$

$$E_{int} \rightarrow 0$$

$$h\nu - KE = I_p$$

$$h\nu - KE_1 = IP_1$$
$$h\nu - KE_2 = IP_2$$
$$h\nu - KE_3 = IP_3 \ldots\ldots$$



Depth of analysis depends on photon energy

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

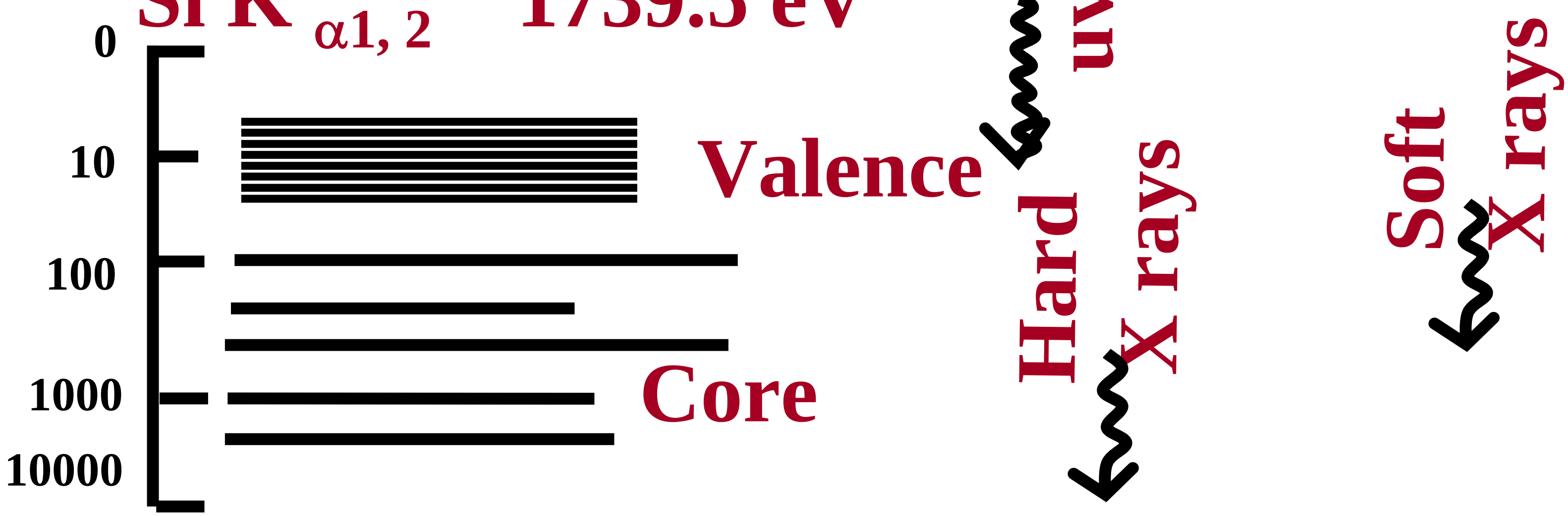
He II 40.8 eV $2\,P \rightarrow 1\,S$ of He^+

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

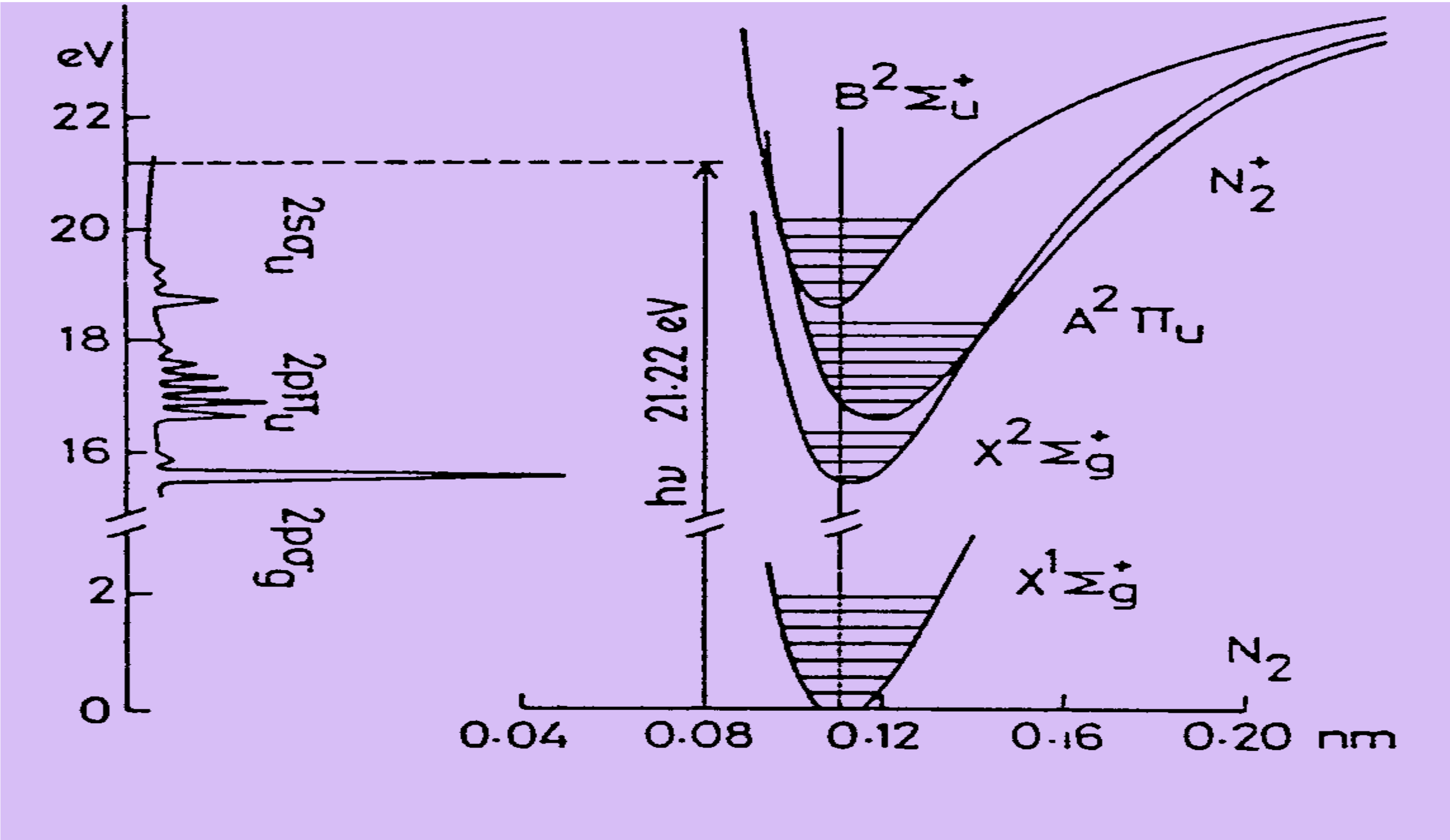
Mg $K_{\alpha 1,2}$ 1253.6 eV ”

Na $K_{\alpha 1,2}$ 1041.0 eV ”

Si $K_{\alpha 1,2}$ 1739.5 eV ”



VALENCE SHELL PHOTOELECTRON SPECTROSCOPY (UPS)



INTERNUCLEAR DISTANCE

$2P\sigma_g \rightarrow$ non bonding **2345 to 2191 cm^{-1}**

$2P\pi_u \rightarrow$ bonding **2345 to 1850 cm^{-1}**

$2S\sigma_u \rightarrow$ weakly antibonding **2345 to 2397 cm^{-1}**

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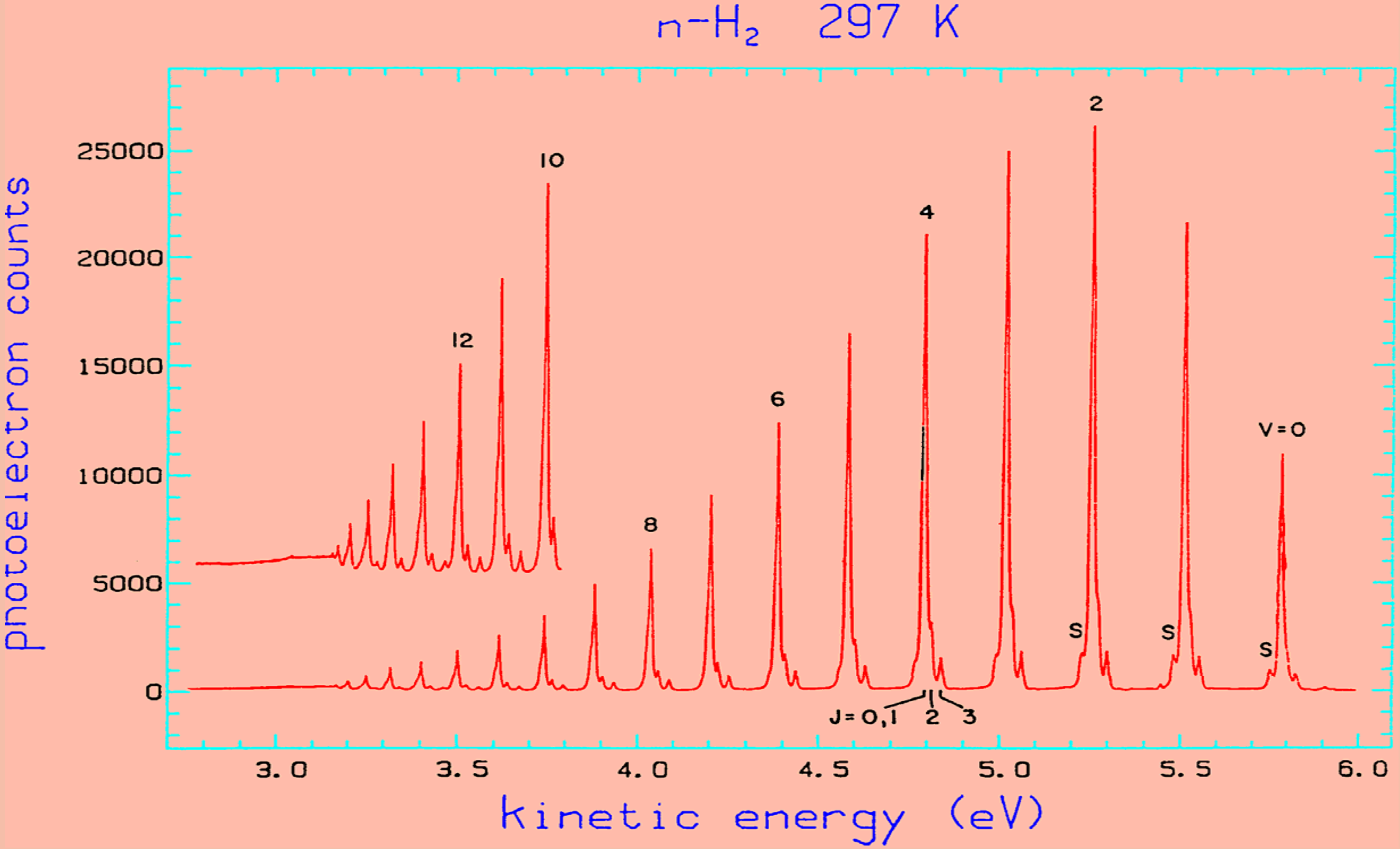
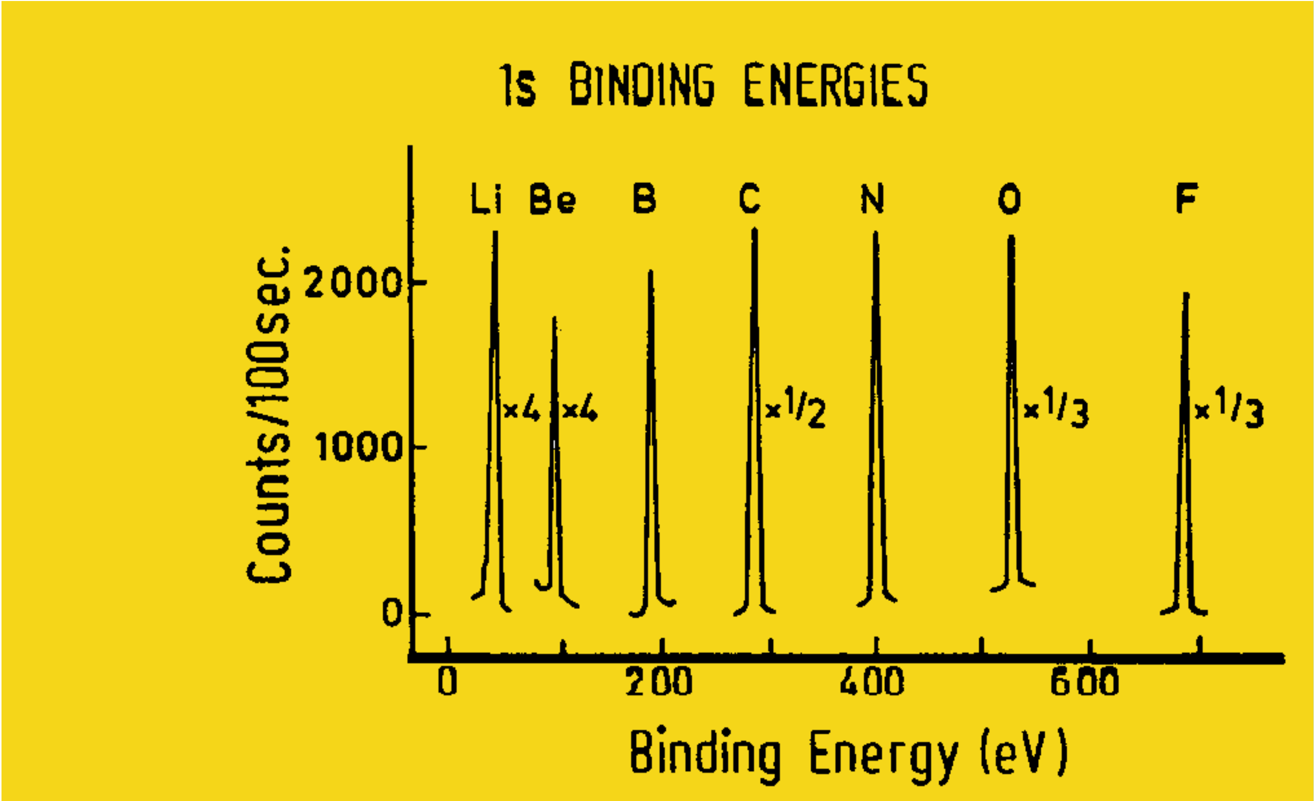
HeI UPS of H_2 Vibrations and Rotations !



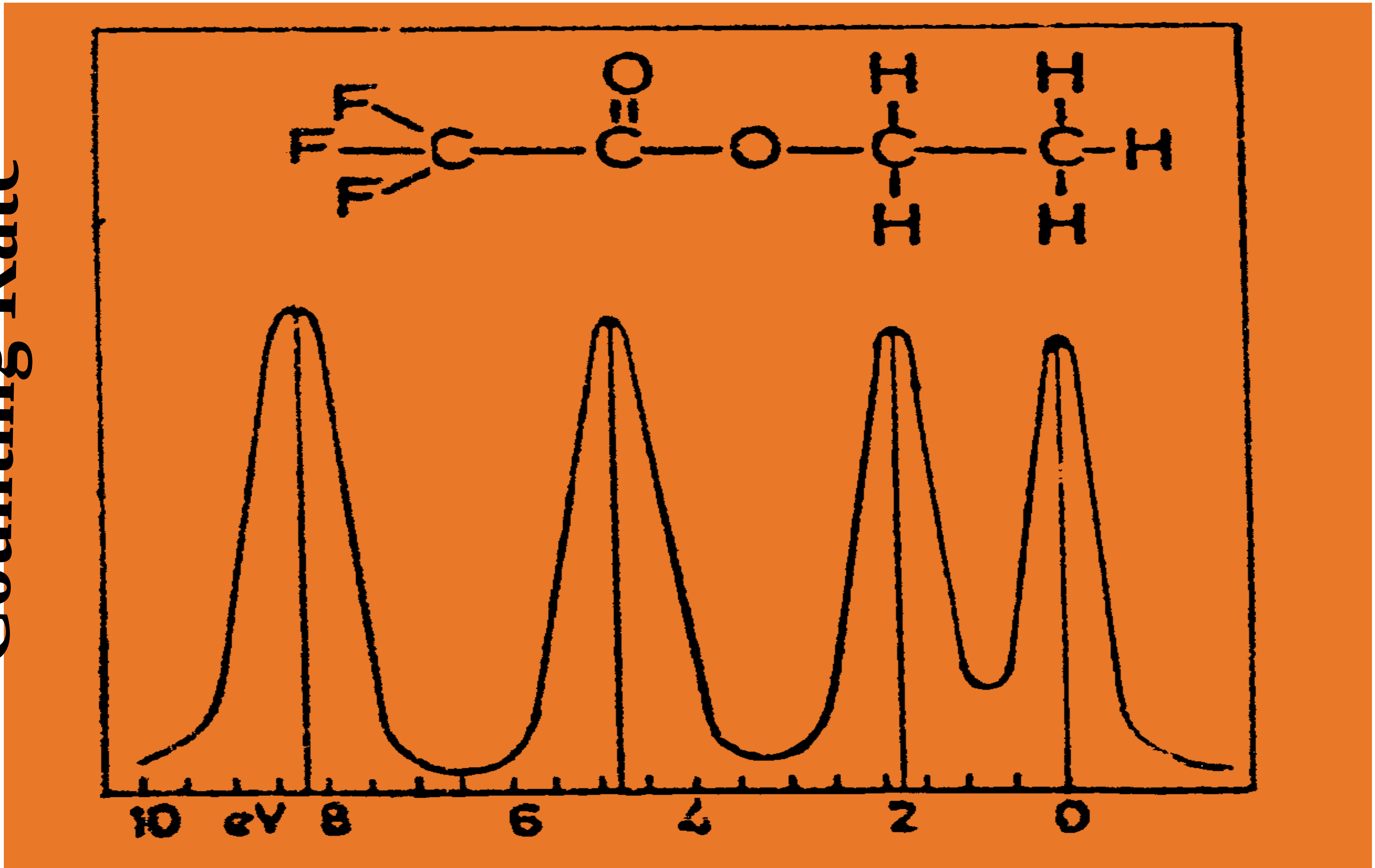
CORE LEVEL PHOTOELECTRON SPECTROSCOPY (XPS)



XPS-spectra of the 1s core levels of Li, Be, B, C, N, O, F (from S. Hüfner).

Chemical analysis – ESCA (qualitative, quantitative)

Counting Rate



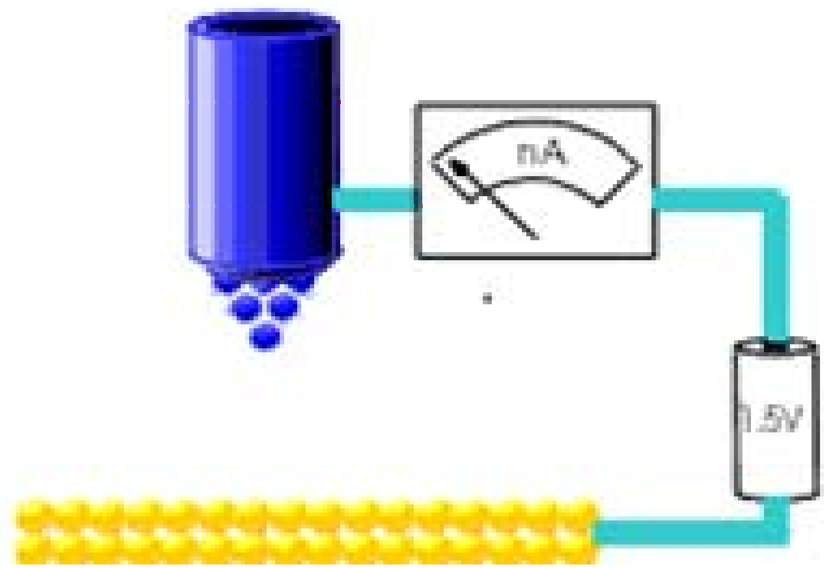
E_B=291.2eV

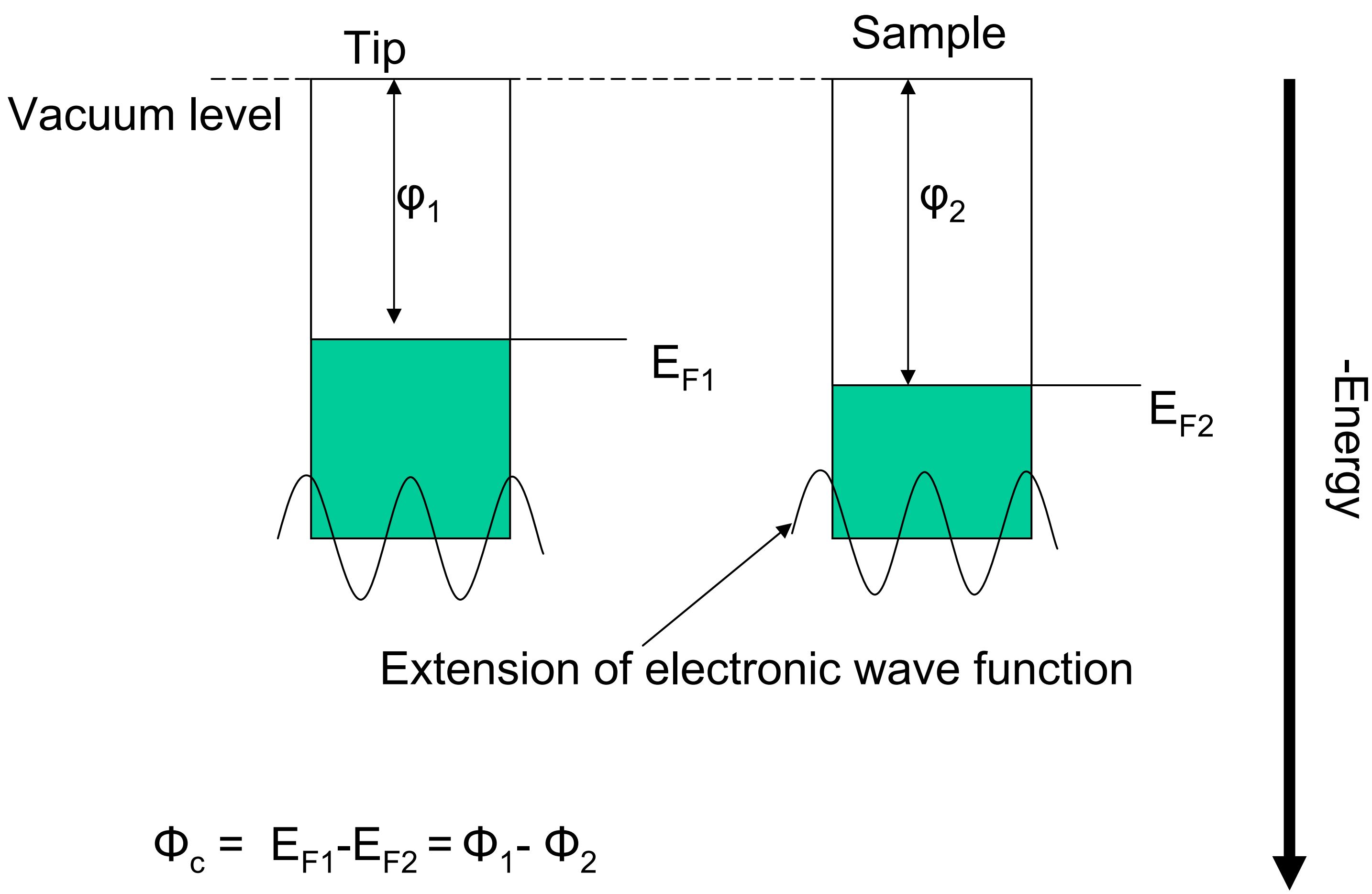
Chemical Shift

Surface sensitivity
Inelastic mean free path

Other techniques

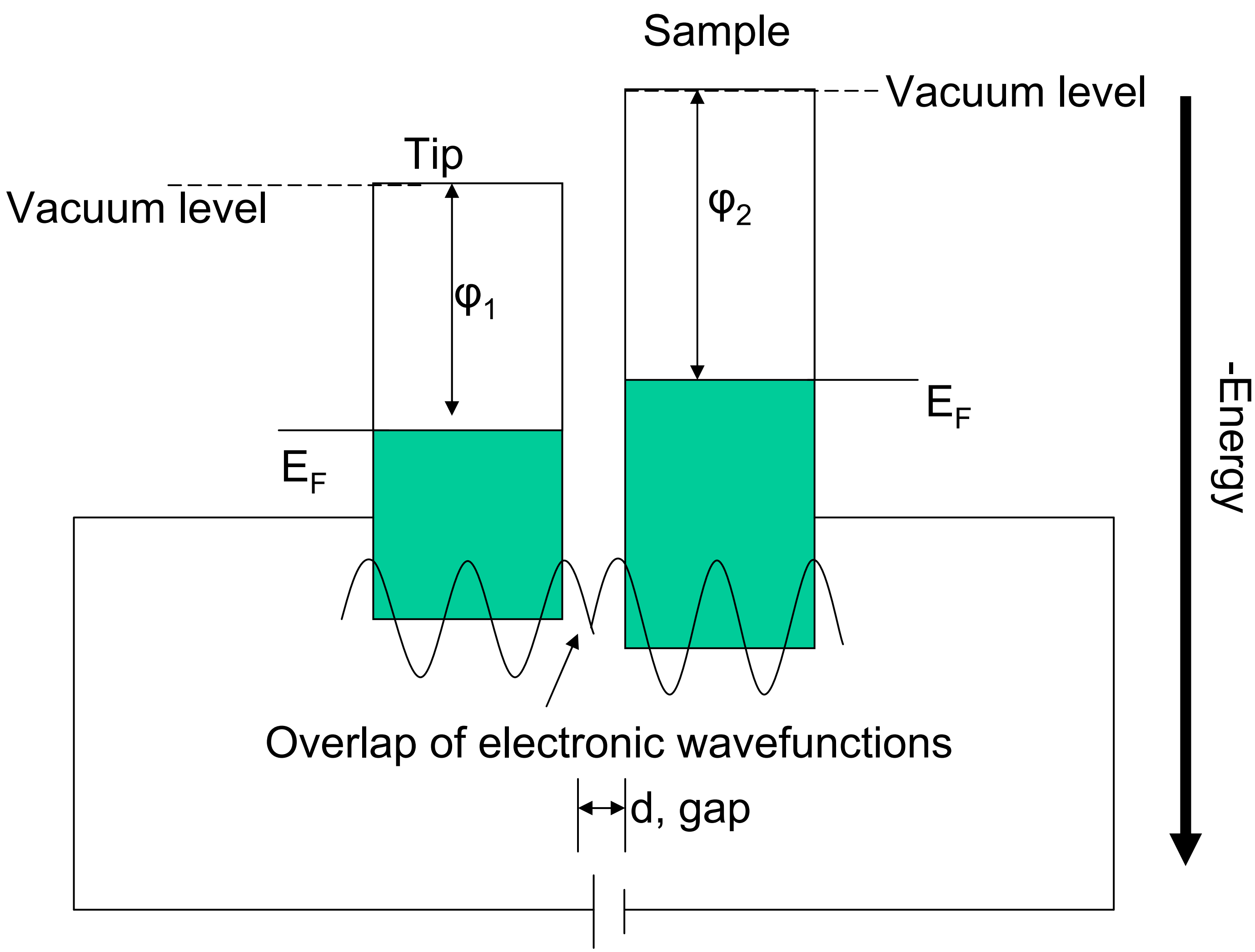
1. Scanning probe microscopy

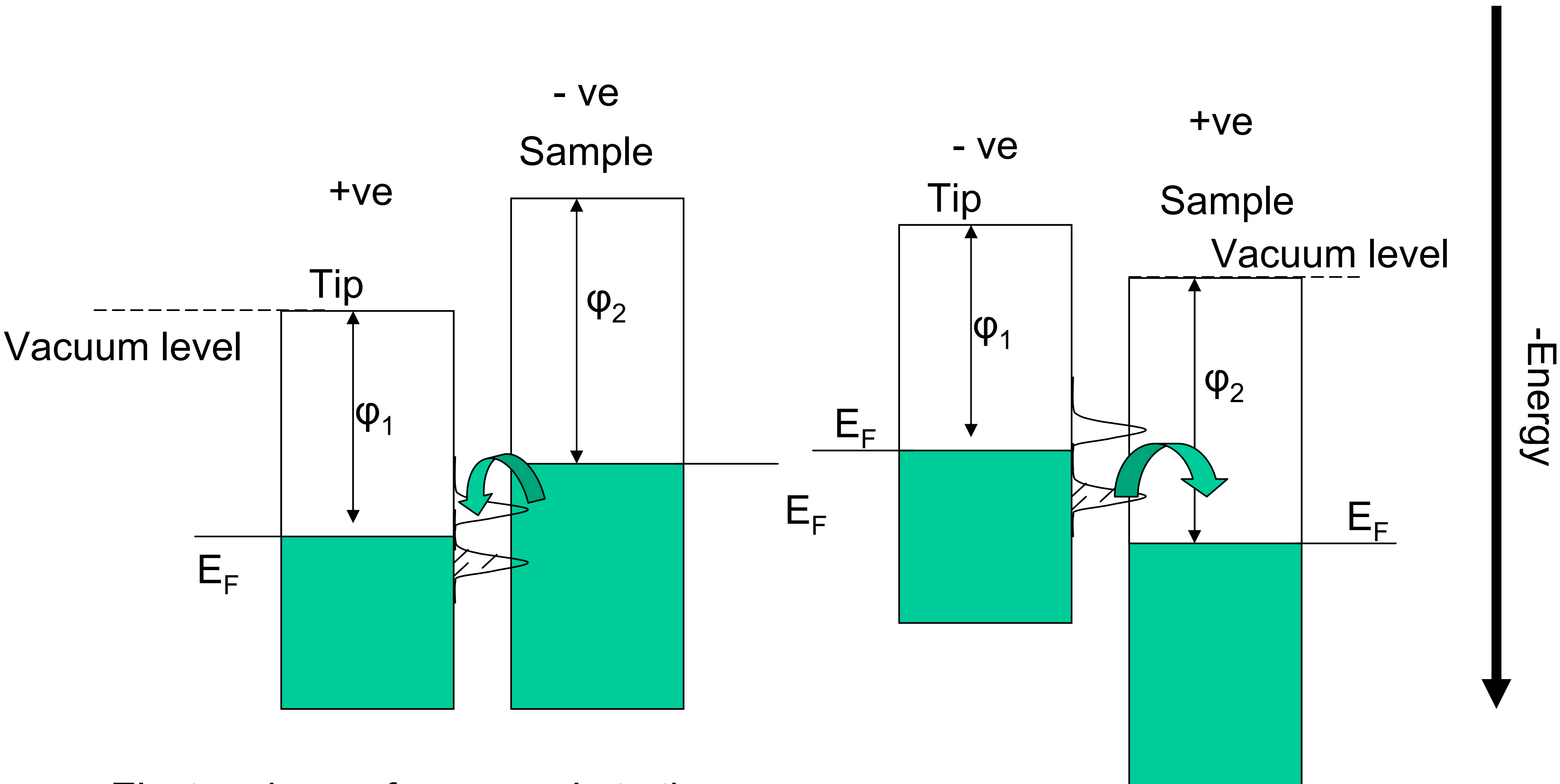




$$\Phi_c = E_{F1} - E_{F2} = \Phi_1 - \Phi_2$$

$I \; \alpha \; \exp(-2kd)$
$k^2 = 2m/\hbar^2(eV_B\text{-}E)$
E- energy of the state from which tunneling occurs
eV_B = Barrier height
Change in 1Å makes an order of magnitude change in tunneling current.

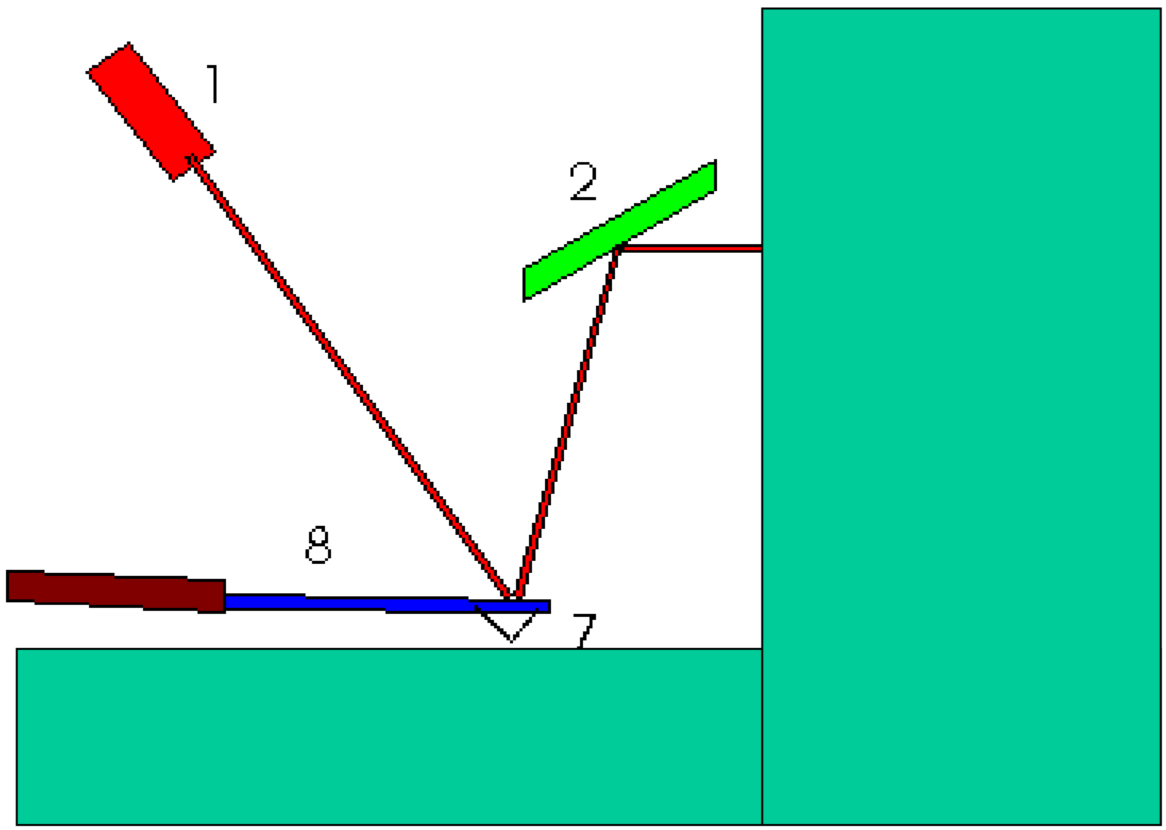




Electron jumps from sample to tip probing occupied states of the sample

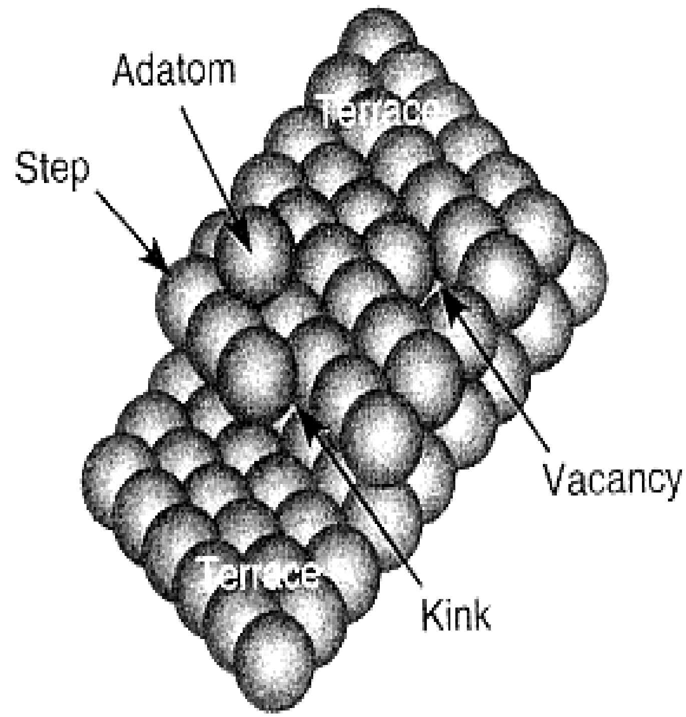
Electron jumps from tip to the sample probing unoccupied states of the sample

Atomic Force Microscopy



Surface structure

Steps, kinks and defects



fcc unit cell

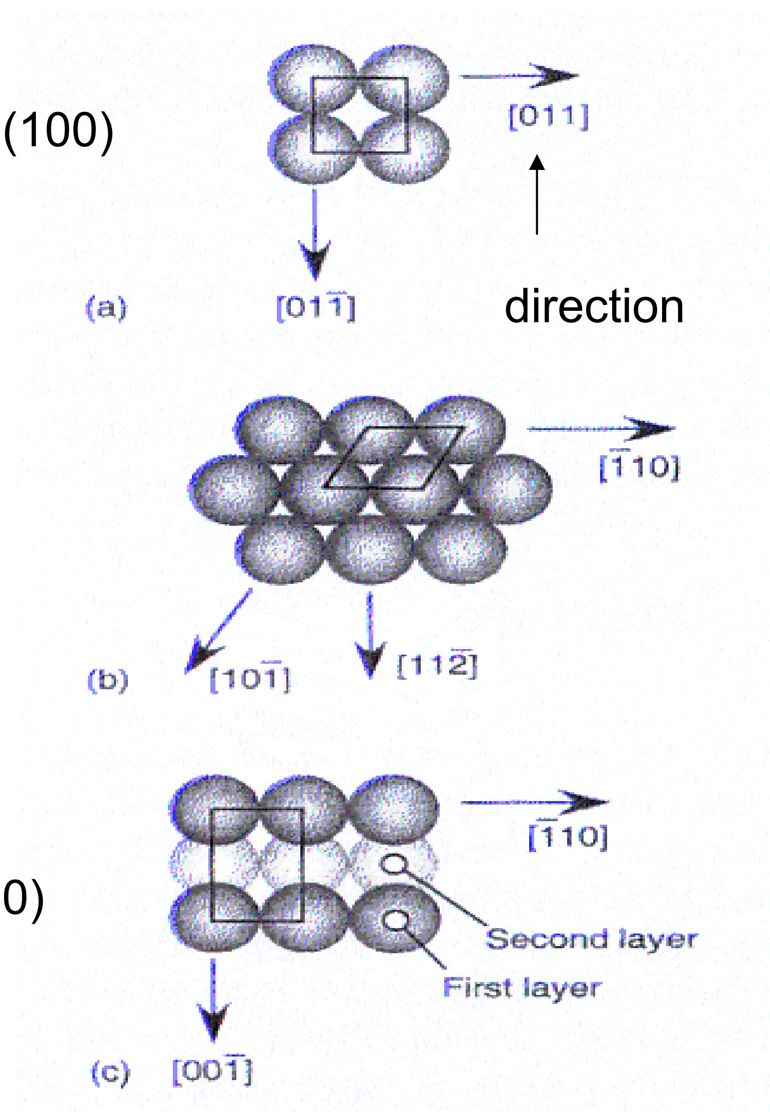
plane → (100)

direction

Direction and plane

(111)

(110)



(1x1) surface for all

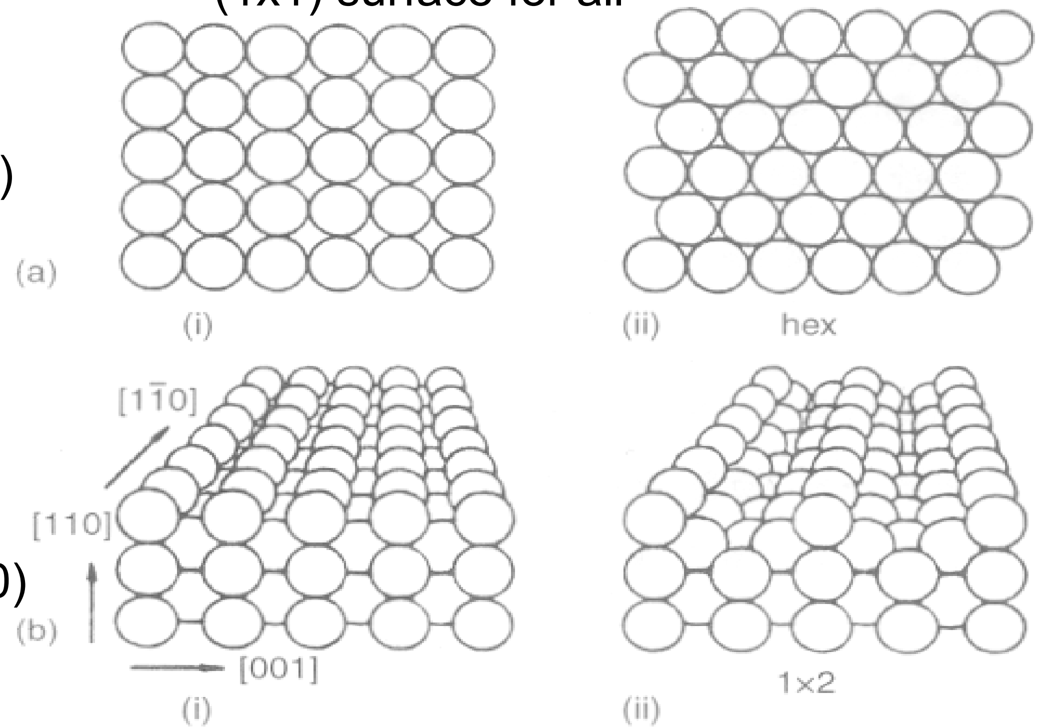
Reconstruction

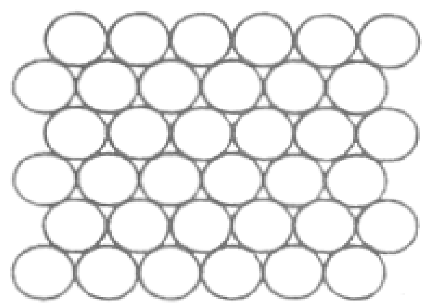
(100)

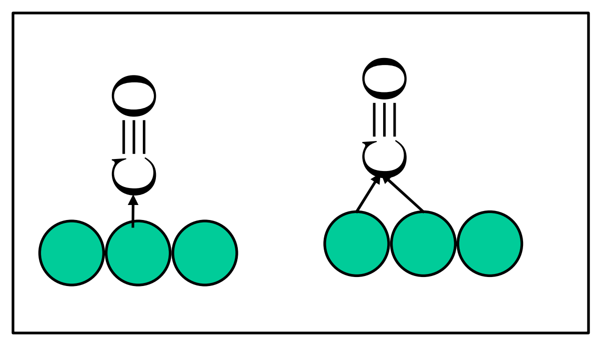
(110)

(111)

planes







Adsorbate structure

Determination of surface structure

AES
IR (RAIRS)
LEED
EELS and surface vibrations
SEXAFS
SPM