

*An introduction to
X-ray photoelectron
spectroscopy*

- *X-ray photoelectron spectroscopy belongs to a broad class of spectroscopic techniques, collectively called, electron spectroscopy.*
- *In general terms, electron spectroscopy can be defined as the energy analysis of electrons ejected or reflected from materials.*
- *All of these spectroscopic techniques yield information on the **ELECTRONIC STRUCTURE.***

*There are, generally
five techniques
collectively called
electron spectroscopy*

X-ray photoelectron spectroscopy
(XPS)

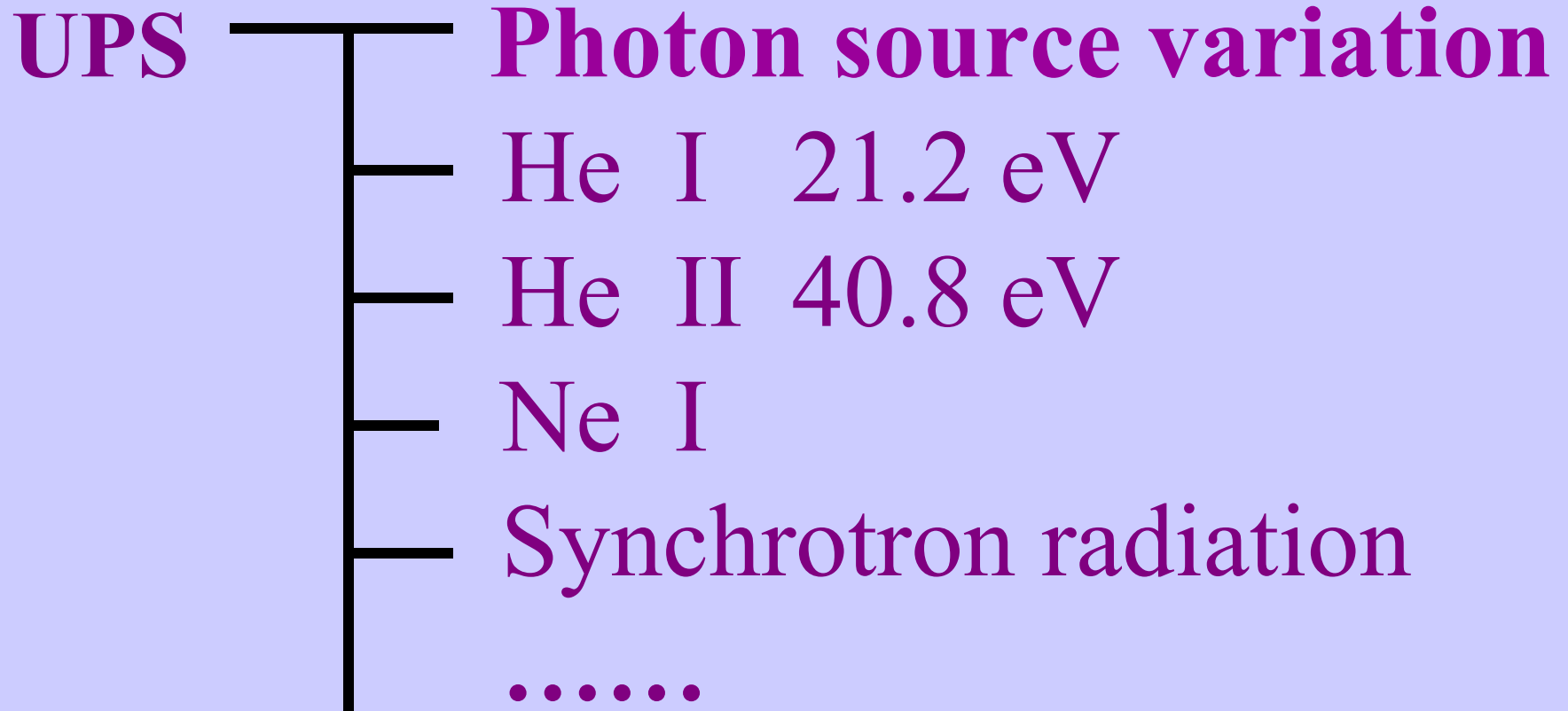
Ultraviolet photoelectron spectroscopy
(UPS)

Auger electron spectroscopy
(AES)

Electron energy loss spectroscopy
(EELS)

Inverse photoemission spectroscopy
(IPS)

There are a range of techniques in each of these



UPS

Variations of the same
basic technique

**One photon
spectroscopy**

Solids

Gases

**Gas
cell**

**Molecular
beams**



**Photoelectron-photoion
coincidence spectroscopy**

**Zero-kinetic energy
photoelectron spectroscopy**

**Multiphoton photoelectron
spectroscopy**

**Photodetachment
spectroscopy**

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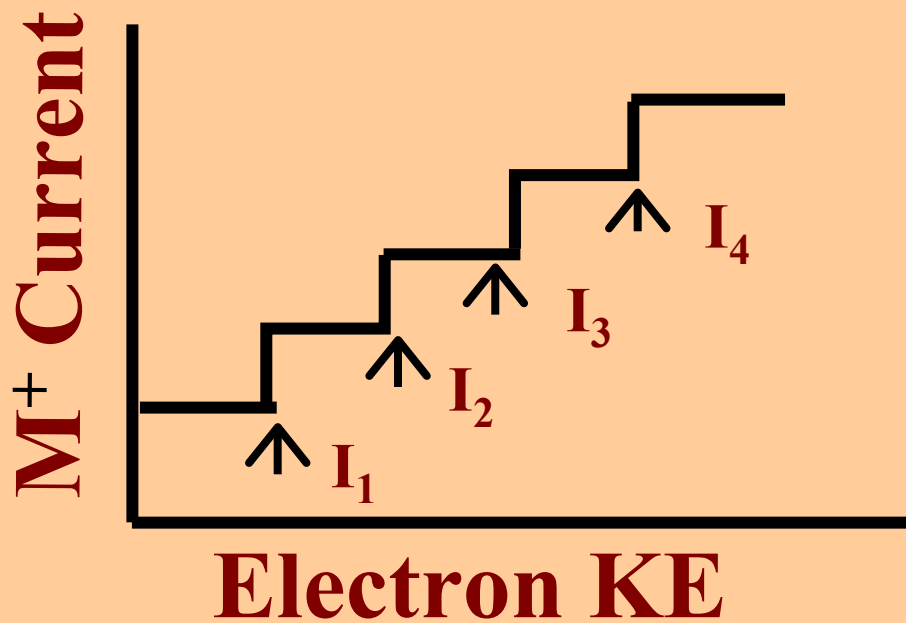
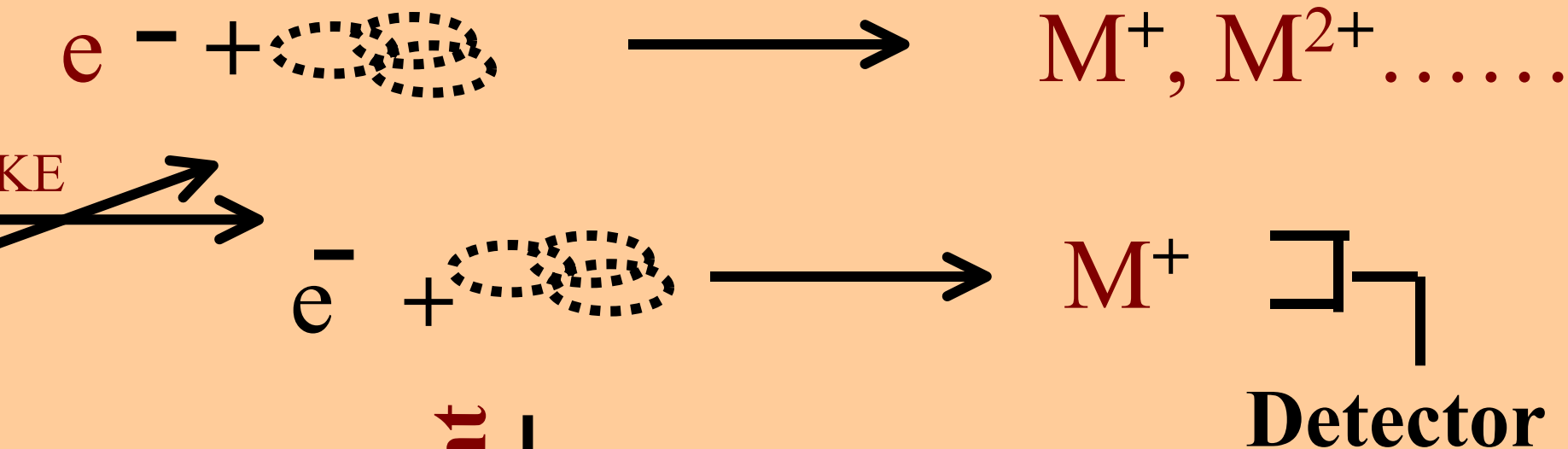
Structure and Properties of Matter

Spectroscopy
Scattering
Physical Properties

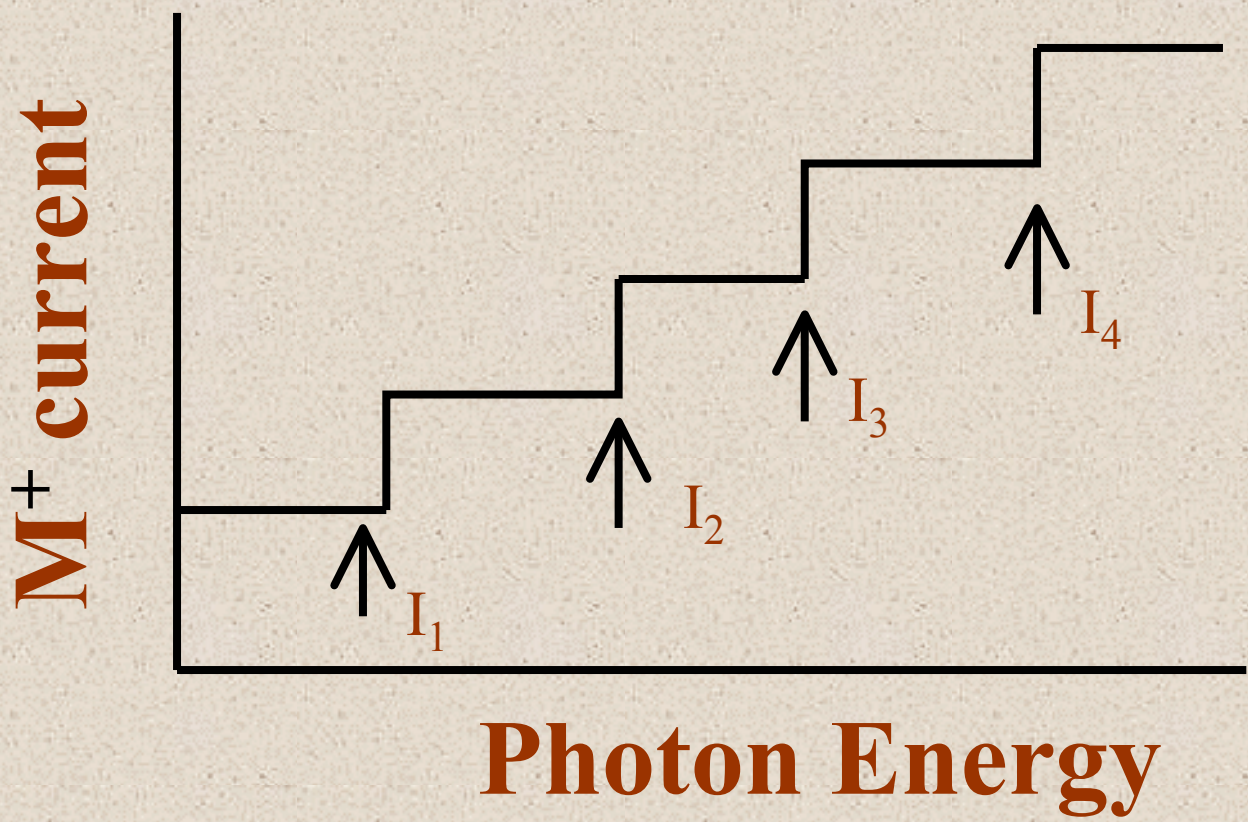
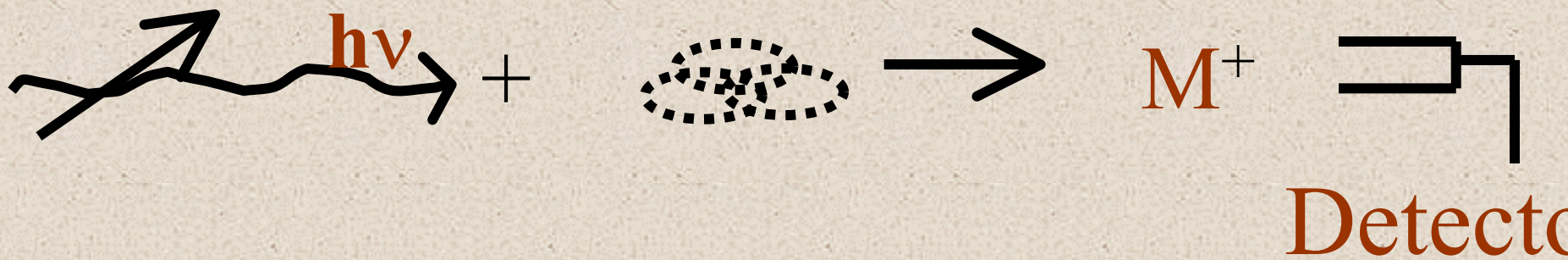
Spectroscopy (pre-1965)

Absorption
Magnetic
Mass

Spectroscopy using electrons

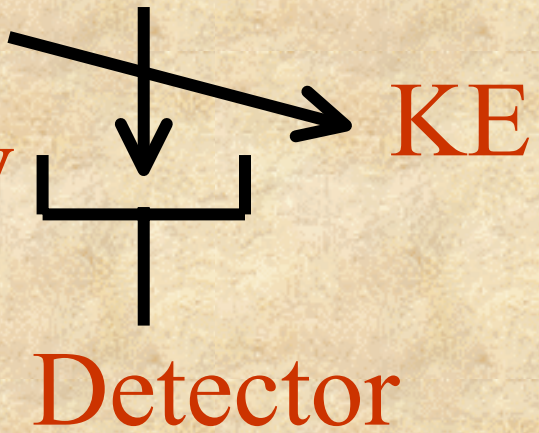


Ionization efficiency curves





(No M^{2+} , generally)



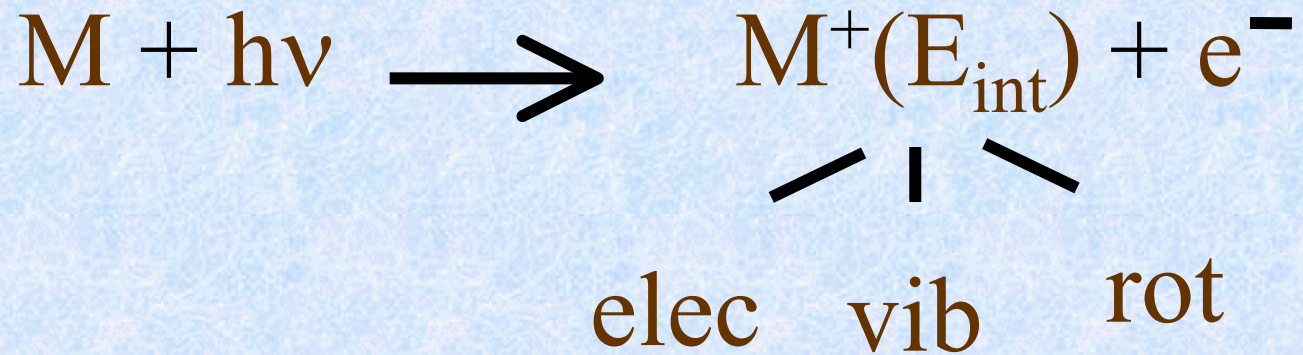
Photoelectron Spectroscopy

Photoelectric effect

Early experiments in 1887

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

Photoion can be excited



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

**Electron and ion separates
with equal momenta.**

$$\mathbf{mu} = \mathbf{MU}$$

The relative velocity,

$$\begin{aligned}\mathbf{V} &= \mathbf{u} + \mathbf{U} \\ &= \mathbf{U} (1 + \mathbf{M}/m) \\ &= \mathbf{u} (1 + m/\mathbf{M})\end{aligned}$$

The kinetic energies,

$$\frac{1}{2} \mathbf{MU}^2 = \frac{1}{2\mathbf{M}} \left(\frac{m \mathbf{MV}}{m + \mathbf{M}} \right)^2$$

$$\frac{1}{2} m\mathbf{u}^2 = \frac{1}{2m} \left(\frac{m \mathbf{MV}}{m + \mathbf{M}} \right)^2$$

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

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

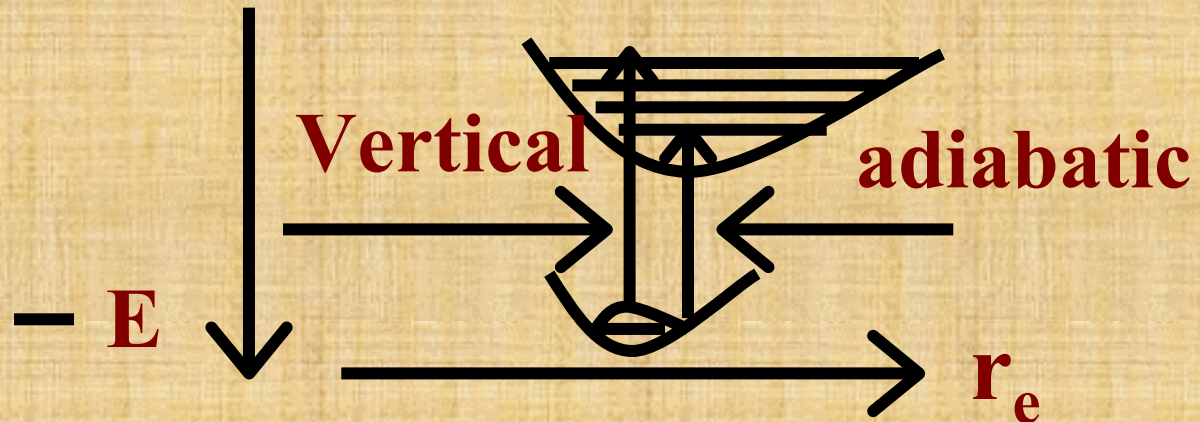
$$E_{\text{int}} \rightarrow 0$$

$$h\nu - \text{KE}_1 = \text{IP}_1$$

$$h\nu - \text{KE} = I_p$$

$$h\nu - \text{KE}_2 = \text{IP}_2$$

$$h\nu - \text{KE}_3 = \text{IP}_3 \dots\dots$$



Depth of analysis depends on photon energy

energy

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

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

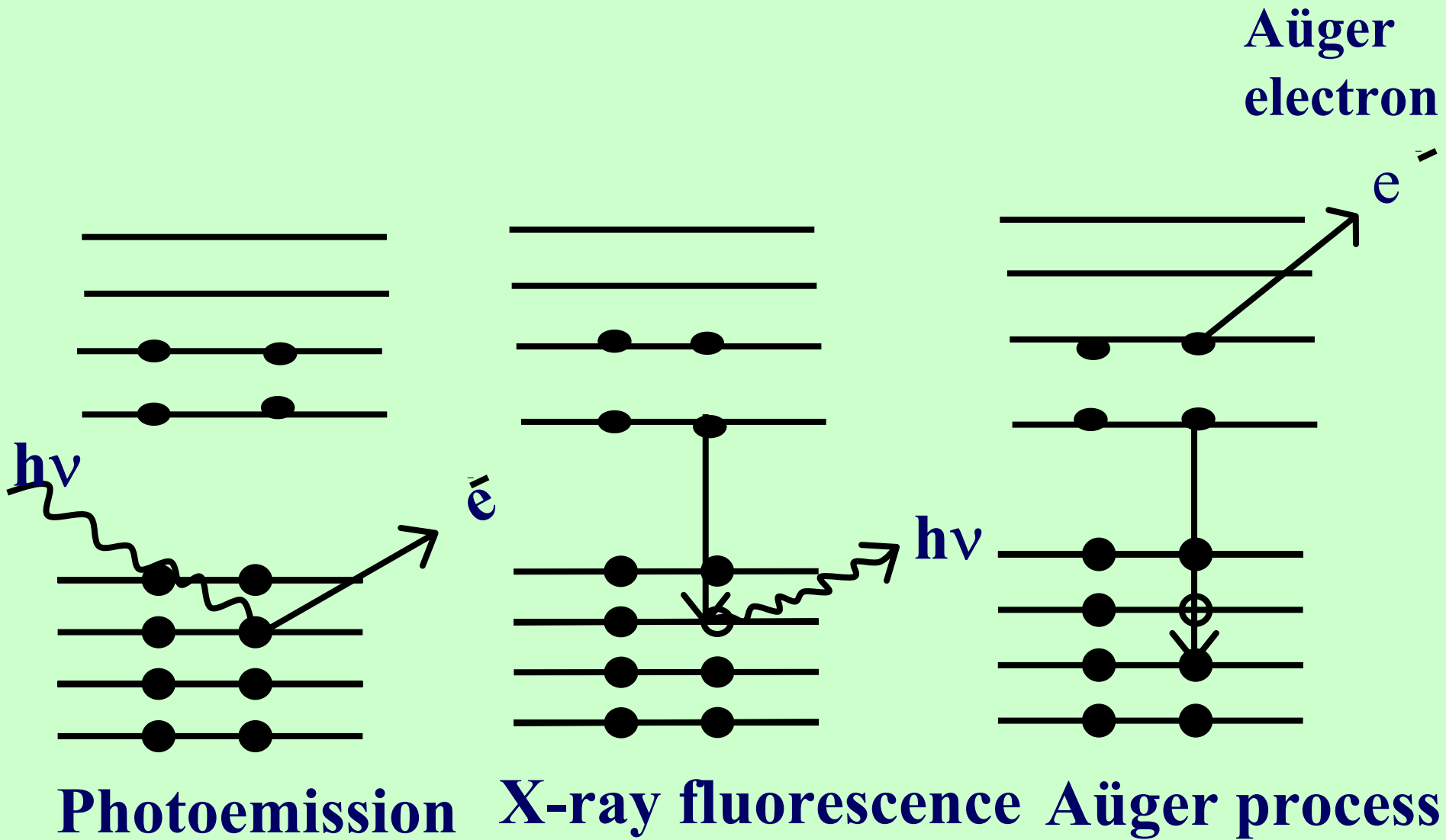
Al $K_{\alpha 1,2}$ 1486.6 eV $2 P^{3/2, 1/2} \rightarrow 1 S$

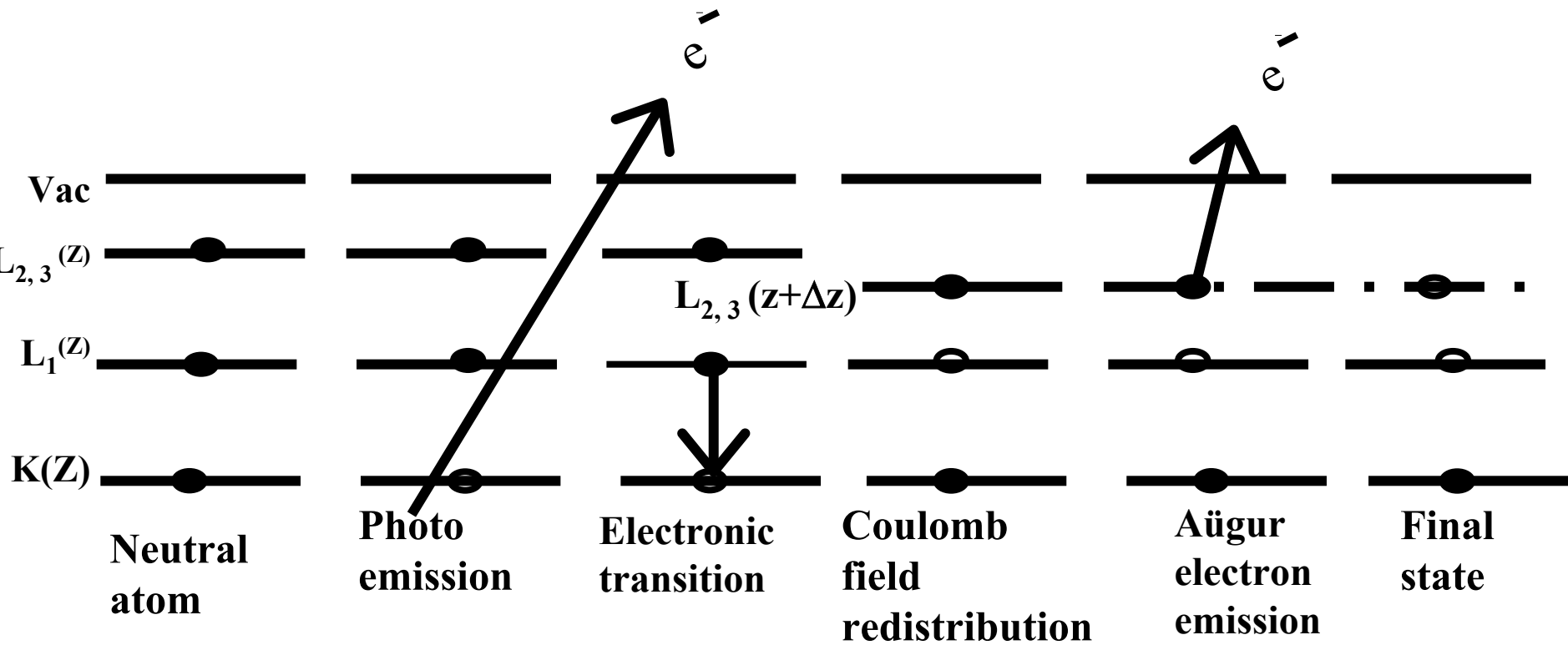
Mg $K_{\alpha 1,2}$ 1253.6 eV ”

Na $K_{\alpha 1,2}$ 1041.0 eV ”

Si $K_{\alpha 1,2}$ 1739.5 eV ”







$$E_{K, L1, L2, 3} = E_k - E_{L1} - E_{L2, 3}$$

$$E_{ABC}^{(Z)} = E_A^{(Z)} - \frac{1}{2} [E_B^{(Z)} + E_B^{(Z+1)}] - \frac{1}{2} [E_C^{(Z)} + E_C^{(Z+1)}]$$

E's are the binding energies.

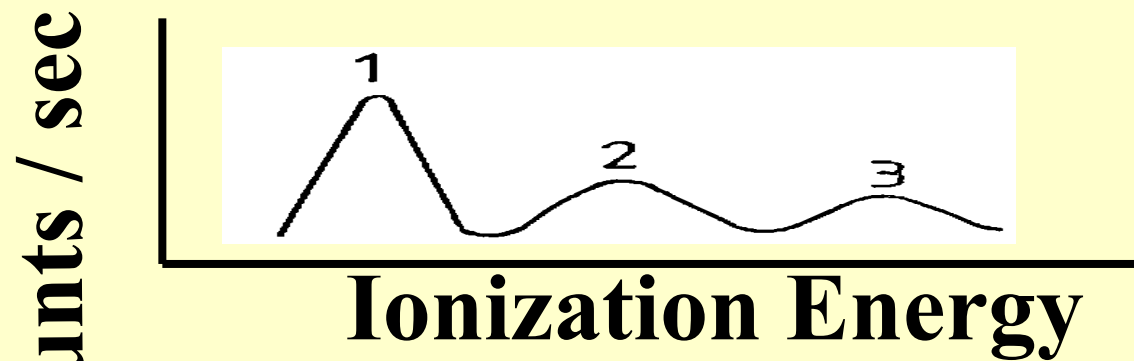
$$E_{ABC} \longrightarrow K L_1 L_{2,3}, K L_1 V, KVV$$

Intense Auger intensities if the valence electron density is high.

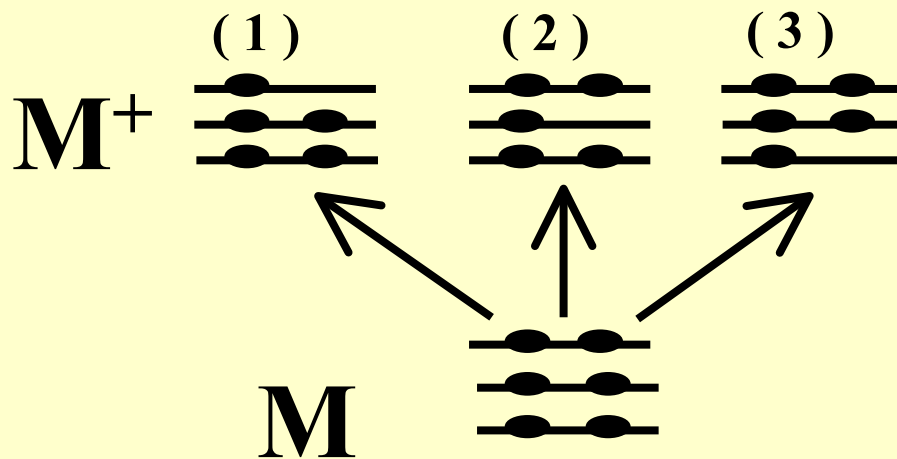
Fluorescence efficiency increases with transition energy. Fluorescence and Auger are comparable when $\Delta E \sim 10,000$ eV.

***VALENCE SHELL
PHOTOELECTRON
SPECTROSCOPY***

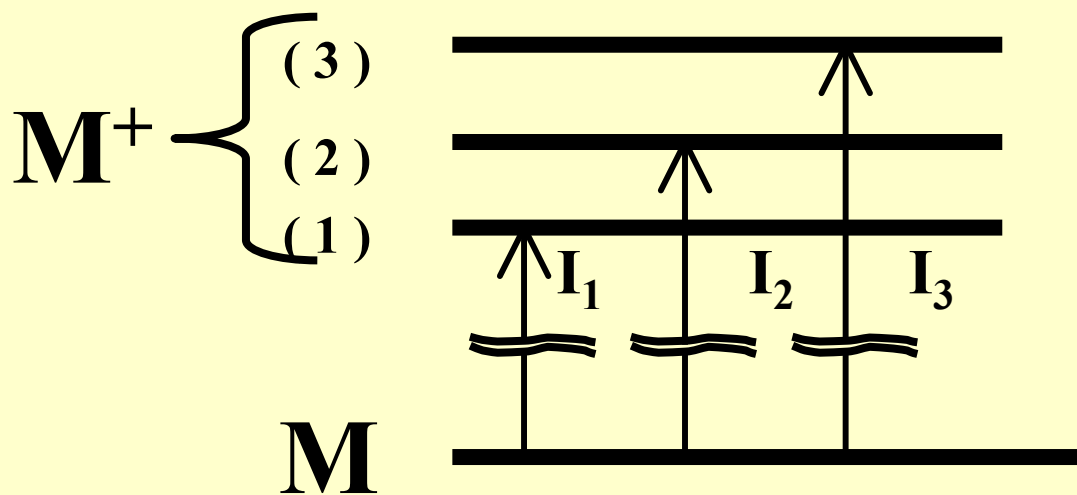
(A)

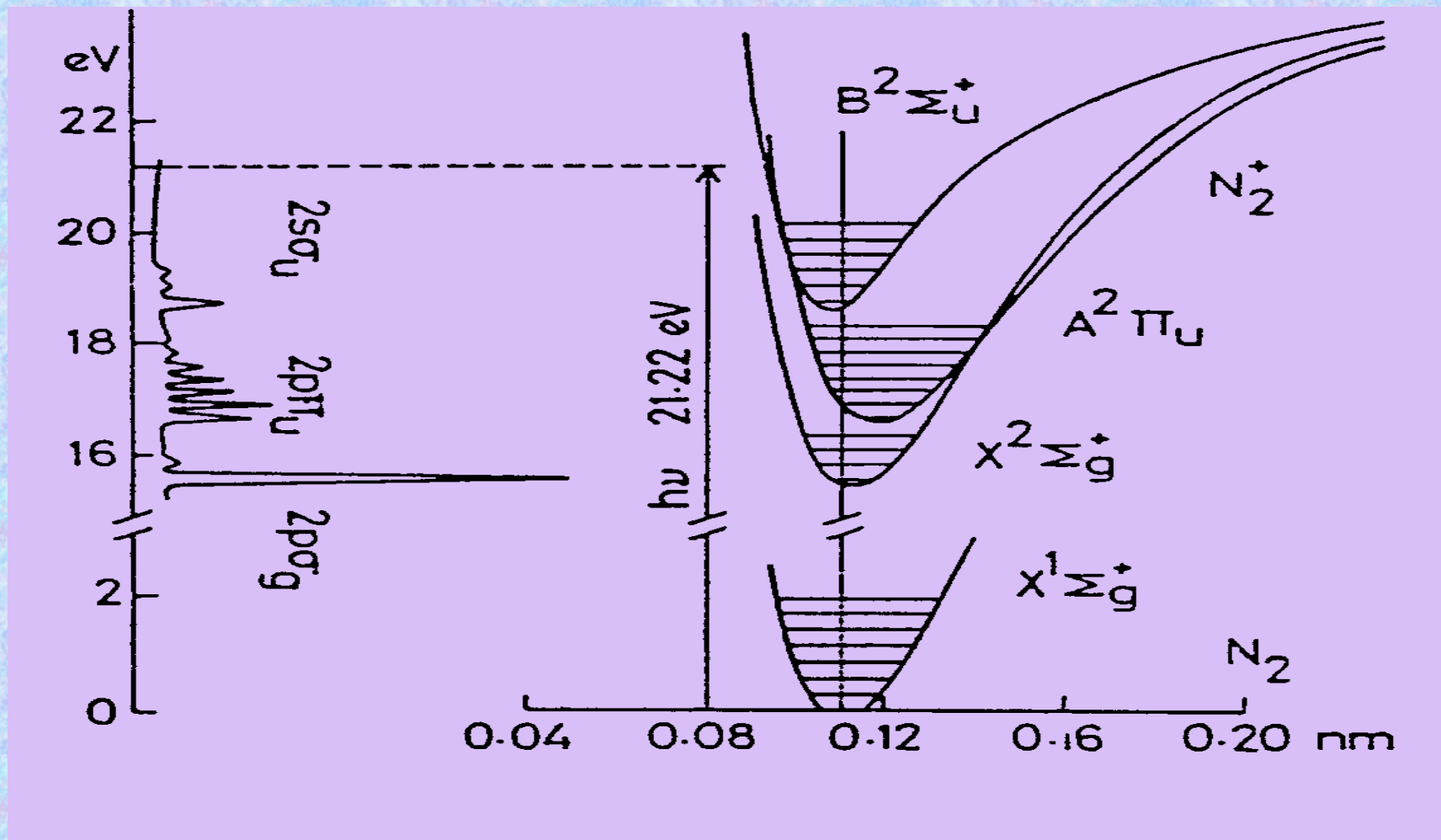


(B)



(C)





INTERNUCLEAR DISTANCE

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

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

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

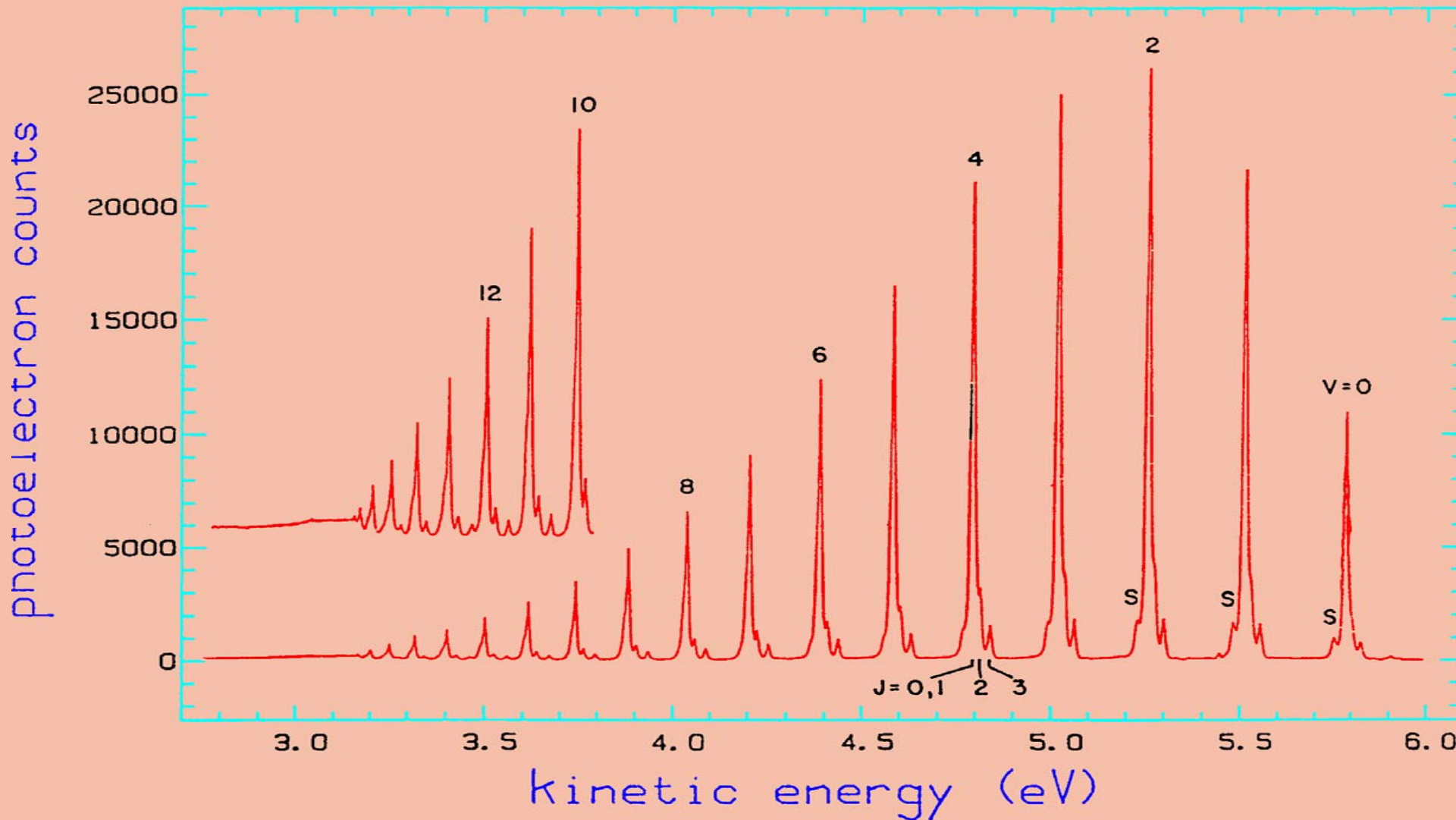
$$\mathbf{E_v = E_0 + \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2}$$

$$\mathbf{D_e = \omega^2 / 4 \omega_e x_e}$$

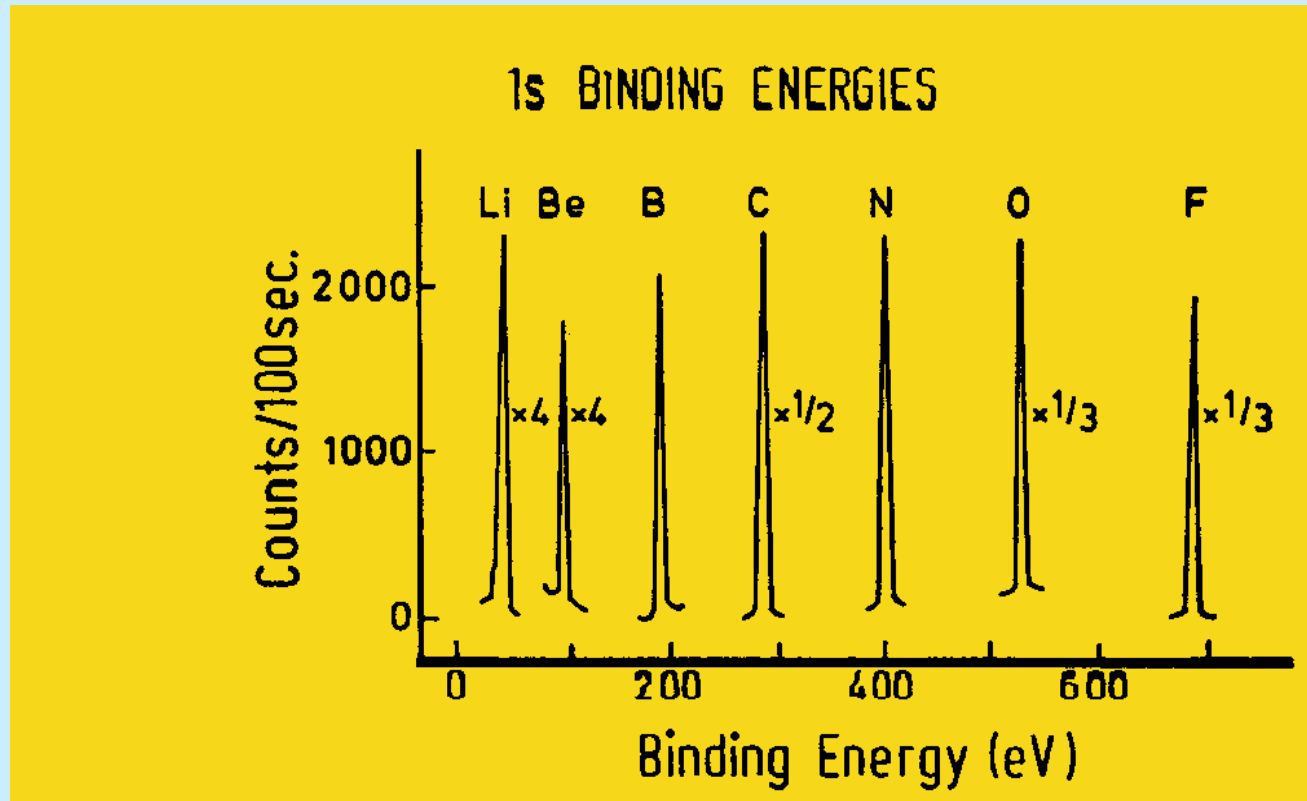
HeI UPS of H₂

Vibrations and Rotations !

n-H₂ 297 K

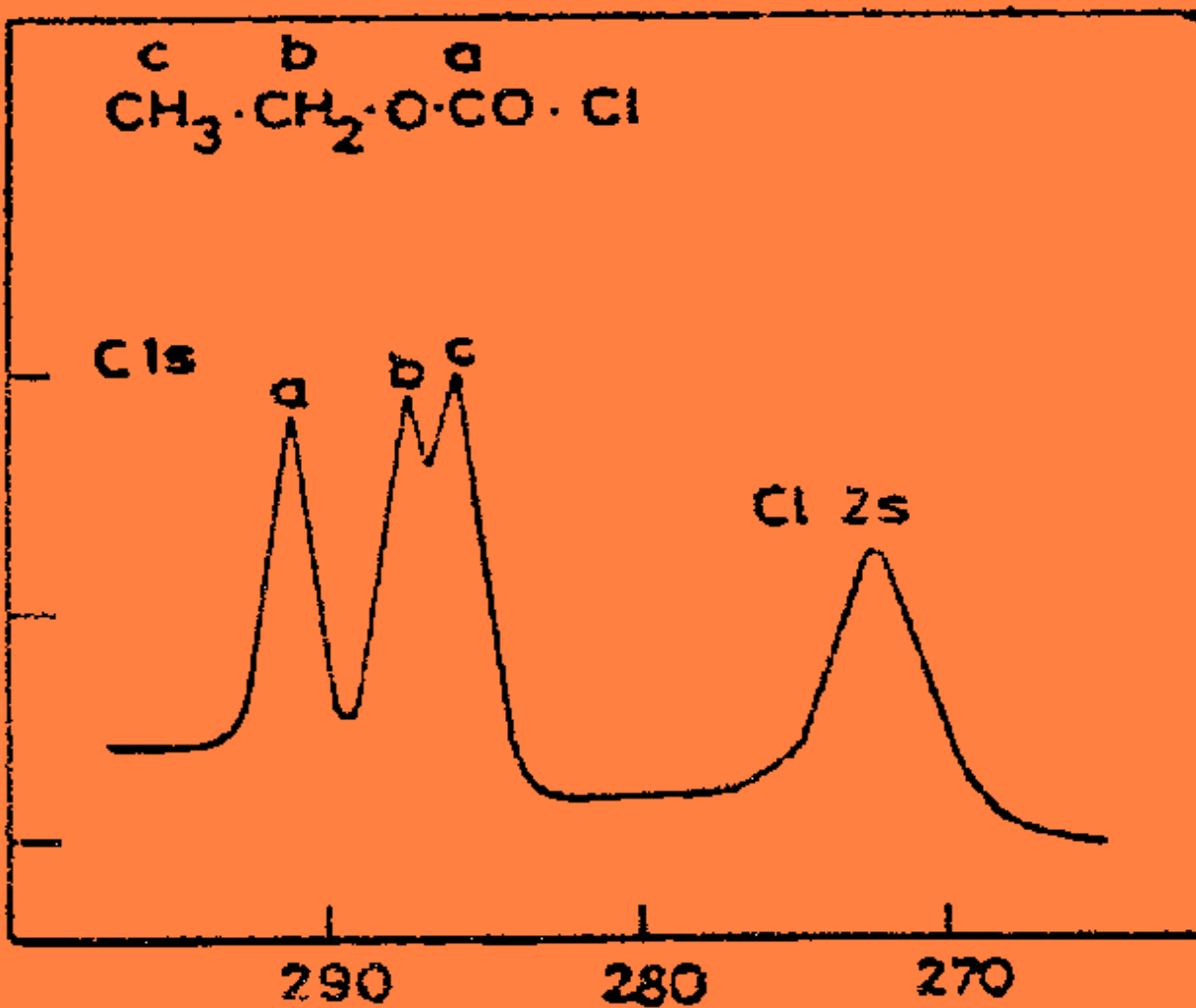


***CORE LEVEL PHOTOELECTRON
SPECTROSCOPY***



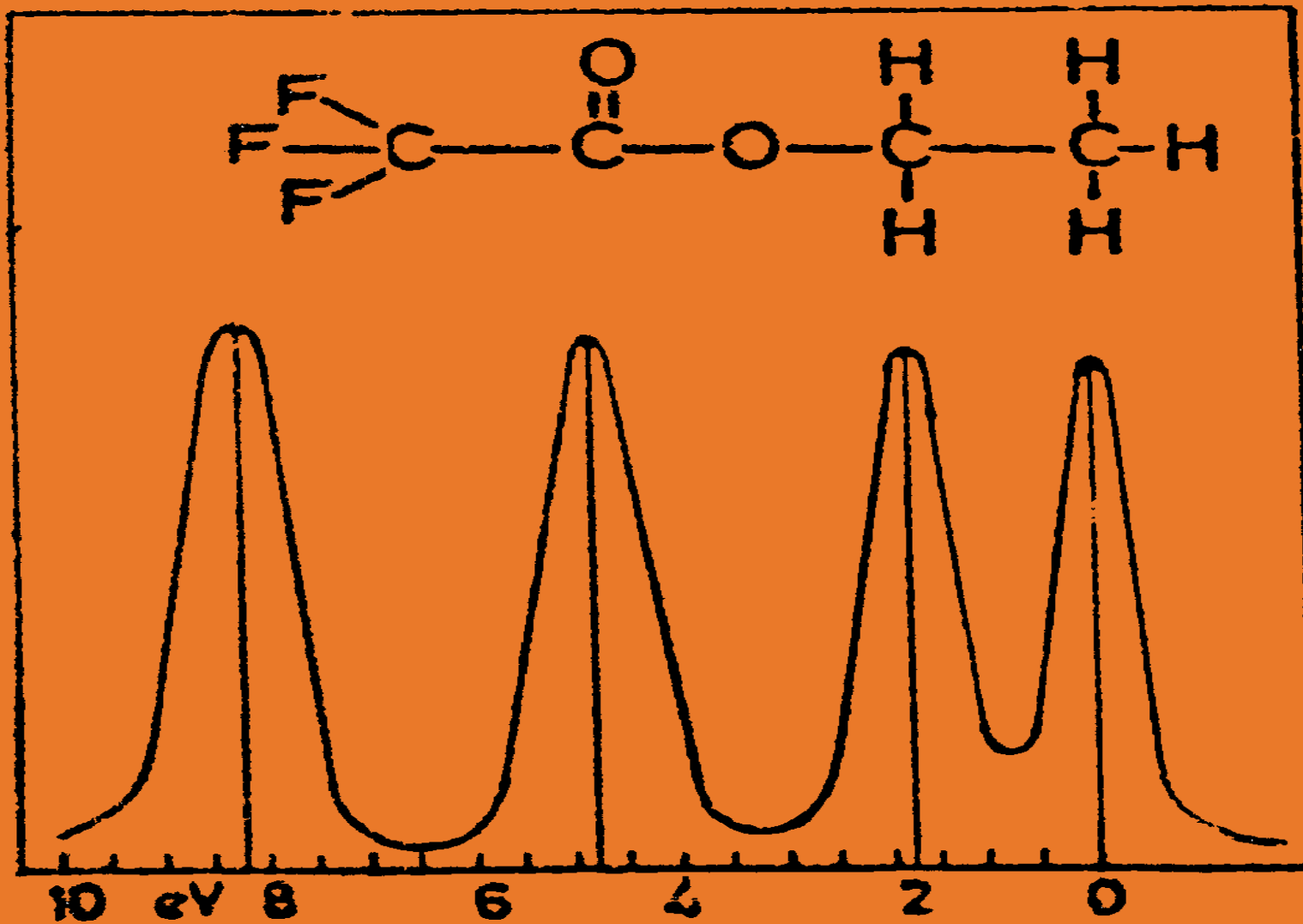
XPS-spectra of the 1s core levels of Li, Be, B, C, N, O, F (from S. Hüfner).

Counting Rate



Binding energy eV

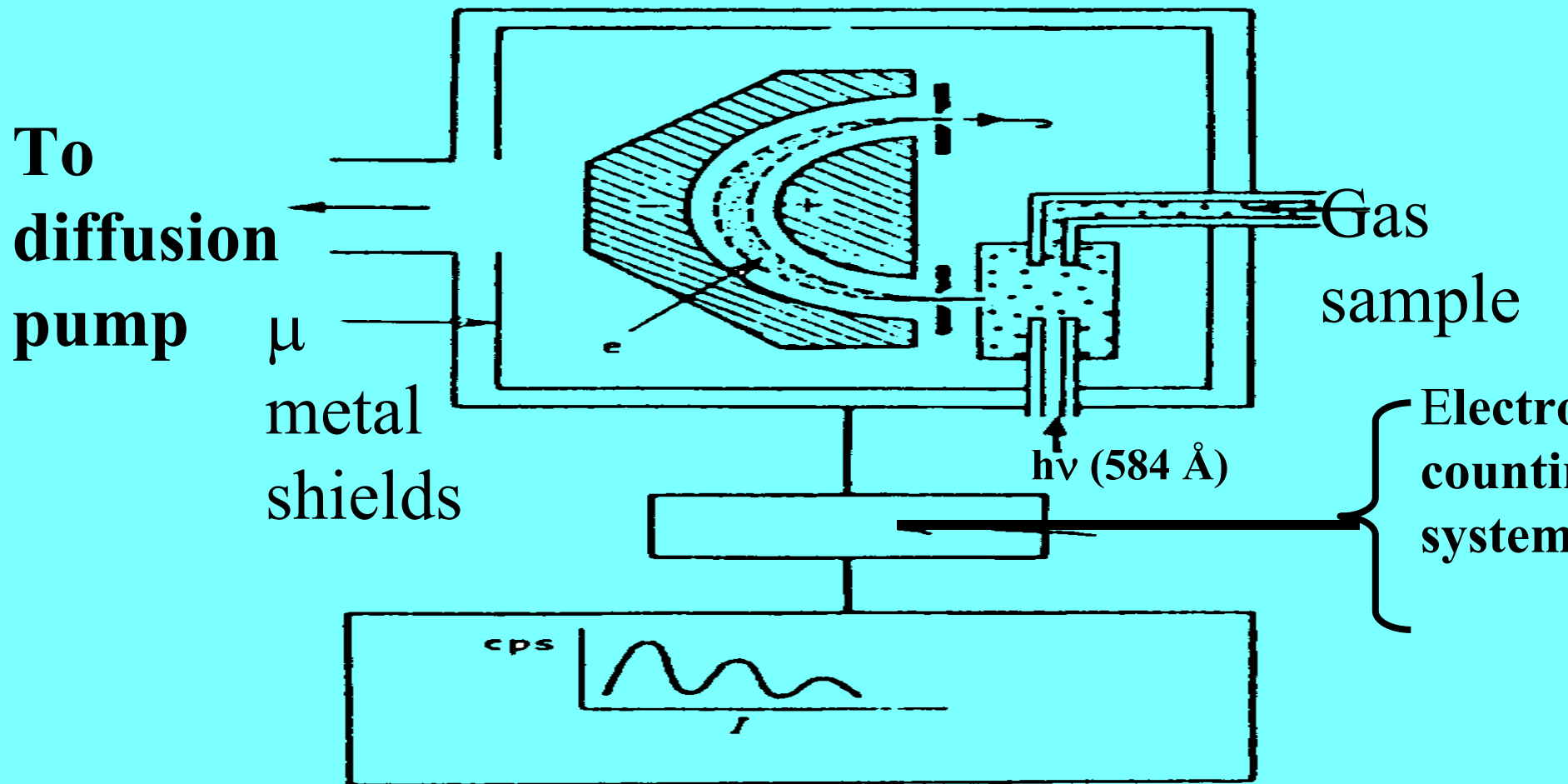
Counting Rate



$E_B = 291.2 \text{ eV}$

Chemical Shift

INSTRUMENTATION



To
diffusion
pump

μ
metal
shields

Gas
sample

$h\nu (584 \text{ \AA})$

Electro
counting
system

cps

t

References

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