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)

Aüger electron spectroscopy (AES)

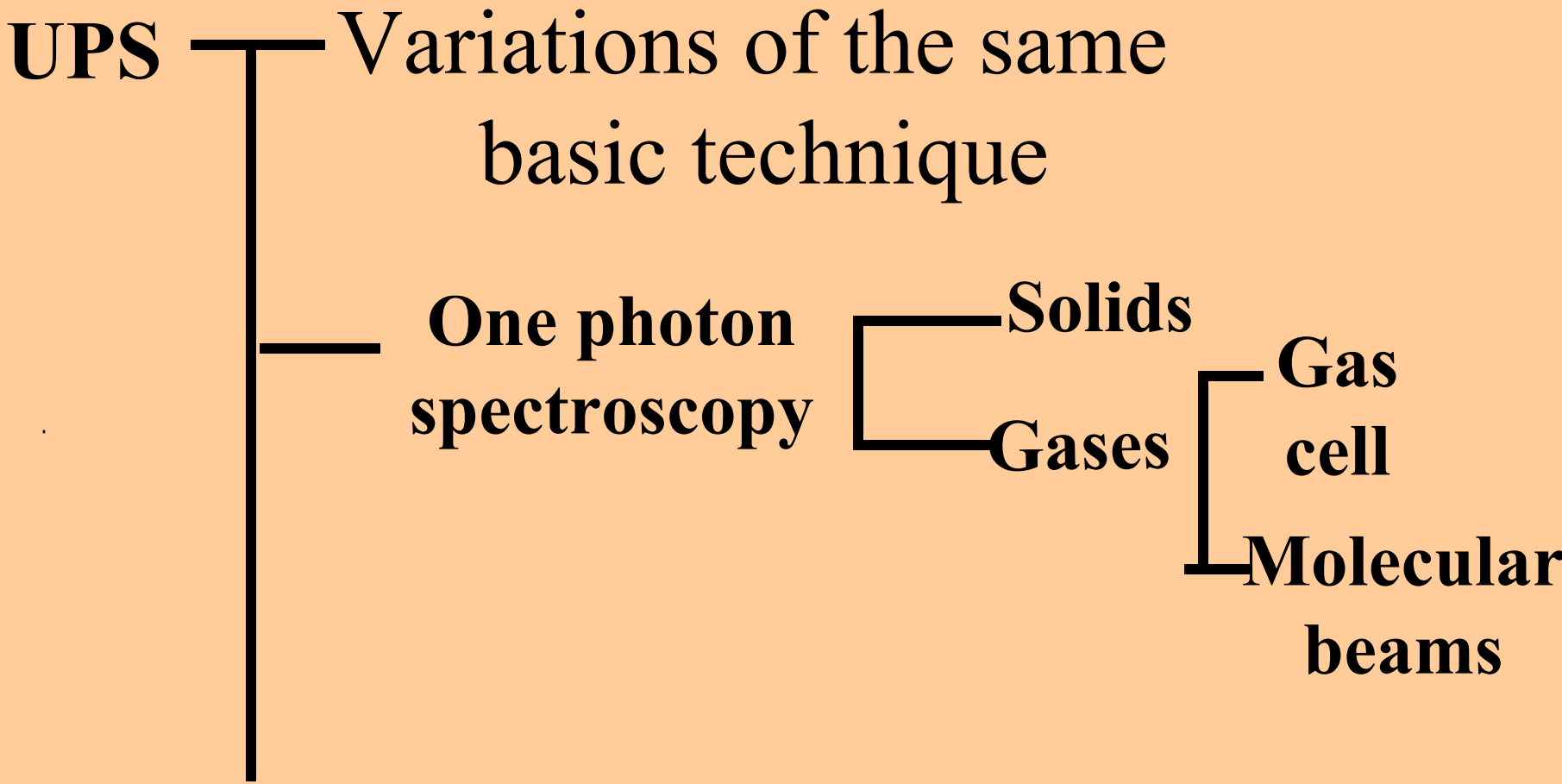
Electron energy loss spectroscopy (EELS)

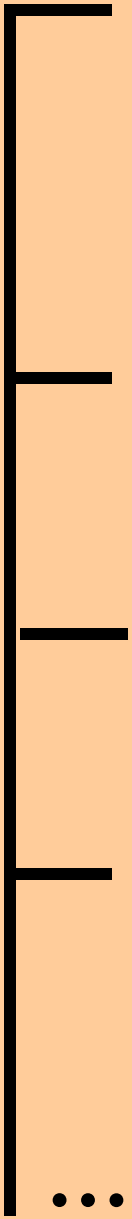
Inverse photoemission spectroscopy (IPS)

There are a range of techniques in each of these

UPS

- **Photon source variation**
  - He I 21.2 eV
  - He II 40.8 eV
  - Ne I
  - Synchrotron radiation
  - ……


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

……..

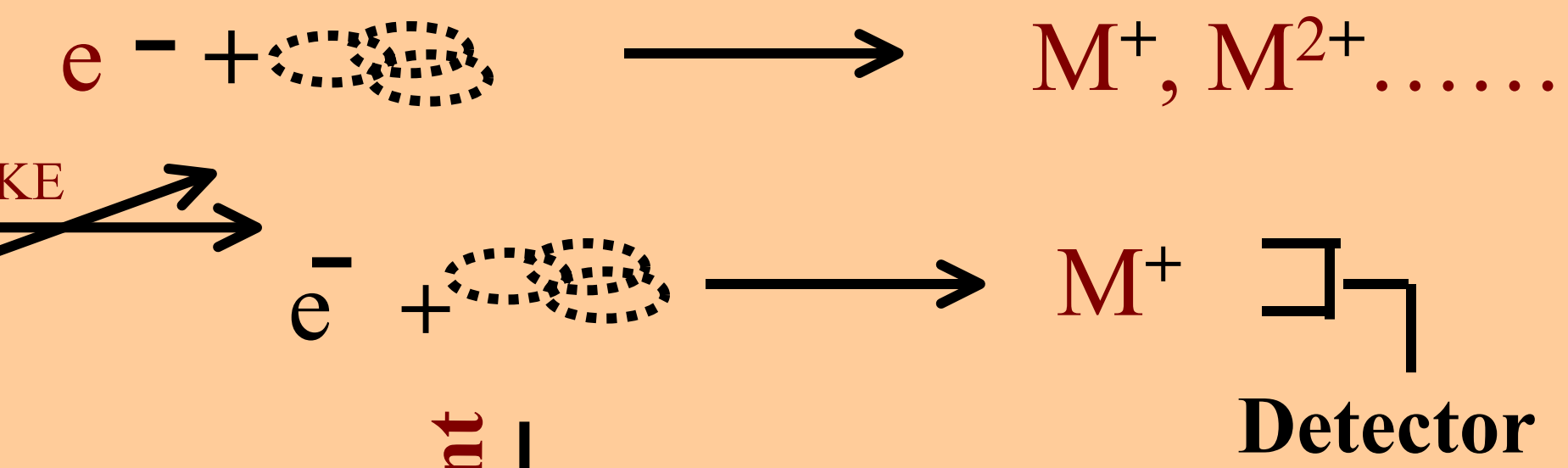
Structure and Properties of Matter

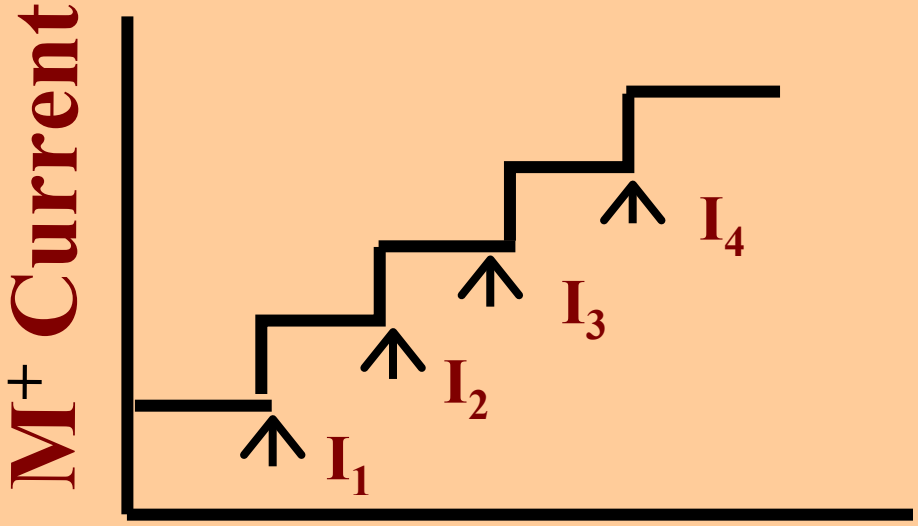
Spectroscopy
Scattering
Physical Properties

Spectroscopy (pre-1965)

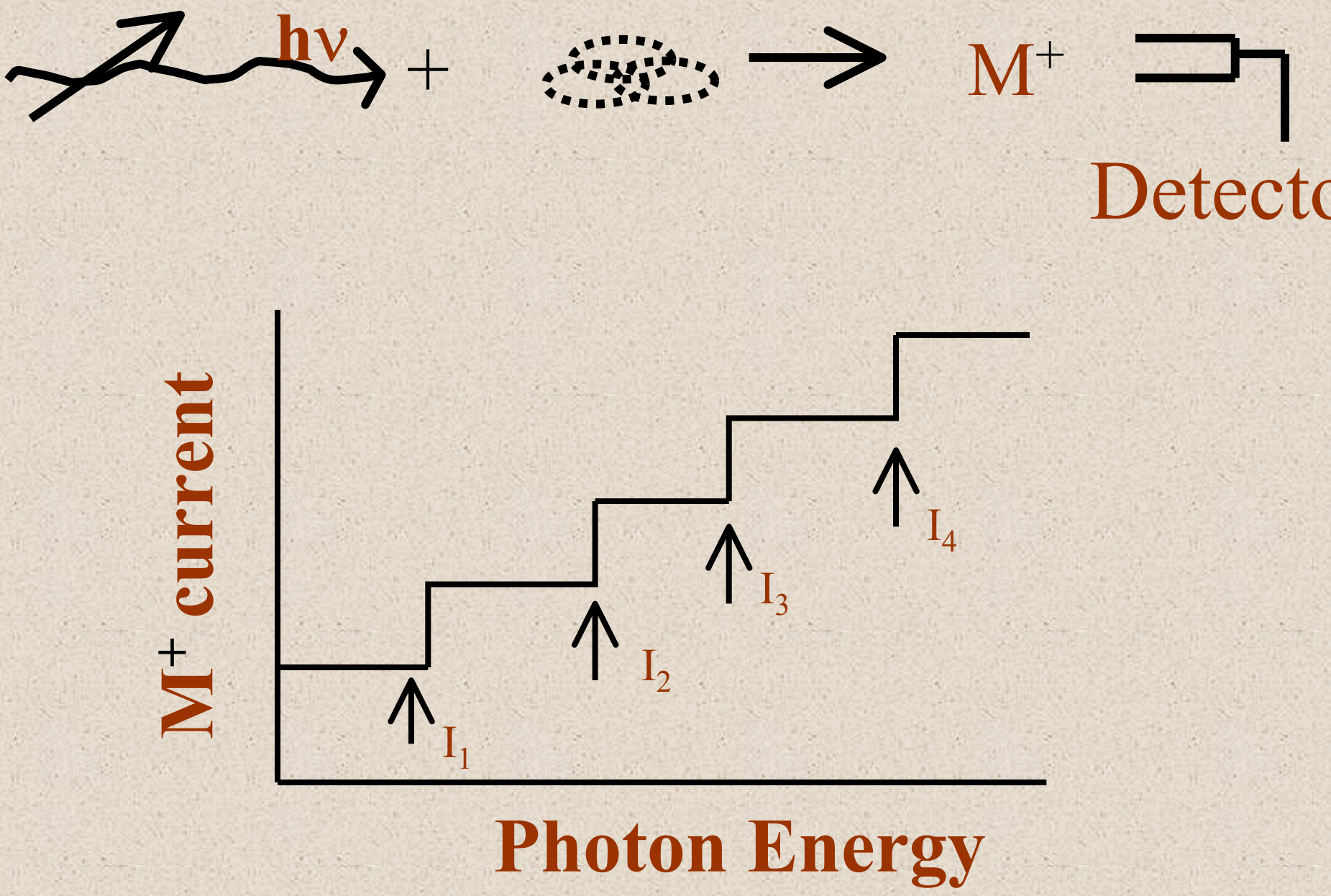
Absorption
Magnetic
Mass

Spectroscopy using electrons





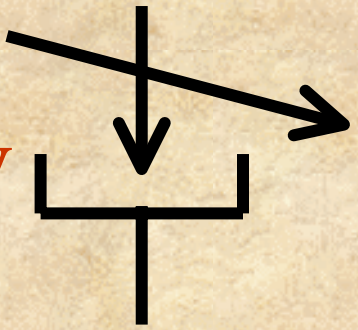
Ionization efficiency curves


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

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

(No M^{2+}, generally)

$M^+ + e^-$



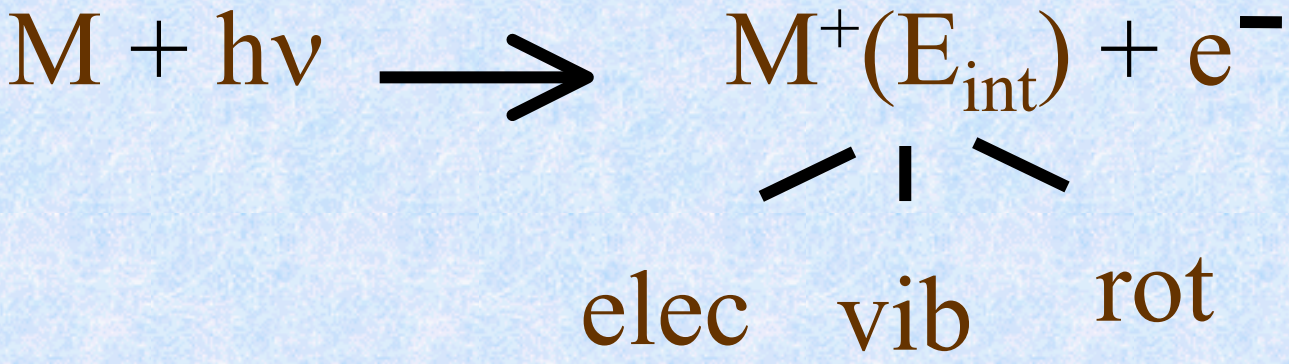
Photoelectron Spectroscopy

Photoelectric effect

Early experiments in 1887

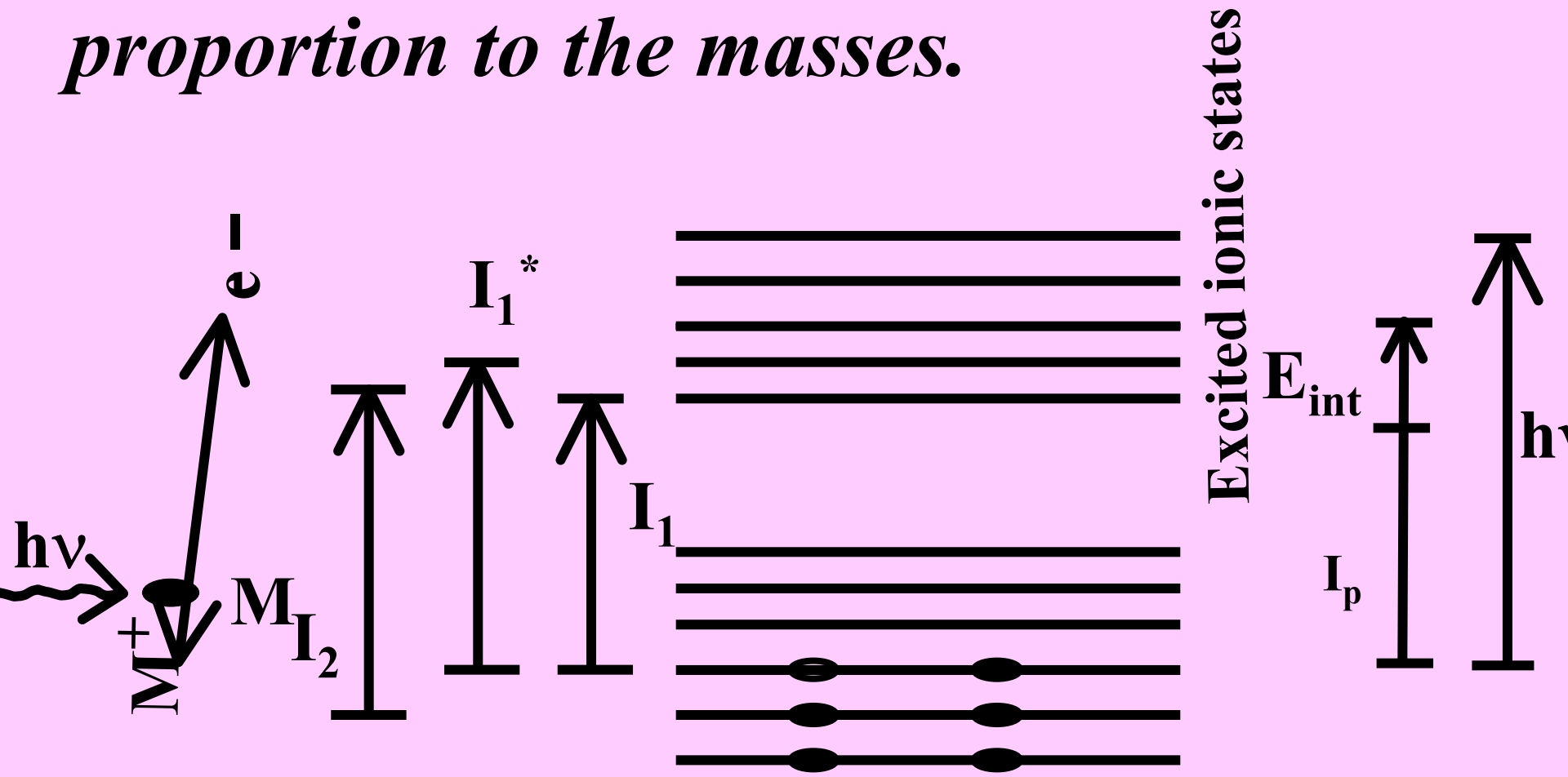
$h\nu = KE + \phi$ 1905

Photoion can be excited



$h\nu - I - E_{int} = $ 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,

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

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

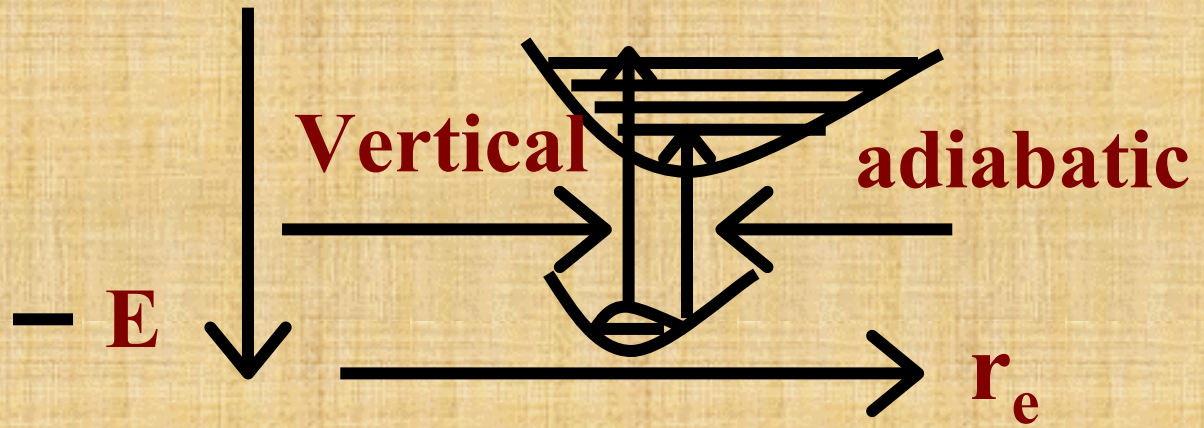
$$h\nu - (I_p + E_{int}) = KE$$

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

$$E_{int} \rightarrow 0$$

$$h\nu - KE = I_p$$

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



Depth of analysis depends on photon energy

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

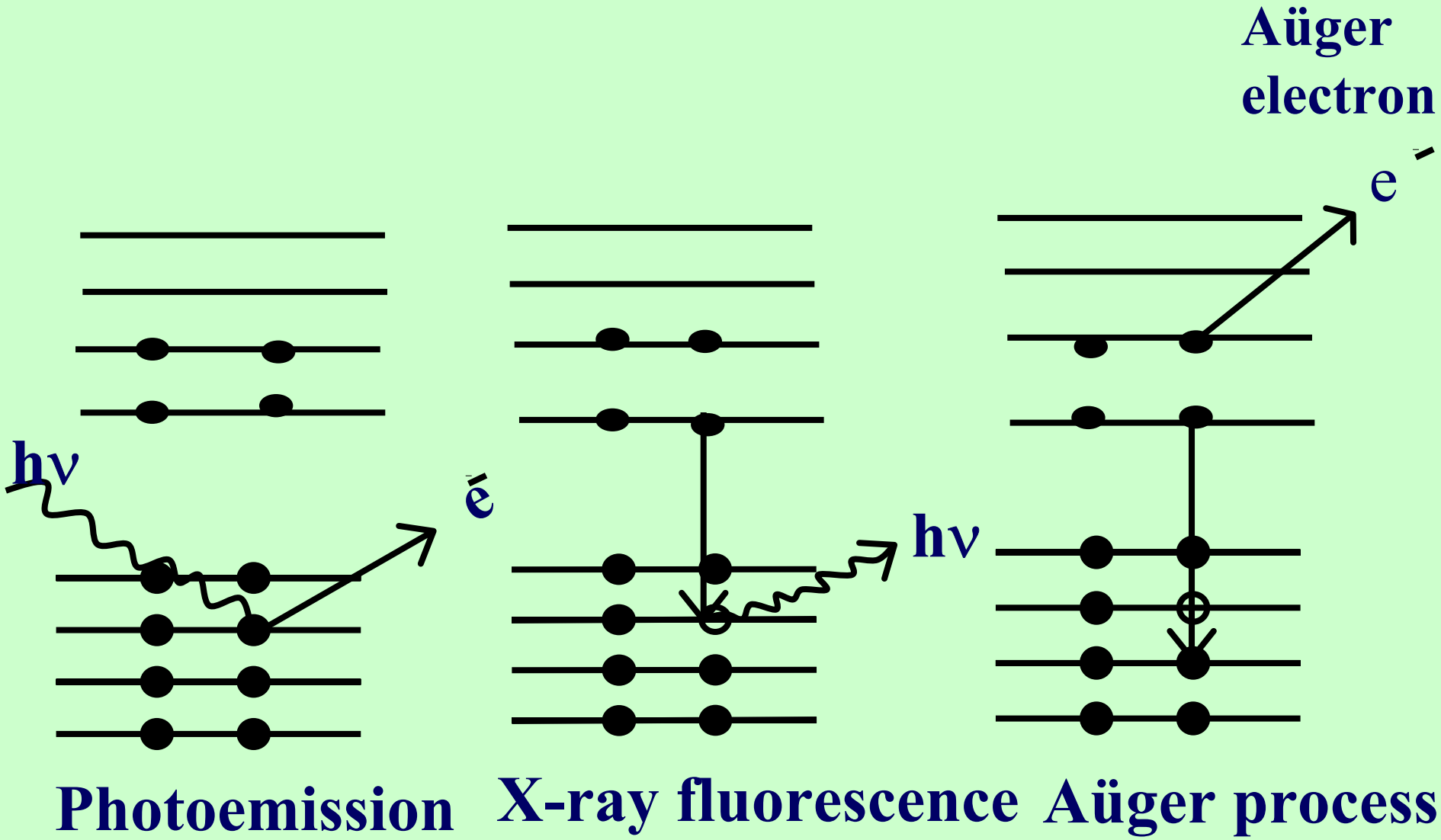
He II 40.8 eV 2 P $\rightarrow$ 1 S of He^+

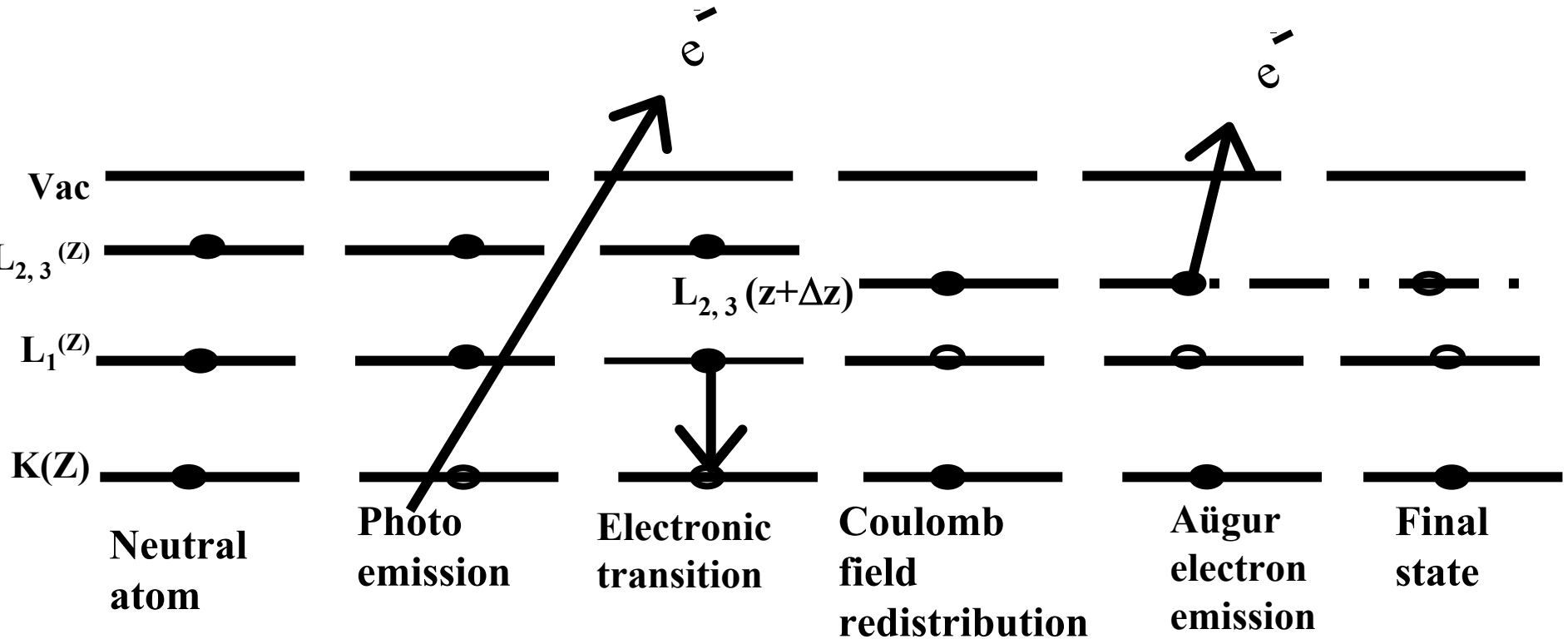
Al $K_{\alpha 1,2}$ 1486.6 eV $2\ P^{3/2,\ 1/2} \rightarrow 1\ S$

Mg $K_{\alpha 1,2}$ 1253.6 eV ”

Na $K_{\alpha 1,2}$ 1041.0 eV ”

Si $K_{\alpha 1,2}$ 1739.5 eV ”


Aüger
electron
e⁻
hν
é
hν
Photoemission
X-ray fluorescence
Aüger process


e⁻
e⁻
Vac
L2, 3 (Z)
L1(Z)
K(Z)
L2, 3 (z+Δz)
Neutral atom
Photo emission
Electronic transition
Coulomb field redistribution
Aügur electron emission
Final state

$$E_{K,\ L\,1,\,L2\,,\,3} = E_k - E_{L1} - E_{L\,2,\,3}$$

$$E_{ABC}^{(Z)} = E_A^{(Z)} - \tfrac{1}{2}\left[\, E_B^{(Z)} + E_B^{(Z+1)} \,\right] - \tfrac{1}{2}\left[\, E_C^{(Z)} + E_C^{(Z+1)} \right.$$

E's are the binding energies.

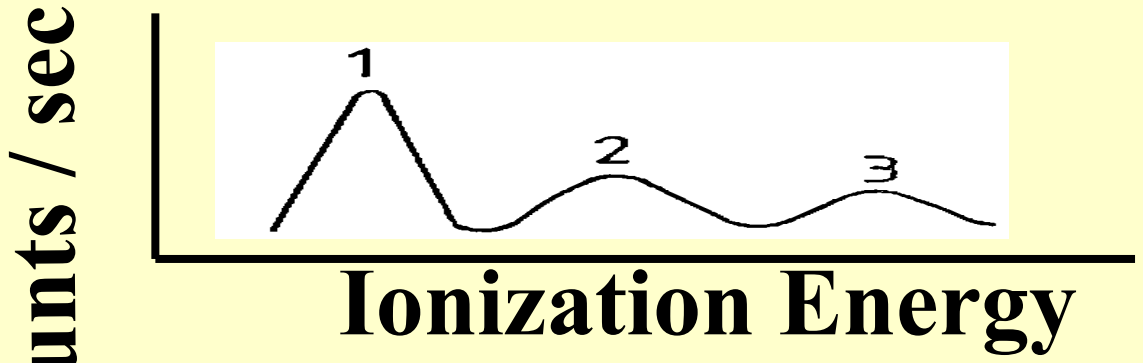
E_{ABC} ⟶ $K\ L_1\ L_{2,\,3}$, $K\ L_1\ V$, KVV

Intense Auger intensities if the valence electron density is high.

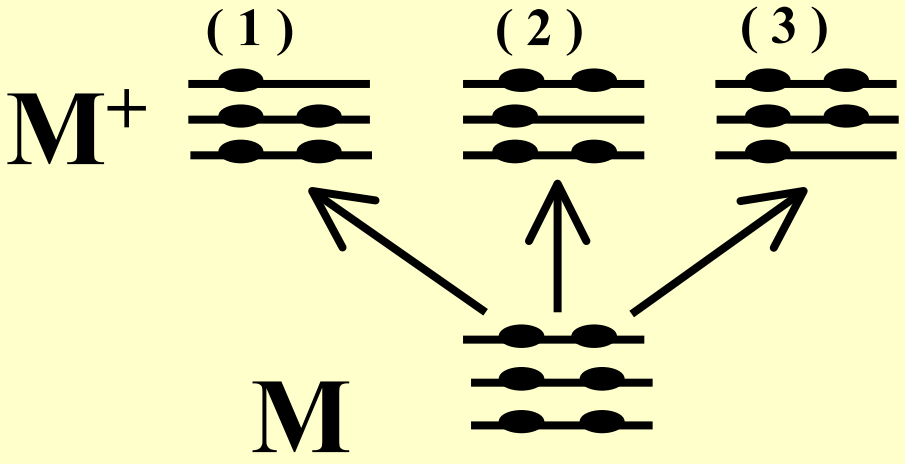
Fluorescence efficiency increases with transition energy. Fluorescence and Auger are comparable when $\Delta E \sim 10{,}000$ eV.

VALENCE SHELL PHOTOELECTRON SPECTROSCOPY

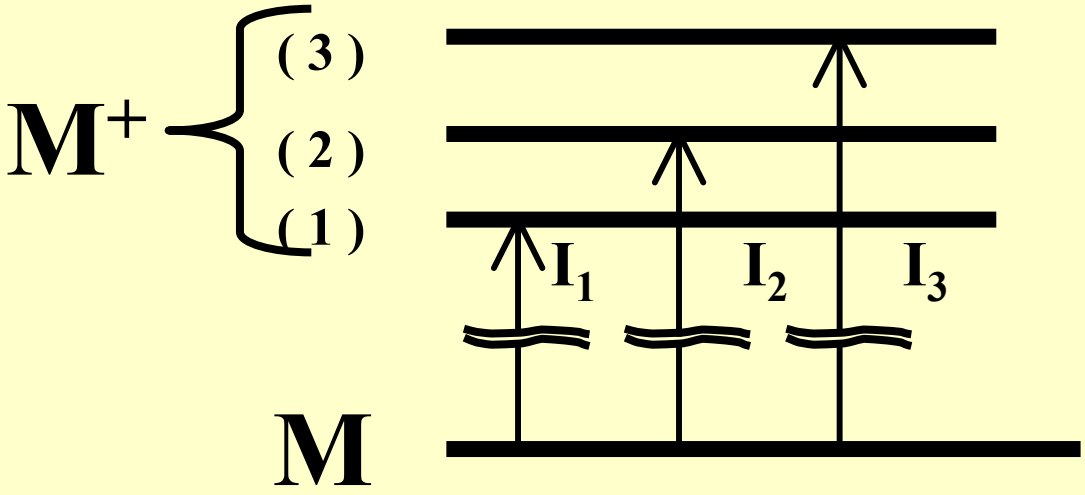
(A)

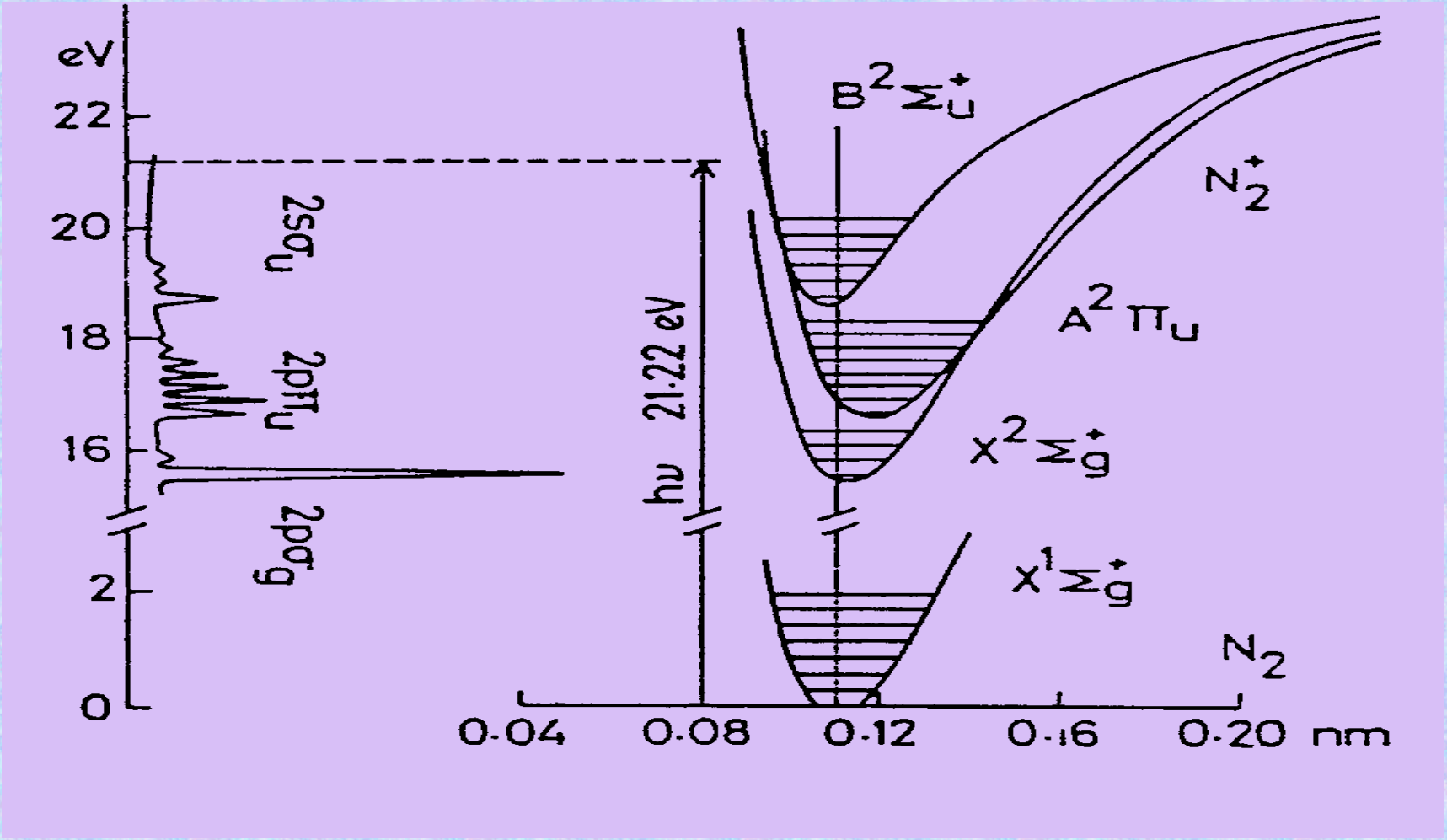


(B)



(C)





INTERNUCLEAR DISTANCE

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

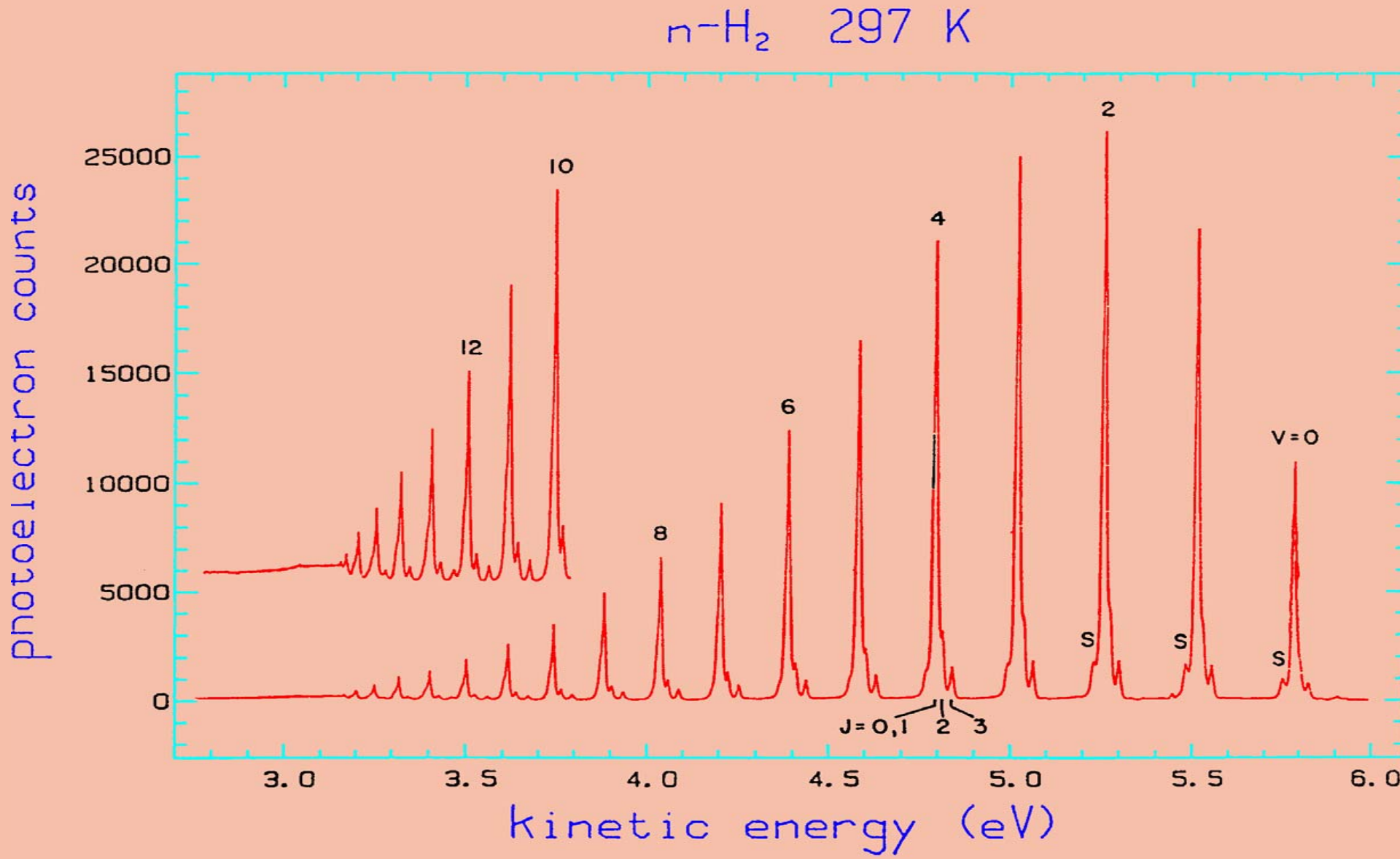
$^2P\pi_u \rightarrow$ bonding 2345 to 1850 cm^{-1}

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

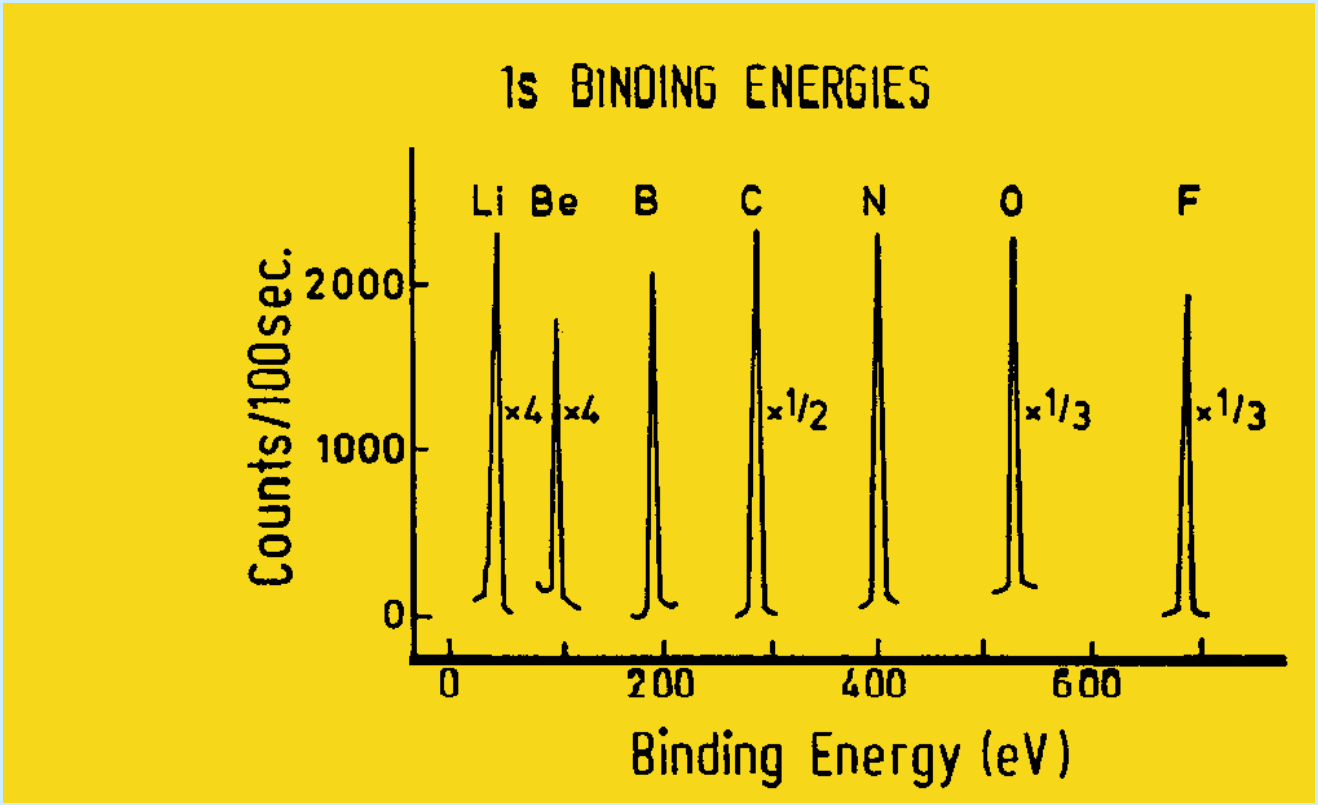
$$E_v = E_o + \omega_e (v + ½) - \omega_e x_e (v + ½)^2$$

$$D_e = \omega^2 / 4\ \omega_e x_e$$

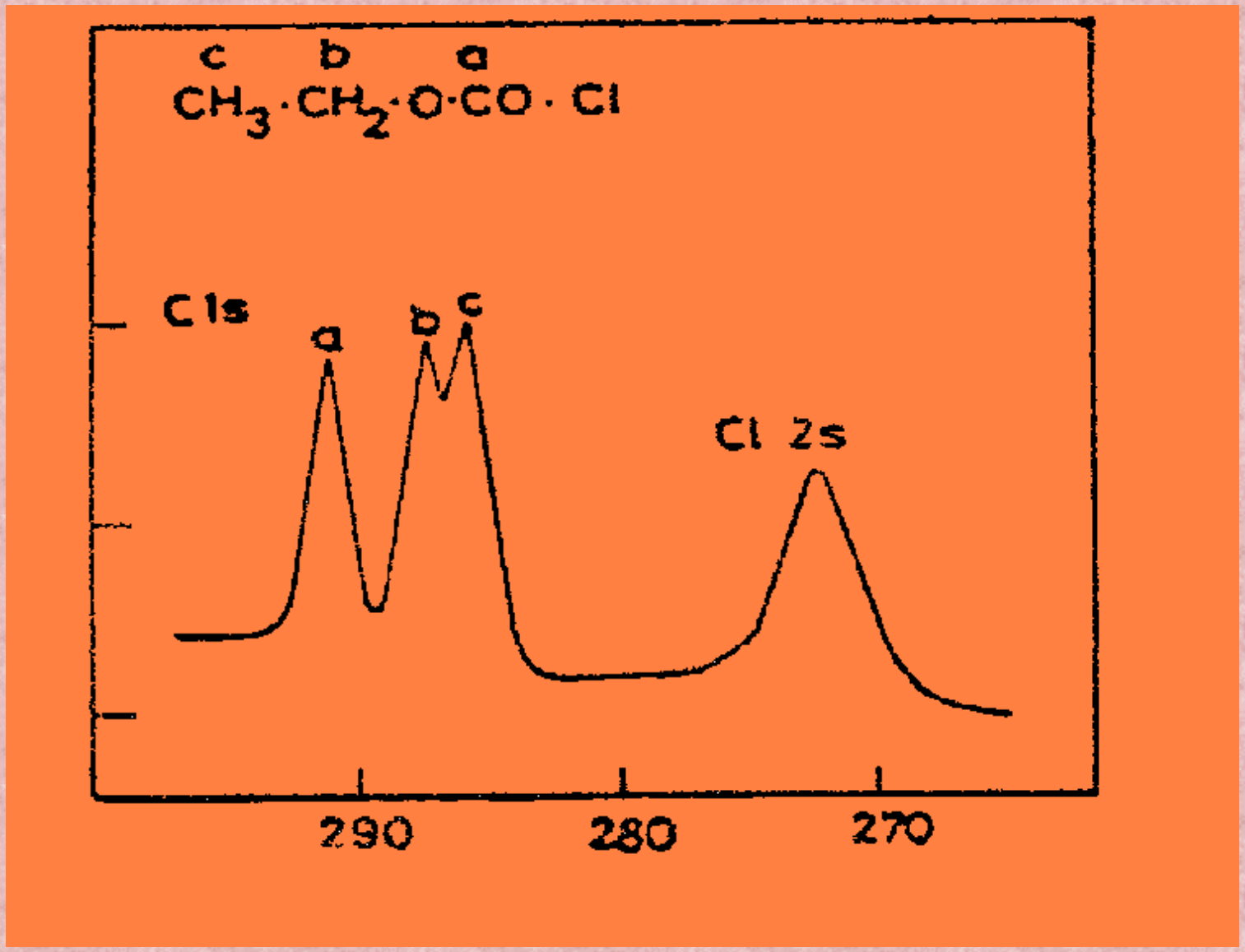
HeI UPS of H_2 Vibrations and Rotations !



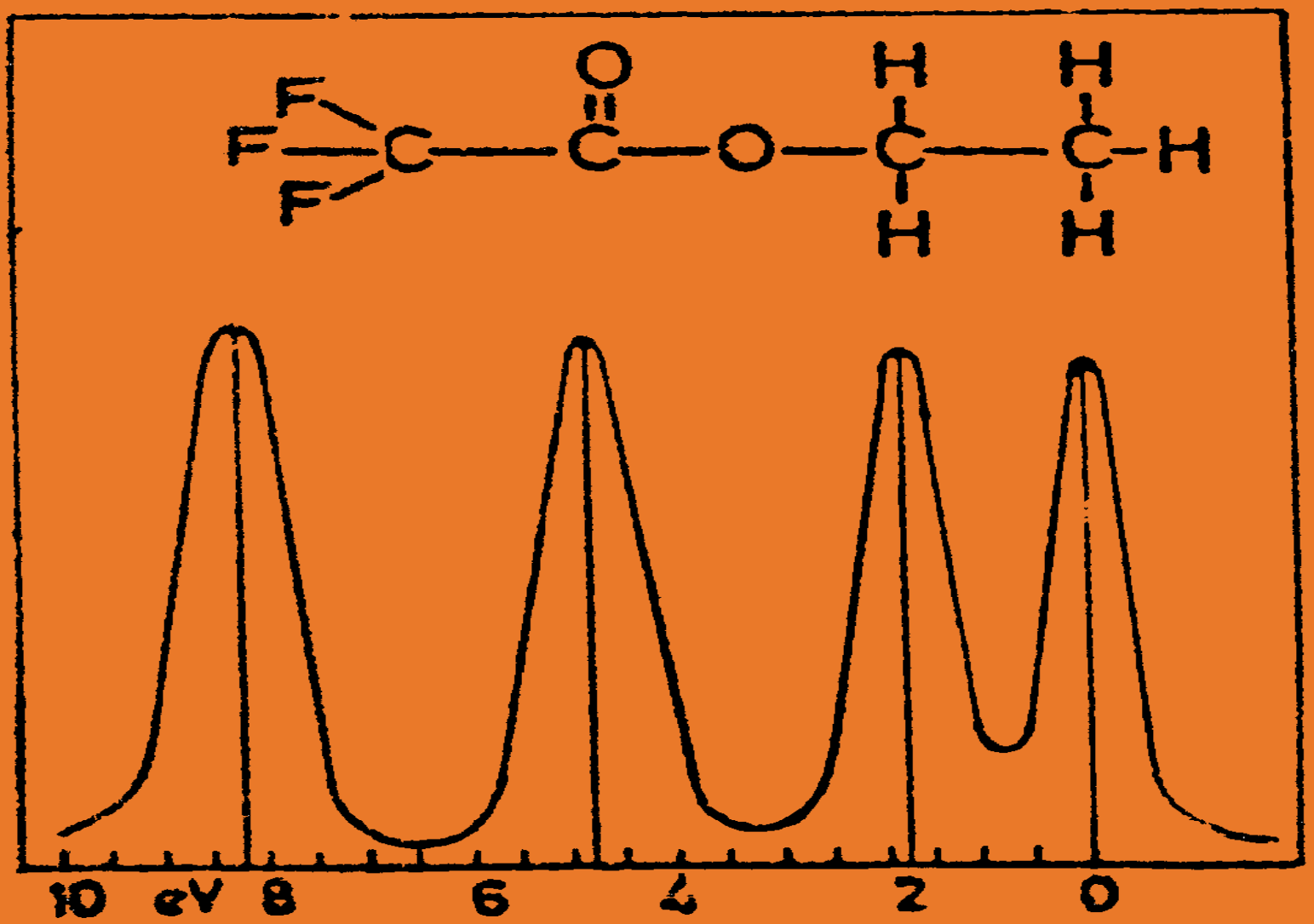
CORE LEVEL PHOTOELECTRON SPECTROSCOPY



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


c b a
CH3·CH2·O·CO·Cl
C 1s
a
b
c
Cl 2s
290
280
270
Counting Rate
Binding energy eV

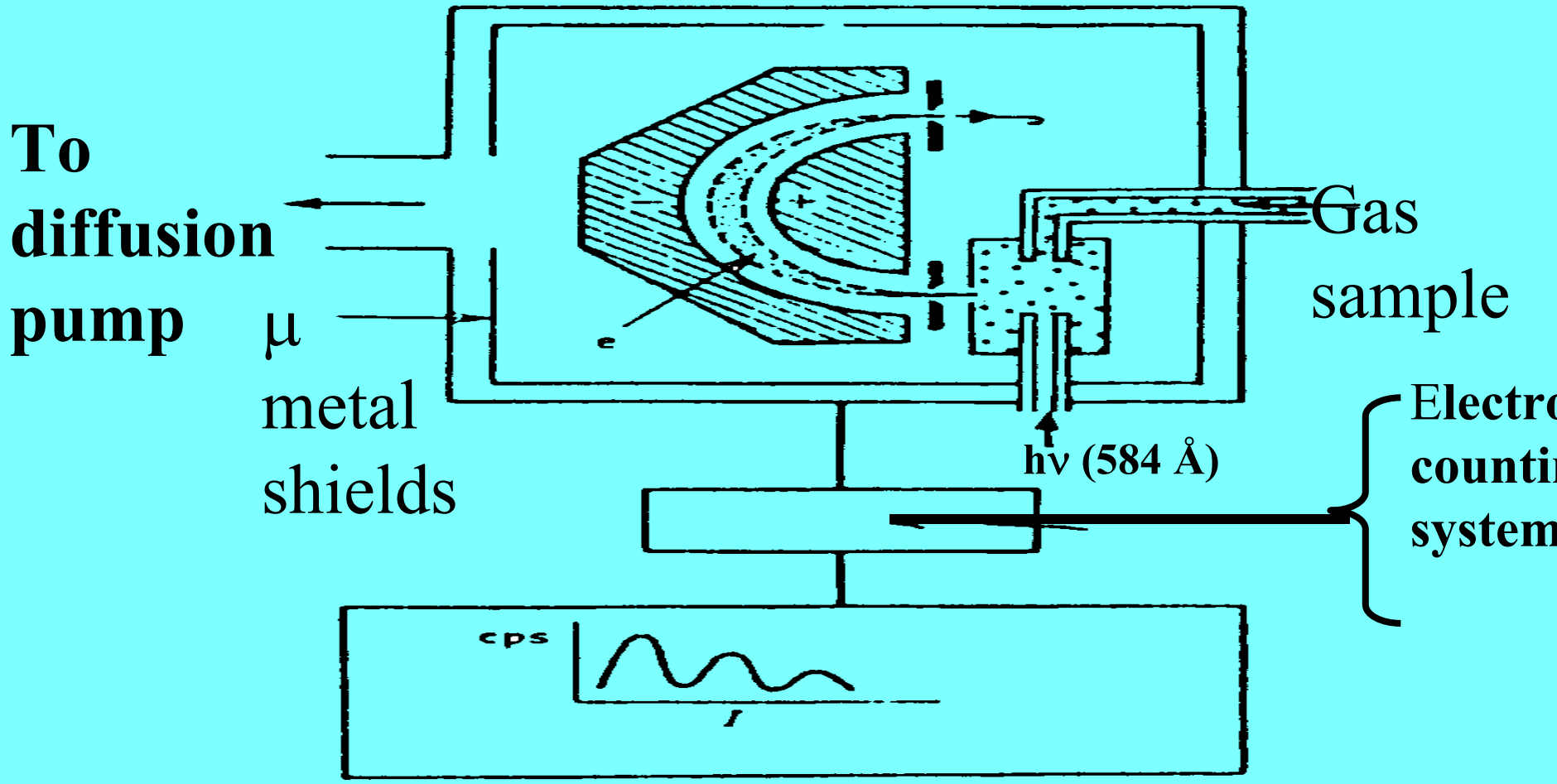
Counting Rate



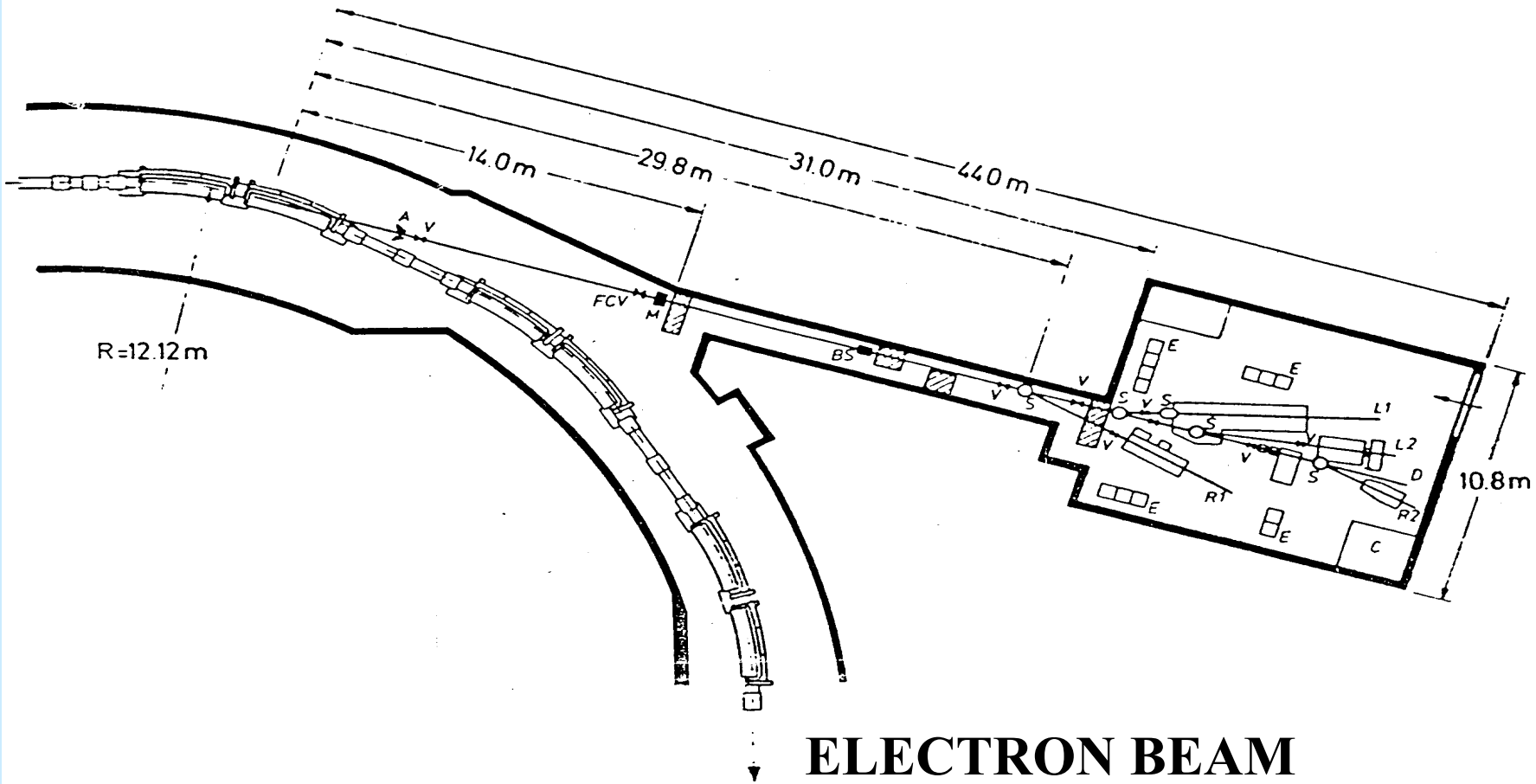
E_B=291.2eV

Chemical Shift

INSTRUMENTATION


To diffusion pump
μ metal shields
Gas sample
e
hν (584 Å)
Electro counti system
cps
I

Synchrotron Radiation and XPS



Layout of the synchrotron radiation laboratory at DORIS.

References

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2. H. Windawi and F. F. L. Ho, Ed. Applied *Electron Spectroscopy for Chemical Analysis* John Wiley & Sons, New York, 1982.

3. D. Briggs and M. P. Seah, Ed. *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, John Wiley & Sons, New York, 1983.

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5. C. R. Brundle and A. D. Baker, Ed., *Electron Spectroscopy: Theory, Techniques and Applications*, Vol. 1-5, Academic press, London, 1978.

6. D. Briggs, Ed., *Handbook of X- ray and Ultraviolet Photoelectron Spectroscopy*, Heyden, London, 1977.

7. K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T Bergmark, L. O. Werme, R. Manne, and Y. Baer, *ESCA Applied to Free Molecules*, North-Holland, Amsterdam, 1969.

8. D. A. Shirley, Ed., *Electron Spectroscopy*, North-Holland, Amsterdam, 1972.