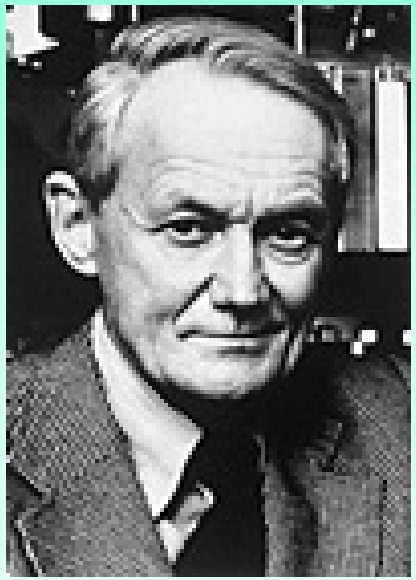
Electron spectroscopy

Lecture 1-2



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

Y653: Electron Spectroscopy

ourse structure

cture 1. Introduction to electron spectroscopies

cture 2. Ultraviolet photoelectron spectroscopy: introduction

cture 3-4. Electron spectroscopies: experimental methods

cture 5-7. Interpretation of UPS, complications, computational methods

cture 8-12. XPS: spectra, interpretation, basic theory of photoelectron spectroscopy

Lecture 13-15: Complications of photoemission, many body effects

Lecture 16-17: Auger electron spectroscopy

Lecture 18-19: Electron spectroscopy case studies: evolution of metallicity, C60, conductivity

Lecture 20-21: Electron spectroscopy case studies: surfaces

Lecture 22-23: Electron spectroscopy case studies: solids, electronic structure

Lecture 24-25: Electron spectroscopy case studies: catalysis

Lecture 26-27: Electron spectroscopy case studies: monolayers, LBs

Lecture 28-29: Electron energy loss spectroscopy of core levels

Lecture 30-31: Electron energy loss spectroscopy of molecules and surfaces

Lecture 32-33: Bremstrahlung isochromat spectroscopy

Lecture 34: Electron spectroscopy with advanced light sources

Lecture 35: Electron spectroscopy: current research

eferences

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C. Smith, Surface Analysis by Electron Spectroscopy, Plenum, New Yor
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T.A. Carlson, Photoelectronand Auger Spectroscopy, Plenum Press, New York, 1975

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

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.

Reviews, papers

- ***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)

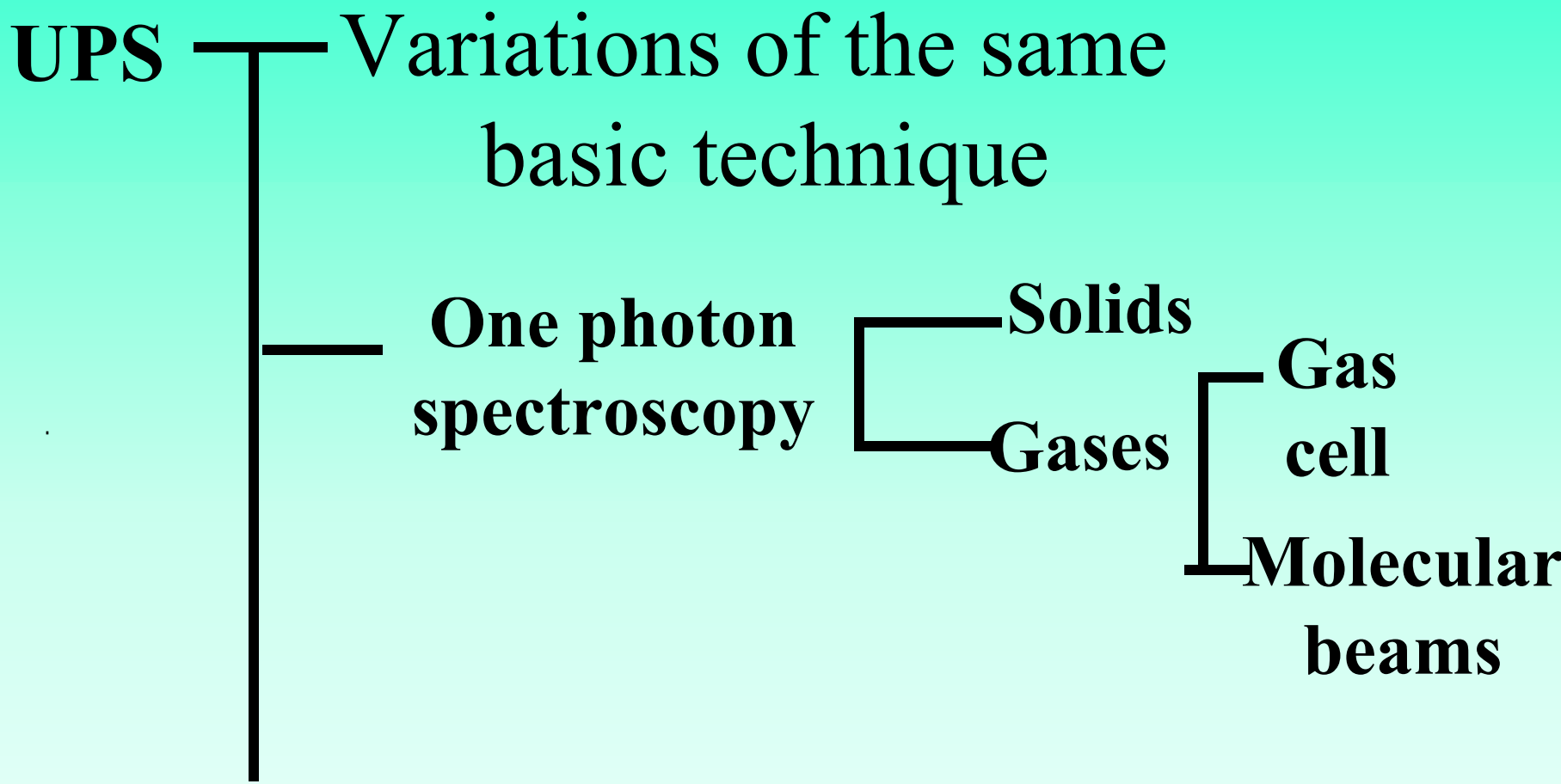
Electron energy loss spectroscopy (EELS)

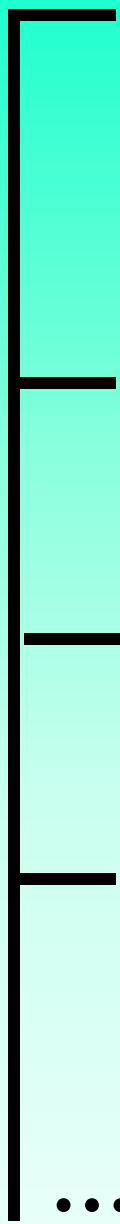
Inverse photoemission spectroscopy (IPS)

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

……..

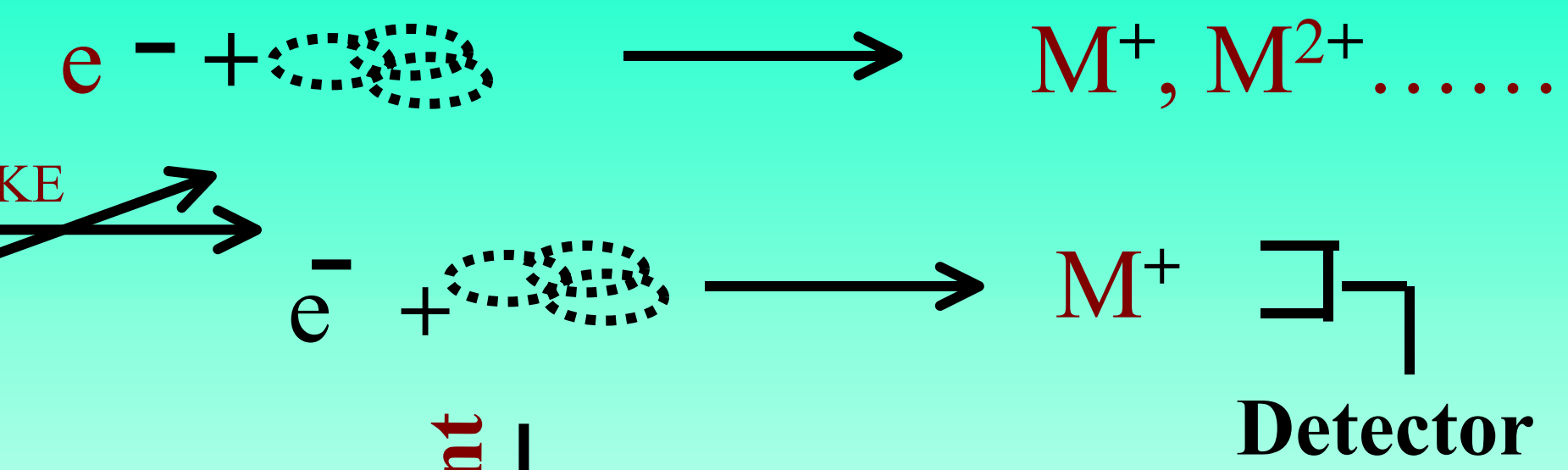
Structure and Properties of Matter

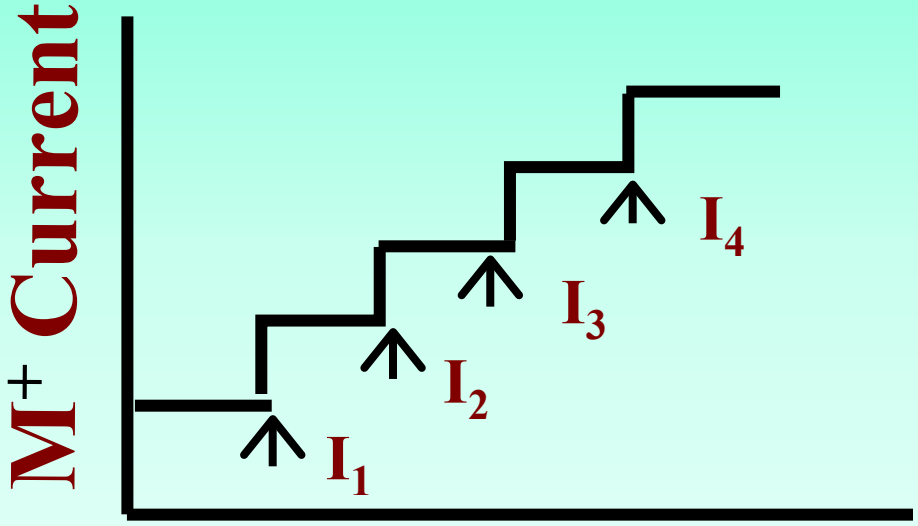
Spectroscopy
Scattering
Physical Properties

Spectroscopy (pre-1965)

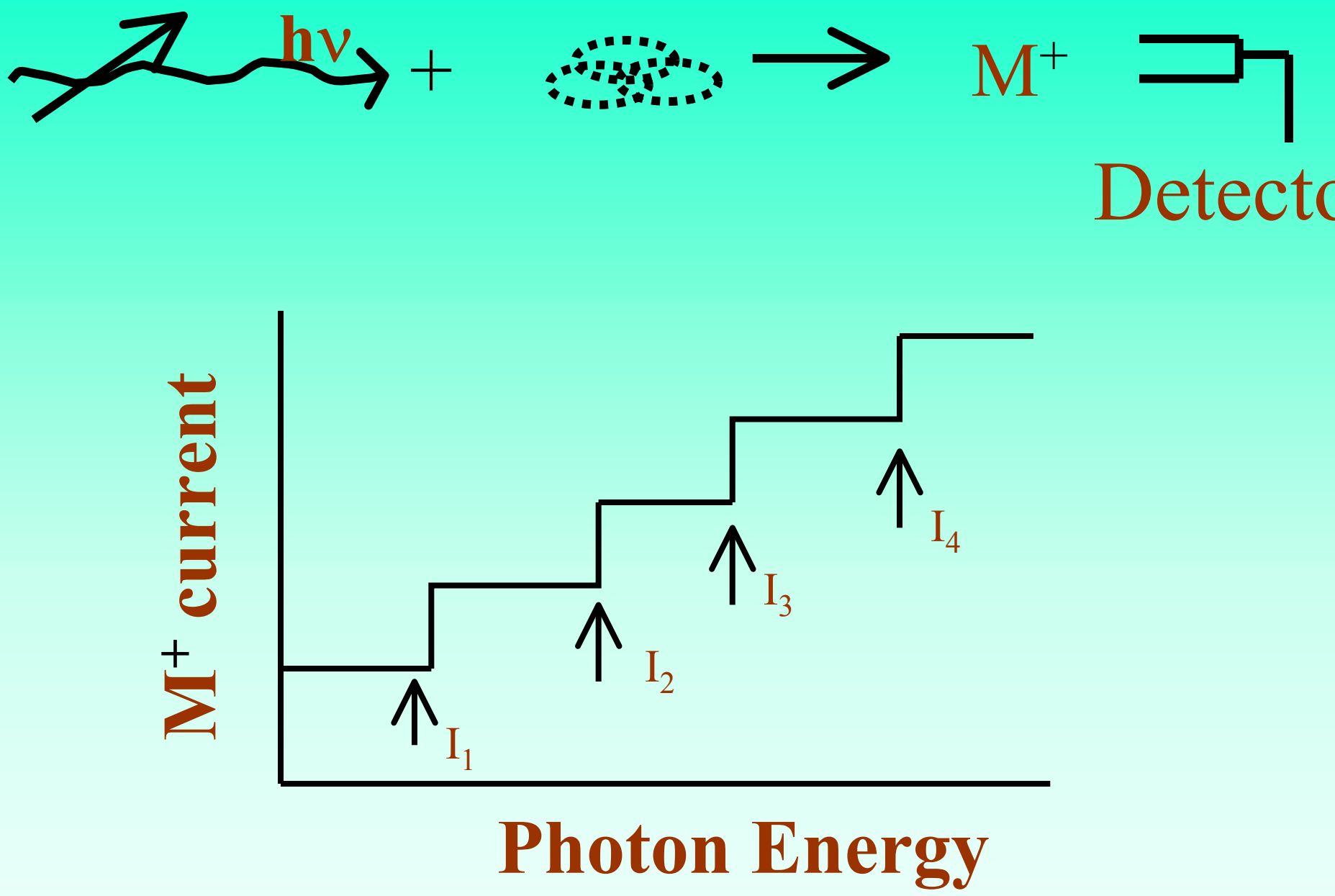
Absorption
Magnetic
Mass

Spectroscopy using electrons



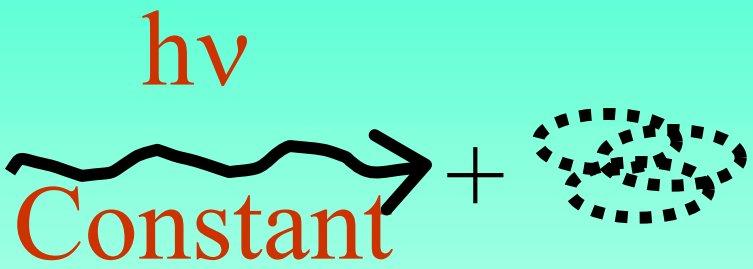


Ionization efficiency curves

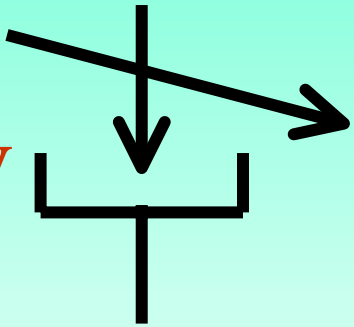

hν
+
M+
Detecto
M+ current
I1
I2
I3
I4
Photon Energy

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

(No M^{2+}, generally)



$M^+ + e^-$



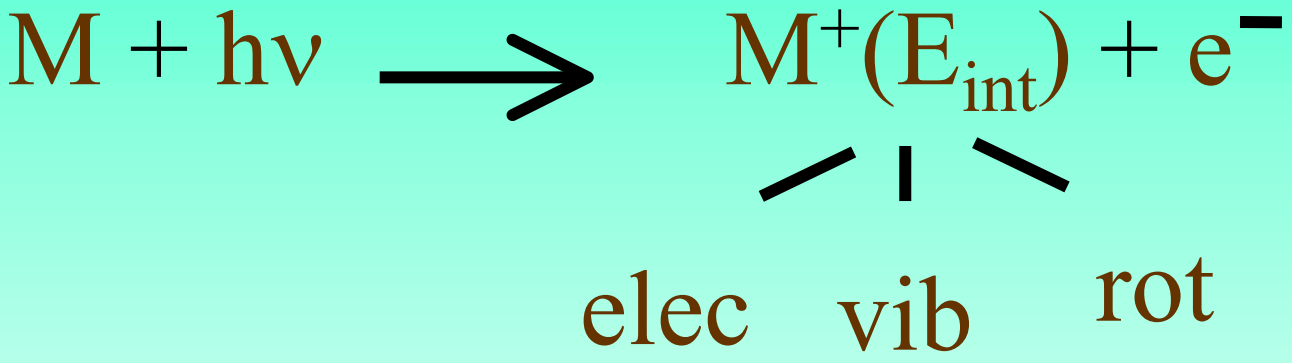
Photoelectron Spectroscopy

Photoelectric effect

Early experiments in 1887

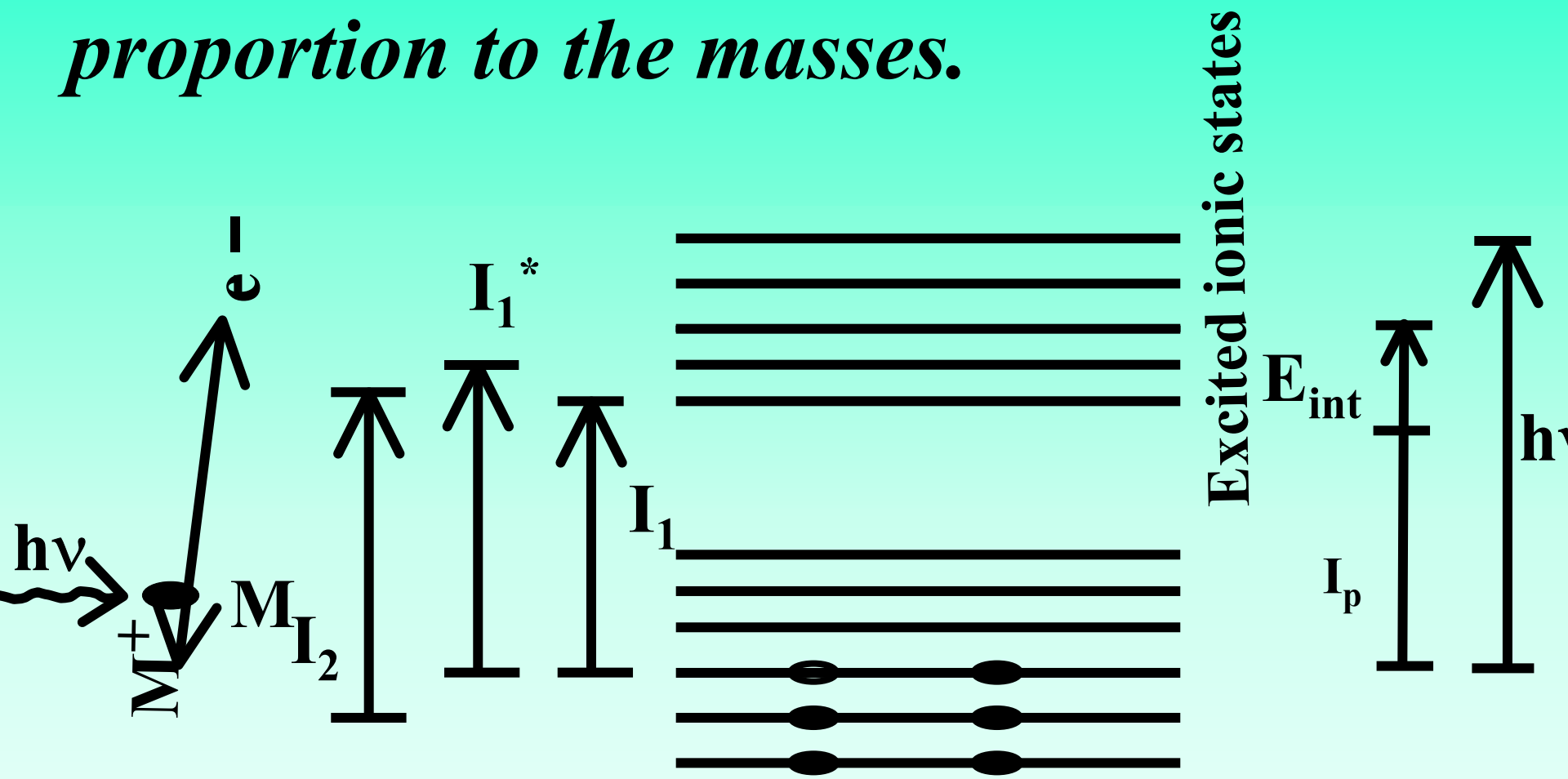
$h\nu = KE + \phi$ 1905

Photoion can be excited



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

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,

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

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

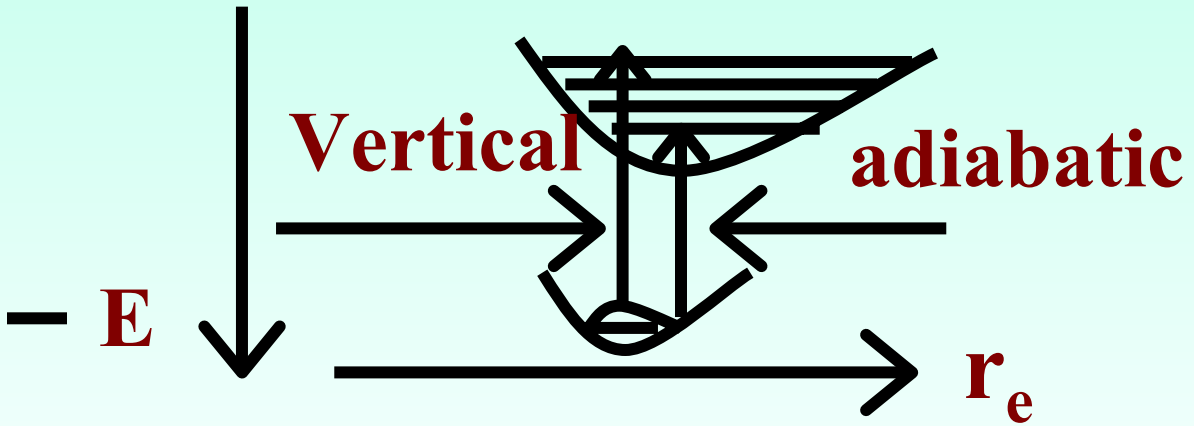
$$h\nu - (I_p + E_{int}) = KE$$

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

$$E_{int} \rightarrow 0$$

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

$$h\nu - KE = I_p$$



Depth of analysis depends on photon energy

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

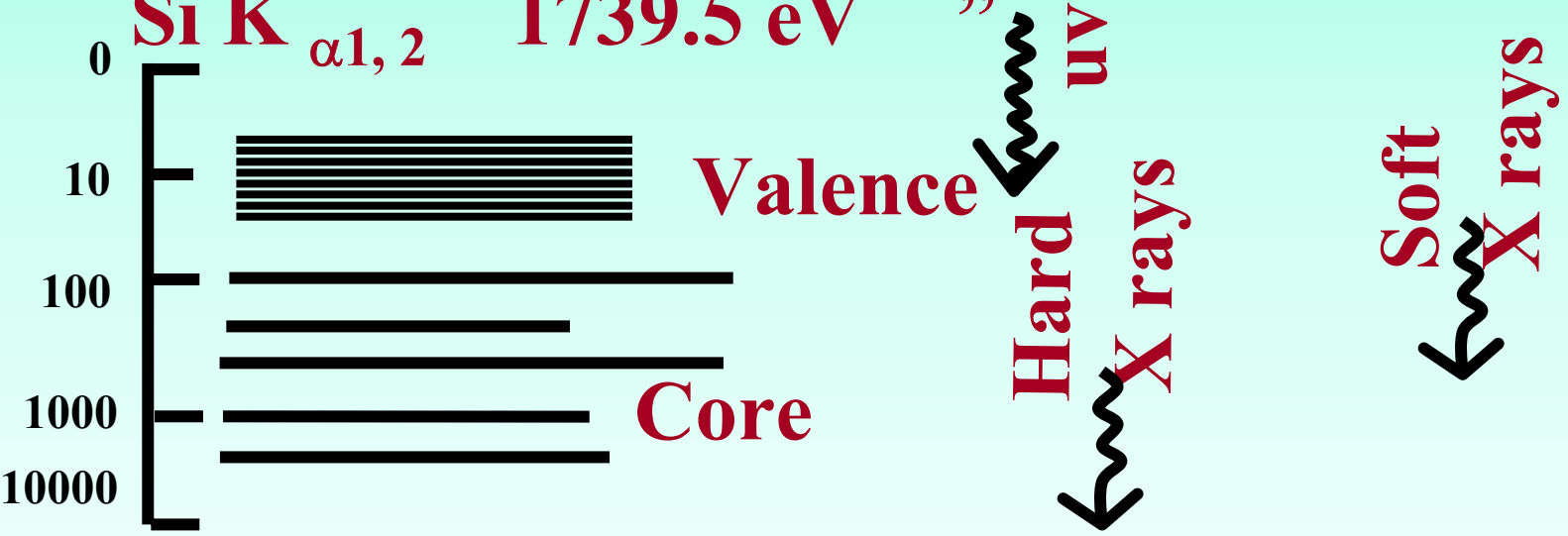
He II 40.8 eV 2 P $\rightarrow$ 1 S of He^+

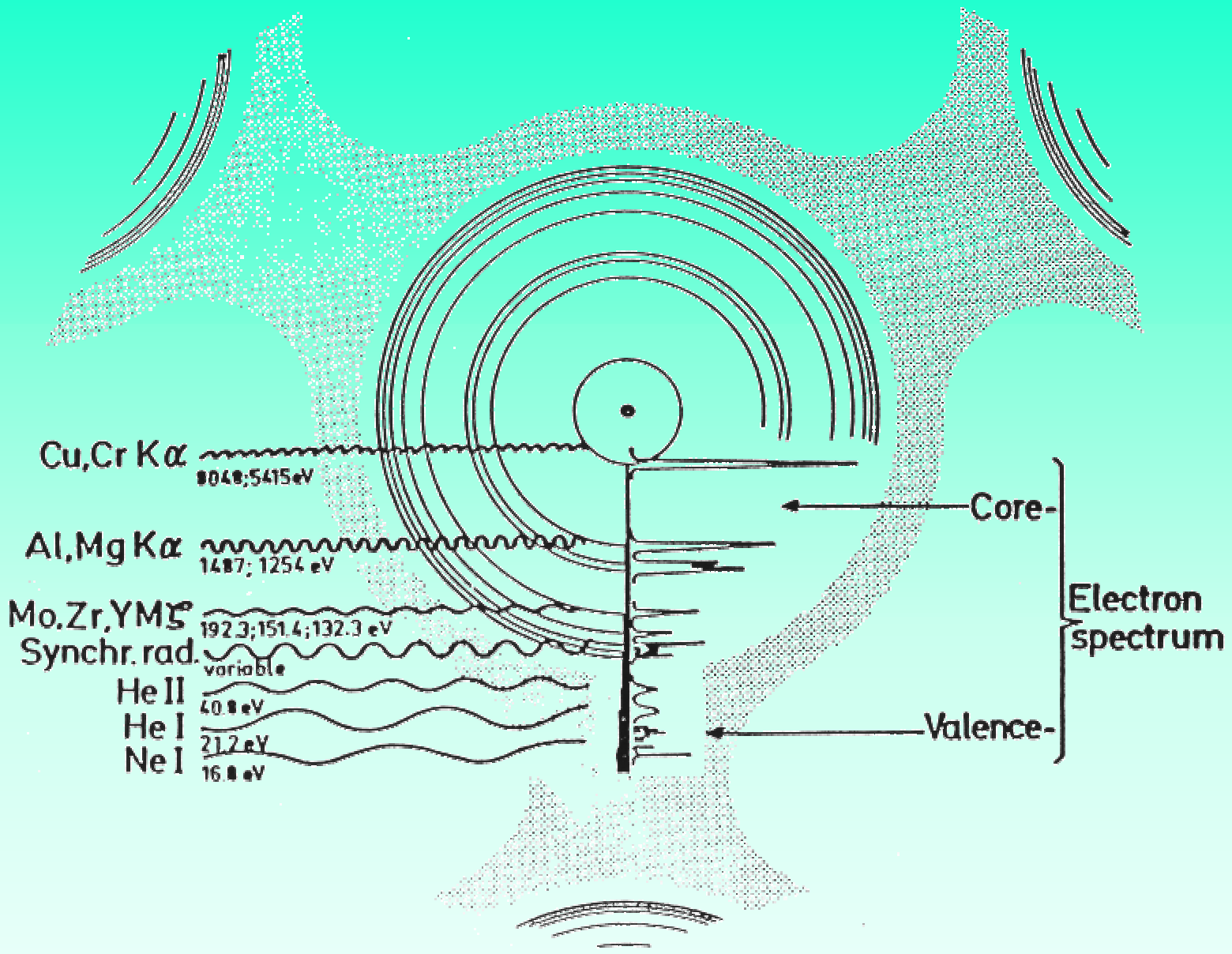
Al $K_{\alpha 1,2}$ 1486.6 eV $2\ P^{3/2,\ 1/2} \rightarrow 1\ S$

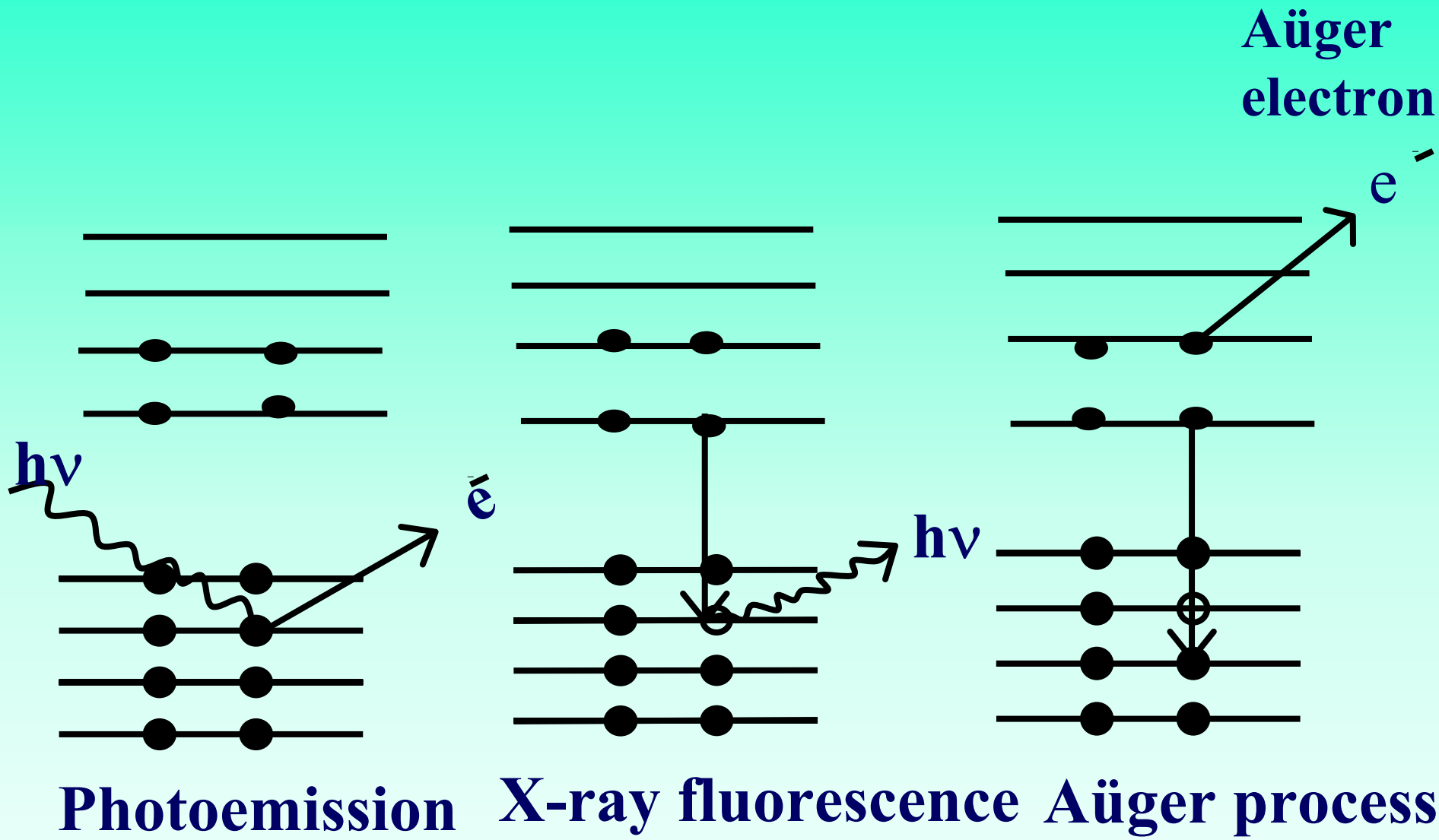
Mg $K_{\alpha 1,2}$ 1253.6 eV ”

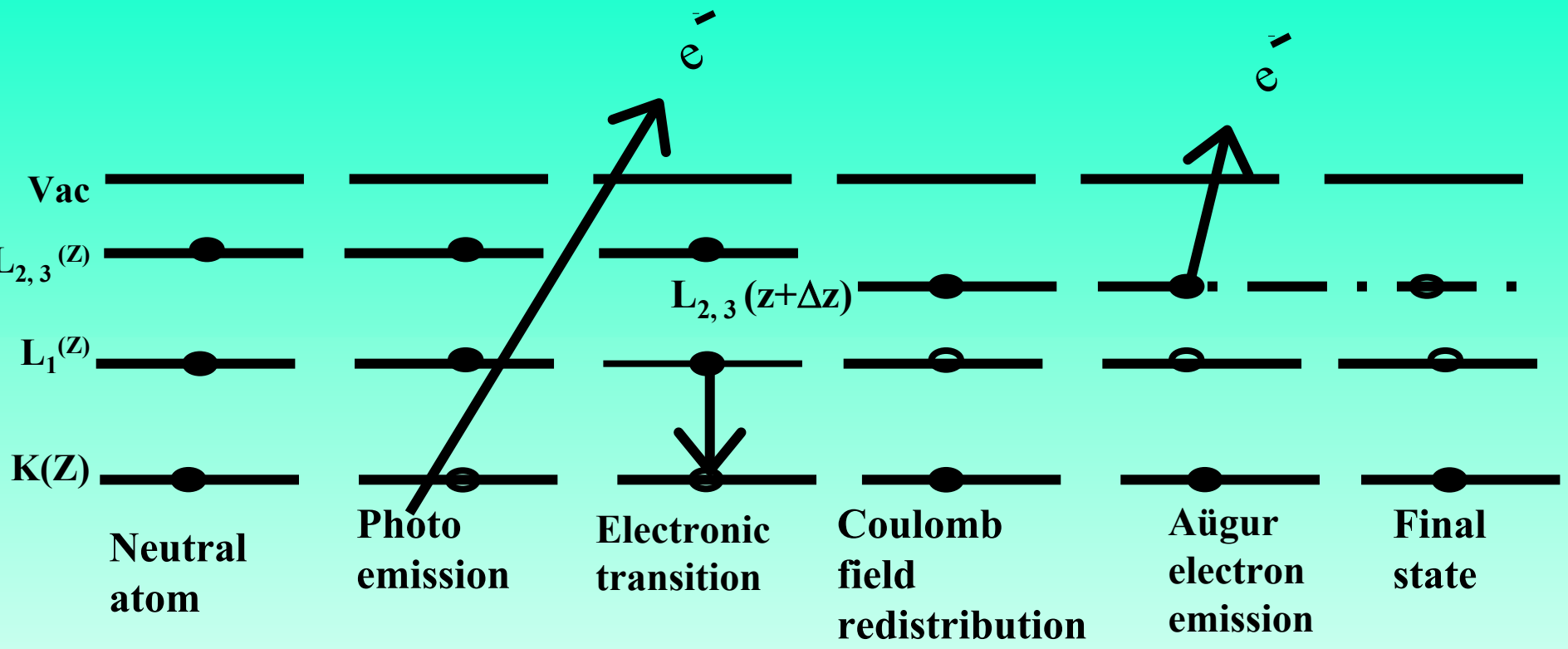
Na $K_{\alpha 1,2}$ 1041.0 eV ”

Si $K_{\alpha 1,2}$ 1739.5 eV ”




Cu,Cr Kα
8048;5415eV
Al,Mg Kα
1487; 1254 eV
Mo,Zr,YMζ
192.3;151.4;132.3 eV
Synchr. rad.
variable
He II
40.8 eV
He I
21.2 eV
Ne I
16.8 eV
Core-
Valence-
Electron spectrum


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


e⁻
e⁻
Vac
$L_{2,3}^{(Z)}$
$L_1^{(Z)}$
K(Z)
$L_{2,3}$ (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.

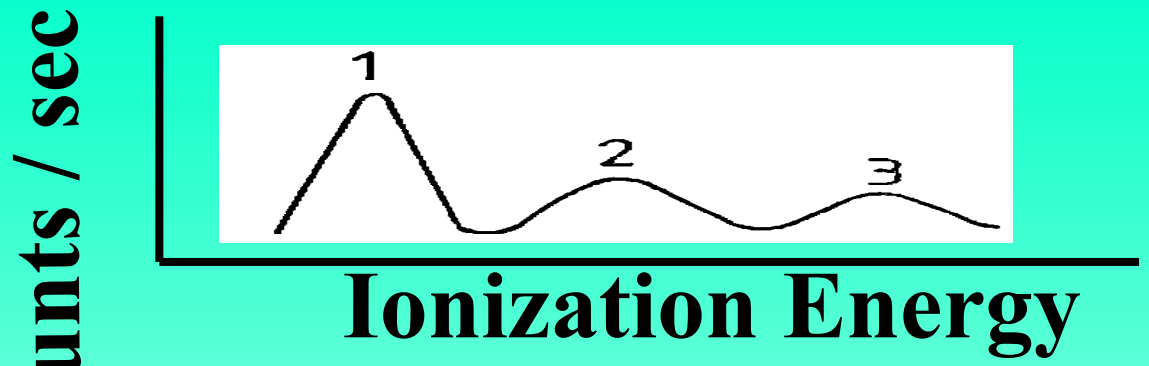
E_{ABC} ⟶ $K\,L_1\,L_{2,\,3}$, $K\,L_1\,V$, KVV

Intense Auger intensities if the valence electron density is high.

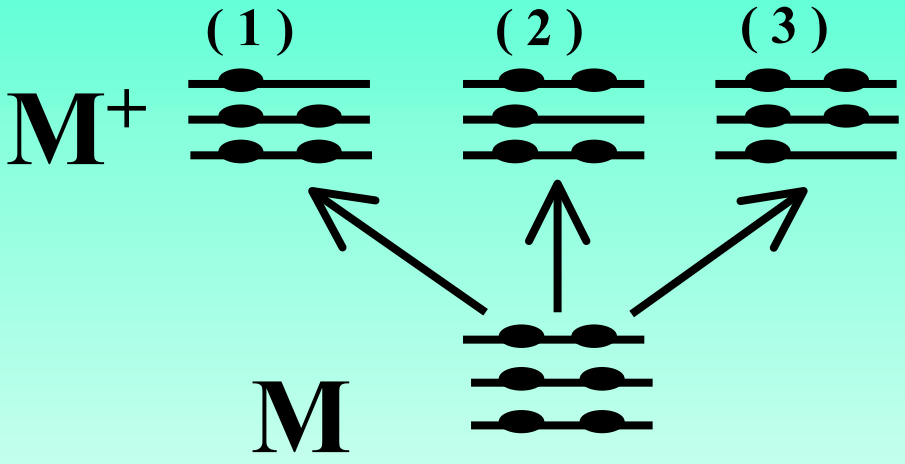
Fluorescence efficiency increases with transition energy. Fluorescence and Auger are comparable when $\Delta E \sim 10{,}000$ eV.

VALENCE SHELL PHOTOELECTRON SPECTROSCOPY

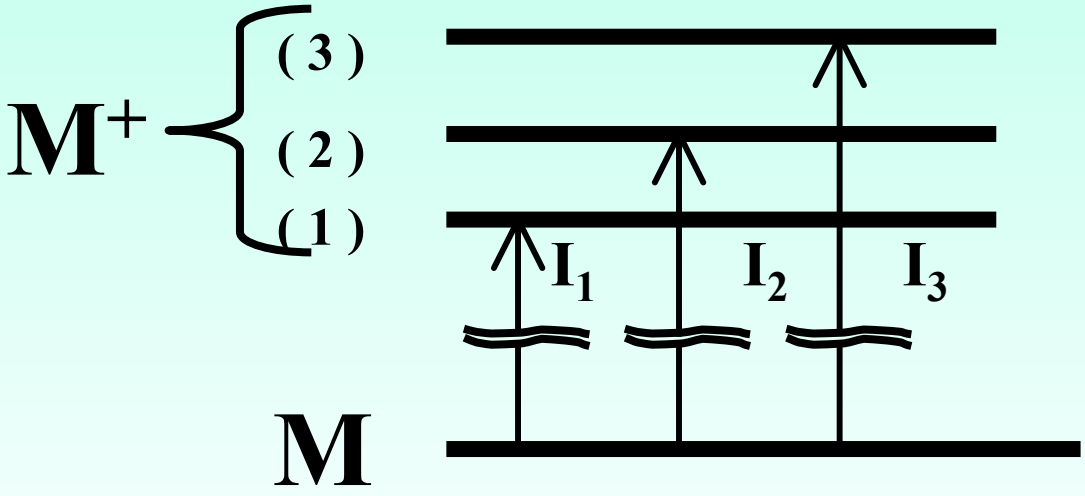
(A)

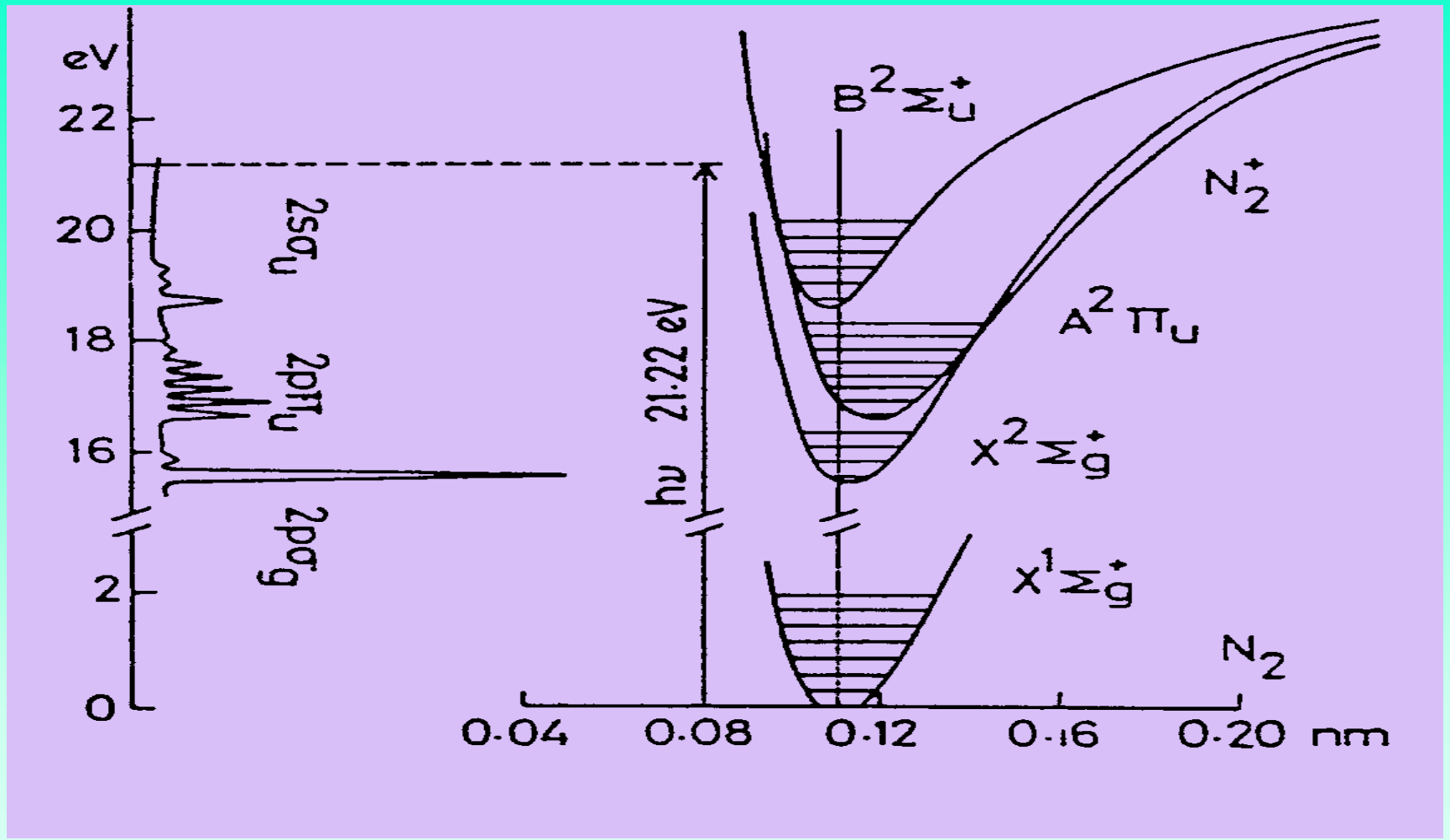


(B)



(C)





INTERNUCLEAR DISTANCE

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

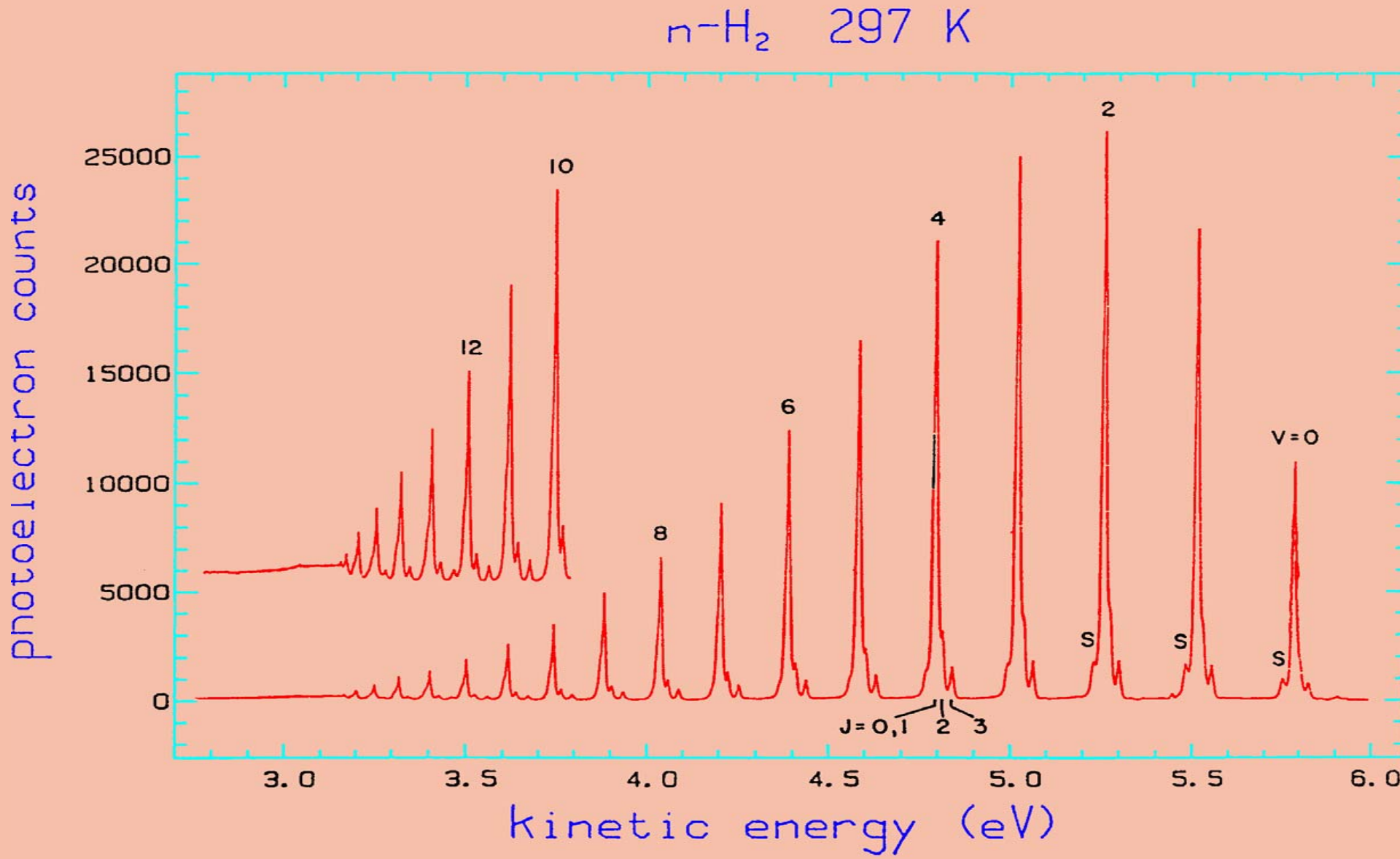
2 P $\pi_u \rightarrow$ bonding 2345 to 1850 cm^{-1}

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

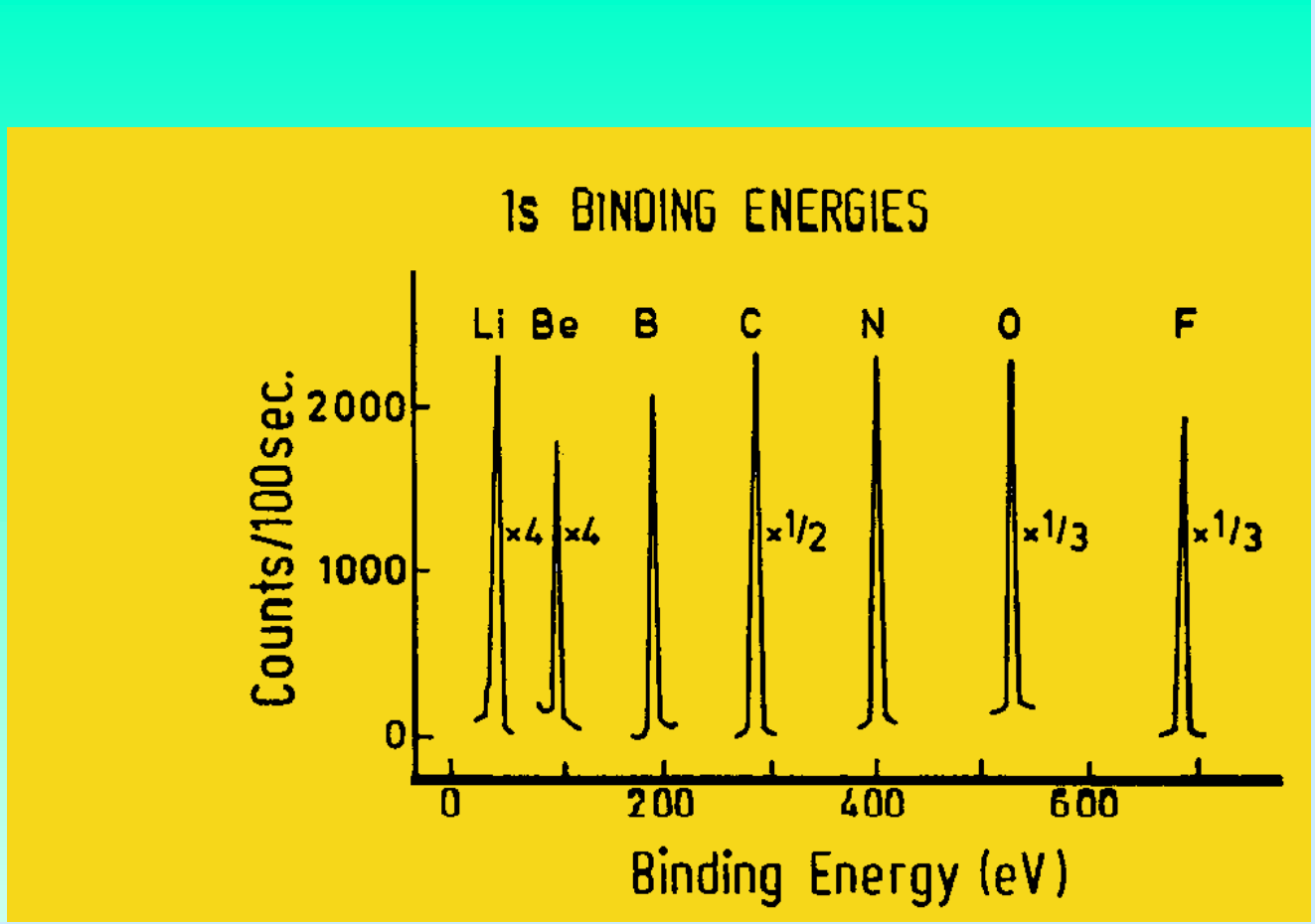
$$E_v = E_o + \omega_e (v + ½) - \omega_e x_e (v + ½)^2$$

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

HeI UPS of H_2 Vibrations and Rotations !

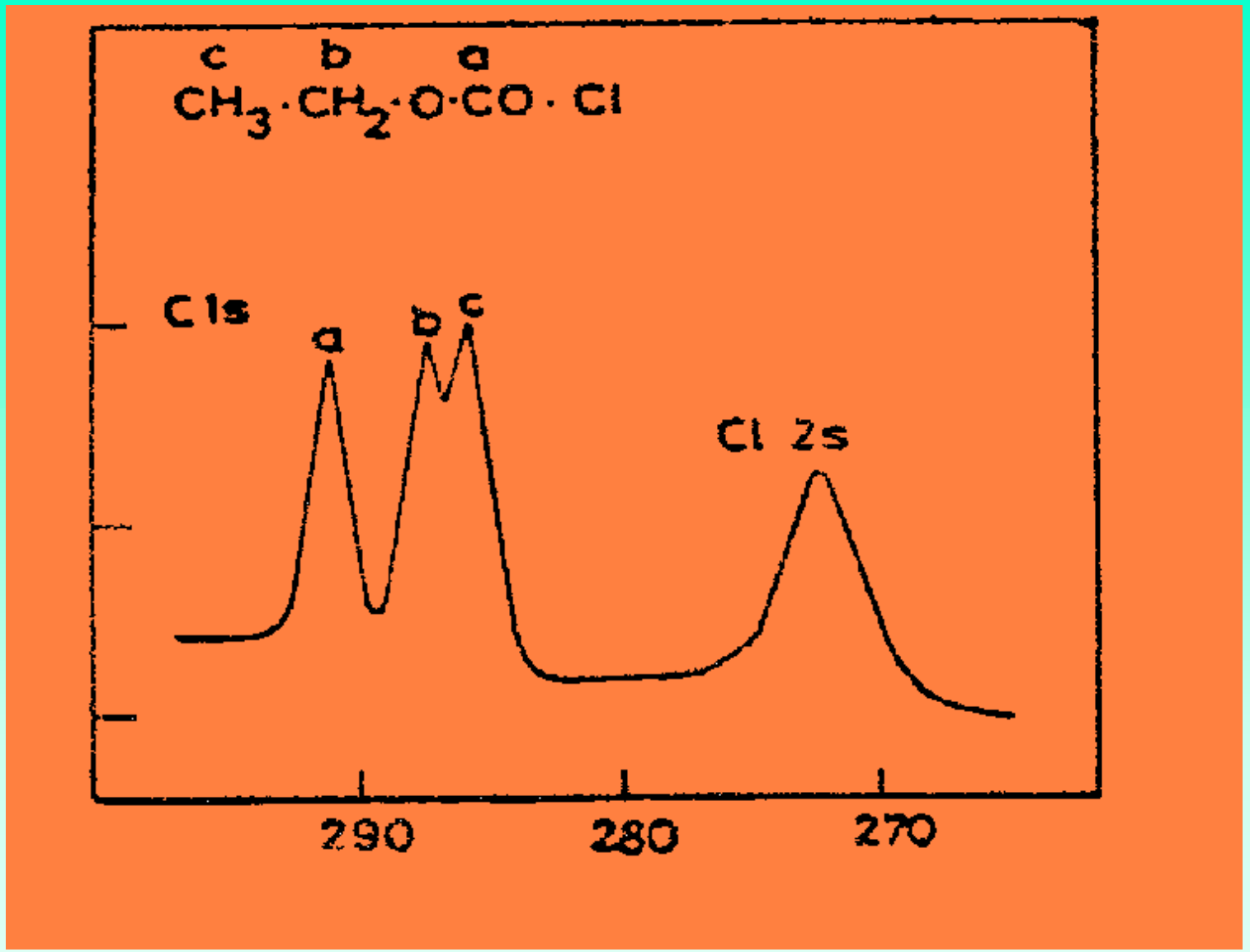


CORE LEVEL PHOTOELECTRON SPECTROSCOPY



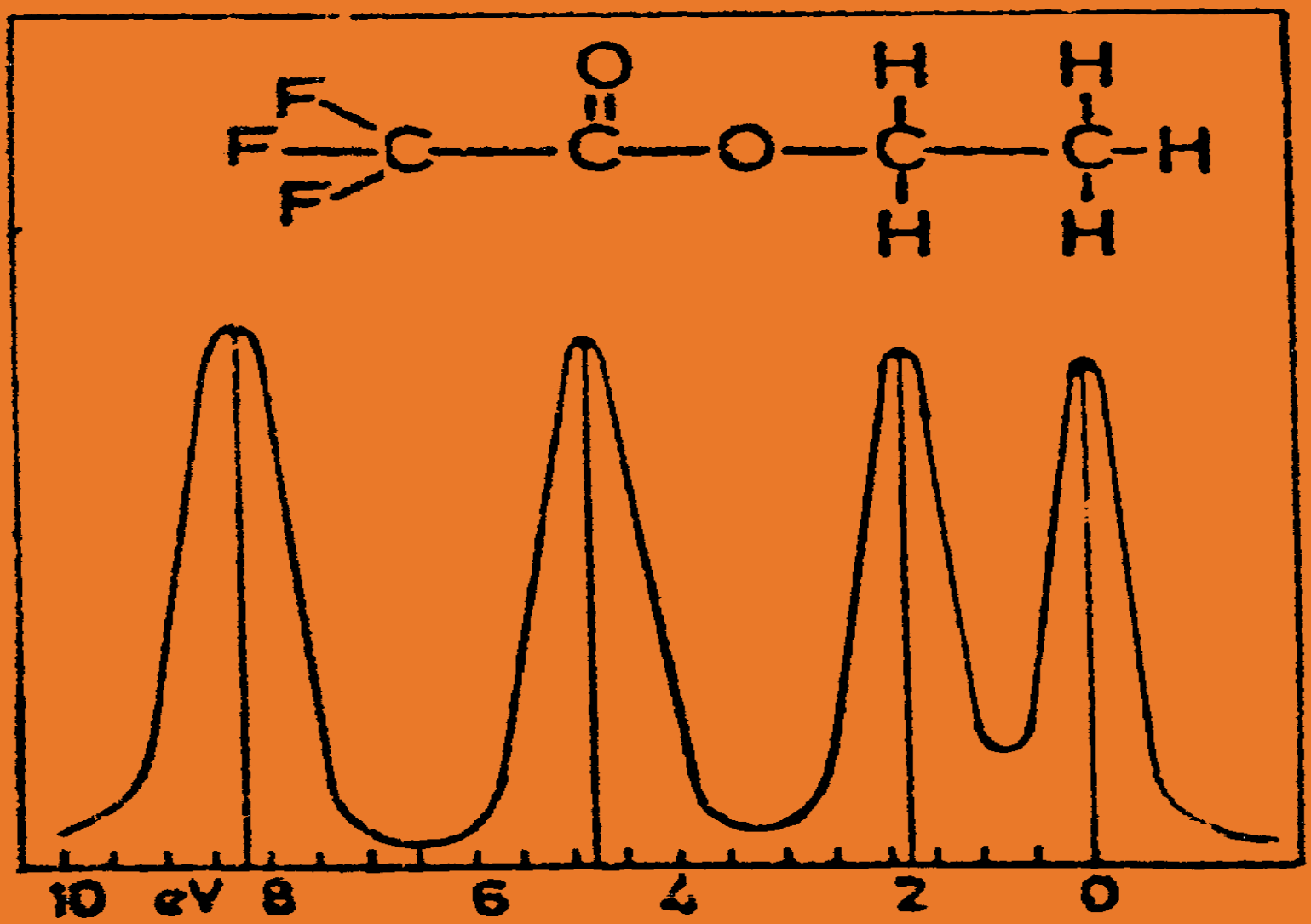
XPS-spectra of the Is core levels of Li, Be, B, C, N, O, F (from S. Hüfner).

Counting Rate



Binding energy eV

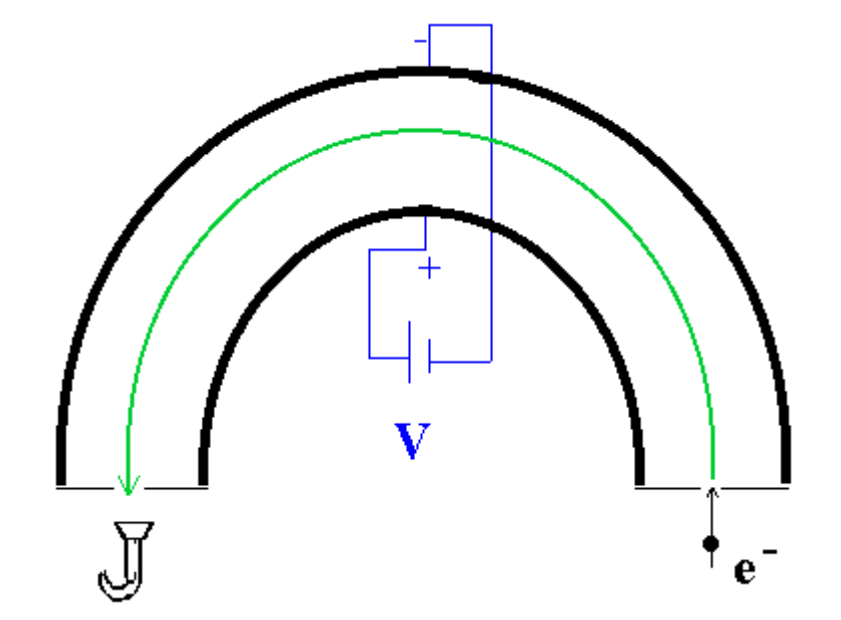
Counting Rate



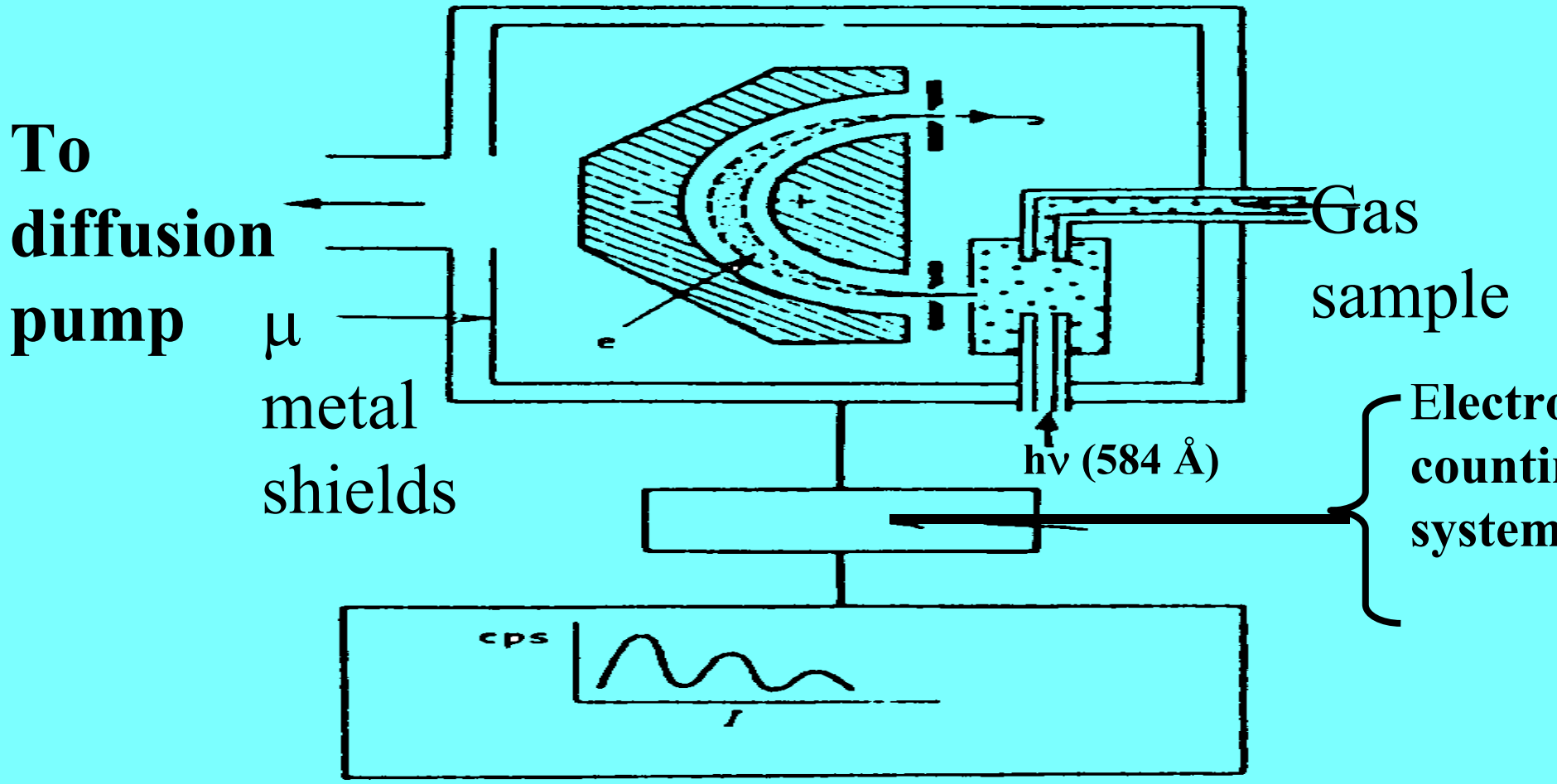
E_B=291.2eV

Chemical Shift

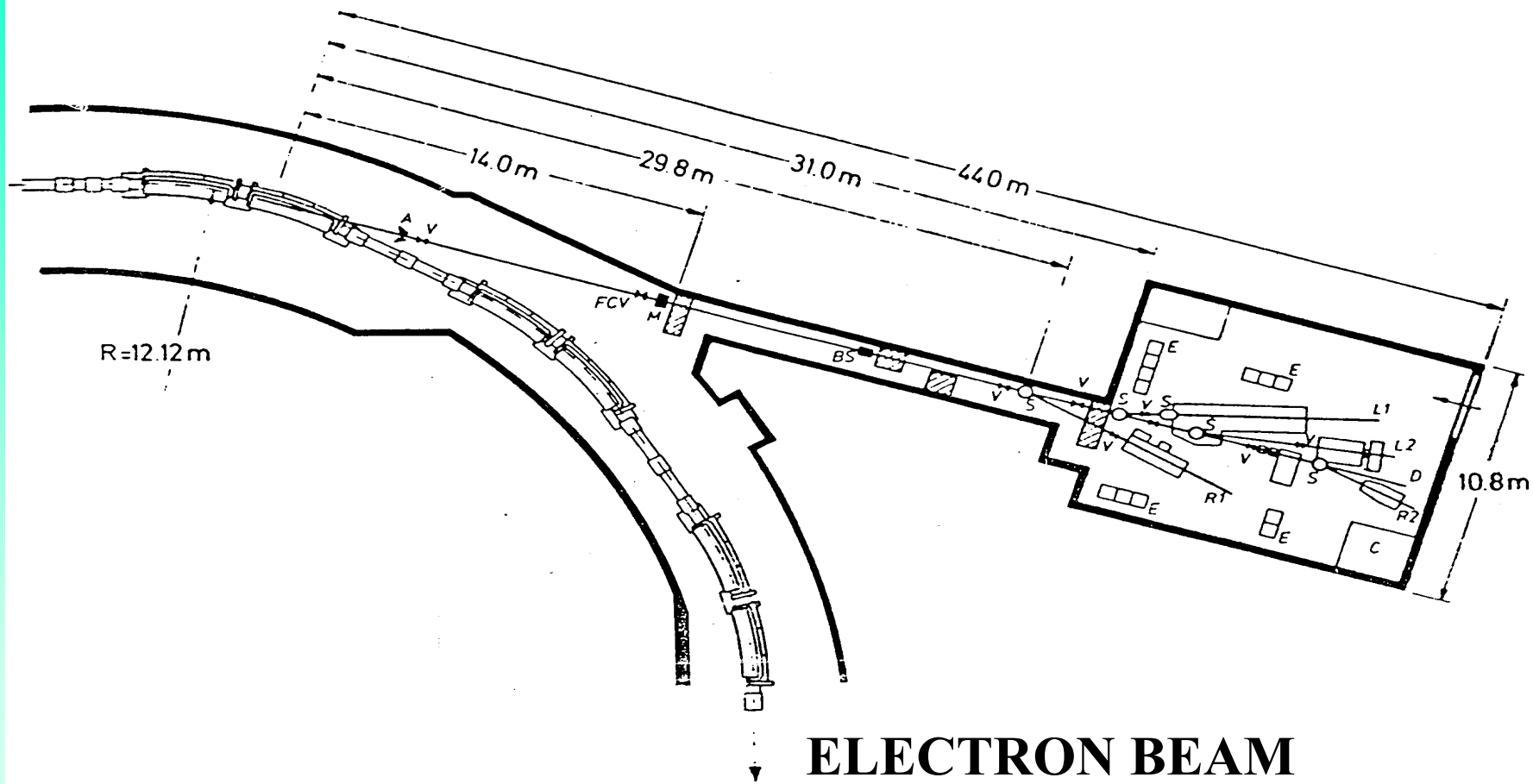
INSTRUMENTATION



Simplest spectrometer


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.