

Electron spectroscopy

Lecture 1-2



Kai M. Siegbahn (1918 -)

½ Nobel Price 1981 – High resolution Electron Spectroscopy

Karl Manne Georg Siegbahn 1924, X-ray spectroscopy

CY653: Electron Spectroscopy

Course structure

Lecture 1,2. Introduction to electron spectroscopies

Lecture 3-5. Electron spectroscopies: experimental methods

Lecture 6-7. Interpretation of UPS, complications, computational methods

Lecture 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: Bremsstrahlung isochromat spectroscopy

Lecture 34: Electron spectroscopy with advanced light sources

Lecture 35: Electron spectroscopy: current research

References

S. Hufner, Photoelectron Spectroscopy, Springer-Verlag, Berlin, 1995.

G. C. Smith, Surface Analysis by Electron Spectroscopy, Plenum, New York, 1994.

C. R. Bundle and A. D. Baker (Ed.), Electron Spectroscopy, Vol. 2., Academic, New York, 1978.

Briggs and Seah, Practical Surface Analysis, John Wiley, New York, 1983.

J. Berkowitz, Photoabsorption, Photoionization and Photoelectron Spectroscopy, Academic Press, New York

T.A. Carlson, Photoelectron and 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

How do you study Structure and Properties of Matter?

Spectroscopy
Scattering
Physical Properties

Spectroscopy (pre-1965)

Absorption
Magnetic
Mass

- *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)

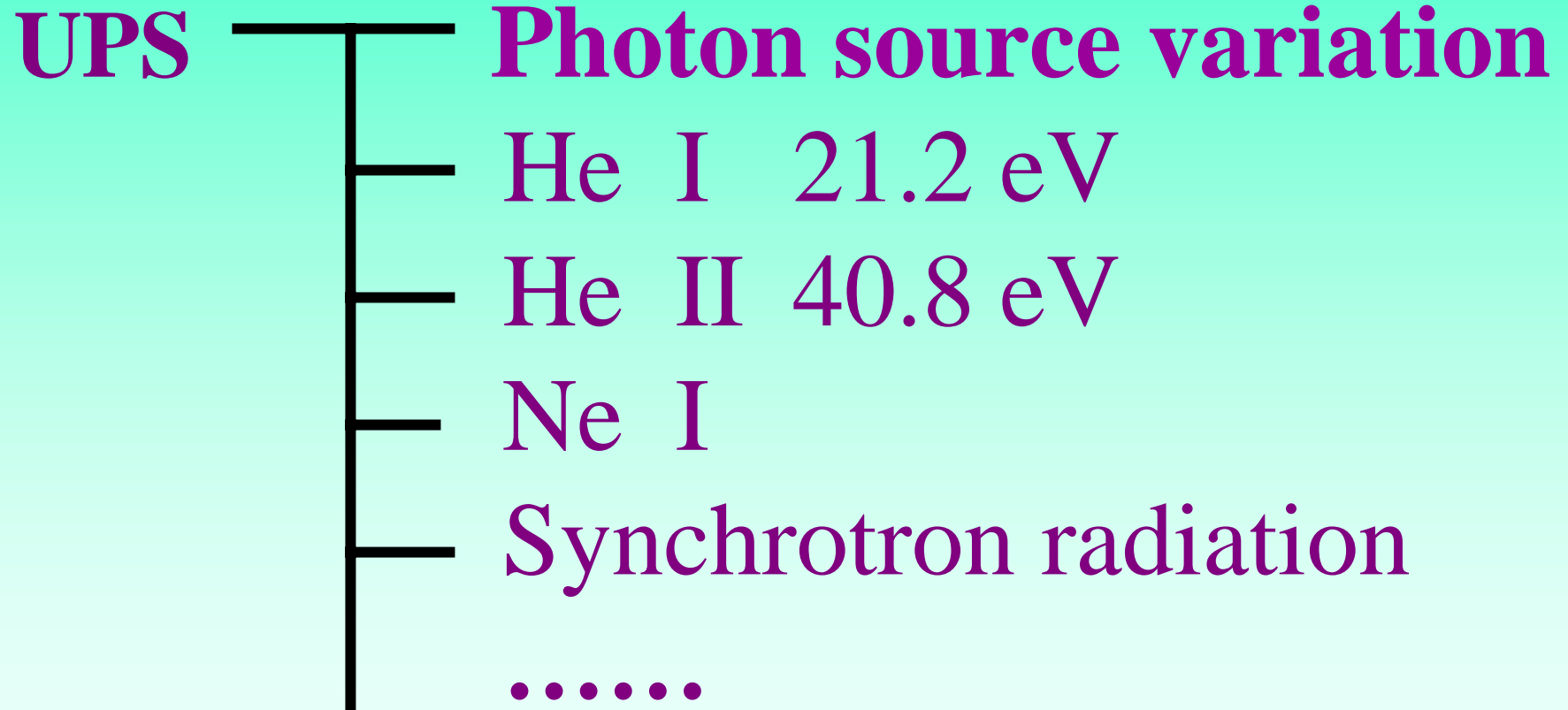
Ultraviolet photoelectron spectroscopy
(UPS)

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**

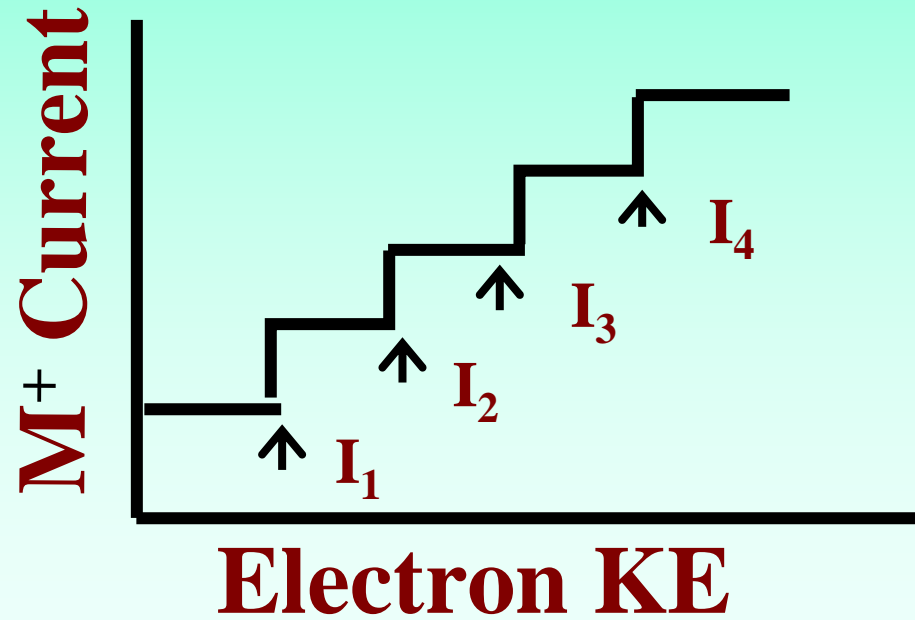
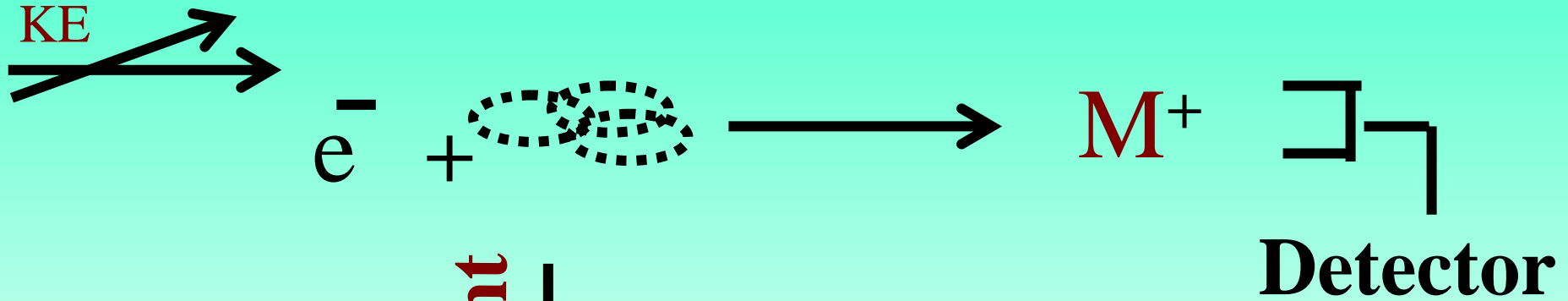
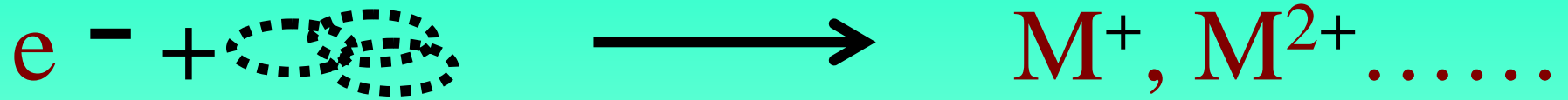
**Zero-kinetic energy
photoelectron spectroscopy**

**Multiphoton photoelectron
spectroscopy**

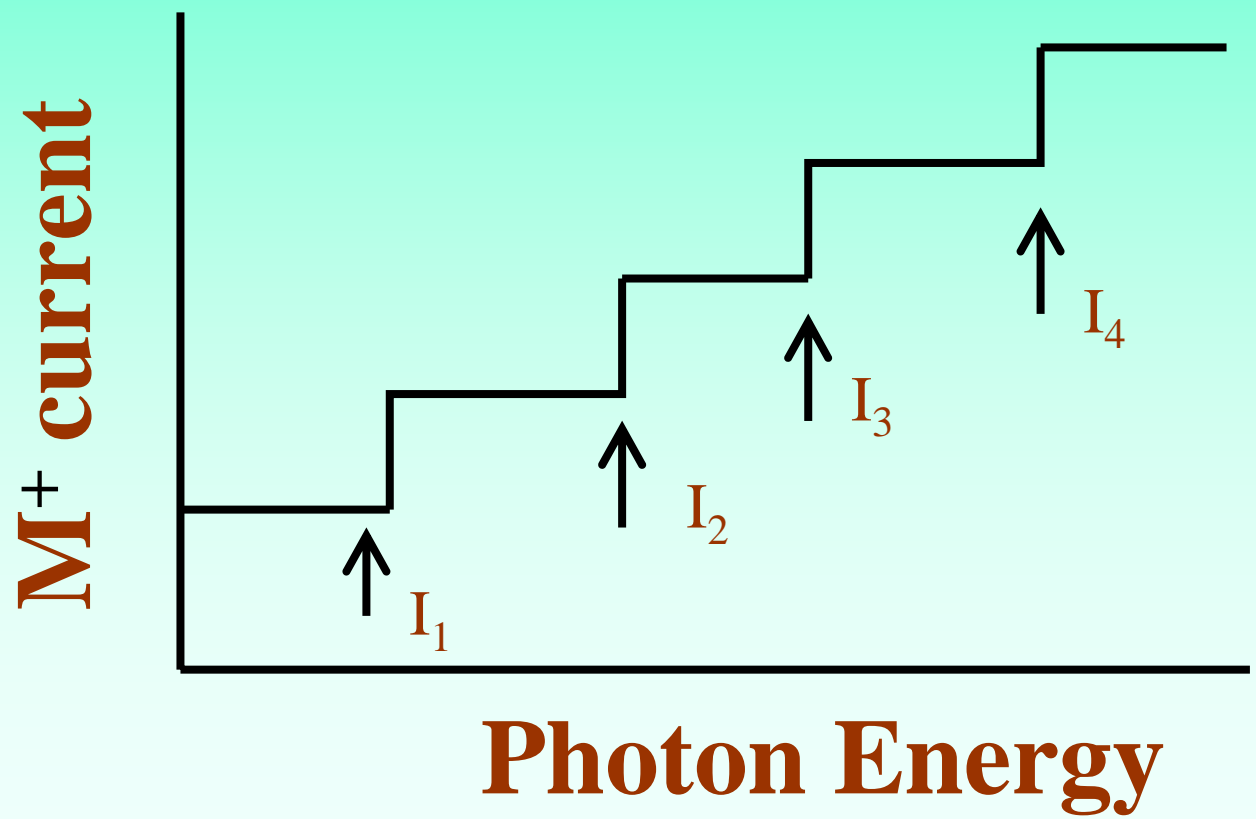
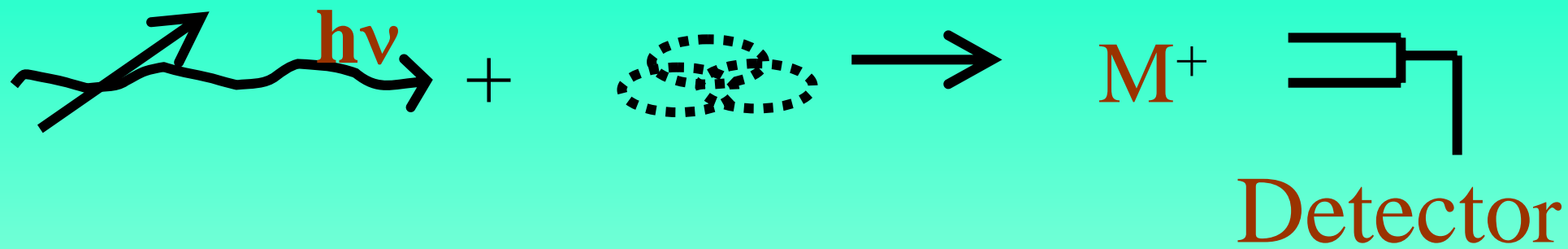
**Photodetachment
spectroscopy**

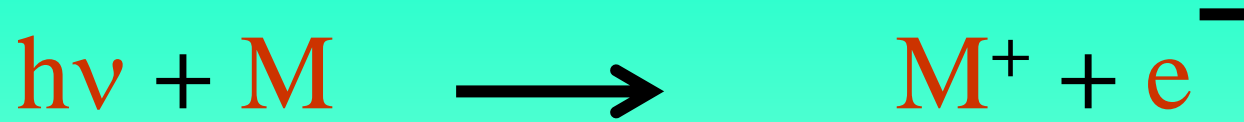
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Spectroscopy using electrons

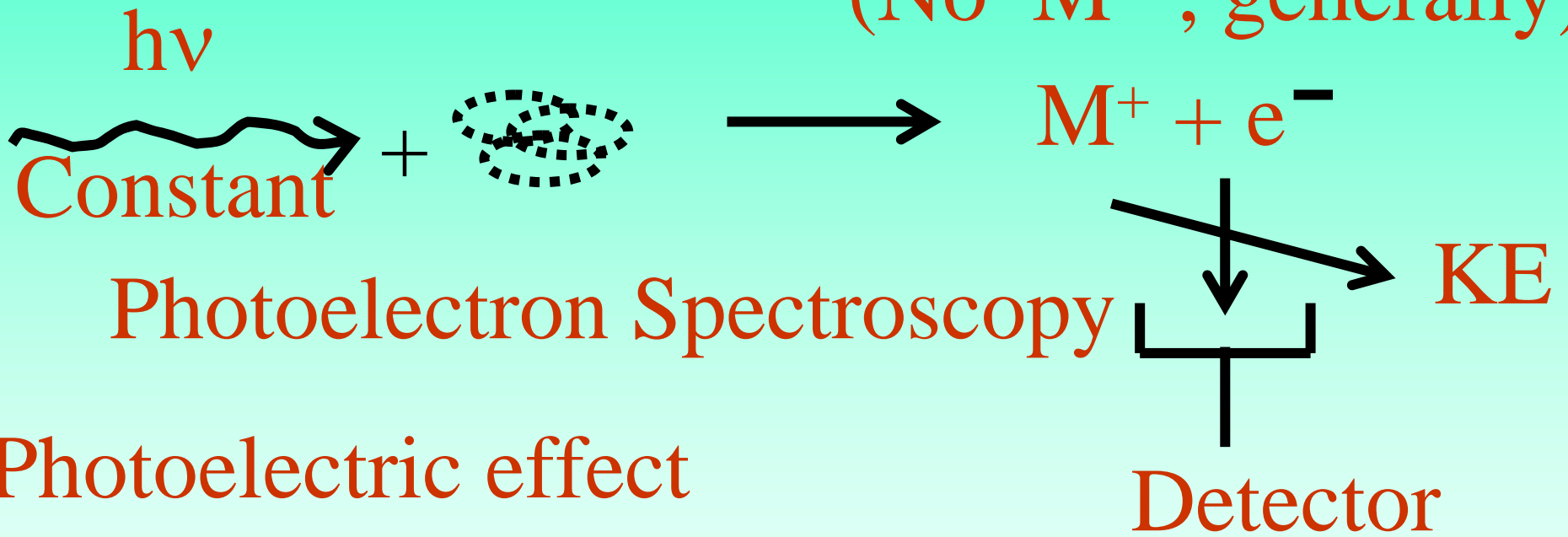


Ionization efficiency curves





(No M^{2+} , generally)



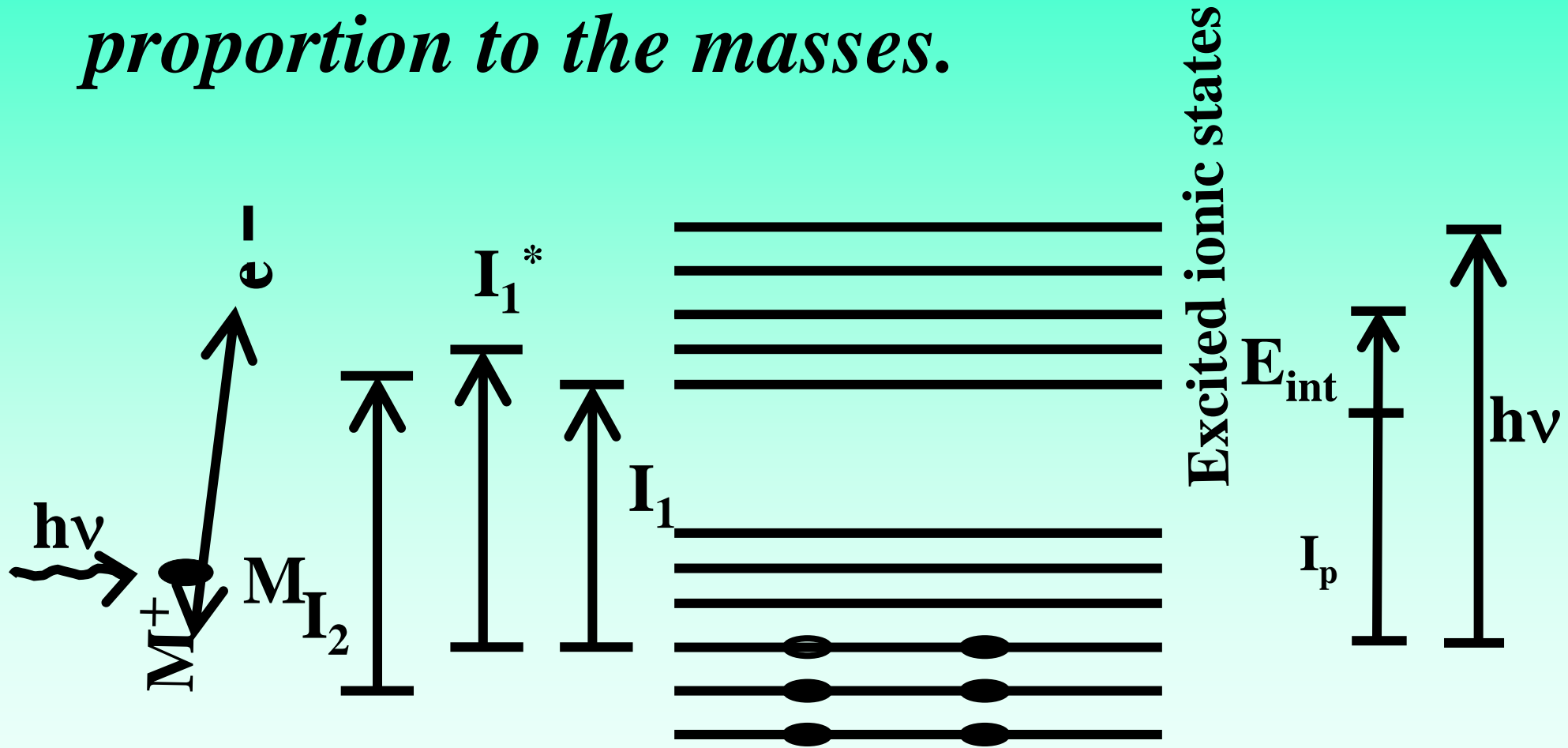
Photoelectron Spectroscopy

Photoelectric effect

Early experiments in 1887

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

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



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

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

The relative velocity,

$$\mathbf{V} = \mathbf{u} + \mathbf{U}$$

$$= \mathbf{U} (1 + \mathbf{M}/m)$$

$$= \mathbf{u} (1 + m/\mathbf{M})$$

The kinetic energies,

$$\frac{1}{2} \mathbf{MU}^2 = \frac{1}{2} \mathbf{M} (\mathbf{V}/1 + \mathbf{M}/m)^2$$

$$\frac{1}{2} \mathbf{mu}^2 = \frac{1}{2} \mathbf{m} (\mathbf{V}/1 + m/\mathbf{M})^2$$

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

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

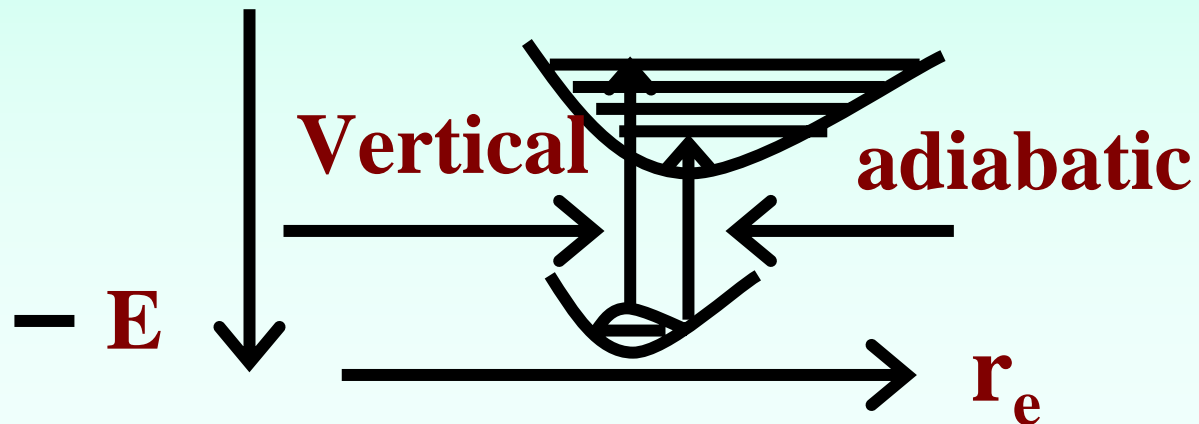
$$E_{\text{int}} \rightarrow 0$$

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

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

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

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



Depth of analysis depends on photon energy

energy

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

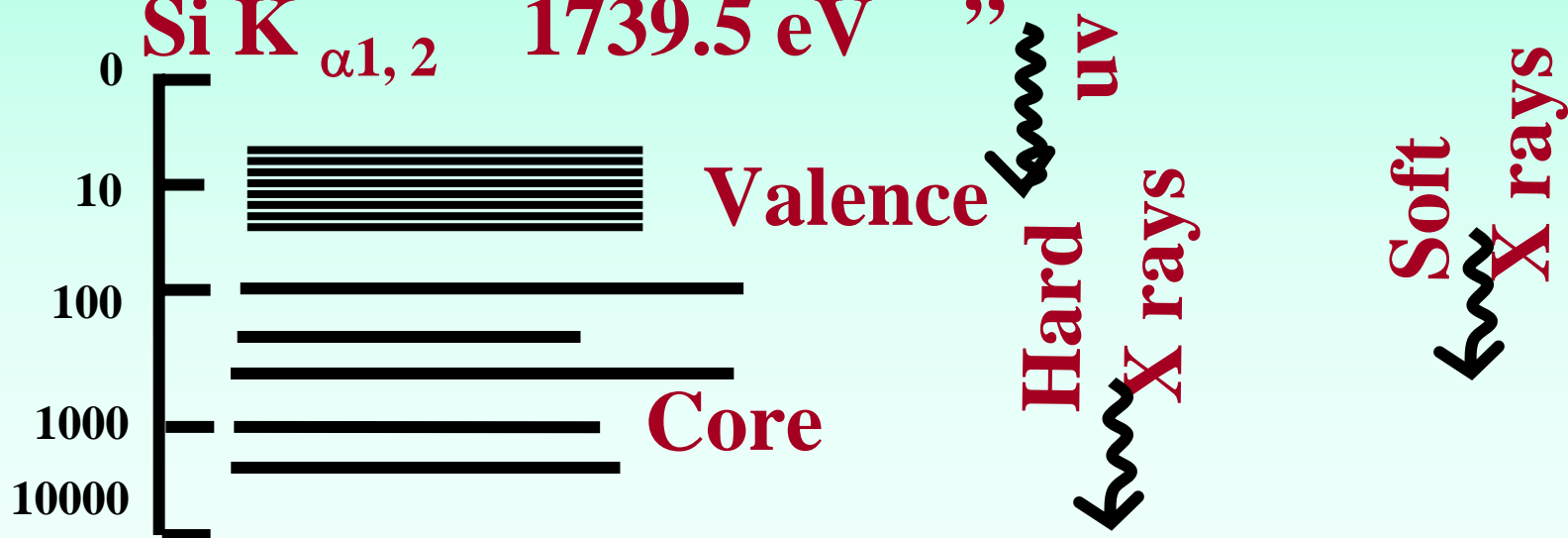
He II 40.8 eV $2P \rightarrow 1S$ of He^+

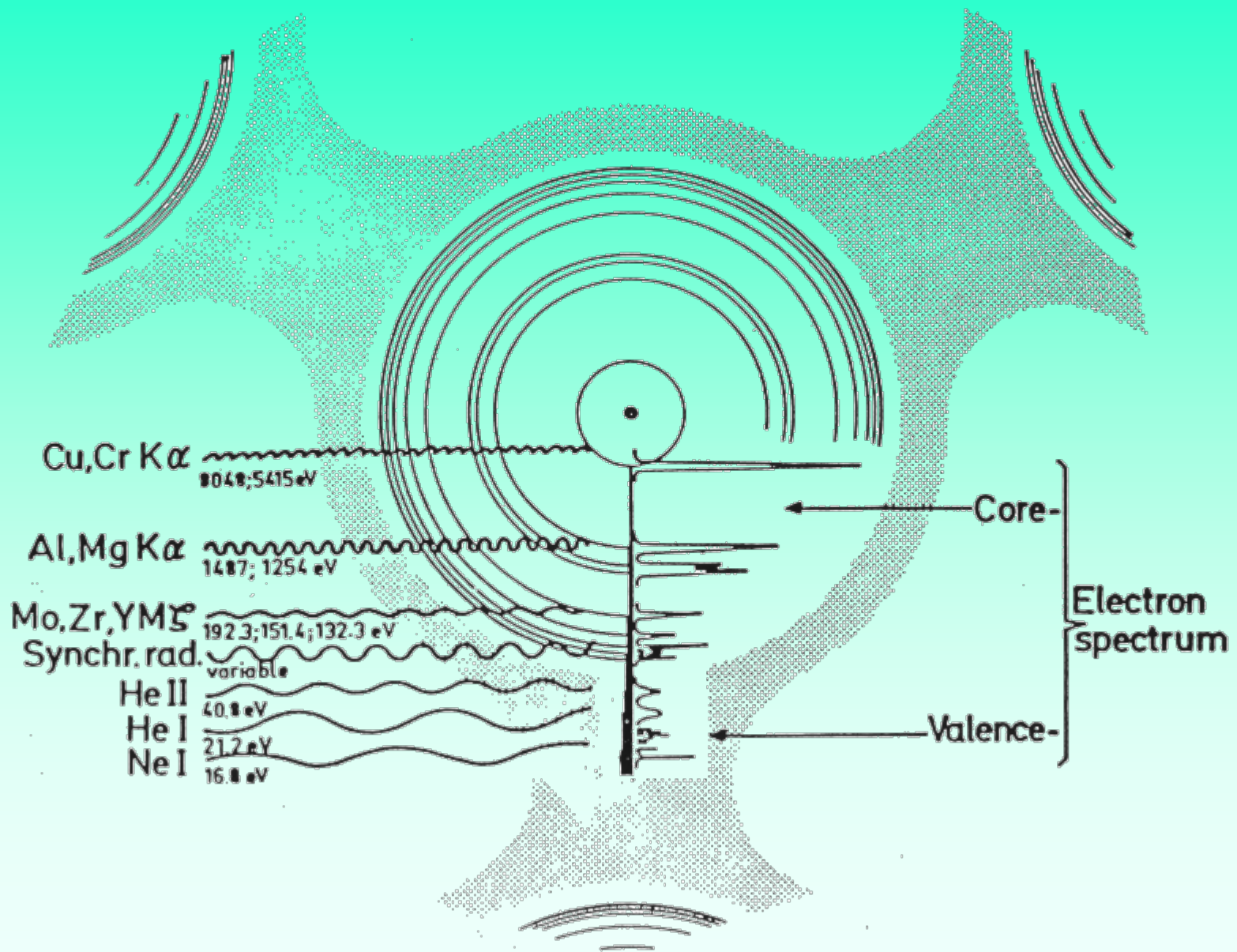
Al $K_{\alpha 1,2}$ 1486.6 eV $2P^{3/2, 1/2} \rightarrow 1S$

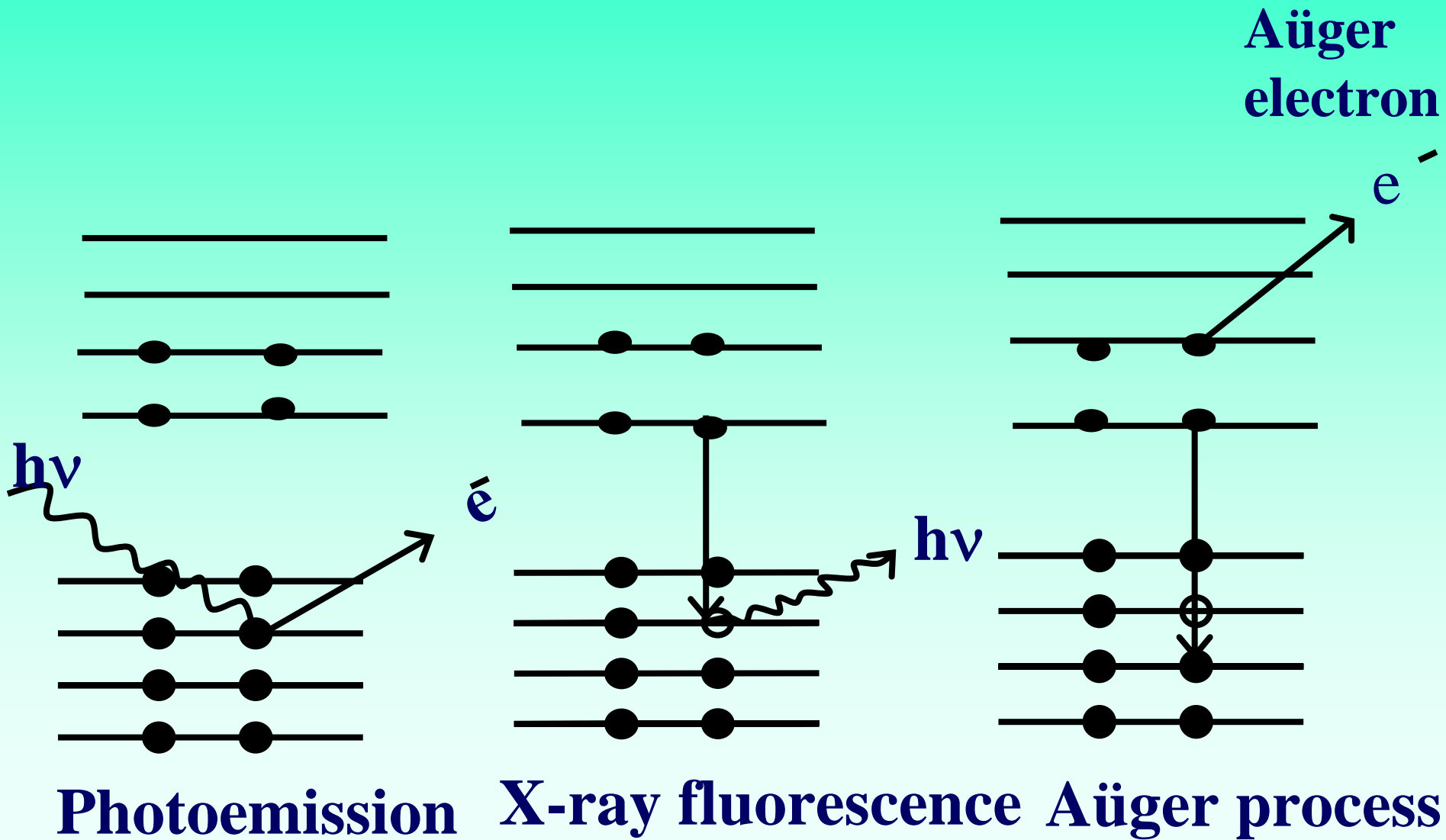
Mg $K_{\alpha 1,2}$ 1253.6 eV ”

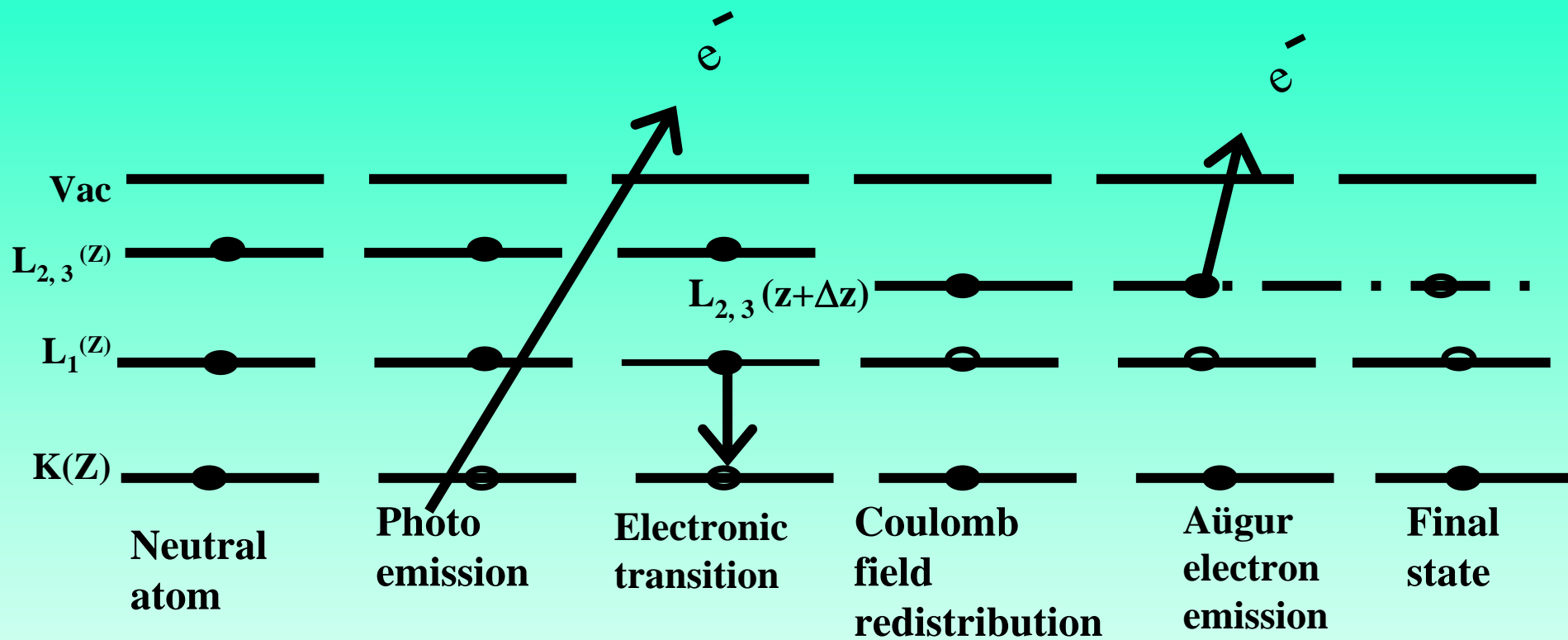
Na $K_{\alpha 1,2}$ 1041.0 eV ”

Si $K_{\alpha 1,2}$ 1739.5 eV ”









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

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

E's are the binding energies.

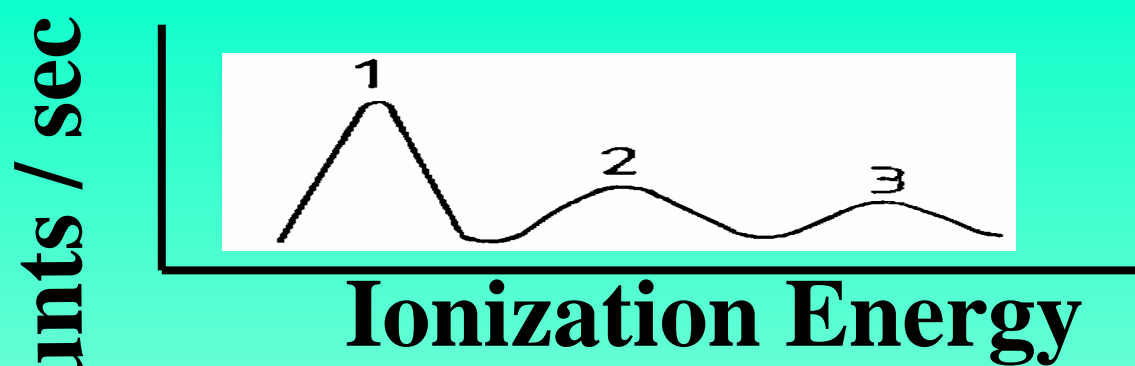
$$E_{ABC} \longrightarrow K L_1 L_{2,3}, K L_1 V, KVV$$

Intense Auger intensities if the valence electron density is high.

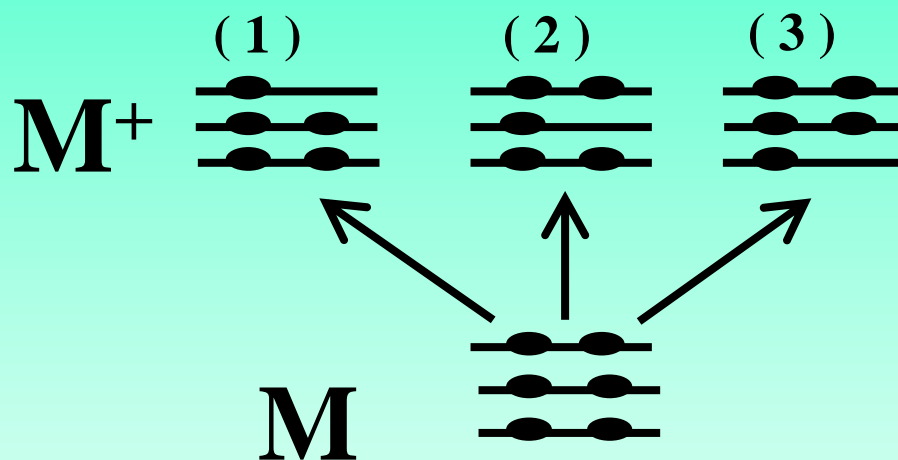
Fluorescence efficiency increases with transition energy. Fluorescence and Auger are comparable when $\Delta E \sim 10,000$ eV.

***VALENCE SHELL
PHOTOELECTRON
SPECTROSCOPY***

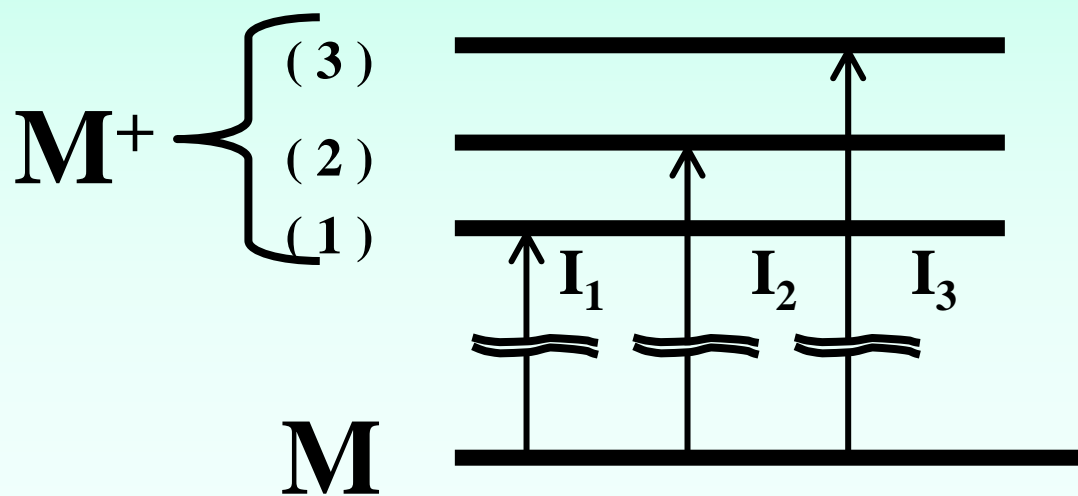
(A)

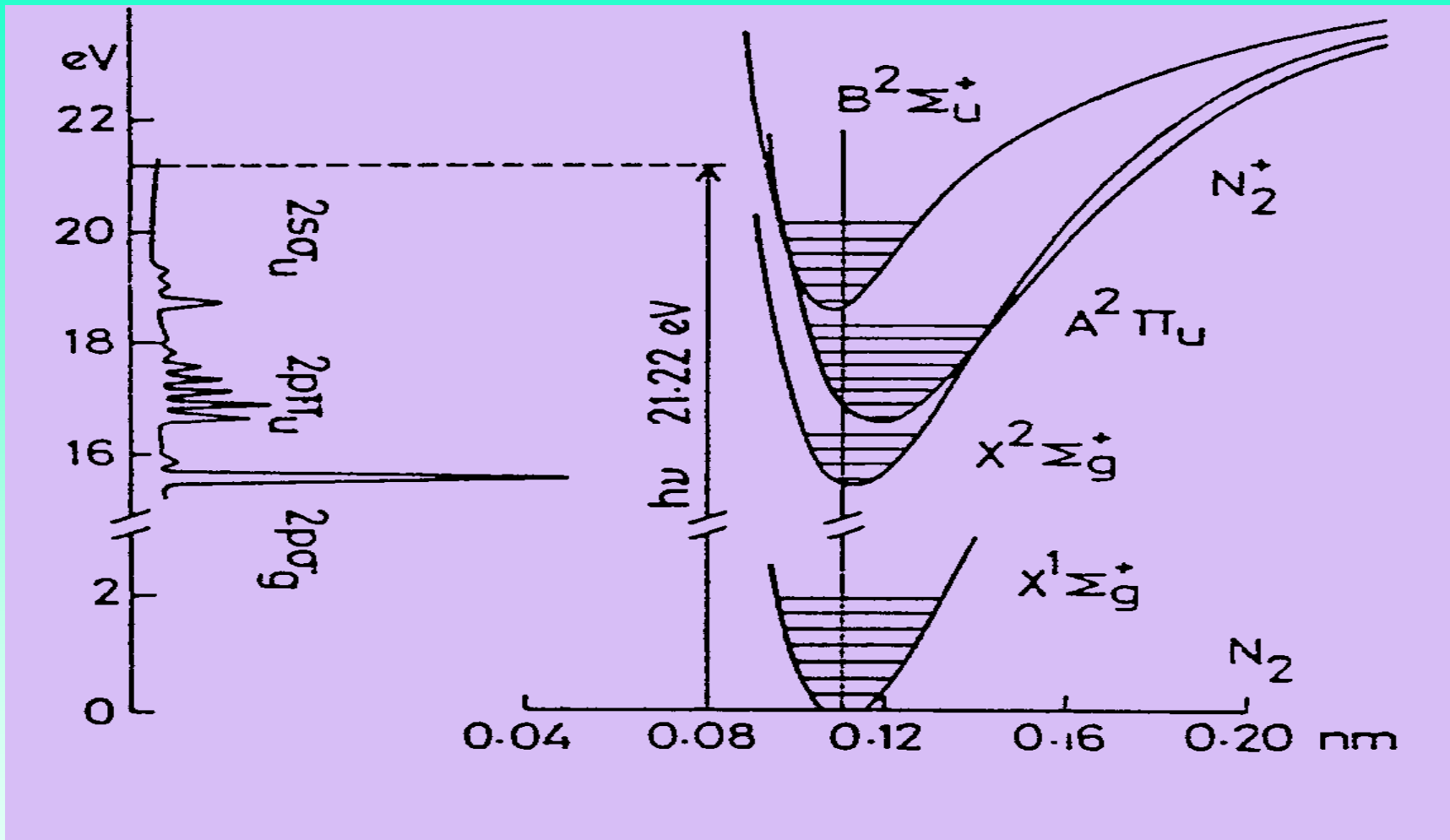


(B)



(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}

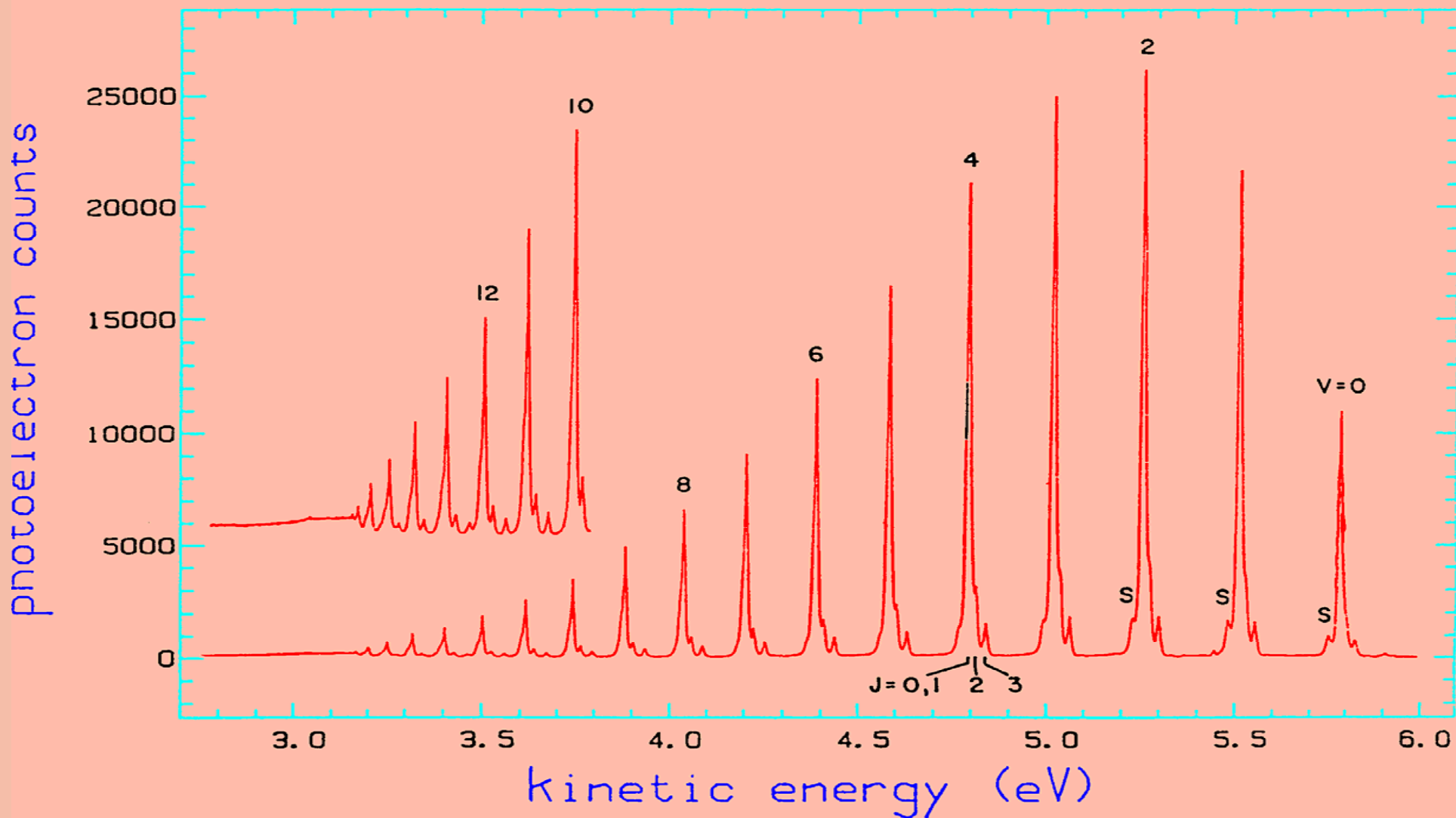
$$\mathbf{E}_v = \mathbf{E}_0 + \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2$$

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

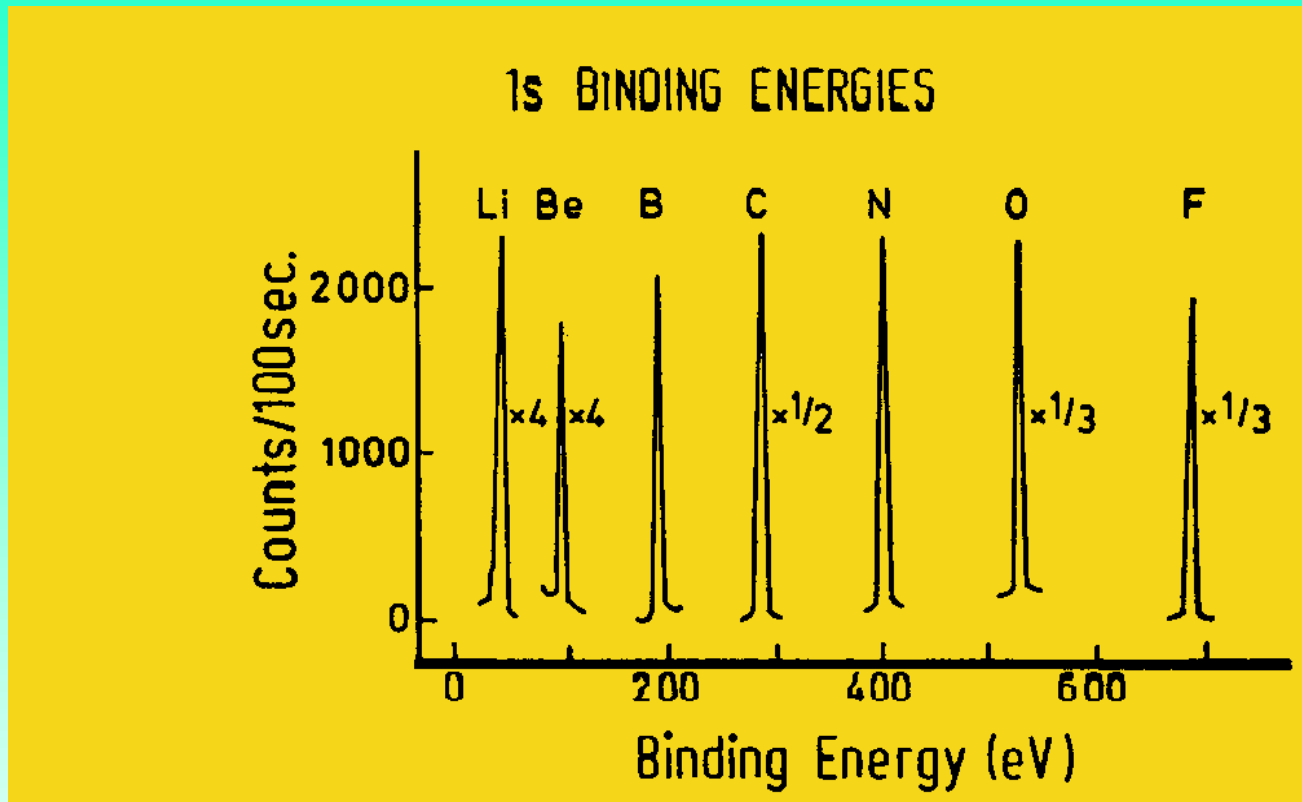
HeI UPS of H₂

Vibrations and Rotations !

n-H₂ 297 K

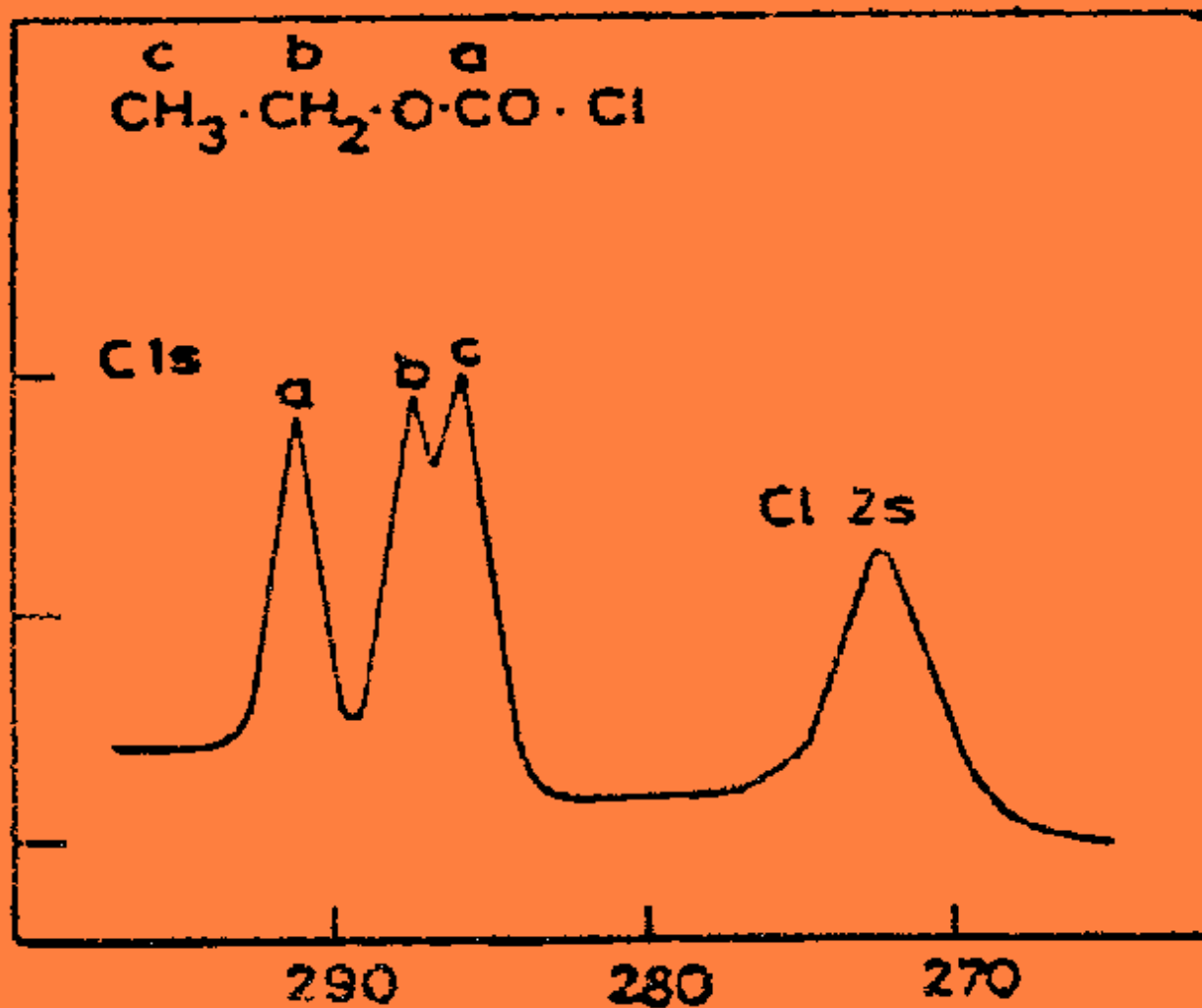


***CORE LEVEL PHOTOELECTRON
SPECTROSCOPY***



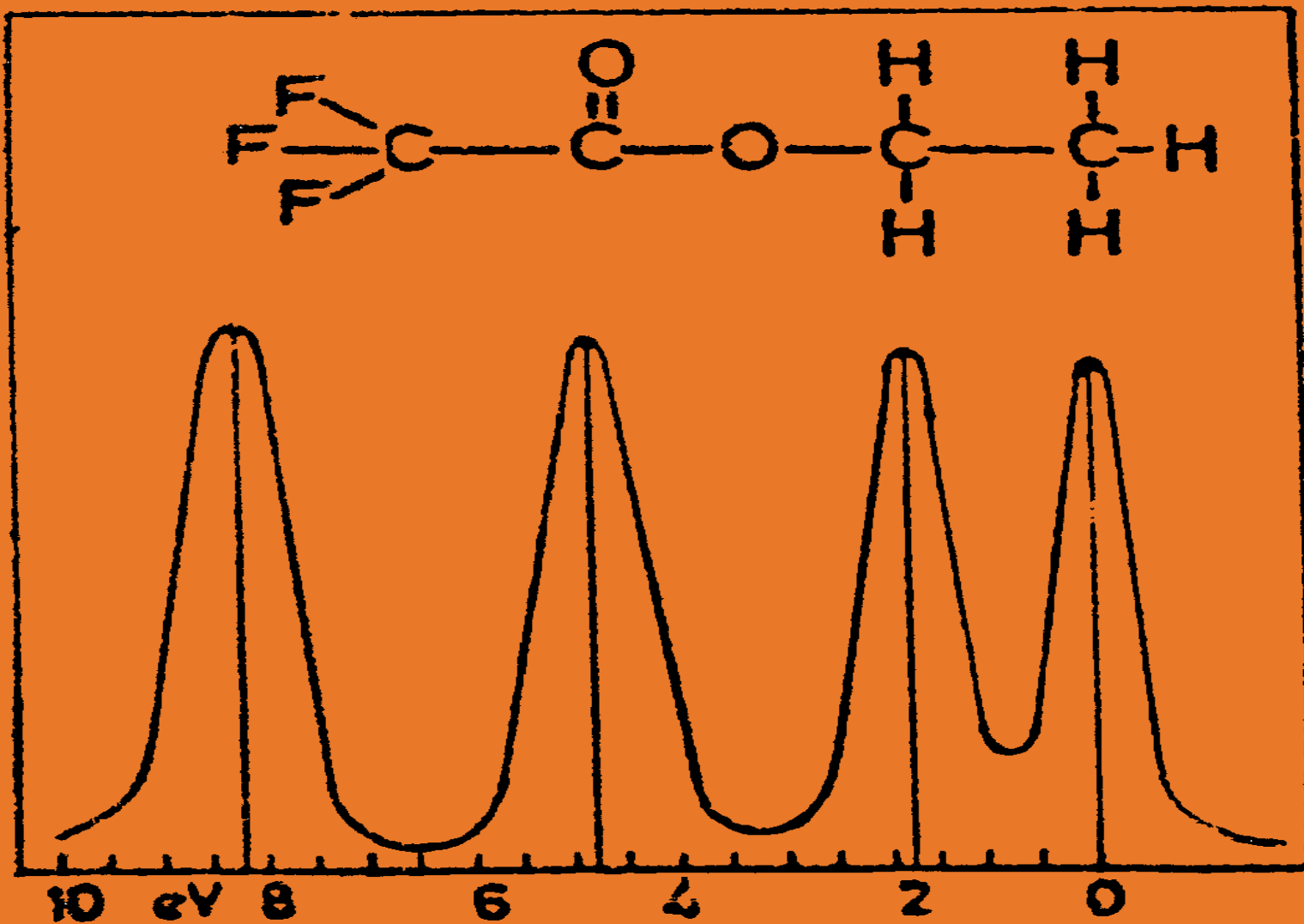
XPS-spectra of the 1s core levels of Li, Be, B, C, N, O, F (from S. Hüfner).

Counting Rate



Binding energy eV

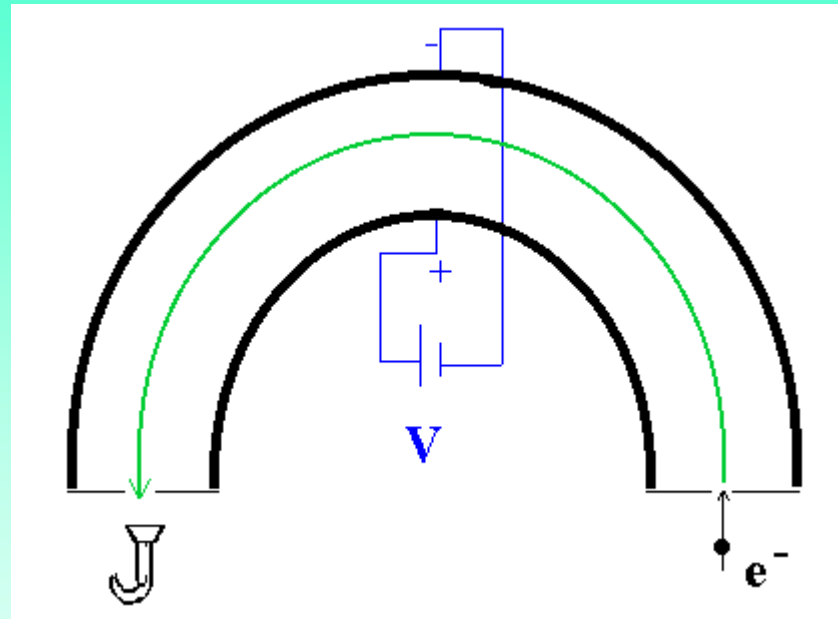
Counting Rate



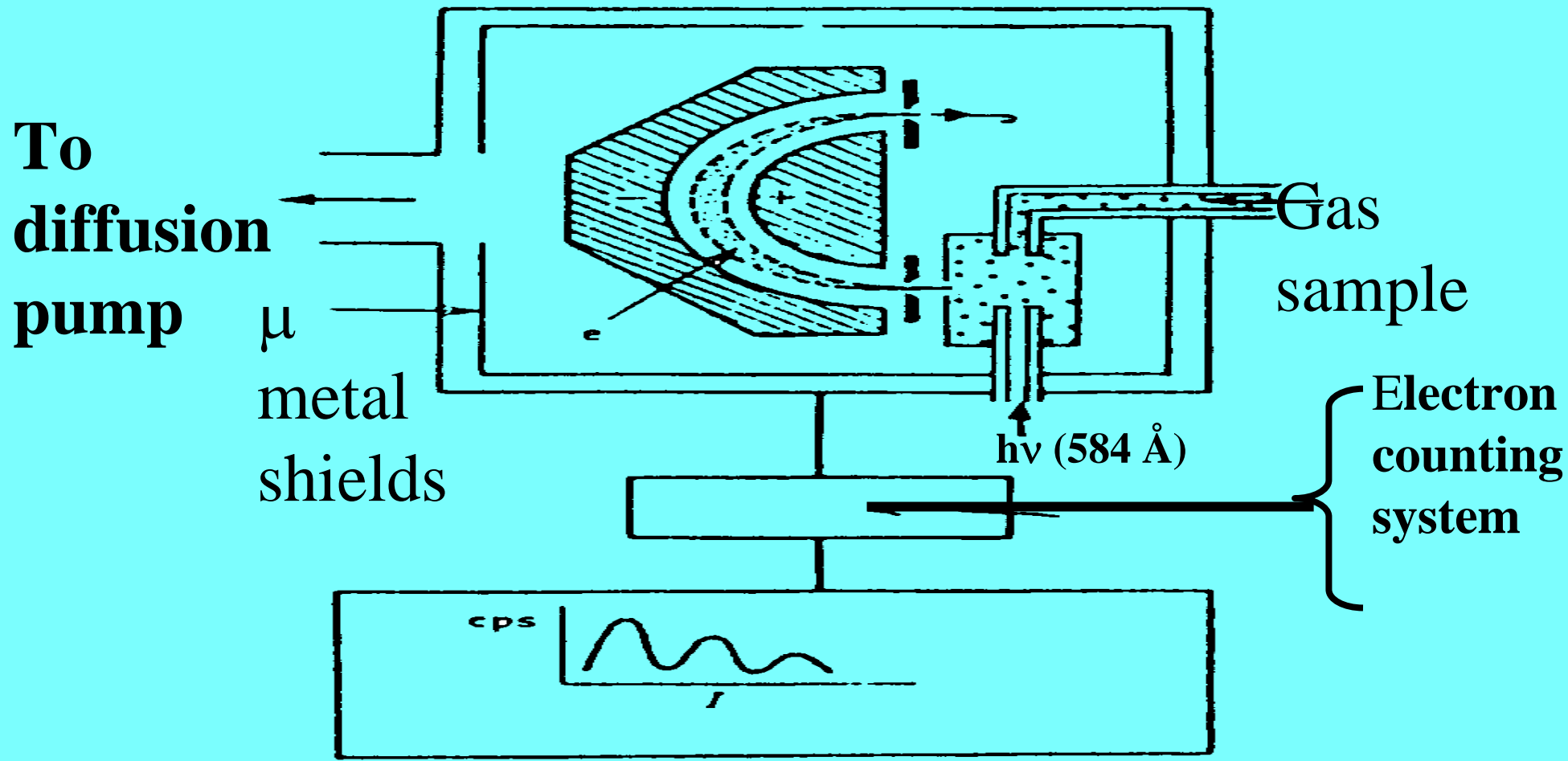
$E_B = 291.2 \text{ eV}$

Chemical Shift

INSTRUMENTATION



Simplest spectrometer



To
diffusion
pump

μ
metal
shields

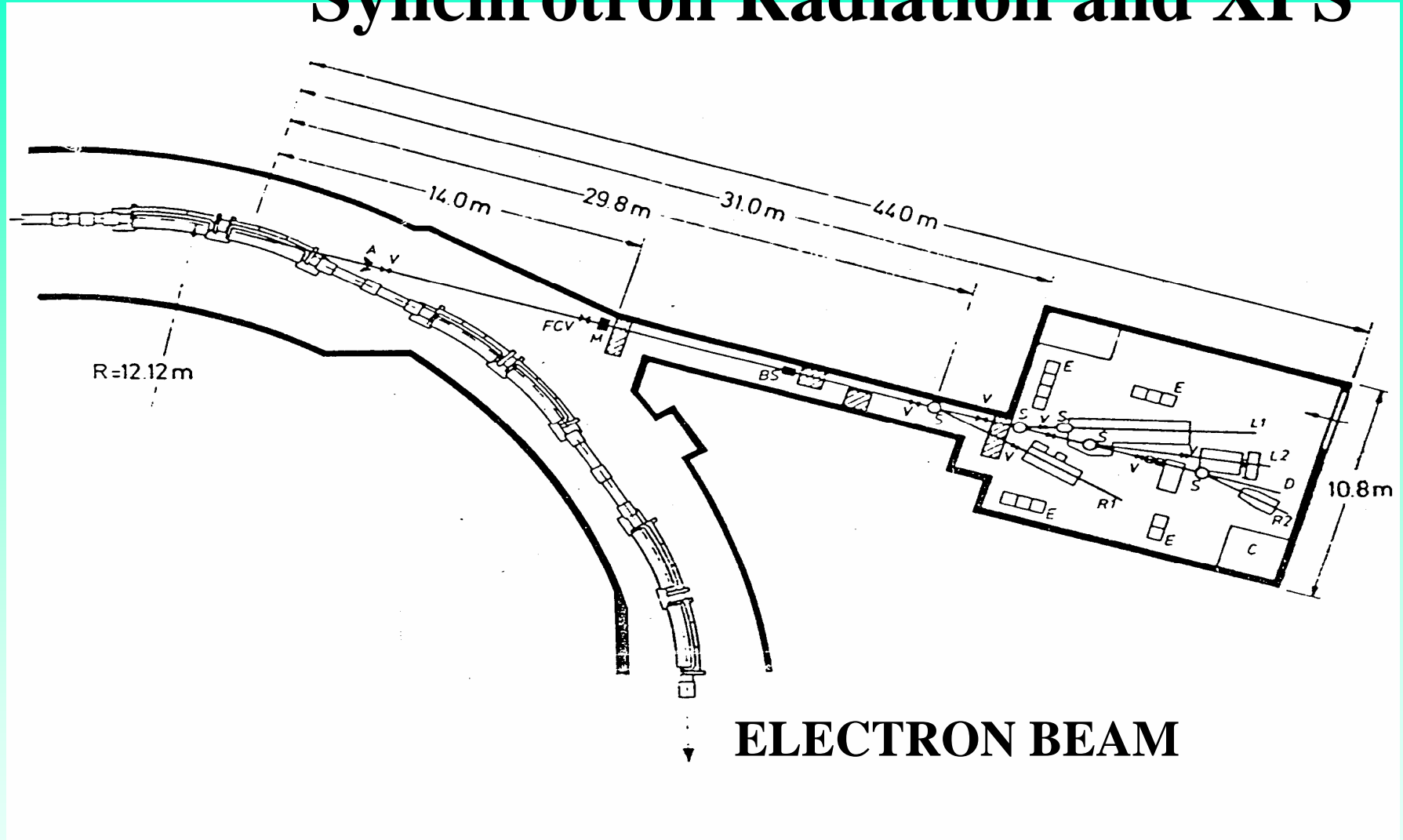
Gas
sample

Electron
counting
system

cps

t

Synchrotron Radiation and XPS



Layout of the synchrotron radiation laboratory at DORIS.