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, C_{60}, 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

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, 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

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)

Aüger electron spectroscopy (AES)

Electron energy loss spectroscopy (EELS)

Inverse photoemission spectroscopy (IPS)

There are a range of techniques in each of these

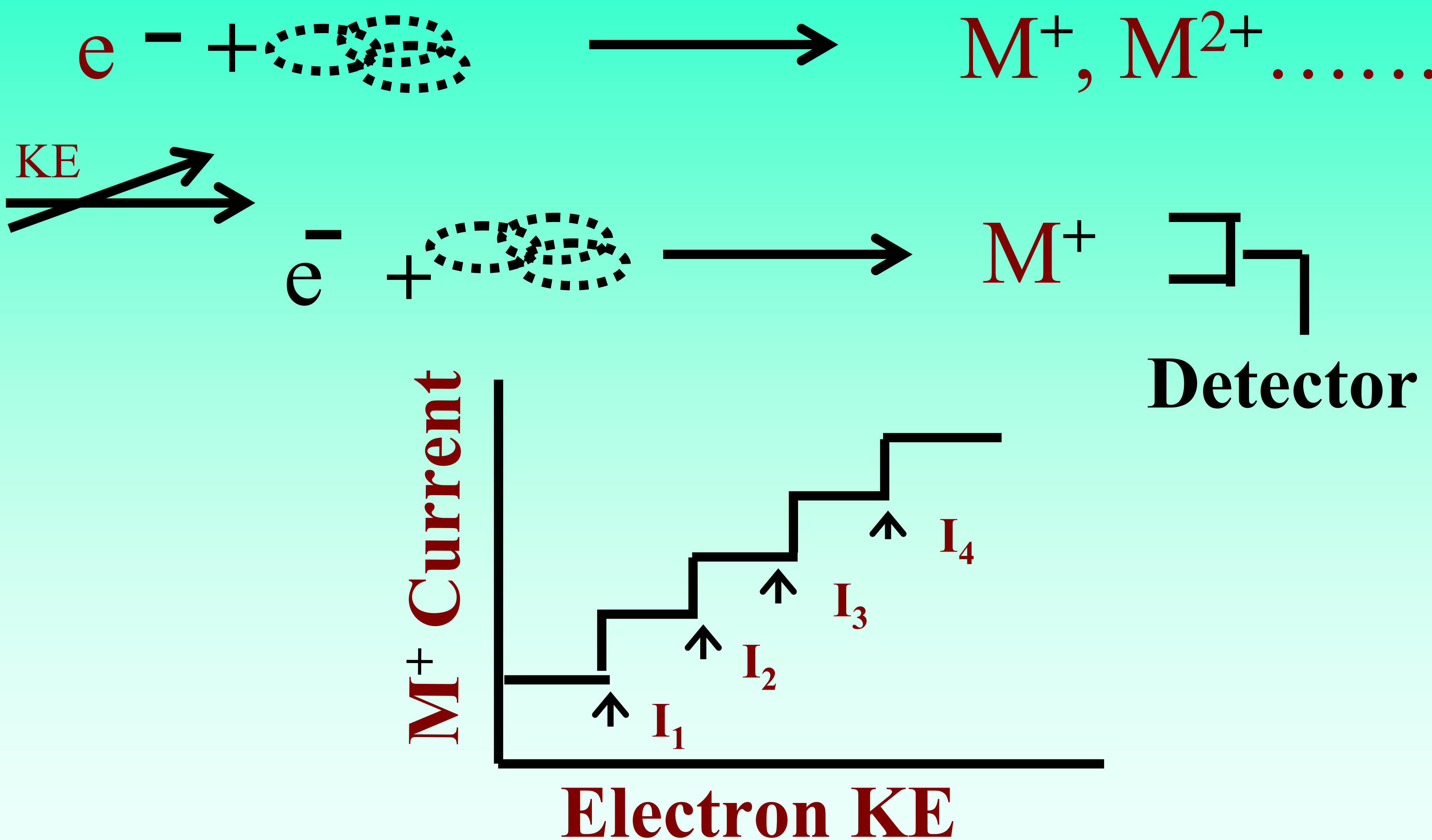
UPS — **Photon source variation**

- He I 21.2 eV
- He II 40.8 eV
- Ne I
- Synchrotron radiation
- ……

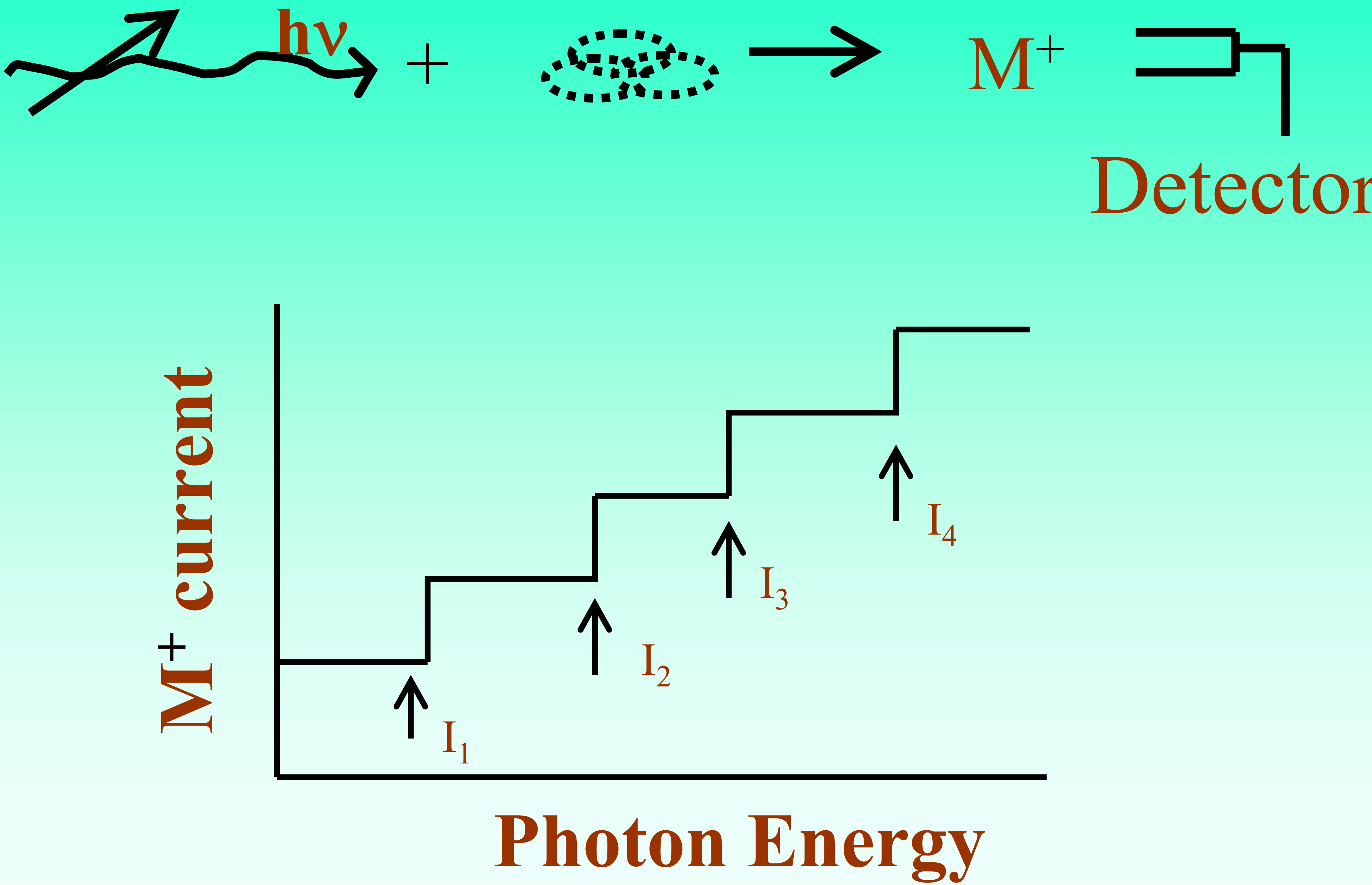
- **UPS**
  - Variations of the same basic technique
  - **One photon spectroscopy**
    - **Solids**
    - **Gases**
      - **Gas cell**
      - **Molecular beams**

- **Photoelectron-photoion coincidence spectroscopy**
- **Zero-kinetic energy photoelectron spectroscopy**
- **Multiphoton photoelectron spectroscopy**
- **Photodetachment spectroscopy**
- **……..**

Spectroscopy using electrons



Ionization efficiency curves


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

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

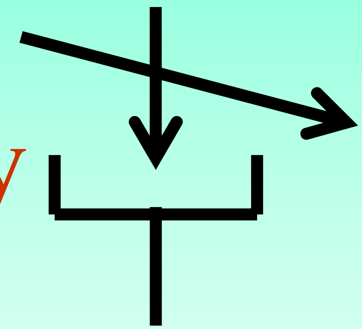
(No M^{2+}, generally)

$h\nu$

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

Constant

Photoelectron Spectroscopy



KE

Detector

Photoelectric effect

Early experiments in 1887

$h\nu = KE + \phi$ 1905

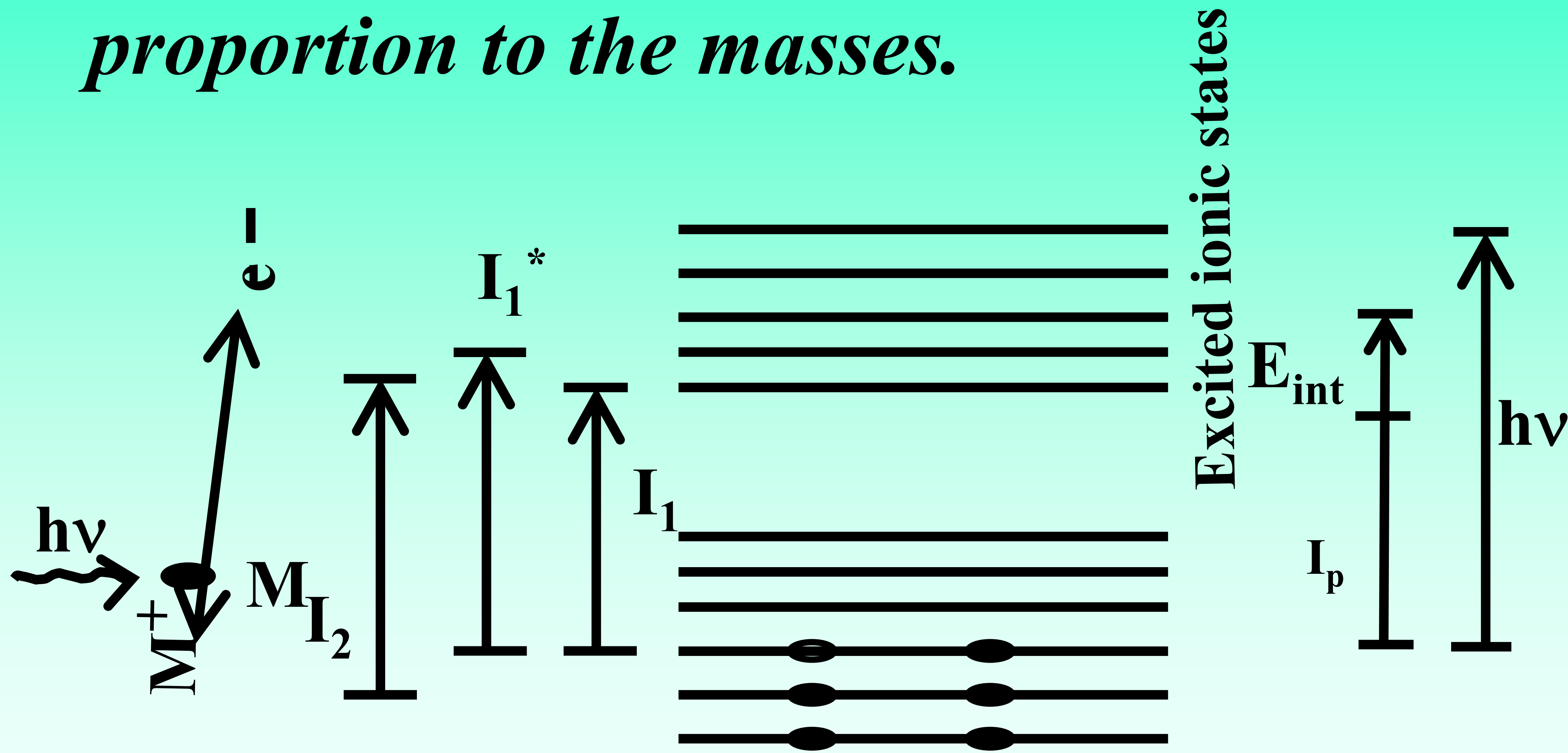
Photoion can be excited

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

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,

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

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

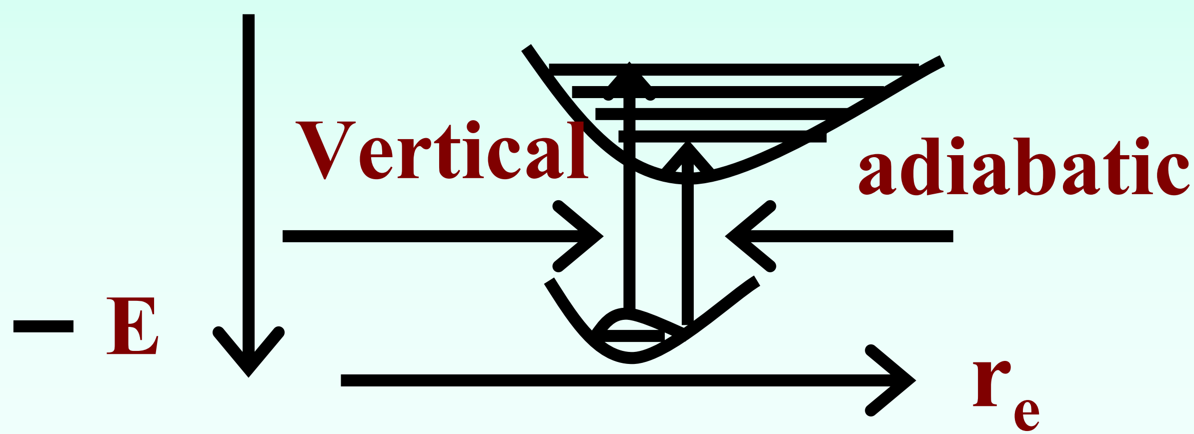
$$h\nu - (I_p + E_{int}) = KE$$

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

$$E_{int} \rightarrow 0$$

$$h\nu - KE = I_p$$

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



Depth of analysis depends on photon energy

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

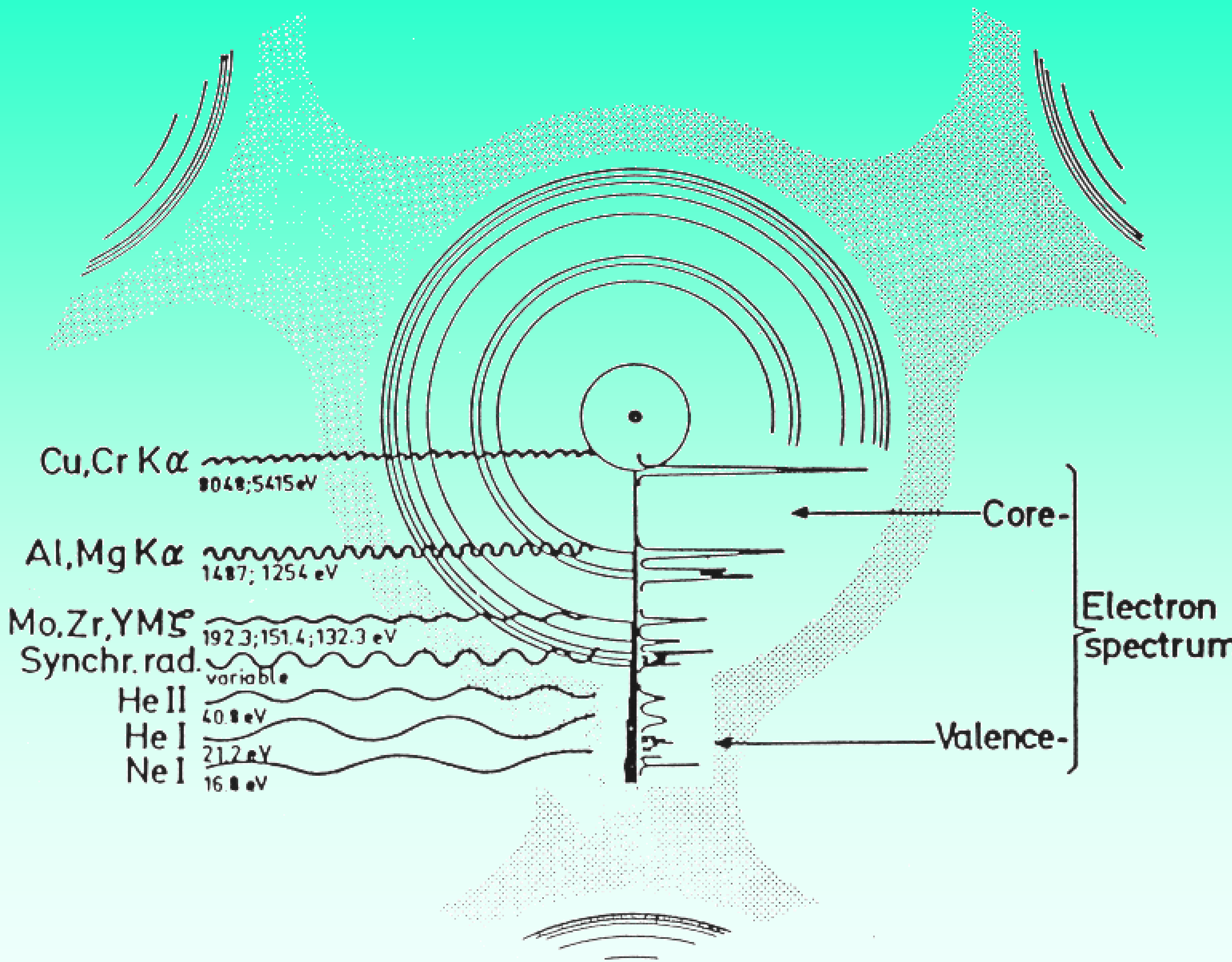
He II 40.8 eV $2\,P \rightarrow 1\,S$ of He^+

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

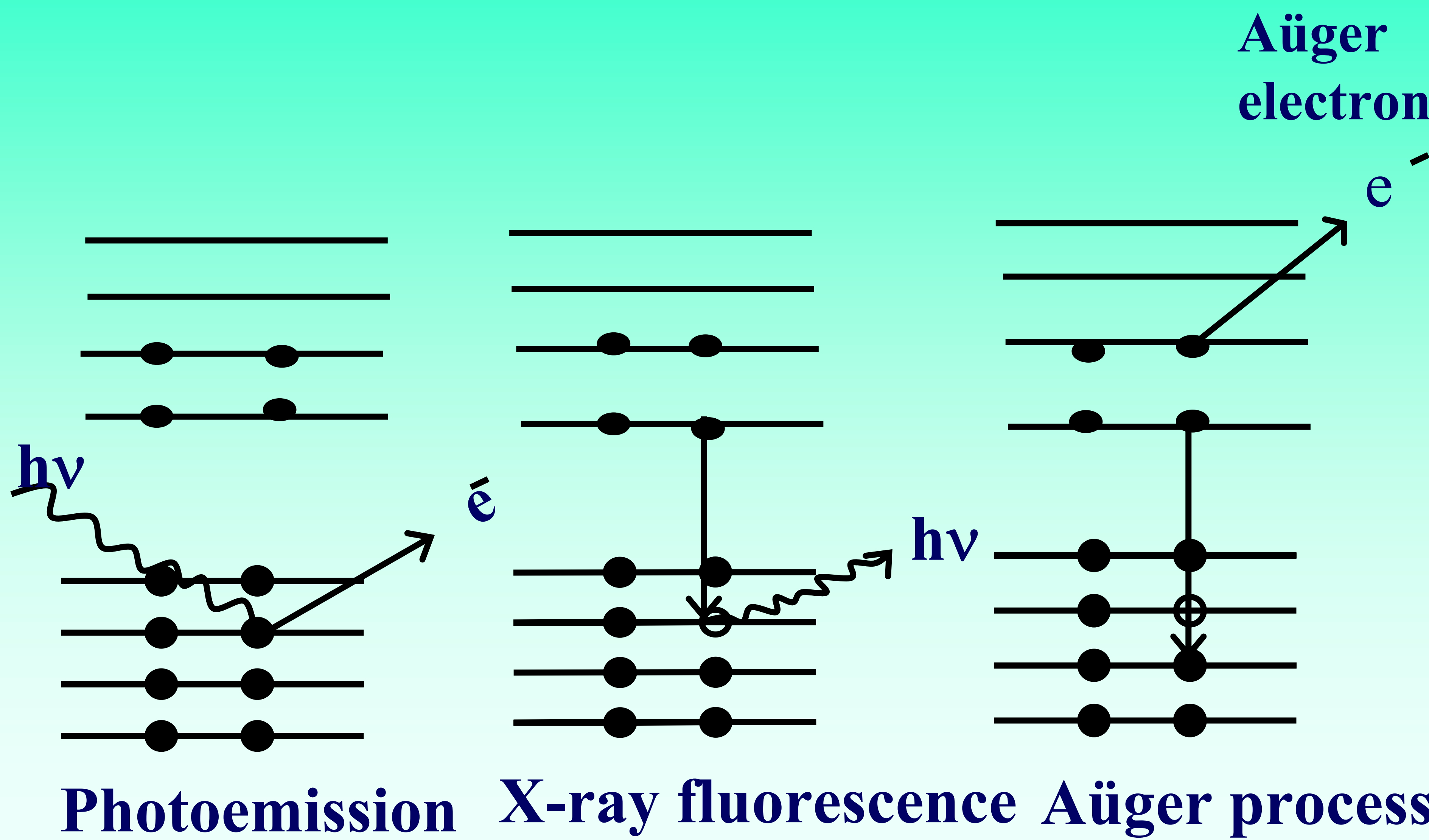
Mg $K_{\alpha 1,2}$ 1253.6 eV ”

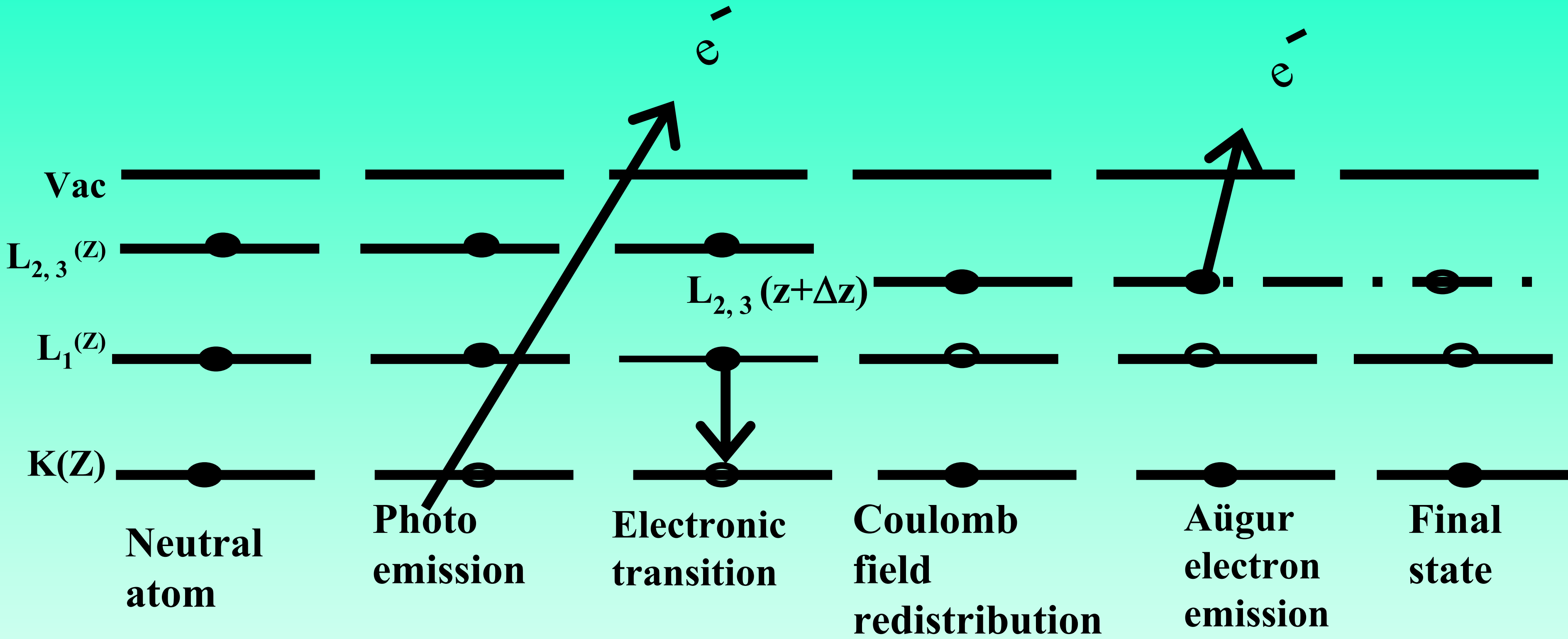
Na $K_{\alpha 1,\,2}$ 1041.0 eV ”

Si K $_{\alpha 1,\,2}$ 1739.5 eV ”



Cu,Cr Kα
8048;5415 eV
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
$L_{2,3}^{(Z)}$
$L_{2,3}$ (z+Δz)
$L_1^{(Z)}$
K(Z)
Neutral atom
Photo emission
Electronic transition
Coulomb field redistribution
Aügur electron emission
Final state

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

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

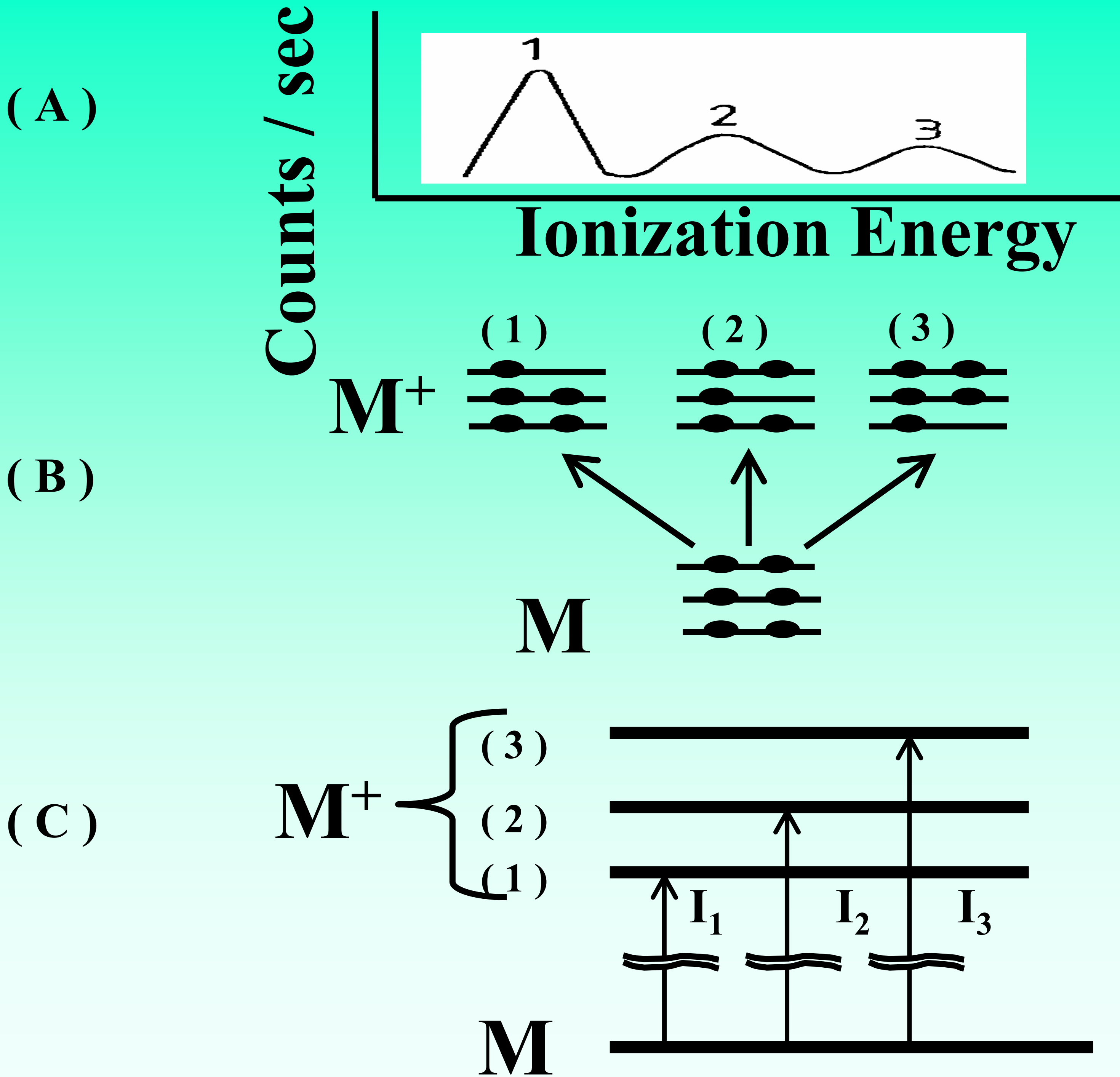
E's are the binding energies.

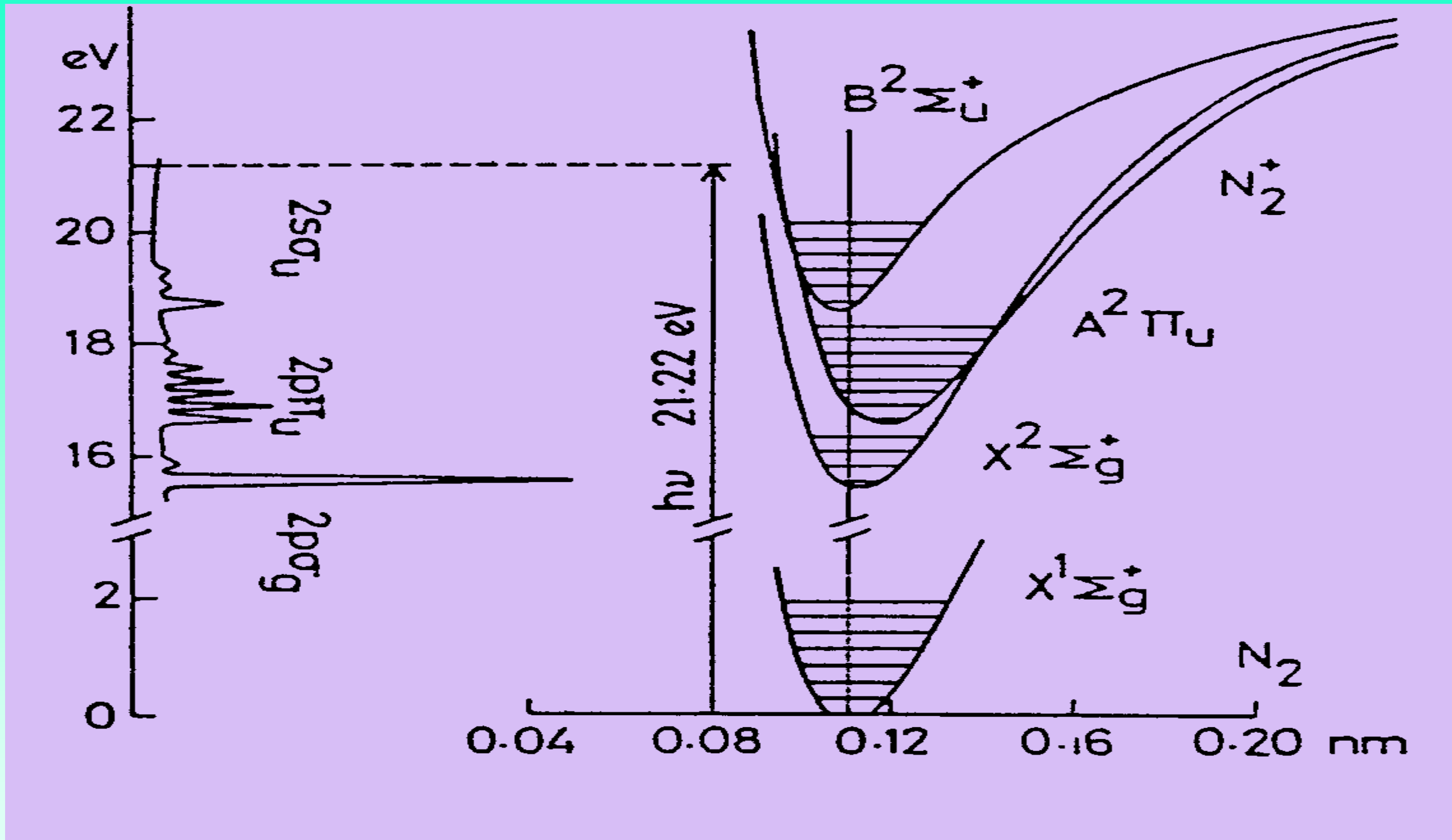
$E_{ABC} \longrightarrow$ $K\,L_1\,L_{2,3}$, $K\,L_1\,V$, KVV

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)
Counts / sec
1
2
3
Ionization Energy
(B)
(1)
(2)
(3)
M^+
M
(C)
M^+
(3)
(2)
(1)
I_1
I_2
I_3
M



INTERNUCLEAR DISTANCE

2 P σ_g → non bonding 2345 to 2191 cm^{-1}

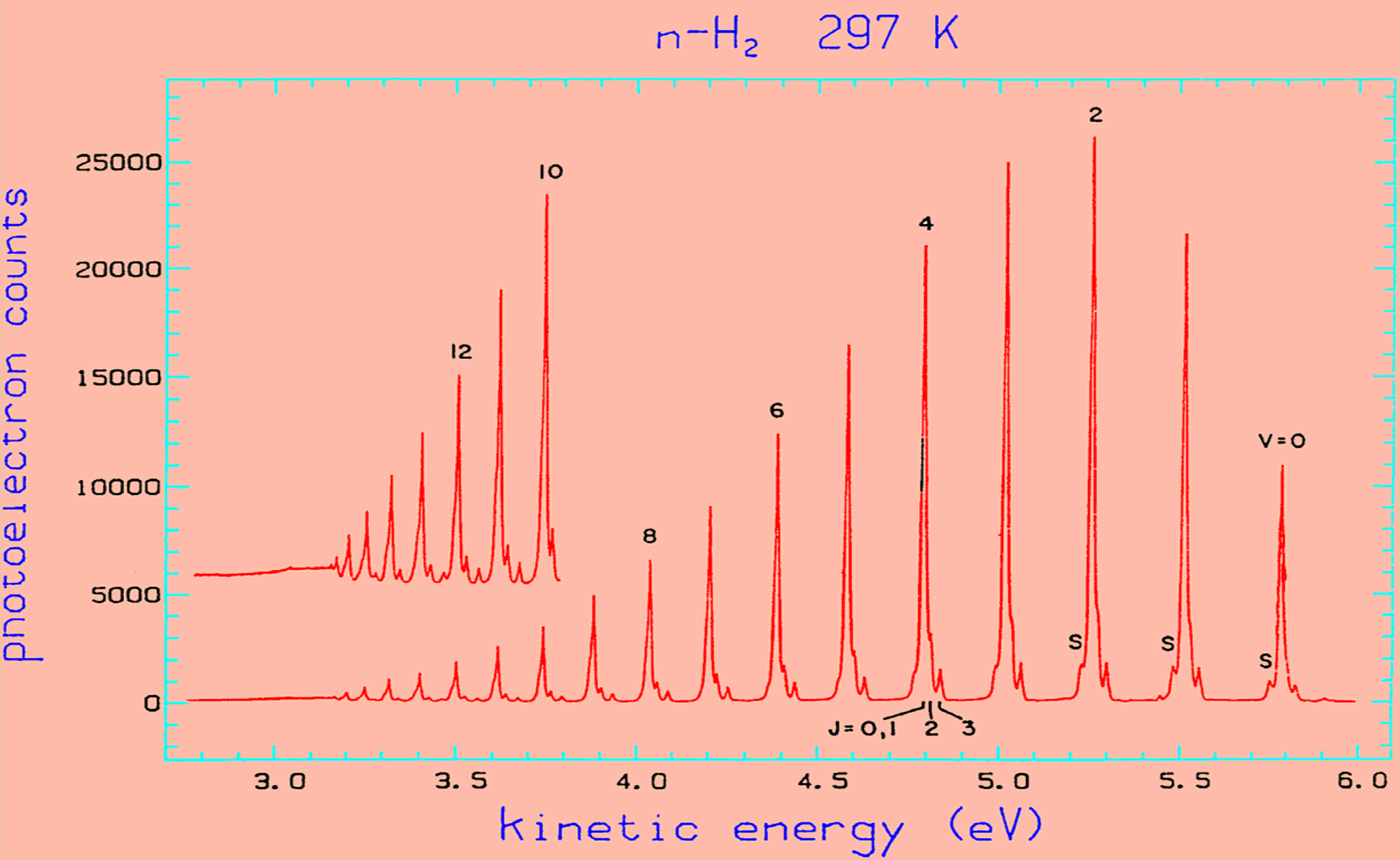
2 Pπ_u → bonding 2345 to 1850 cm^{-1}

2 Sσ_u → weakly antibonding 2345 to 2397 cm^{-1}

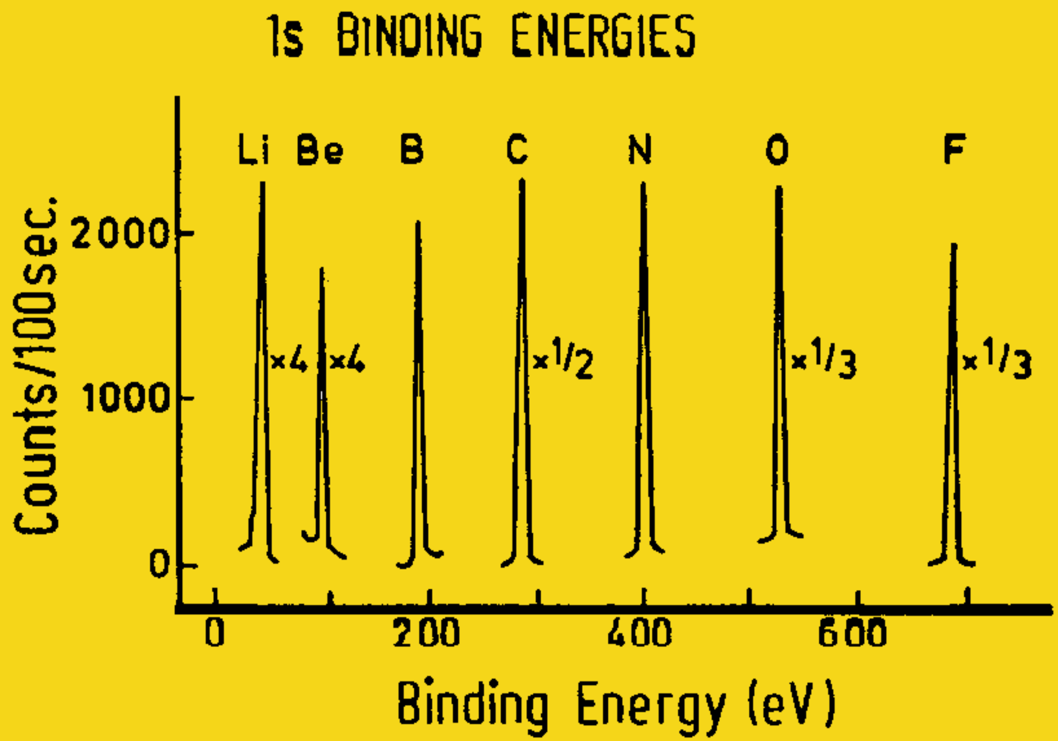
$$E_v = E_o + \omega_e (v + ½) - \omega_e x_e (v + ½)^2$$

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

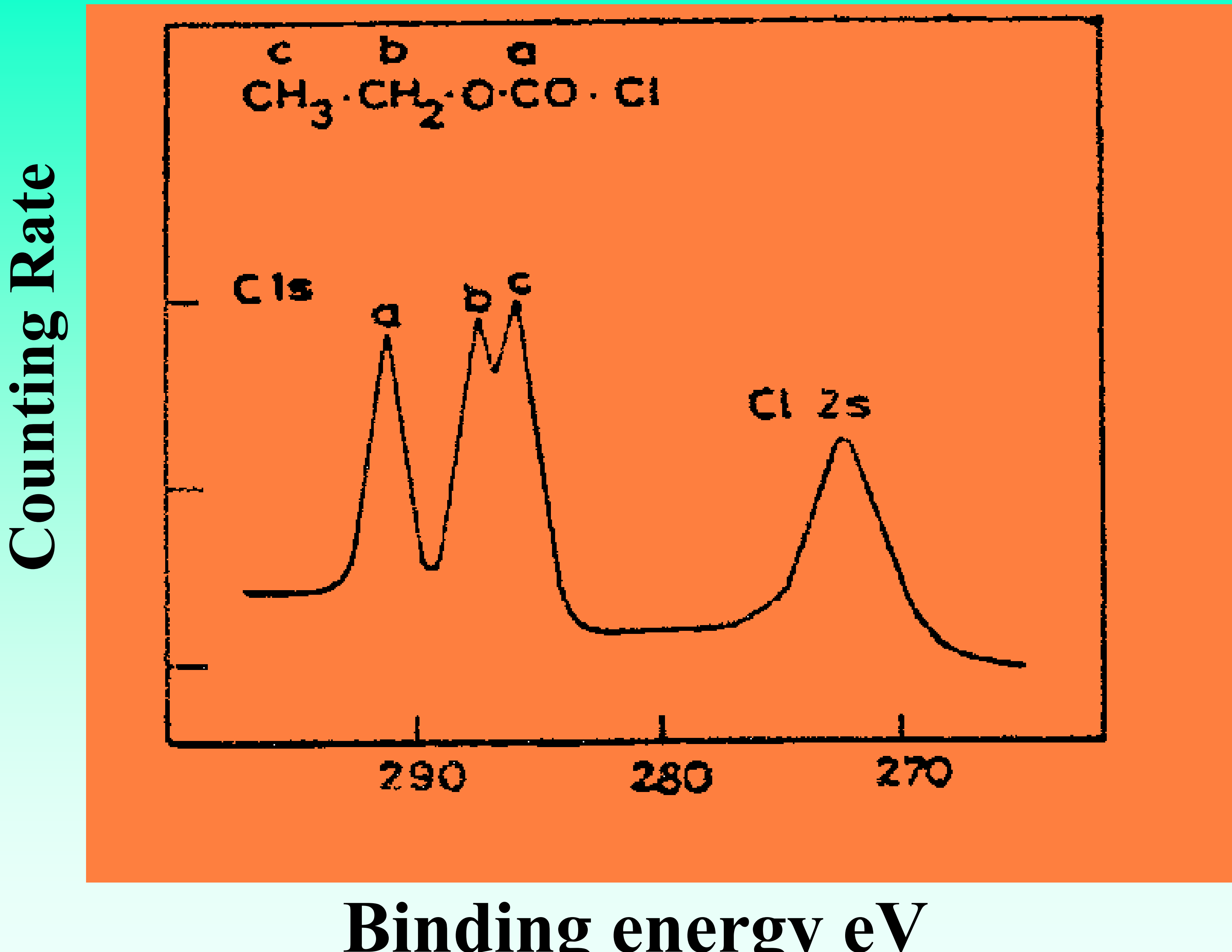
HeI UPS of H_2 Vibrations and Rotations !

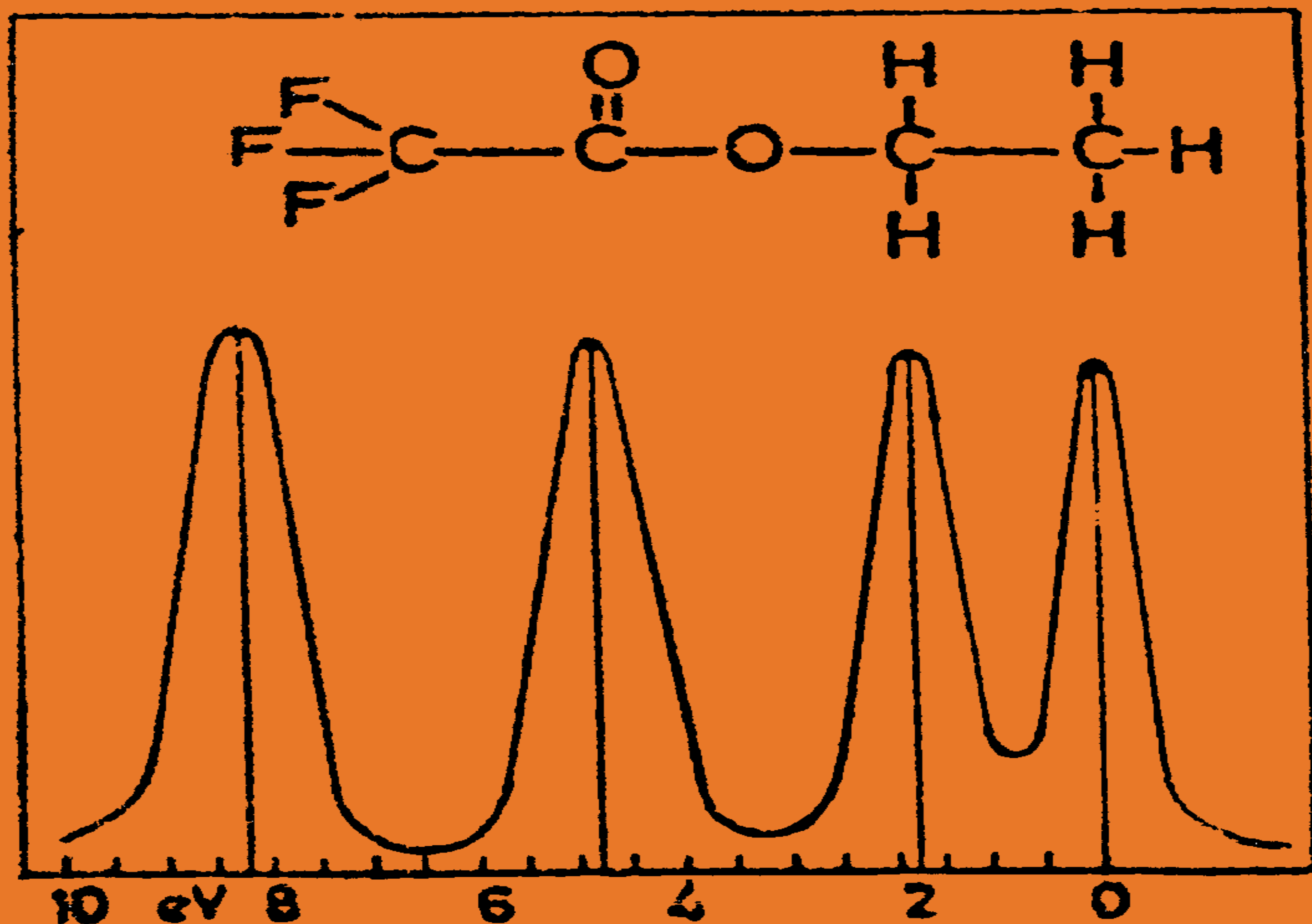


CORE LEVEL PHOTOELECTRON SPECTROSCOPY



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


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

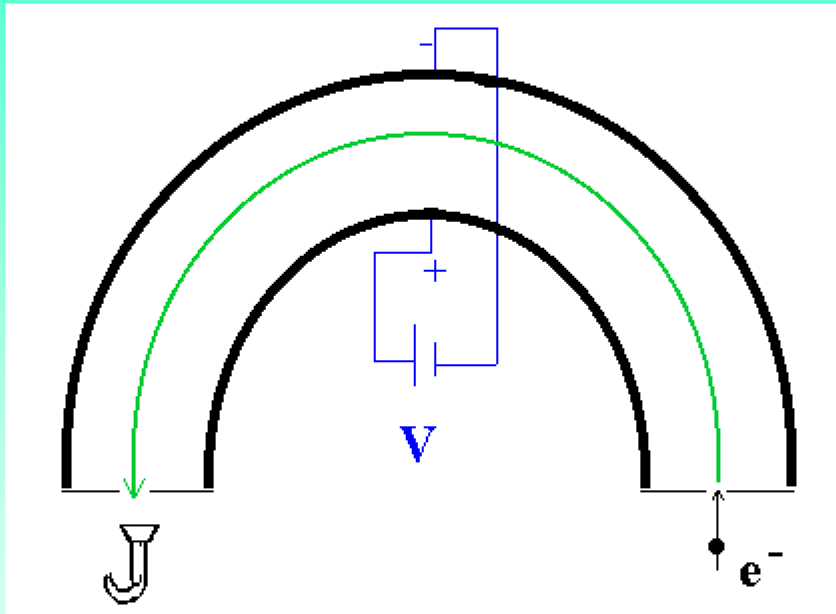


Counting Rate

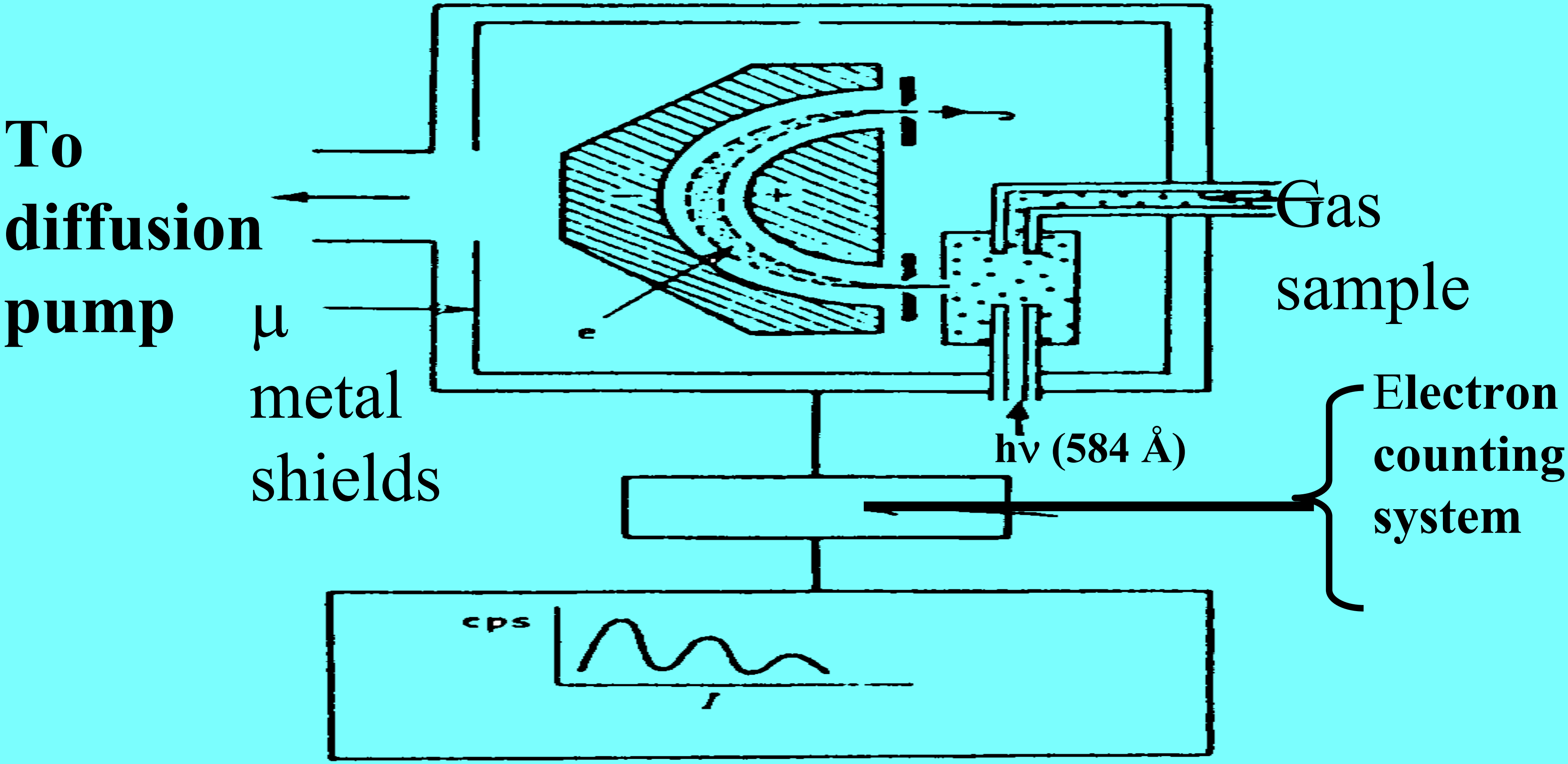
E_B=291.2eV

Chemical Shift

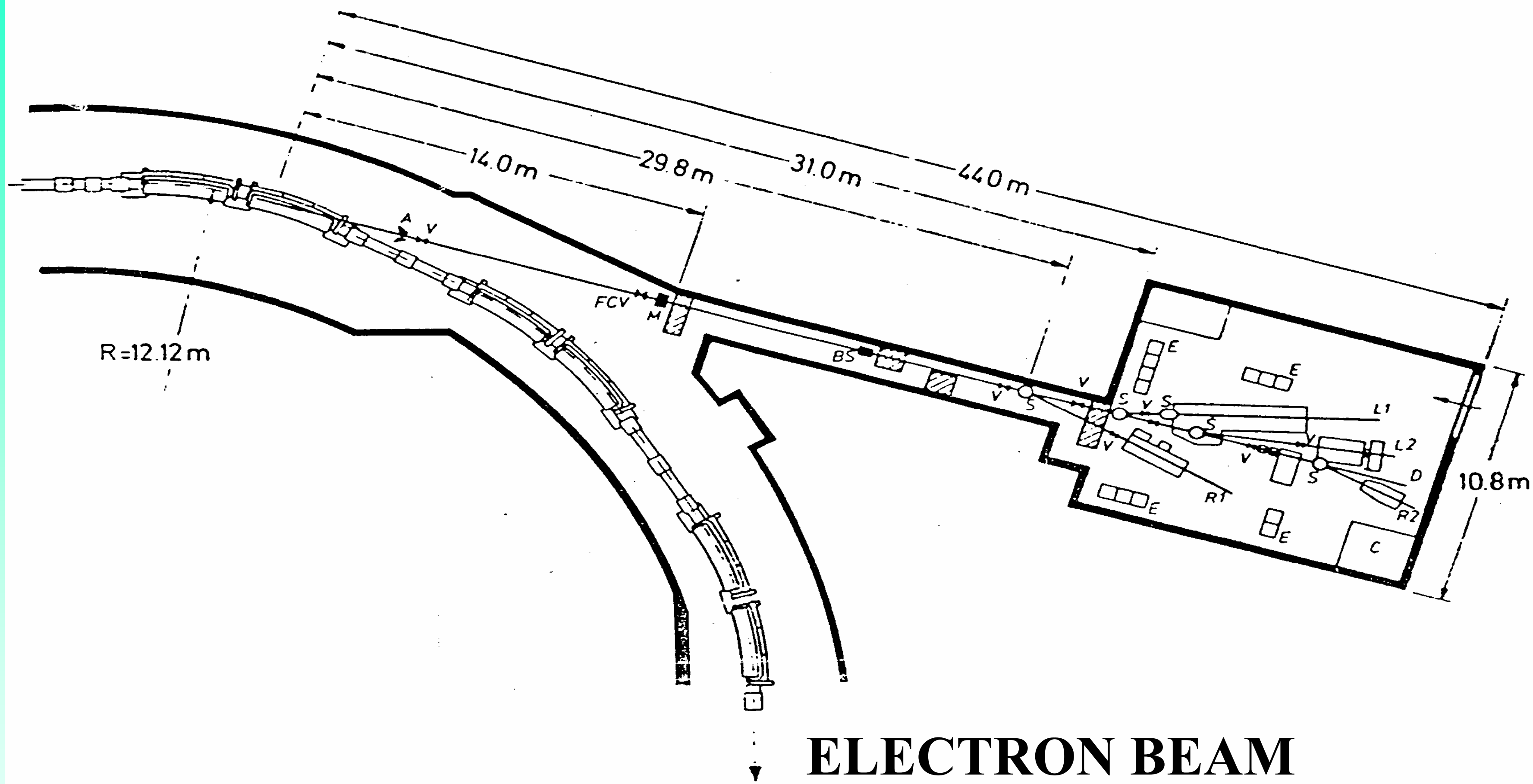
INSTRUMENTATION



Simplest spectrometer


To diffusion pump
μ metal shields
Gas sample
hν (584 Å)
Electron counting system
cps
e

Synchrotron Radiation and XPS



Layout of the synchrotron radiation laboratory at DORIS.