CH 2252 Instrumental Methods of Analysis

Unit – I

www.msubbu.in

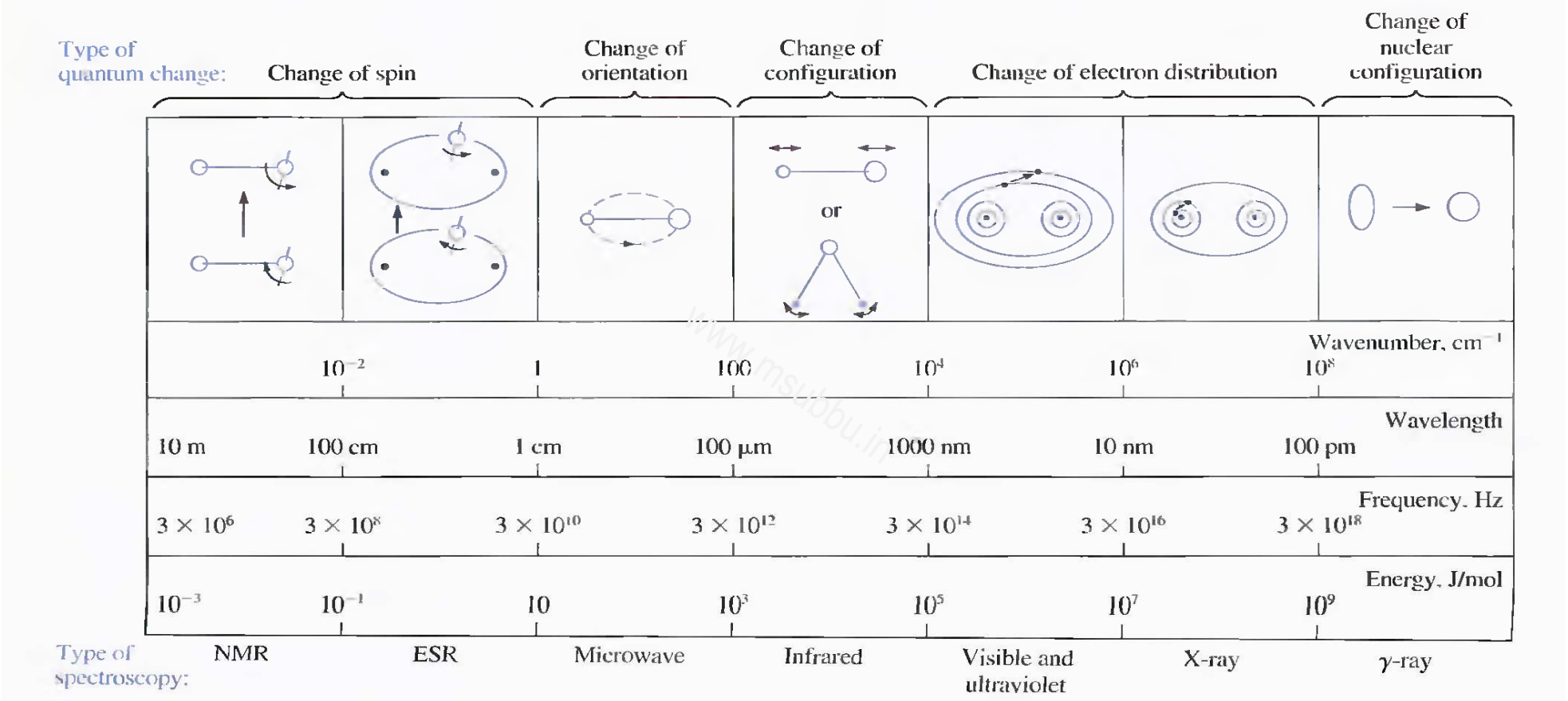
Interactions of Photon with Matter

M. Subramanian

Associate Professor
Department of Chemical Engineering
Sri Sivasubramaniya Nadar College of Engineering
Kalavakkam – 603 110, Kanchipuram (Dist)
Tamil Nadu, India
msubbu.in@gmail.com

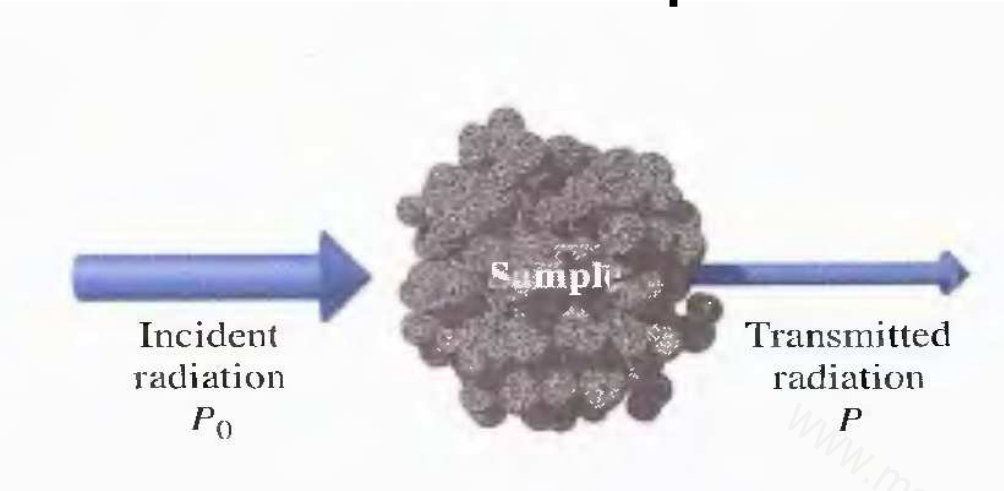
Contents

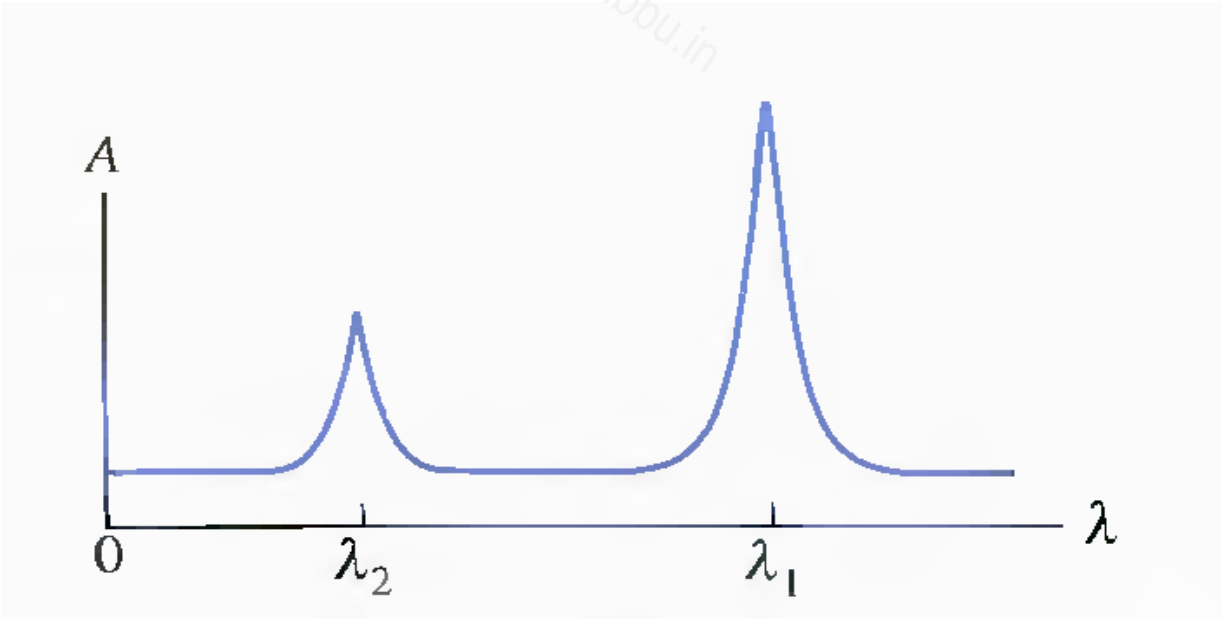
- Interaction of photons with matter, absorbance, & transmittance and their relationship


Type of quantum change:
Change of spin
Change of orientation
Change of configuration
Change of electron distribution
Change of nuclear configuration
or
Wavenumber, cm⁻¹
10⁻²
1
100
10⁴
10⁶
10⁸
Wavelength
10 m
100 cm
1 cm
100 μm
1000 nm
10 nm
100 pm
Frequency, Hz
3 × 10⁶
3 × 10⁸
3 × 10¹⁰
3 × 10¹²
3 × 10¹⁴
3 × 10¹⁶
3 × 10¹⁸
Energy, J/mol
10⁻³
10⁻¹
10
10³
10⁵
10⁷
10⁹
Type of spectroscopy:
NMR
ESR
Microwave
Infrared
Visible and ultraviolet
X-ray
γ-ray

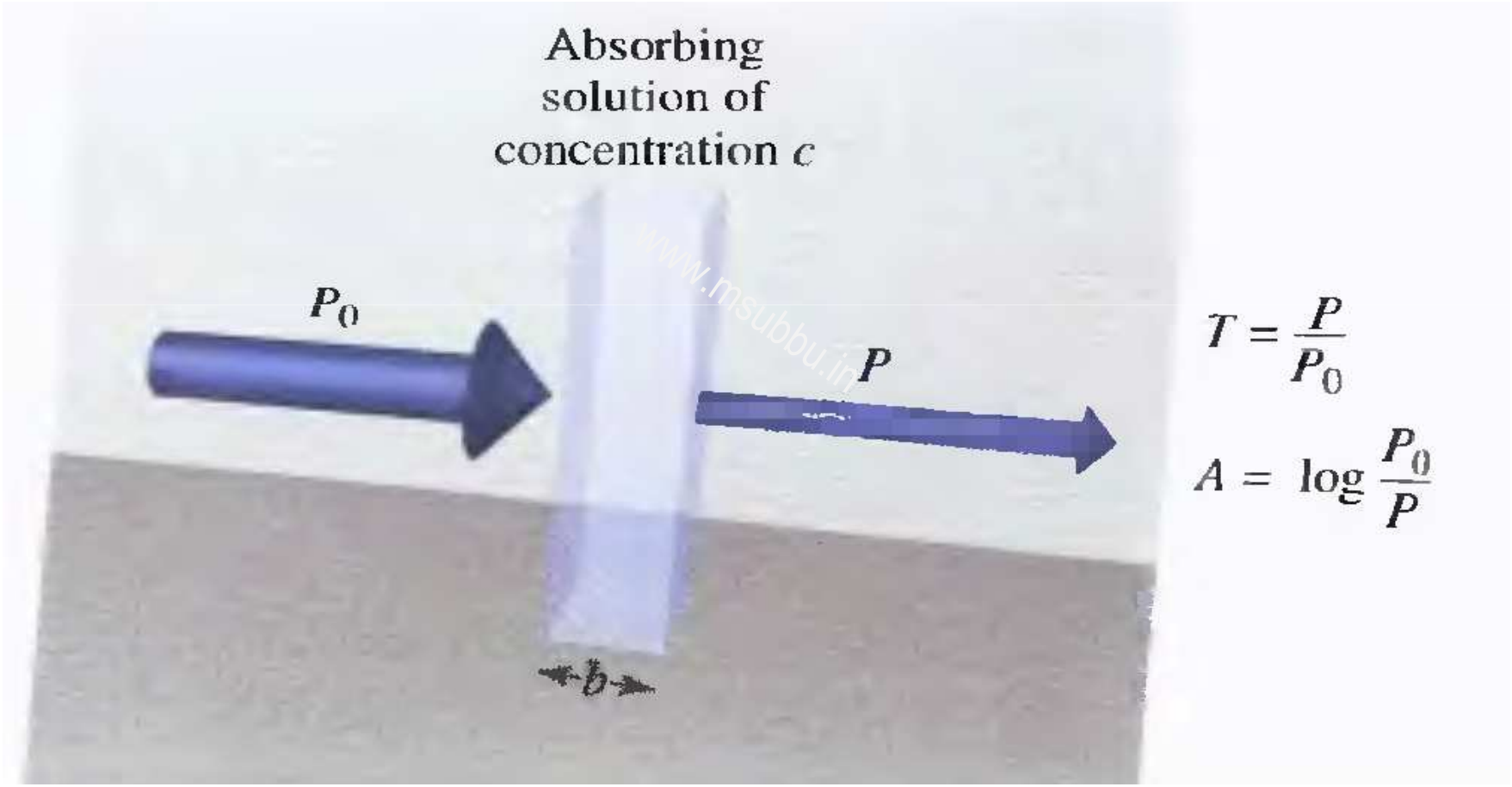
Region of the spectrum	Main interactions with matter
Radio	Collective oscillation of charge carriers in bulk material
Microwave through far infrared	Plasma oscillation, molecular rotation
Near infrared	Molecular vibration, plasma oscillation (in metals only)
Visible	Molecular electron excitation (including pigment molecules found in the human retina), plasma oscillations (in metals only)
Ultraviolet	Excitation of molecular and atomic valence electrons, including ejection of the electrons
X-rays	Excitation and ejection of core atomic electrons
Gamma rays	Energetic ejection of core electrons in heavy elements, excitation of atomic nuclei, including dissociation of nuclei

Absorption of Radiation





Absorbance



log → base 10

Measuring Transmittance and Absorbance

$$A = \log \frac{P_0}{P} \approx \log \frac{P_{\text{solvent}}}{P_{\text{solution}}}$$

Beer-Lambert's law

$$A = abc$$

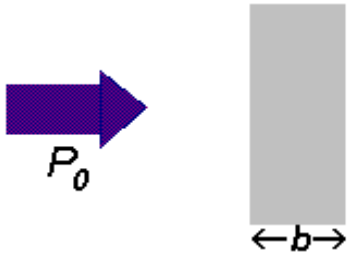
where a is absorptivity ($L.g^{-1}.cm^{-1}$)

$$A = \varepsilon bc$$

where ε is molar absorptivity ($L.mol^{-1}.cm^{-1}$)

Absorbance – Transmittance Relations

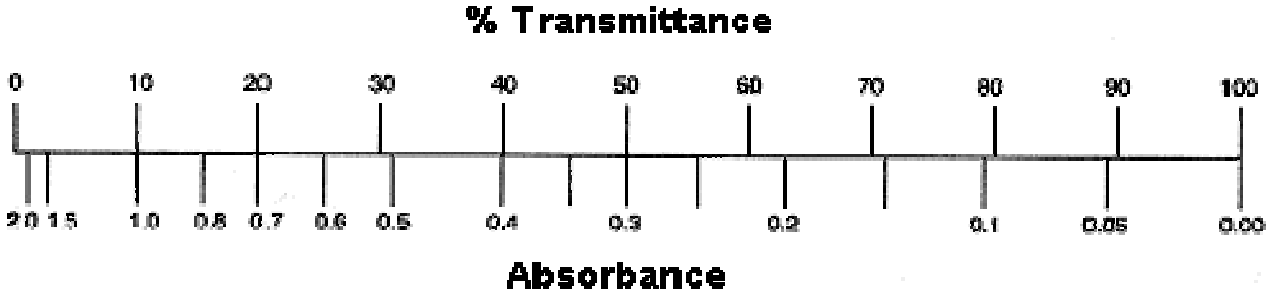
- **Transmittance:** $T = P / P_0$
  % Transmittance: $\%T = 100\ T$
- **Absorbance:** $A = \log (P_0 / P)$

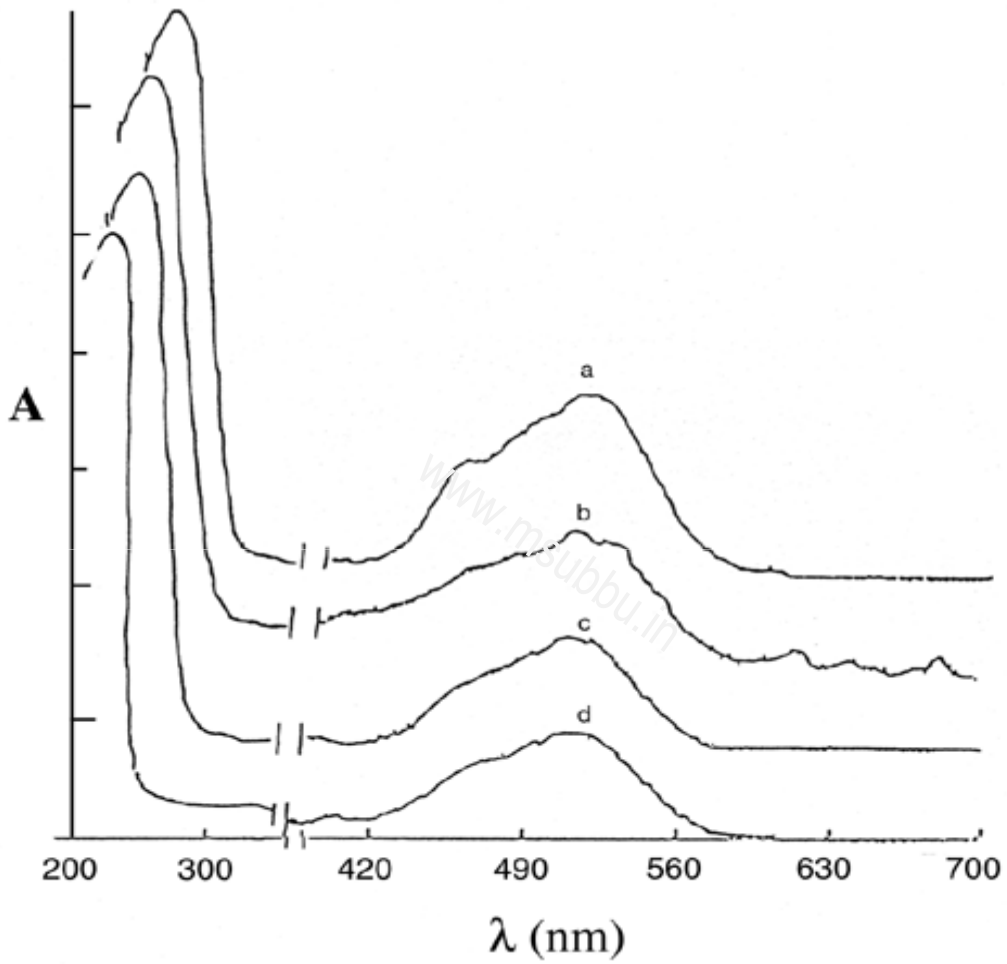


$A = \log (1 / T) \quad = -\log (T)$

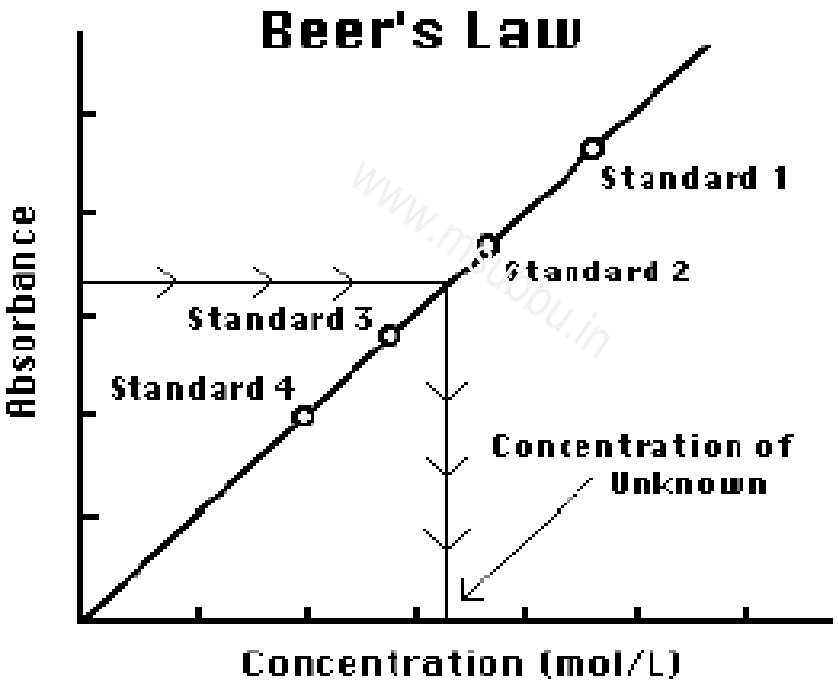
$A = \log (100 / \%T)$

$A = 2 - \log (\%T)$





$$\log \frac{P_0}{P} = \varepsilon bc = A$$



Deviations from Beer-Lambert's Law

- Deviations in absorptivity coefficients at high concentrations (> 0.01 M) due to electrostatic interactions between molecules in close proximity
- Scattering of light due to particles in the sample
- Fluorescence or phosphorescence of the sample
- Changes in refractive index at high analyte concentration
- Shifts in chemical equilibrium as a function of concentration
- Non-monochromatic radiation
- Stray light

Beer-Lambert’s law at high concentrations