بِسْمِ اللهِ الرَّحْمَنِ الرَّحِيمِ

Lecture 2

Advanced Analysis
for Pharmacy Students

By

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# Electronic Spectra and molecular Structre

- Absorption of EMR in the UV-VIS. Region by absorbing groups in the molecule

  (chromophores) lead to **electronic transition** i.e. the electronic system of the molecule transfer from ground state to excited state

Types of Electronic Transitions

- **The outer electrons in an organic molecule may occupy one of three different energy levels :**

- **Sigma (σ) electrons : are bonding electrons which represent valence bonds and are formed from linear overlaps of electronic clouds of S or Sp orbitals . They possess the lowest energy level , i.e. most stable.**

- **Pi (π) electrons : bonding electrons constituting the pi bonds (double bonds) and result from lateral overlap of electronic clouds of P orbitals . They are of higher energy than sigma electrons .**

- **Non-bonding (n-electrons) : these are atomic orbitals of hetero-atoms (N, O, S, halogen) which do not participate in bonding , they usually occupy the highest energy level .**

- **<u>Types of Electronic Transitions</u>**

- **<u>σ - σ *   transition</u> : in vacuum uv e.g. saturated compounds (alkane)**

- σ to π* (carbonyl compounds)

- **<u>π - π*   transition</u> : in 200 - 700 nm region e.g. unsaturated compounds.**

- (alkenes, carbonyl compounds, alkynes, azo compounds)

- η to σ * (oxygen, nitrogen, sulfur, and halogen compounds)

- **<u>n - π*   transition</u> : in 150 - 250 nm region** (carbonyl compounds)
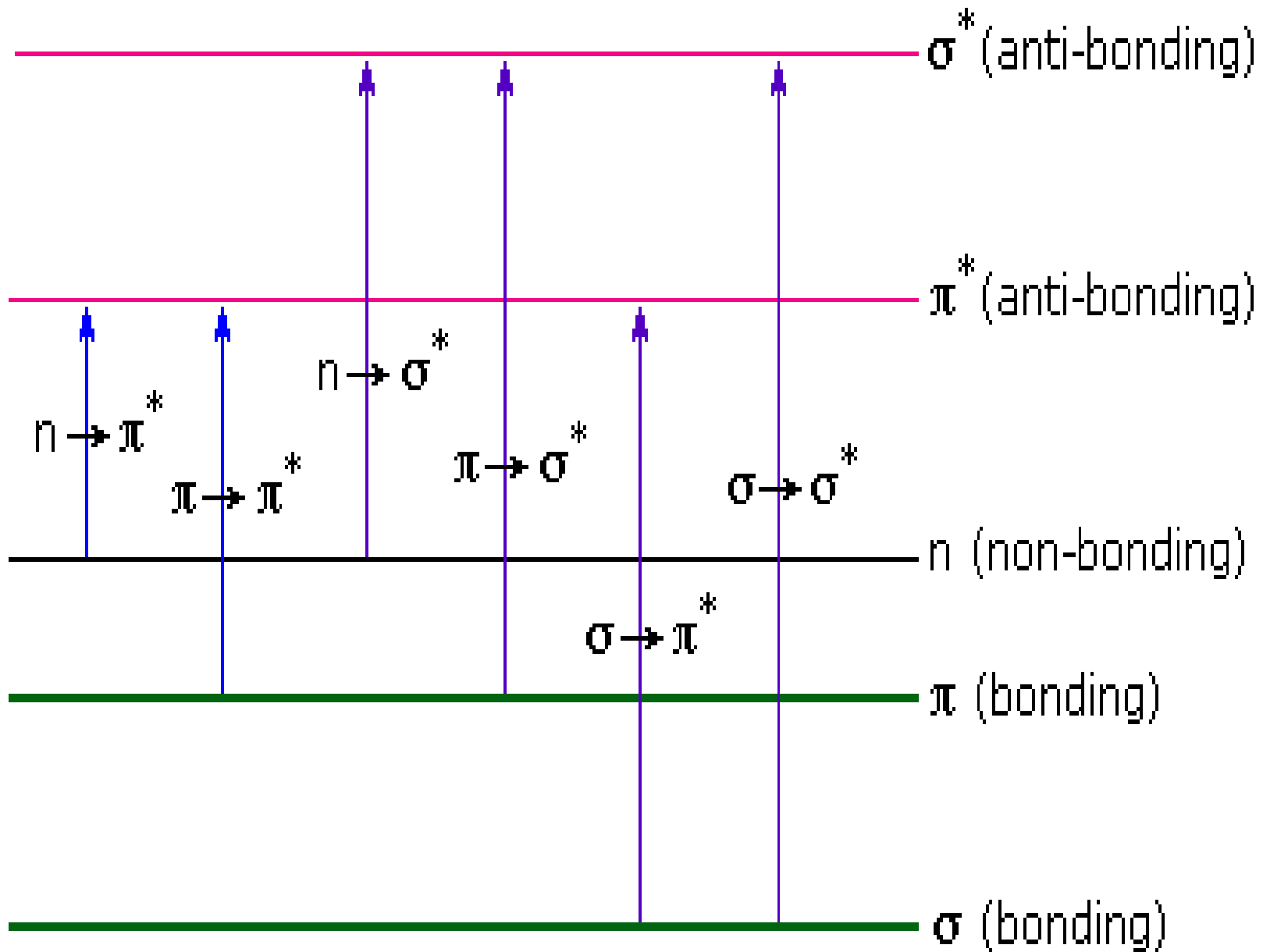
Types of Electronic Transitions

σ to σ^*

Chromophore	λ_{max}
Alkanes	~ 150

π to π^*

Chromophore	λ_{max}
alkenes	~ 175
alkynes	~ 170
Carbonyls	~ 188

η to σ^*

Chromophore	λ_{max}
alcohols, ethers	~ 185
amines	~ 195
sulfur compounds	~ 195

η to π^*

Chromophore	λ_{max}
carbonyls	~ 285

- Most transitions above 200 nm are $\pi - \pi^*$ or $n - \pi^*$

  e.g. in ketones C = O   → $C^+ - O^- \; \pi - \pi^*$ transition

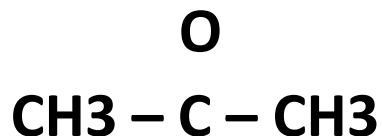   C = O   → $C^- - O^+ \; n - \pi^*$ transition

- $\pi - \pi^*$ transition has greater probability than $n - \pi^*$, so the intensity of absorption band are greater .
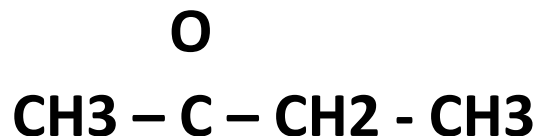
  e.g in $\pi - \pi^*$ ε 1000 - 100000 , in $n - \pi^*$ ε less than 1000

- The spectrum due to chromophore is not markedly

  affected by minor structure change in the molecule

    e.g.   O   O

          CH3 – C – CH3   CH3 – C – CH2 - CH3

            Acetone   2 – butanone

  Have spectra similar in shape and intensity .

- The effect of two isolated chromophores in a molecule (not conjugated) are independent and additive .

    e.g. CH_3-CH_2-CNS λmax at 245 nm with
        ε = 800 (due to –CNS)

    $SNC-CH_2-CH_2-CNS$ λmax at 245 nm with
        ε = 2000 (due to 2– CNS)

- Conjugated double or triple bonds , π orbital overlap, that decrease energy required for excitation i.e. absorption occur at higher λ I.e. bathochromic shift and also increase in the intensity i.e. hyperchromic effect .

- The greater the degree of conjugation the greater the shift
- Benzene : absorbs strongly at 200 nm (ε = 6900) and with a weaker band at 230 – 270 nm (ε = 170) with fine structure .
- Substitution with –OH , -OCH$_3$, -NH$_2$, -NO , -CHO smooth the fine structure of benzene spectrum with bathochromic shift and hyperchromism (due to n – π conjugation .
- Polynuclear aromatic compounds (fused benzene rings) :
- e.g. naphthalene also increase conjugation
- naphthacene (4 rings) λmax at 470 nm and is yellow

 pentacene λmax at 575 nm and is blue .

- <u>Solvents for Spectroscopy</u> :
- The solvent used in spectroscopy must be transparent i.e. has no absorbance during measurement in the specified region . Each solvent has its cutoff point .
- The cutoff-point of any solvent is the lowest wavelength at which the absorbance approach unity (using 1-cm cell, using water as reference) .
- <u>Solvent –Solute interaction</u> : going from nonpolar to polar solvent ; loss of fine structure may occur and λmax may shift . e.g. fine structure of benzene in n-hexane will smoothed for spectrum of benzene in methanol .

Choice of Solvent

Solvent	Minimum Wavelength (nm)
acetonitrile	190
water	191
cyclohexane	195
hexane	195
methanol	201
ethanol	204
ether	215
methylene chloride	220
chloroform	237
carbon tetrachloride	257

ABSORPTION SPECTRA

- **Absorption spectrum is a plot of absorption of radiation vs wavelength . According to the absorbed radiation we can classified the absorption spectra into:**

1 - UV - Spectrum

2 - Visible Spectrum
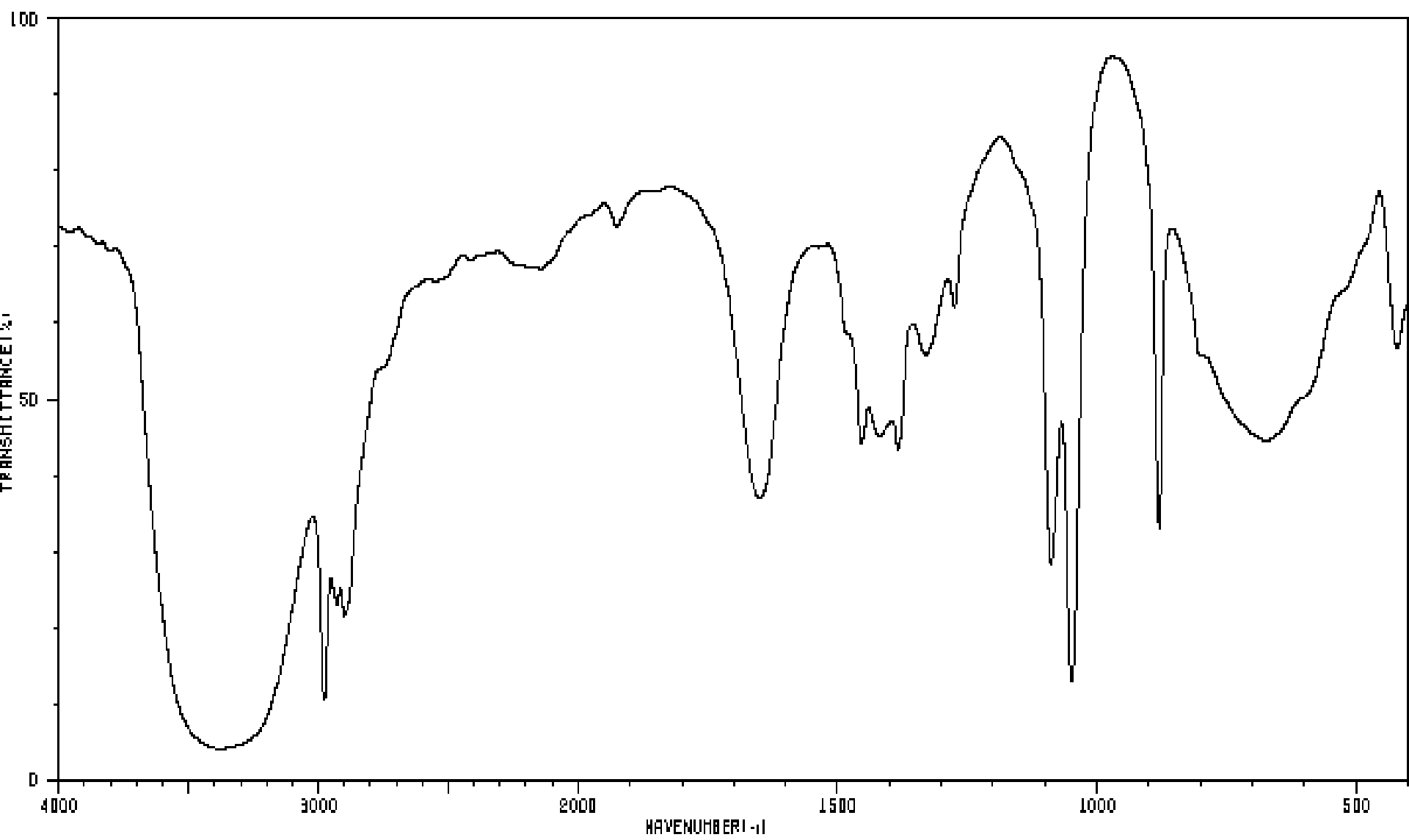
3 - IR - Spectrum

4 - NMR -Spectrum
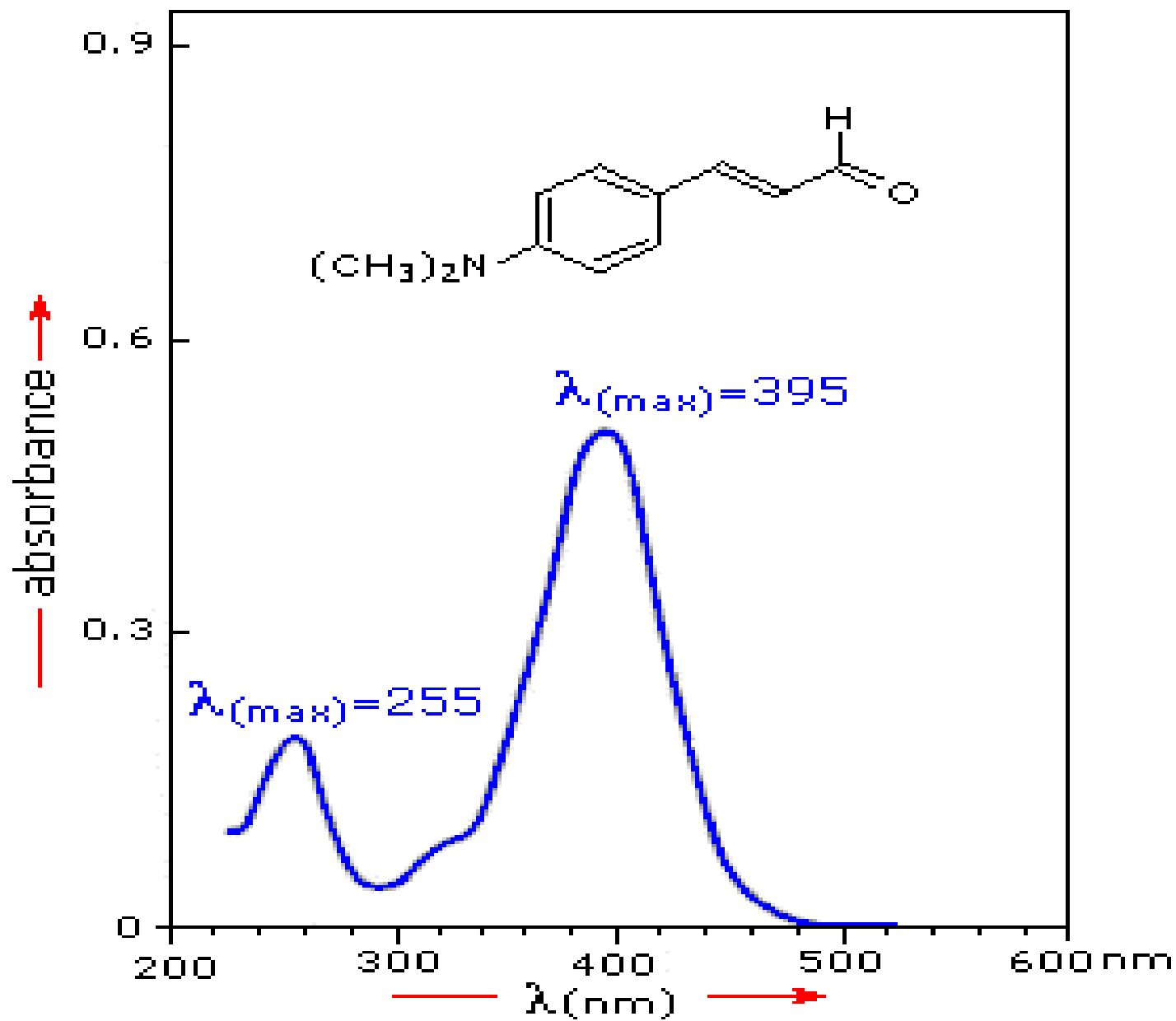
ETHYL ALCOHOL

C_2H_6O

TRANSMITTANCE(%)

WAVENUMBER(-1)

Beer-Lambert Law

Introduction

The Beer-Lambert law (also called the Beer-Lambert-Bouguer law or **simply Beer's law)** is the linear relationship between absorbance and concentration of an absorber of electromagnetic radiation. The general Beer-Lambert law is usually written as:

$$A = a_\lambda \times b \times c$$

where "A" is the measured absorbance, "a" is a wavelength-dependent absorptivity coefficient, "b" is the path length, and "c" is the analyte concentration.

- When working in concentration units of molarity, the Beer-Lambert law is written as:

$$A = \varepsilon_\lambda \times b \times c$$

where ε_λ is the wavelength-dependent molar absorptivity coefficient with units of $M^{-1}\,cm^{-1}$. The subscript is often dropped with the understanding that a value for is for a specific wavelength.

- If multiple species that absorb light at a given wavelength are present in a sample, the total absorbance at that wavelength is the sum due to all absorbers:

$$A = \left(\varepsilon_1 \times b \times c_1\right) + \left(\varepsilon_2 \times b \times c_2\right) + \dots$$

- where the subscripts refer to the molar absorptivity and concentration of the different absorbing species that are present.

FUNDAMENTAL LAWS ON ABSORPTION SPECTROSCOPY

- When monochromatic radiation passes through a cuvette containing absorbing substance , the effect occurring include :

- total light entering   Io

  part is absorbed   Ia   , part is transmitted   It

  part is reflected   Ir   , part is refracted   If

  part is scattered   Is

   where Io = Ia + It + Ir + If + Is

- For a clear solution Is = 0 , Ir and If may be compensated for by means of a control cuvette containing the solvent ,

          So   Io = Ia + It

a - Bouguert - Lambert,s Law

When abeam of a monochromatic radiation enters an absorbing medium , its intensity decreases exponentially with the increase of the thickness of the medium traversed(fig.)

$$\log \frac{I_o}{I} = k\,b \quad (\text{ at constant concentration })$$

(k is a proportionality constant)

b - Beer,s Law

The intensity of a monochromatic radiation decreases exponentially as the concentration of the absorbing medium increases . (fig .   )

$$\log \frac{I_o}{I} = k c \quad (\text{at constant b})$$

(k is a proportionality constant)

c - Beer - Lambert,s Law

$$\log \frac{Io}{I} = abc \qquad (\text{ fig. })$$

$$A = a\,b\,c$$

where A : absorbnce   ,

a : absorpitivity,

b : thickness   cm

c : concentration g/L

- The value of "a" will depend upon the method of expression of the concentration ：

If C is expressed in mole/liter , then "a" is given the symbol Ɛ ($1mol^{-1}cm^{-1}$)and is called _molar absorbitivity_

$$A = Ɛ\, b\, c$$

When c is in gm/100ml , b = 1 cm we get

$$A = A^{1\%}_{1cm}\, b\, c$$

$A^{1\%}$ can be converted easily to Ɛ by the equation

$$A^{1\%}_{1cm} = \frac{Ɛ \times 10}{mol.wt.}$$

THE RELATIONSHIP BETWEEN TRANSMITTANCE , ABSORBTION AND CONCENTRATION

- $T = \dfrac{I}{Io}$

- $\%T = T \times 100$
- or $T = \dfrac{\%T}{100}$

- $A = \log \dfrac{Io}{I}$

- $A = -\log T$

  $A = \log \dfrac{1}{T}$

- $A = a \cdot b \cdot c$

- $T = 10^{-abc}$

- **as** $A = \log \dfrac{1}{T}$ **,** $T = \dfrac{\%T}{100}$

- **then** $A = \log \dfrac{100}{\%T}$

$$A = \log 100 - \log \%T$$

$$= 2 - \log \%T$$

and $\%T = \text{antilog} \ (2 - A)$

- **Example : A sample in a 1-cm cell is determined with a spectrometer to transmit 80% light at a certain wavelength , if the absorpitivity of this substance at this wavelength is 2 , what is the concentration of the substance ?**

- **solution   : the % transmittance is 80%**

$$so\ T\ =\ \%T/\ 100$$

$$=\ 0.8$$

$$as\ A = log\ 1\ /\ T\ \ \ =\ \ a.b.c$$

$$=\ log\ 1\ /\ 0.8\ =\ \ 2\ x\ 1\ x\ c$$

$$log\ 1.2\ \ \ \ \ \ =\ \ 2\ c$$

$$c\ =\ 0.1\ /\ 2\ \ \ \ \ =\ 0.05\ g/L$$

- **Example : A solution containing 1 mg iron (as thiocyanate complex) in 100 ml was observed to transmit 70 % of the incident light .**

a) what is the absorbance of the solution at this wavelength ?

b) what fraction of light would be transmitted by a solution of iron 4 times as concentrated ?

- solution :   a) $T = 0.7$

$$A = \log 1 / 0.7 = \log 1.43 = 0.155$$

$0.155 = a.b.(0.01\ g/L)$

$a.b = 15.5\ L/g$

$A = 15.5\ L/g\ (\ 4 \times 0.01\ g/L\ ) = 0.62$

$A = \log 1 / T = - \log T = 0.62$

$T = 0.24$

- or more directly the absorbance of the new solution :

$$A_1 / A_2 = abc_1 / abc_2 = c_1 / c_2$$

$$A_2 = A_1 \times c_2/c_1$$

$$= 0.155 \times 4/1 = 0.62$$