Unit I

Electro Magnetic Spectrum: Absorption Spectra - UV (Ultraviolet)

What is spectrum?
What is spectroscopy?

VIBGYOR? Visible Spectrum?

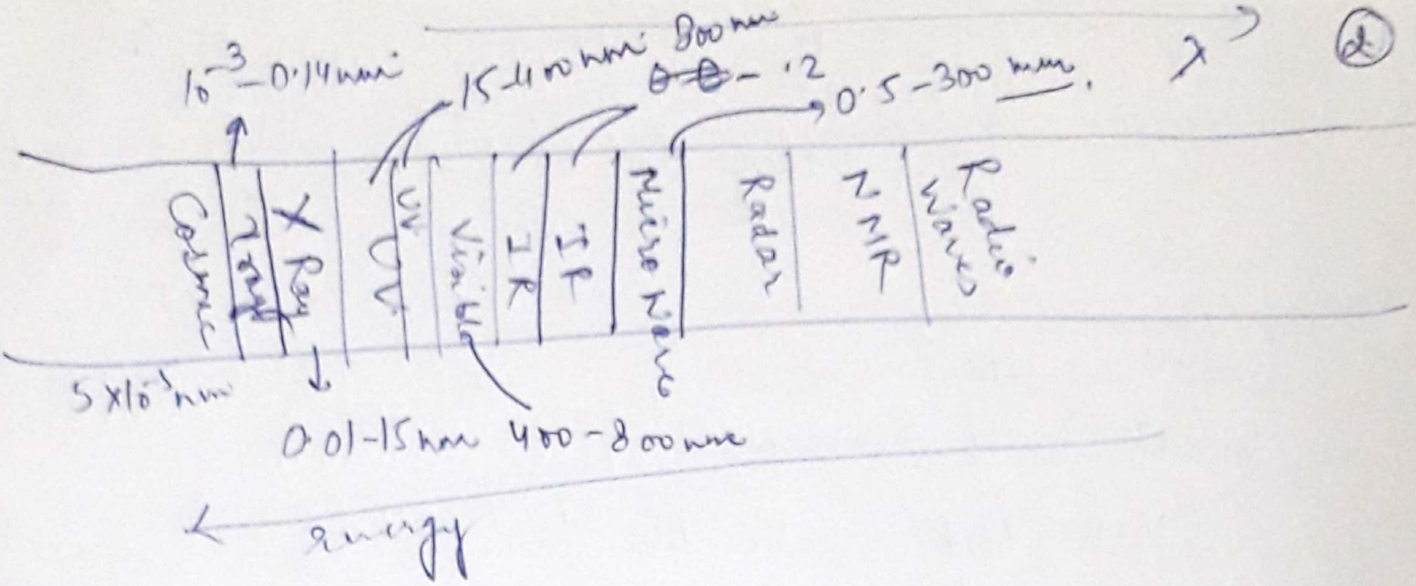
→ The study of interaction between matter and electromagnetic radiations, is called spectroscopy.

→ When a ray of white light (visible light) is allowed to fall on a screen after passing thru a prism, it splits up into seven colours in the form of bands (corresponding to definite λ). This process is called <u>dispersion</u> and the band obtained by this is k/n as <u>spectrum</u>.

→ Range of coloured components is from Red, Orange, Yellow, Green, Blue, Indigo, Violet (VIBGYOR). (Visible Spectrum) $\lambda = 400 - 800$ nm or (4000 A° to 8000 A°)

$$(1\ nm = 10^{-9} m = 10^{-7} cm = 10\ A^{\circ})$$

→ 1800 - 3500 nm (IR Spectrum)
200 - 400 nm (UV Spectrum)] not seen by human eyes.

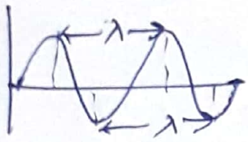


Near Infra red 800 - 2500 nm

Infrared 2500 - 25000 nm

Far infrared 25000 - 250000 nm

a) λ =



$1 A^{\circ} = 10^{-10}$ m

$1 \mu = 10^{-6}$ m

$1 m\mu = 10^{-3} \mu = 10^{-9}$ m

$1 nm = 10 A^{\circ}$

b) Frequency (ν) = inverse to λ

Unit = Hz or cps

$\nu \propto \frac{1}{\lambda}$

(Total no. of waves, which can pass thru a point in one sec)

$E = \frac{hc}{\lambda} = h\nu$

c) Wave number ($\bar{\nu}$) - ($\frac{1}{\lambda}$) (cm^{-1}) Unit

→ Total no. of waves which can pass thru a space of 1 cm.

a) Velocity = Distance travelled by a wave in a unit time is called velocity.

Unit = cm/s or m/s

$$\nu = \frac{c}{\lambda}$$

Types of Spectrum :

→ Absorption Spectrum
→ Emission Spectrum

Absorption Spectrum

when light received from a source is passed thru the absorbing medium under analysis & the transmitted light is viewed with a spectrometer, the spectrum obtained is c/a absorption spectrum.

→ Dark pattern of lines are obtained on a bright screen.

Emission Spectrum

~~An emis~~ It is produced by the emission of radiant energy by an excited atom.

when the radiations emitted from a given light source are seen directly in spectroscopy, then the spectrum obtained is c/a emission spectrum.

→ Continuous
→ Discontinuous

Continuous (In visible spectrum, colours from red to violet appear to be diffused into each other, ∴ change in color appears to be continuous)

e.g. hot iron, hot furnaces etc

Discontinuous

→ Line Spectrum or atomic Spectrum ↓ given by atoms
→ Band Spectrum or Molecular Spectrum ↓ by molecules

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Ultraviolet & Visible Spectroscopy
(100–400 nm) (400–800 nm)

E ⟵

100–190 nm Vacuum UV	190–400 nm Near UV	400–800 nm Visible	IR

⟶ λ

When UV-VIS radiation is passed thru a compound containing multiple bonds, it absorbs some parts of this radiation.
The amount of absorption depends upon λ of radiation & structure of compound.

→ This spectroscopy is also k/n as electronic spectroscopy
→ As It involves promotion of e^- (σ, π, n electrons) from ground state to higher energy state.

→ measures no. of conjugated = bonds & also aromatic conjugation within various molecules.

Absorption Laws :-

1) Lambert's Law
2) Beer's Law

Lambert's Law :- When a beam of monochromatic light passes thru a homogenous absorbing medium, the rate of ↓ of intensity of light with thickness of absorbing medium is ∝ to intensity of incident light.

$$-\frac{dI}{dl} \propto I$$

$$-\frac{dI}{dl} = K \cdot I$$

I = Intensity of light after passing thru a thickness (l) of the medium

$$-\frac{dI}{I} = K \cdot dl$$

dI = infinitesimally small decrease in the intensity of light on passing thru infinitesimally small thickness (dl) of the medium

$-\frac{dI}{dl}$ = Rate of ↓se of intensity of light

K = proportionality constant or absorption coefficient

* It depends upon the nature of absorbing medium

On integration with limits $I = I_0$, when $l = 0$

$$\int_{I_0}^{I} -\frac{dI}{I} = \int_0^l K\,dl$$

or $\ln \frac{I_0}{I} = Kl$

or $2.303 \log_{10}\left(\frac{I_0}{I}\right) = Kl$

or $\log_{10}\left(\frac{I_0}{I}\right) = \frac{Kl}{2.303}$

or $\log_{10}\left(\frac{I_0}{I}\right) = kl$ $\left(k = \frac{K}{2.303}\right)$

$$\log_{10}\left(\frac{I_0}{I}\right) = A$$

$$A = kl$$

(ii) Beer's Law :

Beer explained the effect of concentration of compounds on absorption of light.

When a beam of monochromatic light is passed thru a solⁿ of an absorbing substance, the rate of ↓se of intensity of light with conc. of the sol. is ∝ to the intensity of incident light.

$$-\frac{dI}{dc} \propto I$$

or $$-\frac{dI}{dc} = kI$$

or $$-\frac{dI}{I} = k\,dc$$

$$\int_{I_0}^{I} -\frac{dI}{I} = \int_0^c k\,dc$$

$$\ln\frac{I_0}{I} = k'c$$

$$\log\frac{I_0}{I} = k'c$$

$$A = \log\frac{I_0}{I} = k'c$$

$$\because k' = \frac{k}{2.303}$$

Combining both laws, Beer-Lambert Law can be formulated as -

$$\log_{10}\left(\frac{I_0}{I}\right) = \epsilon c l$$

or $A = \epsilon c l$

A = Absorbance

ϵ = Epsilon (Molar ext. coefficient / Molar absorptivity)

l = Path length

c = Conc. of sol. in mol/l.

If $l = 1$ & $c = 1$ gm mol/l.

then $A = \epsilon$

Molar extinction coefficient is a characteristic property for any compound when temp & λ of light is constant. Its unit is $cm^2/mole$. (7)

Transmittance :-

$$T = 1/A$$

$$\therefore T = \log_{10}(I/I_0)$$

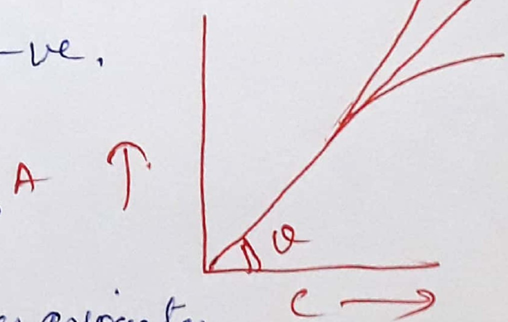
More absorbance, less Transmittance

Limitations of Beer-Lambert's Law :-

(1) In eq $A = \epsilon c l$, If cl is kept const, then (A) should also be constant because for any solute, molar extinction coefficient (ϵ) remains constant.
i.e. A for $c = 1, l = 1$. should be same as that of $c = M/4$ & $l = 4$

but in practice, it is not always possible, because value of ϵ changes $\bar{c}$ change in conc. of solute.

★ (2). For verification of B-L law, a graph b/w absorbance & conc. is plotted & a straight line passing thru origin should be obtained. Deviation may be +ve or -ve.



Reason for deviation

1) when polychromatic radiations or sol. of high conc. is used.
2) when coloured solute ionises, associates or dissociates or hydrolyze in sol^n.
3) when fluorescent compounds are present.