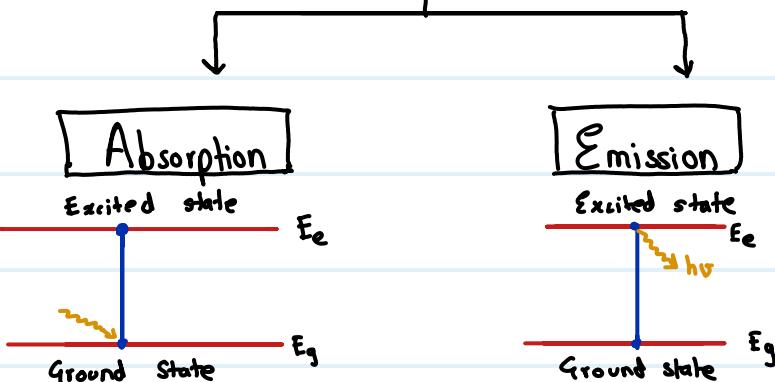


The branch of science dealing with the study of interaction of Electromagnetic radiation with particle is known as spectroscopy.

Electromagnetic Radiation is a form of Radiant energy which has both particle as well as wave nature.

Interaction of Electromagnetic wave and matter



Electromagnetic Spectrum

Cosmic Rays	Gamma Rays	X-Rays	Ultraviolet Rays	Visible	Infrared	Micro waves	Radio Waves
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Advantages of Spectroscopy :-

- 1] Important tool to study atomic & molecular structure in complex organic compounds
 - 2] Less time consuming.
 - 3] Very small amount of sample is required.
 - 4] Cost effective in long run.

Spectra :-

The energy change or frequency of Electromagnetic radiation emitted or absorbed can be recorded (spectra) with the help of instrument, which is known as spectrophotometer.

Types of Spectra:-

- | | |
|---|---------|
| 1] Pure Rotational | E (min) |
| 2] Vibrational Rotational | E (mid) |
| 3] Electronic Band spectra (Transitional) | E (max) |

Spectral Region	Wavelength Involve	Spectroscopy
Micro wave	$1 - 100 \text{ cm}^{-1}$	Microwave Spectroscopy (Rotational Spectroscopy)
Infrared	$500 - 400 \text{ cm}^{-1}$	Infrared Spectroscopy (Vibrational - Rotational Spectroscopy)

Visible &
Ultraviolet

$12500 - 2500 \text{ cm}^{-1}$ (Visible)

$25000 - 70000 \text{ cm}^{-1}$ (UV)

Ultraviolet-visible Spec.

(Electronic Bandspectra)

* Law of Absorptions

- Lambert's Law

It states that when a beam of monochromatic light passes through a homogenous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the incident radiation.

$$I_t = I_0 e^{-kx} \quad \text{--- ①}$$



I_t = Intensity of transmitted light

I_0 = Intensity of incident light

x = thickness or length of the path .

K = absorption coefficient

$$\left\{ -\frac{dI}{I} = K_1 dl \right.$$

$$-\ln I = K_1 l + C$$

$$l=0, I=I_0$$

$$-\ln I_0 = 0 + C$$

$$-\ln I_t = K_1 l - \ln I_0$$

$$\ln \frac{I_0}{I_t} = -K_1 l$$

$$\log \frac{I_0}{I_t} = \frac{K_1}{2.303} l$$

$$2.303 \log \frac{I_0}{I_t} = K_1 l$$

Beer's Law: It states that when a beam of monochromatic light passes through a solution, the decrease of intensity of radiation is directly proportional to the concentration of the solution.

Lambert - Beer's Law

It is combined form of Beer's & Lambert's law.

According to it when a beam of monochromatic light passed through a solution, the decrease in intensity of radiation with thickness of the absorbing material is directly proportional to the intensity of incident radiation as well as Concentration of the solution.

$$I_t = I_0 e^{-Kcx} \quad (\text{acc. to Lambert - Beer's Law})$$

$$\frac{I_t}{I_0} = e^{-Kcx}$$

$$\ln \frac{I_t}{I_0} = -Kcx \quad \text{--- (3)}$$

$$-\log T = \frac{K}{2.303} cx$$

$$-\log T = acx$$

$$\frac{I_t}{I_0} = T \quad (\text{Transmittance})$$

$$\frac{K}{2.303} = a \quad (\text{Absorptivity})$$

$$-\log T = A \quad (\text{Absorbance})$$

$$A = acx$$

$$A = \epsilon c_m x$$

ϵ = molar absorptivity

c_m = molar concentration

$c_m = \frac{\text{Concentration}}{\text{Molar Mass}}$

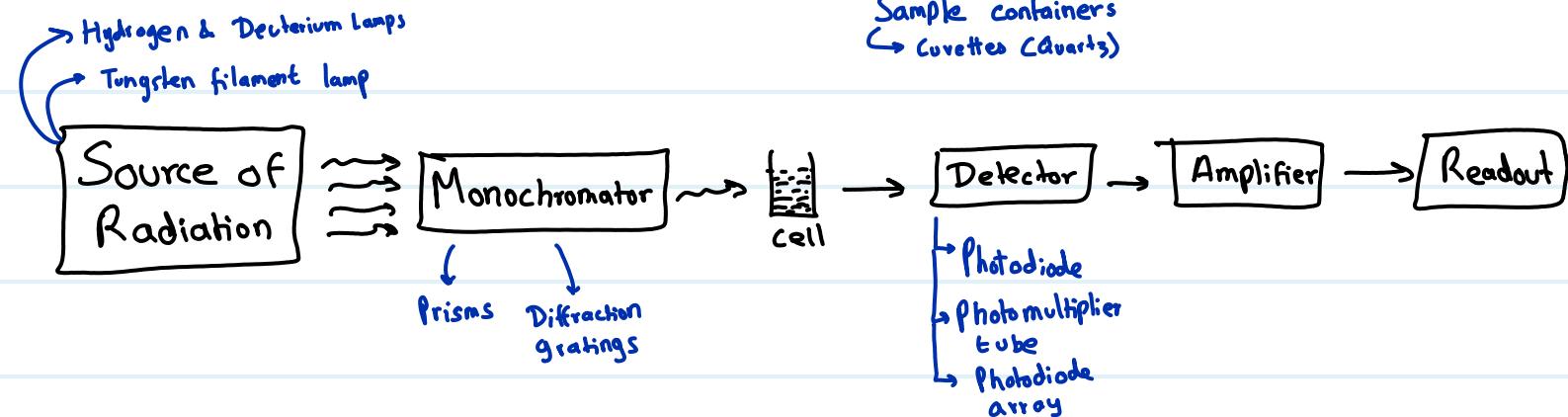
Limitations of Beer-Lambert's Law

- The linearity of Beer-Lambert Law is limited by chemical & instrumental factors
- The law does not hold valid for solutions having conc" greater than $10^{-2} M$.
- Molar extinction coefficient depends on the refractive index of solu" & changes with changes in it.
- Interaction with solvent: hydrogen bonding affects E.
- Scattering of light due to particulates in the sample.
- Fluorescence or Phosphorescence
 - ve deviation in %T & -ve deviation for A
- Shifts in chemical equilibrium as a func of conc".
- Temperature fluctuation and stray light may affect absorbance measurement.

* Single beam spectrophotometer

In single beam spectrophotometer, cell for sample and for blank. are same

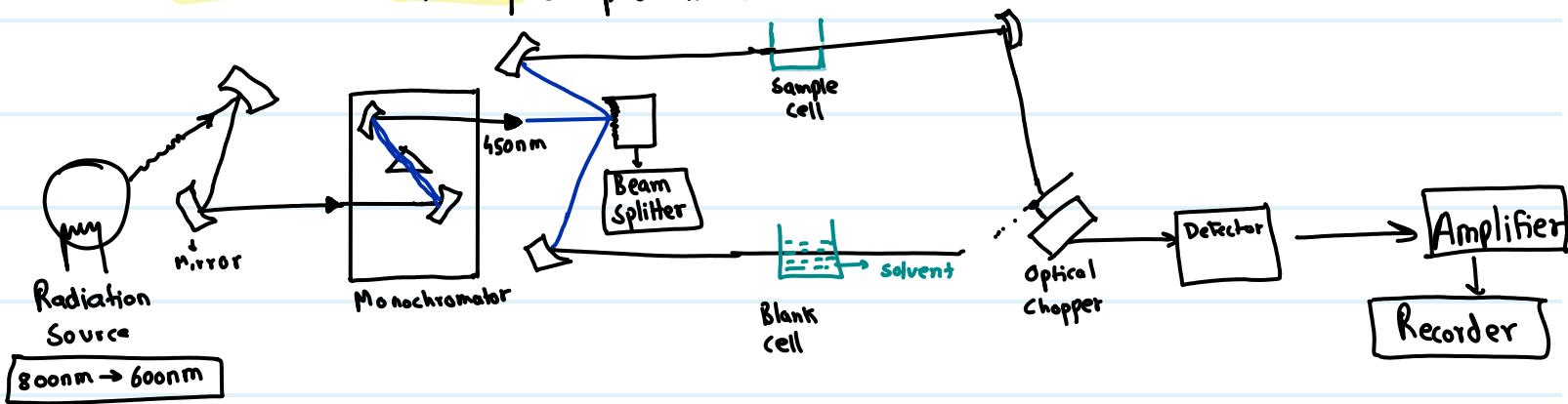
Construction:-



Working :-

- Light beam is focused on monochromator, where after reflection & dispersion nearly monochromatic beam emerges out.
- The emergent monochromatic beam passed through a quartz cuvette containing a sample solution.
- Transmitted radiation from the cuvette is allowed to fall on a photoelectric cell, which converts radiant energy into electrical signal as absorbance.

* Double beam Spectrophotometer



Radiation source \rightarrow H-lamp, D-Lamp, Xe Lamp, Hg Vapour lamp, W filament

Detector: Photovoltaic cell, Phototube, Photo Multiplier tube, Semiconductor detectors

Working:-

- The variation in the intensity of the source light is compensated by splitting the incident beam in 'two light beams' by passing through beam splitter.
- One of the beam passes through the blank solution while other through the sample solution.
- Transmitted radiations from cuvette is allowed to fall on a photo electric cell, which converts

radiant energy into electrical signal as absorbance.

- Simultaneously, absorbance of blank & sample solution can be measured.
- Water is generally used as blank solution.
- Application of UV-Visible Spectroscopy:-

1] Quantitative determination of analyte concentration

2] Identification of inorganic & organic species

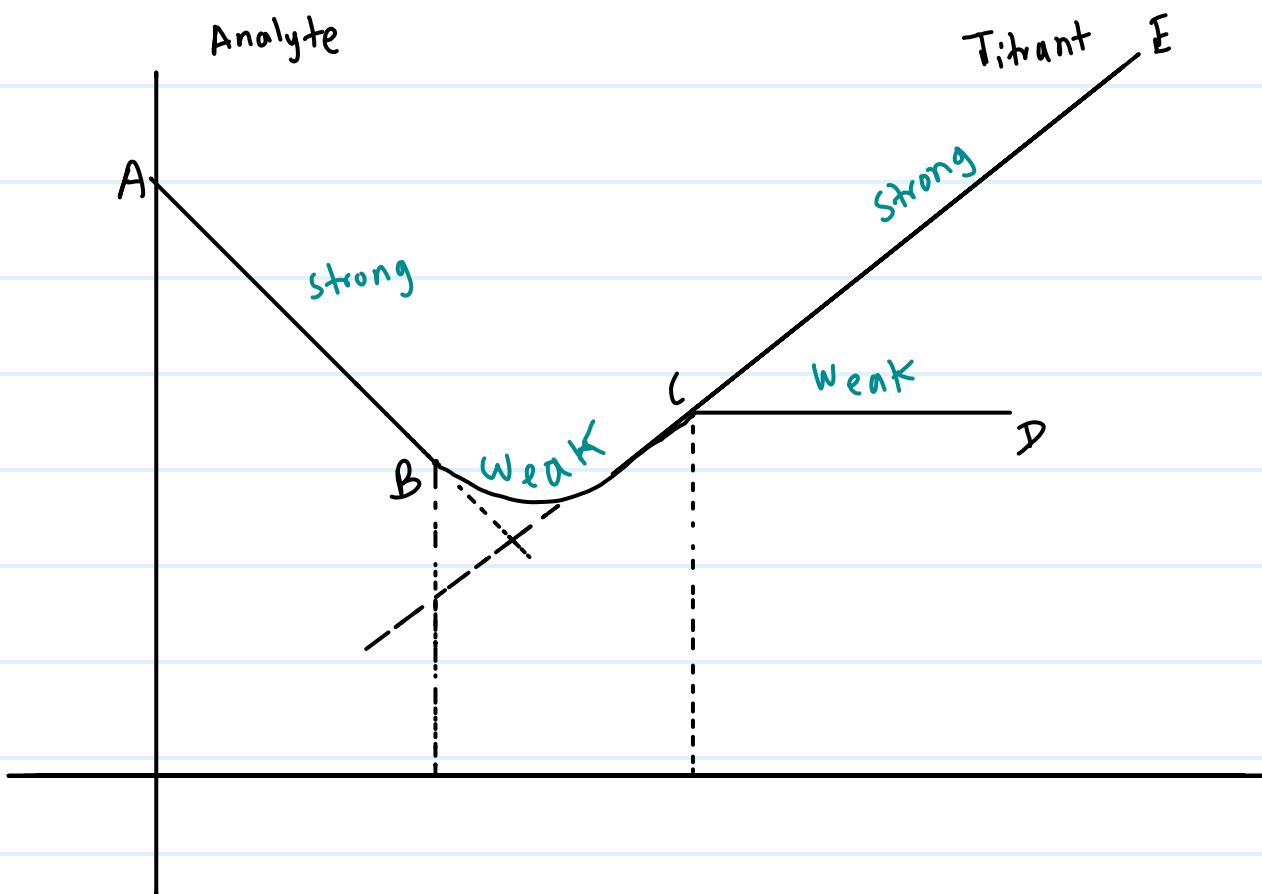
3] Magnitude of molar absorptivity.

4] Used as a detector in HPLC.

5] To study absorbance of organic compounds.

Conductometry

- Conductometry is based on the principle of determination of change in conductivity of different ions in the solution.
- The principle of conductometric titration is changes in the conductance of the solution due to difference in ionic conductance or due to production of more number of ions in the solution.



- Advantages :-

- Coloured soluⁿ can be titrated
- Works for dilute soluⁿ also, as it is based on the changes in the conductance, rather than absolute value of conductance.
- A mixture of weak & strong acids, can also be titrated with relative ease. Thus, making the simultaneous determination possible.

- Limitations:-

- In dilute solutions, obtuse curves are obtained. With obtuse curves it is difficult to locate the equivalence point accurately.
- The overall accuracy of the conductometric titrations is limited as the technique does not permit addition of small increments of the titrant.

Q] A compound having concⁿ 10^{-3} g/L resulted absorbance value 0.20 at $\lambda_{\text{max}} = 510 \text{ nm}$. using 1cm cell. Calculate it's absorptivity and Molar absorptivity values. Molecular weight of compound is 400.

→ concⁿ (c) = 10^{-3} g/L

Absorbance (A) = 0.20

Path length (x) = 1 cm

$$A = \alpha c x$$

$$0.20 = \alpha \times 10^{-3} \times 1$$

$$\alpha = 200 \text{ L/g cm.}$$

$$A = \epsilon c m x$$

$$0.20 = \epsilon \cdot \frac{10^{-3}}{400} \times 1$$

$$\epsilon = 0.8 \times 10^5 \text{ L/mol cm}^{-2}$$

Q] At definite wave length, an absorber when placed in a cell of 1 cm pathlength absorbs 20% of the incident light. If the absorptivity of the absorber at this wave length is 2.0. Find out its Concentration.

→ Path length = 1cm
= 20 %.

absorptivity (a) = 2.0

Considering $I_0 = 100\%$.

$$I_t = 80\%$$

$$A = \log \frac{1}{T} = \log \frac{I_0}{I_t}$$

$$A = \log \frac{100}{80} = 0.969$$

$$A = \alpha c x$$

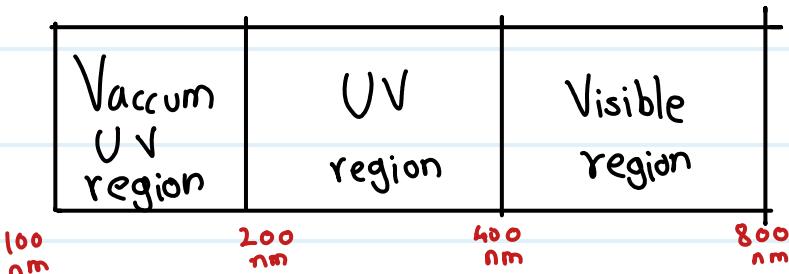
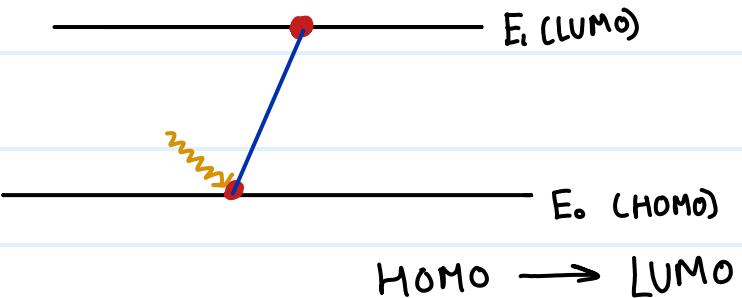
$$0.969 = 2 \times c \times 1$$

$$c = 0.04845 \text{ gm/L}$$

UV - Visible Spectroscopy

UV-visible

Range : 200 - 800 nm



Electronic Transitions :-

Ground State (E_0) \longrightarrow Excited State

HOMO \longrightarrow LUMO

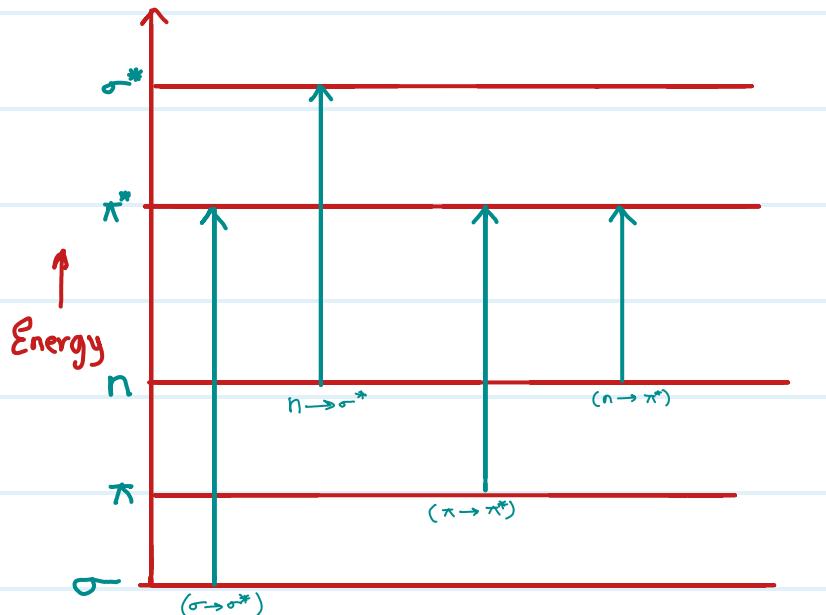
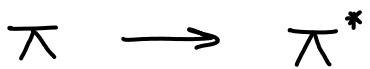
Types of electrons :-

(1) σ electrons - Saturated

(2) π electrons - Unsaturated $=^* =^{\pi}$

3) n electrons - O, N, Cl, F

Types of Transitions :-



1] $\sigma \rightarrow \sigma^*$ transition - C_nH_{2n}, C_nH_{2n+2}

Alkenes, Alkyl

2] $n \rightarrow \sigma^*$ transition - Unsaturated, Non-Bonding $e^- (N, O, S, Cl, F)$

$C_2H_5NO_2, C_2H_5Cl, C_2H_5OH$

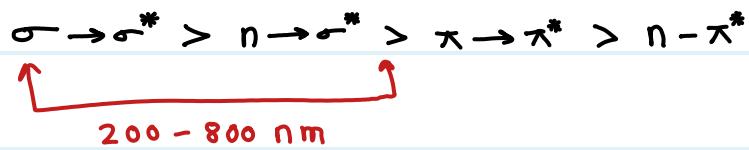
3] $\pi \rightarrow \pi^*$ transition - Unsaturated C_nH_{2n}, C_nH_{2n-2}

C_2H_4, C_2H_2

4] $n \rightarrow \pi^*$ transition - Unsaturated, Non-bonding

$CH_3-\overset{O}{\underset{||}{C}}-H, CH_3-\overset{O}{\underset{||}{C}}-CH_3$

Energy order:-



Selection Rules of UV-Spectroscopy

(1) $\Delta S = 0$

(2) $n \rightarrow \sigma^*$ - forbidden

UV Active / UV Inactive Compounds:-



Saturated - UV Inactive

Unsaturated - UV Active

Chromophores & Auxochromes

Chromophores are unsaturated group (covalently bonded), responsible for electronic absorption. (colour bearing)

Eg: $>C=C<$, $>C=O$

Auxochromes is a saturated group, which are not chromophore themselves but their presence can cause the increase in colour intensity of compounds.

Absorption shift \rightarrow Longer Wavelength

Eg:- Amino grp, OR, NR₂, NHR, -SH etc.

PH Metry

