

Interaction of Radiation with Matter

Electromagnetic Radiation

- Electromagnetic radiation is generated by oscillation or acceleration of an electric charge.
- Electromagnetic radiation propagates in space, without any material medium in the form of transverse waves.
- Electromagnetic radiation consists of discrete packets of energy which are called 'photons'.
- A photon consists of an oscillating electric field (E) & an oscillating magnetic field (M). The electric & magnetic fields are perpendicular to each other & they are also perpendicular to the direction of propagation of photon.

Electric field E

Magnetic field M

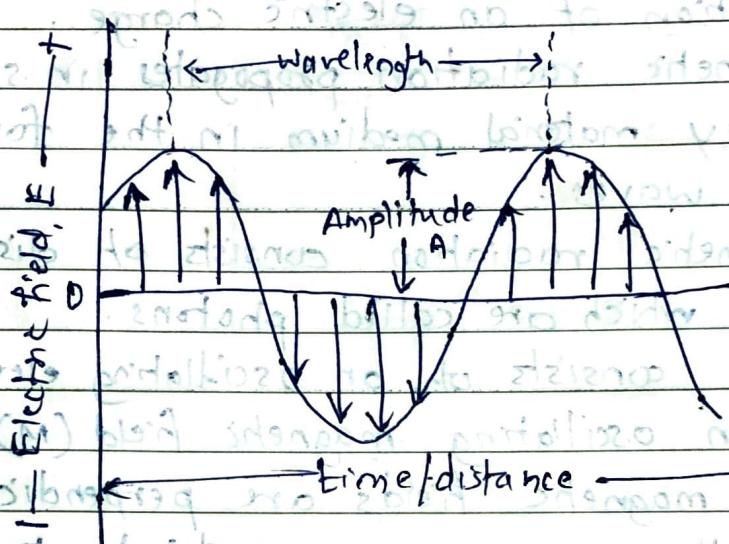
$V_L - V$

Direction of propagation

An electromagnetic wave is characterized by frequency, wavelength & phase.

i) Frequency (ν): It is defined as the no. of times electrical field vector / radiation oscillates in one second.

Unit is Hertz.



Electromagnetic Radiation

e) Wavelength (λ): It is the difference between two nearest parts of the wave in the same phase i.e. distance between two nearest troughs or two nearest crests.

All photons travel at same velocity 'V'.

Relationship between light velocity, wavelength & frequency is

$$V = \lambda \nu$$

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

$\therefore h$ = Planck's constant

$$\nu \text{ (Wavenumber)} = \frac{1}{\lambda}$$

$$\nu = \frac{v}{c_n}, c_n = \text{speed of light}$$

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Electromagnetic Spectrum

Photons present in electromagnetic radiation have different energies & belong to different spectral regions. Thus photons in all these regions have same electromagnetic nature but as their energies are different, they interact differently with matter.

Following are different spectral regions with their frequencies, wavelengths & the type of transition that can occur when photon in these spectral regions interact with matter is shown below:



Region	Gamma rays	X-ray	X-ray	UV	UV	Visible	IR	IR	Far IR
	10^{17} Hz	10^{16} Hz	10^{15} Hz	10^{14} Hz	10^{13} Hz	10^{12} Hz	10^{11} Hz	10^{10} Hz	10^9 Hz
	10^{-10} m	10^{-11} m	10^{-12} m	10^{-13} m	10^{-14} m	10^{-15} m	10^{-16} m	10^{-17} m	10^{-18} m

AK

Lambert - Beer Laws of Absorption

Lambert's Law:

The rate of decrease in intensity of radiation is directly proportional to path length of solution intensity when the monochromatic light passes through a solution of constant concentration.

Mathematically, the law can be written as

$$\frac{dI}{I_0} = -kx \quad \text{or} \quad \frac{-dI}{I_0} \propto kx$$

with thickness

where, I_0 = Intensity (radiant power) of the incident radiation.

dx = Small thickness of solution or path length

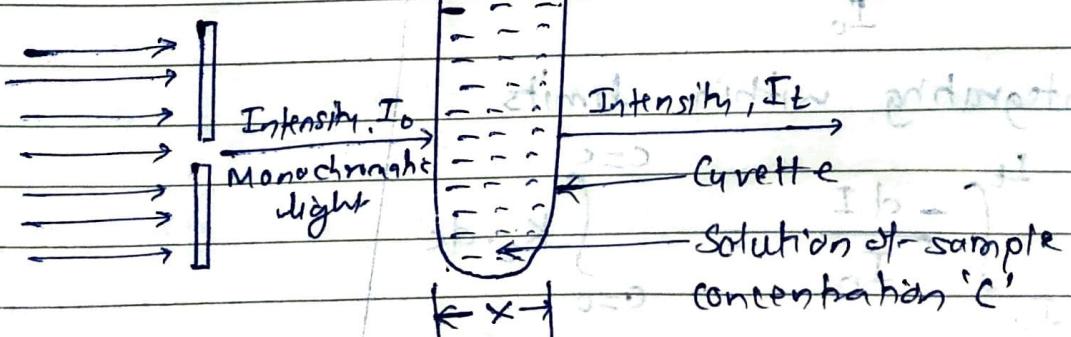
$$dI = \text{Small decrease in intensity of light}$$

$$= I_0 - I_t$$

(Intensity / Radiant Power is the no. of photons per unit area per second)

AK

$$-\frac{dI}{I_0} = k_1 dx$$



Integrating within limits

$$\int_{I_0}^{I_t} \frac{-dI}{I_0} = \int_{x=0}^{x=x} K_1 dx$$

I_0 refers to intensity of source to start with

then we have to start with the law of absorption which

$-(\ln I_t - \ln I_0) = K_1 \cdot x$ now we can get value

of x by dividing both sides by K_1

$\ln \frac{I_0}{I_t} = K_1 \cdot x$ or $I_t = I_0 e^{-K_1 x}$

No reflection and no refraction

Lambert's law can be stated as the intensity of transmitted light (I_t) decreases exponentially as the thickness of absorbing medium increases, for a fixed concentration.

Beer's Law

The rate of decrease in intensity of light is proportional to concentration of solution for a fixed thickness of solution.

Mathematically, the law can be written as

$$-\frac{dI}{I_0} \propto dc$$

Integrating within limits

$$\int_{I_0}^{I_t} \frac{-dI}{I_0} = \int_{c=0}^{c=c} K_2 \cdot dc$$

$$\therefore -(\ln I_t - \ln I_0) = K_2 \cdot c$$

$$\ln \frac{I_0}{I_t} = K_2 \cdot c \quad \text{If } e^{\frac{I_0}{I_t}} \text{ is not written}$$

I_t is bounded by I_0 transmission and c

$$\therefore I_t = I_0 e^{-K_2 \cdot c}$$

Beer's law can be stated as, the intensity of transmitted light decreases exponentially with increase of concentration, for a fixed path length of solution.

Highly dilute solution \rightarrow absorbance \approx zero

Combined Lambert - Beer's Law

Product of absorption factor and path length

Combined Lambert - Beer's law (will be $I = ?$)

$$-\frac{dI}{I_0} \propto dx \quad (\text{Lambert's law for constant conc.})$$

$$-\frac{dI}{I_0} \propto dc \quad (\text{Beer's law for constant thickness})$$

$$-\frac{dI}{I} \propto dx \cdot dc \quad \text{or} \quad -\frac{dI}{I_0} = k' \cdot dx \cdot dc$$

Integrating within limits to get maximum

$$\ln \frac{I_0}{I_t} = k' \cdot x \cdot c$$

$$\text{or } \log \frac{I_0}{I_t} = 2.303 k' \cdot x \cdot c = K \cdot x \cdot c$$

K = absorptivity constant.

The term $\log \frac{I_0}{I_L}$ is defined as absorbance (A)

& the transmittance (T) is defined as $\frac{I_L}{I_0}$

$$A = k \cdot x \cdot c \quad \text{--- Lambert Beer's Law}$$

x is in cm & c is in g/l lit. of soln.

Lambert - Beer's Law can be stated as 'absorption

of a light by solution is directly proportional
to the concentration of solution & the path length.

By taking unit concentration of sample in solution
($c = 1 \text{ mol/l lit}$) & unit length of path ($x = 1 \text{ cm}$)

the absorbance observed will be the value of
the constant in Lambert - Beer's equation.

$$\text{constant } A = E \cdot x \cdot c \quad \text{--- I.B. ---}$$

constant $E = \text{molar absorptivity / molar extinction coefficient}$

$$E \cdot x \cdot c = \frac{I_0}{I_L} \quad \text{--- I.B. ---}$$

There is certain wavelength which is absorbed maximum & it is known as λ_{max} . This wavelength is selected to analyse the sample by spectrophotometer.

$$E \cdot x \cdot c = 2 \times 10^3 \text{ l/mol cm} = \frac{2}{10^{-4}} \text{ mol cm/l}$$

friction (indigo) = 2

UV-Visible Spectroscopy

Principles

1) Lambert-Beer Law

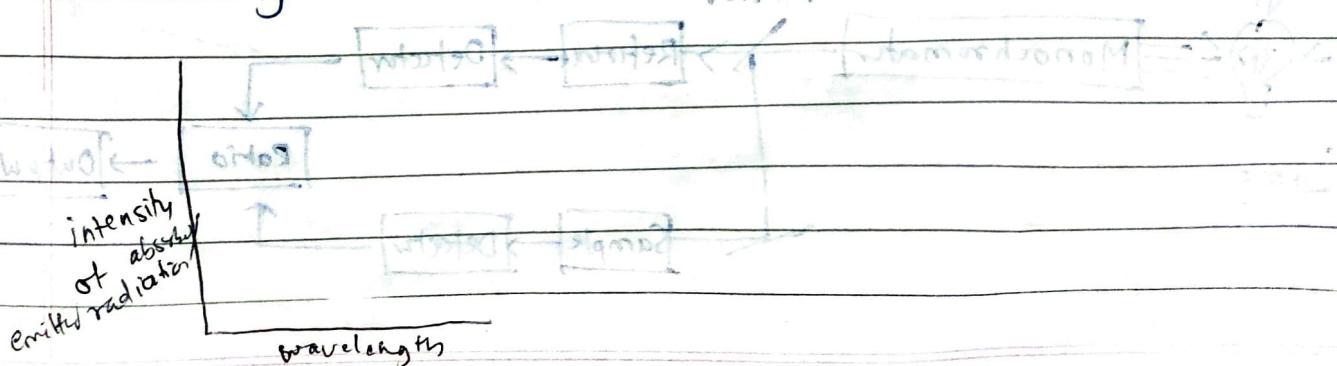
Absorbance of monochromatic light from UV-visible region is proportional to conc. of solution for constant path-length.

2) Transitions -

The absorption of light from UV-visible region causes excitation of bonding electrons in a covalent bond to higher energy antibonding orbitals e.g. $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ non-bonding $\rightarrow \pi^*$

Electrons in stronger covalent bond require all higher energy for excitation which is available from a shorter wavelength UV light. & electrons in a weaker covalent bond require lower energy for excitation which is available in visible light wavelengths.

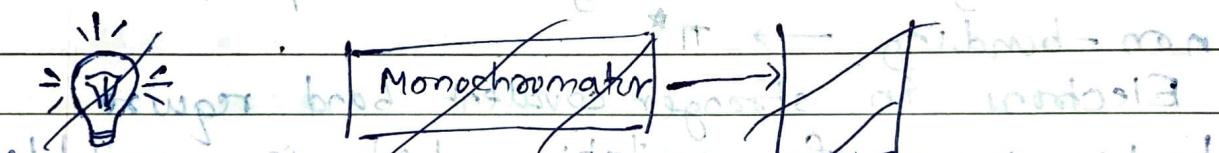
- Spectroscopy measures spectrum of sample containing atoms / molecules
- Spectrum is a graph of intensity of absorbed or emitted radiation by sample versus frequency or wavelength



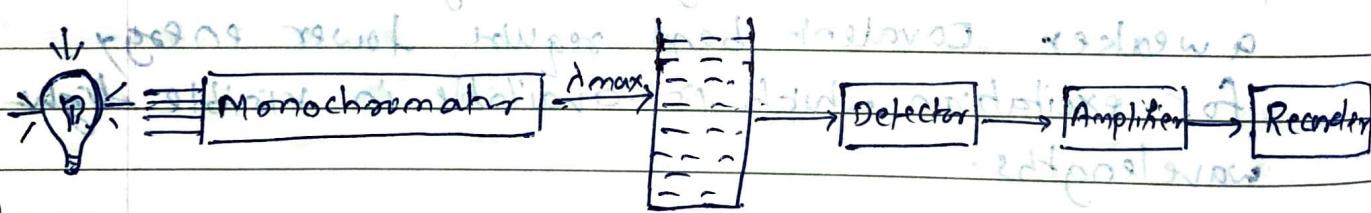
Instrumentation in UV-visible Spectrophotometry

1) Source of radiation : The source should provide radiation of 300 - 1000 nm wavelength range. Tungsten filament lamp is used.

2) Monochromator : A monochromator consists of entrance slit, collimator, a grating prism, exit slit. A good monochromator provides very narrow wavelength band. Glass prisms are used for visible region & quartz prisms are used for UV-region.

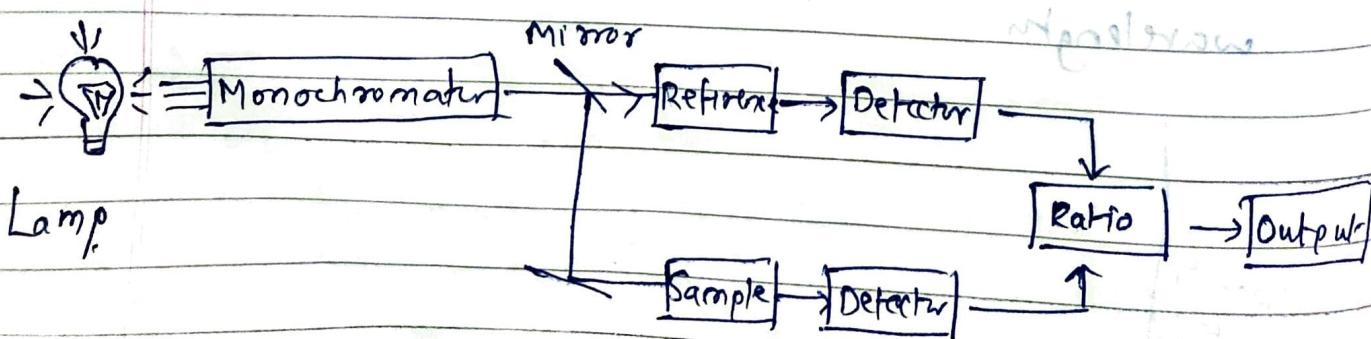


Single Beam Spectrophotometer



Lamp

Double Beam, UV/VIS Spectrophotometer



Gratings are of two types

- (1) Transmission grating
- (2) Reflection grating

Transmission grating consists of series of closely spaced parallel grooves on a transparent material.

Reflection gratings are used commonly & it consists of closely spaced ridges on metallic film.

3) Slits: The slits are used for selecting desired wavelength from dispersed light by monochromator.

4) Sample cell: It holds sample either in form of solution or as such. Glass cuvettes are used in UV spectrosopy. For Visible, glass cuvettes can be used to measure absorbance.

5) Detector: Transmitted light from sample cell falls on the detector where it is converted into electric current. It converts light energy directly into electrical energy. The output current of photo detector is directly proportional to the intensity of light falling on it.

For UV spectrosopy, Photoelectric cell, photovoltaic cell, photo multiplier tube can be used as photo detector.

6) Recorder: It is a display device, which automatically draws spectrum. The signal from monochromator is recorded on X-axis while absorbance of the sample is displayed on Y-axis.

Applications of UV-visible Spectroscopy

- 1) Qualitative Analysis - UV-visible spectroscopy is used for characterizing aromatic compounds & conjugated olefins.
- 2) Detection of impurities - in organic compounds.
- 3) Quantitative Analysis : It can be used to find out molar concentration of the solute under study.

- Ax
- 4) Detection of isomers : e.g. cis or trans isomer.
 - 5) Determination of molecular weight using Beer's law.
 - 6) Determination of structure of several vitamins.

2) To study kinetics of chemical reaction.

For the determination of reaction rate, we can use the method of initial rates. In this method, we take a series of small portions of reactants and add them to a solution containing a suitable catalyst. The reaction starts and the rate of reaction is determined by measuring the change in concentration of one of the reactants over a short period of time. This method is called the initial rate method.

The reaction rate is given by the following equation:

$$Rate = \frac{1}{2} \frac{\Delta [A]}{\Delta t}$$

where $[A]$ is the concentration of reactant A at time t , and Δt is the time interval over which the change in concentration was measured.

Theory of Electronic Transitions

σ -electrons: These electrons are involved in bonds formed by saturated bonds. They are involved in forming ionic compounds and are non-bonding.

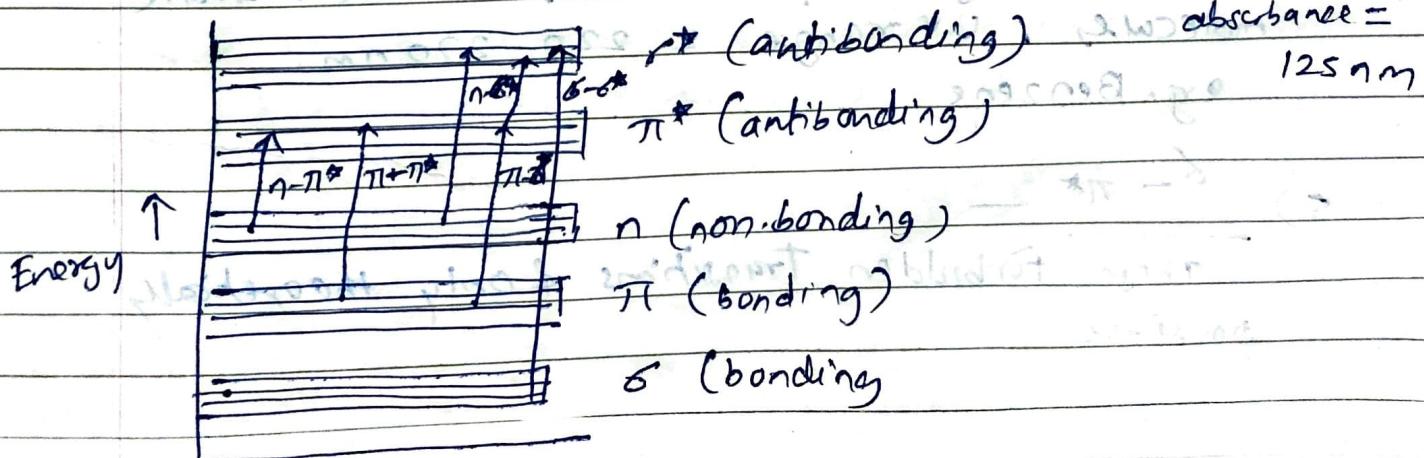
π -electrons: These electrons are involved in unsaturated compounds & aromatics. The energy required to excite them to higher anti-bonding orbital can be acquired from 180 nm - 300 nm.

n-electrons:

These are electrons in outermost energy level (valence shell) of atom, which have not participated in bonding. These are also present in p-orbitals e.g. Nitrogen, O₂, Sulphur etc.

Transitions of Electronic Configuration

1) $\sigma \rightarrow \sigma^*$ - These transitions can occur in saturated compounds. As the energy required for the transition is very large, the absorption band occurs in the UV region (100 - 135 nm) e.g. Methane



2) $\pi - \pi^*$ Transition

These transitions occur in unsaturated compounds, which also contain atoms like oxygen, nitrogen, halogen etc. (Absorption is weak & band is R band)

An e^- from non-bonding orbital is promoted to antibonding π^* orbital.

e.g. $C=O$, $C=S$, $C\equiv N$

$\pi - \pi^*$ require minimum energy & show absorption at 300 nm .

3) $n - \sigma^*$ Transition

Saturated compounds containing atoms with lone pairs (non-bonding e^- s) like O, N, S & halogens are capable of $n - \sigma^*$ transition.

Absorption at $150-250\text{ nm}$

4) $\pi - \pi^*$ transition

- Compounds containing isolated double bond where absorption is high & range is $160-175\text{ nm}$

E-band
Comp. with conjugated double bond where absorption is large & range = $210-280\text{ nm}$.
Band is K-band e.g. Butadiene

- B-bands - given by aromatic & heteroatomic molecules. UV range = $220-270\text{ nm}$.

e.g. Benzene

5) $\delta - \pi^*$

These forbidden transitions & only theoretically possible.

Terms used in UV spectroscopy

1) Chromophore: An unsaturated group responsible for electronic absorption in UV-visible range.

is called chromophore. e.g. $C=C$, $C=O$, $N=N$.

e.g. $CH_3\overset{\text{C}}{||}CH_3$, $\lambda_{max} = 279\text{nm}$, $O\overset{=}{||}O$, $\lambda_{max} = 291\text{nm}$

2) Auxochrome - A saturated group with lone pair of electrons which when attached to chromophore changes both wavelength & intensity of absorption.

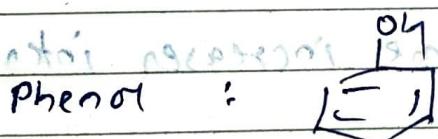
e.g. $-NH_2$, $-OH$, $-Cl$ etc.

e.g.



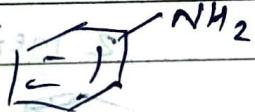
$\lambda_{max} = 255\text{nm}$

Benzene



$\lambda_{max} = 270\text{nm}$

Aniline



$\lambda_{max} = 280\text{nm}$

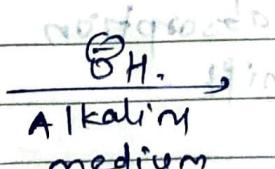
3) Bathochromic shift

The shift of absorption to a longer wavelength due to substitution or solvent effect, is known as bathochromic shift. (Red shift)

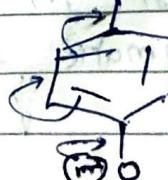
Non bonding e⁻ involved in resonance & not available for transition hence $T_1 \rightarrow T_1^*$ takes place



p-nitrophenol
 $\lambda_{max} = 255\text{nm}$



Alkaline medium



$\lambda_{max} = 285\text{nm}$
High wavelength means low energy $n \rightarrow T_1^*$

4) Hypsochromic Shift (Blue shift)

The shift of absorption to shorter wavelength,

due to substitution / solvent effect. (is Kard)

Non bonding e⁻s available for $n \rightarrow \pi^*$ transition change

Non bonding electrons not available for $\pi \rightarrow \pi^*$ transition

π - p³ + lone pairs of N

Lone pairs of N not available

π - p³ + lone pairs of N

hence $\pi \rightarrow \pi^*$ takes place

for $\pi \rightarrow \pi^*$ transition to $\pi^* \rightarrow \pi^*$ degeneracy plan

$$\lambda_{\text{max}} = 280 \text{ nm} \quad \text{for } \lambda_{\text{max}} = 265 \text{ nm}$$

5) Hyperchromic Shifts

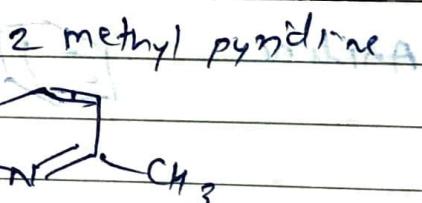
An increase in absorption intensity is known as Hyperchromic shift.

Introduction of autochrome increases intensity of absorption.



$$\lambda_{\text{max}} = 257$$

$$\epsilon = 1750.$$

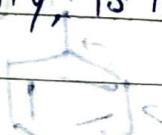
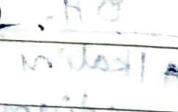


$$\lambda_{\text{max}} = 260 \text{ nm}$$

$$\epsilon = 3560$$

6) Hypochromic Shift

A decrease in absorption intensity is known as Hypochromic shift.





atk

$$\epsilon = 19000$$



2-methyl
naphthalene



$$\epsilon = 10250$$

These shifts & effects on the compound can be summarized as shown below.