

A

SPECTROSCOPY

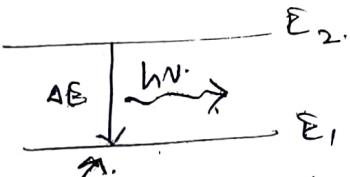
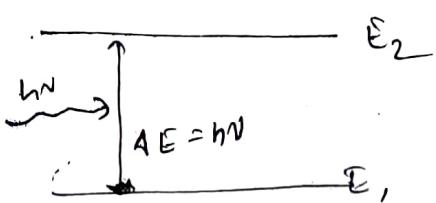
Module - 2 (Chemistry)

Spectroscopy deals with the transitions that a molecule undergoes between its energy levels upon absorption of suitable radiations determined by quantum mechanics selection rules.

Q1

Spectroscopy is the analysis of the electromagnetic radiation scattered or absorbed or emitted by molecules. Spectra are of two types.

Absorption spectrum - results when an atom or molecule undergoes a transition from the lower energy level to the higher one with the absorption of a photon of energy $h\nu$, provided $h\nu$ is exactly equal to the energy difference ($\Delta E = E_2 - E_1$) between the levels.



Emission spectrum - results when the atom or molecule falls from the excited state to the ground state with the emission of a photon of energy $h\nu$.

Spectra can be divided as -

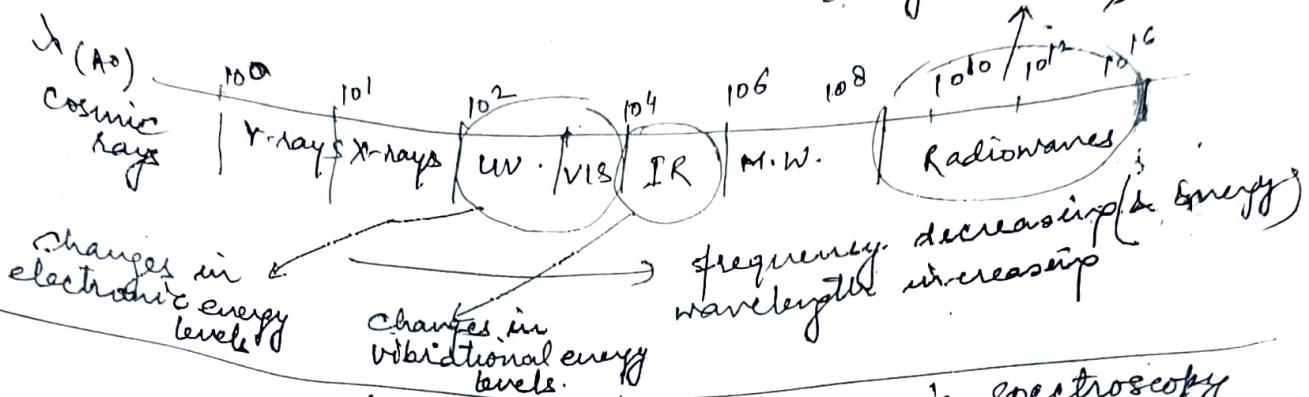
(i) ATOMIC SPECTRA → which arises from the transitions of an electron between the atomic energy levels.

(ii) MOLECULAR SPECTRA → which arises from the transitions of an electron between the molecular energy levels. Molecular spectra gives more information about the st. as it not only includes electronic energy (atomic spectra) but also vibrational energy, rotational energy and translational energy.
Total energy of molecule = $E_{\text{Electron}} + E_{\text{vib.}} + E_{\text{rot.}} + E_{\text{trans.}}$
very small.

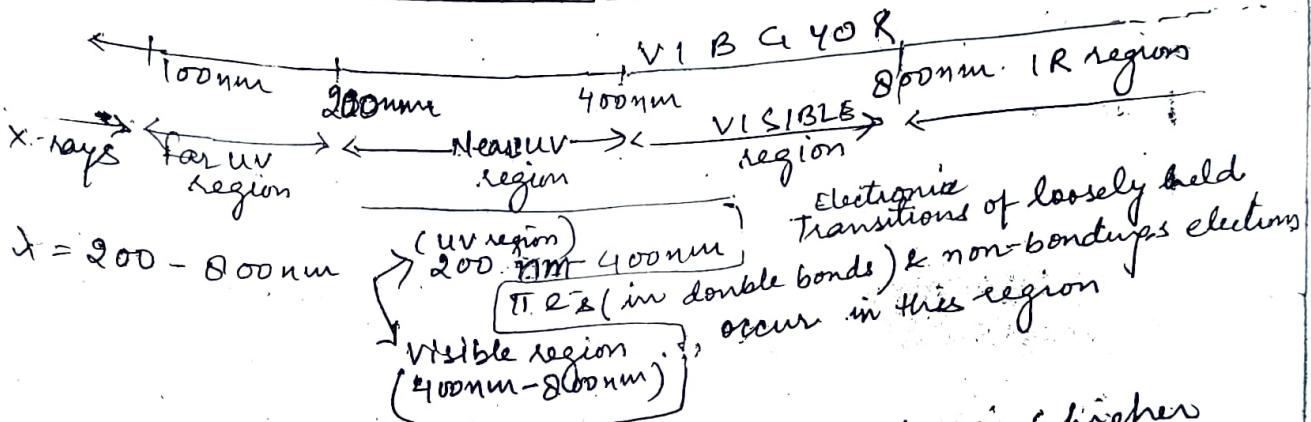
①

The study of interaction between electromagnetic radiation with matter is known as spectroscopy. It is the most powerful technique to study the atomic and molecular structure of the compound.

Spectroscopy uses two types of spectrum depending upon the E.M.R. absorbed or emitted by an atom or molecule changes in nuclear spin state



Ultraviolet-Visible / Electronic Spectroscopy



$\lambda < 200 \text{ nm}$ → vacuum region or far UV-region (higher energy region). & electrons of single bonds excite in this region. In this region the transitions can not be detected through simple spectrophotometer. (O_2 & N_2 interfere)

Principle:- When E.M.R. in UV & VIS. regions is passed through a compound having multiple bonds, some amount of radiations is absorbed. The amount

①

of absorption depends upon the wavelength and structure of the compound. In the molecule, the electrons from lower energy orbitals are excited to higher energy orbitals.

- A UV-visible (& IR) spectrophotometer allows light of a given frequency to pass through a sample and detects the amount of transmitted light and compares the intensity of transmitted light with that of incident light. By the gradual change in frequency, a graph (spectrum) is obtained having absorption or transmittance versus frequency or wavelength. A big absorbance means, a big signal or peak in the spectrum.

The UV spectrum records the wavelength of an absorption maximum i.e. λ_{max} and strength of this absorption

i.e. E_{max} as is defined by the combined Beer-Lambert's law:

It states that when a beam of monochromatic radiation is passed through a homogeneous solution the absorbance is proportional to the product of the concentration and path length.

$$\text{i.e. Absorbance; } A \propto \text{concentration (C)} \times \text{path length (l)}$$

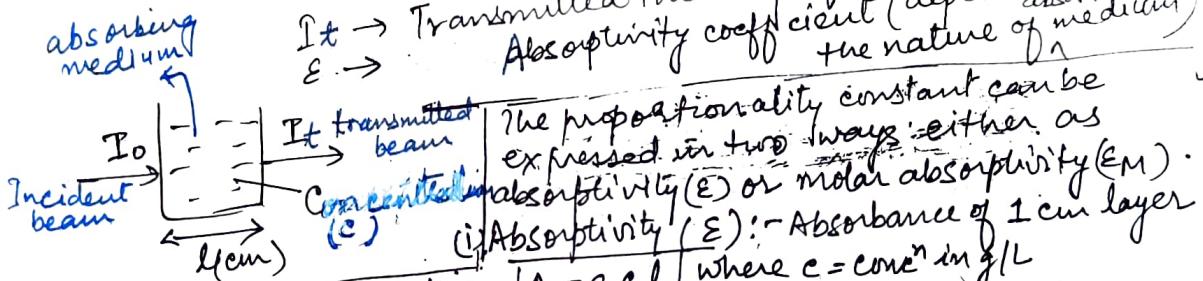
$$\text{or } A = \epsilon \cdot C \cdot l = \log \frac{I_0}{I_t}$$

where $C \rightarrow \text{conc}^n \text{ in g/l}$

$I_0 \rightarrow \text{Incident intensity}$

$I_t \rightarrow \text{Transmitted intensity of radiation}$

$\epsilon \rightarrow \text{Absorptivity coefficient (depends upon absorbing medium + the nature of medium)}$

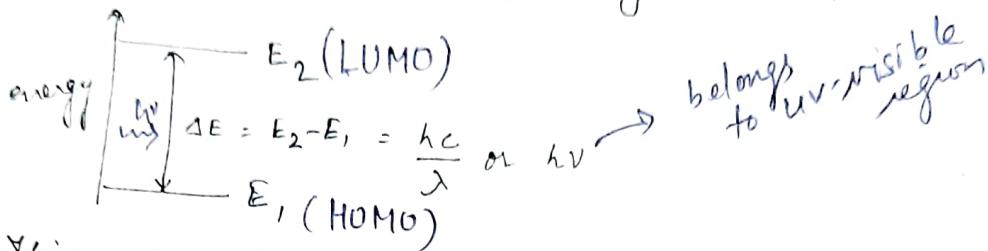


(ii) molar Absorptivity (ϵ_M): - for a specific wavelength is the absorbance of a 1 cm layer of a 1 mol/L solution $A = \epsilon_M \times C_m \times l$, where $C_m \rightarrow \text{conc}^n \text{ in mol/l}$.

Transmittance (T) \rightarrow Ratio of intensities of Transmitted light to that of Incident Intensity. $T = \frac{I_t}{I_0}$. Also, $\% T = \frac{T \times 100}{I_0}$ Thus $\frac{I_t}{I_0} \times 100$ $A = \log \frac{1}{T}$

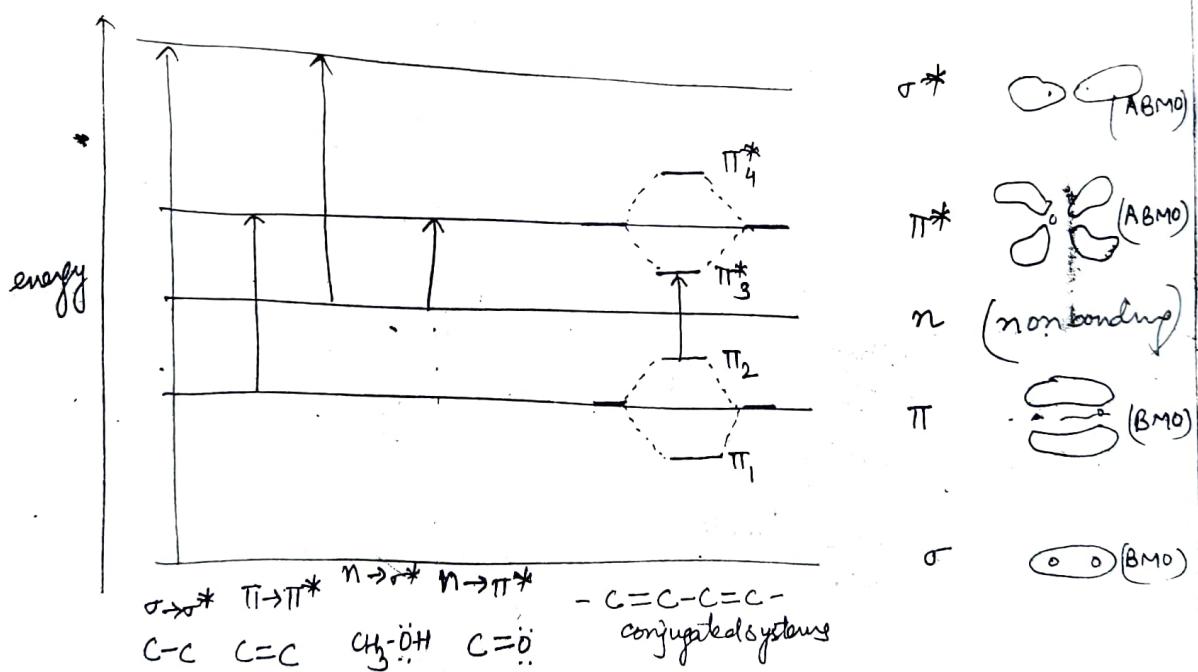
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The absorption of radiation by a molecule occurs only when exactly the right packet of energy (energy) is supplied (right packet means the discrete amount of energy, not fractional, and is specific for any transition).



This absorption of radiation gives different types of excitations or transitions in the molecule.

ELECTRONIC TRANSITIONS:-



Decreasing energy: $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* \rightarrow n \rightarrow \pi^*$

energy decreases ↓
wavelength increases ↑

It requires highest energy or shortest wave length ($\approx 150\text{ nm}$). It is studied in vacuum UV region for specially designed equipment is needed. It is less important for UV spectroscopy. This type of transition e.g. $\text{CH}_4 \rightarrow 121.9\text{ nm}$.

2) $n \rightarrow \sigma^*$

→ It requires lesser energy than $\sigma \rightarrow \sigma^*$. Therefore, the band appears comparatively at longer wavelength. It involves saturated compounds with one hetero atom having lone pair of electrons. e.g. saturated alcohols, ethers, aldehydes, ketones, halides and amines etc. e.g. water at 167 nm , methyl alcohol at 174 nm etc.

3) $\pi \rightarrow \pi^*$ → It requires lesser energy than $n \rightarrow \sigma^*$. It occurs due to the presence of multiple bonds. e.g. alkenes, aromatics, carbonyl compounds etc. In simple alkenes band at $170-190\text{ nm}$ is due to $\pi \rightarrow \pi^*$.

4) $n \rightarrow \pi^*$ → It requires least energy therefore absorbs at longest wave length, approx. $270-300\text{ nm}$. In this transition the lone pairs of e^- on heteroatom is excited to π^* orbitals. For e.g. $>\text{C}=\ddot{\text{O}}$: in ketones and aldehydes etc.

Alkanes $\rightarrow \sigma \rightarrow \sigma^*$ → do not lie in near UV. ($\approx 150\text{ nm}$)

Alkenes $\rightarrow \pi \rightarrow \pi^*$ → $170-190\text{ nm}$
 (Simple) \rightarrow ~~forbidden~~ hence low intensity

Saturated \rightarrow $n \rightarrow \pi^*$ → $\approx 280\text{ nm}$ → allowed hence high " intensity

Aliphatic ketone \rightarrow $n \rightarrow \pi^*$ → $\approx 160\text{ nm}$ → allowed hence high intensity

Conjugated diene \rightarrow $\pi \rightarrow \pi^*$ → $\approx 217\text{ nm}$ → very high " due to conjugation

5.

CONJUGATED SYSTEMS:- In conjugated dienes, the π orbitals of the separate alkene groups combine to give new orbitals π_1 & π_2 (BMO) and π_3^* and π_4^* (ABMO). $\pi_2 \rightarrow \pi_3^*$ transition is of very low energy than $\pi_1 \rightarrow \pi_1^*$ of an unconjugated alkene. Thus λ_{max} of alkene shifts from 171 nm to 217 nm in a conjugated diene. Similarly isolated ketones show $\pi \rightarrow \pi^*$ & $n \rightarrow \pi^*$ transition at shorter wavelength while conjugated ketones at higher wavelength. In conjugated systems, the energy separation between the ground state and excited state is reduced and the system absorbs at longer wavelength (λ_{max}) with larger intensity (E_{max}).

→ longer the conjugation = larger the λ_{max}
 Lycopene → a compound responsible for red colour of tomatoes has 11 conjugated bonds, so the absorption in higher wavelength region makes the molecule coloured.

ABSORPTION AND INTENSITY SHIFT —

When an absorption in a molecule is affected either by any structural environment or by solvent, it gets shifted. The absorption may shift by intensity or by wavelength. The various shifts are:-

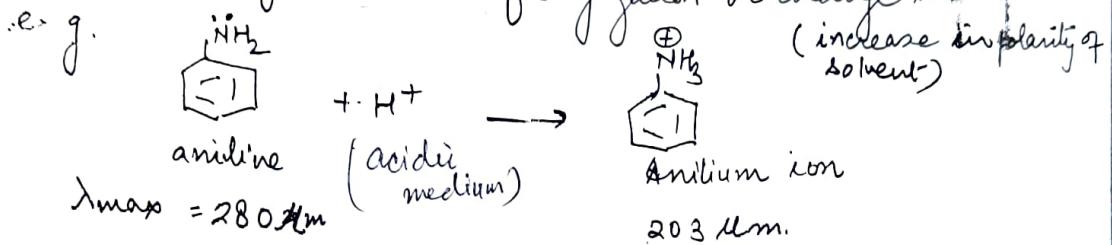
1) BATHOCHROMIC SHIFT:- The shift of an absorption maximum (λ_{max}) towards the red end or higher

wavelength is known as Ballisticnic shift. This is also known as Red-shift.
e.g. c_1 .

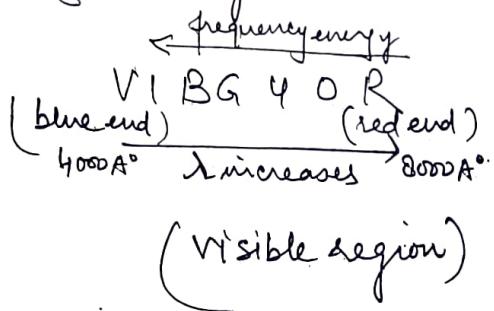
$$\lambda_{\text{max}} = 217 \text{ nm} \quad \rightarrow \quad \text{conjugation is increased} \Rightarrow \lambda_{\text{max}} \uparrow$$

2) HYPOCHROMIC SHIFT:-

HYPERSOCHRONIC SHIFT:- The shift of an absorption maximum towards the blue end or shorter wavelength is known as hypersochronic shift or blue shift. It may be produced by removal of conjugation or change in medium.



Aniline exhibits blue shift in acidic medium because of the removal of conjugation of non bonding e^- with benzene ring in anilinium ion.

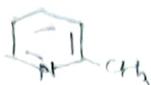


3) HYPERCROMIC SHIFT! — An increase in the intensity of absorption (ϵ_{max}) is known as hyperchromic shift. It is usually by the introduction of an auxochrome.

e.g.



pyridine

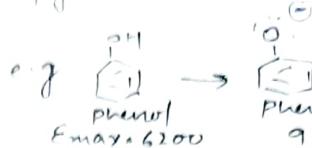


2-methyl pyridine

ϵ_{max} 2750
(intensity of absorption)

3560

λ_{max}

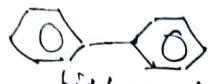


ϵ_{max} 6200

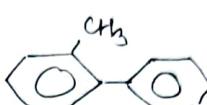
9400

4) HYPPOCHROMIC SHIFT:— The decrease in intensity of absorption (ϵ_{max}) is known as hypochromic shift. It is caused by the group which distorts the geometry of the molecule.

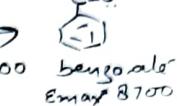
e.g.



ϵ_{max} 19,000

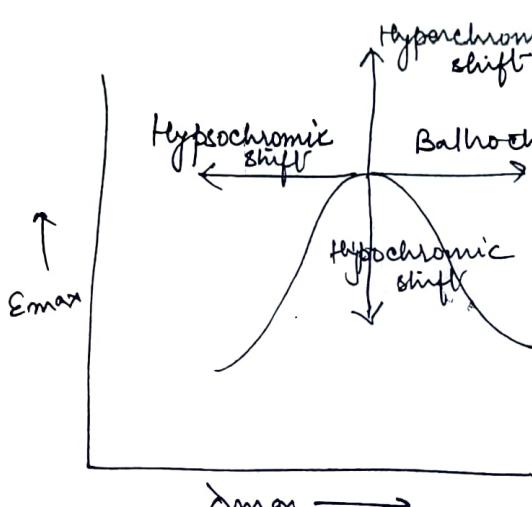


2-methyl biphenyl
 ϵ_{max} 11600



benzoate

ϵ_{max} 8700



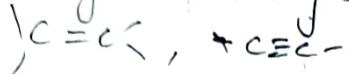
Shifts in ~~to~~ intensity and wavelength in any absorption

CHROMOPHORES

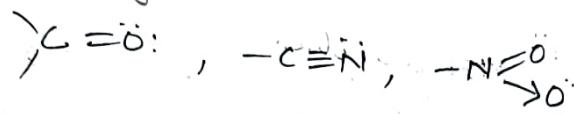
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A chromophore is a covalent unsaturated group responsible for electronic absorptions. The presence of a chromophore changes the energy of electronic transitions. There are two types of chromophores -

- i) chromophores containing π es which undergo $\pi \rightarrow \pi^*$. e.g. Ethylene, acetylenes etc.



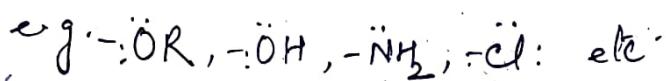
- (ii) chromophores containing π es and nes, they undergo $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. e.g.



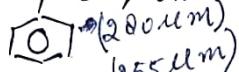
AUXO CHROMES

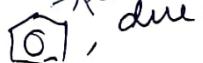
Auxochromes are saturated groups having lone pair of electrons. Auxochromes when attached to a chromophore ~~can~~ increase both the intensity as well as wavelength or λ_{max} .

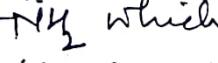
Actually, the auxochromes are the groups which are not responsible for absorption of radiations ~~but~~ are responsible for increasing the conjugation by their nes.



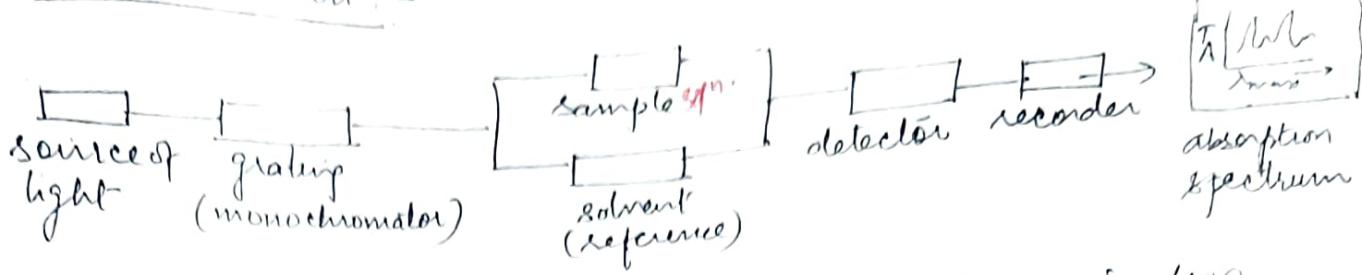
✓ for aniline λ_{max} and ϵ_{max} are higher than in benzene



in benzene  (255 nm), due to the presence of an auxochrome

-NH₂ which increases the conjugation through nes in . Therefore, while benzene is colourless, aniline is yellow in colour.

Instrumentation :-



In detector intensity of sample beam (I_s) $\&$ I_r is less than intensity of solvent beam $I_{(sample)} < I_{(solvent)}$

Tungsten filament lamp \rightarrow for $750 - 350\text{ nm}$

H_2 discharge lamp \rightarrow for below 350 nm

Source of light

Solvents \rightarrow water (polar), ethanol (less polar), (cheap & most common)

hexane (non polar)
 \rightarrow completely transparent to uv light
Cell \rightarrow Quartz with path length $1 - 10\text{ cm}$.



Solvent should be of high purity, chemically inert to sample, transparent.

Concentration of the solution is kept 10^{-5} to 10^{-2} M .

APPLICATIONS:-

1- Qualitative Analysis! - Identification of the compound can be done by comparing absorption spectrum with known compds.

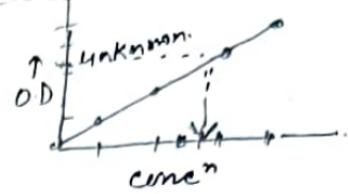
2- Determination of conjugation! - in a given compound is the most important application of this spectroscopy.

3- Quantitative analysis! - This is based on Beer's law.

In the determination of concn of an unknown compound, λ_{max} for compd is selected. Then optical densities (absorbance)

- detection of Geometrical Isomers - The trans isomers absorb at longer λ_{max} than cis. Thus, they can be distinguished by UV-visible spectroscopy.

are measured for some known compds. The O.D. is plotted against concⁿ, which gives a straight line and thus the concⁿ of unknown compd is evaluated.



4) Chemical Kinetics :- Change in concⁿ of either a reactant or product with time is measured.
(Absorbance & concⁿ)

5) Molecular wt determination :- Molecular wt can be determined since the concⁿ used is usually molar concⁿ.

6) Also used for determining tautomeric equilibrium.

✓ 7) Detection of impurity can be done as impurity gives very intense bands of its own in the spectrum.

$$A = E c l \quad \text{or} \quad A = \frac{\epsilon M \times C M \times l}{g/L} \quad \text{Numerical of Boer-Lambert's Law (UV-VIS spect.)}$$

$A \rightarrow$ Absorbance
 $\epsilon M \rightarrow$ Absorptivity (when C is taken in g/L)
 $C \rightarrow$ Concentration
 $l \rightarrow$ path length (cm)
 $\epsilon_M \rightarrow$ molar absorptivity (when C is taken in mol/L)
 $M \rightarrow$ Molar mass

1. A compound having concn 10^{-3} g/L resulted absorbance value 0.20 at λ_{max} 510 nm using 1.0 cm cell. calculate absorptivity and molar absorptivity values. Mol. wt of the compound is 400.

Solⁿ

$$\underbrace{\epsilon \text{ or } a}_{\text{absorptivity}} = \frac{A}{l \times C(g/L)} = \frac{0.20}{1.0 \text{ cm} \times 10^{-3} \text{ g/L}} = 200 \text{ L g}^{-1} \text{ cm}^{-1}$$

$$\underbrace{\epsilon_M}_{(\text{Molar Absorptivity})} = a \times M = 200 \times 400 = 80,000 \text{ L mol}^{-1} \text{ cm}^{-1}$$

Ans.

2. An α, β unsaturated ketone of relative mol. mass 110 has an abs. band with λ_{max} at 215 nm & $\epsilon_M = 10,000$. A solution of this ketone showed abs. $A = 2.0$ with a 1.0 cm cell. Calculate the concn of the ketone in this solution, expressed in g/L.

$$\epsilon_M = a \times M$$

$$a = \frac{10,000}{110} = \frac{100}{11}$$

Now $A = a \times C(g/L) \times l$

$$\text{Or } C(g/L) = \frac{A}{a \times l} = \frac{2.0 \times 11}{1000 \times 1} = \frac{22}{1000} = 2.2 \times 10^{-2} \text{ g/L. Ans}$$

3. A solution of a compound having concn 0.1 g/L gave 0.2 abs. value when measured using 1.0 cm cell. calculate its absorptivity and Molar absorptivity values; given mol.wt of the compd = 200.

$$a = \frac{A}{l \times C(g/L)} = \frac{0.2}{1.0 \times 0.1} = 2 ; \epsilon_M = a \times M = 2 \times 200 = 400 \text{ Ans}$$

4. Calculate the molar absorptivity (ϵ_M) for a solution containing 1.0 mmol dm^{-3} ($1.0 \times 10^{-3} \text{ mol/L}$) of solute when the absorbance of 1 cm cell was 1.5. What would be the value of A for a solution of double this conc'?

Soln.

$$A = \epsilon_M c M \cdot l$$

$$\epsilon_M = \frac{A}{c M \cdot l} = \frac{1.5}{1.0 \times 10^{-3} \times 1 \text{ cm}} = 1.5 \times 10^3 = 1500 \text{ L mol}^{-1} \text{ cm}^{-1}$$

$$A \text{ for double of its conc}' \text{ i.e. } 1.0 \times 10^{-3} \times 2 \text{ mol/L}$$

$$A = 1500 \times (2 \times 1.0 \times 10^{-3}) \times 1 = 3000 \times 10^{-3} = 3 \text{ Ans'}$$

5. When UV light is passed through a solution, the radiant power is reduced to 50%. Calculate absorbance.

Soln. $A = \log_{10} \frac{I_0}{I}$ $\left[I = \frac{50}{100} \times I_0 = 0.5 I_0 \right]$

$$A = \log_{10} \frac{I_0}{0.5 I_0} = \log_{10} 2 = 0.3010 \text{ Ans'}$$

6. Calculate the absorbance, if $\% T = 80$.

Soln. $A = \log \frac{1}{T} = \log \frac{I_0}{I} = \log \frac{100}{80} = 0.097$

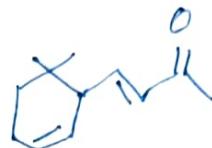
..... or (a) for a solution

Q- Assign the structure (A) and (B) to the respective isomers on the basis of the following uv-data :-

a. isomer shows peak at 228 nm while
b. isomer has a band at 296 nm . Explain .

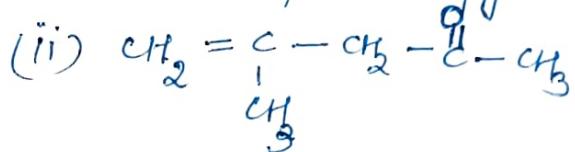
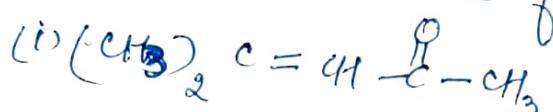


(A)



(B)

Q. How can you distinguish between the following compounds ?
Explain on the basis of uv-visible spectroscopy .



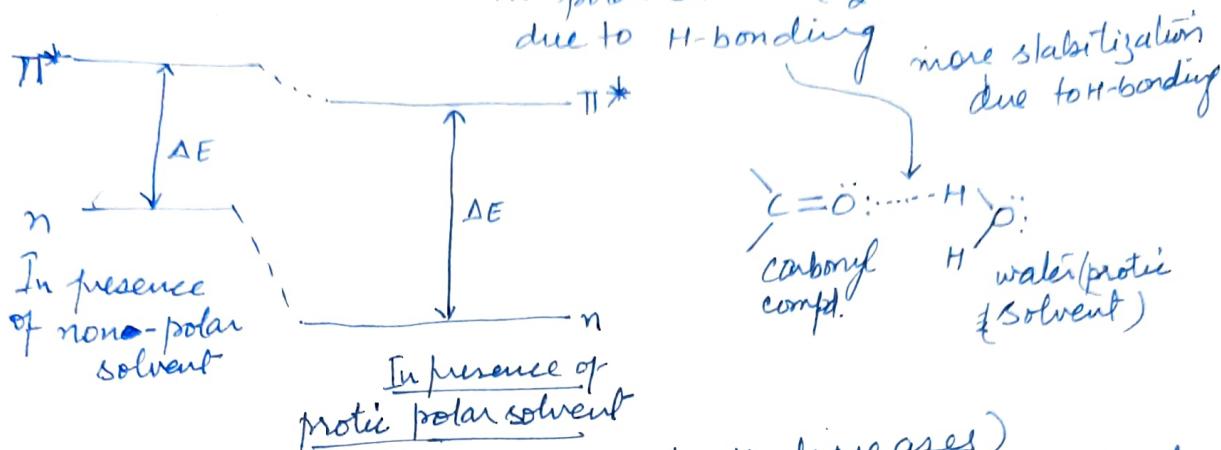
be

Solvent Effect on Absorptions

The most suitable solvent for UV-vis spectroscopy is that which does not absorb in the region under investigation. e.g. ethanol, hexane, methanol, cyclohexane etc.

Unsaturated carbonyl compounds e.g. Butenone $\text{CH}_2=\text{CH}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}(\text{H})_2$ show two different shifts on increasing the solvent polarity.

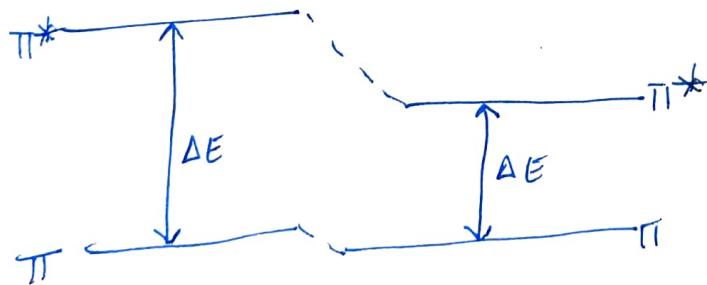
- (i) $n \rightarrow \pi^*$ transition - energy increases for $n \rightarrow \pi^*$ transition in polar solvents (H_2O , alcohols etc.) due to H-bonding



Energy increases (or wavelength decreases)
i.e. Blue Shift due to increase in solvent polarity

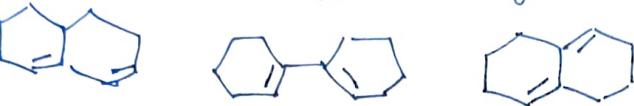
- H-bonding stabilizes (lower the energy) π^* bonding MO more than to π^* .

- (ii) $\pi \rightarrow \pi^*$ transition - Energy decreases in presence of polar solvents, π^* orbitals get more stabilized than π orbitals due to dipole-dipole interaction.
- Absorption moves to longer wavelength i.e. Red shift by increasing the polarity of the solvent.

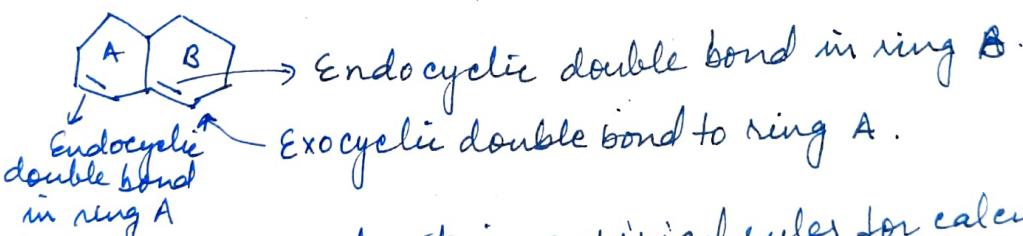
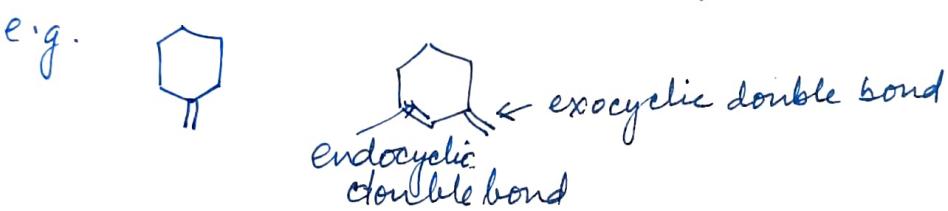


Woodward - Fieser Rules for conjugated dienes

Conjugation of double bonds causes bathochromic shift: longer the conjugation, greater is λ_{max} . The various conjugated systems are:-

- (i) Alicyclic dienes:- Dienes contained in an open chain system - Butadiene is the basic unit in this system.
- (ii) Homoannular dienes:- It is a cyclic diene in which double bonds are in conjugation within the same ring.
e.g. 
- (iii) Heteroannular dienes:- Double bonds which are in conjugation are in different rings.
e.g. 
- (iv) Endocyclic double bonds:- Double bonds present in a ring.
e.g. 

- (v) Exocyclic double bond :- Double bond in which a doubly bonded atom is the part of a ring system.



Woodward proposed certain empirical rules for calculating λ_{max} in dienes which were later modified by Fieser & are known as Woodward Fieser rules.

Acc. to the rules, the absorption takes place at a fixed value for a given diene or triene system. This value is known as Parent value or Basic value. The contribution made by various substituents, exocyclic double bond, endocyclic double bond etc.

are then added to the parent value in order to get the λ_{max} for a given system. As:-

Parent values:-

- (i) Butadiene - 217 nm
- (ii) Cyclic conjugated diene - 217 nm
- (iii) Homoannular conjugated diene = 253 nm
- (iv) Acyclic triene - 245 nm
- (v) Heteroannular diene - 215 nm

increment for each substituent

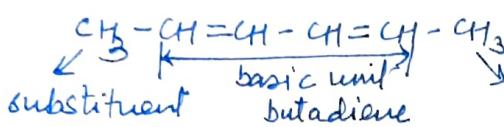
- (i) Alkyl substituent or ring residue = 5 nm
- (ii) Exocyclic double bond = 5 nm
- (iii) Double bond extended conjugation = 30 nm

Auxochrome

- (i) -OR = +6 nm
- (ii) -SR = +30 nm
- (iii) -Cl, -Br = +5 nm
- (iv) -NR₂ = +60 nm
- (v) -OCOCH₃ = 0 nm

Calculation of λ_{max} using N.F.

(i) λ_{max} in UV spectrum of 2,4-hexadiene :-

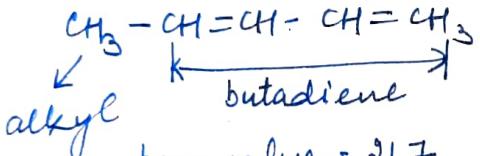


base value = 217 nm

Two alkyls = $2 \times 5 = 10 \text{ nm}$

$$\text{calculated } \lambda_{\text{max}} = \text{Total } 227 \text{ nm} \quad | \quad \text{Observed } \lambda_{\text{max}} = 227 \text{ nm.}$$

(ii) λ_{max} for 1,3-pentadiene



base value = 217

1-alkyl = 5

$$\text{Calculated } \lambda_{\text{max}} = 222 \text{ nm}$$

Observed = 223 nm

(iv) λ_{max} for -

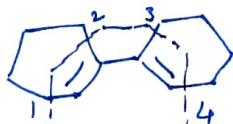


Homoannular diene = 253 nm
3-ring residue = 15 nm

1-exocyclic d.b. = 5 nm
Calculated: 273 nm
 $\lambda_{\text{max obs.}} = 275 \text{ nm}$

Heteroannular = 215 nm
3-ring residue = 15 nm
One exocyclic = 5 nm
Calculated: 234 nm
Observed = 235 nm

(iii) λ_{max} for -



Heteroannular ring = 215 nm

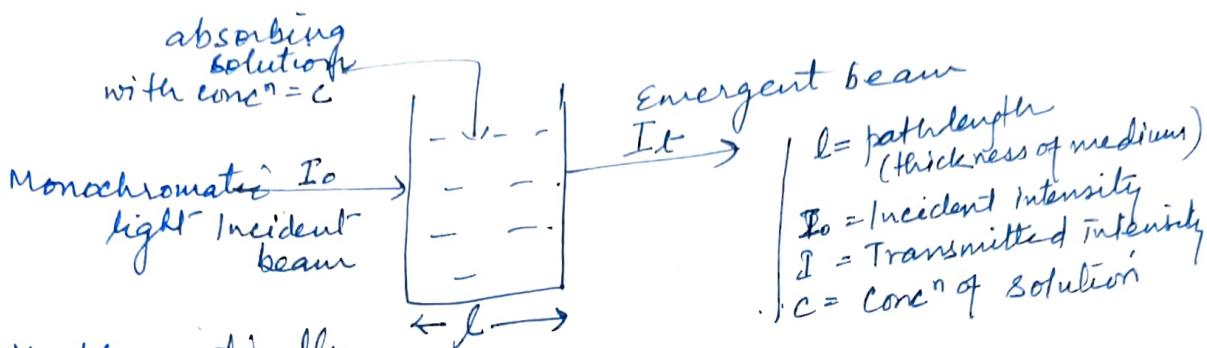
4-ring residues = $4 \times 5 = 20 \text{ nm}$

$$\text{Calculated } \lambda_{\text{max}} = 235 \text{ nm}$$

Observed = 236 nm.

Derivation of Beer-Lambert's law:-

When a beam of monochromatic light is passed through an absorbing medium, the rate of decrease of intensity of radiation to that of thickness of the medium (dl) is directly proportional to the intensity of the incident radiation I as well as concⁿ of the solution 'c'.



Mathematically, according to Beer-Lambert's law -

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

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

$$\frac{-dI}{I} = K C \cdot dl \quad \text{--- (1)}$$

On integrating (1), when $l=0$; $I=I_0$, and at $l=1$; $I=I_t$, we get

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

$$-\ln \frac{I_t}{I_0} = K \cdot C \cdot l$$

$$\text{or } \ln \frac{I_0}{I_t} = K \cdot C \cdot l$$

By taking log base 10,

$$2.303 \log \frac{I_0}{I_t} = K \cdot C \cdot l$$

$$\log \frac{I_0}{I_t} = \frac{K}{2.303} \cdot C \cdot l$$

$$\boxed{\log \frac{I_0}{I_t} = E \cdot C \cdot l}$$

$$\text{where } \frac{K}{2.303} = E$$

E is called as absorptivity
 $\log \frac{I_0}{I_t} = A$ (absorbance)

thus,

$$\boxed{A = E \cdot C \cdot l}$$

Transmittance (T) :- ratio of transmitted intensity to incident intensity.

$$\boxed{T = \frac{I_t}{I_0}}$$

$$\% T = T \times 100$$

thus,

$$\boxed{A = \log \frac{I_0}{I_t} = E \cdot C \cdot l = -\log T}$$

