

Module 2 (II) SPECTROSCOPY SKG

Spectro-radiation 1

Spectroscopy is the branch of science which deals with the determination of the structure of a compound through the interaction of electromagnetic radiation with the matter.

It is the analysis of electromagnetic radiation scattered, absorbed or emitted by molecules. (OR)

Advantages of Spectroscopic methods over classical method

The spectroscopic methods have many advantages over classical methods of analysis and these are as follows -

- (1) Spectroscopic methods take much less time.
- (2) For spectroscopic analysis, only a very small amount of the substance say 1 mg or even less is sufficient.
- (3) Generally the substance remains unchanged during spectroscopic analysis and can be used again and again.
- (4) The spectroscopic methods are comparatively more reliable in establishing the structure and identity of a compound.

Electromagnetic Radiations

Electromagnetic radiation is the stream of energy particles called photons or quanta moving in the direction of propagation and is perpendicular to both the electric field as well as the magnetic field.

- The energy of photon is given by Plank's equation

$$E = h\nu, \nu = \frac{c}{\lambda}, h = \text{Plank's constt}$$
$$= 6.624 \times 10^{-27} \text{ erg-sec}$$
$$= 6.624 \times 10^{-34} \text{ or joule-sec}$$

$E = h \frac{c}{\lambda}$

ν = frequency

c = vel. of light

λ = wavelength

Characteristics of Electromagnetic Radiations

(i) Wavelength - It is the distance between the adjacent crests or trough in particular wave. It is denoted by λ

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

(ii) Wave number - Wave number is the reciprocal of the wavelength expressed in cm. It is total number of waves which can pass through space of one cm. It is denoted by $\bar{\nu}$

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

(iii) Frequency - The number of waves which can pass through a point in one sec. It is denoted as ν and is expressed as cycles/sec. or Hertz

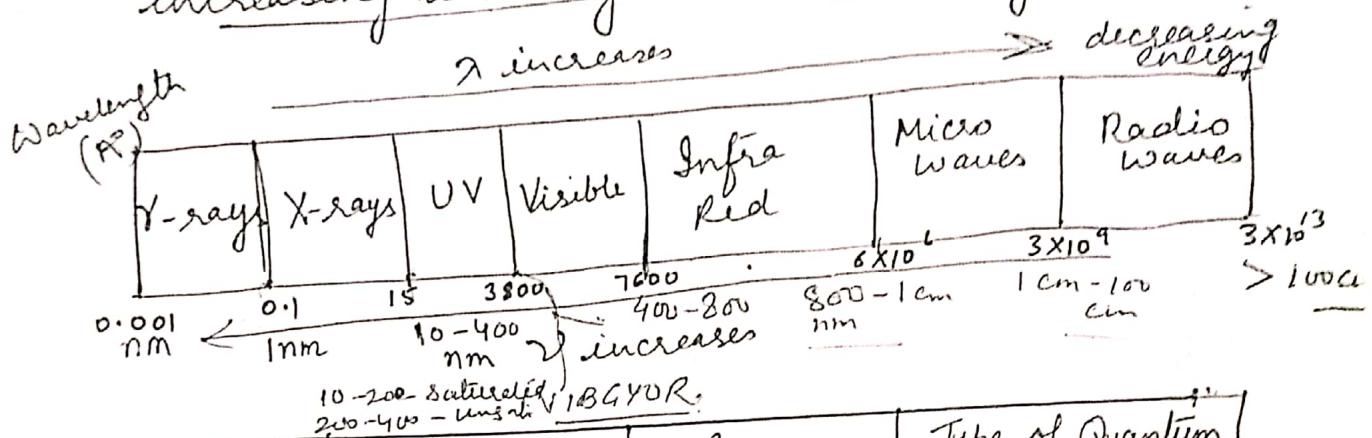
$$\nu = \frac{c}{\lambda}$$

(iv) Energy - Acc. to quantum mechanics, an electromagnetic radiation consists of discrete packets of pure energy called photons or quanta.

$$E = h\nu$$

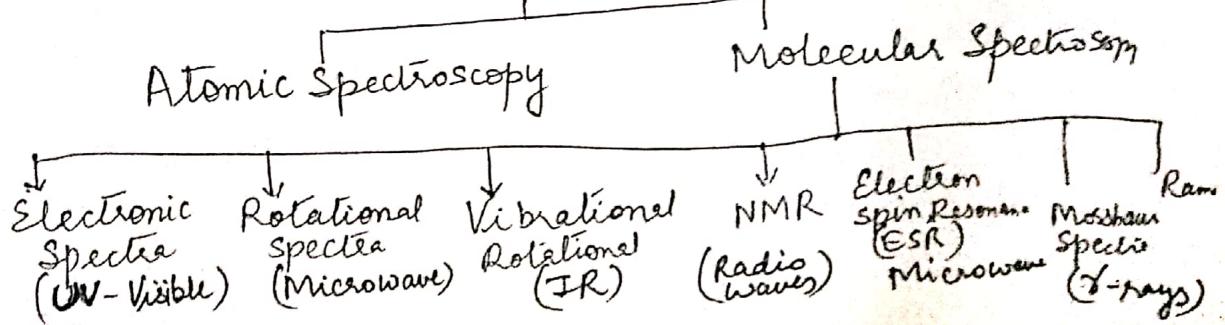
ELECTROMAGNETIC SPECTRUM

Electromagnetic spectrum is the arrangement of electromagnetic radiations in order of their increasing wavelengths or decreasing frequencies.



Spectral Region	Frequency (Hz)	Energy (J/mole)	Type of Quantum Change
γ -rays	$3 \times 10^{18} - 3 \times 10^{20}$	$10^9 - 10^{11}$	Change in Nuclear Configuration
X-rays	$3 \times 10^{16} - 3 \times 10^{18}$	$10^7 - 10^9$	Change in electron distribution
UV & Visible	$3 \times 10^{14} - 3 \times 10^{16}$	$10^5 - 10^7$	" "
I.R.	$3 \times 10^{12} - 3 \times 10^{14}$	$10^3 - 10^5$	Change of configuration
Microwave	$3 \times 10^{10} - 3 \times 10^{12}$	$10^1 - 10^3$	Change of Orientation
ESR	$3 \times 10^8 - 3 \times 10^{10}$	$10^{-1} - 10$	Change of Spin
NMR	$3 \times 10^6 - 3 \times 10^8$	$10^{-3} - 10^{-1}$	Change of spin

TYPES OF SPECTROSCOPY

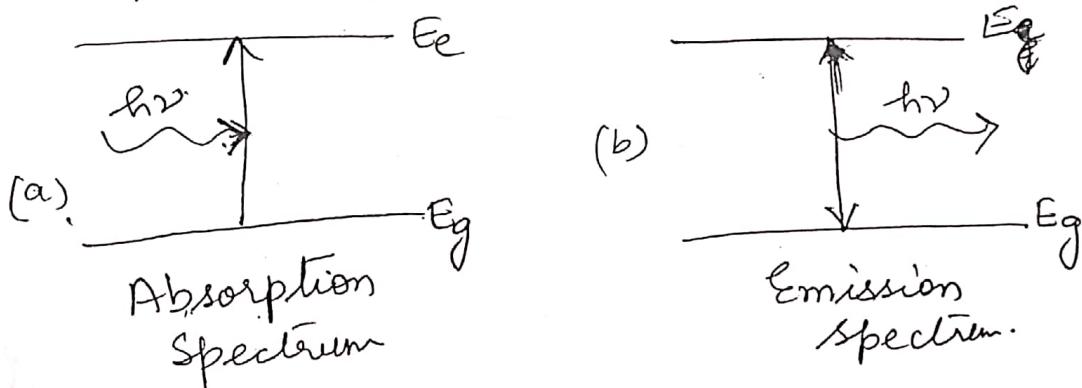


SPECTROMETER

- The energy change or the frequency of the electromagnetic radiation emitted or absorbed can be recorded with the help of an instrument called spectrometer.
- The separation or analysis of a composite radiation into different wavelengths or frequencies constitutes a spectrum.
- Thus spectra so obtained can be broadly classified into two categories.

- (1) Emission Spectrum - When there is a transition from a state of high energy (excited state) to a lower energy (ground state), the excess energy is emitted as a photon of energy $h\nu$ (provided $h\nu$ = equal to the energy difference)
- The spectrum recorded will be emission spectrum.
- (2) Absorption Spectrum -

when there is a transition from a state of lower energy to a state of higher energy i.e. from ground state to the excited state, the energy absorbed will be exactly equal to the energy difference. The spectrum recorded will be absorption spectrum.



Different Types of Molecular Energy

Molecular energy arises due to translational, rotational, vibrational motion and electronic energy.

$$\text{Internal} = E_{\text{tran}} + E_{\text{rot.}} + E_{\text{vib}} + E_{\text{elec}}$$

Translational Energy - The energy associated with the uniform motion of a molecule as a whole through the space is known as translational energy.

Since a molecule can move in X, Y and Z-direction, hence it has three translational degree of freedom. According to kinetic theory of gases -

The total translational energy of a gas molecule

$$= \frac{3}{2} kT$$

The average translational energy along a particular direction $= \frac{1}{2} kT$

where m = Molecular Mass

v = Velocity of the molecule

Rotational Energy - The energy associated with overall rotation of the molecule (with its atoms). The rotational energy.

$$E_{\text{rot.}} = \frac{1}{2} I \omega^2$$

where I = Moment of Inertia

ω = Angular velocity of the rotating molecule

According to quantum mechanics -

$$E_{\text{rot}} = J(J+1) \frac{\hbar^2}{8\pi^2 I}$$

where J = rotational quantum number

\hbar = Plank's constant

I = Moment of Inertia

VIBRATIONAL ENERGY

This energy is due to vibration of the atoms of the molecule about equilibrium positions.

The vibrational energy,

$$E_{\text{vib}} = \left(v + \frac{1}{2}\right) h\nu_0$$

v = Vibrational quantum number having value zero or a positive integer.

ν_0 = vibrational frequency.

When $v=0$, $E_{\text{vib}} = \frac{1}{2} h\nu_0$ = ZERO POINT ENERGY

The vibrational degree of freedom for different molecules are as follows.

Types of Molecule	Vibrational degrees of freedom	Examples
Linear	$3n-5$	$\text{CO}_2, \text{C}_2\text{H}_2$
Non-linear	$3n-6$	$\text{H}_2\text{O}, \text{NO}_2, \text{CH}_4$

ELECTRONIC ENERGY :- This type of energy is due to the motion of electrons i.e. due to various electronic arrangement.

According to Born-Oppenheimer approximation, the total energy of the molecule is given by

$$E = E_{\text{ele}} + E_{\text{vib}} + E_{\text{rot}}$$

The translational energy is negligible as compared to other energies and the increasing order of energy is -

$$E_{\text{ele}} > E_{\text{vib}} > E_{\text{rot}} > E_t$$

UNIT -

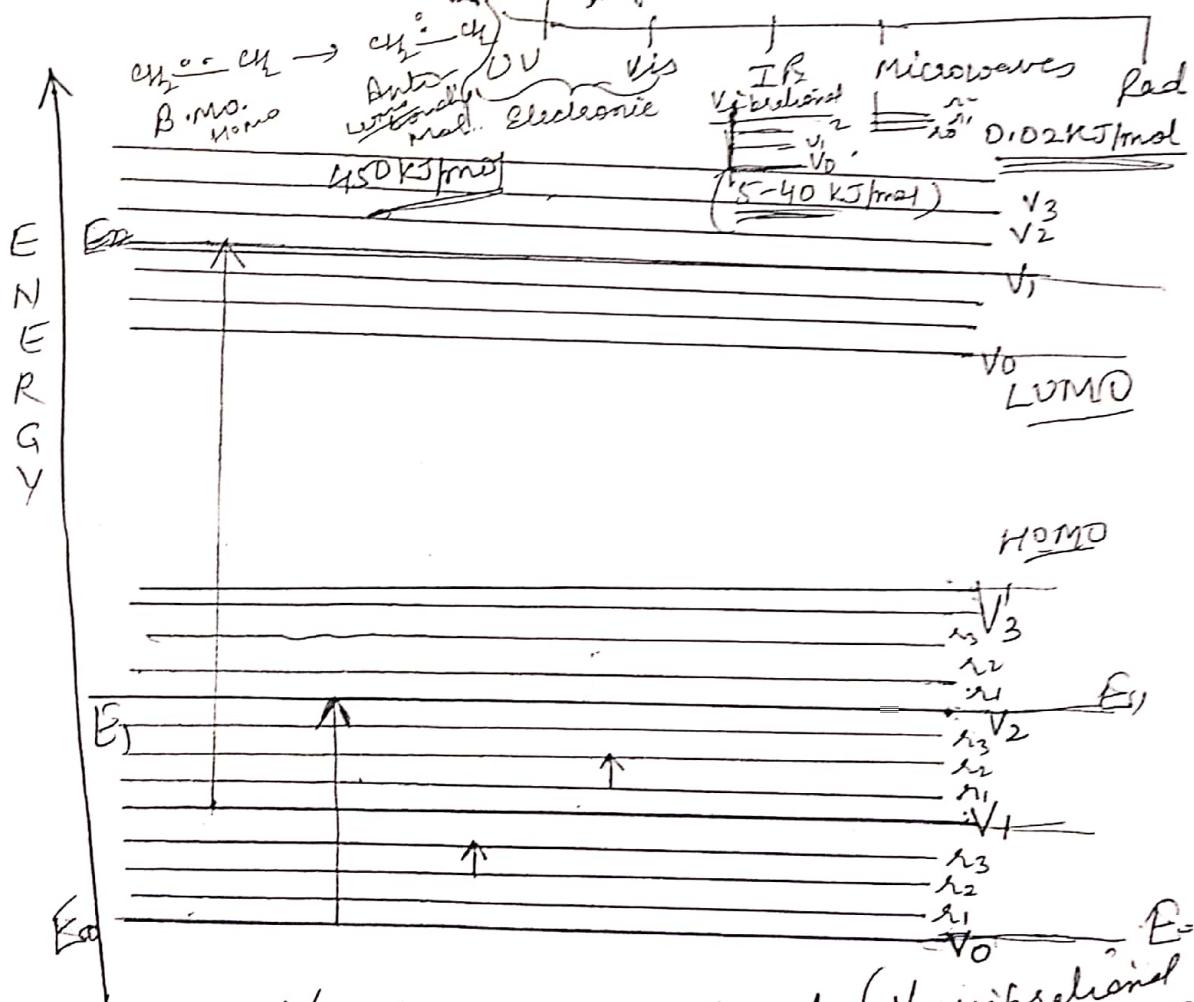
$$1 \text{ Å}^\circ = 0.1 \text{ m} \mu = 10^4 \mu = 10^8 \text{ cm} = 10^{-10} \text{ m}$$

$$1 \text{ nm} = 1 \text{ m} \mu = 10 \text{ Å}^\circ$$

$$1 \text{ Hz} = 1 \text{ cycles/second}$$

$$1 \mu = 1000 \text{ m} \mu = 10^{-4} \text{ cm}$$

very light weight

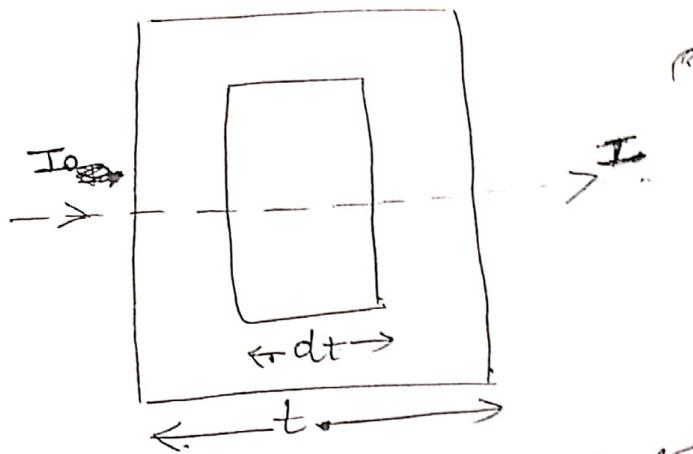


Various energy levels (V - vibrational, ν - rotational)

LAWS OF LIGHT ABSORBANCE

② Lambert's Law - According to this law,

"When a beam of monochromatic light is passed through an absorbing medium, the rate of decrease of intensity of light radiation, with the thickness of the absorbing medium is directly proportional to the intensity of the light."



Let 'I' be the intensity of light radiation ^{after} passing through a medium having thickness 't'

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

where $K = \text{Proportionality Constant}$

$$\text{or } -\frac{dI}{dt} = KI \quad \text{--- (1)}$$

dI = Infinitesimal small decrease in the intensity of light radiation after passing through infinitesimally small thickness ' dt ' of the medium.

$-\frac{dI}{dt}$ = Rate of decrease of intensity of radiation with the thickness.

I_0 = Intensity of radiation before entering

Integrate equation ①

$$\int_{I_0}^I \frac{dI}{I} = -K \int_{t=0}^{t=1} dt$$

$$\ln \frac{I}{I_0} = -Kt \Rightarrow \ln \frac{I_0}{I} = +Kt$$

$$2.303 \log_{10} \frac{I_0}{I} = +Kt$$

where

$\log \frac{I_0}{I}$ = Absorbance A

$\frac{-K}{2.303}$ = Absorption coefficient (E)
of absorbing Medium.

$$A = E \cdot t$$

where I_0 = intensity of incident radiation

I = intensity after passing through the medium.

$$I = I_0 \cdot e^{-kt}$$

$$\text{or } I = I_0 \cdot 10^{-at}$$

where $a = \frac{K}{2.303}$ = Extinction coefficient of the absorbing medium.

I_{abs} be the intensity of radiation absorbed, then,

$$I_{abs} = I_0 - I$$

$$= I_0 - I_0 e^{-Kt}$$

$$I_{abs} = I_0 (1 - e^{-Kt})$$

⑤ BEER'S LAW -

(The Beer's law also takes into consideration the concentration of solution (absorbing medium) along with the thickness of the solution)

This law states that "When a beam of monochromatic radiation is passed through an absorbing medium, the rate of decrease of intensity of radiation with thickness of the absorbing medium is directly proportional to the intensity of incident radiation as well as the concentration of the solution."

$$-\frac{dI}{dt} \propto IC$$

$$-\frac{dI}{dt} = K' \cdot IC \quad \text{--- (1)}$$

where,

K' = Molar absorption coefficient which depends on the nature of absorbing medium

C = conc. of sol in mol/L

I_0 = Intensity of light radiation before entering the absorbing Medium.

$$\int_{I_0}^I \frac{dI}{I} = - \int_{t=0}^{t=x} K' C dt$$

$$\ln \frac{I_0}{I} = -K' C t$$

$$\log_{10} \frac{I_0}{I} = +\frac{K'}{2.303} C t$$

$$A = E.C.t$$

$$I = I_0 e^{-K' C t}$$

$$I = I_0 10^{-a' C t}$$

$$\log \frac{I_0}{I} = a' C t$$

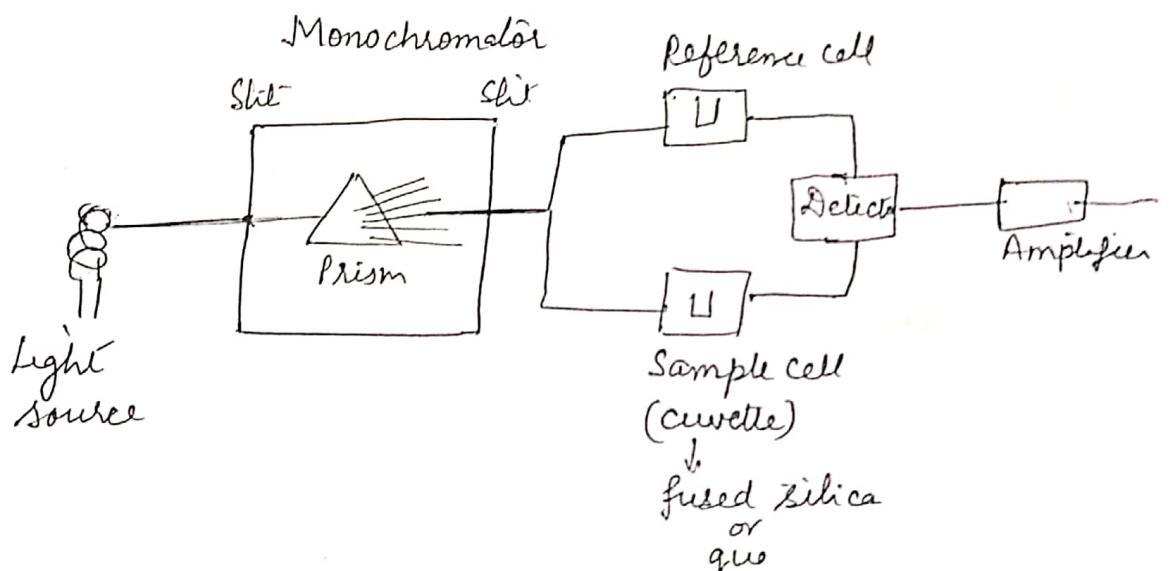
$\frac{K'}{2.303} = \text{Absorption Coefficient of Solution}$

where $a' = \frac{K'}{2.303}$

= Molar extinction coefficient of the absorbing medium

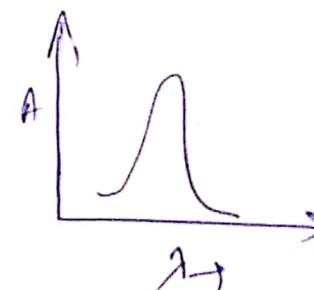
ULTRAVIOLET VISIBLE SPECTROPHOTOMETER

- The instrument used in UV-Visible Spectroscopy is called a UV-Visible spectrophotometer.
- A spectrophotometer is a device which ~~measures~~ detects the percentage transmittance of light radiation when light of certain intensity and frequency is passed through the sample.
- Thus the instrument compares the intensity of the transmitted light with that of the incident light.



UV Visible Spectrophotometer consists of -

- (1) light Source
- (2) Monochromator
- (3) Detector
- (4) Amplifier
- (5) Recording Device



The most suitable light sources are -

(1) Tungsten filament lamp (rich in red ~~filament~~ radiations i.e $\lambda = 375 \text{ nm}$)

(2) Deuterium-discharge lamp (covers the region ~~below~~ above 360 nm).

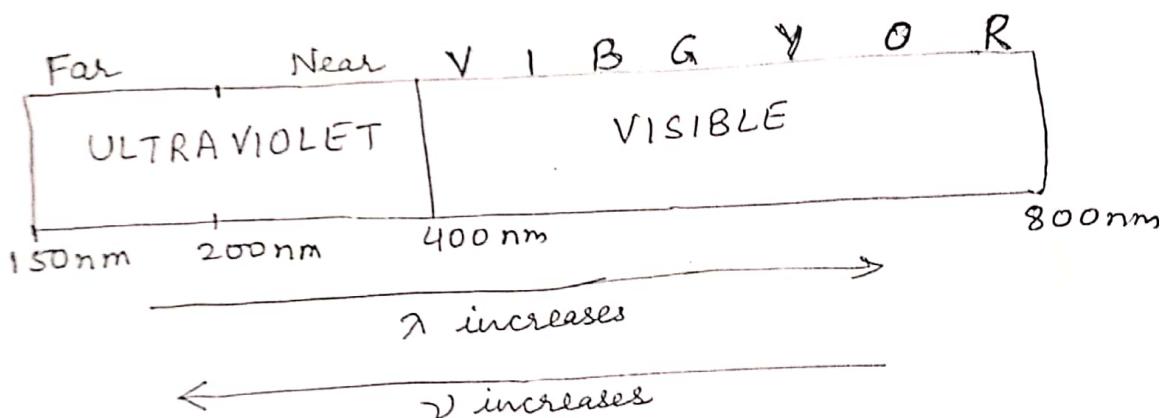
- The primary source of light is divided into two beams of equal intensity. Before dividing it into 2 beams, the incident radiation is dispersed with the help of a rotating prism.
- The various wavelengths of a light source are separated with a prism and then selected by slits such that the rotation of the prism causes a series of continuously increasing wavelengths to pass through the slits for recording.
- The selected beam is monochromatic which is then divided into 2 beams of equal intensity.
- One of the beams of selected monochromatic light is passed through the sample solution and the other beam of equal intensity is passed through the reference solvent.
- The sample may be contained in transparent cells called cuvette. Cuvettes are rectangular in shape, with an internal width of 1cm

- Mostly cuvettes are made up of high quality fused silica or quartz glass because these are transparent throughout the UV, visible and near IR regions.
- This type of spectrometer is called double beam spectrophotometer.
- Sample Preparation - 1 mg of sample is accurately weighed and dissolved in a suitable to make the volume upto 100 ml. A little amount of this solution is taken in a silica cell. The thickness should be 1 cm.

ULTRAVIOLET-VISIBLE SPECTROSCOPY

UV-Visible spectroscopy is also known as electronic spectroscopy because it involves the transition of electrons within a molecule or ion from a lower to higher electronic energy level or vice versa by absorption or emission of radiations falling in the UV-visible range of electromagnetic spectrum respectively.

<u>Region</u>	<u>Wavelength</u>
Visible	400-800 nm = $4000-8000 \text{ Å}^\circ$
Near UV	200-400 nm = $2000-4000 \text{ Å}^\circ$
Far UV	150-200 nm = $1500-2000 \text{ Å}^\circ$



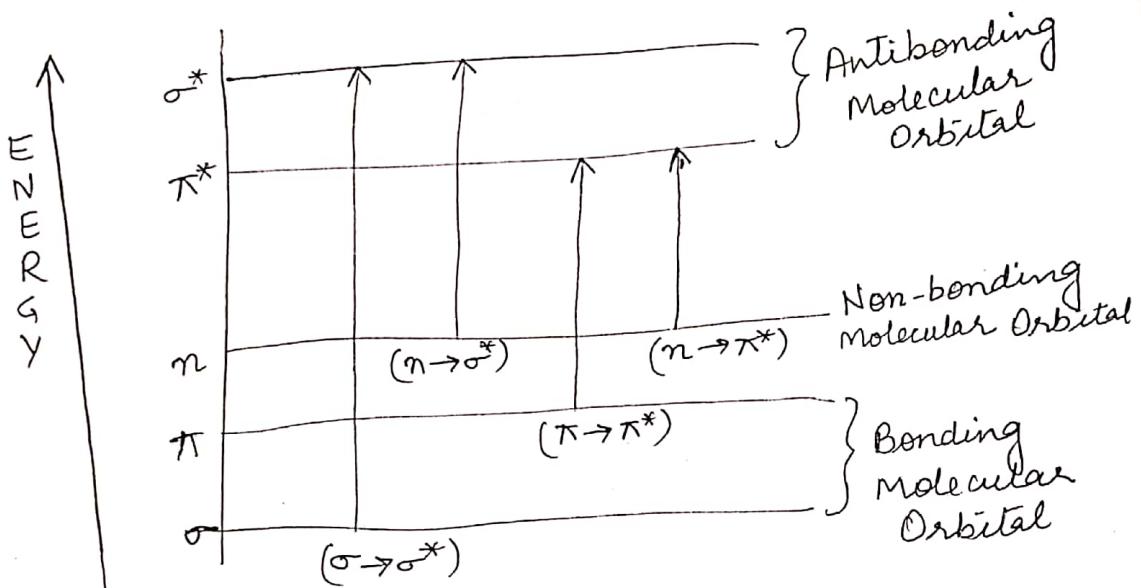
UV-visible spectroscopy is used in determining -

- (1) Molecular Weights
- (2) Detection of impurity
- (3) Dissociation constants of acids & bases
- (4) Kinetics of certain reactions
- (5) The number of conjugated double bonds and also aromatic conjugation .

* The wavelength at which a molecule posses its highest absorptivity coefficient (E_{\max}) is denoted by λ_{\max} .

* In general UV-Visible spectra show only a few broad bands, but IR spectra are usually complex exhibiting a series of sharp peaks.

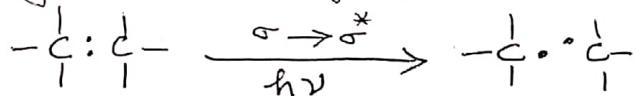
TYPES OF ELECTRONIC TRANSITIONS



Increasing Order of energy required for transition

$$(\text{n} \rightarrow \pi^*) < (\pi \rightarrow \pi^*) < (\text{n} \rightarrow \sigma^*) < (\sigma \rightarrow \sigma^*)$$

(1) $\sigma \rightarrow \sigma^*$ Transitions — This type of transition is possible in saturated hydrocarbons (alkane) where only σ bonds are formed and no atom has non-bonding (n) electrons. Such transitions require energy in the range of 120-150 nm.



e.g. CH_4
& C_2H_6

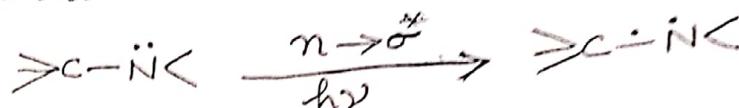
$$\lambda_{\text{max}} \approx 121.9 \text{ nm}$$

$$\lambda_{\text{max}} \approx 135 \text{ nm}$$

(2) $n \rightarrow \sigma^*$ Transitions — The excitation of an e^- from unshared pair to an antibonding σ -orbital is called $n \rightarrow \sigma^*$ transition.

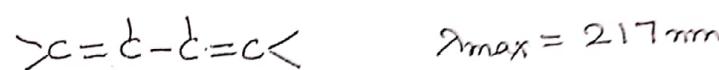
Such transition require less energy compared to $\sigma \rightarrow \sigma^*$ transition.

eg- Saturated halide, (CH_3Cl), Alcohols, ether, aldehyde, Ketone, amine



(3) $\pi \rightarrow \pi^*$ transition : This type of transition takes place in unsaturated compounds containing double or triple bond. The excitation of π -e⁻ requires smaller energy and hence transition occurs at longer wavelength.

eg $\geqslant \text{C} = \text{C} <$, $-\text{C} \equiv \text{C}-$, $-\text{C} \equiv \text{N}$, $-\text{N} = \text{N}:$, $\geqslant \text{C} = \text{O}$



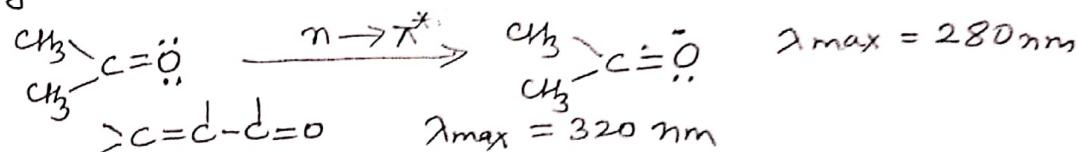
* Benzene : three bonds $\xrightarrow[\hbar\nu]{\gamma_{\max}} 260 \text{ nm (weak)}$
 $\xrightarrow[\hbar\nu]{\gamma_{\max}} 180-200 \text{ nm}$
 $\xrightarrow[\hbar\nu]{\gamma_{\max}} 180-200 \text{ nm (intense)}$

* Ethylene $\text{H}_2\text{C} = \text{CH}_2$ shows intense band at $\sim 174 \text{ nm}$ weak band $\sim 200 \text{ nm}$, both due to $\pi - \pi^*$ transition

* Alkyl substitution of the Olefins makes the absorption to occur at a longer wavelength.

(4) $n \rightarrow \pi^*$ Transition — This type of transition occurs in compounds containing non-bonding electrons on hetero-atoms. The e⁻ gets excited to π^* antibonding orbital. This type of transition requires least energy and hence occurs at longer wavelength.

eg $\geqslant \text{C} = \text{O}$, $\geqslant \text{C} = \text{S}$, $-\text{N} = \text{O}$



eg- Aldehydes & Ketones exhibit two bands

1- $\lambda_{\text{max}} \approx 180-200$ ($\pi-\pi^*$) transition

2- $\lambda_{\text{max}} \approx 280$ nm ($n-\pi^*$) "

* Bands due to $n-\pi^*$ transition is always less intense, \because the e^- s in the n -orbital are situated perpendicular to the plane of the π -bond and hence the probability of the jump of an e^- from n to π^* is low.

CHROMOPHORES - chroma = colour
phorein = to bear

It is defined as "any isolated covalently bonded group that shows a characteristic absorption in the ultraviolet or the visible region". The various types of groups (eg- $C=C$, $C\equiv N$, $C\equiv C$, $C=O$, $N=N$, $N=O$ etc.) which are responsible for $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition are called chromophores.

- They absorb in the common UV (200-400 nm) or Visible (400-800 nm) region. Chromophores can further be classified into two groups :

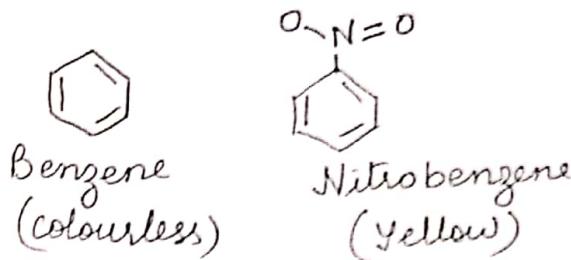
(i) Chromophores which contain $\pi-e^-$ and they undergo $\pi-\pi^*$ transitions.

eg- $>C=C<$, $-C\equiv C-$ etc.

(ii) Chromophores which contain both $\pi-e^-$ as well as non-bonding e^- and undergo $\pi \rightarrow \pi^*$ and $n-\pi^*$ transitions.

eg... $>C=O$, $-C\equiv N$ etc.

Ques - Benzene is colourless while nitrobenzene is yellow.
 Ans - Benzene is colourless but nitrobenzene is yellow due to the presence of chromophoric $-NO_2$ gp.

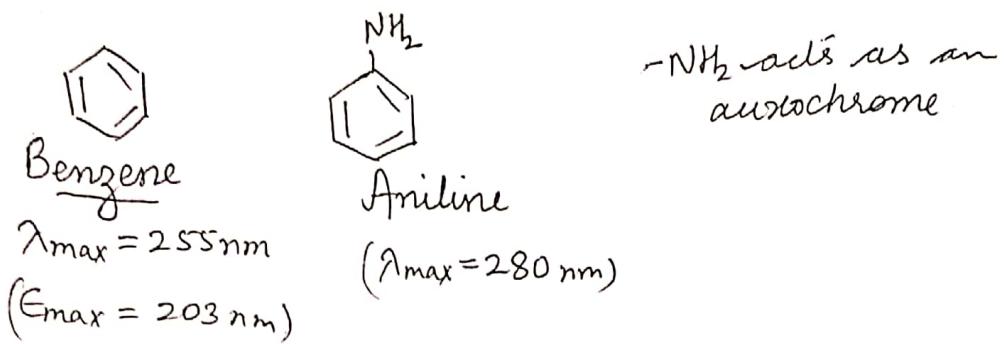


Chromophores and their Transitions

Chromophore	Transition	λ_{max} (nm)	E_{max}
1. $>C=C<$	$\pi \rightarrow \pi^*$	175	~ 15000
2. $-C\equiv C-$	$\pi \rightarrow \pi^*$	196	~ 2000
3. $>C=O$	$n \rightarrow \pi^*$	285	~ 15
	$n \rightarrow \sigma^*$	160	$\sim 18,000$
	$\pi \rightarrow \pi^*$	180	$\sim 16,000$
4. $-N=N-$	$n \rightarrow \pi^*$	338	~ 5
5. $-NO_2$	$n \rightarrow \pi^*$	274	~ 15
6. $\begin{matrix} O \\ \\ -C-NH_2 \end{matrix}$	$\pi \rightarrow \pi^*$	~200	5000
	$n \rightarrow \pi^*$	178	9500
	$n \rightarrow \pi^*$	220	63

AUXOCHROME :- Auxin = Enhancing
 chroma = Colour

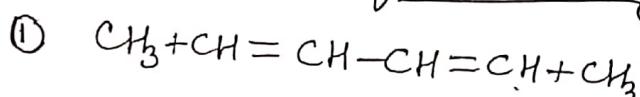
- Groups which are not chromophores themselves but their presence can cause the increase in colour intensity of compounds, are known as auxochrome.
- They shift the absorption maximum towards the red end of the spectrum (longer wavelength)
 e.g. $-OH$, $-NH_2$, $-OR$, $-NR_2$, $-SH$



Auxochrome

- (i) $-\text{OR}$ $+6 \text{ nm}$
- (ii) $-\text{SR}$ $+30 \text{ nm}$
- (iii) $-\text{Cl}, -\text{Br}$ $+5 \text{ nm}$
- (iv) $-\text{NR}_2$ $+60 \text{ nm}$
- (v) $-\text{OCOCH}_3$ 0 nm

Calculation of λ_{\max} using Woodward Fieser Rule -

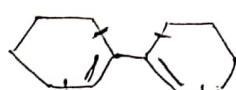


$$\text{Basic Value} = 217$$

(2) Alkyl substituents (2×5) = 10

$$\text{Calculated } \lambda_{\max} = \underline{\underline{227 \text{ nm}}}$$

②



heteroannular diene

Basic value for heteroannular diene = 215

ring residue (4×5)

$= 20$

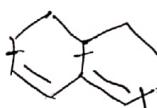
Calculated value λ_{\max}

$= 235 \text{ nm}$

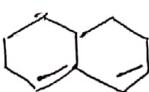
Observed value λ_{\max}

$> 236 \text{ nm}$

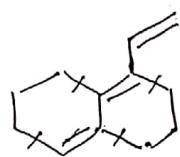
③



or



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



$B.V = 215$

double bond extending
conjugation = 30

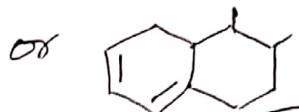
ring residue = 20

exocyclic double bond = 10
 $\lambda_{\max} = 275 \text{ nm}$

Woodward - Fieser Rules for Conjugated Dienes

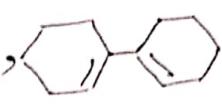
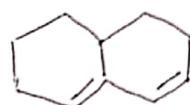
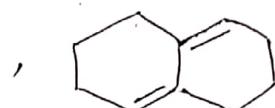
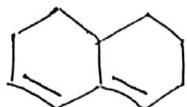
(1) Alicyclic dienes - Dienes contained in an open chain system. Butadiene is the basic unit.
 $\lambda_{\text{max}} = 217 \text{ nm}$

(2) Homoannular diene - It is a cyclic diene in which double bonds are in conjugation within the same ring.



Basic value of $\lambda_{\text{max}} = 253 \text{ nm}$.

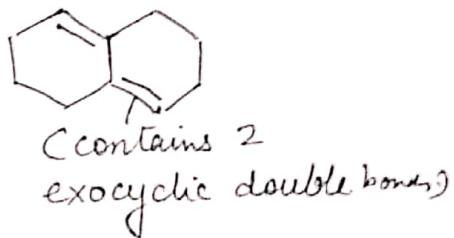
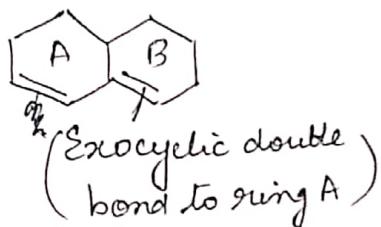
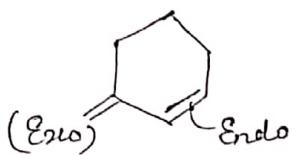
(3) Heteroannular dienes - Double bonds are in conjugation and in different ring



$\lambda_{\text{max}} = 214 \text{ nm}$.

(4) Exocyclic and Endocyclic double bond -

Exocyclic double bond refers to a double bond in which a doubly bonded atom is the part of a ring system.



Parent Values

(i) Butadiene = 217 nm

(ii) Cyclic Conjugated diene = 217 nm

(iii) Acyclic triene = 245 nm

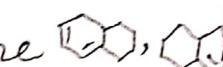
(iv) Homoannular conj. diene = 253 nm

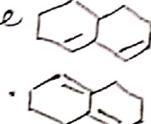
(v) Heteroannular diene = 215 nm

Increment for each substituent

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

Woodward Fieser Rules for Diene & Triene

	Base Value
Acyclic Diene $>\text{C}=\text{C}-\text{C}=\text{C}<$	217 nm
Acyclic Triene	245 nm
Homoannular diene 	253 nm

Heteroannular diene 	214 nm
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Addition for each substituent

-R (alkyl or ring residue)	5 nm
-OR (alkoxy)	6 nm
Exocyclic double bond to one ring 	5 nm

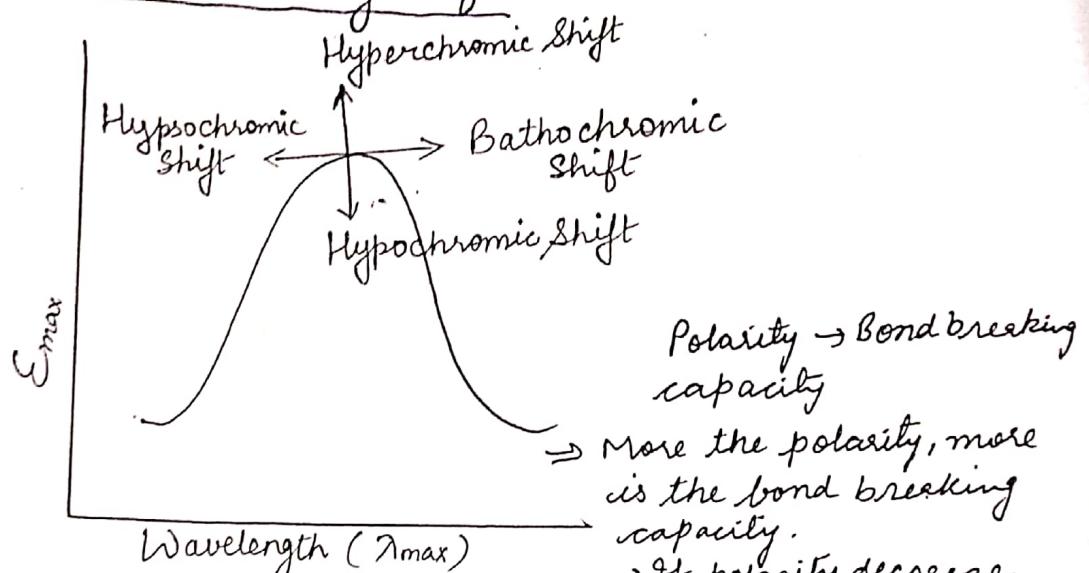
Exocyclic double bond (to 2 rings) 10 nm

Double bond extending Conjugation 30 nm

Auxochrome

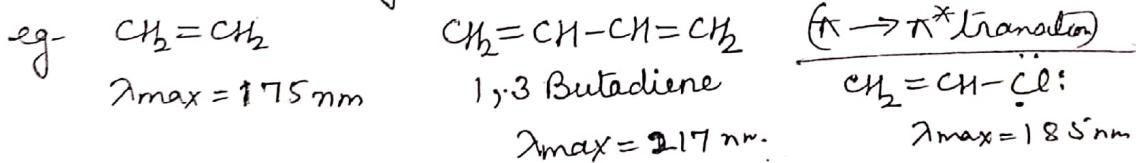
-OR	6 nm
-SR	30 nm
-Cl, -Br	5 nm
-NR ₂	60 nm
-OCOCH ₃	0 nm

Absorption and Intensity Shifts



④ Bathochromic Shift (Red Shift): The shift of an absorption maximum (λ_{max}) ~~wavely~~ towards the longer wavelength is called bathochromic shift or Red shift. It may be due to the presence of an auxochrome or change in the polarity of the solvent.

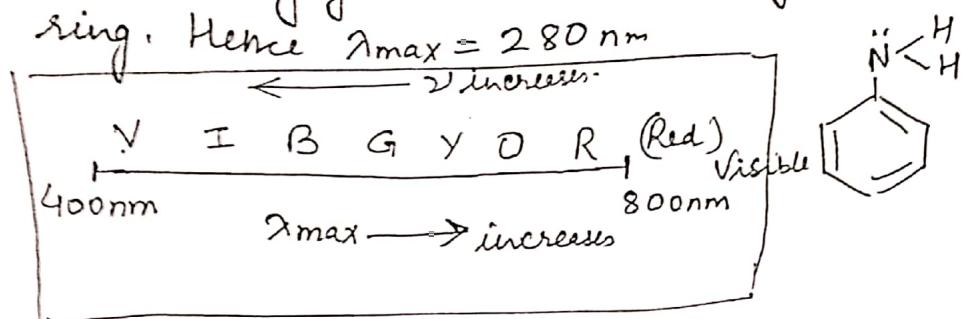
- * The $n-\pi^*$ transition for carbonyl compound experiences bathochromic shift when the polarity of the solvent is decreased.
- * Conversion of phenol to phenolate anion causes bathochromic shift because the non-bonding e^- become available for interaction with the $\pi-e^-$ system of the ring.



⑤ Hypsochromic Shift (Blue Shift): The shift of the absorption maximum (λ_{max}) towards the shorter wavelength is called hypsochromic shift or blue shift. It may be due to increase in polarity of the solvent or removal of conjugation.

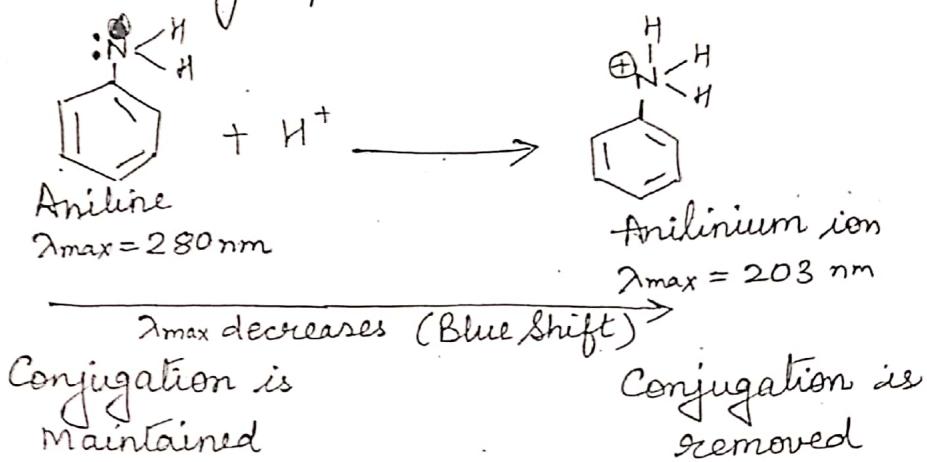
generates in
polarity, so
reduces in
polarity.
So hypsochromic
shift is due to
removal of
conjugation.

e.g. Non-bonding e^- pair present on nitrogen is in conjugation with $\pi - e^-$ of the benzene ring. Hence $\lambda_{max} = 280 \text{ nm}$

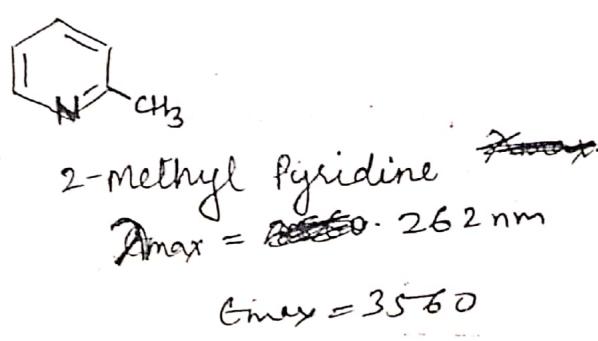
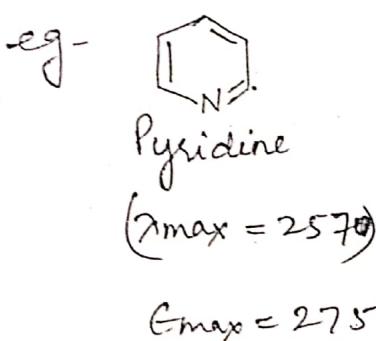


* Aniline exhibits blue shift in acidic solution.

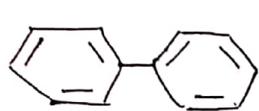
This is because of the formation of anilinium ion which removes the conjugation i.e. electronic pair is no longer present.



② Hyperchromic Shift : It is the effect leading to increase in intensity of the absorption maximum i.e. (E_{max}) increases. The introduction of auxochrome usually increases the intensity of absorption maximum.

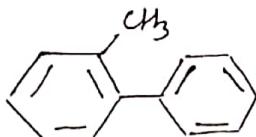


Hypochromic Shift : The decrease in the intensity of absorption (ϵ_{max}) is known as hypochromic shift. It is caused by the groups which distort the geometry of the molecule.



Biphenyl

$$\epsilon_{max} = 19,000$$

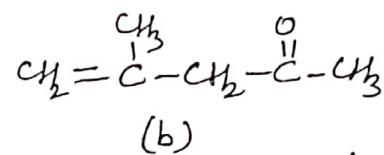
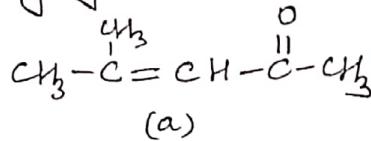


2-methyl biphenyl

$$\epsilon_{max} = 10,250$$

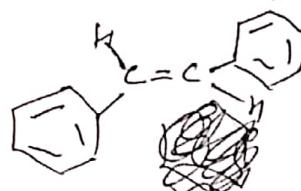
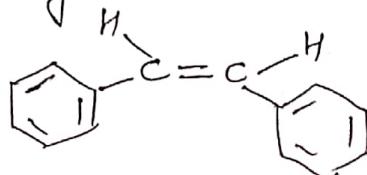
APPLICATION OF UV SPECTROSCOPY

- (1) Extent of Conjugation – UV spectroscopy is widely used to determine the extent of conjugation in polymers. The value of λ_{max} increases with the extent of conjugation.
- (2) Distinction between Conjugated & Non-Conjugated Compounds – UV spectroscopy distinguishes b/w conjugated & non-conjugated compounds.



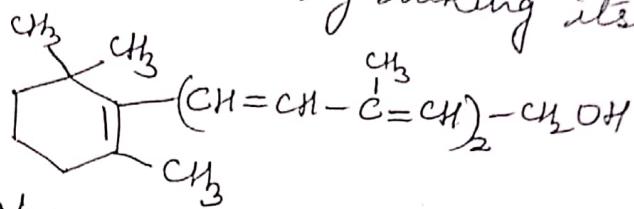
The compound (a) will have longer λ_{max} value because C=O groups is in conjugation with double bond.

- (3) Detection of geometrical isomer – Geometrical isomers can be distinguished by UV-visible spectroscopy. The trans isomers exhibit λ_{max} at slightly longer wavelength than cis-isomers.

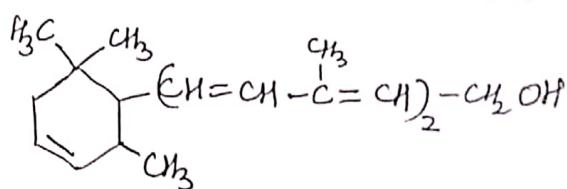


(4) Detection of functional group - In electronic characteristic λ_{max} corresponding spectrum we have to a particular group. The absence of any absorption above $\lambda_{\text{max}} = 200 \text{ nm}$ indicates the absence of conjugation, carbonyl groups and benzene ring in the compound. Therefore, functional groups can easily be identified by UV-visible spectroscopy.

(5) Identification of a compound - Vit. A can be identified in very dilute solutions by taking its UV-spectrum.



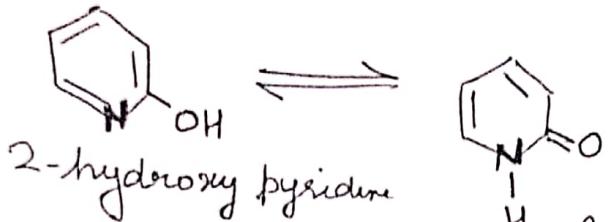
Vit A₁, $\lambda_{\text{max}} = 326 \text{ nm}$



Vitamin A₂, $\lambda_{\text{max}} = 287 \text{ nm}$

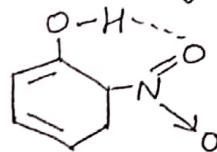
(6) Detection of Impurity - It is a powerful method for the detection of impurity in a number of industrial compounds. The common impurity of benzene in industrial cyclohexane can be detected by its absorption at 255 nm.

(7) Detection of keto-enol tautomerism - If a molecule exists in two tautomeric forms, preference of one over the other can be detected by UV spectroscopy.

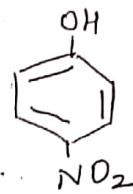


The spectra of these two compounds were found to favour pyridone-2 which is an $\alpha\beta$ -unsaturated ketone. So the equilibrium is shifted towards the right.

(8) Hydrogen Bonding - Intermolecular hydrogen bonding has very little effect on UV absorption but intra molecular hydrogen bonding results in bathochromic shifts due to stabilization of the excited state.



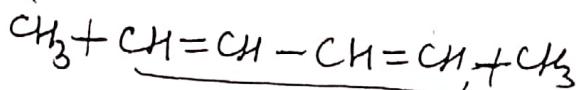
O-nitro phenol
 $\lambda_{max} = 400 \text{ nm}$



P-nitro phenol
 $\lambda_{max} = 329 \text{ nm}$

Numericals

- ① Calculate the absorption max. in UV spectrum of 2,4 Hexadiene



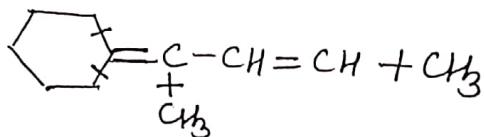
(There are 2 ~~double bonds~~ alkyl substituents)

$$\text{Basic Value} = 217 \text{ nm}$$

$$2 \text{ alkyl Substituent} = \frac{10 \text{ nm}}{(2 \times 5)}$$

$$\text{Calculated Value} = \underline{\underline{227 \text{ nm}}}$$

- ② Calculate the λ_{\max} (absorption max.)



It is a 1,4-butadiene system. There are two alkyl substituents and two ring residues on the double bonds. 1 exocyclic double bond is present.

Absorption max. is calculated as follows—

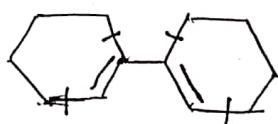
$$\text{Basic Value} = 217 \text{ nm}$$

$$2 \text{ alkyl sub.} = \frac{10 \text{ nm}}{(2 \times 5)}$$

$$2 \text{ Ring Residue} = 10 \text{ nm}$$

$$1 \text{ exocyclic double bond} = \frac{5 \text{ nm}}{242 \text{ nm}}$$

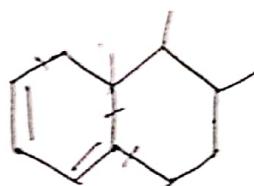
- ③ Calculate the λ_{\max} for



- Heteroannular diene
- 4 ring residues

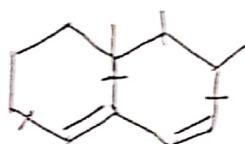
$$\begin{aligned} \text{Basic Value} &= 214 \text{ nm} \\ \text{ring residues } (4 \times 5) &= \frac{20 \text{ nm}}{234 \text{ nm}} \end{aligned}$$

④ Calculate the absorption maximum for the compound.



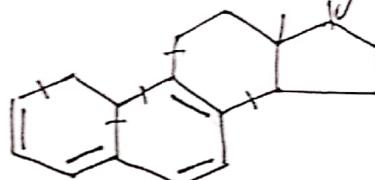
$$\begin{array}{r}
 \text{Basic Value} = 253 \text{ nm} \\
 3 \text{ ring residue} = 15 \text{ nm} \\
 (3 \times 5) \\
 1 \text{ exocyclic double bond} = 5 \text{ nm} \\
 \hline
 273 \text{ nm}
 \end{array}$$

⑤ Calculate the absorption maximum for the comp



$$\begin{array}{r}
 \text{Basic value} = 214 \text{ nm} \\
 3 \text{ ring residue} = 15 \text{ nm} \\
 (3 \times 5) \\
 1 \text{ exocyclic double bond} = 5 \text{ nm} \\
 \hline
 235 \text{ nm}
 \end{array}$$

⑥ Calculate the value of absorption max. for -



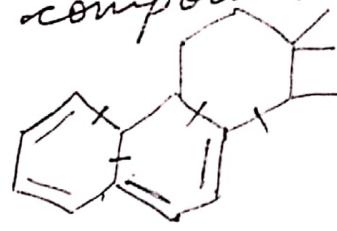
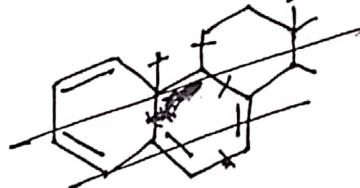
$$\begin{array}{r}
 \text{Basic value} = 253 \text{ nm} \\
 5 \text{ ring residue} = 25 \text{ nm} \\
 (5 \times 5) \\
 2 \text{ double bond extending conjugation} = 60 \text{ nm} \\
 (2 \times 30) \\
 1 \text{ exocyclic double bond} = 5 \text{ nm}
 \end{array}$$

$$\begin{array}{r}
 \hline
 343 \text{ nm}
 \end{array}$$

Note - In case both heteroannular and homoannular conjugated diene system are present in the same compound, then calculations are based on longer wavelength.
i.e. for homoannular i.e. 253 nm.

⑦

Calculate λ_{max} for the compound



$$\text{Basic value} = 253 \text{ nm}$$

$$4 \text{ Ring Residue} = 20 \text{ nm}$$

$$2 \text{ Exocyclic double bond} = 10 \text{ nm}$$

$$1 \text{ double bond extending} = 30 \text{ nm}$$

$$\text{Conjugation} \quad \underline{\hspace{1cm}}$$

$$\text{Calculated Value} = \underline{312 \text{ nm}}$$

UV-absorption in α,β -Unsaturated Carbonyl Compounds

Woodward and Fieser framed certain rules for estimating the absorption max for α,β unsaturated carbonyl compounds. These rules were later modified by Scott and are as follows -

① Basic value = 215 nm

For a compound $C=C=CH-CO-X$, basic value = 215 nm,
(where X is an alkyl gp)

(Aldehyde) If $X \Rightarrow H$, basic value = 207 nm.

(Arid) If $X \Rightarrow OH$ or OR , basic value = 193 nm.

② If double bond and the carbonyl group are contained in a five membered ring, then for such α,β unsaturated comp.,
basic value = 202 nm.



The structural increment for estimating λ_{max} for a given α,β -unsaturated carbonyl comp. are as follows.

- (1) For each exocyclic double bond $= +5 \text{ nm}$
- (2) " " alkyl substituent $= +5$
- (3) " " ring residue $= +5$
- (4) For each alkyl substituent or ring residue at -
 - α -position $= +10 \text{ nm}$
 - β - " $= +12 \text{ nm}$
 - γ or δ " $= +18 \text{ nm}$.
- (5) For each double bond extending conjugation $= +30 \text{ nm}$.
- (6) For homoannular conjugated diene $= +39 \text{ nm}$

chromophore Increment

-OH