UNIT–III

A

ELECTRONIC SPECTROSCOPY

In Spectroscopy, the molecule is exposed to different types of radiations and the responses given by the molecule are recorded with the help of a device called Spectrophotometer, in the form of a graph also known as Spectrum. A molecule when exposed to radiation absorbs part of it and gets excited to higher energy level. The amount and type of wavelength of radiation absorbed by the molecule in order to reach the excited state depends upon the structural features of the molecule. By studying the spectrum thus obtained, it is possible to throw light on the chemical constitution of the molecules.

Spectroscopy is, therefore, the study of molecular responses when it is exposed to certain kind of radiations.

The absorption of different types of radiations such as UV, Visible, Infrared, Microwave, Radiowaves produce different kinds of excitations of the molecule and each excitation provides some important information about the structure. Since in all these methods, the nature of radiation absorbed is studied, the Spectroscopic methods are designated as absorption Spectroscopy.

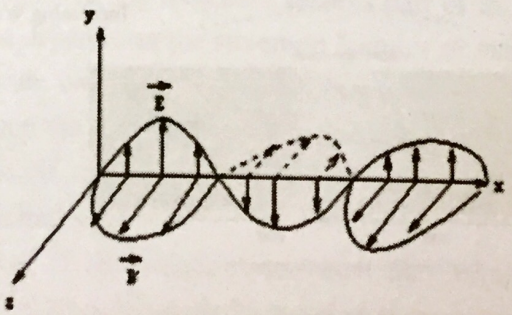
(The Ultra-Violet region, which extends from 200-400 nm and the visible one ranging from 400-800 nm are very useful)

In absorption spectroscopy, the molecule is different kinds of radiations. Therefore it is necessary to study the properties of radiations.

➢ NATURE OF ELECTROMAGNETIC RADIATIONS

Radiations exhibit dual nature i.e. particle and wave form. In studying spectroscopy more emphasis is given on wave form of the radiation.

Radiations when propagate in wave form produce electric and magnetic fields. The directions of their propagation are mutually perpendicular to each other as shown in the fig. (1).



Where X→ Axis of propagation of radiation

Y→ Axis represents direction of magnetic field

Z→ Axis represents direction of electric field.

The various parameters associated with the wave form of radiation are

1. Wave length (λ)
2. Amplitude (a)
3. Energy (E)
4. Frequency (ν)
5. Wave number ($\bar{\upsilon}$)

The units commonly used for the measurement of wave parameters are as under

i) Wave length (λ) is measured in number of units depending on the type of radiation studied

1 A° (Angstrom) = 10^{-8} cm = 10^{-10} m

1 nm (Nanometer) = 10^{-7} cm = 10^{-9} m

1 μ (Micron) = 10^{-4} cm = 10^{-6} m

ii) Frequency (ν) is measured in either Hertz or Cycles per second

1Hz (Hertz) = 1 Cycle per second (cps)

1 KHz (Kilo Hertz) = 10^3 Hertz

1 MHz = 10^6 Hertz

iii) Wave number ($\bar{\upsilon}$) is measured in term of number of waves/cm = cm^{-1} or Kaysers (K) where

1 kayser = 1 cm^{-1}

iv) Energy (E) is measured in ergs or joules

10^7 Ergs = 1 Joule

The spectrum of electromagnetic radiation is shown in the table (1) with increasing wavelengths or decreasing frequencies.

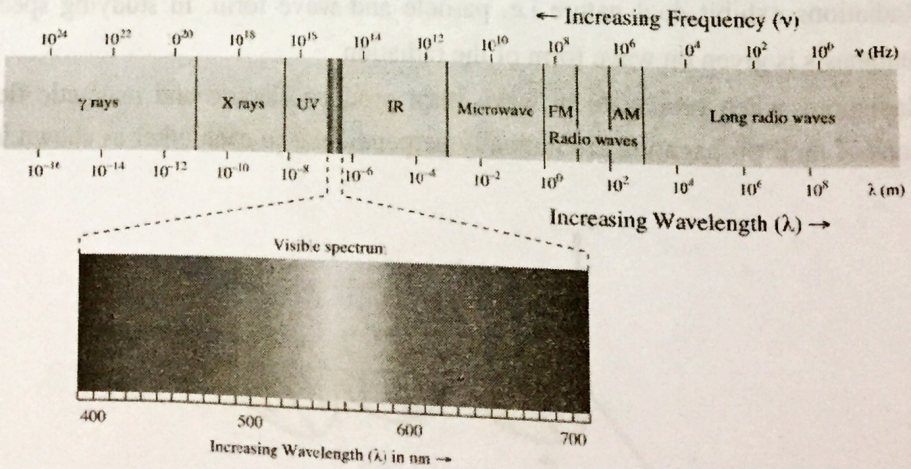
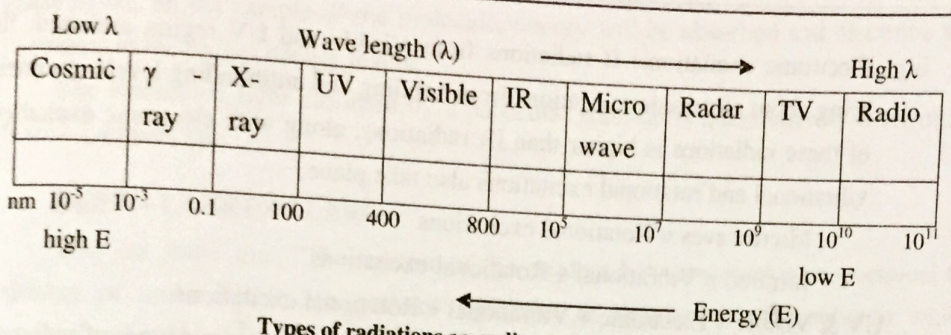


Fig. 3.2 : Electromagnetic spectrum



Types of radiations according to wavelength

Table No. 1

The above table shows that, cosmic rays have the shortest wavelengths, and highest energy and radio waves have the longest wavelengths and lowest energy. As we move from left hand side to right hand side in the above table the wavelength goes on increasing and hence energy and frequency go on decreasing. The visible region represents only a small portion of electromagnetic spectrum (400 – 800 nm). The portion above the visible region is called Infra- red while below it is Ultra –violet region. Although all types of radiations travel as waves with same velocity yet they differ from one another in certain properties

For example, X – rays can pass through glass and muscle tissues. Radio waves pass through air. Visible, Ultraviolet and Infra-red radiation can be bent by reflection or diffraction in a prism. It is observed that when radiation of certain frequency and energy (ΔE equal to hν) are passed through an organic compound, the electrons of the component atoms are excited. In addition the vibrational and rotational energies of the molecules as a whole are quantized. Thus, any wavelength of light that a particular molecule absorbs will be due to changes in the electronic, vibrational and rotational energy levels permissible for its atoms. The wavelengths absorbed are measured and recorded in the form of a spectrum with the help of a device called Spectrophotometer. If we plot the changes in absorption against wavelength, we get absorption bands which are highly characteristic of a compound and the technique provides an excellent tool to elucidate the molecular structure of an unknown compound.

➢ INTERACTION OF RADIATION WITH MATTER

When radiation strikes molecules, the molecule absorbs part of it. The wavelength or frequency of radiation absorbed depends on the structural features of molecules. As a result of absorption of energy, molecule undergoes excitation (higher energy state). The type of excitation produced depends upon the energy of the radiation employed.

i) Rotational excitations: If microwaves are used ($\lambda = 10^5$ to 10^7 nm) molecules undergo rotational excitations.

ii) Vibrational excitations: If IR radiations are used they bring about vibrational excitation. As energy of IR radiation is higher than microwave ($800 - 10^{-5}$) along with vibrational excitations, rotational excitations also takes place.

iii) Electronic excitations: If radiations from Visible and UV region are used, they bring about electronic excitations from bonding and antibonding levels. As energy of these radiations is higher than IR radiations, along with electronic excitations, vibrational and rotational excitations also take place.

Microwaves = Rotational excitations

Infrared = Vibrational + Rotational excitations

UV & Visible = Electronic + Vibrational + Rotational excitations

In the study of spectroscopy, the molecule is exposed to the various types of radiations. The wavelength of the radiation slowly changed from minimum to maximum in the given region and the absorption at every wave length is recorded. A graph wavelength vs Absorbance is then plotted.

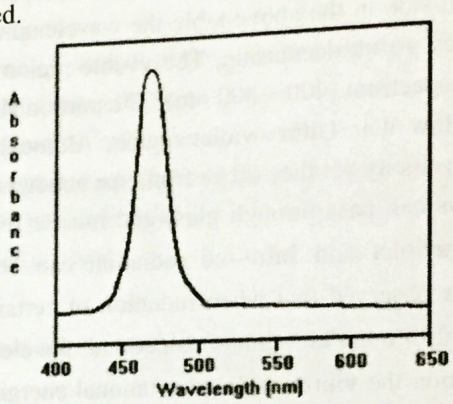


Fig. 3.3 : Graph of wavelength vs Absorbance

We see that, at a particular wavelength the absorption is maximum. The wavelength at which there is maximum absorption observed is called as wavelength maximum (λ max). This is a characteristic property of the molecule and helps in elucidating its structure.

➢ ULTRA–VIOLET (UV) AND VISIBLE SPECTROSCOPY (ELECTRONIC SPECTROSCOPY)

The Ultra violet region, which extends from 200 – 400 nm and the visible region from 400 – 800 nm are more useful to organic chemists. They bring about electronic excitations in the molecule from bonding levels to antibonding levels.

UV – Visible spectroscopy provides information about the structure of the molecule contains double bond or triple bond or conjugated bonds. It also helps in distinguishing conjugated and isolated dienes, dienes and trienes, carbonyl compounds and α, β – unsaturated carbonyl compounds and cis and trans isomers.

Since the energy level of a molecule is quantized, the energy required to bring about the excitation is a fixed quantity. Thus, the electromagnetic radiation with only a particular value of frequency will be able to cause excitation. If a radiation of correct frequency is

made to fall on the sample of the molecule, energy will be absorbed and electrons will be promoted to the higher energy levels.

The amount of light absorbed by a particular solution is quantitatively determined by Beer – Lambert law.

➢ BEER – LAMBERT LAW

This law states that, "The fraction of the incident light absorbed is proportional to the number of molecules in the path of light that is absorbed by the solution which is proportional to its concentration.

$$\log \frac{I_0}{I} A = \varepsilon \times C \times l$$

Where, I_0 = Intensity of incident light,

I = Intensity of transmitted light

A = Absorbance

ε = Extension coefficient

C = Concentration of solution (moles / litre)

l = Length of the cell (cm)

Since concentration and length of the cell are known, absorbance (A) can be calculated by using equation

$$A = \varepsilon \times C \times l$$

The UV spectra are usually recorded as absorption (A) vs wavelength (λ). The intensity of peak is found out by plotting ε or log ε vs wavelength. The intensity of absorption (ε) depends upon following two things

i) Size of the molecule

ii) Change in dipole moment

The value of will be more if change in dipole moment is more. If there is no change in dipole moment the value of ε becomes zero.

➢ INSTRUMENTATION (SPECTROPHOTOMETER):

Spectrophotometer is a device which detects the percentage transmittance of light radiation when light of certain intensity and frequency range is passed through the sample. The modern UV-Visible spectrophotometer consists of following components

(i) **Radiation source:** A deuterium or hydrogen lamps discharge of the range 180-400 nm or tungsten filament lamp of wavelength greater than 375 nm are used as radiation source.

(ii) **Sample container:** It is a quartz or fused silica transparent cell of 1 cm path length. (Glass cell cannot be used as glass absorbs light strongly below 300 nm).

For an accurate work the sample and reference cells should be in optical path length.

(iii) **Monochromator:** The incident radiation is dispersed with the help of a rotating prism and the various wavelengths thus separated are passed through a specially devised slit to select a monochromatic beam of desired wavelength. It is then divided into two beams of equal intensity. (Thus light from the first dispersion is passed through a slit called Monochromator and then sent to second dispersion, light passes through the exit slit.

(iv) **Detector:** Spectrometer electronically subtracts the absorption of the solvent in the reference beam from the absorption of the solution. The signed for the intensity of absorbance Vs corresponding wavelength is automatically recorded on the graph with the help of detector.

(v) **Amplifier:** The amplifier is coupled to a small servomotor, which drives an optical wedge into the reference beam until the Photoelectric cell receives light of equal intensities from the sample as well as reference beams.

(vi) **Recorder:** Amplifier is also coupled with a small servomotor which in turn is coupled to a pen recorder. It records the absorption bands automatically.

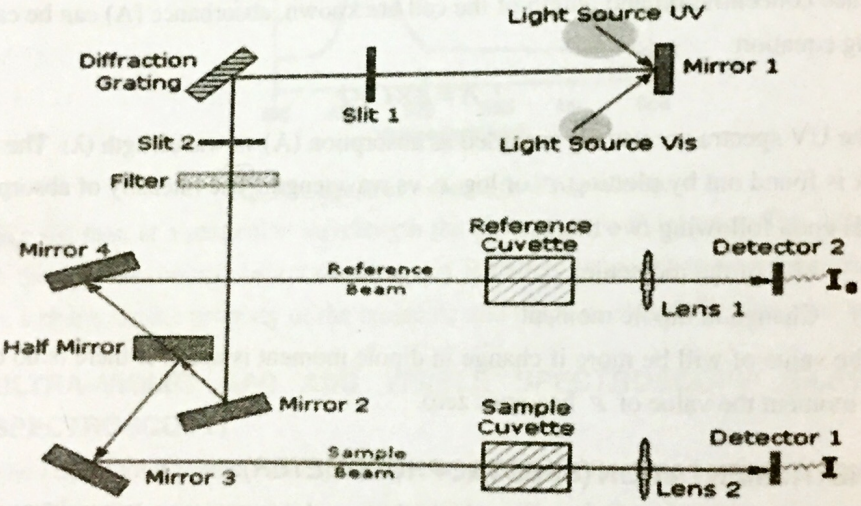


Fig. 3.4 : Ultra-Violet Spectrophotometer

(vii) **Sample and Solvent:** It is essential that a spectrum should be recorded in dilute solutions and solvent must be transparent within the range of wavelength being examined. Only 0.1 mg of pure and dry sample is dissolved in about 100 ml non absorbing solvent like cyclohexane, 1, 4–dioxane, water or 95% ethyl alcohol. (Absolute alcohol cannot be used as it contains traces of benzene which shows peak at 225 nm). Sometimes a sample in pure gaseous state may be used.

The ordinary Spectrometers cover a range 220 – 800 nm. In order to study transitions below 200 nm (Far UV), vacuum ultra violet apparatus is used.

Working

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 intensities of the respective transmitted beams are then compared over the whole wavelength range of the instrument. The spectrophotometer electronically subtracts the absorption of the solvent in the reference beam from the absorption of the solution. The signal for the intensity of absorbance versus corresponding wavelength is automatically recorded on the graph. The spectrum is usually plotted as absorbance (A) against wavelength (λ). The plot is often represented as λ max.

Types of Electronic Transitions

UV – Visible radiations are more energetic. Absorption of these radiations by an organic compound brings about electronic excitations. The process of electronic excitation is accompanied by a large number of vibrational and still larger number of rotational changes.

$$E = E_{electronic} + E_{vibrational} + E_{rotational}$$

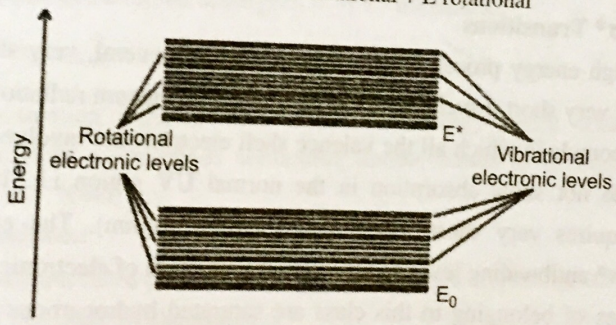


Fig. 3.5 : Energy levels

The absorption of electronic radiation of wavelength 200 – 750 nm can cause excitation of electron from occupied bonding molecular orbital (lower energy) to unoccupied antibonding orbital (Higher energy). This excitation is called electronic excitation.

There are three kinds of electrons present in organic molecule viz.

i) σ – electrons present in Sigma bonds

ii) π - electrons present in pi – bonds

iii) n – nonbonding electrons present as unshared electrons

Sigma (σ) and pi (π) electrons have corresponding higher energy antibonding molecular orbitals (σ^*, π^*), but there is no higher energy antibonding molecular orbital corresponding to non bonding electrons.

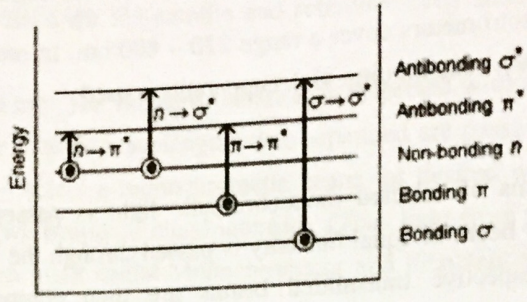


Fig. 3.6 : Electronic transitions

The absorption of electromagnetic radiations by an organic molecule in the UV – VIS region involves promotion of electrons (σ, π, n) from ground state to higher energy state (σ*, π*) as shown in the above figure. The wavelength of absorption depends upon the energy difference ($\Delta E = E_2 - E_1$) between bonding orbital and nonbonding orbital.

The relation between wavelength and energy is $E = hc/\lambda$

From this equation it is clear that, smaller the energy required for excitation of electron, longer is the wavelength absorption. The value of ΔE depends upon molecular structure and hence indirectly the value of λmax is also dependent on the molecular structure. The relative energies for these transitions are in the following order

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

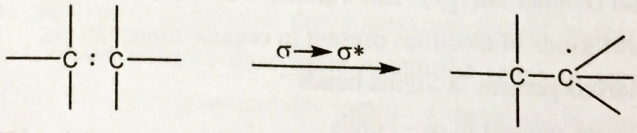
These are four major types of excitations taking place in the molecule.

1. σ → σ* Transitions

It is a high energy process since σ bonds are in general, very strong and absorption takes place at very short wavelength (150 nm) when in vacuum radiations are absorbed. The organic compounds in which all the valence shell electrons are involved in the formation of σ – bonds do not show absorption in the normal UV region i.e. 180 – 400 nm. Such transition requires very short wavelength (below 200 nm). The excitation of σ bond electrons to σ* antibonding level occurs with net retention of electronic spin.

Examples of belonging to this class are saturated hydrocarbons like methane, ethane and other paraffins.

As absorption in this region is beyond the range of ordinary UV Spectrophotometer hence it is less informative.

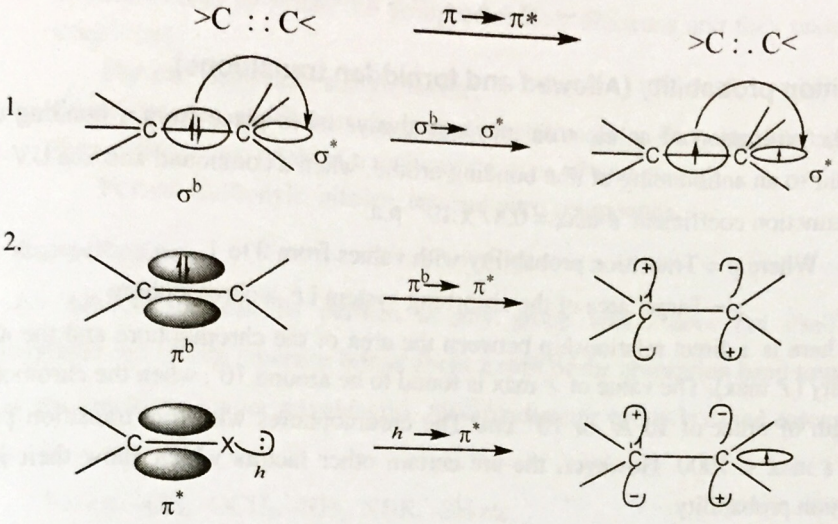


2. π → π* Transitions

In this case the transition of Pi (π) electron from bonding to antibonding (π*) orbital takes place. Compounds containing double or triple bonds and also aromatics show such transitions.

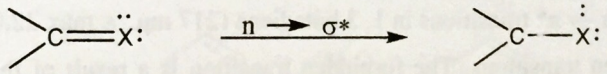
The excitations of π electrons require smaller energy and hence transitions of this type occur at longer wavelength.

For example: Alkenes, Alkynes, Carbonyl compounds, Cyanides, Azo compounds etc.



3. n → π* Transitions

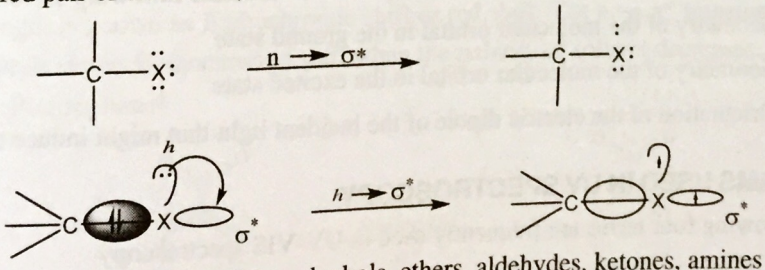
In this type of transition the promotion of electrons from nonbonding (n) orbital to higher energy antibonding π* orbital takes place. Unsaturated compounds containing hetero atoms with unshared pair of electrons undergoes n → π* transition.



This type of transition requires least amount of energy hence occurs at longer wavelengths. For example: Compounds containing double bonds involving hetero atoms such as C=O, C=S, C=N, N=O, etc.

4. n → σ* Transitions

This type of transition takes place in saturated compounds containing one hetero atom with unshared pair of electrons (n electrons).



For example: Saturated halides, alcohols, ethers, aldehydes, ketones, amines etc.

These transitions are less energetic and also occur at longer wavelengths. But the π values for these transitions are very small hence absorption is very weak. Therefore from the point of view of structure determination n → σ* transitions are less significant.

Out of four types of electronic transitions, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are less energetic and absorption occurs in the UV region, hence very useful for structural elucidation of organic molecules. Their relative energies are in the following order

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

Transition probability (Allowed and forbidden transitions)

The promotion of an electron may not always takes place from a bonding orbital or loan pair to an antibonding of non bonding orbital, when a compound absorbs UV-Vis light. The extinction coefficient ε max = 0.87×10^{20} p.a.

Where p = Transition probability with values from 0 to 1

a = Target area of the absorbing system i.e. a chromophore

There is a direct relationship between the area of the chromophore and the absorption intensity (ε max). The value of ε max is found to be around 10^5, when the chromophore has a length of order of 10 A^o or 10^{-7} cm. The chromophores with low transition probability have ε max < 1000. However, the are certain other factors which show their impact on transition probability.

Depending upon the symmetry and the value of ε max, the transition may either be allowed or forbidden.

i) Allowed transition: The transition with the values of Extinction coefficient (ε max) more than 10^4 are usually called allowed transitions.

For ex. $\pi \rightarrow \pi^*$ transitions in 1, 3 butadiene (217 mμ, ε max 22,000).

ii) Forbidden transitions: The forbidden transition is a result of the excitation of one electron from the loan pair present on the hetero atom to an antibonding π^* orbital. The values of ε max for forbidden transitions are generally below 10^4.

For ex. $n \rightarrow \pi^*$ transition in carbonyl compounds (ε max 10-100)

In order to decide whether the transition is allowed or forbidden for symmetrical and totally unsymmetrical molecules, it is important to consider following factors:

a) Geometry of the molecular orbital in the ground state

b) Geometry of the molecular orbital in the excited state

c) Orientation of the electric dipole of the incident light that might induce transition.

➢ TERMS USED IN UV SPECTROSCOPY

Following four terms are frequently used in UV-VIS spectroscopy

1. Chromophore

It is defined as any isolated covalently bonded group that shows a characteristic absorption in the UV-Visible region. The coinage of this word comes from Greek i.e.

Chroma = Colour and Phoros = Bearing. So chromophores are colour bearing units of the molecules.

There are two types of chromophores

i) Chromophores in which the group contains π electrons and they undergo $\pi \rightarrow \pi^*$ transitions.

For ex. Ethylenes, acetylenes etc.

ii) Chromophores which contain both π electrons and n (non bonding) electrons and they undergo two types of transitions i.e. $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$.

For ex. Carbonyls, nitriles, azo and nitro compounds.

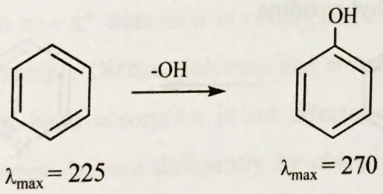
2. Auxochrome

An auxochrome can be defined as any group which does not itself acts as a chromophore but whose presence brings about a shift of the absorption band towards the red end of the spectrum (longer wavelength). An auxochromic group is called colour enhancing group.

For ex. –OH, $-OCH_3$, $-NH_2$, NHR, -SH etc.

The effect of auxochromic group is due to its ability to extend the conjugation of a chromophore by the sharing of non bonding electrons. Thus a new chromophore results which has different value of absorption maximum as well as extinction coefficient.

For ex.

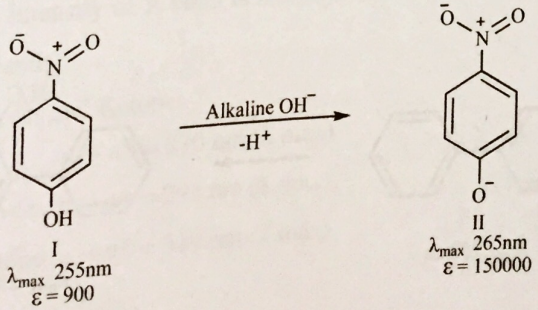


$\lambda_{max} = 225$ $\lambda_{max} = 270$

3. Bathochromic Shift (Red Shift)

An absorption due to auxochrome or by the change of solvent towards longer wavelength is known as Bathochromic shift or red shift. The $n \rightarrow \pi^*$ transition for carbonyl compounds shows Bathochromic shift when the polarity of solvent decreases.

For ex. P-nitrophenol



I
λ_{max} 255nm
$\varepsilon = 900$

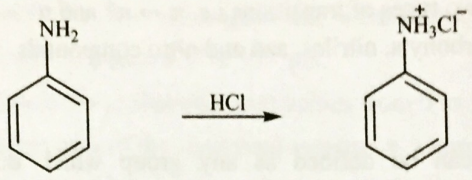
II
λ_{max} 265nm
$\varepsilon = 150000$

As compared to unshared electron pair present on (-OH) the negatively charged oxygen (II) delocalizes more effectively and cause red shift.

4. Hypsochromic shift (Blue shift)

It is an effect in which the absorption is shifted towards shorter wavelength. It may be caused by the removal of conjugation and also by changing the polarity of the solvent.

For ex. Aniline shows blue shift in acidic medium.



(II)

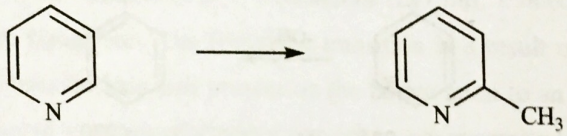
λ_{max} 230nm λ_{max} 203nm

In acidic medium, an unshared pair on nitrogen of aniline is not available for delocalization in cation (II).

5. Hyperchromic shift

Absorption of electromagnetic radiations having greater intensity is called hyperchromic shift (ε value large).

For ex. Pyridine and 2-methyl pyridine



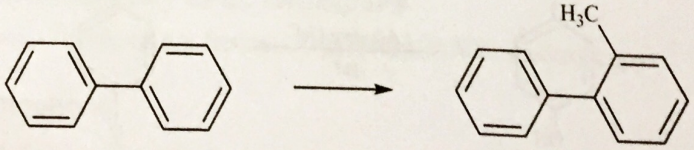
λ_{max} 257nm λ_{max} 262nm

The introduction of auxochrome ($-CH_3$) usually increases intensity of absorption.

6. Hypochromic shift

Absorption of electromagnetic radiation having lesser intensity is called hypochromic shift (ε value small).

For ex. Biphenyls



λ_{max} 250nm λ_{max} 237nm

The introduction of group which distorts geometry of the molecule causes hypochromic shift.

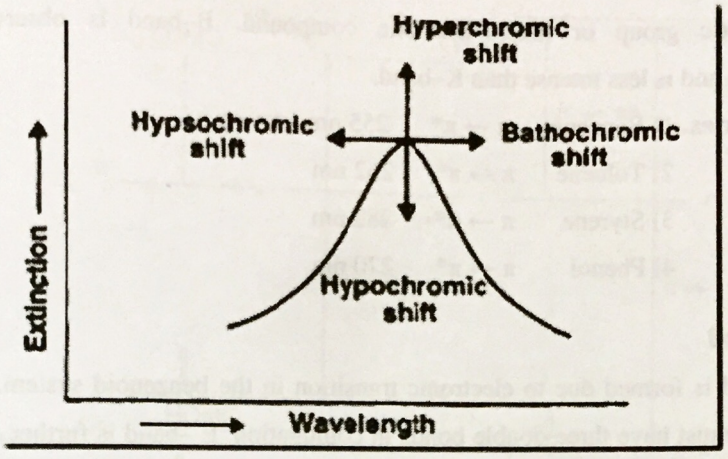


Fig. 3.7 : Absorption and intensity shifts

➢ EFFECT OF SOLVENT ON UV SPECTRUM

The polarity of solvent also affects the various types of band-

1. K-band (K = Konjugierte - German)

K-band is formed due to $\pi \rightarrow \pi^*$ transition in conjugated molecule and intensity of K band is more than 10^4. For example Dienes, polyenes and aromatic compounds substituted by chromophore. Generally K-band absorption is not affected by polarity of solvent but exceptionally 'enes' and 'enones' behave differently by changing the polarity of solvent. Enone shows red shift while changing the polarity of solvent.

2. R-band (R = Radikalartig)

This band is formed due to $n \rightarrow \pi^*$ transition of mostly carbonyl group of aldehydes and ketone. For its formation it is necessary to have lone pair of electrons and a chromophoric group. Intensity of R band is less than 10^4 or even below 100. R –band also known as forbidden bands.

For example: Aldehydes and Ketones

i) Acetone $n \rightarrow \pi^* = 270$ nm (λ max)

ii) Acetaldehyde $n \rightarrow \pi^* = 293$ nm (λ max)

iii) Acetophenone $n \rightarrow \pi^* = 319$ nm (λ max)

3. B-band

B – band is formed due to $\pi \rightarrow \pi^*$ transition in aromatic compound having chromophoric group or hetero–aromatic compound. B–band is observed at longer wavelength and is less intense than K–band.

For ex. 1) Benzene $\pi \rightarrow \pi^*$ 255 nm

2) Toluene $\pi \rightarrow \pi^*$ 262 nm

3) Styrene $\pi \rightarrow \pi^*$ 282 nm

4) Phenol $\pi \rightarrow \pi^*$ 270 nm

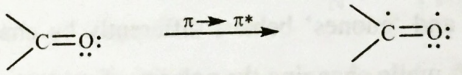
4. E-band

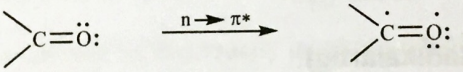
E-band is formed due to electronic transition in the benzenoid system. For E – band compound must have three double bonds in conjugation. E –band is further classified as E_1 and E_2.

For ex.	Compound	E_1- band	E_2–band
1)	Benzene	184 nm	204 nm
2)	Naphthalene	221 nm	286 nm
3)	Anthracene	256 nm	375 nm

➢ UV BAND FOR CARBONYL COMPOUND:

Any compound containing carbonyl group shows two important transitions ie. $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$

1 

2 

In $\pi \rightarrow \pi^*$ transition one π electron is promoted to antibonding π^* orbital whereas in other $n \rightarrow \pi^*$ transition involve one electron from non-bonding orbital get promoted to π^* antibonding orbitals.

The $n \rightarrow \pi^*$transition requires less amount of energy as compared to $\pi \rightarrow \pi^*$ transition; in other words $n \rightarrow \pi^*$ transition occurs at longer wavelength where as $\pi \rightarrow \pi^*$ transition occur at shorter wavelengths.

This can be explain from following M.O. Diagram.

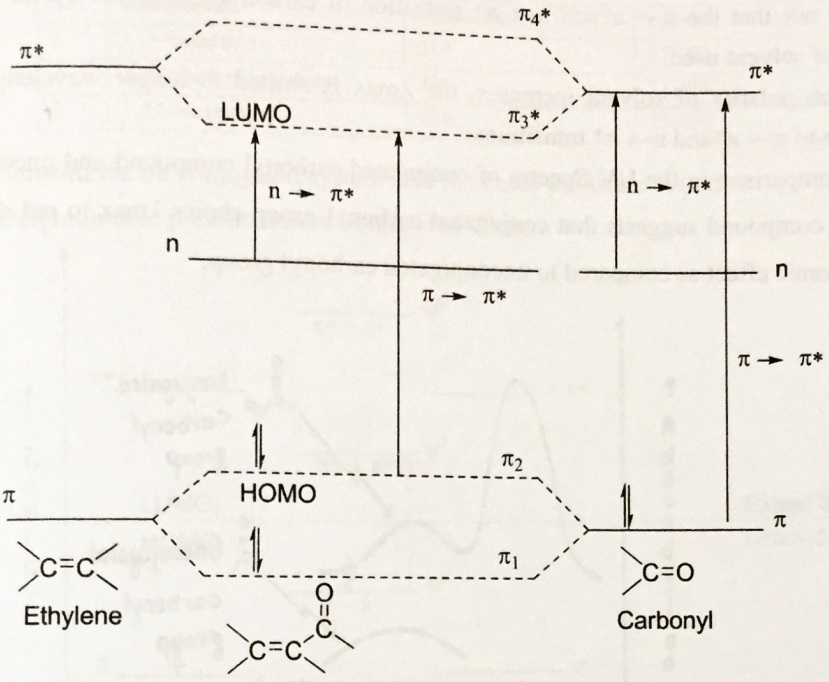


Fig. 3.8 : UV transition in α, β-unsaturated carbonyl compound.

From the M.O. Diagram it is observed that the π_2 level of HOMO component has higher energy than π level of C=C and C=O chromophoric group also the π_3*level of LUMO component has lesser energy and hence it is lower than π^* antibonding orbital of C=C and C=O chromophoric group and thus electron transfer can occur from n→ π_3^* orbital which is called as R-band.

In α, β-unsaturated carbonyl compound, the double bond and carbonyl group are in conjugation and hence due to resonance it increases the single bond character of carbonyl group. Also due to resonance the electron density is spread at four atoms.

The spectra of α, β-unsaturated carbonyl compound is simply the summation of ethylene and carbonyl chromophores. Due to the conjugation, the λmax is shifted to longer wavelength thus bathochromic shift is observed

The energy level diagram shows that π_2 energy level of HOMO is higher than both π energy level of C=C and C=O. Similarly the π_3^* energy level of LUMO is lower than both the π energy level of C=C and C=O chromophore group.

Since the energy level of HOMO and LUMO is less and thus $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition shows bathochromic shift and $n \rightarrow \pi^*$ transition is called R-band.

A weak band at 275 to 295nm with ε max =10-100 is a positive identification of aldehyde or ketonic carbonyl group.

It is not that the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition of carbonyl compound varies with the polarity of solvent used.

When polarity of solvent increases, the λmax is shifted to longer wavelength (Red shift) due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

A comparison in the UV Spectra of conjugated carbonyl compound and unconjugated carbonyl compound suggests that conjugated carbonyl group shows λmax to red shift with hyperchromic effect as compared to unconjugated carbonyl group.

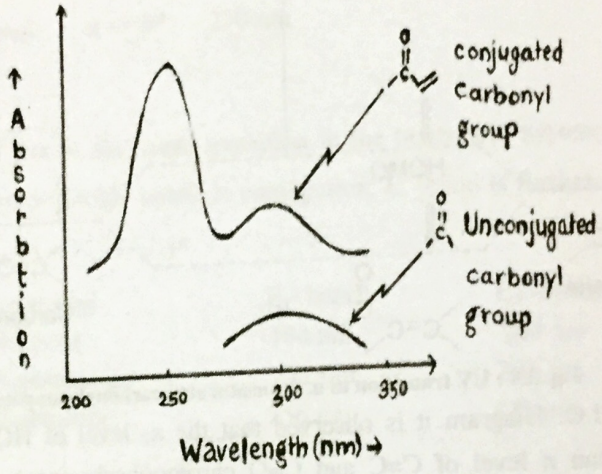


Fig. 3.9 : UV Spectra of conjugated and unconjugated carbonyl compound.

➢ UV BANDS IN DIENES

The ethylene absorbs at 170nm for $\pi \rightarrow \pi^*$ transition while 1,3-butadiene absorbs at 217nm. The reason for this is that 1,3-butadiene has two double bonds which are in conjugation i.e. two chromophoric group are in conjugation due to which electron density is spread over at least four atomic centres. But in ethylene electron density is spread over only two atomic centers.

In general whenever the chromophoric groups are in conjugation; the λmax. is always shifted to longer wavelength causing bathochromic shift (red shift).

The conjugated double bond shifts λmax towards higher wavelength with 15 to 45 nm as compare to isolated double bond, where the interaction of double bond is not posible as in conjugated system.

Also the chromophoric groups are in conjugation then ε_{max} (intensity) is also shifted to higher value. Thus this is the reason so that the $\pi \rightarrow \pi^*$ transition causes a band in the spectrum called as K-band.

The $\pi \rightarrow \pi^*$ transition in conjugated molecule with λ_{max} & ε_{max} value as discuss below.

S.N.	Compound	λmax (nm)	ε max
1	1, 3-Butadiene	217	21,000
2	2,3 Dimethyl butadiene	226	21,400
3	1,2,5 Hexatriene	254	21,400

Substitution on conjugated system also increases the λmax & ε max.

Diagrammatic presentation of conjugated Diene.

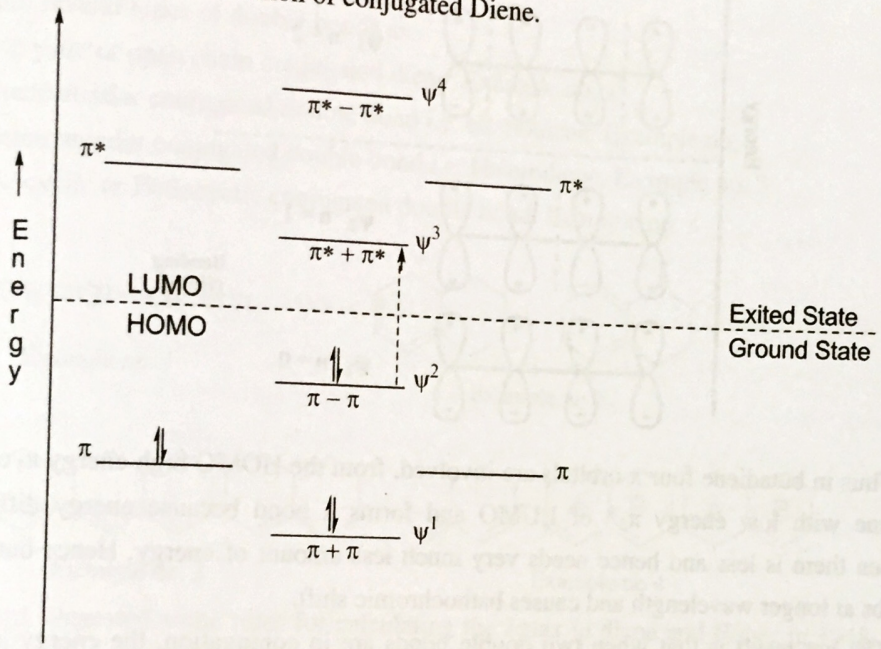


Fig.3.10 : Electronic excitation in conjugated diene

The conjugated butadiene consists of two ethylene unit. The ethylene molecule on excitation gives

$\dot{C}H_2$-$\dot{C}H_2$ diradical at 170nm but the butadiene at 217nm gives various excitations as shown below.

As Diene consist of two ethylene unit with four π bonding orbitals, two from each ethylene unit. The two π orbitals of each ethylene group interact to give two new bonding orbitals ie. Ψ_1 and Ψ_2.

Similarly π antibonding(i.e. π*)orbital produces two new antibonding orbitals ie. $\Psi_3$and Ψ_4.

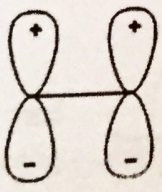


Fig.3.10 a): π bonding orbitals

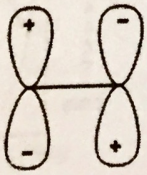
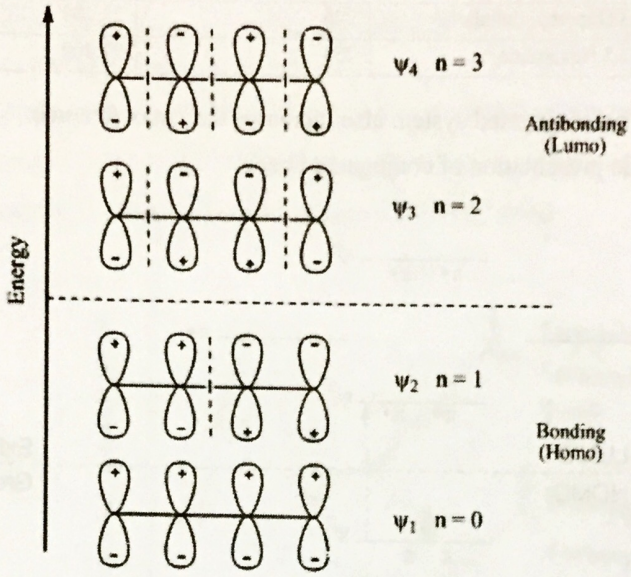


Fig.3.10 b): π* antibonding orbitals

The $\Psi_1, \Psi_2, \Psi_3 \Psi_4$. can be represented as follows.



Thus in butadiene four π orbitals are involved, from the HOMO high energy π_3 orbitals combine with low energy π_3* of LUMO and forms a bond because energy difference between them is less and hence needs very much less amount of energy. Hence butadiene absorbs at longer wavelength and causes bathochromic shift.

The net result is that when two double bonds are in conjugation, the energy level of higher occupied molecular orbital (HOMO) is raised and that of lowest unoccupied molecular orbital (LUMO) i.e. (antibonding) is decreased.

The increase in λmax as well as ε max due to conjugation also is well explained by following graph. (As conjugation increases, the energy gap between HOMO and LUMO decreases)

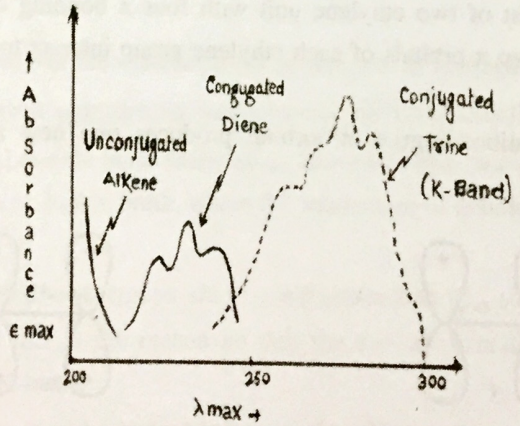


Fig.3.11: Absorption in conjugated and unconjugated systems.

➢ WOODWARD – FISCHER RULES FOR CONJUGATED DIENES

We know that substitution and conjugation of the diene increases the value of λ max and λmax increases towards the longer wavelength.

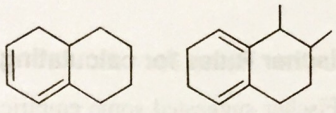
Due to increase in conjugation the conjugated polyene in which five double bonds are in conjugation appears coloured to the naked eye as they absorb high wavelength nearer to visible range.

There are several types of double bonds as:

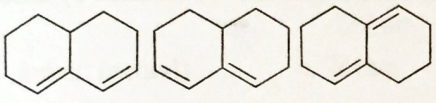
1. Alicyclic or open chain conjugated diene .Example no. 1
2. Homoannular conjugated double bond i.e. Homodiene. Example no. 2
3. Heteroannular conjugated double bond i.e. Heterodiene. Example no. 3
4. Exocyclic or Endocyclic conjugated double bond. Example no. 4

$CH_2{=}CH{-}CH{=}CH_2$

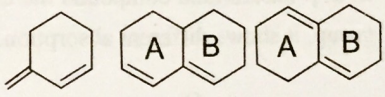
Example no. 1



Examole no 2



Example no. 3



Examole no 4

Woodward suggested some rules for calculating the λmax in diene and Fisher in 1948 modified this rule. According to Woodward Fisher rule each type (above given) of diene has fixed value of absorption called "basic value" and the substitution on the diene increase the λmax and thus they decide the value of substituents which is being added in the basic value to give the λmax of substituted diene.

Parent value

a) Butadiene or cyclic conjugated butadiene	217 nm
b) Acyclic triene	245 nm
c) Homoannular conjugated diene	253 nm
d) Heteroannular conjugated diene	215 nm

Increments for substitution

a) Alkyl substituents	5 nm
b) Ring residue	5 nm
c) Exocyclic double bond	30 nm
d) Double bond extending conjugation	15 nm
e) Bicyclic or strain correction	

Auxochrome

-Cl, -Br	+5 nm
-OR	+6 nm
-SR	+30 nm
$-NR_2$	+60 nm
$-OCOCH_3$	0 nm

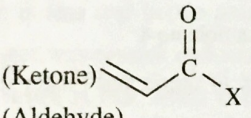
Note

1) If the cyclic diene or open chain conjugated diene is substituted by –Cl or –Br then, 17 nm is added in basic value.
2) The difference between calculated value and observed value of λmax should be lower than 5 nm.

Woodward – Fischer Rules for calculating λmax in α, β carbonyl compounds

Woodward Fischer suggested some empirical rule for the calculation of λmax in α, β unsaturated compound, which was modified by Scott, which are as follows

1) In α, β unsaturated compound the carbonyl carbon has been substituted by different group, it shows different absorption.



(Ketone) If X = R then base value 215 nm

(Aldehyde) If X = H then base value 207 nm

(Acid) If X = OH then base value 193 nm

2) In a cyclic ketone, if α, β unsaturated carbonyl group is a part of six member cyclic ring then basic value is taken as a 215 nm, but if α, β unsaturated carbonyl group is a part of five member ring then base value is taken as 202 nm

   The ε max for such compounds are generally 10^4

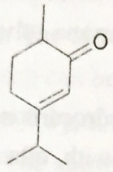
Structural increments for calculation of λmax in α, β unsaturated carbonyl compound

1) Exo-cyclic double bond = +5 nm
2) For each double bond extending conjugation = +30 nm
3) For a homo-anular conjugated diene = +39 nm
4) For each double bond endocyclic in 5 or 7 member ring except cyclo-pent-2 enone. = +5nm
5) Increment of various ouxochrome at various α, β, γ, δ position as follows (with respect to carbonyl group)

Chromophore	α	β	γ	δ (or higher position)
Ring residue	+10	+12	+18	+18
-R	+10	+12	+18	+18
-OR	+35	+30	+17	+31
-OH	+35	+30	-	+50
-OAc	+6	+6	+6	+6
-Cl	+15	+12	-	-
-Br	+25	+35	-	-

1. Calculate the λmax value for the following compounds.

i) α, β unsaturated ketone



Parent system = 215 nm

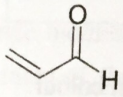
Substituents β (2×12) = 24 nm

λmax (calc) ———

239 nm

λmax (actual) = 241nm

ii) α, β unsaturated aldehyde



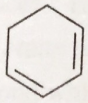
Parent system = 207 nm

λmax (calc) ——

207 nm

λmax (actual) = **210 nm**

iii) Diene system



Parent system = 217 nm

Homoannular diene = 36 nm

Alkyl Substituents (2×5) = 10 nm

λmax (calc) ——

263 nm

λmax (actual) 258 nm

➢ UV SPECTRA OF AROMATIC COMPOUND

As the conjugation in the compound increases, the λmax and ε max value also get shifted to higher value i.e. Bathochromic and hyperchromic effect are observed.

While studying the series of aromatic compounds like, Benzene, Naphthalene, Anthacene, Phenanthrene, etc the increase in aromaticity or conjugation increases the Bathochromic and hyperchromic effect.

The Benzene absorbs at 184nm; 60,000 ε max, 204nm; ε max 7400 with allowed transition and shows a B-band at 254 nm with ε max 204 ie. Forbidden transition. Benzene also shows intensity band between 230 and 270nm.

The B-band at 254nm given by Benzene is fineness structure in hexane solvents while in alcohol it is completely destroyed. (Shown in figure).

It is noted that absorption maxima for Poly-nuclear aromatic hydrocarbon moves to longer wavelength. While comparing the UV spectra of Benzene with other aromatic compounds shows increase in the value of λmax and ε max.

Absorption of Aromatic Compound:

S.N.	Compound Name	λ max.(nm)	max.	Transition.
1	Benzene	184 204 254	60,000 7400 204	Allowed Allowed Forbidden
2	Naphthalene	480	11,000	
3	Pentacene	580	12600	

Pentacene absorbs in visible range (400-800nm) and hence appears blue in colour.

➢ SPECTRA: COMMON UV SPECTRA.

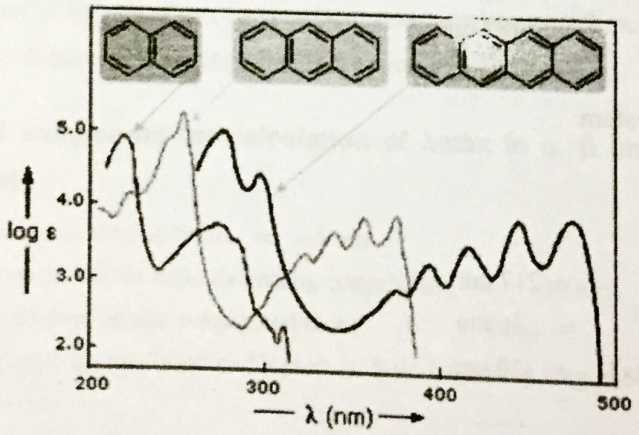


Fig.3.12: Electronic absorption spectra of typical Poly-nuclear aromatic hydrocarbon in Hexane