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ELECTROMAGNETIC SPECTRUM : ULTRAVIOLET ABSORPTION SPECTROSCOPY

CHAPTER

1.1. INTRODUCTION

One of the important fields of activities of an organic chemist is the determination of structural formulae of various substances. In the earlier days, the structure elucidation was mainly based upon the study of classical physical properties (melting point, boiling point, refractive index, etc.) and chemical reactions of the compound. The procedure involved was rather laborious and time consuming. However, in the last fifty years or so some remarkable physical methods have been developed to serve as powerful tools for structure analysis. Of these the most useful and commonly employed methods are the **spectroscopic methods** which are based upon the interaction of electromagnetic radiations with the substance under examination. These methods may further involve the study of ultraviolet (UV), infrared (IR), nuclear magnetic resonance (NMR) and mass spectra.

Mass spectroscopy is employed to determine the molecular mass and molecular formula of the substance while UV and IR are used to determine the nature of functional groups. Finally the NMR spectroscopy is used to know the complete structure including the stereochemistry of the substance.

The major advantages of employing these spectroscopic methods for structure determination and identification of substances are as follows :

- (i) They need very little time and the information obtained is often a permanent record in the form of a chart.
- (ii) The substance is required in very small quantities (of the order of 1 mg.).
- (iii) The methods are extremely sensitive and highly reliable in establishing the structure of compounds and analysis of mixtures of closely related compounds.
- (iv) They can be used for the detection and identification of even very short lived reaction intermediates.
- (v) During the spectroscopic studies (except mass spectroscopy), the compound is not generally affected chemically and can, therefore, be recovered unchanged.
- (vi) Continuous analysis is often possible facilitating the study of reaction rates, etc.

In this chapter, we shall deal with the basic aspects of ultraviolet spectroscopy.

1.2. THE ELECTROMAGNETIC SPECTRUM AND SPECTROSCOPIC STUDIES

1.2.1. Electromagnetic radiations

Many spectroscopic techniques are based upon the interaction of a compound with light or some other form of electromagnetic radiations. It is well known that light and other electromagnetic radiations are different forms of energy which have a dual character; they have the properties of both a wave and a particle. They are called **electromagnetic radiations** because they consist of oscillating electric and magnetic fields which are perpendicular to each other and perpendicular to the direction of motion of the radiations.

Some important characteristics of these radiations are :

- (i) The energy of these radiations is inversely proportional to their wavelength or directly proportional to their frequency. $E \propto \nu \propto \frac{1}{\lambda}$
- (ii) These radiations do not require any physical medium and can be transmitted through empty space. For example, light reaches us from the sun through empty space.
- (iii) All types of electromagnetic radiations travel through space with the same velocity which is 10^8 m s^{-1} .

Electromagnetic radiations can be described in terms of their characteristics such as wavelength and frequency.

1. Wavelength. It is the distance between two adjacent crests or troughs in a particular wave. It is denoted by the symbol λ (lambda).

The wavelength is usually expressed in meters (m), micrometers (μm), nanometers (nm) or angstroms (\AA)

$$1 \mu\text{m} = 10^{-6} \text{ m}; 1 \text{ nm} = 1 \times 10^{-9} \text{ m}; 1 \text{\AA} = 1 \times 10^{-10} \text{ m}$$

An older term for micrometer is micron, μ ($1\mu\text{m} = 1\mu$) and an older term for nanometer is millimicron, $\text{m}\mu$ [$1 \text{ nm} = 1 \text{ m}\mu$]

2. Frequency. It is the number of waves which pass across a point in one second. It is denoted by the symbol v (read as nu).

The frequency is generally expressed in cycles per second (cps) or simply s^{-1} or Hz (Hertz) [$1 \text{ Hz} = 1 \text{ cps}$].

The frequency and wavelength are related to each other as :

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

where c is the constant velocity of light.

3. Wave-number. It is the reciprocal of wavelength and represents the number of waves per centimeter.

It is denoted by the symbol \bar{v} .

Wave number is generally expressed in cm^{-1} (reciprocal centimeters).

Wave number is related to wavelength and frequency as :

$$\bar{v} = \frac{1}{\lambda} = \frac{v}{c}$$

$$\left(\because \lambda = \frac{c}{v} \right)$$

where c is the velocity of radiations in cm (i.e., $3 \times 10^{10} \text{ cm s}^{-1}$).

In SI system, the unit of wave number is m^{-1} .

4. Energy of electromagnetic radiations. Electromagnetic radiations are associated with discrete energy units called quanta or photons. The energy of a photon is directly proportional to its frequency or inversely proportional to its wavelength as shown by the following equation :

$$E = h v = \frac{hc}{\lambda}$$

where h is Planck's constant ($6.625 \times 10^{-34} \text{ J s}$).

1.3. ELECTROMAGNETIC SPECTRUM

Visible light, which can be detected by the human eye constitutes only a very small part of electromagnetic radiations. The full range of these radiations is indeed very large and their wavelengths vary from a very small fraction of a meter to many kilometers. The arrangement of entire range of electromagnetic radiations in increasing order of their wavelengths or decreasing order of their frequencies is known as electromagnetic spectrum. The complete electromagnetic spectrum, alongwith common names used to identify different ranges of wave lengths, is shown in fig. 1.1.

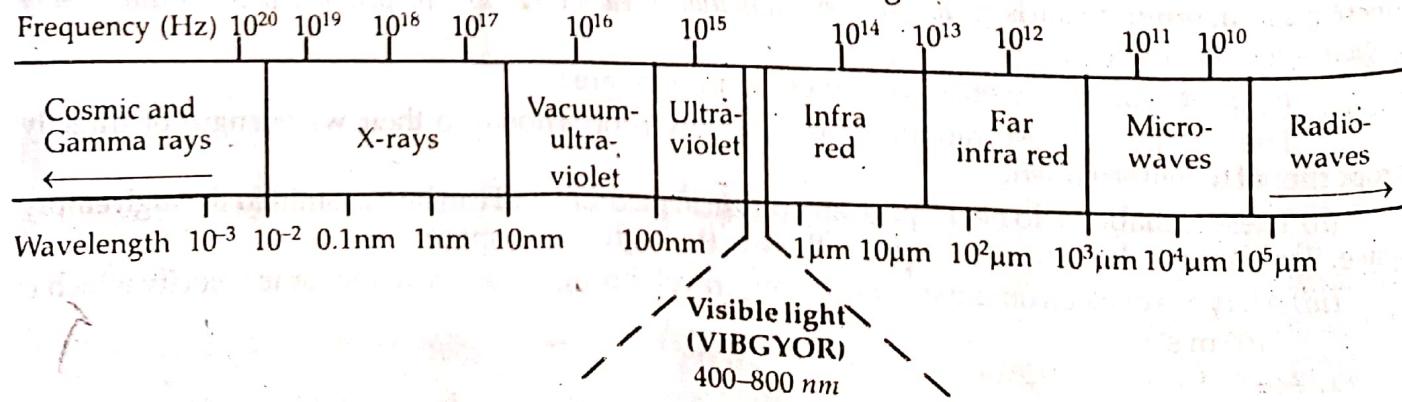


Fig.1.1. Approximate ranges of wavelengths and frequencies of electromagnetic radiations. (Not to scale)

Of the complete electromagnetic spectrum, spectroscopic techniques are concerned primarily with **radiofrequency** radiations (NMR), **infra-red** radiations (IR) and **ultraviolet-visible** radiations (UV).

1.3.1. Principle of absorption spectroscopy

It is interesting to note that practically all the important spectroscopic methods used for structural analysis belong to the field of **absorption spectroscopy** which studies the absorption of electromagnetic radiation in relationship to molecular structure. When a beam of electromagnetic radiation is passed through a substance, the radiation may be either absorbed or transmitted depending upon the wavelength of the radiation and molecular structure of the substance. Absorption of radiation would naturally bring about an increase in the energy of the molecule; the energy gained being directly proportional to the frequency or inversely proportional to the wavelength of radiation. *The increase in energy of a molecule may lead to electronic excitation whereby electrons are raised to higher energy levels. Alternatively it may bring about an increase only in the vibrational or rotational energy of the molecule.*

Electronic excitation can be caused by only **high energy** radiations such as **ultraviolet** and **visible** radiations. On the other hand, vibrational and rotational energy levels can be raised even by **relatively low energy infrared** radiations.

A very important condition for a molecule to absorb electromagnetic radiation is that the energy of a photon of the radiation must be equal to the energy difference between two vibrational or rotational or electronic energy states of the molecule. In other words, the particular wavelength of radiation that a given molecule can absorb is determined by changes in vibrational or rotational or electronic states that are **permitted** to a molecule of that structure. The absorption of radiation is observed instrumentally by passage of radiation through a sample of substance and automatic analysis of the intensity of transmitted radiations. A record of the amount of radiation absorbed or transmitted by a given sample as a function of wavelength of radiation is called **absorption spectrum**.

One might expect an absorption spectrum to consist of a series of lines but actually the spectrum is made of absorption bands with peaks of maximum intensity. The instrument used for recording a spectrum is known as **spectrophotometer** or **spectrometer**.

Having discussed the principle of spectroscopy, we proceed further to discuss ultraviolet spectroscopy in some detail.

1.4. ULTRAVIOLET SPECTROSCOPY

Ultraviolet spectroscopy involves the measurement of **absorption of light** in the visible and ultraviolet regions (visible region 400-800 nm ; UV region 200-400 nm) by the substance under investigation. Since the absorption of light involves the transition from one **electronic energy level** to another within a molecule, UV spectroscopy is also known as **electronic spectroscopy**.

It will be quite appropriate at this stage to study the laws which govern the absorption of light.

1.4.1. The Absorption Laws

There are two laws which express respectively the relationship between absorption of light by a substance and its molar concentration and the length of the path through which the light passes.

These are :

1. **Beer's Law.** According to this law, "When a beam of monochromatic light is passed through a substance dispersed in a non-absorbing solvent, the absorption of light is directly proportional to the molar concentration of the absorbing substance."

2. Lambert's Law. This law states that, "When a beam of monochromatic light is passed through a substance, the absorption of light is directly proportional to the path length of the sample of the substance."

3. Beer-Lambert Law. The two laws stated above can be combined to get a general absorption law, termed as **Beer-Lambert Law**. It may be stated as, "The absorption of light by a substance at a particular wavelength is proportional to the number of molecules of the substance in the path of light".

Mathematically :

$$\log \frac{I_0}{I} \propto c \quad (\text{Beer's law})$$

$$\log \frac{I_0}{I} \propto l \quad (\text{Lambert's law})$$

∴ Beer-Lambert law may be expressed as :

$$\log \frac{I_0}{I} \propto cl$$

or $\log \frac{I_0}{I} = \epsilon \cdot cl$ (ϵ is read as *epsilon*)

where, I_0 = Intensity of incident light

I = Intensity of transmitted light

c = Concentration of the absorbing substance in mol L^{-1}

l = Path length or thickness in cm of the cell containing the sample

ϵ = Proportionality constant known as **molar absorptivity** (sometimes referred to as **molar extinction coefficient** or simply **extinction coefficient**).

The expression $\log \frac{I_0}{I}$ is termed **optical density** or **absorbance** (A). It is a measure of absorption of radiation by a sample. Therefore, Beer-Lambert law may also be expressed mathematically as :

$$A = \log \frac{I_0}{I} = \epsilon \cdot cl$$

Limitations of Beer-Lambert Law. Beer-Lambert law is strictly obeyed when dealing with the UV spectra of *single* species. However, if a sample contains different structural forms of the molecules in equilibrium with each other such as in case of keto-enol tautomers, the law is not obeyed.

It is also not applicable if the solute sample and solvent interact with each other to form complexes.

4. Molar absorptivity (ϵ). It is a proportionality constant which relates the observed absorbance (A) at a particular wavelength (λ) to the molar concentration of the absorbing substance and the length (l) of the path of light in cm. It may be expressed as :

$$\begin{aligned} \epsilon &= \frac{\log I_0/I}{cl} \\ &= \frac{A}{cl} \quad (\because \log I_0/I = A) \end{aligned}$$

Molar absorptivity is a measure of the intensity of absorption at a particular wavelength and has the dimensions of $\text{cm}^2 \text{ mol}^{-1}$ but these units are seldom used.

It is a characteristic property of a compound and is not affected by its concentration or the length of the path of light. Its value ranges from zero to 10^6 . Values above 10^4 constitute **high intensity absorptions** while values below 10^4 are **low intensity absorptions**.

Percent transmission. Since $\frac{I_0}{I}$ is the ratio of intensity of incident light (I_0) to the transmitted

light (I), the transmittance (T) of a sample will be naturally given by the relation :

$$T = \frac{I}{I_0}$$

$$\therefore \% \text{ transmittance} = 100 \times \frac{I}{I_0}$$

Problem 1.1. The molar absorptivity of a conjugated diene (molecular mass = 110 g mol^{-1}) is 13,100. Compute the concentration of this diene in methanol which is required to give the absorbance of 1.6. The path length of light is 1.00 cm. Express your answer in (i) mol L^{-1} and (ii) g mL^{-1} .

Solution. According to Beer-Lambert Law :

$$A = \epsilon c l$$

$$c = \frac{A}{\epsilon l} = \frac{1.6}{13100 (\text{cm}^2 \text{ mol}^{-1}) \times 1.00 (\text{cm})} = 1.22 \times 10^{-4} \text{ mol L}^{-1}$$

Since the molecular mass is 110 g mol^{-1} ,

$$\begin{aligned} 1.22 \times 10^{-4} \text{ mol L}^{-1} &= 1.22 \times 10^{-4} \times 110 \text{ g L}^{-1} \\ &= \frac{1.22 \times 10^{-4} \times 110}{10^3} \\ &= 1.23 \times 10^{-5} \text{ g mL}^{-1} \end{aligned}$$

1.5. MECHANICS OF RECORDING THE UV SPECTRUM : PRESENTATION OF THE SPECTRUM

Excellent ultraviolet spectrophotometers are now available which can conveniently record the spectra over the range 200–800 nm (200–400 nm is known as *near ultraviolet region* while 400–800 nm is *visible region*). Since oxygen of the atmosphere strongly absorbs light at about 200 nm and below, the use of wavelengths shorter than 200 nm (for ultraviolet region) is not practicable unless **special vacuum techniques** are employed.

The ultraviolet spectra are always recorded on a wavelength scale in **millimicrons ($m\mu$)** or **nanometers (nm)**.

Procedure. For recording the ultraviolet spectrum, the given compound is generally dissolved in some suitable solvent which does not itself absorb light in the region under examination. The commonly employed solvents are **95% ethanol, hexane and water**.

The solution of the compound is placed in a suitable transparent container which does not absorb light in the region being studied; generally a **quartz cell** of 1 cm path length is used for this purpose. (Glass cannot be used since it absorbs strongly in ultraviolet region.) At the same time some solvent is taken separately in another quartz cell which serves as a **reference cell**. The sample solution and the solvent are then exposed to the ultraviolet and visible radiations in a spectrophotometer in which a **hydrogen discharge lamp** is usually employed as a source of light in the ultraviolet region (200–400 nm) while a **tungsten filament lamp** is used for the visible region (400–800 nm) of the radiation.

The spectrometer operates by comparing the amount of light in the beam transmitted through the sample with the reference beam which passes through the reference cell. This compensates for any absorption of light by the cell and the solvent. In this way, the spectrometer measures the amount of light absorbed by the compound at each wavelength of the ultraviolet and visible region. This absorption gets recorded on a chart paper as a plot of wavelength of the entire region (on the horizontal axis) versus the absorbance (A) of light at each wavelength (on the vertical axis). The

spectrum obtained consists of a small number of broad peaks ; quite often only one peak is seen.

UV spectrometer. A simplified diagram of UV-visible spectrometer is shown in fig. 1.2. It consists of the following parts :

1. A source of radiations which emits all wavelengths of UV (or visible) radiations. The commonly used source of light in the UV region is the hydrogen or deuterium discharge lamp while a tungsten filament lamp is used for producing visible light.
2. A monochromator which separates the radiations into individual wavelengths. The single wavelength of radiation is split into two beams one of which passes through the sample cell while the other passes through the reference cell.
3. A detector which continuously measures the intensity ratio of the beams transmitted through the sample and the solvent respectively.
4. A recorder chart paper which automatically records the absorption of light at each wavelength as a graph of absorbance versus wavelength.

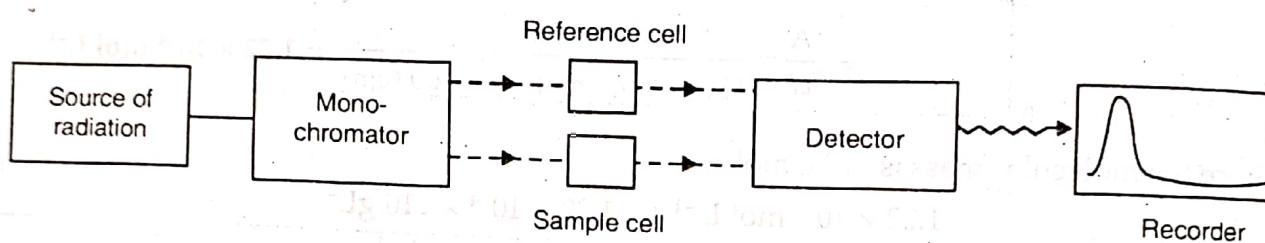


Fig. 1.2. UV spectrometer

Presentation of the spectrum. The ultraviolet spectrum of 1, 3-butadiene ($\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$) in hexane is shown in Fig. 1.3. It may be seen that absorption of ultraviolet radiations by 1, 3-butadiene begins at wavelength below 200 nm and continues upto about 260 nm. The absorption is maximum at 217 nm (top of the peak).

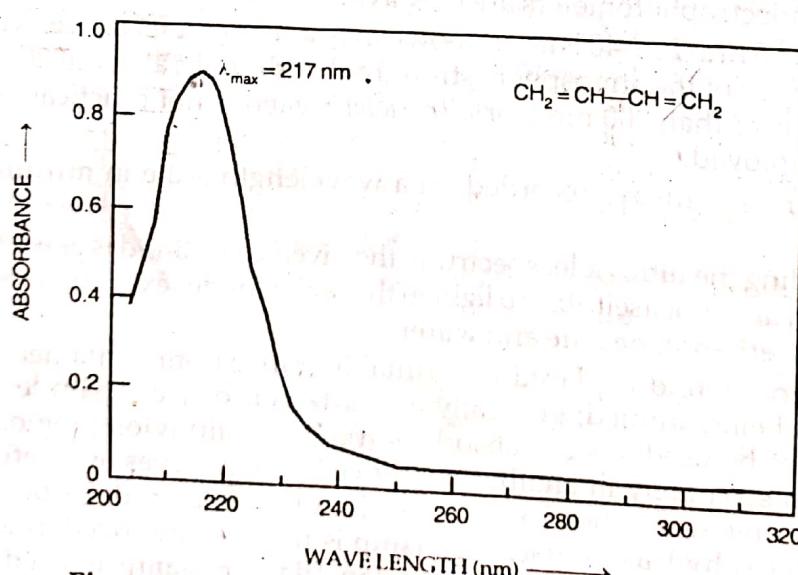


Fig. 1.3. The ultraviolet absorption spectrum of 1, 3-butadiene.

The spectrum is reported as a single absorption peak using the notation $\lambda_{\text{max}} = 217 \text{ nm}$.

In reporting the UV spectrum for analytical purposes, the molar absorptivity ϵ (which indicates the intensity of absorption) at the wavelength of maximum absorbance is also quoted alongwith λ_{max} . For example, the molar absorptivity of 1,3-butadiene at $\lambda_{\text{max}} = 217$ is 20900. Therefore, the UV spectrum is reported as : 1, 3-butadiene, $\lambda_{\text{max}} = 217 \text{ nm}$ ($\epsilon = 20900$)

Sometimes the ultraviolet absorption curves are also presented by plotting molar absorptivity against wavelength. For example, the ultraviolet spectrum of acetone in hexane (Plotted as ϵ versus wavelength) is shown below in Fig. 1.3(a). It may be seen that the maximum molar absorptivity (ϵ) is about 15 at $\lambda_{max} = 279$ nm.

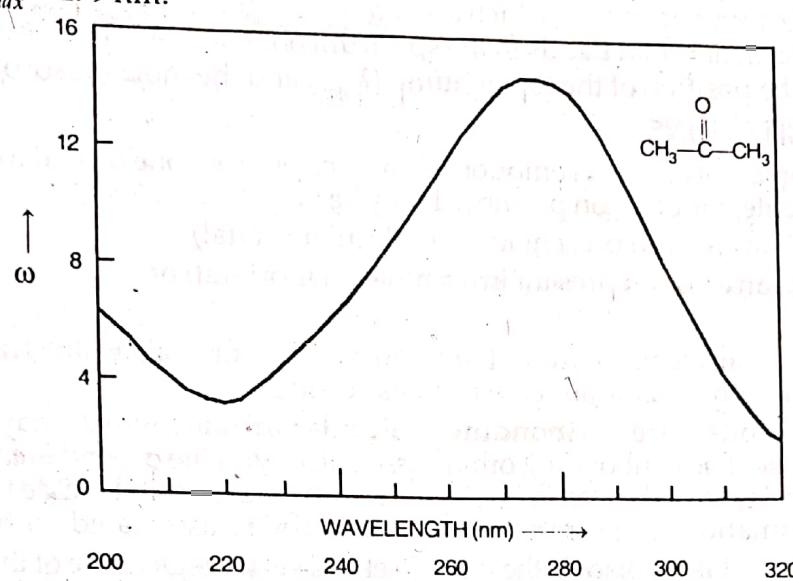


Fig.1.3 (a) The ultraviolet spectrum of acetone in hexane (ϵ versus λ).

Since the UV spectra generally show broad peaks and valleys, the actual spectra are rarely used. The spectral information is given by listing the value or values of λ_{max} alongwith the molar absorptivity for each value of λ_{max} .

1.6. PRINCIPLE OF UV SPECTROSCOPY

Absorption of visible and ultraviolet light produces changes in the electronic states of molecules associated with the excitation of an electron from a lower to a higher energy level. But it must be noted that *each electronic level in a molecule is associated with a number of vibrational sub-levels (with small energy separations) and each vibrational level in turn is associated with a number of rotational sub-levels (with still smaller energy separation)*. Therefore, in its transition to higher energy level, an electron can go from *any* of the sub-levels—*corresponding to various vibrational and rotational states*—in the ground state to *any* of the sub-levels in the excited state (Fig. 1.4).

Appearance of broad bands and not sharp peaks in the spectrum. If the electronic excitation in the molecule had occurred without any accompanying changes in vibrational and rotational sublevels, the spectrum would have consisted of sharp lines (as in the case of absorption spectra of atoms) with each line representing a change in electronic state. But due to the mixing of

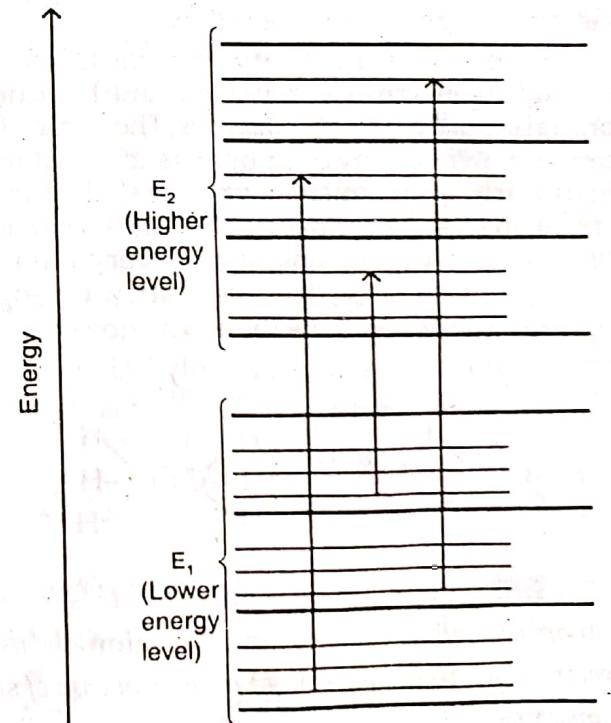


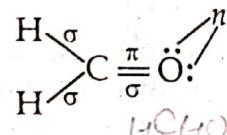
Fig.1.4. Electronic excitation from the ground state to the excited state accompanied by changes in vibrational and rotational sub-levels. (Thick lines indicate vibrational energy sub-levels and thin lines indicate rotational energy sub-levels)

vibrational and rotational changes with electronic changes in the molecules, there will be a large number of possible transitions requiring only slightly different energies. This will require the absorption of a large number of wavelengths which are very close to each other. As a result the absorption spectrum contains a large number of lines which are too close together to be distinguished separately and are recorded in the form of **broad bands** in the spectrum obtained. As stated earlier, the spectrum is described in terms of the position of the top of hump (λ_{max}) and the molar absorptivity (ϵ_{max}).

1.7. ELECTRONIC EXCITATIONS

Electronic transition involves the promotion of an electron from one orbital to another orbital of higher energy. In a molecule, the electron promoted may be :

- A σ electron (i.e., an electron present in a σ molecular orbital)
- A π electron (i.e., an electron present in a π molecular orbital) or



(iii) An n electron (i.e., an electron present in a non-bonding orbital) as illustrated with the help of electron pairs in formaldehyde as shown the right hand side.

The higher energy orbitals are **antibonding molecular orbitals** which may be vacant in the ground state of the molecule. The antibonding orbital associated with the σ -bond is called the σ^* (sigma star) orbital and that associated with π -bond is called the π^* (pi star) orbital. Since the n electrons are not concerned in bond formation, there are no antibonding orbitals associated with them.

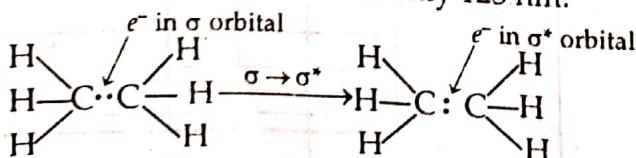
The electronic transitions taking place in the ultraviolet and visible regions are of the following types:

- $\sigma \rightarrow \sigma^*$
- $n \rightarrow \sigma^*$
- $n \rightarrow \pi^*$ and
- $\pi \rightarrow \pi^*$

Fig. 1.5 gives a general idea of the relative amounts of energies required for various types of electronic excitations.

A brief account of the various types of electronic transitions is as follows :

(i) $\sigma \rightarrow \sigma^*$ **Transitions.** *Transitions in which a σ bonding electron is excited to an antibonding σ^* orbital are called $\sigma \rightarrow \sigma^*$ transitions.* These transitions can be shown only by compounds such as saturated hydrocarbons in which all valence shell electrons are involved in the formation of σ bonds. The energy required for these transitions is very high and consequently these occur at very short wavelengths. For example, in methane the absorption of energy for such transitions occurs at only 125 nm.



Since these wavelengths are lesser than 200 nm and fall in the **vacuum UV region**, the usual spectroscopic technique cannot be used in case of such transitions.

(ii) $n \rightarrow \sigma^*$ **Transitions.** *These are the electronic excitations from a non-bonding atomic orbital to an antibonding σ^* orbital.* Compounds having non-bonding electrons on hetero atoms such as oxygen, nitrogen, sulphur or halogens can show $n \rightarrow \sigma^*$

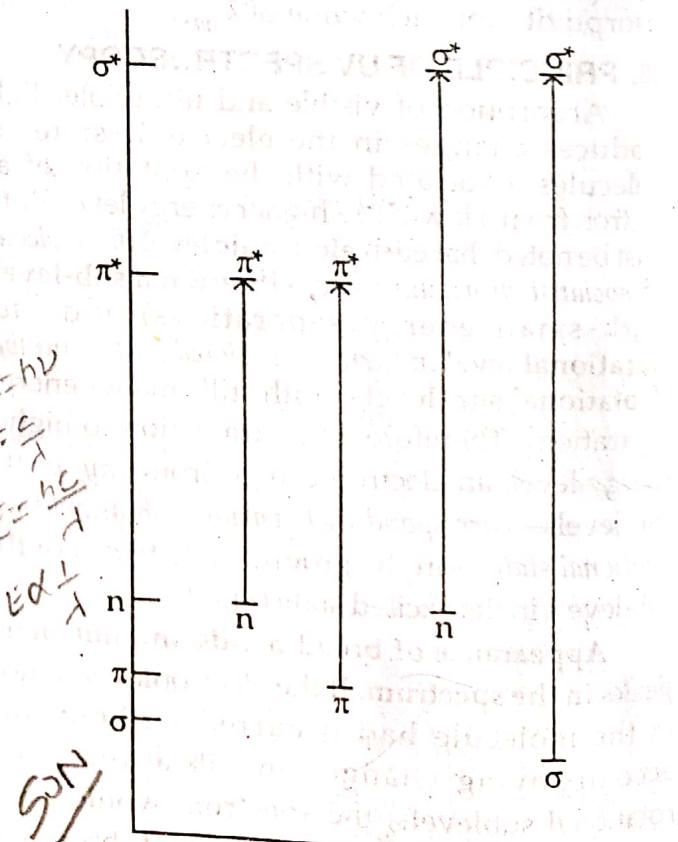
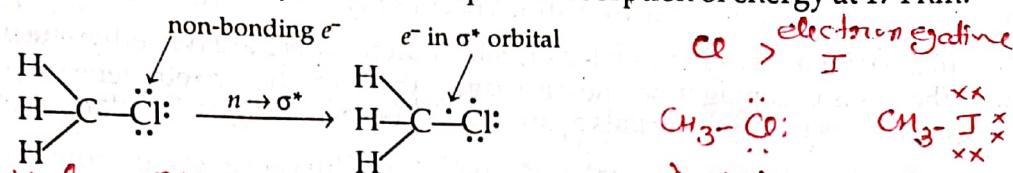


Fig. 1.5. Energies required for different types of electronic excitations.

transitions. These transitions are of lower energy and hence occur at longer wavelength than $\sigma \rightarrow \sigma^*$ transitions.

For example, $n \rightarrow \sigma^*$ transition in methyl chloride requires absorption of energy at 174 nm.



Effect of Size of Halogen Atom:

The energy required for these transitions decreases with the decrease in the electronegativity of the hetero atom and therefore, the wavelength of absorption increases. For example, methyl chloride absorbs at 174 nm while in methyl iodide absorption takes place at 258 nm. Similarly amines absorb at higher wavelength than alcohols as nitrogen has lesser electronegativity than oxygen.

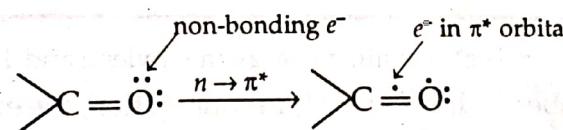
This observation can be attributed to the fact that greater the electronegativity of the hetero atom, more firmly the non-bonding electrons are held by it and, therefore, more energy is required for $n \rightarrow \sigma^*$ transition.

Effect of H-bonding

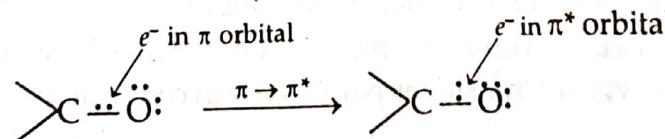
Hydrogen bonding of the compound with the solvent also shifts the absorption to shorter wavelength.

But in general, $n \rightarrow \sigma^*$ transitions are not of much importance.

(iii) $n \rightarrow \pi^*$ Transitions. These are the transitions in which an electron in a non-bonding atomic orbital is promoted to an antibonding π^* orbital. Compounds having double bonds between hetero atoms, e.g., C=O, C=S and N=O, show these transitions which appear as weak absorption bands. These transitions require only small amounts of energy and take place within the range of ordinary ultraviolet spectrophotometer. However, the intensity of absorption is generally very low. For example, the carbonyl group of saturated aldehydes or ketones exhibits an absorption of low intensity at about 285 nm.



(iv) $\pi \rightarrow \pi^*$ Transitions. The transitions in which a π electron is excited to an antibonding π^* orbital are called $\pi \rightarrow \pi^*$ transitions. These have relatively higher energy requirement than $n \rightarrow \pi^*$ transitions and absorption generally take place outside the ordinary ultraviolet region for simple molecules containing isolated unsaturated centres. But the intensity of absorption is very high. For example, the $\pi \rightarrow \pi^*$ transition for simple aldehydes or ketones produces an absorption band of high intensity at about 180 nm. For a simple alkene like ethylene, such a transition takes place in still far ultraviolet region (about 175 nm).



Effect of conjugation. Conjugation of double bonds lowers the energy required for the electronic transition. As a result, molecules containing conjugated systems such as >C=C-C=C< and

>C=C-C=O absorb the radiations of longer wavelengths than in case of non conjugated systems and absorption bands appear in the ordinary ultraviolet range. For instance 1,3-butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) shows λ_{max} 217 nm in contrast to ethylene which shows λ_{max} 175 nm.

To understand the effect of conjugation on λ_{max} , let us start with ethylene which is the simplest unconjugated alkene. The double bond in ethylene consists of a sigma bond formed by the combination of sp^2 hybrid orbitals of two carbon atoms and a π bond formed by the combination of unhybridised

$2p$ orbitals. Due to the large difference in the energies of π bonding and π^* antibonding molecular orbitals (fig. 1.6), $\pi \rightarrow \pi^*$ transition takes place with the absorption of radiation below 200 nm (175 nm for ethylene). Therefore these transitions occur only in far ultraviolet region.

In a conjugated system such as 1, 3-butadiene, there are two ethylene units in conjugation with each other. Due to conjugation, the π bonding orbitals of the two ethylene units interact with each other to form two new bonding orbitals π_1 and π_2 of different energies. Similarly there is formation of two π^* orbitals (i.e. π anti bonding orbitals) π_3^* and π_4^* of different energies from the two ethylene units. The energy difference between highest occupied π molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for 1, 3-butadiene is less than it is for ethylene (Fig. 1.6). As the HOMO-LUMO energy gap becomes smaller, the position of energy absorption moves to longer wavelength (217 nm for 1, 3-butadiene) which falls within the ordinary ultraviolet region.

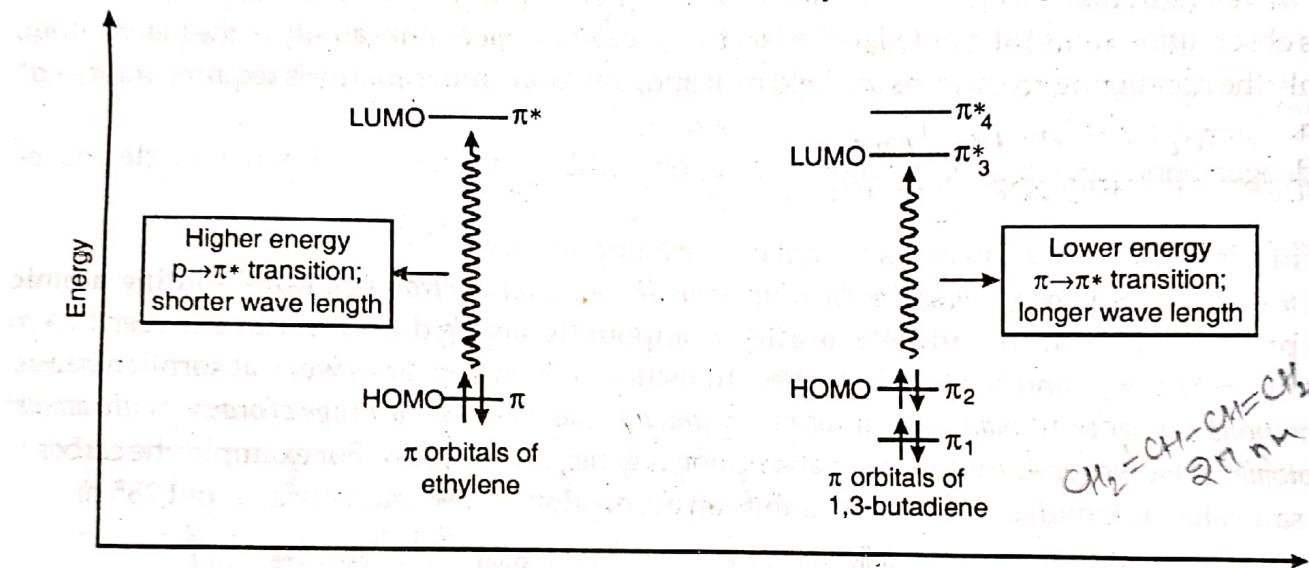


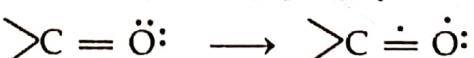
Fig. 1.6. Comparison of $\pi \rightarrow \pi^*$ transition energy in ethylene and 1, 3-butadiene.

With the increase in the number of double bonds in conjugation, the energy difference between HOMO and LUMO further decreases, so that absorption moves to still longer wavelengths. Thus spectrum of 1, 3, 5, 7 octatetraene ($\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH}_2$), in hexane, exhibits λ_{max} 290 nm ($\epsilon_{max} = 52000$). If there are enough double bonds in conjugation, absorption will ultimately move into the visible region and the compound will be coloured. For example, β -carotene, a naturally occurring yellow pigment containing 11 double bonds in conjugation, owes its colour to absorption in the visible part of light ($\lambda_{max} = 455$ nm).

Another effect of conjugation is that with the increase in conjugation, the number of possible UV transitions increases and the spectrum becomes more complex.

To sum up the above discussion on electronic transitions, it may be stated that the organic chemist is primarily interested in two types of transitions particularly in conjugated systems. These are :

$n \rightarrow \pi^*$: for example,



and $\pi \rightarrow \pi^*$: for example,



In may be noted that transitions to antibonding π^* orbitals are associated only with unsaturated centres in the molecules.

1.8. TRANSITION PROBABILITY

It is interesting to note that it is not necessary that exposure of a compound to ultraviolet or visible light must always lead to an electronic transition. On the other hand, the probability of a particular electronic transition depends upon the value of molar absorptivity (ϵ_{max}) and certain other factors. Accordingly transitions have been divided into two categories :

(i) Allowed transitions. Prob. of occ is very high $\epsilon_{max} \geq 10^4$ e.g. $n \rightarrow n^*$

(ii) Forbidden transitions. " " " Low $\epsilon_{max} < 10^4$ e.g. $n \rightarrow n^*$

(i) **Allowed transitions.** These are transitions which have $\epsilon_{max} 10^4$ or more and the probability of their occurrence is very high. These are generally due to $\pi \rightarrow \pi^*$ transition. For example, $\pi \rightarrow \pi^*$ transition in 1,3-butadiene which shows absorption at 217 nm and has ϵ_{max} 20900 represents an allowed transition. The π and π^* orbitals involved in these transitions lie in the same plane and can undergo overlapping to a large extent in the excited state. Therefore, $\pi \rightarrow \pi^*$ transitions are highly probable.

(ii) **Forbidden transitions.** These are transitions for which ϵ_{max} is generally less than 10^4 . These are usually related to $n \rightarrow \pi^*$ transition. For example, $n \rightarrow \pi^*$ transition of a saturated aldehyde or ketone showing weak absorption near 290 nm and having ϵ_{max} less than 100 is a forbidden transition.

It should be clearly understood that forbidden transition does not mean that such a transition cannot take place at all. It just tells us that the probability of the transition is very low. To clarify this statement, let us consider the $n \rightarrow \pi^*$ transition. The orbital containing the non-bonding electrons present on the hetero atom lies in a plane perpendicular to the plane of π^* molecular orbital. The regions in space belonging to these orbitals can overlap only to a very small extent. As a result the probability of excitation of n electrons to π^* orbitals is very low.

1.9. CONCEPT OF CHROMOPHORE AND AUXOCHROMES

1.9.1. Chromophore *Chromophores are the functional groups which absorb electromagnetic radiations & may or may not impart colour to any compound.*

The term chromophore was originally used to denote a functional group or some other structural feature, the presence of which imparts a colour to a compound. For example, nitro group is a chromophore since its presence in a compound imparts yellow colour to the compound. But these days the term chromophore is used in a much broader sense. It is now defined as any group which exhibits absorption of electromagnetic radiations in the visible or ultraviolet region. It may or may not impart any colour to the compound.

Table 1.1 lists some simple chromophore groups alongwith their λ_{max} , ϵ_{max} and the type of transition involved.

Table 1.1. Some simple chromophoric groups

Chromophore	Transition	Approximate value of λ_{max} (nm)	Approximate value of ϵ_{max}	Solvent
$>\text{C}=\text{C}<$ $-\text{C}\equiv\text{C}-$	$\pi \rightarrow \pi^*$	175	15,000	Vapour Hexane
	$\pi \rightarrow \pi^*$	175	10,000	
$>\text{C}=\text{O}$	$\pi \rightarrow \pi^*$	180	10,000	Hexane
	$n \rightarrow \sigma^*$	160	18,000	
OH $-\text{C}=\text{O}$	$n \rightarrow \pi^*$	285	15	Methanol Ethanol
	$n \rightarrow \pi^*$			
$-\text{N}=\text{N}-$ $-\text{NO}_2$	$n \rightarrow \pi^*$	205	60	Methanol
	$n \rightarrow \pi^*$	338	5	
O $-\text{C}-\text{NH}_2$	$n \rightarrow \pi^*$	274	15	Methanol Hexane
	$\pi \rightarrow \pi^*$	178	9500	
	$n \rightarrow \pi^*$	220	63	Hexane

It may be seen that chromophores are of two types :

(i) Chromophores such as $>\text{C}=\text{C}<$ and $-\text{C}\equiv\text{C}-$ which contain π electrons and undergo $\pi \rightarrow \pi^*$ transitions.

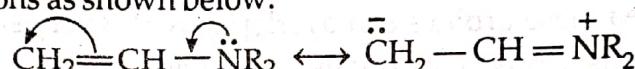
(ii) Chromophores such as $>\text{C}=\text{O}$, $-\text{N}=\text{N}-$ and NO_2 which contain both π and n electrons. They can undergo $\pi \rightarrow \pi^*$ as well as $n \rightarrow \pi^*$ transitions.

Two compounds having the same chromophoric group generally exhibit absorption at near the same wavelength (λ_{max}) and have nearly the same molar absorptivity (ϵ_{max}). Therefore, it should be possible to identify the presence of a particular functional group in an unknown compound by the comparison of its UV spectrum with the data of already known compounds. But the position of absorption maximum and the intensity of absorption can be modified by a number of factors (as discussed below in sec. 1.9.3).

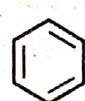
1.9.2. Auxochrome

An auxochrome is a group which itself does not act as a chromophore but when attached to a chromophore it shifts the absorption maximum towards longer wavelength alongwith an increase in the intensity of absorption. Some commonly known auxochromic groups are $-\text{OH}$, $-\text{NH}_2$, $-\text{OR}$, $-\text{NHR}$ and $-\text{NR}_2$.

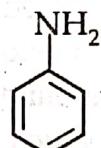
All auxochromes contain one or more non-bonding pair of electrons. When an auxochrome is attached to a chromophore, it leads to conjugation or helps in extending conjugation by sharing of its non-bonding pair of electrons as shown below.



Due to conjugation, there is a decrease in energy difference between the ground state and excited state of the group. As a result, the absorption shifts to longer wavelength. At the same time there is an increase in the intensity of absorption. For example, when the auxochrome $-\text{NH}_2$ group is attached to benzene ring, it increases λ_{max} as well as ϵ_{max} as given below :



Benzene



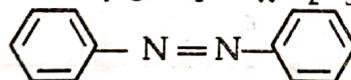
Aniline

$$\lambda_{max} = 255 \text{ nm} \xrightarrow{\text{increases to}} \lambda_{max} = 280 \text{ nm}$$

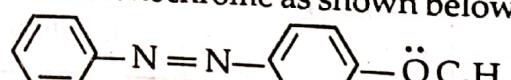
$$\epsilon_{max} = 203 \text{ nm} \xrightarrow{\text{increases to}} \epsilon_{max} = 1430$$

$(-\text{NH}_2$ acts as auxochrome by extending the conjugation in benzene by the participation of non-bonding pair of electrons in conjugation).

Similarly, ethoxy group ($-\ddot{\text{O}}\text{C}_2\text{H}_5$) acts as an auxochrome as shown below :



Azobenzene

*p*-Ethoxyazobenzene

$$\lambda_{max} = 320 \text{ nm} \xrightarrow{\text{increases to}} \lambda_{max} = 385 \text{ nm}$$

$$\epsilon_{max} = 21,000 \xrightarrow{\text{increases to}} \epsilon_{max} = 42,000$$

1.9.3. Change in position and Intensity of absorption

For isolated chromophore groups such as $>\text{C}=\text{C}<$ and $-\text{C}\equiv\text{C}-$, absorption occurs in the ultraviolet region which cannot be easily studied. But the position of absorption maximum and the intensity of absorption can be modified in different ways by some structural changes or change of solvent as given below.

(i) **Bathochromic shift or red shift.** It involves the shift of absorption maximum towards longer wavelength. It can be brought about by three different methods as given below.

(a) **By attachment of an auxochrome to the chromophore.** When an auxochrome such as $-\text{OH}$ or $-\text{NH}_2$ is attached to a chromophore, it leads to conjugation or helps in extending conjugation. As a result, absorption shifts to longer wavelength (as already explained under sec. 1.9.2).

(b) **By conjugation of two or more chromophoric groups.** Bathochromic shift is also produced if two or more chromophores are present in conjugation in a molecule. For example, as already stated ethylene shows $\pi - \pi^*$ transition at 170 nm while 1, 3-butadiene (where two double bonds are in

conjugation) shows λ_{max} at 217 nm.

(c) **By change of solvent.** It is also possible to achieve bathochromic shift by change of solvent. For example, use of a solvent of lower polarity (such as hexane) produces a red shift in the $n \rightarrow \pi^*$ absorption of carbonyl compounds. (This is discussed in detail in sec. 1.10).

(ii) **Hypsochromic shift or blue shift.** It involves the shift of absorption maximum towards shorter wavelength. It may be brought about as follows :

(a) **By removal of conjugation in a system.** For example, protonation of aniline causes a blue shift from 280 nm to 203 nm. This is because anilinium ion thus formed, $\text{C}_6\text{H}_5\text{NH}_3^+$, has no lone pair of electrons on nitrogen which can conjugate with benzene ring.

(b) **By change of solvent.** Change of solvent can also be used to bring about hypsochromic shift. For example, use of a solvent of higher polarity (such as water) causes a blue shift in the $n \rightarrow \pi^*$ absorption of acetone. (Discussed in detail in sec. 1.10).

(iii) **Hyperchromic effect.** This effect involves an increase in the intensity of absorption. It is usually brought about by introduction of an auxochrome. For example, introduction of methyl group in position 2 of pyridine increases ϵ_{max} from 2750 to 3560 for $\pi \rightarrow \pi^*$ transition (λ_{max} shifts from 257 nm to 262 nm).

(iv) **Hypochromic effect.** It involves a decrease in the intensity of absorption. It is brought about by groups which distort the geometry of the molecule. For example when a methyl group is introduced in position 2 of biphenyl, hypochromic effect takes place due to distortion caused by methyl group.

As a result ϵ_{max} decreases from 19000 to 10250 (λ_{max} shifts from 250 nm to 237 nm).

It may be noted that bathochromic shift is generally accompanied by hyperchromic effect while hypsochromic shift is accompanied by hypochromic effect.

The various kinds of absorption and intensity shifts have been summed up in fig. 1.7.

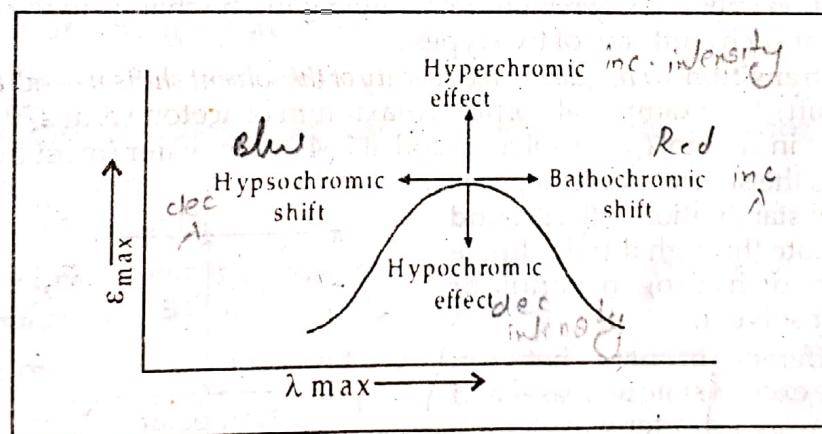


Fig. 1.7. Various kinds of absorption and intensity shifts.

1.10. SOLVENT EFFECTS AND CHOICE OF SOLVENT

1.10.1. Solvent effects

The solvent used for dissolving a compound under examination has a profound effect on the UV spectrum of the compound as given below :

(1) **Effect on fine structure.** As a result of interactions of solute with solvent molecule, the fine structure of the absorption bands is blurred out and a smooth curve is obtained. This smoothing out of the spectrum deprives us of much useful information about complex molecules. The smoothing out effect is more in polar solvents than in non-polar solvents.

The fine structure of UV spectrum is best observed in vapour phase.

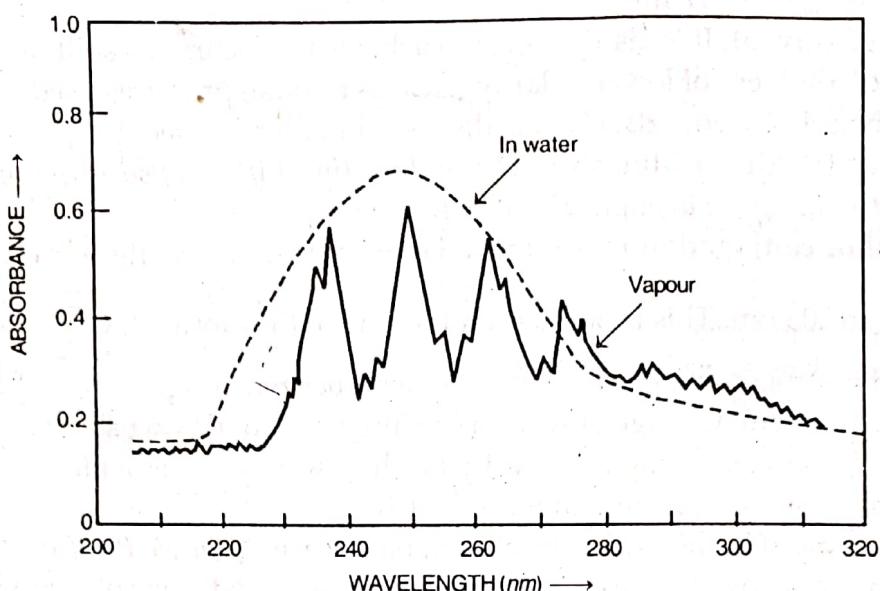


Fig. 1.8. Smoothing out effect on the UV spectrum in a polar solvent; fine structure of the spectrum in vapour state, smoothing out of the structure in water.

(2) Effect on the position and intensity of absorption maximum. Changing the polarity of the solvent may also lead to changes in the position and intensity of absorption maximum.

Effect on non-polar compounds. In general, changes in polarity of the solvent do not cause any significant shift in the spectra of non-polar compounds such as dienes and conjugated hydrocarbons. For example, the absorption maximum for non-polar compounds is practically the same in alcohol (polar solvent) as well as in hexane (non-polar solvent).

Effect on polar compounds. In case of polar compounds such as α, β -unsaturated carbonyl compounds, the absorption maximum generally gets shifted with the change in the polarity of solvents. It has been observed that such shifts are of two types :

(i) Shift in $n \rightarrow \pi^*$ transition. (i) Increase in the polarity of the solvent shifts $n \rightarrow \pi^*$ transitions to shorter wavelength (i.e. blue shift). For example, absorption maximum of acetone is at 279 nm in hexane (non-polar solvent), at 270 nm in ethanol (polar solvent) and at 264 nm in water (most polar solvent).

This shift towards the shorter wavelength is mainly due to the greater stabilisation of the ground state than the excited state through dipole-dipole interaction, formation of hydrogen bonds or solvation with the polar solvent.

As a result, the difference in energy between the ground state and the excited state increases and the absorption shifts towards shorter wavelength (Fig.1.9).

Let us for example, consider the blue shift of the $n \rightarrow \pi^*$ carbonyl absorption. The carbonyl group is more polar in the ground state than in the excited state. Therefore, the extent of hydrogen bonding between the ground state and the polar solvent like water and alcohol is much more than between the excited state and the solvent. In other words, ground state is stabilised to a greater extent and undergoes greater lowering of energy than the excited state. Consequently the energy difference between the two states increases and the absorption shifts towards the shorter wavelength.

(ii) Shift in $\pi \rightarrow \pi^*$ transition. Increase in the polarity of the solvent shifts $\pi \rightarrow \pi^*$ transitions to longer wavelength (i.e., red shift). For example, it has been observed that as compared to solution in hexane, solution in ethanol generally shows a red shift of about 10—20 nm.

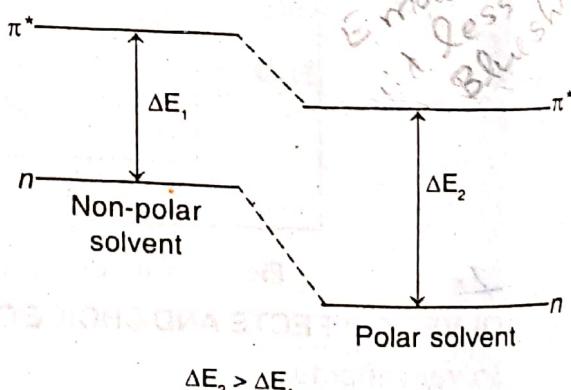


Fig. 1.9 Greater stabilisation of ground state; blue shift.

The shift of $\pi \rightarrow \pi^*$ absorption towards longer wavelength is largely due to the greater stabilisation of excited state relative to ground state through dipole-dipole interaction or solvation. As a result, the energy difference between the ground state and the excited state decreases and the absorption shifts towards larger wavelength.

For example, the molecule of ethylene is more polar in the excited state than the ground state due to greater polarity of π^* orbital compared to π orbital. As a result the π^* M.O. will be relatively more stabilised by dipole-dipole interaction with the polar solvent as compared to stabilisation of the ground state. Therefore, lesser energy will be required for such a transition and the absorption will shift towards larger wavelength.

(iii) Shift in $n \rightarrow \sigma^*$ transitions. $n \rightarrow \sigma^*$ transitions are very sensitive to hydrogen bonding. For example, alcohols and amines form hydrogen bonding with the solvent molecules due to the presence of non-bonding electrons on the hetero atom. As a result, more energy is required for $n \rightarrow \sigma^*$ transition in polar solvents and shift towards lower wavelength takes place.

To sum up :

(i) If a group is more polar in the ground state than in the excited state, increasing the polarity of the solvent shifts the absorption to shorter wavelength.

(ii) If a group is more polar in the excited state than in the ground state, increasing the polarity of the solvent shifts the absorption to longer wavelength.

1.10.2. Choice of solvent

A suitable solvent for ultraviolet spectroscopy should meet the following requirements.

(i) It should be transparent in the wavelength region under examination i.e. it should not itself absorb radiations in the region being examined.

(ii) It should be less polar so that it has minimum interaction with the solute molecules and has no effect on the fine structure of absorption bands and the position of absorption bands.

The most commonly employed solvent is 95% ethanol. It is cheap, has good dissolving power and does not absorb radiations above 210 nm. In other words, it is transparent above 210 nm. Commercial ethanol should not be used as it contains some benzene which undergoes absorption in the UV range at about 280.

Some other solvents which are transparent above 210 nm are *n*-hexane, cyclohexane, methanol, water and ether.

Hexane and other hydrocarbons are sometimes preferred to polar solvents because they have minimum interactions with the solute molecules.

Benzene, chloroform and carbon tetrachloride cannot be used because they absorb in the range of about 240—280 nm.

1.11. SOME CHARACTERISTIC ABSORPTION BANDS

Table 1.2 lists the wavelengths of maximum absorption and corresponding molar absorptivities or extinction coefficients for some typical ultraviolet bands of simple molecules containing different groups.

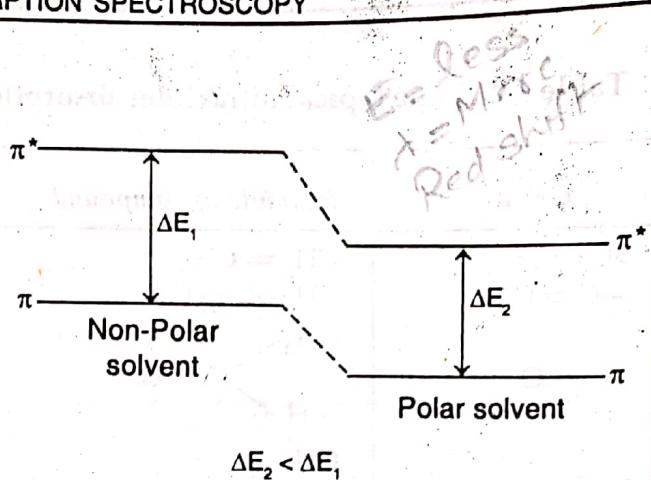


Fig. 1.10. Greater stabilisation of excited state; red shift.

Table 1.2. Some typical ultraviolet absorption bands due to the presence of different groups

Group	Example of compound	λ_{max} (in m μ or nm)	ϵ_{max}	Solvent
$>C=C<$	$CH_2=CH_2$	171	15,530	Vapour
$-C\equiv C-$	$CH_3-C\equiv CH$	187	450	Cyclohexane
$>C=O$	CH_3 $C=O$ H CH_3 $C=O$ CH_3 CH_3-C O OH	160 180 290 166 189 279	20,000 10,000 17 16,000 900 17	Vapour Hexane Vapour Hexane
$-C(=O)OH$		208	32	Ethanol
$>C=C-C=C<$	$CH_2=CH-CH=CH_2$	217	20,900	Hexane
$>C=C-C\equiv C-$	$CH_2=CH-C\equiv CH$	219	7600	Ethanol
$>C=C-C=O$	$CH_3-CH=CH-CH=O$ $CH_3-CH=CH-C=O$ CH ₃ 320 224 314	228 218 320 224 314	7800 18,000 30 9750 38	Hexane Ethanol
Benzenoid ring		203.5 254	7400 204	Water
		217 269	600	Water
		245.5	9800	Water

*The vapour state refers to the use of the compound in the neat form (i.e. without employing any solvent).

Example 1.1. Which of the following compounds do you expect to absorb ultraviolet radiation?

Why or why not?

- (i) Acetaldehyde (ii) Benzene (iii) Cyclohexane (iv) Ethanol (v) Heptane (vi) Aniline (vii) Butadiene

Solution.

(i) Acetaldehyde. It shows absorption at around 290 nm due to low energy $n-\pi^*$ transition.

(ii) Benzene. It absorbs in the UV region at about 255 nm due to $\pi-\pi^*$ transition.

(iii) Cyclohexane. It does not absorb in the UV region because it involves only high energy $\sigma-\sigma^*$ transition.

(iv) Ethanol. It does not absorb in the UV region since it involves only $\sigma-\sigma^*$ and $n-\sigma^*$ transitions.

(v) **Heptane.** Due to only $\sigma - \sigma^*$ transition, there is no absorption in the UV range.

(vi) **Aniline.** Due to the presence of auxochrome, NH_2 group, attached to benzene, it shows absorption at about 280 nm.

(vii) **Butadiene.** It contains a conjugated system and shows strong absorption at about 217 nm.

Example 1.2. The UV spectrum of acetaldehyde has two peaks of $\lambda_{\max} = 290 \text{ nm}$ and $\lambda_{\max} = 180 \text{ nm}$. What type of electronic transitions is responsible for each of these transitions?

Solution. $\lambda_{\max} = 290 \text{ nm}$ is due to $n \rightarrow \pi^*$ transition

$\lambda_{\max} = 180 \text{ nm}$ is due to $\pi \rightarrow \pi^*$ transition.

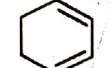
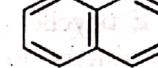
Problem 1.2. Of the following compounds, which can absorb UV radiation :

- (i) Benzene (ii) 1,3-Pentadiene (iii) Heptane (iv) Ethanol (v) Ethylene (vi) Benzoic acid (vii) Nitrobenzene
(viii) Water.

[Ans. (i) (ii), (v), (vi) and (vii)]

Problem 1.3. Which of the following compounds would you expect to exhibit UV absorptions in the 200–400 nm range :

- (i) 1,3-cyclohexadiene (ii) 1,4-cyclohexadiene (iii) Cyclohexene (iv) Naphthalene.

Ans. 1, 3-Cyclohexadiene () and naphthalene () would exhibit UV

absorption in the 200–400 nm range because they contain conjugated double bonds and would therefore undergo $\pi \rightarrow \pi^*$ transition in the 200–400 nm range.

Problem 1.4 Two isomeric ketones having the formula $\text{CH}_2=\text{CH}-\text{CHCOCH}_3$ and $\text{CH}_3-\text{CH}=\text{C}-\text{COCH}_3$

were subjected to ultraviolet spectroscopy. One isomer exhibited $\lambda_{\max} 235 \text{ nm}$ ($\epsilon_{\max} 12000$) while the other did not show any high intensity absorption above 200 nm. Which isomer shows $\lambda_{\max} 235 \text{ nm}$ ($\epsilon_{\max} 12000$) ?

Ans. The isomer $\text{CH}_3-\text{CH}=\overset{\text{O}}{\underset{\parallel}{\text{C}}}=\text{C}=\text{CH}_3$ would show high intensity absorption above 200 nm

due to $\pi - \pi^*$ transition in a conjugated systems. Therefore it shows $\lambda_{\max} 235 \text{ nm}$ ($\epsilon_{\max} 12000$).

The other isomer contains isolated ethylenic bond and carbonyl group. Due to ethylenic bond it can have $\pi \rightarrow \pi^*$ transition only below 200 nm. Due to carbonyl group, it can have $\pi \rightarrow \pi^*$ transition above 200 nm but it would of very low intensity.

1.12. WOODWARD-FIESER RULES FOR CALCULATING ABSORPTION MAXIMA*

By studying the ultraviolet absorption spectra of a large number of compounds, Woodward (1941) deduced certain rules for correlating λ_{\max} with molecular structure. Since then, these rules have been modified by Scott and Feiser as a result of more experimental data. The modified rules, known as Woodward-Fieser rules, enable us to calculate the position of λ_{\max} for a given structure by relating the position of λ_{\max} with the position and degree of substitution of chromophore.

The calculated values are generally within 2 or 3 nm of experimental values.

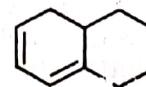
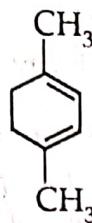
We will now consider these rules briefly for different classes of compounds.

1.13. WOODWARD-FIESER RULES FOR CALCULATING λ_{\max} IN CONJUGATED DIENES, TRIENES AND POLYENES

Before we consider the rules for dienes, trienes, etc., it will be useful to explain some terms involved in discussing the rules.

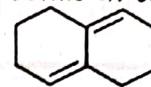
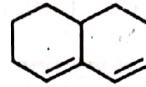
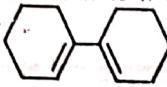
(1) **Homoannular diene.** It is a cyclic diene which contains conjugated double bonds in the same ring.

*Not included in the syllabus of various universities of Punjab

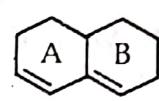
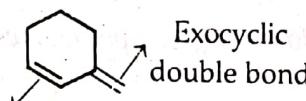
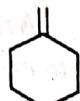
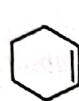


For example :

(2) **Heteroannular diene.** It is a cyclic diene in which double bonds in conjugation are present in different rings. For example :



(3) **Endocyclic double bond.** It is a double bond present in a ring as shown below in (a).



Endocyclic
double bond
(a)

Exocyclic
double bond
(b)

Endocyclic
double bond
(c)

Ring A has one endocyclic
and one exocyclic double
bond. Ring B has one
endocyclic double bond only.
(d)

(4) **Exocyclic double bond.** It is a double bond in which one of the doubly bonded atoms is a part of ring system as shown above in (b).

WOODWARD-FIESER RULES FOR CONJUGATED DIENES, TRIENES, POLYENES, ETC.

According to these rules, each type of diene or triene system has a certain fixed value at which absorption takes place. This constitutes the **basic value** or **parent value**.

The contributions made by various alkyl substituents or ring residues, double bonds extending conjugation and polar groups such as $-\text{Cl}$, $-\text{Br}$ and $-\text{OR}$ are added to the basic value to get λ_{\max} for a particular compound.

The parent values and contributions of different substituents/groups are given in table 1.3.

Table 1.3. Parent values and increments for different substituents/groups.

(a) Parent Values

- (i) Acyclic conjugated diene
- (ii) Homoannular conjugated diene
- (iii) Heteroannular conjugated diene

217 nm

253 nm

214 nm

(b) Increments

- (i) Each alkyl substituent or ring residue
- (ii) Exocyclic double bond
- (iii) Each double bond extending conjugation

5 nm

5 nm

30 nm

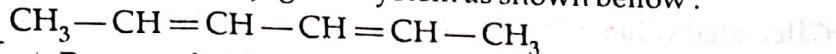
(c) Auxochromes :

$-\text{OR}$	30 nm
$-\text{SR}$	6 nm
$-\text{Cl}, -\text{Br}$	30 nm
$-\text{NR}_2$	5 nm
$-\text{OCOCH}_3$	60 nm
	0 nm

To illustrate the above rules, a few examples are given ahead :

Example 1.3. On the basis of Woodward-Fieser rules, calculate λ_{\max} for 2, 4-hexadiene, $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH}_3$.

Solution. 2, 4-Hexadiene is an acyclic conjugated diene having two methyl substituents attached to either side of the conjugated system as shown below:



∴ Parent value for acyclic conjugated diene = 217 nm

Two alkyl substituents, $2 \times 5 = 10$ nm

Calculated value of λ_{\max} = 227 nm

Observed value of λ_{\max} for 2, 4-hexadiene is 227 nm.

Example 1.4. Calculate λ_{\max} for 1, 4-dimethylcyclohexa-1, 3-diene, $\text{H}_3\text{C}-\text{C}_6\text{H}_3-\text{CH}_3$.

Solution. The given compound is a homoannular diene having two alkyl substituents and two ring residues (as shown below by dotted lines).



∴ Parent value for homoannular diene = 253 nm

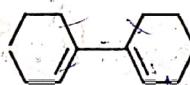
Two alkyl substituents, $2 \times 5 = 10$ nm

Two ring residues, $2 \times 5 = 10$ nm

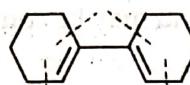
∴ Calculated value = 273 nm

Observed value = 265 nm

Example 1.5. Compute λ_{\max} for the compound:



Solution. The given compound is a heteroannular diene having 4 ring residues as shown below.



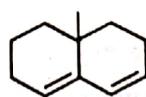
∴ Parent value for heteroannular diene = 214 nm

Four ring residues, $4 \times 5 = 20$ nm

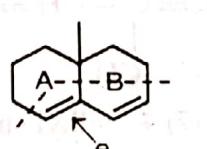
∴ Calculated value = 234 nm

Observed value = 236 nm

Example 1.6. Calculate λ_{\max} for the compound having the structure:



Solution. According to the given structure, it represents a heteroannular diene having three ring residues and one exocyclic double bond marked 'e' (This double bond is exocyclic with respect to ring B). That is:



∴ Parent value for heteroannular diene = 214 nm

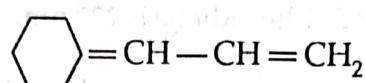
Three ring residues, $3 \times 5 = 15$ nm

One exocyclic double bond = 5 nm

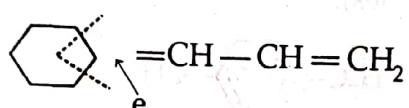
∴ Calculated value = 234 nm

Observed value = 235 nm

Example 1.7. Calculate λ_{\max} for 3 - cyclohexylidenepropene



Solution. 3 - Cyclohexylidenepropene is a conjugated diene having two ring residues and an exocyclic double bond marked shown below.



∴ Parent value for conjugate diene = 217 nm

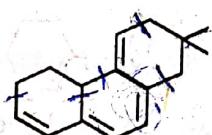
Two ring residues $2 \times 5 = 10$ nm

One exocyclic double bond = 5 nm

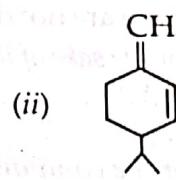
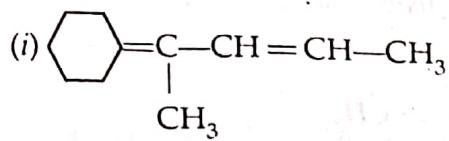
∴ Calculated value = 232 nm

Observed value = 236.5 nm

Example 1.8. Compute λ_{\max} for the following compound:



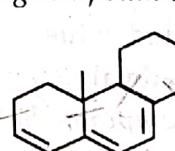
Problems 1.6. Calculate λ_{\max} for the following compounds :



[Ans. (i) Parent conjugated diene + 2 alkyi substituents + 2 ring residues + exocyclic double bond = $217 + 10 + 10 + 5 = 242$ nm]

(ii) Parent heteroannular diene + 2 ring residues + exocyclic double bond = $214 + 10 + 5 = 229$ nm]

Problem 1.7. Compute λ_{\max} for the following compound.



Handwritten calculations:
 $253 - 20 = 233$
 $233 - 30 = 203$
 $203 - 30 = 173$
 $173 - 30 = 143$
 $143 - 30 = 113$
 $113 - 30 = 83$
 $83 - 30 = 53$
 $53 - 30 = 23$
 $23 - 30 = -7$

[Ans. Parent homoannular diene + Four ring residues + Two exocyclic double bonds + one double bond extending conjugation = 313 nm.]

1.14. WOODWARD-FIESER RULES FOR α, β -UNSATURATED CARBONYL COMPOUNDS

Woodward-Fieser rules for calculating λ_{\max} for α, β -unsaturated carbonyl compounds modified by Scott may be summed up as given in table 1.4.

Table 1.4. Parent values and increments for different substituents/groups

(a) Parent Values

- (i) α, β -unsaturated acyclic or six membered ring ketone 215 nm
- (ii) α, β -unsaturated five-membered ring ketone 202 nm
- (iii) α, β -unsaturated aldehyde 207 nm

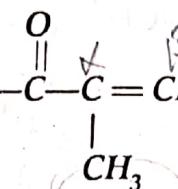
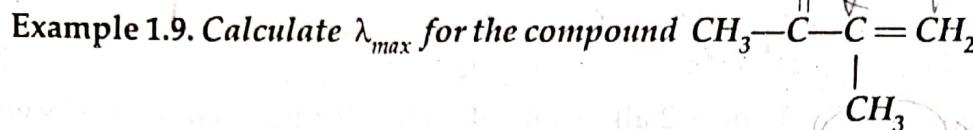
(b) Increments

- (i) Each alkyl substituent or ring residue
 - at α position 10 nm
 - at β position 12 nm
 - at γ and higher positions 18 nm
- (ii) Each exocyclic double bond 5 nm
- (iii) Double bond exocyclic to two rings simultaneously 10 nm
- (iv) Double bond extending conjugation 30 nm
- (v) Homoannular conjugated diene 39 nm
- (vi) Auxochromes:

	Position		
	α	β	γ
—OH	35	30	50
—OR	35	30	17
—SR	—	85	—
—OCOCH ₃	6	6	6
—Cl	15	12	—
—Br	25	30	—
—NR ₂	—	95	—

In these compounds, the actual spectra obtained are affected considerably by the nature of solvent employed. Therefore, a solvent correction is applied to the calculated value to obtain the λ_{max} for that particular solvent. However, we are not discussing the solvent corrections at this stage.

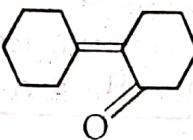
A few examples are given below for the sake of illustration of the above rules :



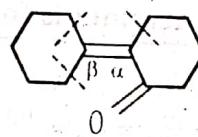
Solution. The given compound is an α, β -unsaturated acyclic ketone having an alkyl substituent in α -position.

Parent value for α, β -unsaturated acyclic ketone	= 215 nm
One alkyl substituent in α -position	= 10 nm
Calculated value	= 225 nm
Observed value	= 220 nm

Example 1.10. Compute λ_{max} for the compound having the structure :

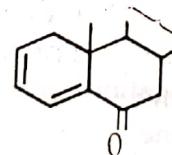


Solution. The given compound is an α, β -unsaturated six-membered ring ketone. It has one ring residue at α -position and two at β -positions and has double bonds exocyclic to two rings as shown below :

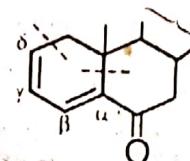


Parent value for α, β -unsaturated 6 membered cyclic ketone	= 215 nm
One ring residue at α -position	= 10 nm
Two ring residues at β -position,	$2 \times 12 = 24$ nm
Double bond exocyclic to two rings	$2 \times 5 = 10$ nm
Calculated value	= 259 nm
Observed value	= 256 nm

Example 1.11. Compute λ_{max} for the structure :



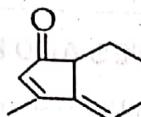
Solution. The given structure represents an α, β -unsaturated six membered ring ketone having a ring residue at α -position and another ring residue at δ -position. It has an exocyclic double bond, a double bond extending conjugation and a homoannular diene component.



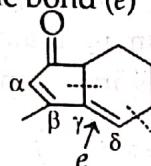
Parent value	= 215 nm
One α -ring residue	= 10 nm

One δ ring residue	= 18 nm
One exocyclic double bond	= 5 nm
One double bond extending conjugation	= 30 nm
One homoannular conjugated diene	= 39 nm
∴ Calculated value	= 317 nm
Observed value	= 319 nm

Example 1.12. Calculate λ_{\max} for the following compound :

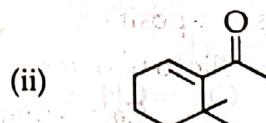
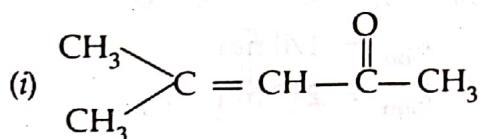


Solution. The given compound is a α, β -unsaturated five membered ring ketone having a methyl group at β -position, a ring residue at γ -position, a ring residue at δ -position, a double bond extending conjugation and an exocyclic double bond (e) as shown below.



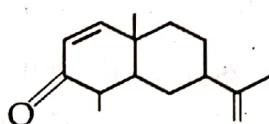
∴ Parent value for α, β -unsaturated five membered cyclic ketone	= 202 nm
One alkyl substituent at β -position	= 12 nm
One ring residue at γ -position	= 18 nm
One ring residue at δ -position	= 18 nm
One exocyclic double bond	= 5 nm
One double bond extending conjugation	= 30 nm
∴ Calculated value	= 285 nm
Observed value	= 287 nm

Problem 1.8. On the basis of Woodward-Fieser rules, calculate λ_{\max} for the following compounds :

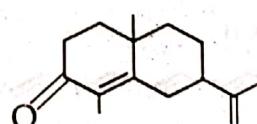


- Ans.**
- (i) Parent α, β -unsaturated acyclic ketone (215 nm) + 2 β -alkyl substituents ($2 \times 12 = 24$ nm) = 239 nm
 - (ii) Parent value (215 nm) + One α ring residue (10 nm) + β ring residue (12 nm) + β -alkyl substituent (12 nm) = 249 nm]

Problem 1.9. A given compound is expected to have the structure either A or B. Its UV spectrum shows λ_{\max} at 252 nm. Predict its actual structure.



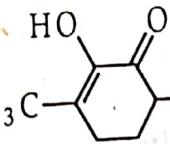
(A)



(B)

- [Ans.** Calculate λ_{\max} for both A and B. (A = 215 + 12 for β ring residue = 227; B = 215 + 10 for alkyl group at α -position + 2 \times 12 for 2 β ring residues + 5 for exocyclic double bond = 254).
The actual structure is B.]

Problem 1.10. Compute the λ_{\max} for 2-hydroxy-3,5-dimethylcyclohex-2-en-1-one.



[Ans. The given compound is $\text{H}_3\text{C}-\text{C}(\text{H}_3)-\text{CH}=\text{CH}-\text{C}(\text{H}_3)=\text{O}-\text{CH}_2$

Parent α, β -unsaturated six membered ring ketone (215 nm) + one —OH group at α -position (35 nm) + one alkyl group at β -position (12 nm) + one β ring residue (12 nm) = 274 nm.]

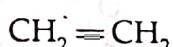
1.15. ULTRAVIOLET SPECTRA OF CONJUGATED ENES AND ENONES

It has already been studied that the presence of conjugated systems in a molecule plays a very important role in ultraviolet spectroscopy. If a molecule contains two chromophoric groups separated from each other by two or more single bonds, their effect on the UV spectrum of the molecule is generally additive. But if the two chromophoric groups are conjugated, they are *practically equivalent to a new chromophore* and a markedly different spectrum is obtained. To illustrate this statement, we now consider the ultraviolet spectra of conjugated enes and enones.

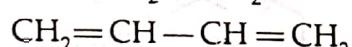
1.15.1. Ultraviolet spectra of conjugated enes

The UV spectra of all enes, whether conjugated or non-conjugated, involve the $\pi \rightarrow \pi^*$ transitions. Still the spectra of conjugated enes are markedly different from non-conjugated enes. This is basically due to the fact that in conjugated enes, the energies of π and π^* orbitals are much closer together than in simple enes. As a result, the conjugated system requires lesser excitation energy as compared to non-conjugated system and, therefore, the absorption shifts to longer wavelength. All acyclic conjugated dienes exhibit **red shift** of about 40 nm with respect to unconjugated enes, giving intense signal in the region 215–230 nm. Extended conjugation gives rise to additional red shift alongwith increase in intensity.

λ_{\max} values of the following polyenes clearly illustrate the effect of conjugation and its extent on λ_{\max} of conjugated enes.

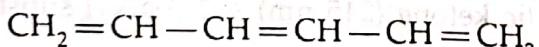


$$\lambda_{\max} = 170 \text{ nm}$$



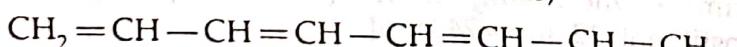
$$\lambda_{\max} = 217 \text{ nm}$$

1, 3-Butadiene (2 double bonds)



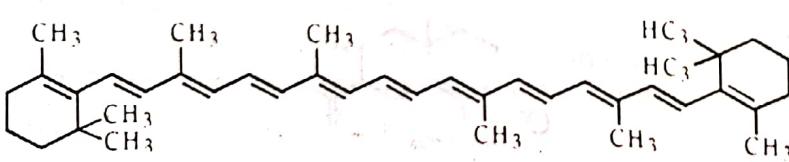
$$\lambda_{\max} = 258 \text{ nm}$$

1, 3, 5-Hexatriene (3 double bonds)



$$\lambda_{\max} = 290 \text{ nm}$$

1, 3, 5, 7-Octatetraene (4 double bonds)



$$\lambda_{\max} = 455 \text{ nm}$$

β -carotene (11 double bonds)

The UV spectrum of a conjugated diene (2,5-dimethyl-2,4-hexadiene) in methanol is shown in fig. 1.11 for the sake of illustration.

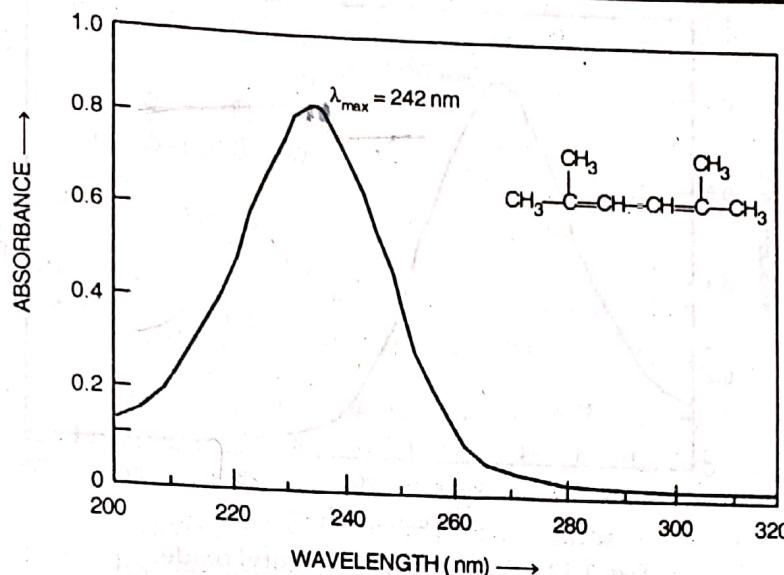


Fig. 1.11. UV spectrum of 2,5-dimethyl-2,4-hexadiene.

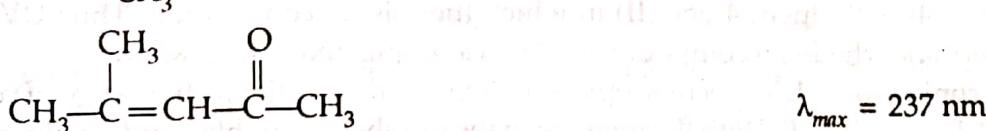
It may be seen that there is a broad absorption band in the region between 210 nm and 260 nm and the absorption is maximum at 242 nm.

1.15.2. Ultraviolet spectra of conjugated enones

Conjugated enones (*i.e.* ketones in which carbonyl group is in conjugation with a carbon-carbon double bond) exhibit strong absorption in the 215-250 nm due to $\pi \rightarrow \pi^*$ transition and weak absorption in the 310-330 nm range due to $n \rightarrow \pi^*$ transition. As compared to unconjugated ketones, there is a red shift in both the types of absorptions due to conjugation.

It may be noted that the weak $n \rightarrow \pi^*$ band is sometimes not observed at all because it is masked by the very intense ($\epsilon \approx 10,000$) $\pi \rightarrow \pi^*$ band.

λ_{max} values of $\pi \rightarrow \pi^*$ absorption bands of some enones are given below.



The UV spectrum of a conjugated ene, mesityl oxide ($\text{CH}_3-\text{C}=\text{CH}-\text{C}=\text{O}$) in ethanol is shown in fig. 1.12 for the sake of illustration.

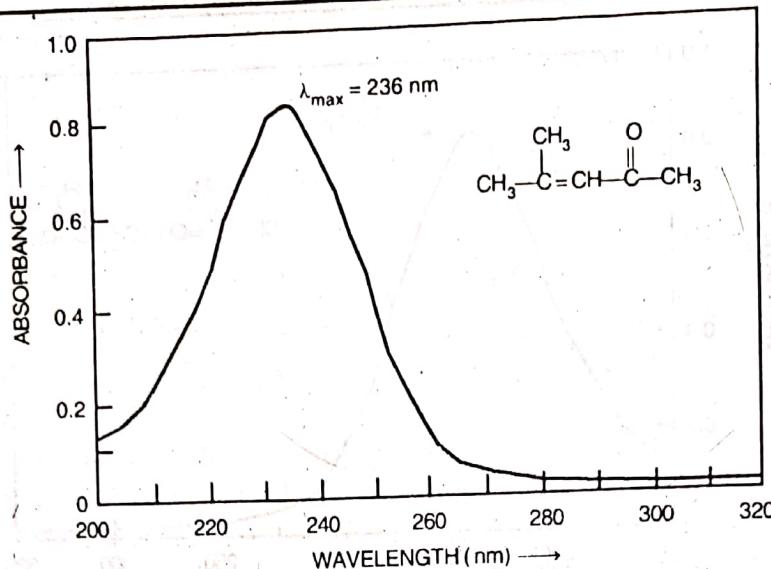


Fig. 1.12. UV spectrum of mesityl oxide.

The spectrum shows $\pi \rightarrow \pi^*$ absorption band at $\lambda_{max} = 236$. The $n \rightarrow \pi^*$ band ($\lambda_{max} = 315$) is not observed in the spectrum.

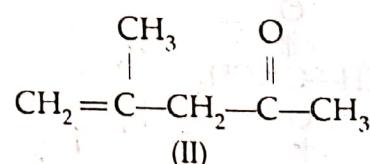
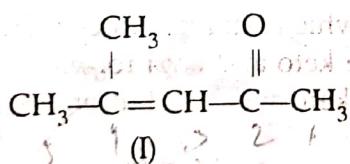
1.16. INTERPRETATION OF ULTRAVIOLET SPECTRA : APPLICATIONS OF ULTRAVIOLET SPECTROSCOPY

The interpretation of ultraviolet spectra of unknown compounds can be very useful in deriving structural information about the compounds. The main applications of ultraviolet spectroscopy are as follows :

- 1. Detection of conjugation.** Ultraviolet spectrum helps to show whether a given compound contains certain groups in conjugation with each other or not. The conjugation may be
 - between two or more carbon-carbon double (or triple) bonds
 - between carbon-carbon and carbon-oxygen double bonds or
 - between double bonds and an aromatic ring.

UV spectrum can also reveal the presence of an aromatic ring itself and the number and location of substituents attached to the carbons of the conjugated system.

For example, let us compare the UV spectra of 4-methylpent-3-ene-2-one(I) and 4-methylpent-4-ene-2-one(II) :

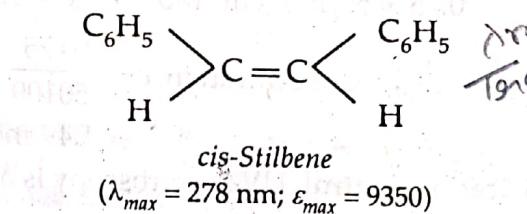
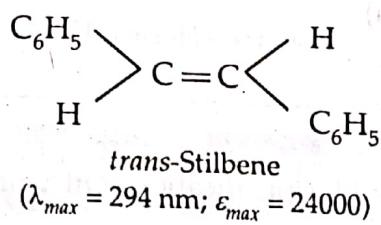


Since 4-methylpent-3-ene-2-one(I) has the carbon-carbon double bond and the carbonyl group in conjugation with each other, both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ absorption bands in it will be at longer wavelength than in 4-methylpent-4-ene(II) in which there is no conjugation. Thus UV spectrum enables us to determine whether a compound contains a conjugated system or not.

2. Extent of conjugation. UV spectroscopy is also employed to estimate the extent of conjugation in polyenes $R-(CH=CH)_n-R$. With the increase in the number of double bonds (or increase in the value of n), the absorption shifts to longer wavelength. For compounds having 8 or more double bonds, the absorption may shift to even visible region of light. Thus by determining the λ_{max} of a given polyene, it may be possible to know the number of double bonds in conjugation.

3. Determination of configuration of geometrical isomers. In case of geometrically isomeric compounds, the *trans* isomers exhibit λ_{max} at slightly longer wavelengths and have larger mol

absorptivities than the *cis* forms. For example, of the two stilbenes ($C_6H_5-CH=CH-C_6H_5$), the *trans* isomer shows $\lambda_{max} = 294$ nm ($\epsilon = 24000$) while the *cis* isomer has $\lambda_{max} = 278$ nm ($\epsilon = 9350$).



trans *cis*

The above observation can be justified in terms of steric hindrance. In the *trans* isomer, the bulky groups lie on either side of the double bond and there is no steric hindrance. As a result, the ethylenic double bond and the π -bonds of benzene ring lie in the same plane and the π orbital overlap of the conjugated system is quite effective. Therefore, the *trans* isomer absorbs at longer wavelength.

In the *cis* isomer, the bulky groups lie on the same side of the double bond giving rise to steric hindrance. Therefore, the ethylenic double bond and π -bonds of benzene are forced to be non-planar. Due to this distortion, the π -orbital overlap is not so effective. The decrease in π -orbital overlap leads to decrease in conjugation. Hence, the *cis* isomer absorbs at shorter wavelength.

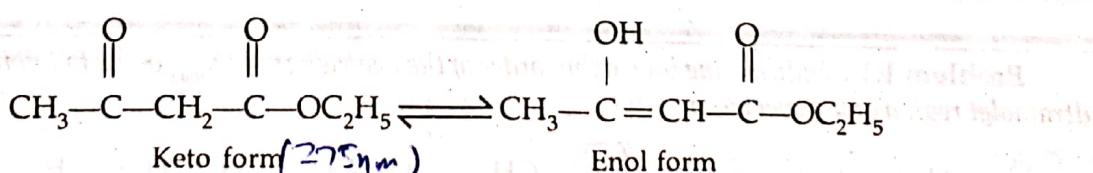
4. Detection of functional groups. UV spectrum can be used for the detection of certain functional groups and other structural features if the absorption takes place above 200 nm.

Even the *absence* of any absorption above 200 nm is of some utility as it shows the absence of conjugation, carbonyl group and benzene rings in the compound.

5. Determination of strength of hydrogen bonding. If a compound forms hydrogen bonds with protic solvents such as water and alcohol, it is possible to find the strength of hydrogen bonding by comparing the λ_{max} in the protic solvent with λ_{max} in a non-polar solvent. For example, carbonyl compounds form hydrogen bonds between water and carbonyl oxygen. As a result the energy of n electrons of carbonyl oxygen in the ground state decreases by an amount equal to the strength of the hydrogen bond. Consequently the $n-\pi^*$ transition of the carbonyl compound requires more energy and therefore it is shifted to lower wavelength. For example, $n-\pi^*$ transition of acetone in hexane (non-polar solvent) takes place at 279 nm but in water (protic solvent) it occurs at 264 nm.

From the above hypsochromic shift of 15 nm, the strength of hydrogen bond between water and acetone can be calculated.

6. Study of keto-enol tautomerism. In case of compounds which exhibit keto-enol tautomerism, UV spectra show characteristic absorption bands of both the keto and enol forms. For example, ethyl acetoacetate which exists as an equilibrium mixture of keto and enol tautomers shows two



absorption bands for the keto and enol forms respectively. The keto form has $\lambda_{max} = 275$ nm with very low intensity ($\epsilon = 16$) while the enol form has $\lambda_{max} = 244$ nm with very high intensity ($\epsilon = 16000$).

7. Quantitative analysis. UV spectroscopy provides a very sensitive method of quantitative analysis. It is based upon Beer-Lambert law which relates the absorbance (A) of a substance with its concentration (c), path length (l) and molar absorptivity (ϵ) ; that is :

$$A = \epsilon cl$$

For example, we can find the concentration of vitamin A in a sample by determining the

absorbance of the given sample. Pure vitamin A has $\lambda_{max} = 325 \text{ nm}$ ($\epsilon = 50,100$). If the given sample when taken in a cell with a path length of 1 cm shows an absorbance of 0.75 at 325 nm, concentration can be calculated as follows :

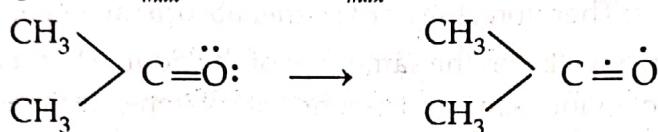
$$0.75 = 50,100 (\text{cm}^2 \text{ mol}^{-1}) \times c \times 1.00 \text{ (cm)} \quad (A = \epsilon c)$$

$$\therefore \text{Concentration, } c = \frac{0.75}{50100} \\ = 1.49 \text{ mol L}^{-1}$$

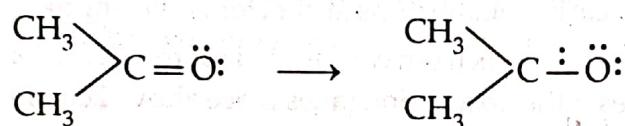
8. Purification control. UV spectroscopy is also used for purification control in dye stuff and pharmaceutical industries.

Example 1.13. The UV spectrum of acetone shows two important peaks at $\lambda_{max} = 279 \text{ nm}$ ($\epsilon_{max} 15$) and $\lambda_{max} = 189 \text{ nm}$ ($\epsilon_{max} 900$). Identify the electronic transition for each peak.

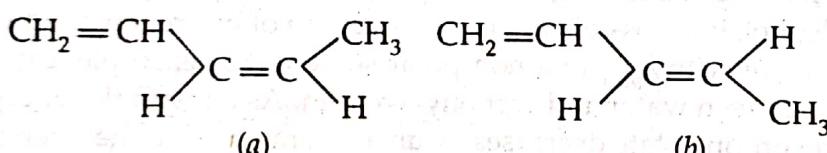
Solution. The peak at $\lambda_{max} = 279 \text{ nm}$ ($\epsilon_{max} 15$) is due to $n \rightarrow \pi^*$ transition. That is :



The peak at $\lambda_{max} = 189 \text{ nm}$ ($\epsilon_{max} 900$) is due to $\pi \rightarrow \pi^*$ transition. That is :



Example 1.14. The following dienes have λ_{max} at 176 nm, 211 nm and 215 nm respectively. Find out which is which.



(a)

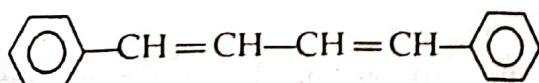
(b)

(c)

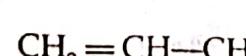
Solution. Of the three compounds, (c) represents an isolated pentadiene while (a) and (b) are conjugated pentadienes. It is obvious that (c) would absorb at the shortest wavelength. In other words the compound showing $\lambda_{max} = 176 \text{ nm}$ must be (c).

Further, (a) and (b) are geometrically isomeric conjugated pentadienes. Since in such cases the *trans* isomer usually absorbs at slightly higher wavelength than the *cis* isomer, the compound exhibiting λ_{max} at 215 nm should be the *trans* isomer, i.e., (b). As such the compound with $\lambda_{max} = 211 \text{ nm}$ must be (a).

Problem 1.11. Indicate the increasing order of the wavelength of λ_{max} of the following compounds in the ultraviolet region of the spectrum.



(a)



(b)



(c)

[Ans. (c) < (b) < (a)]

Problem 1.12. Which of the following compounds, if any, can give an ultraviolet spectrum showing λ_{max} at : (i) 218 ($\epsilon = 18000$), (ii) 245.5 ($\epsilon = 9800$), (iii) 186.5 ($\epsilon = 450$), (iv) 415 ($\epsilon = 63,000$).