

## Ultraviolet and Visible Spectroscopy

### ELECTROMAGNETIC RADIATIONS

Visible light is a form of energy which can be described by two complementary theories i.e. Corpuscular theory and wave theory . Neither of these theories can explain all the properties of light, some properties of light such as photochemical effect ,black body radiations can be explained only by the corpuscular theory ,while the other properties of light such as diffraction ,interference etc can be explained only by the wave theory .

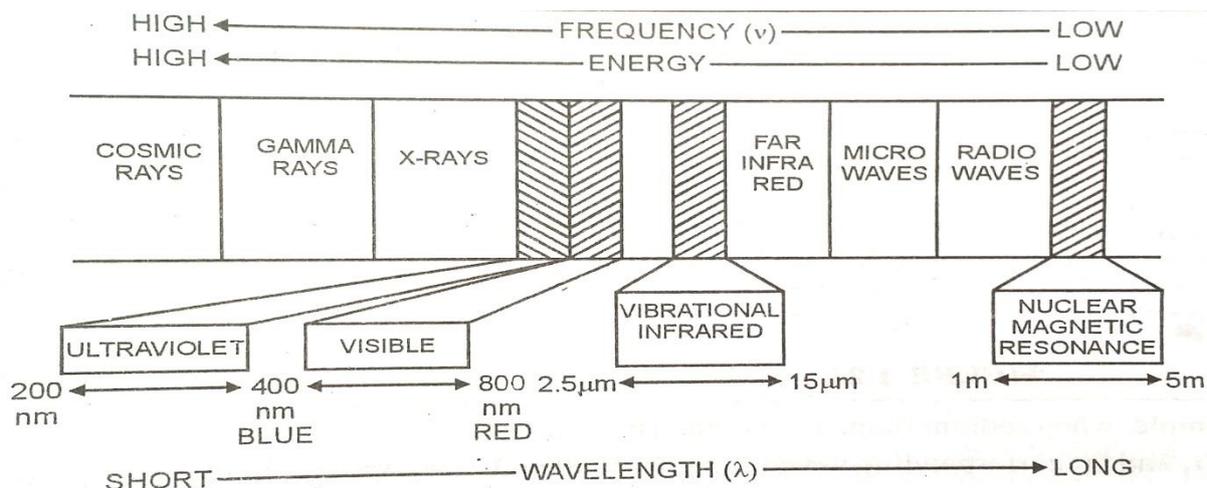
### Electromagnetic wave theory

Wave theory was put forward by James Maxwell in 1864 .According to this theory

- 1.Energy is emitted from any source continuously in form of waves or radiations and the energy thus emitted is called radiant energy. The most common example of radiant energy is heat,light X-rays etc.
- 2.Each radiation consists of mutually perpendicular oscillating electric and magnetic fields both of which are perpendicular to the direction of propagation of the radiation .
- 3.All radiations have wave character and travel with the velocity of light i.e.  $3 \times 10^{10}$

### ELECTROMAGNETIC SPECTRUM

The field of spectroscopy deals with the study of absorption or emission of electromagnetic radiations .We are familiar with the number of different types of electromagnetic radiations such as cosmic rays, X-rays ,Ultra violet light ,visible light ,infra red radiations ,radio waves radar waves etc.All the electromagnetic radiations travel with the same velocity i.e. $3 \times 10^{10}$  cm/sec but differ from one another in the wave length of their waves .The arrangement of all types of electromagnetic radiations in the order of their increasing wavelength or decreasing frequency is called the electromagnetic spectrum.



**Spectroscopy** is the study of the interaction between matter and electromagnetic radiation—radiant energy that displays the properties of both particles and waves. Several different spectrophotometric techniques are used to identify compounds. Each employs a different type of electromagnetic radiation. We will start here by looking at ultraviolet and visible (UV/Vis) spectroscopy

**UV/Vis spectroscopy** provides information about compounds with conjugated double bonds. Ultraviolet light and visible light have just the right energy to cause an electronic transition—the promotion of an electron from one orbital to another of higher energy. Depending on the energy needed for the electronic transition, a molecule will absorb either ultraviolet or visible light. If it absorbs **ultraviolet light**, a UV spectrum is obtained; if it absorbs **visible light**, a visible spectrum is obtained. Ultraviolet light is electromagnetic radiation with wavelengths ranging from 180 to 400 nm (nanometers); visible light has wavelengths ranging from 400 to 780 nm. (One nanometer is or 10 Å.) **Wavelength** is inversely related to the energy: The shorter the wavelength, the greater is the energy. Ultraviolet light, therefore, has greater energy than visible light.

$$E = hc/\lambda$$

$h$  = Planck's constant

$c$  = velocity of light

$\lambda$  = wavelength

The normal electronic configuration of a molecule is known as its **ground state**—all the electrons are in the lowest-energy molecular orbitals. When a molecule absorbs light of an appropriate wavelength and an electron is promoted to a higher energy molecular orbital, the

molecule is then in an **excited state**. Thus, an **electronic transition** is the promotion of an electron to a higher energy MO. The relative energies of the bonding, nonbonding, and antibonding molecular orbitals are shown..

Ultraviolet and visible light have sufficient energy to cause only the two electronic transitions shown in Figure 8.5. The electronic transition with the lowest energy is the promotion of a nonbonding (lone-pair) electron (n) into a antibonding molecular orbital. This is called an (stated as “n to star”) transition. The higher energy electronic transition is the promotion of an electron from a bonding molecular orbital into a antibonding molecular orbital, known as a (stated as “ to star”) transition. This means that only organic compounds with electrons can produce UV Vis spectra.

## **PRINCIPLES OF UV SPECTROSCOPY**

Whenever UV radiation is passed through the solution of an organic compound, it is either absorbed or transmitted depending up on the wavelength and its molecular structure of the organic compound. As a result of the absorption of the energy an electron gets excited from the electronic state to some higher electronic state. During this absorption process, some of the molecules of the organic compound will collide with the photons of the radiant energy. Although a large number of such photon molecule collisions are possible, but only those will result in absorption of energy in which the energy of the photon exactly matches the difference in energies of the electron in the ground and the excited electronic states of the molecule

If  $E_0$  and  $E_1$  are the energies of the ground and the first excited electronic states of the molecule respectively and  $\Delta E$  is the difference in energy

$$\Delta E = (E_1 - E_0) = h\nu = hc/\lambda$$

### **The Beer–Lambert Law**

Wilhelm Beer and Johann Lambert independently proposed that at a given wavelength, the absorbance of a sample depends on the amount of absorbing species that the light encounters as it passes through a solution of the sample. In other words, absorbance depends on both the concentration of the sample and the length of the light path through the sample. The relationship among absorbance, concentration, and length of the light path is known as the **Beer–Lambert law** and is given by

$$A = \epsilon cl$$

Where

$$A = \text{absorbance of the sample} = \log I_0/I$$

$I_0$  = intensity of the radiation entering the sample

$I$  = intensity of the radiation emerging from the sample

$c$  = concentration of the sample, in moles/liter

$l$  = length of the light path through the sample, in centimeters

$\epsilon$  = molar absorptivity (liter mol<sup>-1</sup> cm<sup>-1</sup>)

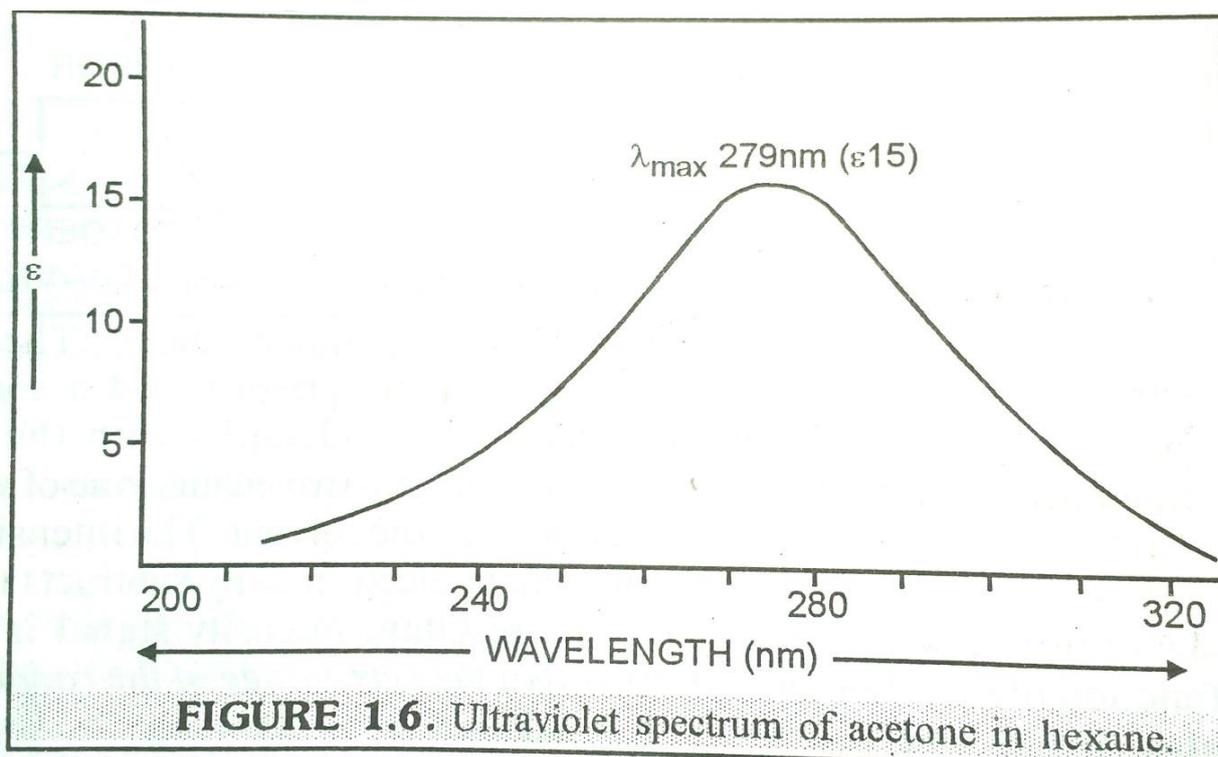
### **Molar absorptivity**

The **molar absorptivity** (formerly called the extinction coefficient) of a compound is a constant that is characteristic of the compound at a particular wavelength. It is the absorbance that would be observed for a 1.00 M solution in a cell with a 1.00-cm path length. The molar absorptivity of acetone, for example, is 9000 at 195 nm and 13.6 at 274 nm. The solvent in which the sample is dissolved when the spectrum is taken is reported because molar absorptivity is not exactly the same in all solvents. So the UV spectrum of acetone in hexane would be reported as 195 nm ( hexane); 274 nm ( hexane). Because absorbance is proportional to concentration, the concentration of a solution can be determined if the absorbance and molar absorptivity at a particular wavelength are known.

$$\epsilon = A/cl$$

### **PRESENTATION OF SPECTRA**

The ultraviolet-visible spectrum is generally recorded as a plot of absorbance versus wavelength. It is customary to then replot the data with either  $e$  or  $\log e$  plotted on the ordinate and wavelength plotted on the abscissa. Figure 7.4, the spectrum of benzoic acid, is typical of the manner in which spectra are displayed. However, very few electronic spectra are reproduced in the scientific literature; most are described by indications of the wavelength maxima and absorptivities of the principal absorption peaks. For benzoic acid, a typical description might be



**FIGURE 1.6.** Ultraviolet spectrum of acetone in hexane.

## SOLVENTS

The choice of the solvent to be used in ultraviolet spectroscopy is quite important. The first criterion for a good solvent is that it should not absorb ultraviolet radiation in the same region as the substance whose spectrum is being determined. Usually solvents that do not contain conjugated systems are most suitable for this purpose, although they vary regarding the shortest wavelength at which they remain transparent to ultraviolet radiation. Table 7.1 lists some common ultraviolet spectroscopy solvents and their cutoff points or minimum regions of transparency. Of the solvents listed in Table 7.1, water, 95% ethanol, and hexane are most commonly used. Each is transparent in the regions of the ultraviolet spectrum in which interesting absorption peaks

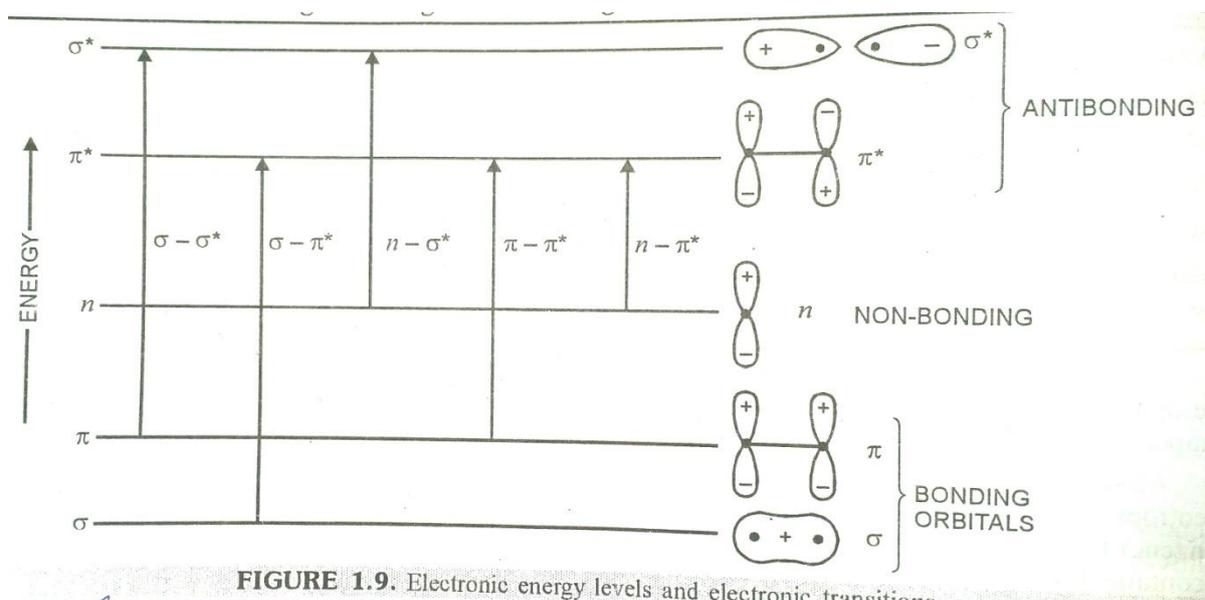
from sample molecules are likely to occur. A second criterion for a good solvent is its effect on the fine structure of an absorption band. Figure 7.5 illustrates the effects of polar and nonpolar solvents on an absorption band. A nonpolar solvent does not hydrogen bond with the solute, and the spectrum of the solute closely approximates the spectrum that would be produced in the gaseous state, in which fine structure is often observed. In a polar solvent, the hydrogen bonding forms a solute–solvent complex, and the fine structure may disappear

Acetonitrile	190 nm	<i>n</i> -Hexane	201 nm
Chloroform	240	Methanol	205
Cyclohexane	195	Isooctane	195

## Types of Electronic transitions

The absorption of electronic transition by organic compounds in the UV and Visible region occurs due to excitation of electrons from bonding or non-bonding molecular orbitals (ground state) to the antibonding molecular orbitals (excited state) which are usually vacant in the ground state of the molecule.

The electronic transitions that occur in UV and visible region are of following types:

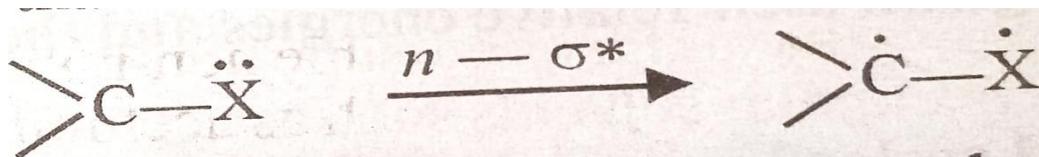


- (i) **Transitions.** ( $\sigma \rightarrow \sigma^*$ ) Transitions in which an electron is excited from sigma-bonding MO to sigma star antibonding MO are called  $\sigma \rightarrow \sigma^*$  transitions. These transitions are shown by only those compounds which all the electrons are involved in  $\sigma$ -bond formation i.e., in saturated hydrocarbons. These require very high energy. Therefore, these transitions occur at short wavelengths or high frequency and are usually found in vacuum or far ultraviolet region. For example, methane absorbs at 125nm and propane at 135nm.



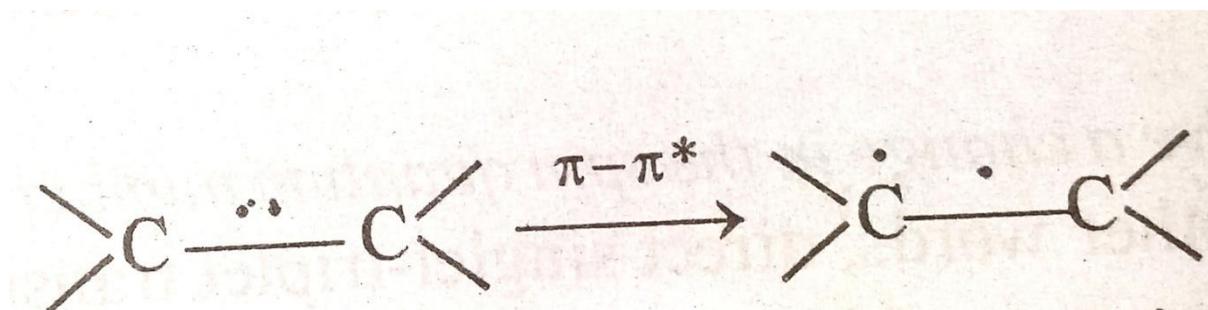
- (ii) **n**— $\sigma^*$  Transitions in which a non-bonding electron is excited to  $\sigma^*$  antibonding MO are called n— $\sigma^*$  transitions. These transitions occur in those compounds which contain heteroatoms such as oxygen, nitrogen, sulphur, halogens etc. For example alcohol, ethers, alkyl halides, amines, aldehydes and ketones show this

type of transition. These transitions require lower energy than  $\sigma-\sigma^*$  transitions and hence occur at longer wavelengths than  $\sigma-\sigma^*$  transitions



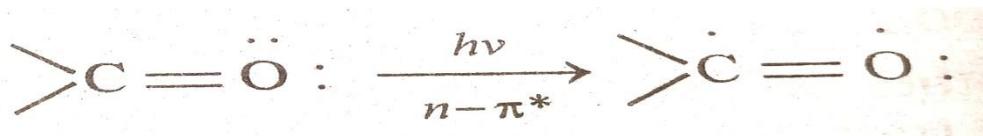
In fact the energy required for these transitions depends up on the electronegativity of the heteroatom. Lower the electronegativity, higher the wavelength of absorption. For example methyl alcohol absorbs at  $\lambda_{\max}$  258.

(iii)  $\pi-\pi^*$  Transitions. transitions in which a  $\pi$ -electron is excited to a antibonding orbital  $\pi^*$  MO are called  $\pi-\pi^*$



This type of transition occurs in saturated compounds containing double bonds and also in aromatic compounds. These transitions generally require a large amount of energy and hence occur at short wavelength. For example organic compounds containing isolated unsaturated centre, the absorption due to  $\pi-\pi^*$  transition occurs well outside the range of ordinary spectrophotometers. In saturated aldehydes and ketones the  $\pi-\pi^*$  transition produces a n absorption band of high intensity at about 285nm.

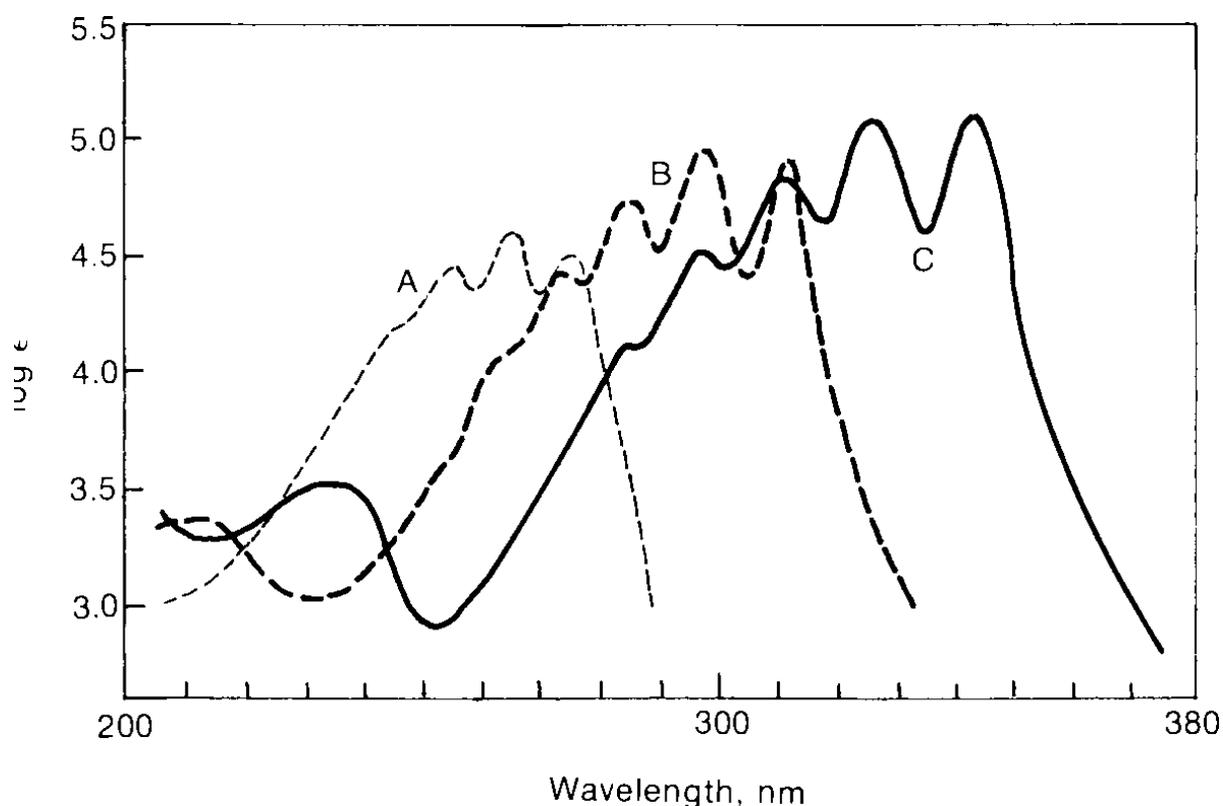
(d)  $n-\pi^*$  transitions. transitions in which an electron is excited from the non bonding atomic orbital to the  $\pi^*$  MO are called  $n-\pi^*$  transitions.



All organic compounds containing a double bond between carbon and some hetero atom such as  $C=O$ ,  $C=S$ ,  $C=N$  etc this type of transition.

### THE EFFECT OF CONJUGATION

One of the best ways to bring about a bathochromic shift is to increase the extent of conjugation in a double-bonded system. In the presence of conjugated double bonds, the electronic energy levels of a chromophore move closer together. As a result, the energy required to produce a transition from an occupied electronic energy level to an unoccupied level decreases, and the wavelength of the light absorbed becomes longer. Figure 7.10 illustrates the bathochromic shift that is observed in a series of conjugated polyenes as the length of the conjugated chain is increased.



### THE EFFECT OF CONJUGATION ON ALKENES

The bathochromic shift that results from an increase in the length of a conjugated system implies that an increase in conjugation decreases the energy required for electronic excitation. This is true and can be explained most easily by the use of molecular orbital theory. According to molecular orbital (MO) theory, the atomic  $p$  orbitals on each of the carbon atoms combine to make  $p$  molecular orbitals. For instance, in the case of ethylene (ethene), we have two atomic  $p$  orbitals,  $f_1$  and  $f_2$ . From these two  $p$  orbitals we form two  $p$  molecular orbitals,  $y_1$  and  $y_2^*$ , by taking linear combinations. The bonding orbital  $y_1$  results from the addition of the wave functions of the two  $p$  orbitals, and the antibonding orbital  $y_2^*$  results

from the subtraction of these two wave functions. The new bonding orbital, has an energy lower than that of either of the original  $p$  orbitals; likewise, the antibonding orbital has an elevated energy.

## Chromophoric group

The term chromophoric was originally applied to a system which imparts colour to a compound (Greek, chromophorus=color carrier) . For example, nitro group is a chromophore since it imparts yellow colour to a compound. Similarly, aryl conjugated azo group (Ar---N=N---Ar) is a chromophore since it imparts colour to the azo dyes. But now the term chromophore is used in a much broader sense. Thus, a chromophore is now defined as any functional group that absorbs electromagnetic radiations irrespective of the fact whether it imparts colour to the compound or not.

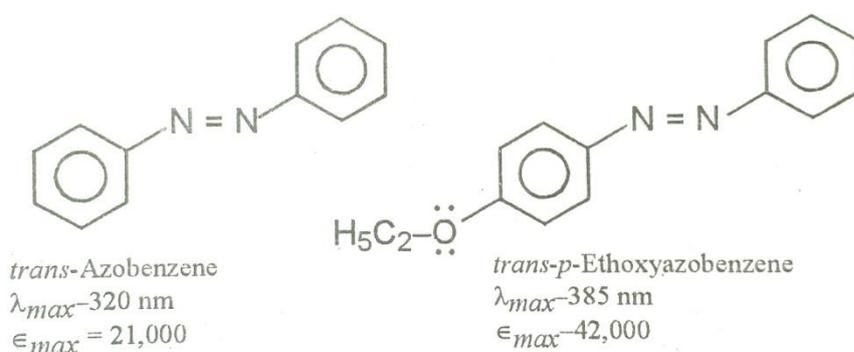
For example, a carbonyl group is a chromophore since it absorbs in the UV region at round 279 nm with a molar extinction coefficient of about 15.

Chromophores such as  $>C=C<$  and  $-C=C-$  which contains  $\pi$ - electrons and hence undergo  $\pi$ - $\pi^*$  transitions.

2. Chromophores such as  $>C=O$ ,  $-N=N-$ ,  $-NO_2$  etc. Which contain both  $\pi$ - and  $n$ - electrons and hence undergo  $\pi$ -  $\pi^*$  and  $n$ -  $\pi^*$  transitions.

## AUXOCHROMES

Groups which themselves do not show any characteristic absorption above 200 nm but which when attached to a given chromophore usually cause a shift of the absorption band to longer wavelength with a simultaneous increase in the intensity of the absorption band are called auxochromes. Some common examples of auxochromic groups are  $-OH$  (hydroxyl),  $-SH$  (sulphydryl) and their derivatives such as  $-OR$ ,  $-NHR$ ,  $-NR_2$ ,  $-SR$  etc . and some of the halogens. For illustrations, consider the following examples;

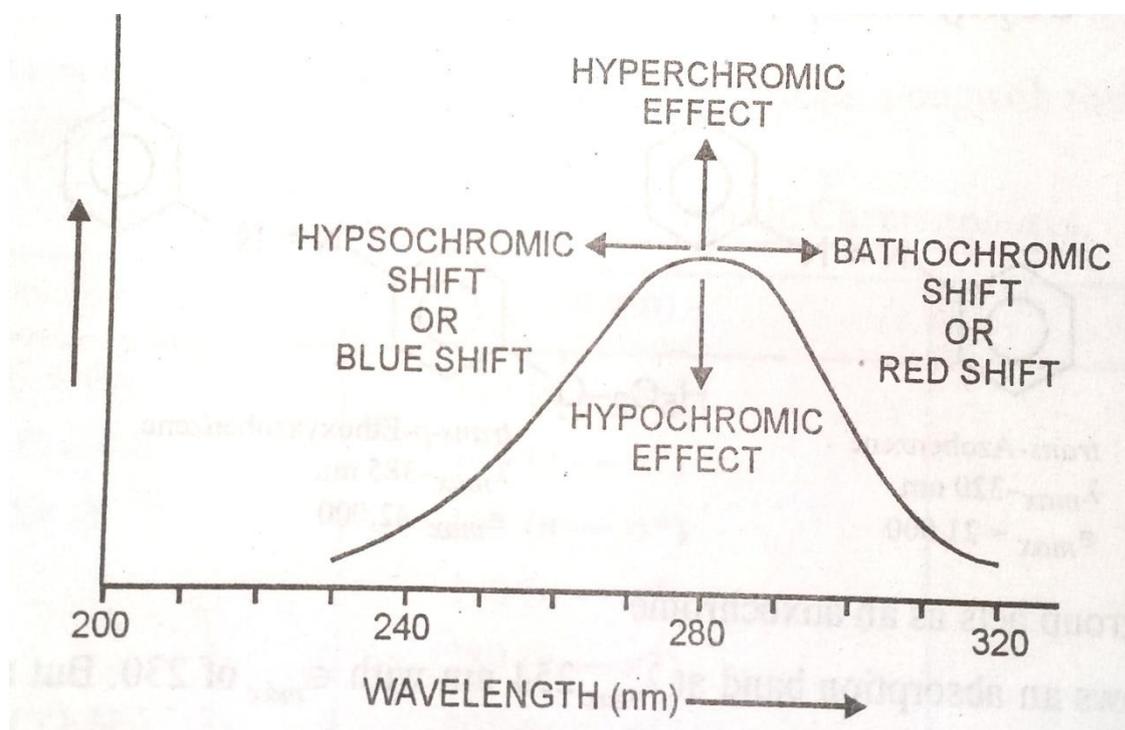


1. Trans-azobenzene absorbs at 320 nm with  $\epsilon_{\max} = 21,000$ . However, the presence of an auxochrome such as ethoxy group ( $-\text{OC}_2\text{H}_5$ ) at the p-position shifts the  $\lambda_{\max}$  to 385 nm with the intensity ( $\epsilon_{\max} = 42,000$ ).

2. Benzene shows an absorption band at  $\lambda_{\max}$  254 nm with  $\epsilon_{\max}$  of 230. But aniline shows  $\lambda_{\max}$  at 280 nm with  $\epsilon_{\max}$  of 1430.

Thus,  $-\text{NH}_2$  GROUP ACTS AS AN AUXOCROME. However, the anilinium ion which does not contain non-bonding electrons shows  $\lambda_{\max}$  at 254 nm ( $\epsilon_{\max}$  160) which is characteristic of the benzene ring.

**1. Bathochromic shift or Red shift.** The shift of absorption maxima to longer wavelength is called bathochromic shift or the red shift. This can be achieved by the following three ways.



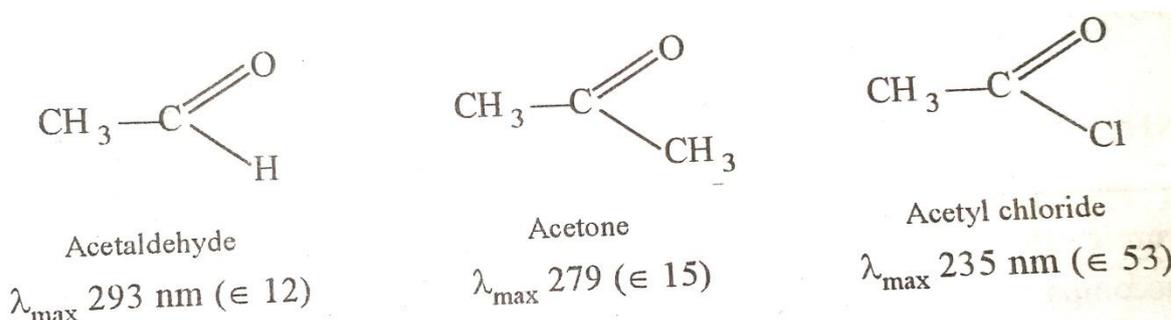
(a) By attaching an auxochrome to the carbon-carbon double bond or the benzene ring. As discussed above, placement of an auxochrome such as ethoxy group at the p-position of trans-azobenzene shifts its longest wavelength absorption band by 65 nm to a longer wavelength and also increases its intensity two-fold, i.e., trans-p ethoxyazobenzene;  $\lambda_{\max}$  385 nm ( $\epsilon$  21,000).

(b) By conjugation of two chromophores. For example, ethylene absorbs strongly at 175 nm ( $\epsilon$  15,000) in the far UV region, but when two double bonds are brought in conjugation, just as in butadiene, the  $\pi-\pi^*$  transition undergoes a bathochromic shift with a hyperchromic effect, and butadiene absorbs at 270 nm ( $\epsilon$  21,000).

(c) By decreasing the polarity of the solvent. For example, acetone shows a  $\lambda_{\max}$  at 264.5 nm in  $\text{H}_2\text{O}$  due to  $n-\pi^*$  excitation. If hexane is used as a solvent, the absorption maximum shifts to 279 nm.

**2. Hypsochromic shift.** A shift of absorption maxima to shorter wavelength is called hypsochromic shift or the blue shift. This may be caused by the following factors.

(i) By attaching an auxochrome to the  $\text{C}=\text{O}$  group. For example,  $n-\pi^*$  transition of acetaldehyde appears at 293 nm but it undergoes a hypsochromic shift when its H-atom is substituted by an auxochrome.



(ii) By increasing the polarity of the solvent. For example,  $n-\pi^*$  transition of acetone in hexane appears at 279 nm ( $\epsilon$  15) but this absorption shifts to lower wavelength and appears at 264.5 nm in water. As already explained this blue shift is due to H-bonding which lowers the energy of the electrons thereby increasing the energy gap between the  $n$ - and  $\pi^*$ -orbitals.

**3. HYPERCHROMIC EFFECT.** This effect leads to an increase in molar absorptivity. Further, bathochromic effect is often accompanied by hyperchromic effect. E.g., when phenol is converted into phenoxide ion both the primary and secondary bands of phenol show a bathochromic shift with hyperchromic effect.

**4. Hypochromic effect.** This effect leads to a decrease in molar absorptivity. Further, hypsochromic shift is often accompanied by hypochromic effect. E.g., benzoic acid is converted into benzoate ion; or aniline is converted into anilinium ion, both the primary and secondary bands exhibit hypsochromic shifts with hypochromic effect.

### WOODWARD-FIESER RULES FOR CALCULATION OF $\lambda_{\text{MAX}}$ OF SIMPLE CONJUGATED DIENES

Woodward formulated certain empirical rules for calculating the  $\lambda_{\max}$  for long wavelength  $\pi-\pi^*$  transition for dienes and polyenes. These rules were later by FIESER in 1959. According to these rules, each diene has a certain fixed basic value and the value of the  $\lambda_{\text{MAX}}$  upon the following points:

- (I) the alkyl substituents or ring residues present on the diene system.

- (II) The number of double bonds extending conjugation beyond the diene system.
- (III) The presence of polar groups or auxochromes such as  $-X(=Cl, Br \text{ etc.})$ ,  $-OR$ ,  $-SR$ ,  $-NH_2$ ,  $-OCOCH_3$  etc.

**Example 1. calculate the  $\lambda_{max}$  for the most intense band in the UV spectrum of 2,3-dimethyl-1,3-butadiene.**

**Solution** (I) the structure of 2,3-dimethyl-1,3-butadiene is

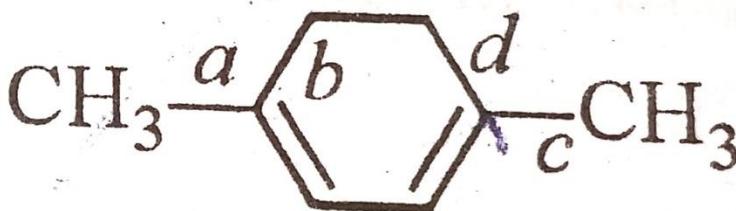
It has two methyl substituents at positions 2 and 3 (marked as a and b) Thus, parent value for acyclic diene = 214 nm

Two substituents (2x5) = 10 nm

Calculated  $\lambda_{max}$  = 224 nm

The observed  $\lambda_{max}$  is 226 nm.

**Example 2. calculate the  $\lambda_{max}$  for the most intense band in the UV spectrum of 1,4-dimethylcyclohexa-1,3-diene.**



**Solution.** The structure of 1,4-dimethylcyclohexa-1,3-butadiene is

It is a homoannular diene with two methyl substituents marked as (a) and (c) and two ring residues, marked as (b) and (d).

Therefore, parent value for homoannular diene = 253 nm

Two methyl substituents, (2x5) = 10 nm

Two ring residues, (2x5) = 10 nm

Calculated  $\lambda_{max}$  = 273 nm

The observed  $\lambda_{max}$  = 265 nm

Example 3. Calculated  $\lambda_{max}$  for the diene.

Solution. the given compound is heteroannular diene with four ring residues

Parent value for heteroannular diene = 214 nm

Four ring residues (4x5) = 20 nm

Calculated value = 234 nm

Observed value = 236 nm

**WOODWARD-FIESER RULES FOR CALCULATION OF  $\lambda_{MAX}$  for  $\pi$ -  $\pi^*$  (transition) absorption band of  $\alpha\beta$ - unsaturated carbonyl compounds :Enones**

Woodward and Fieser examined the UV spectra of a number of  $\alpha\beta$ -unsaturated compounds in ethanol and formulated a set of empirical rules which help us to predict the  $\lambda_{max}$  of  $\pi$ -  $\pi^*$  transition in an unknown compound. These rules are summarised table 1.6.

**Solvent correction.** Since  $\pi$ -  $\pi^*$  absorption band is strongly affected by polarity of the solvent, therefore, to convert  $\lambda_{max}$  values obtained in other solvents to standard ethanol solvent, the following corrections have been proposed

SOLVENT	CORRECTION	SOLVENT	CORRECTION
METHNOL	0	CYCLOHEXANE	+11
CHLOROFORM	+1	DIOXAN	+5
ETHER	+7	WATER	-8
HEXANE	+11		

**BASE VALUES :**

- |   |        |
|---|--------|
| (1) $\alpha,\beta$ -unsaturated acyclic or six-membered ring Ketone | 215 nm |
| (2) $\alpha,\beta$ -unsaturated five-membered ring Ketone           | 202 nm |
| (3) $\alpha,\beta$ -unsaturated aldehydes                           | 207 nm |
| (4) $\alpha,\beta$ -unsaturated acids or esters                     | 197 nm |

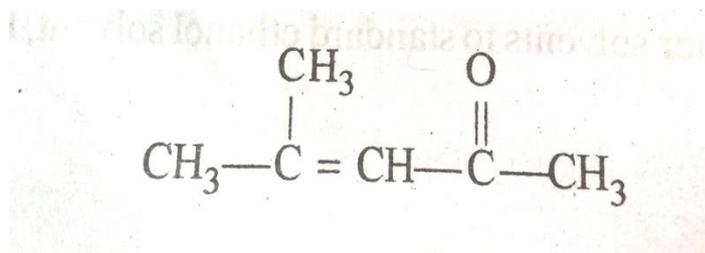
Increments:

- |  |       |
|--|-------|
| (1) Each alkyl group or ring residue       |       |
| $\alpha$                                   | 10 nm |
| $\beta$                                    | 12 nm |
| $\gamma$ and higher                        | 18 nm |
| (2) Each double bond extending conjugation | 30 nm |
| (3) Each exocyclic double bond             | 5 nm  |
| (5) Homoannular diene component            | 39 nm |

(i-e, two double bonds which are conjugated with C=O group lie in the same ring )

**Auxochromes                      position**

Example. Calculate  $\lambda_{\max}$  for the following compound



Solution. The given compound is an  $\alpha,\beta$ -unsaturated Ketone having two alkyl substituents (i.e., methyl) at  $\beta$ -position.

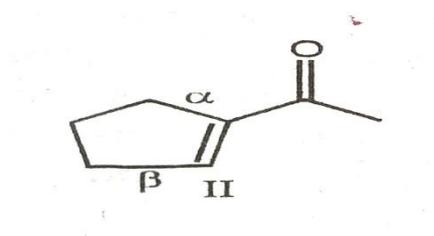
Basic value for  $\alpha,\beta$ -unsaturated acyclic ketone = 215 nm.

Two alkyl substituents at  $\beta$ -position, (2x12) = 24 nm

Therefore, Calculated  $\lambda_{\max}$  = 239 nm

The observed value is 237 nm ( $\epsilon_{\max} = 12,500$ )

**Example.** Calculate the  $\lambda_{\max}$  for the compound below;



Basic value for the  $\alpha,\beta$ -unsaturated five membered ring ketone = 202 nm

One  $\alpha$ -residue = 10 nm

One  $\beta$ -ring residue = 12 nm

Therefore, Calculated  $\lambda_{\max}$  = 224 nm

**Application for UV spectroscopy.** Some important applications of UV spectroscopy are discussed below;

**1. Detection of functional groups.** UV spectroscopy has been used to detect the presence or the absence of certain functional groups in organic molecules. E.g., if an organic compound does not show  $\lambda_{\max}$  above 200 nm, it cannot contain a conjugated chromophore (i.e.,  $C=C-C=C$ ), an aldehyde or a keto group, a benzene ring.

**2. Detection Impurities.** Compounds with large  $\lambda_{\max}$  can be detected when present as impurities even at a concentration provided the sample itself does not show any absorption in the of impurities.

**3. IDENTIFICATION OF GEOMETRICAL ISOMERS.** UV spectroscopy can be used to distinguish between a pair of geometrical isomers. In general, trans-compounds absorb at longer wavelengths with higher extinction coefficient than the corresponding cis-isomers.

**4. Detection of formation of charge-transfer complexes.** UV spectroscopy is quite useful in detecting the formation of charge complexes as discussed below:

Many electro rich organic (i-e, donor) molecules such as mesitylene, aromatic hydrocarbons such as naphthalene, anthracene etc. Phenols and aromatic amines are to form charge transfer complexes with electronic deficient (i-e, acceptor) molecules such as picric acid, tetracyanoethylene (TCNE) etc.

**5. Determination of extent of conjugation.** One of the most important uses of UV-spectroscopy is to detect and estimate the extent of conjugation in a polyene,  $R-(CH=CH)_N-R$ . Butadiene itself absorbs at 217 nm. But addition of each double bond shifts the absorption maxima to the longer wavelength by about 30 nm. Greater the number of such conjugated double bonds, longer is the wavelength of absorption.