

# ULTRAVIOLET AND VISIBLE SPECTROSCOPY

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## 19.1 INTRODUCTION

Spectroscopy involves interaction of electromagnetic radiation with matter. Electromagnetic radiation is considered as waves of energy propagated from a source in space and consists of oscillating electric and magnetic field at right angles to each other. Each electromagnetic radiation has characteristic wavelength ( $\lambda$ ), frequency ( $v$ ) or wave number,  $\bar{v} = \left(\frac{1}{\lambda}\right)$ . The absorption or emission of electromagnetic radiation is quantized

and each quantum of radiation is called photon. The energy ( $E$ ) of a photon is given by Planck's law, i.e.  $E = hv$ , where  $h$  is Planck's constant and  $v$  is the frequency of radiation. Some important electromagnetic radiations are radio wave, microwave, infrared, visible, ultraviolet, X-ray and gamma rays with decreasing order of wavelength or increasing order of frequency or energy. Molecule or ion may absorb energy from electromagnetic radiation of suitable wavelength (or frequency) resulting in:

- Electronic excitation caused by absorption of UV-visible radiation leading to UV-visible spectroscopy.
- Molecular rotation by absorption of microwave radiation leading to microwave spectroscopy.
- Vibrational excitation caused by absorbing infrared radiation leading to infrared spectroscopy.

The instrument used for investigation of such absorption phenomena is called spectrophotometer.

Magnetic nuclei as well as unpaired electron present in the molecular system/ion may give rise to resonant absorption of electromagnetic radiation when the sample is placed in a magnetic field. The electromagnetic radiation used for such phenomena are microwave and radio frequency leading to electron spin resonance (ESR) and nuclear magnetic resonance (NMR) respectively.

## 19.2 PRINCIPLE AND THEORY OF UV-VISIBLE SPECTROSCOPY

The UV-visible spectral method involves UV-visible spectroscopy. This arises due to absorption of ultraviolet (UV) or visible radiation by sample resulting in electronic transition within the molecule or ion. The relationship between the energy absorbed in an electronic transition, the frequency ( $v$ ), wavelength ( $\lambda$ ) and wave number ( $\bar{v}$ ) of radiation producing the transition is

$$\Delta E = hv = h \frac{c}{\lambda} = h\bar{v}c \quad (19.1)$$

where  $h$  is Planck's constant,  $c$  is the velocity of light.

$\Delta E$  is the energy absorbed during electronic transition in a molecule or ion from a lower energy state ( $E_1$ ) (ground state) to a high-energy state ( $E_2$ ) (excited state)

$$\Delta E = E_2 - E_1 = h\nu$$

(19.2)

The wavelength corresponding to such transition is given by,

$\lambda = \frac{hc}{\Delta E}$ , which usually falls in the range of 200 nm-800 nm of the electromagnetic spectrum, which covers the UV and visible region of electromagnetic radiation as shown in Figure 19.1.

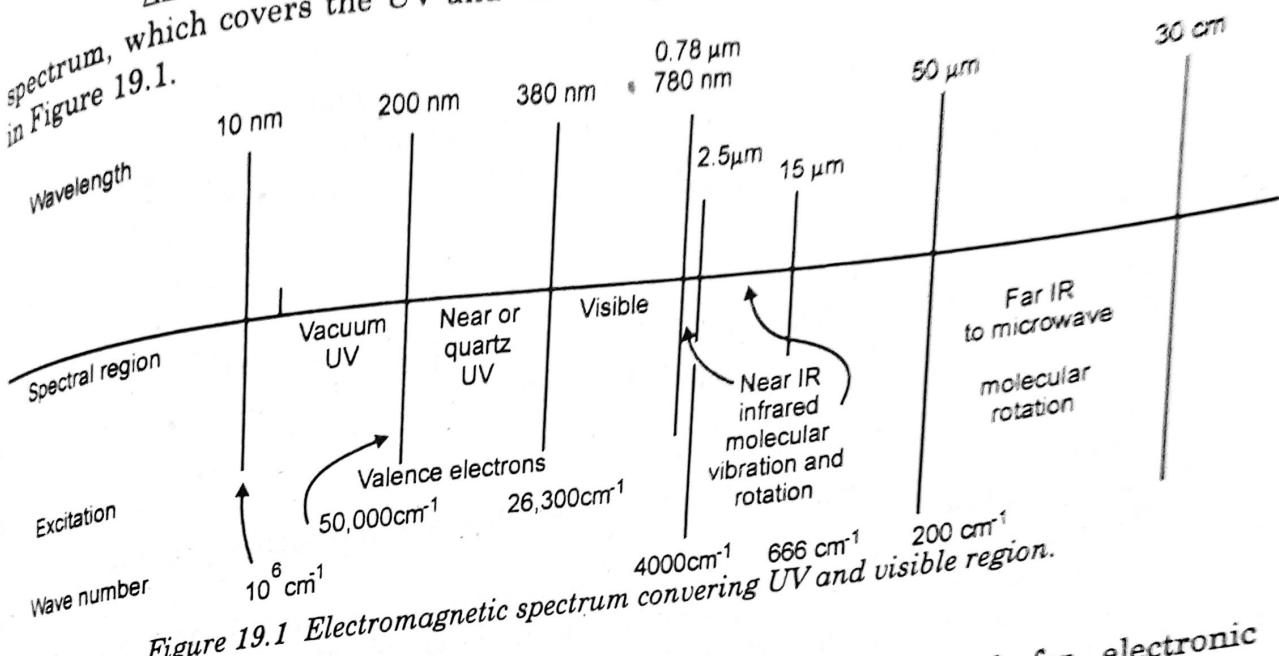


Figure 19.1 Electromagnetic spectrum covering UV and visible region.

### Example 19.1

Find the wavelength of electromagnetic radiation required for electronic transition between two electronic states of energy difference  $8.0 \times 10^{-12}$  ergs. Give comment on the result.

### Solution

Given

$$\begin{aligned} \Delta E &= h\nu = 8.0 \times 10^{-12} \text{ ergs} \\ \lambda &= \frac{hc}{\Delta E} = \frac{6.62 \times 10^{-27} \text{ ergs} \times 3 \times 10^{10} \text{ cms}^{-1}}{8 \times 10^{-12} \text{ erg}} \\ &= 2.5 \times 10^{-5} \text{ cm} \\ &= 2.5 \times 10^{-5} \times 10^8 \text{ Å} \\ &= 2500 \text{ Å} \\ &= 250 \text{ nm} \end{aligned}$$

This wavelength corresponds to ultraviolet region of electromagnetic spectrum.

### Absorption Laws

There are two laws which govern the absorption of light by the molecule. These are:

(i) Lambert's law and

(ii) Beer's law.

### Lambert's law

It states that "when a beam of monochromatic radiation passes through homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation."

Mathematically, the law can be expressed as

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

(19.3)

Where  $I$  = intensity of radiation after passing through a thickness  $x$  of the medium.  $dI$  = infinitesimally small decrease in the intensity of radiation on passing through infinitesimally small thickness  $dx$  of the medium.  $-\frac{dI}{dx}$  = rate of decrease of intensity of radiation with thickness of the absorbing medium.

### Beer's law

The law states that "when a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the concentration of the solution."

Mathematically, this law is stated as

$$-\frac{dI}{dx} \propto C$$

(19.4)

where  $C$  = Concentration of the solution in moles/liter.

Combining E.q. (19.4) with Eq. (19.3), we get

$$-\frac{dI}{dx} \propto C I$$

(19.5)

Equation (19.5) is known as Lambert-Beer's law which is stated as follows.

### Lambert-Beer's law

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

Mathematically, this law is stated as:

$$-\frac{dI}{dx} = k C I$$

(19.6)

where  $k$  = proportionality constant or absorption coefficient. Its value depends upon the nature of the absorbing medium.

Let  $I_0$  be the intensity of the radiation before entering the absorbing medium ( $x=0$ ), then  $I$ , the intensity of radiation, after passing through any thickness, say  $x$  of the medium so that

$$\int_{I_0}^I \frac{dI}{I} = - \int_{x=0}^{x=x} k C dx$$

(19.7)

$$\ln \frac{I}{I_0} = -k C x$$

$$\frac{I}{I_0} = e^{-kcx}$$

Equation (19.7) can also be written as

$$\log \left( \frac{I}{I_0} \right) = -\frac{k}{2.303} C x = -\epsilon C x$$

$$\log \left( \frac{I_0}{I} \right) = \epsilon C x$$

(19.8)

$$\text{or } A = \epsilon Cx$$

where  $\epsilon = \frac{k}{2.303}$  and  $A = \log \frac{I_0}{I}$ , is called absorbance or optical density of the solution.

The absorption spectrum is generally studied by monitoring the intensities of the incident ( $I_0$ ) and transmitted radiation ( $I$ ). If  $C$  is the molar concentration of absorbing species in mole  $\text{dm}^{-3}$  (mole liter $^{-1}$ ), then absorption of UV or visible light is governed by Lambert-Beer's law,

$$A = \log \frac{I_0}{I} = \epsilon Cx \quad (19.9)$$

where  $A$  is absorbance or optical density,  $\epsilon$  is molar absorptivity or molar extinction coefficient of the absorbing medium and  $x$  is the thickness of the absorbing medium (or path length) respectively. The path length may also be expressed as  $l$  so that  $A = \epsilon Cl$ .

The ratio  $\frac{I}{I_0}$  is called transmittance,  $T$  and  $\frac{I}{I_0} \times 100$  is called percentage transmission.

$\%T$ . There exists a relationship between absorbance,  $A$ , the transmittance,  $T$  and molar absorption coefficient ( $\epsilon$ ) which is given by

$$A = \epsilon CX = \log \frac{1}{T} = -\log T \quad (19.10)$$

Again

$$\%T = \frac{I}{I_0} \times 100$$

$$\begin{aligned} \log \%T &= \log \frac{I}{I_0} + \log 100 \\ &= -\log \frac{I_0}{I} + 2 \\ &= -A + 2 \end{aligned}$$

$$A = 2 - \log (\%T) \quad (19.11)$$

Unit of  $\epsilon$ :

In the relation  $\epsilon = \frac{A}{C\ell}$  it is clear that if the conc 'C' is expressed as mole lit $^{-1}$  and 'l'

is cm then unit of ' $\epsilon$ ' will be mole $^{-1}$  lit cm $^{-1}$  as  $A$  is a dimensionless quantity.

**Example 19.2** The molar absorptivity of a particular solute is  $2.0 \times 10^4$  mole $^{-1}$  lit cm $^{-1}$ . Calculate the % of transmittance through a cuvette with a 5.00 cm light path for a  $10^{-6}$  M solution.

**Solution**

Given

$$\epsilon = 2.0 \times 10^4$$

$$C = 10^{-6} \text{ M}$$

$$l = 5 \text{ cm}$$

$$\begin{aligned} \text{Absorbance, } A &= \epsilon C\ell = 2.0 \times 10^{-6} \times 5 \\ &= 10 \times 10^{-2} = 10^{-1} = 0.1 \end{aligned}$$

$$\log (\%T) = 2 - A = 2 - 0.1 = 1.9$$

$$\%T = \text{Anti log of } 1.9 = 79.43$$

**Example 19.3**

Calculate the energy associated with radiation having wavelength of 200 nm absorbed per mole of absorbing species.

**Solution**

From the relation  $\Delta E = \frac{hc}{\lambda}$  the energy absorbed per mole by the absorbing species will be given by  $\frac{Nhc}{\lambda}$  (where N is the Avogadro's number). Substituting the values of N, h, c and  $\lambda$ , the energy absorbed in kJ/mol is equal to  $11.9809 \times 10^4 / \lambda$ , where  $\lambda$  is expressed in nm.

Here  $\lambda = 200$  nm.

$$\begin{aligned}\text{The energy absorbed in kJ/mole} &= \frac{11.9809 \times 10^4}{200} \\ &= 5.99045 \times 10^2 \text{ kJ/mole} \\ &= 1.4263 \times 10^2 \text{ k cal/mole}\end{aligned}$$

**Nature of Electronic Spectrum**

Since the absorption (or emission) of visible or UV energy is quantized (i.e.  $E = nhv$ ), the absorption spectrum resulting from a single electronic transition is expected to contain single discrete line (sharp line). Again electronic transition is very rapid compared to nuclear motion. The former occurs generally without changes in internuclear distance. This is known as *Franck Condon principle*. However, in a molecular species the spectra appear as *band spectra*. This is because electronic excitation arising from absorption of UV or visible energy is accompanied by vibration and rotational energy changes in the molecule resulting the overall shape of absorption band to be broad. This is displayed by plotting molar absorptivity (or absorbance) or even transmittance taken as ordinate

against the corresponding values of wavelength (nm or  $\text{\AA}$ ) or wave number (in  $\text{cm}^{-1}$ ) taken as abscissa. In some cases logarithm of molar extinction coefficient is plotted against the wavelength or frequency. These plots are shown in Figures 19.2(a), (b) and (c)

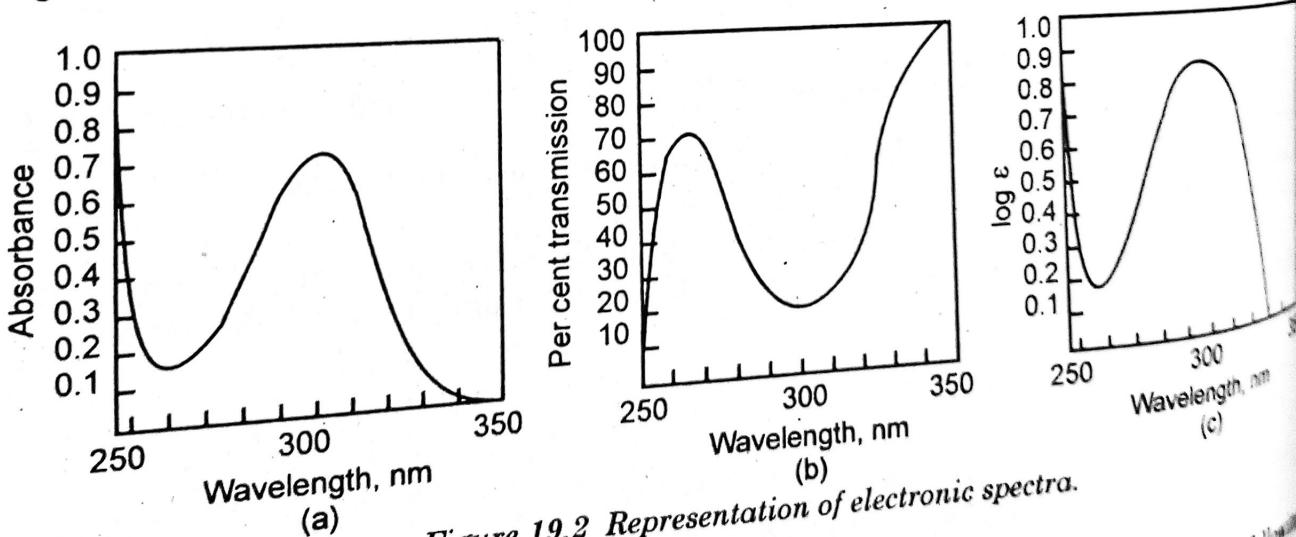


Figure 19.2 Representation of electronic spectra.

**19.3 SELECTION RULES FOR ABSORPTION**

The position of absorption band and its intensity is governed by the following selection rules:

**1. Energy requirement:**

The position of absorption band corresponds to the wavelength of radiation whose energy is equal to that required for an electronic transition, i.e.  $\lambda = \frac{hc}{\Delta E}$ .

**2. Symmetry of ground and excited state:**

For electronic transition to take place, both the ground and excited state wave function cannot be  $u$  (ungerade or antisymmetric) or  $g$  (gerade or symmetric) whereas  $g \leftrightarrow u$  or  $u \leftrightarrow g$  transition is allowed. Thus  $u \rightarrow u$  or  $g \rightarrow g$  transition is forbidden. This is called *Laporte Rule*.

**3. Spin selection rule:**

Electronic transition takes place between states of the same spin multiplicity (i.e. singlet-singlet or triple-triplet) whereas singlet-triplet or vice versa is forbidden.

**4. Only one electron transition is allowed:**

The transition of only one electron from lower energy state to higher energy state by absorption of UV or visible radiation gives rise to more intense band whereas transition involving two or more than two electrons is forbidden giving rise to less intense band (even not detected).

**19.4 INSTRUMENTATION INVOLVED IN UV-VISIBLE SPECTROSCOPY**

The commercially available instrument for the measurement of absorption in UV-visible region is called UV-visible spectrophotometer. The essential components of a UV-visible spectrophotometer are:

**Radiation source**

- (a) For visible region (~ 350 nm to 800 nm): Tungsten incandescent filament lamp.
- (b) For UV-region (~ 175 nm to 400 nm): Hydrogen or deuterium discharge lamp, Xenon discharge lamp and mercury arc are used. A radiation source must satisfy the following conditions:
  - (a) Providing sufficient radiant energy so that the transmitted energy can be detected at the end of the optical path.
  - (b) Sufficiently stable so that fluctuations are reduced.
  - (c) Supplying continuous radiation over the entire wavelength of required region.

**Monochromatic system**

For an effective absorption by the sample, a narrow beam of required wavelength from a continuous source is provided by the monochromatic system. It consists of an entrance slit, a collimating lens or a concave mirror to produce a parallel beam of radiation, a dispersing element to disperse the polychromatic radiation into its component wavelength, a focusing lens and an exit slit on the focal plane. The dispersing element includes a prism or diffraction gratings. The prisms are made of glass for visible region and of quartz or fused silica for UV-region.

**Sample cells** The cells that contain samples for analysis should fulfil the following three main conditions:

They must be uniform in construction. The thickness must be constant and the surface facing the incident light must be optically flat.

The materials used for the construction of the cell should be inert to solvent.

The most commonly used cells are made of quartz or fused silica. These are readily available in matched pairs where sample cell is almost identical to the

reference cell where the solvent is taken. Rectangular cells with path length of 1 cm are commonly used.

#### Radiation detector

A detector is a device which converts radiant energy into an electrical signal for measurement. These include:

- Photo voltaic cell (or barrier-layer cell)
- Photo emissive cell (photo cell or phototube)

The sensitivity of a photo emissive cell can be increased considerably by employing photo multiplier tube.

#### Signal processors and read out system

The signal from the detector is amplified by an external electronic amplifier and may include galvanometer, potentiometer, pen recorder or oscilloscope. For recording resulting the movement of attenuator wedge (optical wedge). As the recorder pen is linked to the attenuator wedge, the movement of the latter moves the former up and down on a chart paper fixed on a rotating drum. If the motor which drives the former up and down is also made to drive the drum on which chart paper is fixed, then it is possible to obtain slot of wavelength versus optical wedge position which becomes wavelength versus transmittance or absorbance.

#### Power supply

The power supply serves the following:

- Decrease line voltage to the instruments operating level with a transformer.
- Converts AC to DC with a rectifier if direct current is required by the instrument.
- Smooth out any ripple which may occur in the line voltage in order to deliver constant voltage to the source lamp and instrument.

## 19.5 TYPES OF UV-VISIBLE SPECTROPHOTOMETER

The spectrophotometer may be classified as single beam and double beam. In single beam spectrophotometer, radiation is first passed through the solution under analysis. In double beam, the radiation is split into two equal halves, one-half passes through the cell containing the sample while the other half passes through the second cell (reference cell) containing the solvent (blank solution). The signal for the absorption due to the reference is automatically subtracted from that due to sample cell giving rise to the signal corresponding to the absorption of component of the sample solution. The double beam type may have two matched detectors or the radiation may be flashed alternatively over two paths to a simple detector. Some important types of single beam and double beam UV-visible spectrophotometer are given below.

#### Manual (non-recording) spectrophotometer

- Single beam direct reading spectrophotometer
  - Single beam null balance spectrophotometer
  - Double beam null balance spectrophotometer
- Other examples are Unicom SP600 and Unicom SP500

#### Automatic or recording spectrophotometer

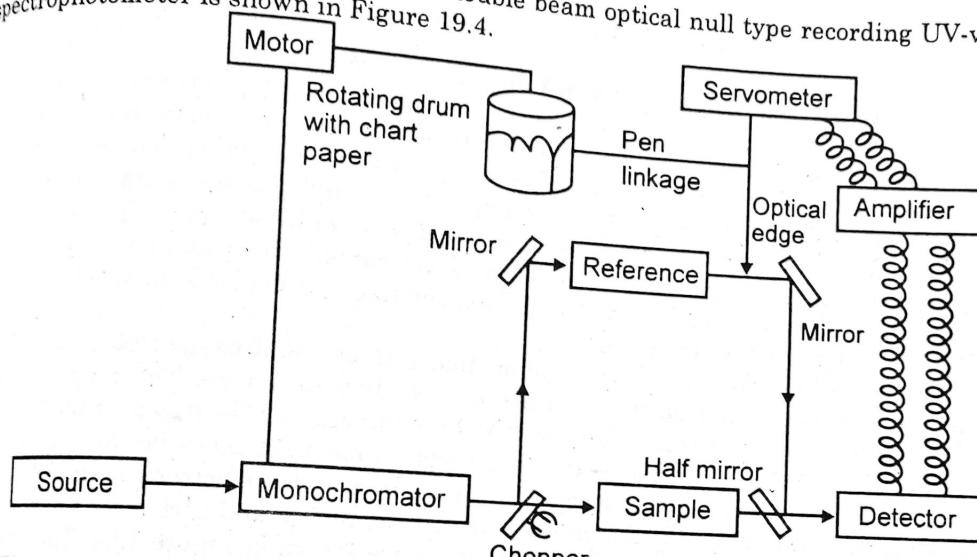
Almost all recording spectrophotometers are of double beam type. However, commercially available recording double beam spectrophotometers are direct reading optical null and potentiometric null types as exemplified below.

**Example**  
Spectronic-20  
Beckmann model DU-1  
Cary model-16

**Example**

- (a) Direct reading double beam recording spectrophotometer  
Beckmann model BD-G
- (b) Optical null double beam recording spectrophotometer  
Perkins Elmer model-202
- (c) Potentiometric null double beam spectrophotometer  
Cary model-14

The block diagram of a typical double beam optical null type recording UV-visible spectrophotometer is shown in Figure 19.4.



**Figure 19.3** Block diagram of a double beam optical null type UV-visible spectrophotometer.

**Working Principle**

Radiation from a source is allowed to pass through the monochromatic system. The resulting narrow beam of radiation through monochromator encounters a chopper. The chopper driven by synchronous motor is rotating mirror, which permits the beam to pass straight during the half of its period of rotation. During the other half, the beam encounters the reflecting surface which turns it at right angle directing it upwards as shown in figure 19.3. The direction as desired may be changed again by other stationary mirror. Thus two beams are obtained by the single beam emerging from the monochromator. One beam passes through the sample cell while the other passes through a reference cell (containing solvent). The alternating beams reach the detector where they recombine to give a resultant ac signal. The outputs (ac signals) are amplified and then transmitted to the recorder where the absorbance or transmittance is recorded on a chart paper as a function of wavelength.

**Choice of Solvent**

Many solvents are available for use in the UV region. Three common solvents are cyclohexane, 95% ethanol and 1, 4-dioxane. Cyclohexane may be freed of aromatic and olefinic impurities by percolating through activated silica gel and is transparent down to about 210 nm. Aromatic compounds, particularly poly-nuclear aromatics, are usually soluble and their spectra generally retain their fine structure when determined in cyclohexane. The fine structure is often lost in more polar solvent. 95% ethanol is good choice when a more polar solvent is required. It is transparent down to 210 nm. Commercial ethanol should not be used as it contains benzene, which absorbs strongly in

UV region. 1, 4-dioxane can be purified by distillation from methanol. Methanol contamination can be removed by the addition of ethanol followed by distillation to remove benzene-methanol azeotrope. 1, 4-dioxane is transparent down to 220 nm.

## 19.6 TYPES OF ELECTRONIC TRANSITION

Depending on the nature of absorbing species, electronic transitions may be of the following types:

- Transitions involving  $\sigma$ ,  $\pi$  and non-bonding ( $n$ ) electrons.
- Transitions involving d or f electrons.
- Charge transfer transitions.

### Transitions Involving $\sigma$ , $\pi$ and $n$ (Non-bonding Electrons)

The electrons in molecules can be classified as sigma ( $\sigma$ ), pi ( $\pi$ ) and non-bonding ( $n$ ) electrons. The  $\sigma$  electrons are associated with single covalent bonds. Since they are tightly bound, radiation of high energy is required for their excitation. The excitation is from a bonding MO ( $\sigma$ -MO) to an anti-bonding ( $\sigma^*$ -MO) and the resulting transition is known as  $\sigma \rightarrow \sigma^*$  transition. The electrons associated with multiple bonds (double or triple bonds) are known as  $\pi$ -electrons. The  $\pi$ -electrons are rather easily excited to the higher level. Here, the transition of an electron is from a bonding pi MO ( $\pi$ -MO) to anti-bonding pi MO ( $\pi^*$ -MO) resulting  $\pi \rightarrow \pi^*$  transition.

If a molecule contains a hetero atom like nitrogen and oxygen etc., the hetero atom has unshared electron pairs which are non-bonding in nature. These non-bonding electrons can be excited to either  $\sigma^*$  MO or  $\pi^*$  MO resulting  $n \rightarrow \sigma^*$  or  $n \rightarrow \pi^*$  transitions. It is to be noted that  $\sigma \rightarrow \pi^*$  and  $\pi \rightarrow \sigma^*$  transitions do not take place because these are Laporte forbidden. The absorbing species involving  $\sigma$ ,  $\pi$  and  $n$  electrons mainly include organic molecules and inorganic anions such as nitrate, nitrite and carbonate anions, etc. The various energy levels and electronic transitions are shown in Figure 19.4. The energy required for various transitions obey the following order

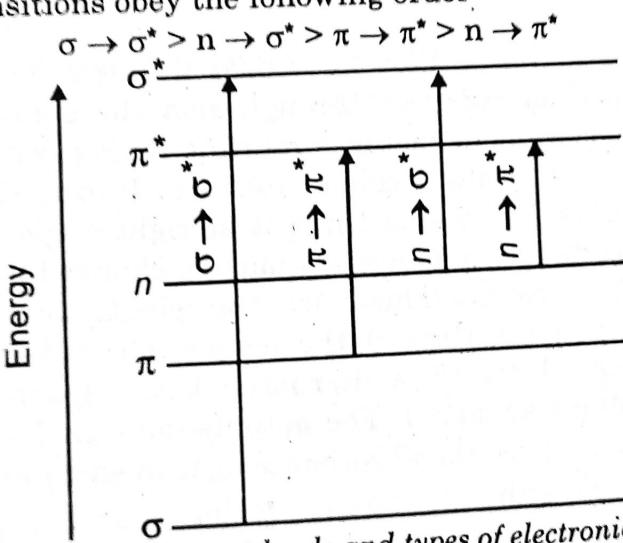


Figure 19.4 Various energy levels and types of electronic transition.

#### $\sigma - \sigma^*$ transition

This transition can occur in compounds in which all the electrons are involved in the formation of single bonds ( $\sigma$ -bond only) and there is no lone pair of electron. Example of such transitions are saturated hydrocarbon like methane, ethane, etc. Such transition requires radiation of very short wavelength (less than 150 nm or high energy). The usual spectroscopic measurement cannot be done below 200 nm, since oxygen (present in air) begins to absorb strongly. To study such high energy transition (below 200 nm), the entire

path length must be evacuated. Thus the region of transition below 200 nm is called *vacuum ultraviolet region*. The region is less informative. Methane which contains only C - H  $\sigma$ -bond can undergo  $\sigma \rightarrow \sigma^*$  transition exhibiting absorption peak at 125 nm. Ethane has an absorption peak at 135 nm which also must arise from the same type of transition but here electrons of C - C bond appear to be involved. Since the strength of the C - C bond is less than that of C - H bond, less energy is required for excitation, as a result, absorption occurs at lower wavelength. Thus organic molecules in which all the valence shell electrons are involved in the formation of  $\sigma$ -bonds do not show absorption in the normal ultraviolet region, i.e. 180-400 nm.

#### $n \rightarrow \sigma^*$ transition

This type of transition takes place in saturated compound containing one hetero atom with unshared pair of electrons. Examples of such transitions are saturated alkyl halides, alcohols, ethers, amines, etc. Such transition is brought about by radiation in the region of 150 to 250 nm. The absorption data for some typical compounds involving  $n - \sigma^*$  transition are given below.

Compounds	$\lambda_{\text{max}}(\text{nm})$	$\epsilon_{\text{max}}$
Water	167	1480
$\text{CH}_3\text{OH}$	184	150
$\text{CH}_3\text{OCH}_3$	184	2520
$(\text{CH}_3)_3\text{N}$	227	900

The molar absorptivities ( $\epsilon$ ) for this type of absorption are intermediate in magnitude and usually in the range  $100-3000 \text{ mole}^{-1} \text{ lit cm}^{-1}$ .

In saturated alkyl halides, the energy required for such a transition decreases with the increase in the size of halogen atom (or decrease in the electro-negativity of the atom). For example, the  $n$  electrons on chlorine atoms are comparatively difficult to excite. The absorption maximum ( $\lambda_{\text{max}}$ ) for methyl chloride is 172-175 nm whereas that for methyl iodide is 258 nm as  $n$  electrons on iodine atom are loosely bound because of its increase in size and less electro-negativity value.  $\epsilon_{\text{max}}$  is also higher compared to methyl chloride. Similarly amines absorb at higher wavelength as compared to alcohol and hence the extinction coefficient for amines will be larger.

Thus, when absorption measurements are made in UV-region, compounds such as aliphatic alcohol and alkyl halide are commonly used as solvent, because they start to absorb at 260 nm. However, these solvents cannot be used when measurement are to be made in 200 - 260 nm. In such cases saturated hydrocarbons which only give rise to  $\sigma - \sigma^*$  transition must be used. However, the drawback is that these are poor solvating agent.

#### $n \rightarrow \pi^*$ transition

This type of transition can occur in unsaturated bond containing at least one hetero atom like O, N, S and halogen with  $n$  electrons. Examples of such transition are aldehydes and ketones, etc. This type of transition requires least amount of energy out of all the transitions discussed above and hence occurs at longer wavelength. Saturated aldehydes ( $\text{C}=\text{O}$ ) show both types of transitions, i.e. low energy  $n \rightarrow \pi^*$  and high energy  $n \rightarrow \pi^*$  occurring around 290 nm and 180 nm respectively. In aldehydes and ketones  $n \rightarrow \pi^*$  transition arises from excitation of a lone pair of electrons in a  $2p$  orbital of oxygen atom with the anti-bonding  $\pi$  orbital of carbonyl group. When hydrogen is replaced by alkyl group as in ketone, this results in shift of band to shorter wavelength.

**Summary of various electronic transitions**

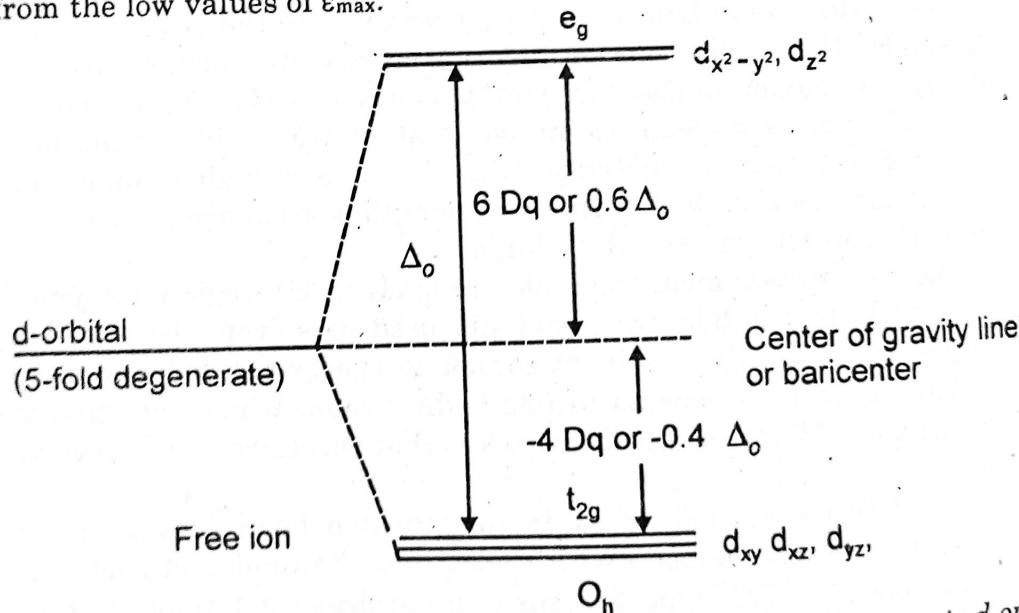
The probable transitions and the region where the various electronic transitions take place are stated below for easy understanding.

Nature of transitions	Absorption range	$\epsilon_{\max}$
	$\lambda_{\max}$ (in nm)	
$\sigma \rightarrow \sigma^*$ transition	125-150 nm	—
$n \rightarrow \sigma^*$ transition	150-200 nm	100-4000
$\pi \rightarrow \pi^*$ transition	170-200 nm	1000-1000000 (very high)
$n \rightarrow \pi^*$ transition	200-700 nm	10-100 (very low)

A number of inorganic anions exhibit  $\lambda_{\max}$  in the UV region due to  $n \rightarrow \pi^*$  transitions, e.g.  $\text{NO}_3^-$  (313 nm),  $\text{CO}_3^{2-}$  (217 nm) and  $\text{NO}_2^-$  (360 nm).

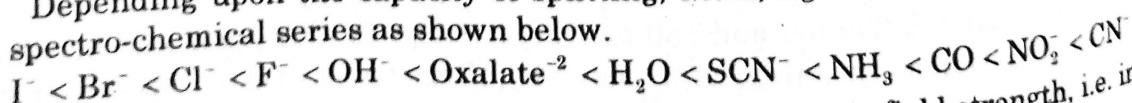
**Absorbing Species Involving d or f Electrons**

In transition metals (d-block elements) there are incomplete d orbitals. The ligand fields created by the ligands cause splitting of d orbitals. For example, in octahedral field, the penta degenerate d orbitals get split up to three-fold degenerate,  $t_{2g}$  and two-fold degenerate,  $e_g$  set by  $\Delta$  (10 Dq) called crystal field splitting energy as shown in Figure 19.5. On being excited, the electron in  $t_{2g}$  orbitals absorbs energy equal to the crystal field splitting energy and moves to  $e_g$  orbitals in octahedral field. Since the values  $\Delta$  is low, absorption takes place in the visible region, as a result, transition metal complexes are coloured. Such type of transitions is called d-d transition as  $t_{2g}$  and  $e_g$  set belong to the same d orbitals. For the f-block elements, transitions are also possible due to f orbital electrons. However, the band obtained due to f-f transition is narrow due to screening of inner orbitals from external influence. However, such transition is Laporte forbidden as reflected from the low values of  $\epsilon_{\max}$ .

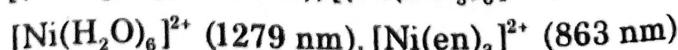
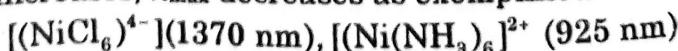


**Figure 19.5** Octahedral crystal field splitting of five-fold degenerate d-orbital.

Depending upon the capacity of splitting, i.e.  $\Delta$ , ligands are arranged in a series called spectro-chemical series as shown below.



In this series, the ligands are arranged in order of their field strength, i.e. in order of  $D_q$  values. As  $D_q$  increases,  $\lambda_{\max}$  decreases as exemplified



### Charge Transfer Spectral Absorption

For charge transfer transitions absorbing species should contain both electron donor and electron acceptor. A charge transfer is always followed by a change in the dipole moment, hence such transitions are allowed and occur with high intensity (10000 to 10,000). If the separation between the states is more, the transition may occur in the UV region. But in many cases the charge transfer transition involves low energy and occurs in the visible region making the compounds coloured. For example, in  $\text{MnO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$ , the central metal ions are  $\text{Mn}^{+7}$  and  $\text{Cr}^{+6}$  with no unpaired electrons. They, however, show purple and orange colours. This is because of charge transfer from  $\text{O}^{2-}$  to  $\text{M}^{m+}$ . As transfer of electrons from  $\text{O}^{2-}$  takes place at lower energy leading to absorption in visible region resulting in the colour of the above ions.

### 19.7 THE CONCEPT OF CHROMOPHORE AND AUXOCHROME

The absorption of radiation in the visible and UV regions depends primarily on the number and arrangement of electrons in the absorbing molecules or ions. This led to the concept of chromophore and auxochrome discussed below.

#### 1. Chromophore

It may be defined as covalently bonded unsaturated group of atoms responsible for the absorption of radiation in the visible and UV region. Two types of chromophores are known in organic molecules.

- (i) Chromophores which contain the  $\pi$ -electrons only and undergo  $\pi \rightarrow \pi^*$  transitions. Such chromophores contain unsaturated (double or triple) bonds such as ethylenic group, ( $\text{C} = \text{C}$ ) and acetylenic group ( $\text{C} \equiv \text{C}$ ).
- (ii) Chromophores which contain both  $\pi$ -electrons and  $n$  (non-bonding) electrons. Such chromophores undergo two type of transitions, i.e.  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$ .

Example of this type include carbonyl group, ( $>\text{C} = \text{O}$ ) (azo group (-N=N-), nitrile (- $\text{C} \equiv \text{N}$ ), nitro groups (-NO<sub>2</sub>), carboxyl, amido, azo methane, nitrate and nitrite group (-ONO<sub>2</sub>), etc.

#### 2. Auxochrome

The term auxochrome applies to an atom or group of atoms which does not give rise to absorption band of its own, but changes the absorption characteristics of chromophore (both intensity and wavelength) when conjugated to it. Some of the important characteristics of auxochrome are:

- (i) An auxochrome does not give rise to absorption band of its own but when conjugated to a chromophore, both the intensity and wavelength of absorption band are changed.
- (ii) It may be an atom or group of atoms.
- (iii) It is colour enhancing group.

For example, absorption maxima of benzene is 255 nm ( $\epsilon_{\max} = 203$ ). When an auxochrome like amino group is substituted in benzene as in aniline, its absorption maximum shifts to longer wavelength at 280 nm and  $\epsilon_{\max}$  becomes higher ( $\epsilon_{\max} = 1430$ ). The effect of the auxochrome is due to its ability to extend the conjugation of a chromophore by sharing of its non-bonding electrons. Thus an auxochrome must have at least one atom with unshared pair/pairs of electrons. Such atoms are generally present in the molecule in the form of a polar group like -OH, -NH<sub>2</sub>, -O-CH<sub>3</sub> or halogen atom (X), etc.

**19.8 SHIFTING OF ABSORPTION BAND AND CHANGE IN INTENSITY**

The wavelength and intensities of the absorption bands due to chromophore are sensitive to nature of the solvent, inductive effect and pH, etc. It is useful to define the following terminology with regard to change in wavelength and intensity.

**Bathochromic shift**

A shift of  $\lambda_{\max}$  to longer wavelength (also called red shift) due to the presence of an auxochrome or change of solvent. The  $n \rightarrow \pi^*$  transition for carbonyl compounds experience bathochromic shift when the polarity of solvent is decreased.

**Hypsochromic shift**

A shift of  $\lambda_{\max}$  to shorter wavelength (also called blue shift). It may arise due to removal of conjugation or change in polarity of the solvent.

**Hyperchromic effect**

Increase in the intensity of an absorption band usually with reference to  $\epsilon_{\max}$ . The introduction of an auxochrome increases the intensity of absorption band.

**Hypochromic effect**

Decrease in the intensity of an absorption band usually with reference to  $\epsilon_{\max}$ . The removal of an auxochrome decreases the intensity of absorption band.

The absorption and intensity shifts are shown in Figure 19.6. The introduction of group which disturbs the geometry of a group causes such type of shift.

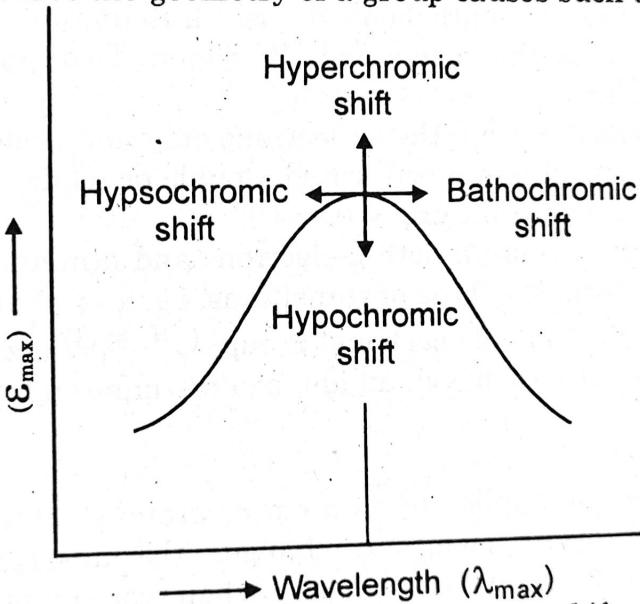
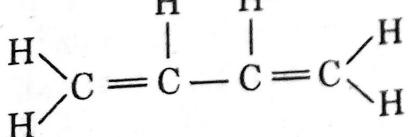
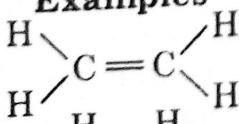


Figure 19.6 Absorption and intensity shift.

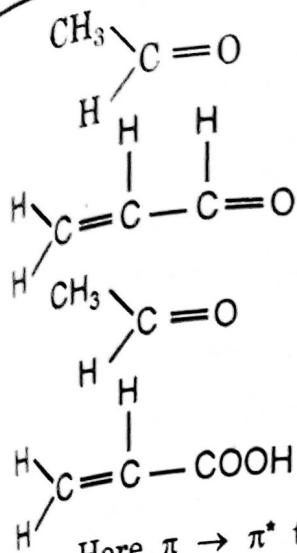
The following factors influence the values of  $\lambda_{\max}$  and  $\epsilon_{\max}$ .

**1. Effect of Conjugation of Chromophore**

According to MO theory,  $\pi$  electrons can further be delocalized by the conjugation process. The effect of this delocalization is to lower the energy level of  $\pi^*$  orbital and hence to shift the absorption maximum to longer wavelength. Some typical examples are

**Examples**

Chromophore	$\lambda(\text{nm})$	$\epsilon_{\max}$	Transition
Ethylene	171	15530	$\pi \rightarrow \pi^*$
Butadiene	217	20900	$\pi \rightarrow \pi^*$



	Acetaldehyde	180	10000	$\pi \rightarrow \pi^*$
		290	17	$n \rightarrow \pi^*$
	Crotonaldehyde	218	18000	$\pi \rightarrow \pi^*$
		320	30	$n \rightarrow \pi^*$
	Acetic acid	208	32	$n \rightarrow \pi^*$
	Crotonic acid	206	13500	$\pi \rightarrow \pi^*$
		242	250	$\pi \rightarrow \pi^*$

Here  $\pi \rightarrow \pi^*$  transition is one that corresponds to  $- \text{C} = \text{C} -$  system of the molecules. Thus, when the chromophores are separated in a molecule by only single bond, conjugation occurs. In other words, in conjugated systems there are alternate multiple bonds such as,  $-\text{C} = \text{C} - \text{C} = \text{C} - \text{C} = \text{C} -$  or  $-\text{C} = \text{C} - \text{C} = \text{O}$  system. The effect of conjugation can also be illustrated by observing that the wave length of absorption maximum is 265 nm for divinyl ethylene  $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH}_2$ ; whereas for non-conjugated counterpart such as diallyl ( $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH} = \text{CH}_2$ ), is 180 nm. In case of extensive conjugation i.e. when the molecule contains a number of conjugated double bonds, the wavelengths of absorption maxima become sufficiently high and hence the absorption occurs in the visible region and the compounds appears coloured. For example  $\beta$ -carotene with eleven conjugated double bonds is yellowish green in appearance and absorb in the region of 420 – 480 nm.

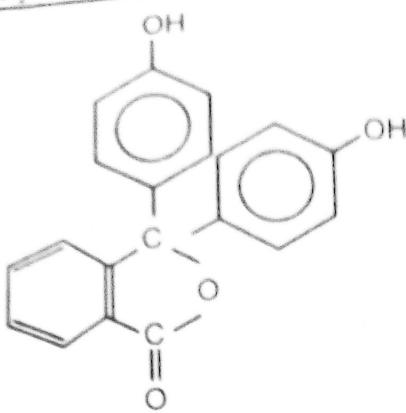
A system containing two double bonds in conjugation may be cis isomer or trans isomer. The cis isomer absorbs at a lower wavelength as compared to trans isomer due to slight decrease in conjugation because of crowding.

## 2. Additive Characteristics

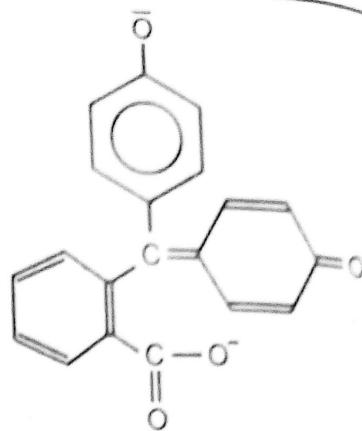
When a molecule contains two or more chromophores separated by more than one single bond, the absorption of radiation by the molecules become additive. In other words, the total absorption is the sum of absorption characteristic of each chromophore. For example, diallyl  $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH} = \text{CH}_2$  contains two ethylenic linkages separated by three single bonds. It absorbs radiation about the same wavelength as ethylene but the amount of radiation absorbed for similar concentration is approximately double that of ethylene.

## 3. Effect of Aromatic Rings

In aromatic system, the benzene ring is the simplest chromophore. Two or more benzene rings in conjugation giving rise to polycyclic compounds result in the absorption of radiation corresponding to higher wavelengths in the visible region. For example, the corresponding values of  $\lambda_{\max}$  for benzene, naphthalene and anthracene are 268, 311 and 476 nm respectively. But when the chromophores are substituted into the benzene nucleus, the resulting compounds have different absorption spectrum from that of benzene itself and the substituent chromophores. This arises because of mutual electrostatic interaction between the chromophores. Compounds with the same number of carbon atoms as that in benzene, but with double bond arranged as in benzoquinone are much more effective chromophores than the benzene itself. For example, phenolphthalein possesses different structures in acidic and basic solution, as shown below.



Colourless molecule in acidic medium



Phenol phthalein in acidic and basic medium

Red anion in basic medium

It is because in basic solution (because of extended conjugation) the entire anion forms a chromophore whereas in acidic solution, the molecule contains three separate benzene rings (here conjugation is not extended) and hence less chromophoric.

#### 4. Effect of Substitution of Auxochrome

As discussed earlier, auxochrome causes a bathochromic (red) shift of  $\lambda_{\text{max}}$  and hyperchromic shift in the intensity of absorption band.

For example, the benzene ring is much less effective as a chromophore. But substitution of some polar groups into the benzene nucleus increases the wavelength of absorption maxima in the visible region and hence also the absorption value. The effect of some auxochromes on the absorption characteristic of benzene in solvent hexane are as follows.

#### Effect of auxochromes on benzene chromophore in solvent hexane

Auxochrome	Compound	$\lambda_{\text{max}}$	$\epsilon_{\text{max}}$
$-\bar{N}H_2$	Benzene	256	250
$-OH$	Aniline	280	200
$-Cl$	Phenol	275	200
$-Br$	Chloro benzene	265	360
	Bromo benzene	245	295

#### Effect of Solvent Polarity

The polarity of the solvent has pronounced effect on the position and intensity of bands arising due to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions. In fact, the shifts exhibited by the bands on increasing the polarity of the solvent can be used to identify the type of transition.

#### Effect of solvent polarity on $n \rightarrow \pi^*$ transition

The effect of solvent on the absorption characteristics has been illustrated below by taking mesityl oxide (4-methyl-3-pentene-2-one) as an example.

Solvent	$\lambda_{\text{max}}$	$\epsilon_{\text{max}}$	Transition
Hexane	230	12,600	$\pi \rightarrow \pi^*$
	329	47	$n \rightarrow \pi^*$
Water	243	10,000	$\pi \rightarrow \pi^*$
	303	60	$n \rightarrow \pi^*$

These data indicate that the wavelength due to  $n \rightarrow \pi^*$  absorption is shifted by nm to shorter wavelength (higher energy) in the more polar solvent. Thus increased polarity of solvent causes a hypsochromic shift (blue shift) for  $n \rightarrow \pi^*$  band.

**Causes of hypsochromic shift of  $n \rightarrow \pi^*$  transition in polar solvent**

The solvation is most effective with polar hydrolytic solvent like water or alcohol in which hydrogen bond formation between the solvent proton and non-bonded electron pair is extensive. As a result the energy of the  $n$ -orbital is lowered by an amount approximately equal to the energy of hydrogen bond as diagrammatically represented in Figure 19.7(a). A blue shift, also roughly corresponding to the energy of hydrogen bond, is therefore, observed. The effect of solvent polarity on  $\pi \rightarrow \pi^*$  transition is just opposite to that of  $n \rightarrow \pi^*$  transition. Thus the band at 230 nm in hexane is shifted to 243 nm in water. The increase in polarity in this case has caused a bathochromic shift (red shift).

**Effect of solvent polarity on  $\pi \rightarrow \pi^*$  transition**

The effect of solvent on the absorption characteristics has also been illustrated by taking mesityl oxide (4-methyl-3-pentene-2-one) as an example.

These data as mentioned above indicate that the wavelength due to  $\pi \rightarrow \pi^*$  absorption is shifted by 13 nm to higher wavelength (lower energy) in the more polar solvent. Thus increase of polarity of solvent causes a bathochromic shift. (red shift) for  $\pi \rightarrow \pi^*$  band.

**Causes of bathochromic shift of  $\pi \rightarrow \pi^*$  in polar solvent**

This is due to fact that  $\pi^*$  orbital is more polar than the  $\pi$  orbital and then  $\pi^*$  orbital is stabilized to a greater extent in the presence of a polar solvent as shown diagrammatically in Figure 19.7(b) resulting red shift.

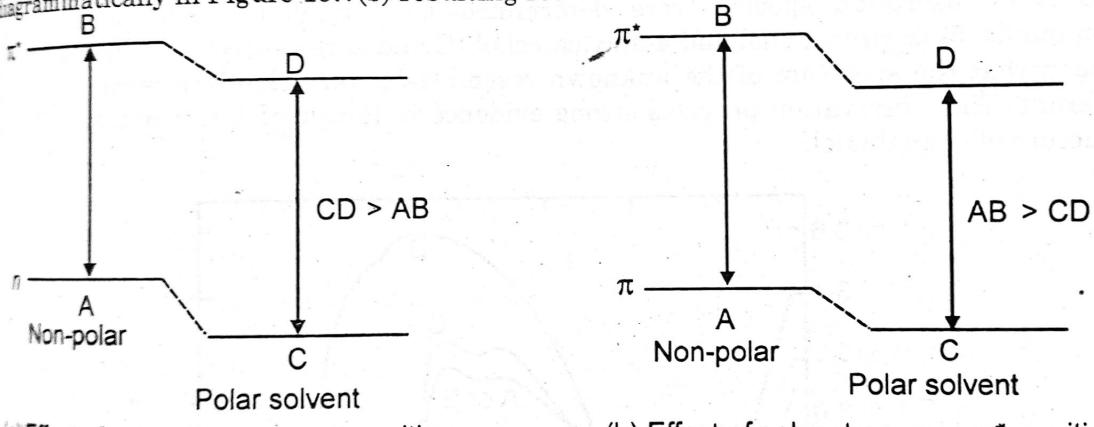


Figure 19.7

#### Stereo Chemical Factors

Since co-planarity is essential for efficient overlap of  $\pi$ -orbitals, factors which affect the co-planarity will influence the position and intensity of absorption maxima. The common factors are:

- Restricted rotation around single bonds and
- Absence of rotation around double bonds.

#### Restricted rotation around single bonds

The effect of hindered rotation around a single bond is best illustrated by the UV spectra of diphenyls. The parent molecule diphenyl can readily achieve co-planarity since there is no restriction for rotation about C - C single bond between the two benzene rings. If larger groups are present in ortho position, rotation at around the single bond is restricted and hence co-planarity cannot be C - C single bond causes loss of co-planarity. It is seen that the loss of co-planarity results in a marked decrease in the value of molar absorptivity.

**Absence of rotation about double bonds**

This is best illustrated by considering the data presented below for two compound such as cinnamic acid and stilbene which can exhibit geometrical isomerism.

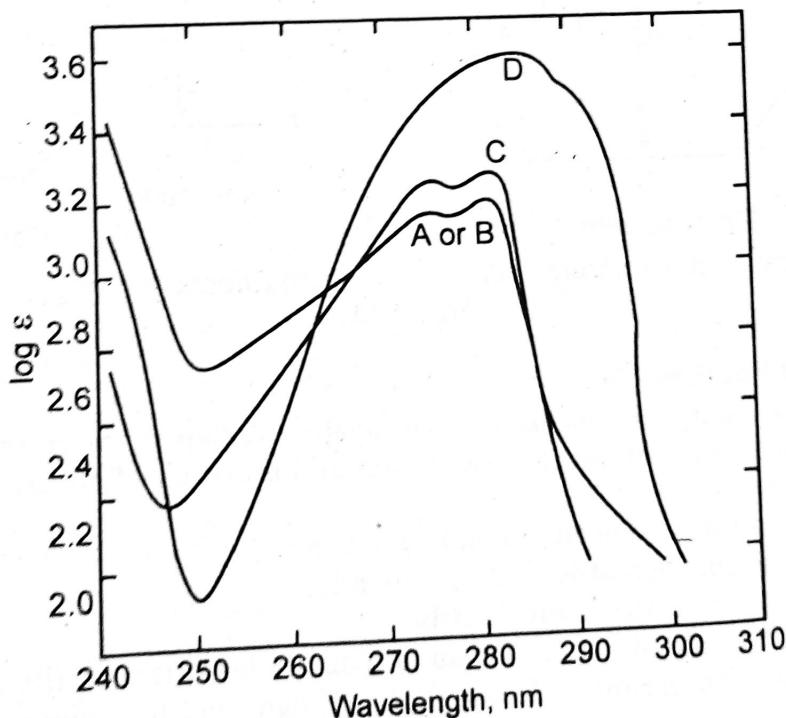
Compound	Cis-isomer		Trans-isomer	
	$\lambda_{\text{max}}$	$\epsilon_{\text{max}}$	$\lambda_{\text{max}}$	$\epsilon_{\text{max}}$
cinnamic acid	168	10,700	272	15,900
stilbene	278	9550	294	24,000

On each pair of geometrical isomers, the 'cis' form would be expected to be more sterically hindered and the 'trans' form would be expected to achieve co-planarity of the electron system more readily.

## 19.9 APPLICATION OF UV-VISIBLE SPECTROSCOPY

### Structural Analysis

UV-visible spectra provide a valuable tool in the identification of unsaturated organic compounds and in the elucidation of their structure. Information concerning a compound of unknown structure can sometimes be obtained by a direct comparison of its absorption spectrum with those of model compound of known structure. For example, investigation of the compound cannabidiol (a substance isolated from Minnesota wild hemp), chemical evidence showed its structure to be either A or B as shown in Figure 19.8. UV absorption spectra were determined for cannabidiol and for the model compounds, 5-amylresorcinol and 4-amylcatechol (C and D respectively) in Figure 19.8. It is seen that the spectrum of the unknown resembles C very closely whereas D is quite different. This observation provides strong evidence in favour of A rather than B for the structure of cannabidiol.



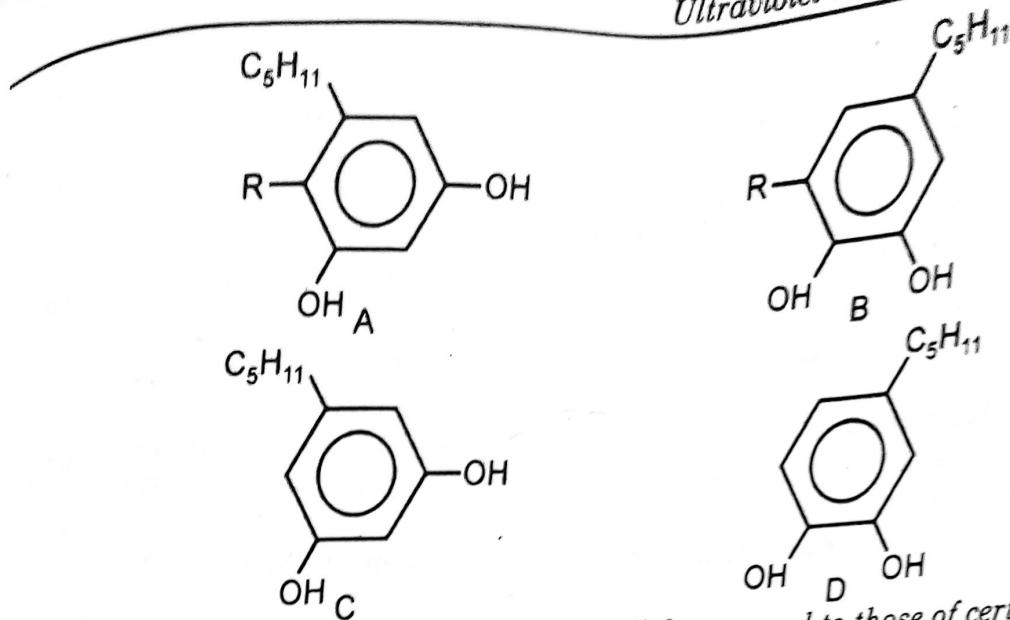


Figure 19.8. Absorption spectrum of cannabidiol compared to those of certain phenol.

#### Empirical Rules for Calculation of Absorption Maxima ( $\lambda_{\max}$ )

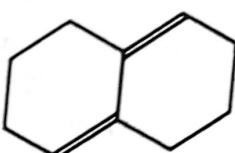
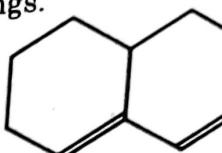
Woodward and Fieser formulated empirical rules for calculation of  $\lambda_{\max}$  for different dienes, triens (polyenes),  $\beta$ -tones and aldehydes as discussed below.

##### Alicyclic dienes or diene

These are contained in an open chain, where 1,3 butadiene system ( $C = C - C = C$ ) is present, the basic value is 217 nm.

##### Heteroannular diene

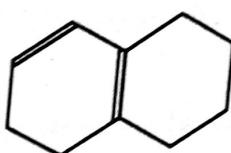
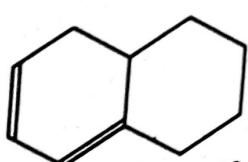
A heteroannular diene means that the two double bonds in conjugation are present in different rings.



Basic unit for such system is 214 nm.

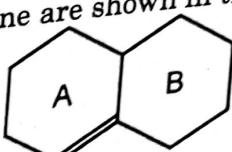
##### Homoannular diene

A homoannular diene means that the two double bonds in conjugation are present in the same ring.

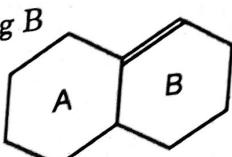


Basic unit of such system is 253 nm.

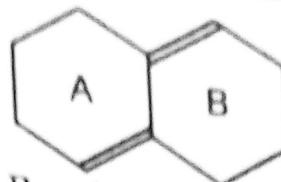
Exocyclic and endocyclic diene are shown in the following examples.



Double bond exocyclic to ring B



Double bond exocyclic to ring A



Double bond (A) as exocyclic to ring B and double bond (B) as exocyclic to ring A.  
The creation of exocyclic double bond causes an additional bathochromic shift of 5 nm.  
**Increments for each substituent**

1. Alkyl substituents or ring residue on the double bond causes bathochromic shift 5 nm.
2. Each double bond with extended conjugation causes bathochromic shift of 30 nm.
3. The presence of polar groups auxochrome such as  $-Cl$ ,  $-Br$ ,  $-OR$ ,  $-SR$ , etc. causes bathochromic shift of  $\lambda_{max}$  as shown below.

Auxochromes	Bathochromic shift
$-OR$	+ 6nm
$-SR$	+ 30nm
$-Cl$ , $-Br$	+ 5nm
$-NR_2$	+ 60nm
$-OC-CH_3$	0

### Example 19.9

Predict the  $\lambda_{max}$  values for the following compounds.

Solution

(a) Basic value = 217 nm

2-alkyl substituent  $\frac{(2 \times 5)}{227} = 10$

(b) Basic value = 217 nm

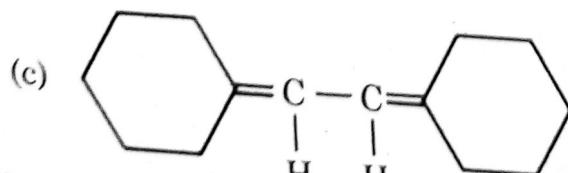
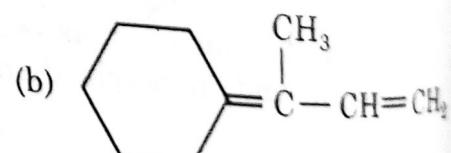
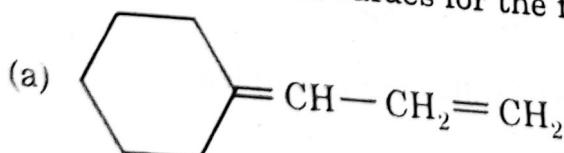
2-alkyl substituent  $\frac{(2 \times 5)}{227} = 10$

(c) Basic value = 217 nm

1-alkyl substituent  $\frac{(1 \times 5)}{222} = 5$

### Example 19.10

Predict the  $\lambda_{max}$  values for the following system.



Solution

(a) Basic value 217 nm

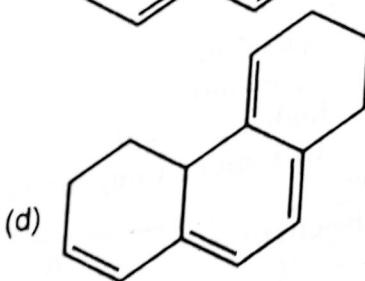
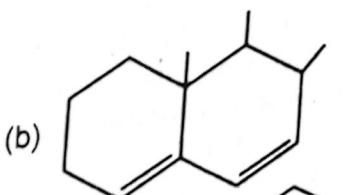
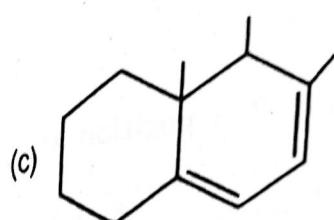
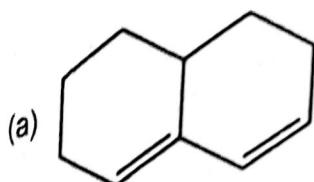
2-alkyl substituents  $(2 \times 5) = 10$

$$1\text{-exocyclic bond } \frac{(1 \times 5) = 5}{232 \text{ nm}}$$

(b) Basic value 217 nm  
 3-alkyl substituents  $3 \times 5 = 15$   
 $1\text{-exocyclic bond} = \frac{(1 \times 5) = 5}{237 \text{ nm}}$

(c) Basic value of 217 nm  
 4-ring residue  $(4 \times 5) = 20$   
 $2\text{-exocyclic bond} = \frac{(2 \times 5) = 10}{247 \text{ nm}}$

**Example 19.11**  
 Predict the  $\lambda_{\max}$  for the following system



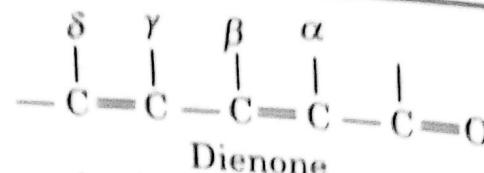
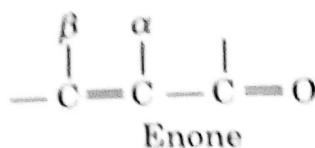
**Solution**  
 (a) Basic value (heteroannular) 214 nm  
 $3\text{-ring residue} (2 \times 5) = 10 \text{ nm}$   
 $1\text{-exocyclic double bond} \frac{(1 \times 5) = 5}{234 \text{ nm}}$

(b) Basic value = 214 nm (hetero annular)  
 $3\text{-ring residue} (3 \times 5) = 15 \text{ nm}$   
 $1\text{-exocyclic double bond} \frac{(1 \times 5) = 5}{234 \text{ nm}}$

(c) Basic value (homoannular diene) 253 nm  
 $4\text{-ring residue} (4 \times 5) = 20 \text{ nm}$   
 $1\text{-exocyclic double bond} \frac{(1 \times 5) = 5}{278 \text{ nm}}$

(d) Basic value 253 nm  
 $2\text{-extended double bond} (2 \times 30) = 60 \text{ nm}$   
 $3\text{-exocyclic double bond} (3 \times 5) = 15 \text{ nm}$   
 $5\text{-ring residue} \frac{(5 \times 5) = 25}{353 \text{ nm}}$

Enones ( $\alpha, \beta$  unsaturated ketone)  
 Woodward and Fieser framed certain empirical rules for estimating absorption maximum for  $\alpha, \beta$  unsaturated carbonyl compound. The  $\lambda_{\max}$  is calculated for  $\pi \rightarrow \pi^*$  asized below.



Base value for  $\alpha, \beta$  unsaturated ketone (cyclic/six-membered) = 215 nm.  $\lambda_{\text{max}}$   
 compound containing  $= \text{CH}-\text{COX}$ ; basic value is 215 if X is alkyl group.

- (i) If X = H, the base value = 207 nm (Aldehyde).
- (ii) If X = OH, the base value = 198 nm (Acid).
- (iii) If double bond and carbonyl group in conjugation are present in five-membered ring, then for  $\alpha, \beta$  unsaturated ketone, basic value = 202 nm.

### Structural increment

(i)	For each exocyclic double bond	
(ii)	Double bond extending conjugation	+ 5 nm
(iii)	For a homoannular conjugated diene	+ 30 nm
(iv)	For each double bond endocyclic in five or seven-membered ring except cyclo-Pent-2-enone	+ 39 nm + 5 nm

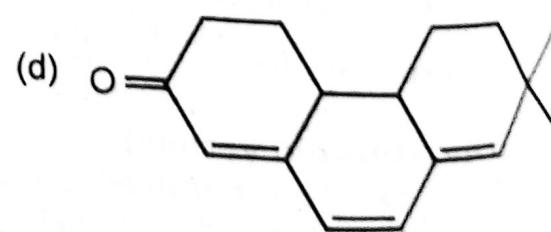
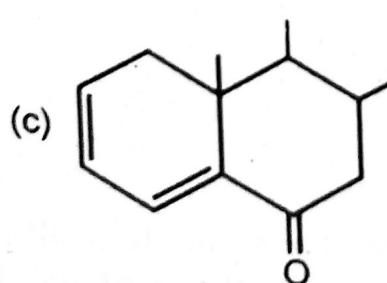
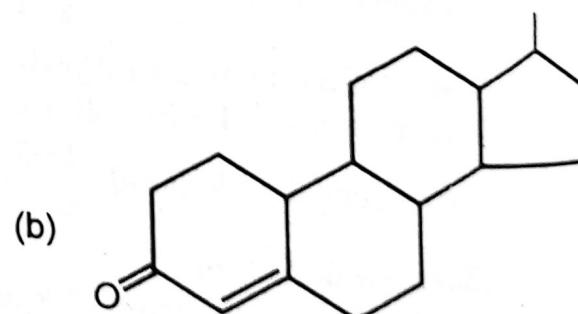
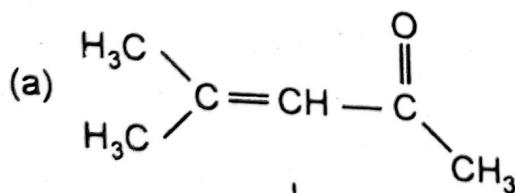
For each alkyl substituent	
$\alpha$ -position	
$\beta$ -position	+10 nm
$\gamma$ -position	+12 nm
or $\delta$ -position	+18 nm
or higher position	

Increment (nm) for various auxochrome in the various  $\alpha, \beta, \gamma$  position are given below:

Auxochrome	$\alpha$	$\beta$	$\gamma$	$\delta$ or higher
$-OH$	+35	+30		
$-OAC$	+6	+6	+6	50
$-Cl$	+15	+12		+6
$-Br$	+25	+35		
$-OR$	+35	+30	17	
$-SR$		+85		
$-NR_2$	—	+95		31

### Example 19.12

Predict  $\lambda_{\text{max}}$  for the following system.



### Solution

(a)	Base value 215 nm 2- $\beta$ -alkyl (substituent) $\frac{(2 \times 12) = 24}{\lambda_{\max} = 239 \text{ nm}}$
(b)	Base value 215 nm 2- $\beta$ -alkyl $(2 \times 12) = 24 \text{ nm}$ 1-exocyclic double bond $\frac{(1 \times 5) = 5 \text{ nm}}{\lambda_{\max} = 244 \text{ nm}}$
(c)	Base value 215 nm Base value homonuclear dien 39 nm 1- $\alpha$ ring residue $(1 \times 10) = \text{nm}$ 1- $\delta$ ring residue $(1 \times 18) = 18 \text{ nm}$ 1- exocyclic double bond $(1 \times 5) = 5 \text{ nm}$ 1- double bond extending $(1 \times 30) = 30 \text{ nm}$ $\lambda_{\max} = 317 \text{ nm}$
(d)	Base value 215 nm 1- $\beta$ ring residue $(1 \times 12) = 12 \text{ nm}$ 1- $\delta$ ring residue $(3 \times 18) = 54 \text{ nm}$ 2- For higher $\delta$ $(2 \times 30) = 60 \text{ nm}$ 2- double bond extending conjugation 2-exocyclic double bond $\frac{(2 \times 5) = 10}{\lambda_{\max} = 351 \text{ nm}}$

**Correction for change in the polarity of solvent**  
 It may be noted that the value of  $\lambda_{\max}$  is changed due to change in the polarity of the solvent i.e.  $\lambda_{\max}$  is solvent dependent. More polar solvent will experience hydrogen bonding with the carbonyl group and  $\pi \rightarrow \pi^*$  transition will experience blue shift. Solvent corrections may be noted as follows.

Solvent	Correction (n)
Ethanol	0
Methanol	0
Dioxane	+5
Chloroform	+1

#### Rule for calculating $\lambda_{\max}$ for derivatives of acyl benzene

Like Woodward-Fieser rules, Scott devised a set of rules for calculating  $\lambda_{\max}$  for the derivatives of acyl benzene. These rules help in estimating the position of absorption maximum in ethanol in a number of monosubstituted aromatic ketones aldehydes, acids and esters.

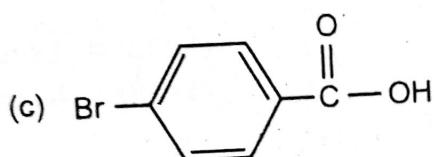
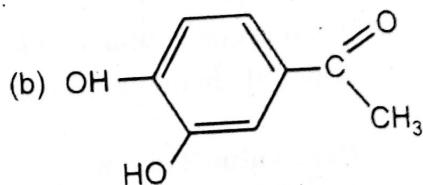
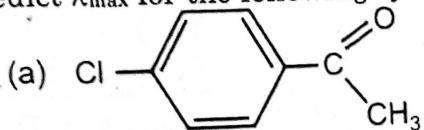
For a compound of  $\text{C}_6\text{H}_5 - \overset{\underset{\text{O}}{\parallel}}{\text{C}} - \text{X}$ , the rules are summarized below:

The basic value is 246 nm, if X is an alkyl group or alcylic residue.

If X is halogen atom, the basic value becomes 250 nm.

The basic value is 230 nm, if X = -OH or -OR. The structural increment in nm for further substitution on the aromatic ring in the Ortho, Meta and Para positions are given below.

Auxochrome	Increment in nm position of the substituent		
	Ortho	Meta	Para
Alkyl	+3	+3	+10
OH, OR	+7	+7	+25
Cl	0	0	+10
Br	+2	+2	+15
NH <sub>2</sub>	+13	+13	+58
NHCOCH <sub>3</sub>	+20	+20	+45
NR <sub>2</sub>	+20	+20	+85
-O-	+11	+20	+75

**Example 19.13**Predict  $\lambda_{\max}$  for the following systems.**Solution**

(a)

$$\begin{array}{r} \text{Basic value} = 246 \text{ nm} \\ 1 - P - \text{Cl} (1 \times 10) = 10 \text{ nm} \\ \hline \lambda_{\max} = 256 \text{ nm} \end{array}$$

(b)

$$\begin{array}{r} \text{Basic value} = 246 \text{ nm} \\ 1 - m - \text{OH} (1 \times 7) = 7 \text{ nm} \\ 1 - P - \text{OH} (1 \times 25) = 25 \text{ nm} \\ \hline \lambda_{\max} = 278 \text{ nm} \end{array}$$

(c)

$$\begin{array}{r} \text{Basic value} = 230 \text{ nm} \\ 1 - P - \text{Bromo} (1 \times 15) = 15 \text{ nm} \\ \hline \lambda_{\max} = 245 \text{ nm} \end{array}$$

**2. Quantitative Analysis**

For determination of the concentration of a substance, wavelength of its maximum absorption is selected. The absorbance of the solution of the compound is measured for different concentrations of the solution known as standard solution. Then absorbance is plotted against the concentration of the solution which produces a straight line. This plot may be used as a calibration curve for unknown sample. The solution of the unknown sample is put on the spectrophotometer and its absorbance is measured. Corresponding to this absorbance the concentration of unknown sample can be measured from calibration plot as shown in Figure 19.9

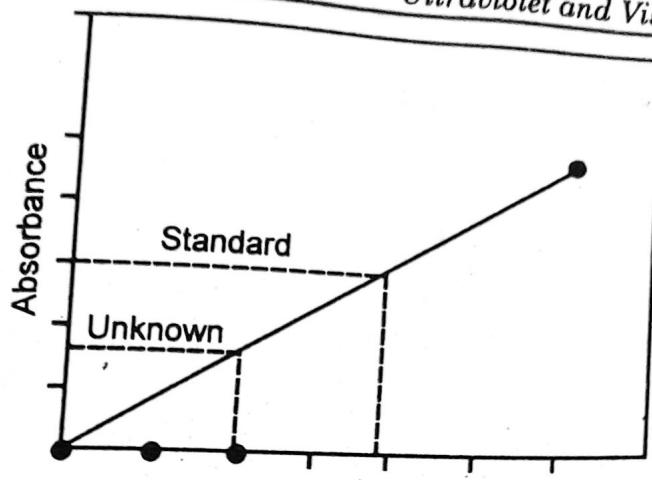


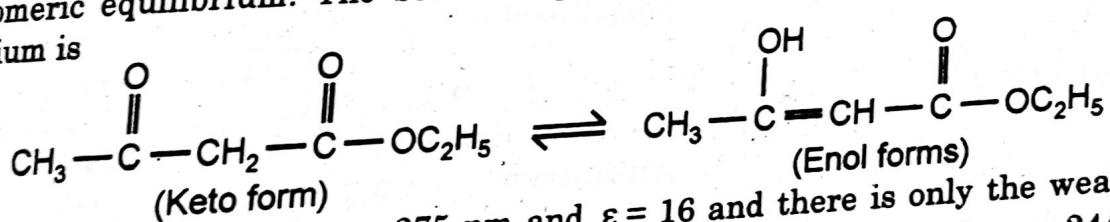
Figure 19.9 Calibration plot.

### 5. Detection of Impurities

UV absorption spectroscopy is one of the best methods for detecting impurities especially in organic compounds. For example, in nylon manufacture, the starting materials like adipic acid and hexa methylene diamine should be very pure. If the starting materials are not pure, the nylon obtained will be of very poor quality. The purity of these materials can be tested by UV absorption spectroscopy. Traces of unsaturated and aromatic impurities can be detected because the starting materials are transparent at the near UV-region.

### 4. Study of Tautomeric Equilibria

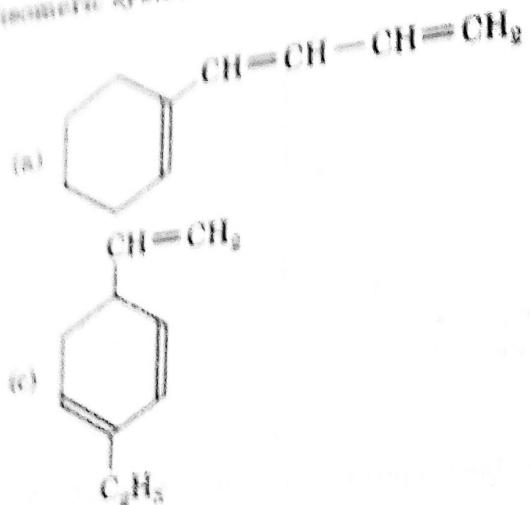
UV spectroscopy can be used to determine the various keto and enol forms present in tautomeric equilibrium. The best example is that in ethyl aceto acetate where the equilibrium is



The keto form has  $\lambda_{\max} = 275 \text{ nm}$  and  $\epsilon = 16$  and there is only the weak  $n \rightarrow \pi^*$  band of the isolated carbonyl group. On the other hand, enol form has  $\lambda_{\max} = 244 \text{ nm}$  and  $\epsilon = 1600$ . Thus from the strength of the 244 nm band, one can measure the proportion of tautomers present in the ethyl aceto acetate.

Besides the above, UV-visible spectral method can also be applied to chemical kinetics, molecular weight determination, spectrophotometric titration, octahedral-square planar equilibria, square-planar-tetrahedral equilibria, geometrical isomerisation etc.

Problem 19.14 Explain how the ultraviolet spectrum can be used to decide between the following isomeric systems.



Solution  
 $\lambda_{\text{max}}$  for (a)

$$\begin{aligned} \text{Base} & - 217 \text{ nm} \\ \text{Extent} & - 30 \text{ nm} \\ \text{No. of alkyl group} & - 2 \times 5 = 10 \text{ nm} \\ & \underline{\quad 257 \text{ nm}} \end{aligned}$$

$\lambda_{\text{max}}$  for (b)

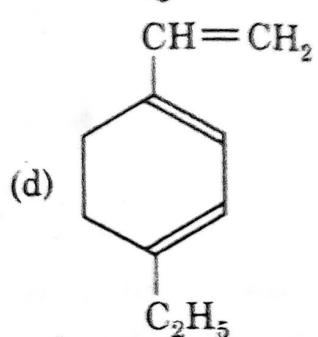
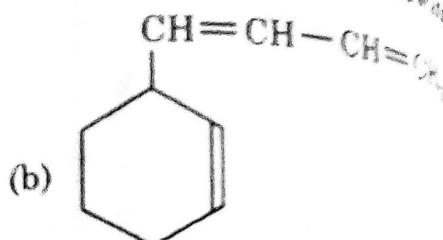
$$\begin{aligned} \text{Base} & - 217 \text{ nm} \\ \text{Substituent} & - 5 \text{ nm} \\ \text{Base} & - 222 \text{ nm} \end{aligned}$$

$\lambda_{\text{max}}$  for (c)

$$\begin{aligned} \text{Base} & - 253 \text{ nm} \\ \text{Substituent} & - 5 \times 3 = 15 \text{ nm} \\ & \underline{\quad 268 \text{ nm}} \end{aligned}$$

$\lambda_{\text{max}}$  for (d)

$$\begin{aligned} \text{Base} & - 253 \text{ nm} \\ \text{1-extended conjugation} & - 30 \text{ nm} \\ \text{Substituent} & - 3 \times 5 = 15 \text{ nm} \\ & \underline{\quad 298 \text{ nm}} \end{aligned}$$



## QUESTIONS

**Answer the following questions.**

- Q.1. Mention the range of near UV or quartz region in nm.  
Q.2. What is the limit of molar extinction coefficient?  
Q.3. Name the radiation source used in UV-visible spectrometry.  
Q.4. Give the example of compound showing  $n \rightarrow \pi^*$ ,  $n \rightarrow \sigma^*$  transition.  
Q.5. Why does conjugation shifts  $\lambda_{\text{max}}$  to longer wavelength?  
Q.6. Name some of the solvents used in UV-spectroscopy.  
Q.7. Mention the relation between probability of a transition and molar extinction coefficient.  
Q.8. What is the effect of H-bonding to UV absorption?  
Q.9. What is the range of  $\epsilon_{\text{max}}$  for allowed transition? Is  $\pi \rightarrow \pi^*$  transition is allowed or forbidden?  
Q.10. What type of transition are observed in benzophone?  
Q.11. Which of the following compound have higher  $\lambda_{\text{max}}$ .  
(a)  $\text{H}_2\text{N}-\text{C}_6\text{H}_5$   
(b)  $\text{Cl}-\text{H}_3\text{N}^+-\text{C}_6\text{H}_5$   
Q.12. Why is ethanol a good solvent in ultraviolet?  
Q.13. Discuss the various absorption laws involved in UV-visible spectral method.  
Derive Lambert-Beers law.  
Q.14. Discuss the various electronic transitions involved in organic molecules. Write a note on various electronic spectral bands. Give your comments on their original and characteristics.  
Q.15. Discuss the effect of solvent polarity in  
(i)  $n - \pi^*$  transition,  
(ii)  $\pi - \pi^*$  transition  
Q.16. Draw the schematic diagram for a double beam spectrophotometer and write its working principles.  
Q.17. (a) Explain the following  
(i) half bandwidth  
(ii) oscillator strength and transition moment integral  
(b) Write the various selection rules involved in UV-visible spectroscopy  
Q.18. Discuss the following  
(a) The effect of some of auxochrome absorption characteristics of benzene.  
(b) The effect of stereochemical factors on the electronic absorption band.  
Q.19. What are the empirical rules for calculation of absorption maxima in case of polynes? Explain by giving suitable examples.  
Q.20. What are the empirical rules for calculation of absorption maxima for  $\alpha-\beta$  unsaturated ketone? Explain by giving suitable examples.  
Q.21. Discuss the various rules for calculation of absorption maxima in case of acyl benzene.  
Q.22. Write the basic principle involved in UV-visible spectroscopy.