

UV - VISIBLE SPECTROSCOPY

Study of interaction of electromagnetic radiation with matter is called spectroscopy. The structure of atoms and molecules can be determined from spectroscopy. The spectra can be of the following two types —

- (i) emission spectra
- (ii) absorption spectra

Emission spectrum : When a solid is heated or electric discharge is passed through a gas, light is emitted. On examining this light by a spectroscope, a spectrum is produced. It is known as **emission spectrum**. Emission spectra can be divided into three types as —

- (i) continuous spectra
- (ii) line spectra
- (iii) band spectra

Absorption spectrum : When white light is passed through a coloured solution or vapour, black bands are observed in the continuous region. And the spectra obtained are called **absorption spectra**.

Atomic spectra : The structure and energy levels of atoms are obtained from their atomic spectra. They have usually discrete, well separated lines. Hence, they are called **line spectra**. E.g. in the study of hydrogen, five series of spectral lines are obtained. They are Lyman, Balmer, Paschen, Brackett and Pfund series.

Molecular spectra : The structure, stability and other valid informations of molecules can be obtained from their molecular spectra. They are usually in the form of bands. Hence, they are known as **band spectra**. Each band consists of closely placed many lines.

Nature of light : According to de Broglie, light has wave, particle duality. Light can be regarded as energy. When a molecule absorbs

light, its energy is increased. The energy absorbed by one molecule is called **one quantum** of energy.

The energy absorbed by one molecule (E) is proportional to the frequency of light radiation (ν):

$$E \propto \nu \quad \text{_____ (1)}$$

$$\text{or, } E = h\nu \quad \text{_____ (2)}$$

Here, h is called Planck constant. Its value is

(i) 6.625×10^{-27} erg sec.

(ii) Its S.I. unit is 6.625×10^{-34} Joule sec.

One quanta of energy is given in terms of erg or joule as the unit of frequency is sec^{-1} . Frequency is expressed in hertz (Hz) also. Thus the S.I. unit for energy is joule.

The energy absorbed by one mole of the substance is called **one Einstein**.

$$1 \text{ Einstein energy} = N h \nu \quad \text{_____ (3)}$$

Here, N = Avogadro number. Its value is 6.023×10^{23}

The frequency of radiation (ν) is inversely proportional to the wave length (λ) as given below.

$$\nu \propto \frac{1}{\lambda} \quad \text{_____ (4)}$$

$$\text{or, } \nu = \frac{c}{\lambda} \quad \text{_____ (5)}$$

where, c = velocity of light. Its value is, 3×10^{10} cm sec^{-1} . In S.I. unit, it is 3×10^8 m sec^{-1}

Wave length of radiation (λ) can be given in terms of (i) Angstrom (\AA) (ii) cm (iii) m (iv) micron (μ) (v) milli micron ($\text{m}\mu$) (vi) nanometer (nm). The inter relationship between them are given as

$$\begin{aligned} 1 \text{ \AA} &= 1 \times 10^{-8} \text{ cm} \\ &= 1 \times 10^{-10} \text{ m} \quad (\because 100 \text{ cm} = 1 \text{ m}) \\ &= 0.1 \times 10^{-9} \text{ m} \\ &= 0.1 \text{ nm} \quad (\because 1 \text{ nm} = 1 \times 10^{-9} \text{ m}) \\ &= 0.1 \times 10^{-3} \times 10^{-6} \text{ m} \end{aligned}$$

$$= 0.1 \times 10^{-3} \mu \quad (\because 1 \mu = 1 \times 10^{-6} \text{ m})$$

$$= 0.1 \text{ m}\mu \quad (\because \text{milli} = \frac{1}{1000} = 1 \times 10^{-3})$$

Hence, $1 \text{ \AA} = 1 \times 10^{-8} \text{ cm} = 1 \times 10^{-10} \text{ m} = 0.1 \text{ nm} = 0.1 \text{ m}\mu$
and, $1 \text{ nm} = 1 \text{ m}\mu = 10 \text{ \AA}$

The reciprocal of wave length is called wave number ($\bar{\nu}$)

$$\text{i.e., } \bar{\nu} = \frac{1}{\lambda} \quad (6)$$

The unit of wave number is decided by the wave length. However, wave number is usually given as cm^{-1} . Combining all equations, we obtain

$$E = h\nu = h \frac{c}{\lambda} = hc \cdot \frac{1}{\lambda} = hc \bar{\nu} \quad (7)$$

From the above equation, the energy (E) is

- (i) directly proportional to frequency (ν) and wave number ($\bar{\nu}$)
- (ii) inversely proportional to wave length, (λ)

WORKED EXAMPLES

1. The wave length of radiation is 400 nm. Calculate its (i) wave number (ii) frequency in S.I. units.

Wave number, $\bar{\nu}$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{400 \text{ nm}} = \frac{1}{400 \times 10^{-9} \text{ m}} = \frac{10^9}{400} \text{ m}^{-1}$$

$$= 2.5 \times 10^6 \text{ m}^{-1}$$

Frequency ν

$$\nu = c \bar{\nu} \text{ sec}^{-1}$$

$$= 3 \times 10^8 \times 2.5 \times 10^6 \text{ sec}^{-1} = 7.5 \times 10^{14} \text{ sec}^{-1}$$

II method

$$\text{Frequency, } \nu = \frac{c}{\lambda} = \frac{3 \times 10^8}{400 \times 10^{-9}} \text{ sec}^{-1}$$

$$= \frac{3}{4} \times 10^{15} \text{ sec}^{-1}$$

$$= 7.5 \times 10^{14} \text{ sec}^{-1}$$

2. Calculate (i) One quanta (ii) One Einstein energy for a radiation of wave length 5000 \AA

One quanta energy

$$E = h\nu = h \frac{c}{\lambda} \text{ J}$$

Here, $h = 6.625 \times 10^{-34} \text{ J sec}$; $c = 3 \times 10^8 \text{ m sec}^{-1}$; $\lambda = 5000 \text{ \AA}$

$$\lambda = 5000 \times 10^{-10} \text{ m} = 5 \times 10^{-7} \text{ m}$$

$$\therefore E = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{5 \times 10^{-7}} \text{ J} = 3.975 \times 10^{-19} \text{ J}$$

One Einstein Energy

$$E = N h \nu = N h \frac{c}{\lambda} \text{ J}$$

Here, $N = \text{Avogadro number} = 6.023 \times 10^{23}$

$$E = \frac{6.023 \times 10^{23} \times 6.625 \times 10^{-34} \times 3 \times 10^8}{5 \times 10^{-7}}$$

$$= 2.394 \times 10^5 \text{ J}$$

$$= 2.394 \times 10^2 \times 10^3 \text{ J}$$

$$E = 239.4 \text{ kJ} \quad (\because 1 \text{ kJ} = 1 \times 10^3 \text{ J})$$

3. The energy of activation of a reaction is 200 kJ mol^{-1} . Calculate the minimum frequency of radiation required for the reaction.

Use

$$E = N h \nu \text{ J}$$

$$\text{or, frequency, } \nu = \frac{E}{N h} \text{ sec}^{-1}$$

Given.

$$E = 200 \text{ kJ} = 200 \times 10^3 \text{ J}; \quad N = 6.023 \times 10^{23}$$

$$h = 6.625 \times 10^{-34} \text{ J sec}$$

$$\therefore \nu = \frac{2 \times 10^5}{6.023 \times 10^{23} \times 6.625 \times 10^{-34}} \text{ sec}^{-1}$$

$$\nu = 5.102 \times 10^{14} \text{ sec}^{-1}$$

PROBLEMS FOR EXERCISE

- Calculate (i) Wave number (ii) Frequency and (iii) One quantum of energy for the radiation of 2000 Å.
(Ans: (i) $5 \times 10^6 \text{ m}^{-1}$; (ii) $1.5 \times 10^{15} \text{ sec}^{-1}$; (iii) $9.938 \times 10^{-19} \text{ J}$)
- Calculate (i) wave number (ii) frequency and (iii) one Einstein of energy for the radiation of 800 nm.
(Ans: (i) $1.25 \times 10^6 \text{ m}^{-1}$ (ii) $3.75 \times 10^{14} \text{ sec}^{-1}$ (iii) 150 kJ mol^{-1})

Different type of molecular energies

The absorption takes place when the energy of the incident electromagnetic radiation is equal to the energy difference between two quantized energy levels of the absorbing species. The various quantized energy levels are _____

- Translational energy, E_{tra}
- Rotational energy, E_{rot}
- Vibrational energy, E_{vib}
- Electronic energy, E_{ele}

We shall discuss them in brief.

(i) Translational energy levels

These energy levels are very close to each other. It is calculated using, $E_{\text{tra}} = \frac{1}{2} mv^2$

Where, m = mass and v = linear velocity

(ii) Rotational energy levels

This is associated with the rotation of the molecule with atoms. It is calculated using the formula,

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

Where, J = rotational quantum number and it may be 0,1,2,.....

I = moment of inertia

h = Planck's constant.

It appears in the microwave region which is a very low energy region.

(iii) Vibrational energy levels

This is associated with the vibrations of atoms in a molecule. It is calculated using

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

where, v = vibrational quantum number and it can be 0,1,2,.....
 ν = vibrational frequency.

It appears in the infrared region. The wave length is from 8000 Å to 350000 Å. The frequency is from 3.75×10^{14} to $8.6 \times 10^{12} \text{ sec}^{-1}$. This is the low energy (about 10 kJ) region.

(iv) Electronic energy levels

The energy due to the motion of electrons while nuclei are at rest is called electronic energy.

This appears in the ultra violet and visible region.

The wave length of radiation is 1000 Å to 8000 Å

The frequency is $3 \times 10^{15} \text{ sec}^{-1}$ to $375 \times 10^{14} \text{ sec}^{-1}$

The energy of one Einstein is about 500 kJ.

Origin of molecular spectra

Consider a diatomic molecule AB consisting of the atoms A and B. The electrons in these atoms can exist in a number of energy levels, as in all atoms in general. If electronic transition was the only mode by which the molecules could absorb or emit energy, molecular spectrum would also have been a line spectrum similar to that shown by atoms. But in the case of molecules, the complication is caused by the fact that a molecule may utilise the absorbed energy not only for electronic transitions like atoms, but also in setting the molecules

rotating as a whole or setting nuclei of the constituent atoms in vibration with respect to each other. In the case of molecular spectra therefore we may consider —

- (i) Electronic transition.
- (ii) Rotational motion.
- (iii) Vibrational motion.

The rotational and vibrational motions are also quantized like electronic level transitions.

Because of simultaneous change in electronic energy state as well as rotational and vibrational energy states of the molecule, molecular spectra are actually observed in the form of a number of closely spaced lines in the form of a band. Such spectra are called **band spectra**. These appear in regions of short wave length because energy required for electronic transition is usually large.)

The occurrence of quantized vibrational and rotational motions gives rather a complicated picture of the energy levels of a molecule as shown in fig 8.1. The values of n represent different electronic energy levels of the molecule. The vibrational and rotational energy levels corresponding to different in values are grouped together. Thus, the energy levels, included in the group for which $n = 1$ represents the lowest energy levels of the molecule. Similarly, the energy levels included in the group for which $n = 2$ gives the energy states of the next higher electronic level, and so on.

Each electronic level consists of a number of vibrational sublevels represented by the vibrational quantum numbers are shown on the right. The various values of v , i.e. $v = 0, 1, 2, \dots$ give the various vibrational quantum numbers belonging to the same electronic ($n = 1, 2, 3$, etc) level.

Each of the vibrational quantum numbers in its turn, is associated with a number of rotational quantum numbers designated by the various values of J ($= 0, 1, 2$, etc) as shown in the figure on the left.

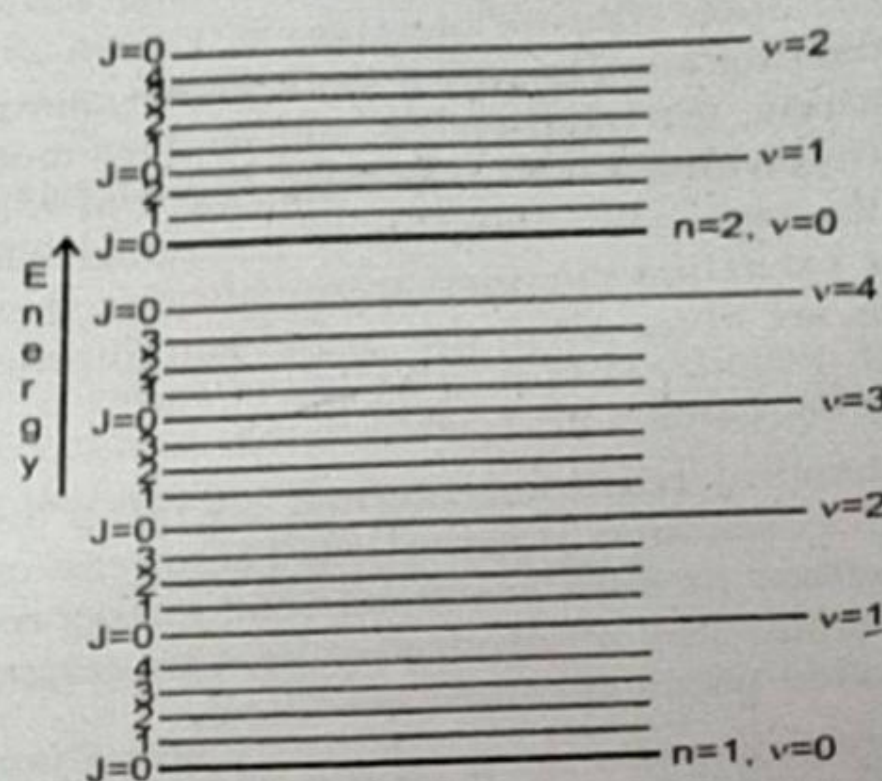


Fig. 8.1

The energy required for exciting emissions is lowest for rotational, higher vibrational and still higher for electronic transitions as:

$$E_{\text{elec}} > E_{\text{vib}} > E_{\text{rot}}$$

Thus, if excitation energy is adjusted to be so small as to produce only transition from one rotational quantum level to another, the vibrational level and the electronic level remaining the same, the emission spectra observed would correspond to changes in the rotational quantum numbers only. Such a spectrum is known as **rotational spectrum**. Since the energies involved in such spectra are small, these occur in **microwave region**.

If on the other hand, the excitation energy is sufficiently large to cause transition from one vibrational quantum level to another, the electronic level remaining the same, emission spectra observed would correspond to changes in the vibrational quantum numbers. But since changes in vibrational levels also involve changes in rotational levels, what we actually observe is a **vibrational rotational spectrum**. Since energies involved are relatively higher, such spectra are observed in the **infrared region**.

If still higher excitation energies are applied, electronic transition may take place. These will be accompanied by vibrational level changes and each vibrational level change, in turn, will be accompanied by

$$\log \frac{I}{I_0} = \frac{-k}{2.303} x = -ax \quad (9)$$

$$\frac{I}{I_0} = 10^{-ax} \quad (10)$$

$$I = I_0 10^{-ax}$$

Where, a = extinction coefficient of the absorbing medium.

It is related to absorption coefficient k , by the expression,

$$a = \frac{k}{2.303} = 0.4342 k$$

$$\text{and } k = 2.303 a$$

(iii) Lambert Beer's law or Beer's law

Statement: 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, the law may be written as,

$$\frac{-dI}{dx} \propto IC \quad (1)$$

$$\text{or, } \frac{-dI}{dx} = k' IC \quad (2)$$

$$\text{On rearranging, } \frac{-dI}{I} = k' C dx \quad (3)$$

where, k' = molar absorption coefficient
 C = concentration of the solution.

Let I_0 be the intensity of radiation before entering the absorbing solution (i.e. when $x = 0$).

Integrating the equation (3) with suitable limits,

$$\int_{I_0}^I \frac{dI}{I} = -k' C \int_0^x dx \quad (4)$$

$$\ln \frac{I}{I_0} = -k' Cx \quad (5)$$

$$\frac{I}{I_0} = e^{-k' Cx} \quad (6)$$

$$\text{or } I = I_0 e^{-k' Cx} \quad (7)$$

Changing the natural logarithm to the base 10, the equation (7) may be written as,

$$I = I_0 10^{-a' Cx} \quad (8)$$

Where, a' is called molar extinction coefficient of the absorbing solution. It is related to molar absorption coefficient of the absorbing solution, k' by the expression,

$$a' = \frac{k'}{2.303} = 0.4342 k' \quad (9)$$

$$\text{and } k' = 2.303 a'$$

Testing of Beer's law

From Beer's law it follows that if we plot absorbance, A against concentration, C , a straight line passing through the origin should be obtained as in fig 8.2. But, there is usually a deviation from a linear relationship between concentration and absorbance. In other words, an apparent failure of Beer's law may insure. Deviations from the law are reported as positive or negative according to whether the resultant curve is concave upwards or concave downwards.

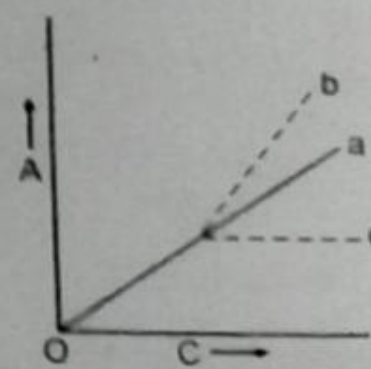


Fig. 8.2

Deviations from Beer's law can arise due to the following factors

- Beer's law will hold over a wide range of concentration provided the structure of the coloured ion or the coloured non electrolyte in the dissolved state does not change with concentration.
- Deviations may occur if the coloured solute ionises, dissociates or associates in solution.
- Deviations may also occur due to the presence of impurities that fluoresce or absorb at the absorption of wave length.
- Deviations may occur if monochromatic light is not used.
- Deviations may occur if the width of the slit is not proper

(vi) Deviations may occur if the solution undergoes polymerisation.

(vii) Beer's law cannot be applied to suspensions.

Explanation of terms used in absorption spectra

1) Absorbance, A

$$A = \log \frac{I_0}{I} = \log \frac{P_0}{P}$$

Where, I_0 and I are the intensity of incident radiation and transmitted radiation. I_0/I is called, opacity.

P_0 and P are the power of incident radiation and transmitted radiation.

A is also called as optical density (D) or extinction coefficient.

2) Transmittance, T

$$T = \frac{I}{I_0} = \frac{P}{P_0}$$

3) Absorptivity, a

$$a = \frac{A}{xC}$$

4. Molar absorptivity, E

$$E = \frac{A}{Cx} = \log \frac{I_0}{I}$$

WORKED EXAMPLES

1. A monochromatic radiation is incident on a solution of 0.05 M of an absorbing substance. The intensity of the radiation is reduced to one fourth of the initial value after passing through 10 cm length of the solution. Calculate the value of molar extinction coefficient as well as molar absorption coefficient of the substance.

Use $\frac{I}{I_0} = 10^{-a' Cx}$

Given $\frac{I}{I_0} = 0.25; C = 0.05 \text{ M}; x = 10 \text{ cm}$

$$\log \frac{I}{I_0} = -a' Cx$$

$$\log 0.25 = -a' \times 0.05 \times 10$$

$$\log 4 = 0.5 a'$$

$$0.5 a' = 0.6021$$

$$a' = \frac{0.6021}{0.5} = 1.204$$

Molar absorption

$$\text{coefficient, } k' = 2.303 a' = 2.303 \times 1.204 = 2.773$$

2. A substance when dissolved in water at 10^{-3} M concentration absorbs 10% of an incident radiation in a path of 1 cm length. What should be the concentration of the solution in order to absorb 90% of the same incident radiation?

Use $\frac{I}{I_0} = 10^{-a' Cx}$

Given

I. Absorption = 10%

$$\therefore \frac{I}{I_0} = 90\% = 0.90; C = 10^{-3} \text{ M}; x = 1 \text{ cm}$$

$$0.90 = 10^{-a' \times 10^{-3} \times 1}$$

$$\text{Taking log, } \log 0.90 = -a' \times 10^{-3}$$

$$\text{or } \log \frac{1}{0.90} = 10^{-3} a'$$

$$0.0458 = 10^{-3} a'$$

$$\therefore a' = \frac{0.0458}{10^{-3}} = 45.8$$

II. Absorption = 90%. $\therefore \frac{I}{I_0} = 10\%; a' = 45.8; x = 1 \text{ cm}$.

$$0.1 = 10^{-45.8 \times 1 \times C}$$

Taking log, $\log 0.1 = -45.80'$

$$\log \frac{1}{0.1} = \log 10 = 1 = 45.80'$$

$$\therefore C = \frac{1}{45.8} = 0.0218 \text{ M}$$

3. When a monochromatic light is passed through a cell of 1 cm length, the intensity of the radiation is reduced to 10%. If the same radiation is passed through a cell of length 8 cm what is the concentration of the solution? Calculate the length of the cell in order to have 25% absorbance.

Use $2.303 \log \frac{I_0}{I} = a \times x$

Given

(1) $I_0 = 100\%$ $I = 90\%$ $x = 1 \text{ cm}$ $a = ?$

$$2.303 \log \frac{100}{90} = a \times 1$$

$$= 2.303 \times 0.0458 = a$$

Extinction coefficient, $a = 0.1055$

(2) $I_0 = 100\%$ $I = ?$ $a = 0.1055$ $x = 8 \text{ cm}$.

$$2.303 \log \frac{100}{I} = 0.1055 \times 8$$

$$\log \frac{100}{I} = \frac{0.1055 \times 8}{2.303} = 0.3664$$

$$\frac{100}{I} = \text{Antilog } 0.3664 = 2.327$$

$$I = \frac{100}{2.327} = 43\% \text{ or } 0.43$$

(3) $I_0 = 100\%$ $I = 25\%$ $a = 0.1055$ $x = ?$

$$2.303 \log \frac{100}{25} = 0.1055 \times x$$

$$2.303 \times 0.6021 = 0.1055 \times x$$

$$x = \frac{2.303 \times 0.6021}{0.1055} = 13.1 \text{ cm.}$$

PROBLEMS FOR EXERCISE

- When a radiation was passed through a cell of 2 cm length, the intensity has reduced to 20%. Calculate the
 - Concentration of the solution, if it is passed through 10 cm cell.
 - Thickness of the cell in order to have 50% absorbance.
(Ans: a = 0.1116; I = 59.8%; x = 6.20 cm)
- 70% transmittance was observed using a cell of 2 mm thickness. If a cell of 0.05 mm thickness is used, what is the percentage of transmittance? (Ans: 91.87%)
- When a monochromatic light was passed through a cell of 1 cm thickness having 0.2M solution, 90% light was absorbed. Calculate (i) Transmittance (ii) Absorbance (iii) Coefficient of absorption.
(Ans: (i) 0.1 (ii) 1 (iii) 0.4 lit mol⁻¹ cm⁻¹)
- When a monochromatic light was passed through a cell of 1 cm thickness, 10% light was absorbed. Calculate the percentage of light absorbed if it is passed through a cell of 5 cm thickness. (Ans: 41%)

Instrumentation

When a molecule absorbs light in the ultra violet and visible region, changes in energy and electronic arrangement take place. Usually in electronic spectra the following two parameters are determined —

- quantity of light absorbed
- decrease in the intensity of light radiation when it passes through a medium.

The absorption maximum (ϵ_{max}) for a particular electronic transition depends on the energy. The wave length at which the absorption maximum occurs is called, λ_{max} .

We shall discuss few instruments used to determine the energy of absorption or emission.

1. Photometers

These instruments give the relative intensity of two electromagnetic radiations or the derivative of the ratio.

2. Spectrometers

In this instrument, there will be two slits namely, entrance slit and exit slit. The exit slit may be one or more in number. There will be a filter also.

Using a spectrometer, it is possible to study some selected wave length in a particular spectral region or to study all possible wave lengths individually in a given spectral region.

3. Spectro photometers

These instruments contain spectrometer and other accessories. They record the relative intensity of two electromagnetic radiations or the derivative of the ratio. The two light rays may be separated by time or position or both.

4. Photocolorimeters

The amount of sample is determined by comparing the colour of the experimental solution with a standard solution using photocolorimeter. This is divided in to two types based on number of light paths as —

- (i) single beam photocolorimeter
- (ii) double beam photocolorimeter.

In single beam instrument, radiation is first passed through the cell containing the solvent alone and then to the experimental solution.

In double beam instruments, the beam is split into two equal halves one half of radiation passes through the sample solution and the other half passes through a blank (solvent).

The double beam operation facilitates automatic recording and at the same time errors that arise due to fluctuation in the applied voltage, detector response etc. are minimised.

Photocolorimeters are further divided into two types as —

- (i) single cell photocolorimeter
- (ii) double cell photocolorimeter.

Block diagram of single cell photocolorimeter

The important components of a single cell photocolorimeter are

- (i) light source (ii) filter (iii) cell
- (iv) barrier type photocell (v) recorder.

Schematic diagram of a photoelectric colorimeter is shown in fig 8.3.

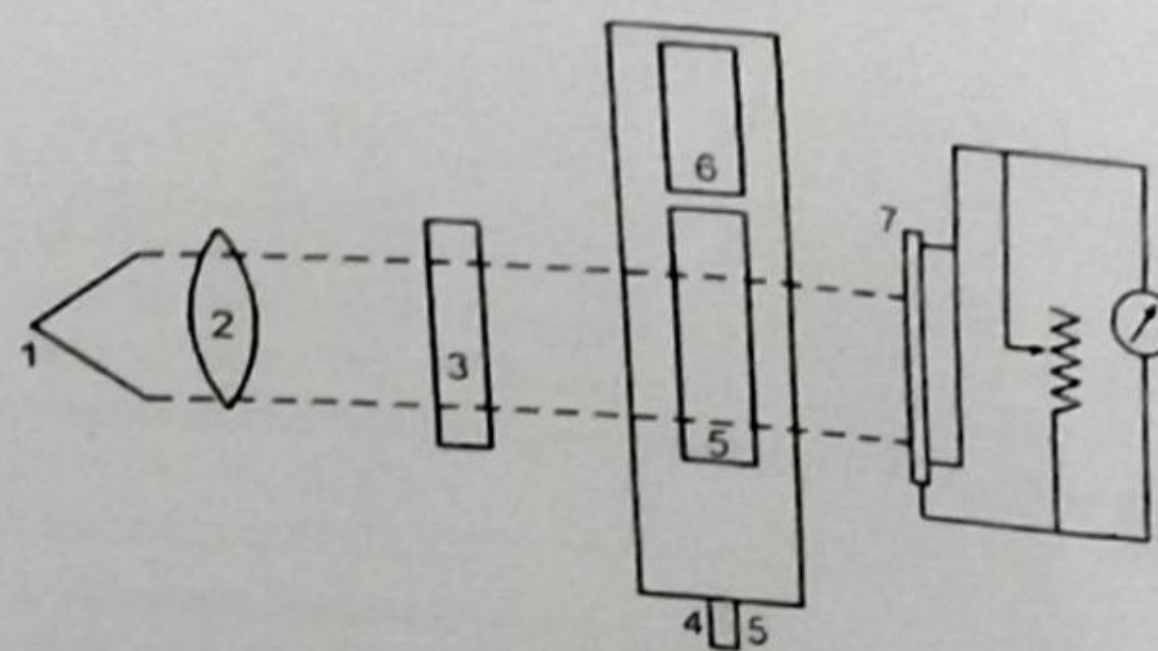


Fig 8.3

- 1. Light source
- 2. Collimating lens
- 3. Filter
- 4. Movable holder
- 5. Solution
- 6. Solvent
- 7. Barrier type photocell

Block diagram of spectrophotometer

Schematic diagram of a spectrophotometer is shown in figure 8.4.

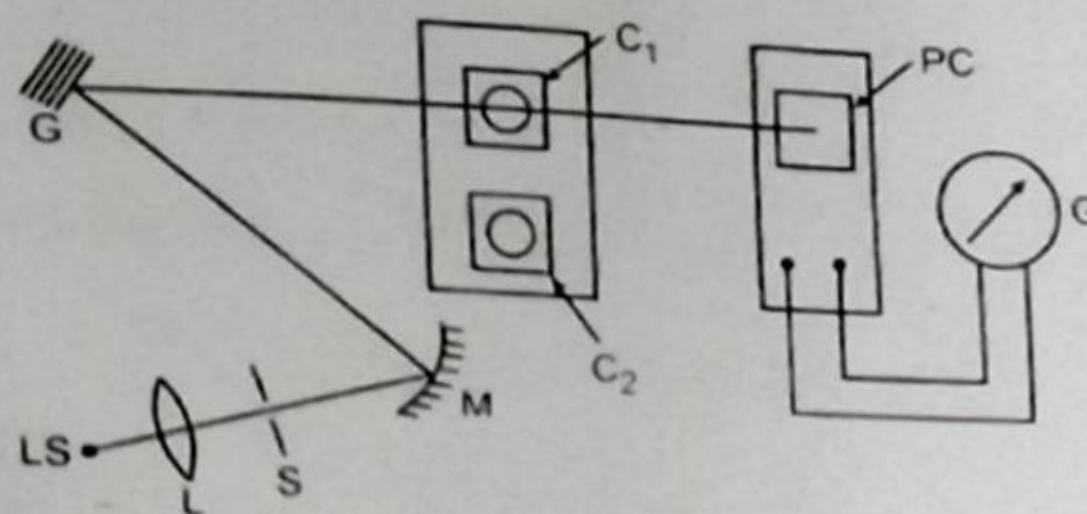


Fig 8.4

LS is the source of light radiation. Hydrogen discharge tube is used to obtain ultra violet radiation of wave length 200-250 nm. Tungsten lamp is used as source to obtain radiation of wave length 100-320 nm. The light rays emerging from LS first pass through a lens L and then to a slit S. when the ray falls on mirror M, it is reflected

so as to fall on grating G. At grating, separation of light occurs because light of different wave lengths is dispersed at different angles. The light of required wave length emerging from grating passes through the experimental solution taken in the cell C_1 . Then it passes through galvanometer G to the photocell PC. PC records the intensity of light radiation. Then, the same light passes through the pure solvent taken in the cell C_2 and then to photocell via galvanometer. Photocell records the intensity of radiation as before.

Molar absorption, ϵ or $\log \epsilon$ values are taken in the y - axis. The values of wave length λ are taken in x - axis. We obtain a graph as shown in figure. This gives the value of λ_{max} .

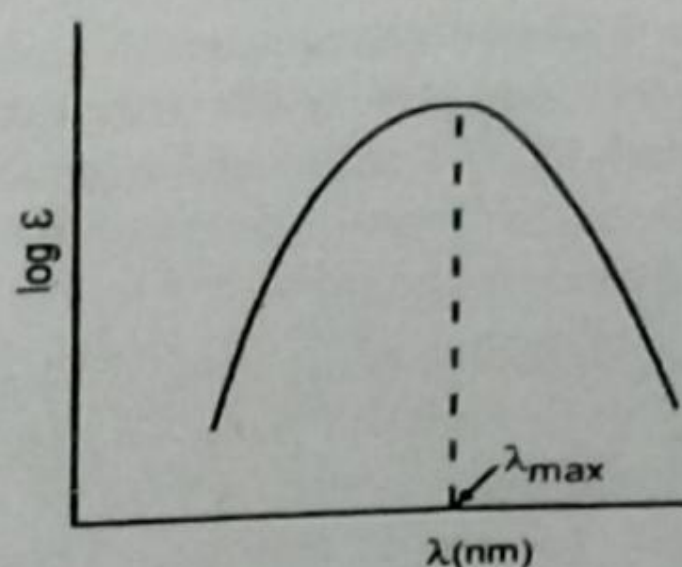


Fig. 8.5

Comparison of photocolorimeter with spectrophotometer

- 1) The precision of spectrophotometer is higher than that of photo-colorimeter.
- 2) Using a spectrophotometer it is possible to record the actual absorption lines.
- 3) Beer's law is followed in spectrophotometer.
- 4) The absorption power varies from one instrument to another in the case of photo colorimeter.
- 5) Filters are used in photo colorimeters. Monochromators are used instead of filters in spectrophotometers. Gratings or prisms are used as monochromators in spectrophotometers to obtain better results.

Description of components of photo colorimeter and spectrophotometer.

Radiation source

A continuous source of radiant energy covering the region of spectrum in which the instrument is designed to work is required.

The wave length range of visible light lies between 4000 Å to 7500 Å. In this region, a tungsten filament lamp is most widely used.

If colorimetric analysis is carried out in the ultra violet region of the spectrum, the source used is a hydrogen lamp.

The following are the requirements of a radiation source —

- (i) It must be stable
- (ii) It must be of sufficient intensity for the transmitted energy to be detected at the end of the optical path.
- (iii) It must supply continuous radiation over the entire wave length region in which it is used.

2. Filters

A source is generally emitting a continuous spectra. Hence, a device is required to select a narrow band from wave lengths of continuous spectra. For this selection, filters or monochromators or both are used.

A light filter is device that allows light of the required wavelength to pass through but absorbs light of other wave lengths wholly or partially. Thus, a suitable filter can select a desired wave length band. It means that a particular filter may be used for a specific analysis. If analysis is carried out for several species, a large number of filters have to be used and interchanged. This method is very useful for routine analysis.

Filters are of two types —

- (i) absorption filters.
- (ii) interference filters.

Absorption filters : They work by selective absorption of unwanted wave lengths. An absorption filter is a solid sheet of glass that has been coloured by a pigment which is dissolved or dispersed in the glass. Dyed gelatin or similar materials can also be used as absorption filters. The following table 8.1. briefly describes the absorption characteristics of some common filters.

Table 8.1
Absorption characteristics of common filters

S.No.	Colour of filters	Approximate wave length (nm)
1.	Yellow	450
2.	Orange	500
3.	Red	575
4.	Purple	450-650
5.	Blue	400-475
6.	Green	575-700

Interference filters : These filters function on interference phenomena at desired wave length, thus permitting rejection of unwanted radiation by selective reflection. Narrower band widths are obtained with interference filters.

In order to prepare an interference filter, a semi transparent metal film is deposited on a plate of glass. Then it is coated with a thin layer of some dielectric material like magnesium fluoride followed by another coating of a thin film of metal. Finally another plate of glass is kept over the film for mechanical protection.

Monochromators : A monochromator successfully isolates band of wave lengths usually much more than a narrower filter. The essential elements of a monochromator are an entrance slit, a dispersing element (a prism or grating) and an exit slit. The function of a prism or a grating is to disperse the heterochromic radiation into its component wave lengths.

Material of construction should be selected with care to suit the range in which it has to work. For example —

- (i) Normal glass for visual range
- (ii) Quartz for ultra violet region
- (iii) Alkali halides for infra red region are used.

In modern monochromators, two dispersing components are present. They may be

- (i) two prisms or
- (ii) two gratings or
- (iii) one prism and one grating.

Slits

There are two types of slits —

- (i) entrance slit
- (ii) exit slit

The main function of the entrance slit is to provide a narrow source of light so that there should be no overlapping of monochromatic images. From this, the exit slit selects a narrow band of dispersed spectrum for observation by the detector. The usual practice is that both entrance and exit slits have equal width. Under such conditions the width of a monochromatic image of the entrance slit is such that it will just be passed by the exit slit.

Gratings

Generally gratings are difficult to be prepared. Hence, replica gratings are prepared from an original grating. This is done by coating the original grating with a film of an epoxy resin which after setting is removed to yield replica. Then, replica is made reflective by aluminizing its surface. Replica gratings are cheaper than prisms. But the main defect of the gratings is that they produce more than one order of diffraction. Such defects can be removed by employing filters in front of the entrance slit to absorb interfering radiations. However, one may use two gratings to eliminate stray light.

Cell

The cell holding the sample (usually a solution) should be transparent to the wave length region being recorded. For visible region, they are generally made of colour corrected fused glass. The thickness of the cell is generally 1 cm (internal distance). Cells may be rectangular or cylindrical in shape or cylindrical with flat ends. The cell made up of quartz is employed for ultra violet region.

Detection of radiation

In order to detect radiations, three types of photosensitive devices are used. They are —

- (i) photovoltaic cells (barrier layer cells)
- (ii) phototubes (photo emissive tubes)
- (iii) photomultiplier tubes.

We shall discuss these types one by one.

Photovoltaic cell

This cell is also known as barrier layer or photonic cell. This cell operates without the use of the battery. It consists of a metal base plate like iron or aluminium which acts as one electrode. On its surface, a thin layer of a semiconductor like selenium is deposited. Then the surface of the selenium is covered by a very thin layer of silver or gold which acts as a second collector electrode.

When the radiation is incident on the surface of the selenium, electrons are generated at the selenium silver interface. These electrons are collected by the silver. The accumulation of electrons on the silver surface creates an electric voltage difference between the silver surface and the base of the cell and if the external circuit has a low resistance, a photo current will flow which is directly proportional to the intensity of the incident radiation beam. If this cell is connected to a galvanometer, a current will flow which will vary with the intensity of the incident light.

Photo tubes

These cells are also known as photo emissive cells. A variety of cells are available for the ultra violet and visible wave length regions.

A photo tube consists of an evacuated glass bulb. Inside the bulb, there is a light sensitive cathode in the form of a half cylinder of metal. The inner surface of cathode is coated with a light sensitive layer such as cesium or potassium oxide and silver oxide. A metal ring inserted near the centre of the bulb acts as an anode.

When radiation is incident upon the cathode, photo electrons are emitted. These are attracted and collected by an anode. Then, these are returned via the external circuit. Due to the flow of these electron, current is produced. This current may be amplified by electronic means. It is taken as a measure of the amount of light striking the photosensitive surface.

Phototubes are more sensitive than photovoltaic cells.

Photomultiplier tubes

The sensitivity of a photo emissive tubes can be increased considerably by employing the photomultiplier tubes.

A photomultiplier tube consists of an electrode covered with a photoemissive material. This tube also contains a large number of plates known as dynodes. Each dynode is covered with a material

which emits several electrons, for each electron striking on its surface. Also, each dynode is charged at a successively higher potential.

When the light radiation is incident upon the cathode surface, electrons are ejected. These are accelerated to the sensitive surface of the dynode where secondary electrons are emitted in greater number than initially striking the plate. These electrons in turn are accelerated to the surface of another dynode maintained at a higher potential where the number of electrons is again increased by a factor of 4 or 5. The process is repeated several times until a large number of electrons arrive at a collector. The number of electrons falling on the collector measures the intensity of light incident on the cathode surface. Most photomultiplier tubes have about 10 dynodes. Each dynode is maintained at 75 to 100 V more positive than the preceding dynode. By a photomultiplier tube, the over all amplification factor of about 10^6 can be achieved.

2) Theory of electronic transitions

As seen earlier, the ultra violet and visible radiations cause transitions of bonding electrons in elements. This electronic transition involves changes in rotational and vibrational levels also. This is called Born - Oppenheimer approximations.

$$\text{i.e; } E_{\text{total}} = E_{\text{ele}} + E_{\text{vib}} + E_{\text{rot}}$$

Hence, electronic spectra are complex, band spectra. Let the energy change involving electronic transition be ΔE and is given as,

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

$$\text{and frequency, } \nu = \frac{\Delta E_{\text{ele}} + \Delta E_{\text{vib}} + \Delta E_{\text{rot}}}{h}$$

Here, ΔE_{ele} = Energy change for electronic transition.

ΔE_{vib} = Energy change for vibrational transition.

ΔE_{rot} = Energy change for rotational transition.

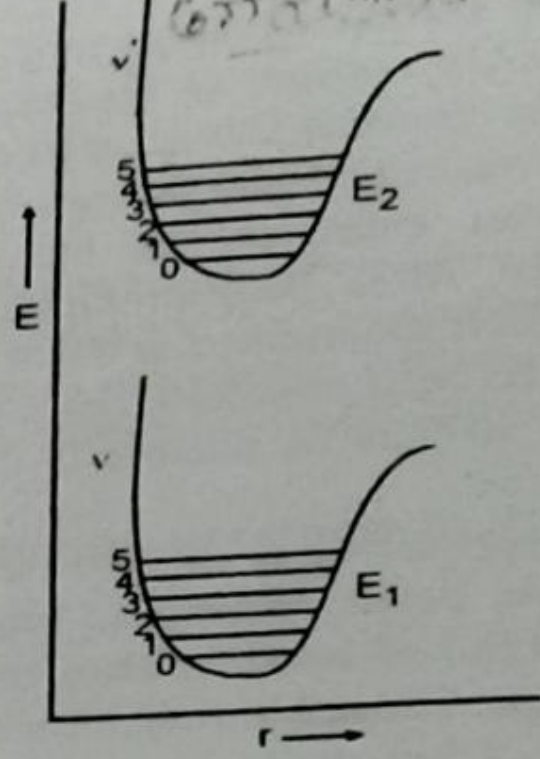
Though the electronic spectra are complex and band spectra, they are more important for the following reasons —

- (i) They appear in uv and visible region
- (ii) It can be photographed.
- (iii) Even non polar molecules like N_2 , H_2 give electronic spectra incorporating vibrational and rotational transitions.

(iv) Using electronic spectra, various parameters like moment of inertia (I), bond length (r_0), fundamental vibrational frequency (ν_0), force constant (k), dissociation energy (D) can be calculated.

Types of electronic transitions — *pre-dissociation energy*

In order to understand the types of electronic transitions of a diatomic molecule, it is important to know about the variation of potential energy with respect to internuclear distance in any two electronic transitions. This is shown in fig. 8.6.



In the figure—

- E = potential energy
- r = internuclear distance.
- E_1 = ground state of electronic level
- E_2 = excited state of electronic level
- ν = the vibrational levels in the ground state electronic level.
- ν' = the vibrational levels in the excited state electronic level.
- 0, 1, 2, ... = vibrational quantum numbers.

Fig. 8.6

The electronic transition from E_1 to E_2 is depend on the position of E_1 to position E_2 which is decided by the following three factors—

- (i) The transitions may involve $0, \pm 1, \pm 2, \dots$ and it need not be $\Delta \nu = \pm 1$ as in vibrational transitions.
- (ii) **Frank Condon principle** : During absorption of light, one electron is assumed to get excited. This excitation is very rapid. So, vibrating molecule does not change its internuclear distance during the transition.

This suggests the vertical transitions on potential energy diagram.

- (iii) The vibrational transition in the ground state electronic level commences at $\nu = 0$ and it can be end up with $\nu = 1, 2, \dots$ of excited electronic level. These have high probability. In other words, during electronic transition, there is no restriction on

the changes in the vibrational quantum number (ν). These are explained in the fig 8.7.

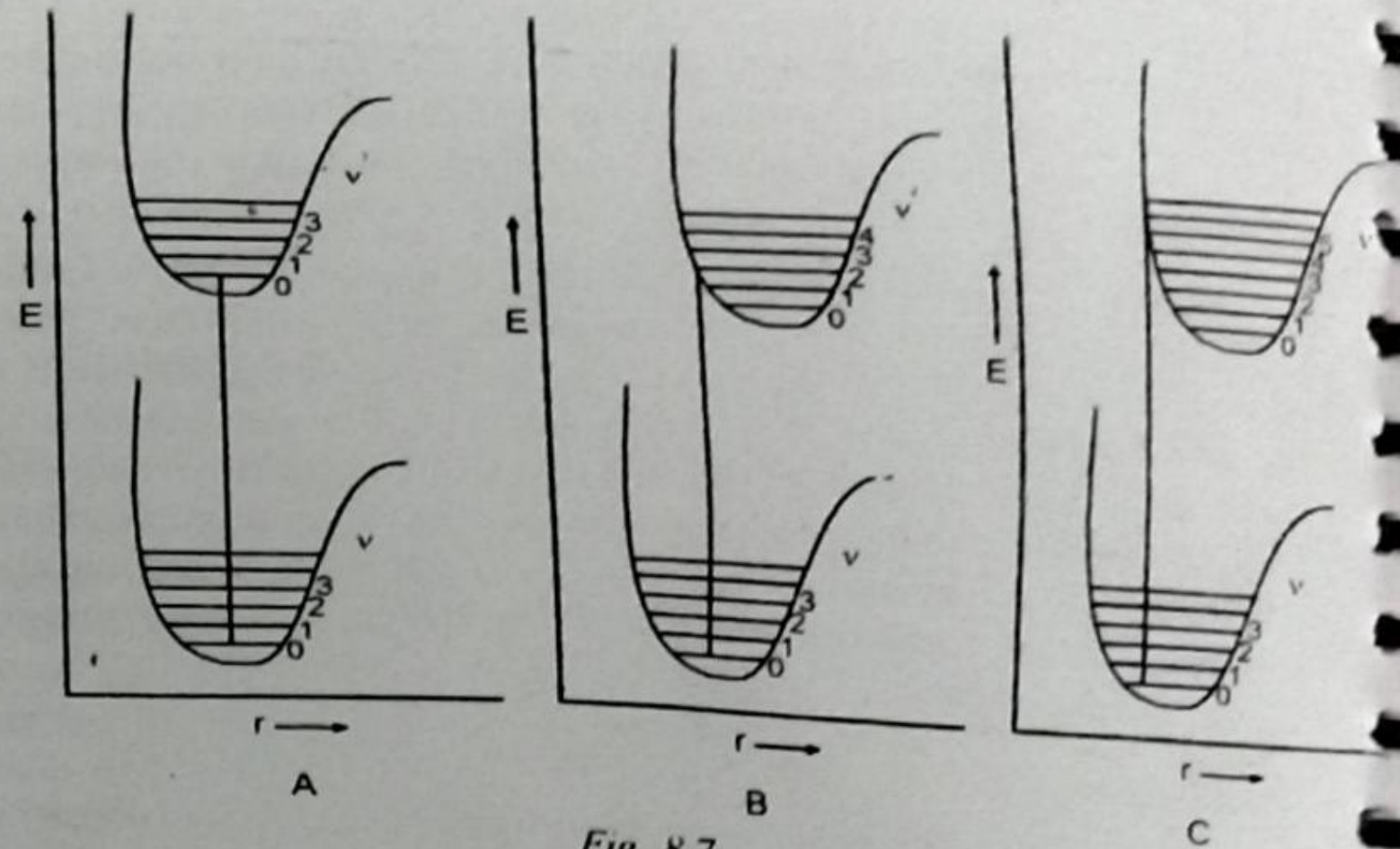


Fig. 8.7

1. Figure 8.7. A indicates the transition from $\nu = 0$ to $\nu' = 0$
 2. Figure 8.7 B shows the transition from $\nu = 0$ to $\nu' = 2$
 3. Figure 8.7 C exhibits the transition from $\nu = 0$ to $\nu' = \infty$.
- This indicates the dissociation of the molecule. All the three types of transitions occur in accordance with Frank Condon principle.

Let us explain the figure 8.7 B. There are two potential energy curves for it. One is for the ground state and the other is for the first excited state. In the excited state, the bonds existing in the molecule will be weaker than in the ground state. Hence, the potential energy minimum of the excited state will lie in the longer internuclear distance than in the ground state. According to quantum mechanics, the vibrational transitions of the

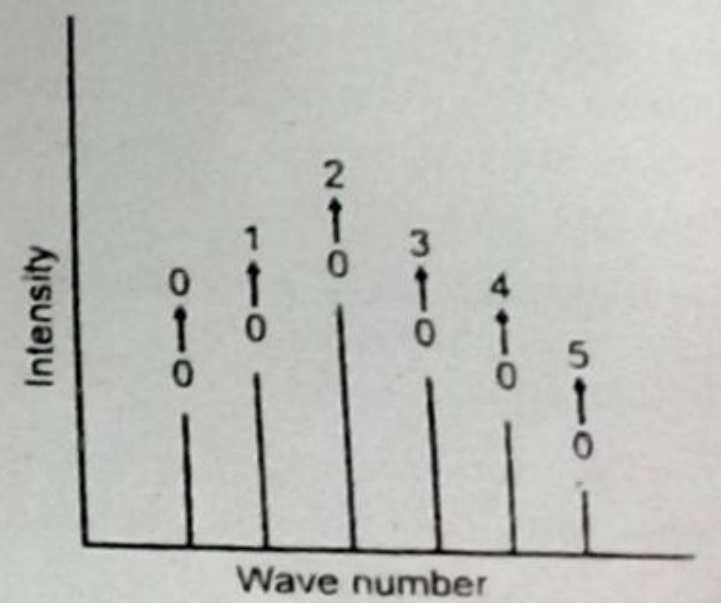


Fig. 8.8

ground electronic level will lie at the centre. When one photon energy is incident to the molecule at this stage, the highly probable transition from $\nu = 0$ $\nu' = 2$ will take place as per the Frank - Condon principle. All other transitions to other vibrational level of excited electronic level will take place with less probability. This is explained in the fig 8.8.)

Selection rule

- Electronic transitions between the same l values are forbidden. Only those transitions are allowed, when $\Delta l = \pm 1$. Here, l is the azimuthal quantum number.
- Electronic transitions between the states of same spin multiplicity are allowed.

Types of Electronic Transitions

The absorbing species may include transitions involving -

- σ , π and n (non - bonding) electrons.
- d and f electrons.
- Charge transfer electrons.

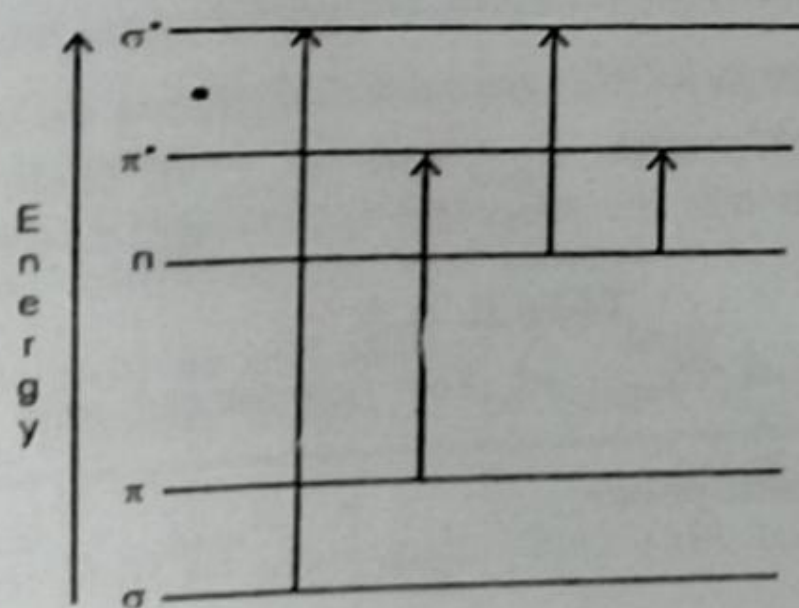
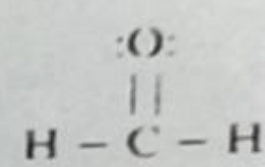


Fig. 8.9

- $\sigma - \sigma^*$ Transitions : Saturated hydrocarbons involve this type of transitions.
- $\pi - \pi^*$ Transitions : This corresponds to promotion of an electron from a bonding π orbital to an antibonding π^* orbital.
- $n - \sigma^*$ Transitions : Saturated compounds with lone pair of electrons show this type of transitions.

4. $n - \pi^*$ Transitions : Unsaturated molecules containing oxygen, nitrogen and sulphur show this type of transition. Formaldehyde (HCHO) serves as an example to explain all these transitions.



The transitions are given in the figure 8.9. From the figure, the energies required for the transitions are in the order.

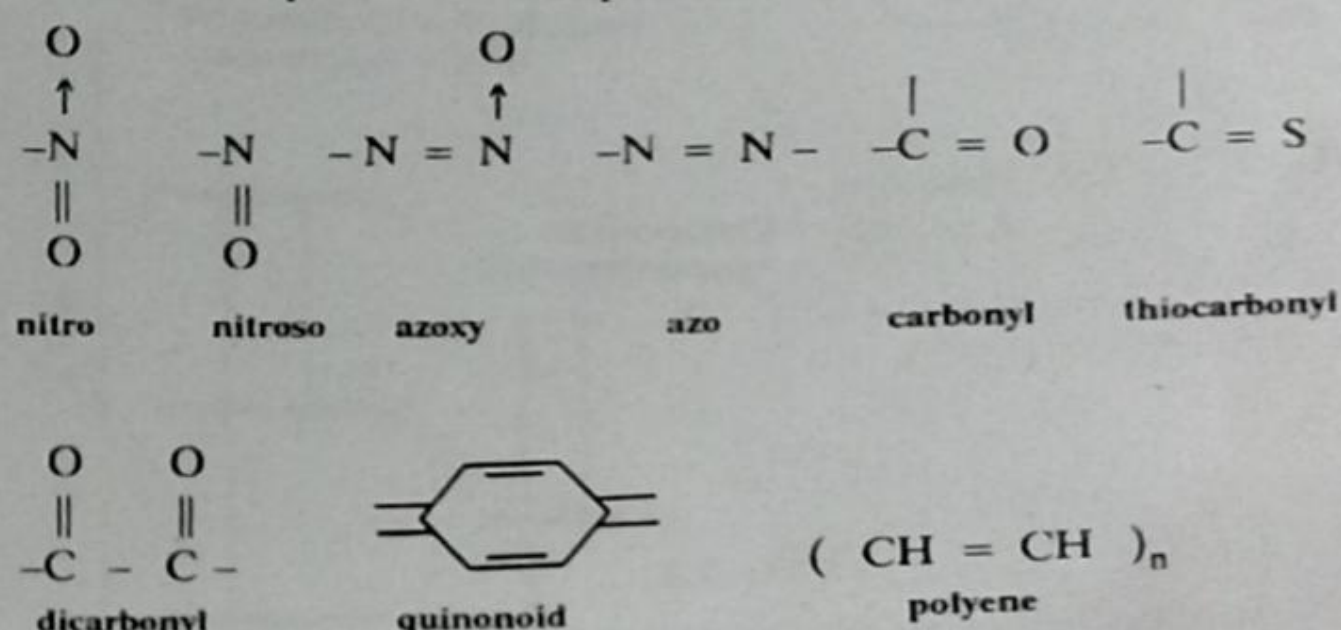
$$\sigma - \sigma^* > n - \sigma^* > \pi - \pi^* > n - \pi^*$$

Some Important Definitions

Chromophores

Colour usually appeared in an organic compound when it contained **unsaturated groups** which should more appropriately be called **groups with multiple bonds**. Otto Witt in 1876 called these groups with multiple bonds as Chromophores.

A few important chromophores are -



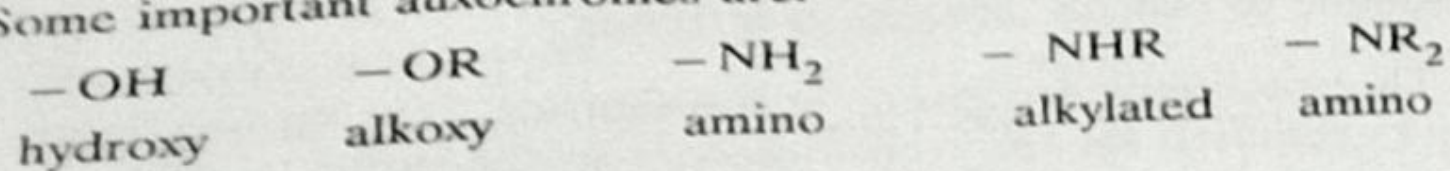
Chromogen : The compound containing the chromophoric group is called chromogen. It has been noticed that chromogens containing only one **chromophore** are usually yellow. Depth of the colour increases with the number of the chromophores.

A single $\text{C} = \text{C}$ group as in ethylene does not produce any colour. The colour, however, develops if a number of these groups are present in conjugation. For example, $\text{CH}_3(\text{CH} = \text{CH})_6\text{CH}_3$ is yellow in colour.

Auxochromes : Certain groups, which could not cause any colour effects in the absence of chromophore groups, do have an important

effect in colour when they are introduced into a compound containing a chromophore group. Witt described such groups as **auxochromes** or **colour augmenters** or **deepeners**.

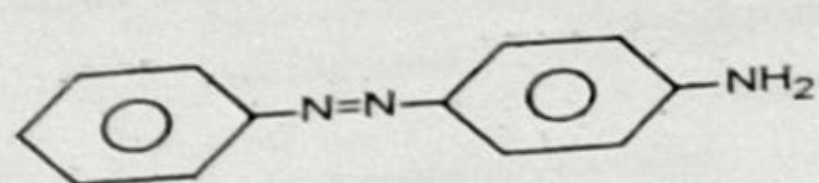
Some important auxochromes are.



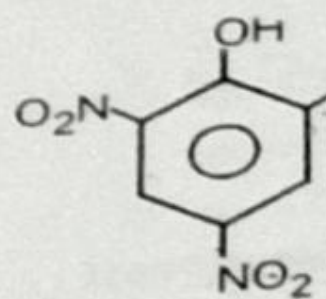
Auxochromes are salt forming groups and perform two functions -

- They deepen the colour of the chromogen
- Their presence is necessary to make the chromogen, a dye.

Examples



p-Aminoazobenzene
Here, N=N = Chromophore
NH₂ = Auxochrome



Picric Acid
Here, NO₂ = Chromophore
OH = Auxochrome

Table 8.2.

Differences between chromophore and auxochrome

S.No.	Chromophore	Auxochrome
1.	This group is responsible for the colour in the molecule.	This does not impart colour to the molecule but increases the colour of the chromophore.
2.	Does not form salt.	Forms salt
3.	It contains at least one multiple bond.	It contains lone pairs of electrons.

4.	Eg: -NO ₂ , -NO, -N=N-, -CO 	-OH, -OR, -NH ₂ , -NHR, -NR ₂
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λ_{\max} and intensity of absorption bands

Each molecules depending upon its nature and structure, absorbs at different wave length of electromagnetic radiation. The wave length at which the absorption is maximum is called λ_{\max} . The intensity of absorption bands at λ_{\max} is given by ϵ_{\max} which is calculated using -

$$\epsilon = \frac{A}{Cx} = \frac{\log \frac{I_0}{I}}{Cx}$$

Here, $\log \frac{I_0}{I} = A =$ absorption of the solution.

C = concentration of the solution.

x = path length or thickness of cell in cm.

I_0 = intensity of incident radiation.


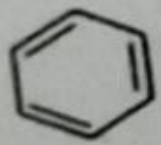
I = intensity of the transmitted ray.

Using the above formula, λ_{\max} and ϵ_{\max} of some chromophores of organic compounds are given in the following table 8.3.

TABLE 8.3.

λ_{\max} and ϵ_{\max} of few chromophores

S.No.	Chromophore	λ_{\max} (nm)	$\epsilon_{\max} \times 10^{-2}$ (m ² mol ⁻¹)
1.	-C=C-	170	16000
2.	-C=C-C=C-	220	21000
3.	-C=C-C=C-C=C-	260	35000
4.	-C≡C-	170	10000
5.	 -C=O	166 280	18000 15

6.	$\begin{array}{c} \\ -C=N- \end{array}$	190	5
7.	$-C=C-C=O$	240 320	10000 30
8.	$-C=C-C=C-C=O$	270 350	15000 100
9.		245 435	20000 150
10.		184 204	60000 7400

Note: It can be noted in the above table, there are more than one λ_{\max} (ϵ_{\max}) for few compounds. The first λ_{\max} corresponds to $\pi - \pi^*$ transition and the other may correspond to $n - \pi^*$ transition. The ϵ_{\max} for the latter is very low.

The λ_{\max} of an absorption may be shifted to higher or lower wave length for various reasons. Similarly, the value of ϵ_{\max} may become higher or lower. Previously, these shifts and effects have been designated in the following way and now they are no more in use.

1. **Bathochromic shift or red shift**: A shift of an absorption maximum, λ_{\max} towards longer wave length is called bathochromic shift.

2. **Hypsochromic shift or blue shift** is a shift towards shorter wave length.

3. **Hyperchromic effect** is an effect leading to increased absorption intensity.

4. **Hypochromic effect** is an effect leading to decreased absorption intensity.

Factors which influence λ_{\max} and ϵ_{\max}

1. **Solvent Effect**: The following solvents are employed for electronic

Water, hexane, cyclohexane, methanol, ethanol, ether, methylene dichloride, chloroform.

When an electronic spectrum of a compound in different solvents is recorded, the λ_{\max} and ϵ_{\max} do vary considerably. The variations observed by changing the solvent of low polarity to high polarity are the following -

- Conjugated dienes and aromatic hydrocarbons do not exhibit much solvent effect.
- α, β unsaturated carbonyl compounds show two types of shifts. They are -
 - The band corresponding to $\pi - \pi^*$ transition shows red shift.
 - The band corresponding to $n - \pi^*$ transition exhibits blue shift.

This is explained in the following figure. 8.10.

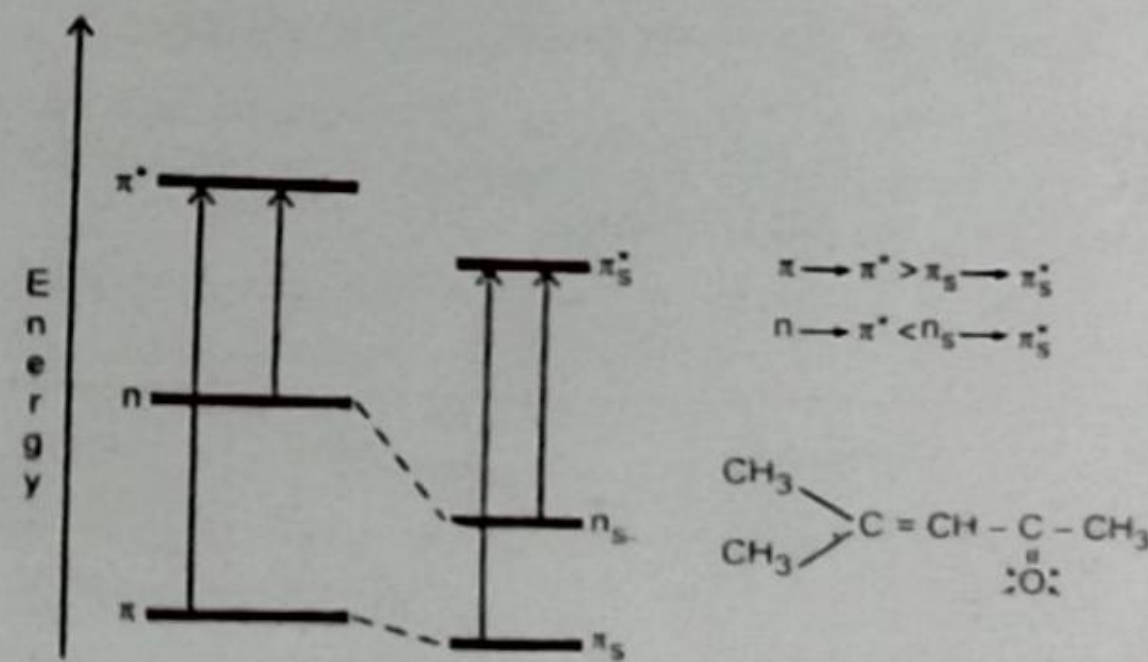


Fig. 8.10.

Explanation

- The solvents with low polarity stabilise the π , π^* and n orbitals.
- Water and ethanol which have hydrogen bondings stabilise n orbitals more.
- Due to the presence of solvent, π^* orbitals are more stabilised than π - orbitals. This may be due to the enhanced polarisation of π^* orbitals than π - orbitals.

(iv) The net result of solvent effect may be summarised in the following way –

- $\pi - \pi^*$ transition exhibits red shift.
- $n - \pi^*$ transition exhibits blue shift.

The above conclusions are drawn by the electronic spectral studies of mesityl oxide in various solvents as reported in the following table.

TABLE 8.4.

S.No.	Solvent	$\pi - \pi^*$ (nm)	$n - \pi^*$ (nm)
1.	n - hexane	230	327
2.	ether	230	326
3.	ethanol	✓ 237	315
4.	water	245	305

Note : Wave length is inversely proportional to energy, $\lambda \propto \frac{1}{E}$

2. Conjugation Effects : The λ_{\max} of the compound increase as we increase the conjugation in the compound. This fact can be easily deciphered from the following table.

TABLE 8.5.

S.No.	Compound	λ_{\max} (nm)	Number of conjugation.
1.	ethylene, $\text{CH}_2 = \text{CH}_2$	170	zero
2.	1,3 - butadiene, $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$	220	one
3.	trans - 1,3,5-hexatriene	260	two
4.	vitamin A ₁	325	five

Thus, the molecule with more than ten conjugated structures will have λ_{\max} at 450 nm. This is the reason for the yellow colour of polyene compounds. The orange of red colour of tomato and carrot is due to the presence of extended conjugated structures in them.

3. Substituent Effects : The λ_{\max} of aromatic compounds is affected by the substituents as below –

- When alkyl groups ($-\text{CH}_3$, $-\text{C}_2\text{H}_5$ etc.) are present, they shift λ_{\max} to the higher wave length (red shift)
- Groups having lone pair of electrons are substituted ($-\text{OH}$, $-\text{NH}_2$, $-\text{OR}$, $-\text{NHR}$, $-\text{NR}_2$), they also shift λ_{\max} to the higher wave length.
- When the availability of non bonding electrons varies, the position of λ_{\max} also varies. For example, when p - nitrophenol is reacted with sodium hydroxide, we obtain p - nitrophenolate ion which exhibits red shift. On the other hand, when amines are treated with acids, they show blue shift.

4. Stereochemistry factors : The structure of chromophores is much affected by (i) angular strain (ii) steric hindrance (iii) geometrical isomerism. Due to these, the extent of overlap of orbitals decreases. These also affect the extent of conjugation which are reflected in the λ_{\max} values. These are explained with biphenyl compounds and stilbenes.

a) Biphenyl compounds. The unsubstituted biphenyl does not possess planar structure because the benzene rings are present at 45° to each other. (fig A).

In the ortho substituted biphenyl compounds (Fig B), the angle between the two benzene rings increases which decreases the overlap of π - orbitals. This causes blue shift with low ϵ_{\max}

b) Stilbenes. If an alkene exhibits geometrical isomerism, the trans isomer (Fig - C, trans - stilbene) will absorb at higher wave length with high ϵ_{\max} than the cis-isomer (Fig - D, cis - stilbene). This is due to more π - orbital overlap in the trans compound than in cis compound.

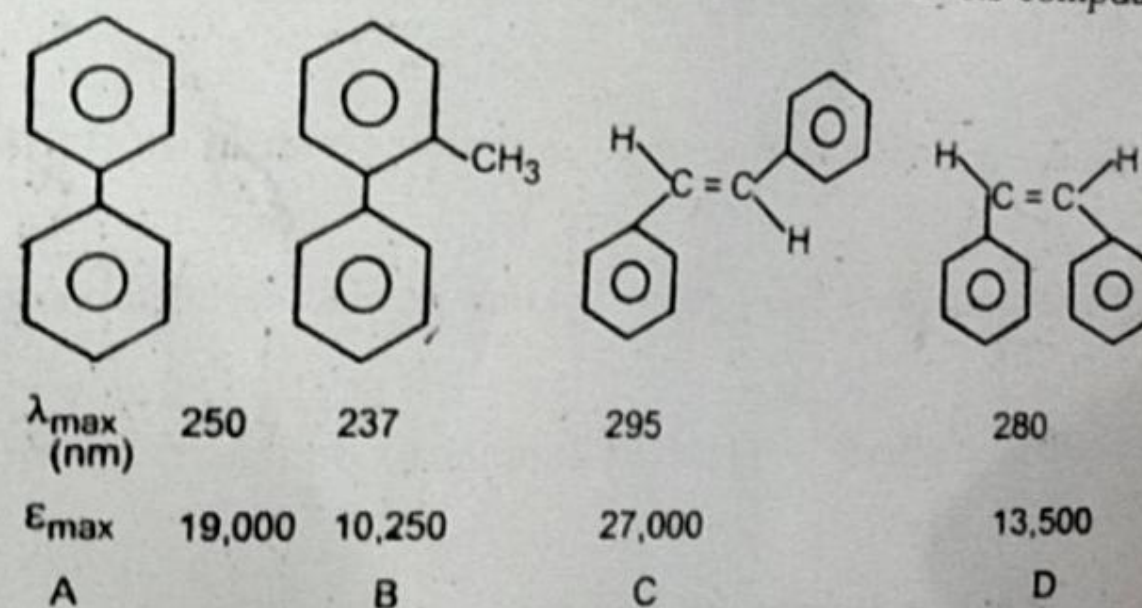


Fig.

Applications of uv - visible spectroscopy

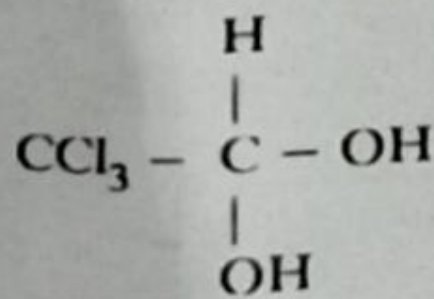
- 1) Electronic spectra are useful in the determination of the atomic groupings present in organic molecules. Few examples are given in the table 8.6.

Table 8.6.

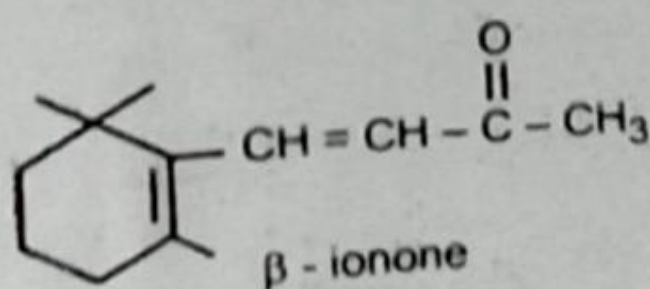
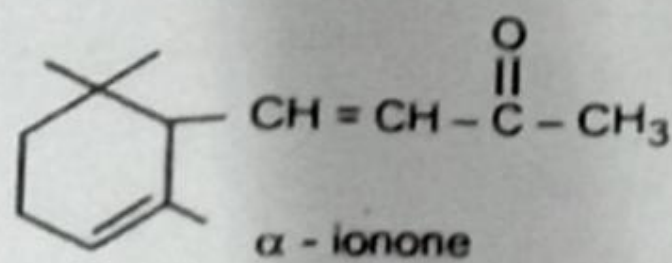
S.No.	Atomic group	Example.	λ_{\max} (Å)
1.	$\begin{array}{c} \diagdown \\ \text{C} = \text{C} \\ \diagup \end{array}$	$\text{CH}_2 = \text{CH}_2$	1710
2.	$\begin{array}{c} \\ -\text{C} = \text{O} \end{array}$	$\text{CH}_3 - \text{CH} = \text{O}$	1600, 1800, 2900
3.	$-\text{NO}_2$	$\text{CH}_3 - \text{NO}_2$	2010, 2740

- 2) UV - Visible spectrum is useful to confirm structures.

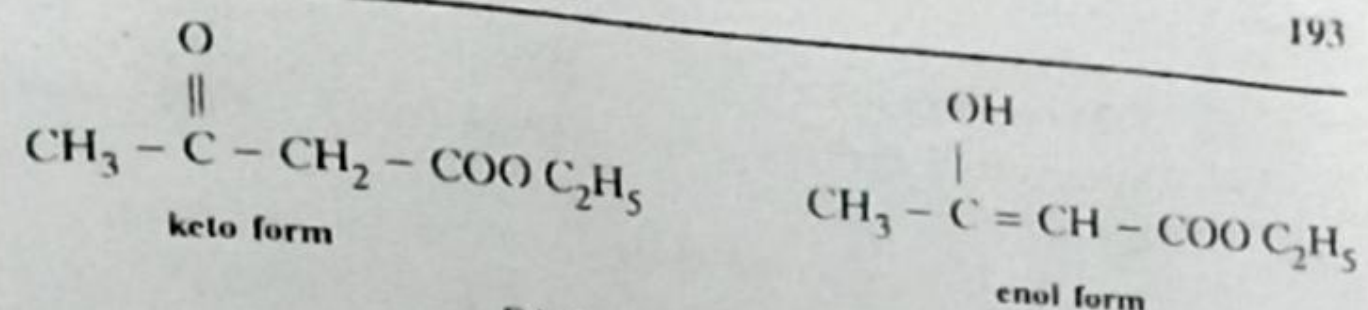
a) Chloral hydrate shows expected carbonyl band at 2900 Å but no such band is found in aqueous solution. Hence, its structure is



b) α - ionone shows a peak at 2280 Å indicating only two conjugated bonds. β - ionone has a band at 2960 Å showing a larger conjugated system.



- 3) The percentage of various keto - enol forms present can be determined from their electronic spectra.



Ethyl aceto acetate (EAA)

The keto form of EAA has λ_{\max} at 2750 Å where as the enol form has λ_{\max} at 2440 Å. From the band intensity, concentrations of tautomeric forms can be calculated.

- 4) The impurities in organic compounds can be detected using electronic spectra. The bands due to impurities are very intense. Hence, purification is carried out until there is no absorption band due to impurities. For example, cyclohexane will contain benzene as impurity. Benzene absorbs at 2550 Å.
- 5) UV - visible spectroscopy can be used to study the kinetics of a reaction. Concentration of either reactant or product changes with time. We know that absorbance is directly proportional to the concentration. Hence, absorbance is measured at different intervals of time. From the data obtained, the kinetics of the reaction is studied.)

QUESTION BANK

- 1) Explain: a) emission spectrum b) absorption spectrum.
- 2) Distinguish between atomic spectra and molecular spectra.
- 3) What are quanta and Einstein?
- 4) Explain the symbols ν , λ , c and $\bar{\nu}$
- 5) Write the relationship existing among ν , $\bar{\nu}$, c and λ .
- 6) Write the S.I unit for λ , c .
- 7) Describe the different type of molecular energies.
- 8) Why molecular spectra are called band spectra?
- 9) Explain the different molecular spectra.
- 10) State and explain Grotthus - Draper law.
- 11) Explain fluorescence.
- 12) State a) Lambert's law b) Beer's law
- 13) Explain the method of testing Beer's law.
- 14) Mention few factors responsible for the deviation of Beer's law.
- 15) Explain the various terms used in absorption spectra.