d) Most of the organic molecules except free radicals are in triplet state

8.8 SUMMARY

In this unit you had studied that in the presence of ligands, the five fold degeneracy of d orbitals of a metal ion is removed. By absorption of energy in the visible region of spectra, the electrons can undergo d–d transitions. The origin of colours of transition metal complexes can be explained in the light of d–d and charge transfer electronic transitions and the crystal field theory. You have also studied various processes by which de-activation of an electronic state takes placed.

8.9 TERMINAL QUESTIONS

1. The e_g orbitals are higher in energy than the t_{2g} orbitals in octahedral environment but the order is reversed in tetrahedral arrangement. Explain.

2. Give the absorption spectrum of $Ti_2(SO_4)_3$ and explain the type of electronic transition taking place.

3. HgS, $KMnO_4$ and K_2CrO_4 — all are intensely coloured, though there is no possibility of d–d transitions in them. Explain.

8.10 ANSWERS

Self Assessment Questions

1. a) i) T   ii) T   iii) T   iv) F

   b) i) reverse   ii) centre of symmetry

   iii) octahedral   iv) polarizability   v) point

2. In charge-transfer spectra, the greater the reducing power of the ligand, the lower is the energy at which the charge transfer band occurs. As Br^- ion has a greater reducing power than the Cl^- ion, the charge-transfer bands occur at 36,000 cm^{-1} and 44,000 cm^{-1} in the spectra of $[PtBr_4]^{2-}$ and $[PtCl_4]^{2-}$, respectively.

3. a) T   b) T   c) T   d) F

Terminal Questions

1. See Section 8.3

2. See Section 8.3

3. The intense colours of HgS, $KMnO_4$ and K_2CrO_4 are due to charge-transfer transitions as there is no possibility of d–d transition in any of them. The red colour of HgS is due to the transition $S^{2-}(n) \rightarrow Hg(6s)$ i.e., due to the transfer of lone pair electrons of sulphide ion to the empty $6s$ orbital of the mercury (II) ion. The intense colours of $KMnO_4$ and K_2CrO_4 are due to the transfer of lone pair electrons on O^{2-} ion to the empty t_{2g} orbitals on Mn^{7+} and Cr^{6+} ions. You should note that Mn^{7+} and Cr^{6+} are examples of d^0 ions, whereas Hg^{2+} has a d^{10} configuration.

UNIT 9 OPTICAL SPECTROSCOPY: INSTRUMENTATION AND SAMPLING

Structure

9.1 INTRODUCTION

In the earlier units on different kinds of spectra namely — rotational, vibrational, electronic and Raman — we have looked into the origin of a particular spectra and the information it can give us about the molecular structure. However, we had not discussed how these spectra are experimentally obtained. Since there is a lot of similarity in the experimental techniques in obtaining different kinds of spectra, we shall learn them in this unit. At the same time each one of them differs in detail from the other and hence they have been treated separately in different sections. You would notice that nmr, esr and mass spectra have not been included here since their experimental techniques are quite different from the ones discussed in this unit. Hence the experimental techniques associated with nmr, esr and mass spectra are included in their respective units. The spectrum of a sample is recorded with the help of an instrument called spectrometer or spectrophotometer. A spectrometer generally records some function of radiant power (e.g. percent absorption or transmission) transmitted through the sample at different wave lengths in the given region. A spectrophotometer gives us the ratio of the radiant power of two electromagnetic beams. Since the absorption spectrum is much more intense than the emission spectrum, we generally record the absorption spectrum of a sample. In this unit, we shall deal with absorption spectrometers used in different regions of spectrum.

Objectives

After studying this unit, you should be able to:

- describe the different components of various spectrophotometers,
- explain the various terms like signal to noise ratio, resolving power etc. associated with spectrometers,
- describe the various sampling techniques,
- correlate slit-width with resolving power,
- differentiate between single beam and double beam spectrometers, and
- draw a block diagram of a spectrometer.

9.2 SPECTROSCOPIC COMPONENTS

In this section, we shall discuss the main features of spectrometers, followed by the differences in components as per requirements of the various regions of a spectrum. First of all, we need a suitable source of electromagnetic radiation which must provide a continuous and sufficient radiant energy over the whole region of spectrum under study. Its intensity must also not change during the time when spectrum is being recorded. For different regions of spectrum, we would, naturally, need different sources of radiation and these have been discussed in Sub-section 9.2.1.

Next we shall require some optical devices to guide the radiations on to the sample and to the detector. These include slits, lenses, mirrors, prisms/gratings, monochromators etc. Since monochromators are common to all types of spectrometers, we shall discuss them in Sub-section 9.2.2. Other optical parts are discussed at suitable places simply because the optical set up requirements may be different for different instruments. The sample itself could be in gaseous, liquid or solid state and hence, different sample handling techniques are required. These techniques have been discussed separately in Section 9.3.

Finally, after the radiations have passed through the sample, we detect and record them with the help of detectors. These have been discussed in Sub-section 9.2.3. The detectors are in turn connected to amplifiers and a recorder to produce a plot of absorbance or transmittance as the wavelength or frequency varies. The function of a detector is to convert the radiation falling on it to electrical current which is amplified by the recorder. We can sumup the above information in a block diagram given below (Fig. 9.1.).
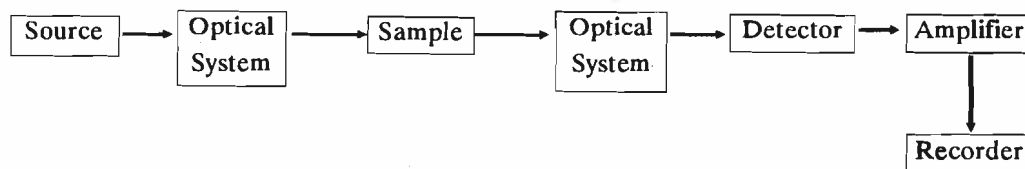

Fig. 9.1 : Block diagram of a spectrometer.

9.2.1 Sources

As stated earlier the source should produce continuous and steady radiations in given region of spectrum. It should also not contain any strong emission lines. Keeping these factors in mind, the following sources have been found useful and are commonly used for different regions.

Microwave : Reflex Klystron valve is the main source of radiations in microwave region. It emits radiations of a narrow range of frequency and therefore, it does not require any monochromator. The frequency of the region is controlled by the voltage

applied to the Klystron valve. Thus by slowly changing the voltage, we can scan the whole region of the spectrum. The only difficulty with Klystron valve is that it emits radiations of very small frequency range. Microwaves cannot be directed by optical devices. On the other hand, the microwaves can be directed along a rectangular metal tube called a waveguide.

Infrared : The source for infrared region is usually a filament which is maintained at red or white heat by an electric current. The two most commonly used are known as Nernst glower and Globar filament. The Nernst glower is made of zirconium and yttrium (rare earths) oxides in the form of a hollow rod of approximately 2 mm in diameter and 30 mm in length. It is heated to about 2000°C when it furnishes maximum radiations at about 7000 cm^{-1}. The Globar filament is made of silicon carbide. It is heated to about 1500°C when it furnishes maximum radiation at about 5000 cm^{-1}. It produces less intense radiations than Nernst glower. However, the Globar filament is employed for working at higher wavelengths, the reason being that its radiant power output decreases more slowly than the Nernst glower.

Raman : The common exciting source of Raman spectrometers is a mercury discharge lamp. It gives a series of characteristic lines at 253.7, 365, 404.7, 435 8 and 546.1 nm. A single wavelength is used as a souce. The other wavelengths are cut off by the use of suitable filters. The most commonly used radiation corresponds to 435.8 nm. Since the intensity of Raman spectrum is proportional to the fourth power of the frequency of the exciting line, it is useful to employ high frequency. Too high a frequency may cause photodecomposition or may cause overlap of Raman shifts. Thus a line with optimum value is selected. More recently, however, laser sources have replaced the mercury discharge lamps which provide extreme monochromatic radiations of high intensity. The commonly employed helium-neon laser emits a strong line at 632.8 nm. Except for the high cost, it has all the other advantages like high intensity, monochromatic character and no filter is required. It has the added advantage that it can be used for coloured solutions and much smaller samples.

Ultraviolet and Visible Region: For work in ultraviolet region, a hydrogen discharge lamp is used. It can be used between 200 nm to 375 nm. The intensity of the lamp increases almost threefold by replacing hydrogen with deuterium. Other high intensity lamps are known but are not commonly used due to various difficulties.

For visible region, the common source is the tungsten filament incandescent lamp. It can be used between 350 to 800 nm region and is operated at a temperature of about 3000°C.

9.2.2 Monochromators

In order to restrict the band of wavelength passing through the sample, we require some optical devices known as monochromators. These monochromators consist of a dispersing device which splits the polychromatic beam into a spectrum. The two common devices used for this purpose are prisms and gratings, the only exception being microwave region, where waveguides are used. In addition to a prism or grating, the monochromator has two slits. One of the slits sharply defines the incoming beam. The other exit slit is placed after the dispersing medium and its function is to allow only a narrow beam of radiation to fall on the sample. Two important characteristics of a dispersing device are shown in Fig. 9.2. The nominal wavelength is the wavelength of band centre. The range of wavelengths between two points at which the transmittance is one half of the maximum transmittance is known as band pass width. It is essentially the width of the exit slit. The band pass width depends on the nature of the dispersing unit and the focal length of the monochromator. The band pass width also depends on the ruling of the grating and since it remains constant for a particular grating, the band pass width for a given slit remains constant throughout the spectrum in case of grating spectrometers. In prism spectrometers, the band pass width changes with wavelength

because the dispersion of the prism changes with the wavelength. We know from our previous knowledge that the dispersion of polychromatic radiation into a spectrum is caused due to the variation of refractive index with wavelength. Hence, the separation of two wavelengths depends upon the dispersion power of the prism material. The separation of wavelengths is not uniform throughout and the separation becomes smaller at higher wavelengths. Glass and quartz are used as prism materials for the visible spectrum; glass is preferred as prism since its dispersion power is three times than that of quartz. However, glass is not transparent in the ultraviolet region and hence quartz prisms are used for this region.
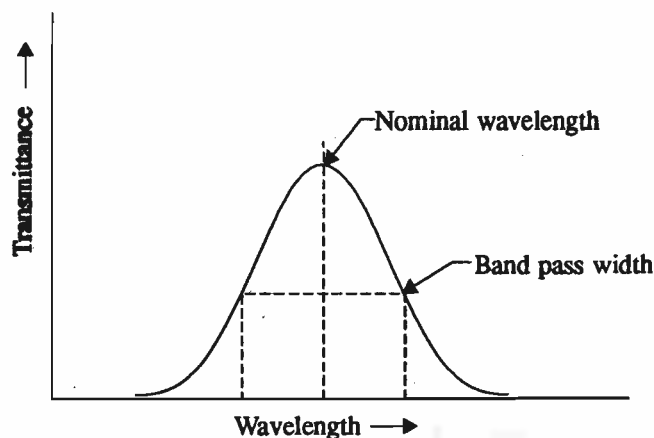

Fig. 9.2: Transmittance characteristics of a monochromator.

The dispersal of a polychromatic beam into a spectrum can also be achieved by means of a grating. A grating consists of a large number of parallel lines on a highly polished surface. Generally, there are about 600 lines per millimeter for ultraviolet and visible regions. Each ruled groove in a grating acts as a scattering centre for light rays and the light spreads out over a range of angles.

9.2.3 Detectors

It is quite obvious that different regions of spectrum would require different detector systems. In this section, we shall discuss the various detectors used for different regions of spectrum.

For microwave region, a quartz crystal is generally employed as a detector. It is mounted on a cartridge made up of a tungsten wisker held in point contact with the crystal. It detects the radiations focussed upon it and converts the microwave power to a direct current output. The signal it gives is amplified and fed to the recorder. It is quite sensitive and easy to use. Instead of quartz crystal, superhetrodyne radio receiver or silicon-tungsten crystal may also be used.

In case of Raman spectrum, especially when mercury arc lamp is used as a source, we must use extremely sensitive detectors. The detectors commonly employed for this purpose are either photomultiplier tubes or a photographic plate. A photomultiplier tube consists of a phototube and a series of electrodes known as diodes. A phototube is simply a glass bulb which is partially coated internally with a thin layer of photosensitive material such as potassium oxide or silver oxide leaving a small portion uncoated to permit the entry of light. The coated layer is attached to the negative end of a battery. A metal ring at the centre of the bulb is made the anode by joining it to the positive end of the battery. The whole bulb is evacuated. When light falls on the cathode, the photosensitive layer emits electrons which are attracted towards the anode and a current flows through the outside circuit.

As mentioned above, in a photomultiplier tube the emitted electrons are made to fall successively on a series of electrodes which are charged successively at higher

49

potentials. Each of these electrodes is covered with a material which emits several electrons for each electron that fall on its surface. The net effect is the amplification of the current many times.

In the case of infrared spectrometers, the detectors are generally of two kinds :
(i) Golay cell (ii) bolometer or thermocouple. Both of them are basically thermal detectors which give response at all the frequencies in the region.

Golay cell : When infrared radiations are allowed to fall on a gas enclosed in a small cell, it heats up the gas causing the change in pressure within the cell. These changes in pressure are recorded. This type of cell is bulky and expensive and hence less commonly used. Bolometers and Thermocouples on the other hand make use of photoconductivity phenomenon.

Bolometers: We know that the resistance of a metallic conductor changes with temperature. When infrared radiations fall on a thin metal conductor, its temperature changes which causes a corresponding change in its resistance. The changes in the resistance can be measured with the help of a Wheatstone bridge. The bolometer forms one arm of the bridge and the other balancing arm of the bridge consists of a similar metal strip but which is not exposed to the radiation. If no radiation falls on the bolometer, no current would flow and the bridge would remain balanced. However, when infrared radiations fall on the bolometer, a current would start flowing through the galvanometer due to change in the resistance. The current flowing through the galvanometer would then be directly proportional to the radiations falling on the bolometer.

Thermocouples: In a thermocouple, two wires of different semiconductor materials with high thermoelectric efficiency are joined together at the two ends. The infrared radiations are made to fall at one of the joints (hot junction), the other joint (cold junction) is kept at a constant temperature. This difference of temperature causes an electrical potential difference between the two joints. The potential difference would depend upon the amount of radiation falling on the hot junction and is thus a measure of the radiation.

The ultraviolet or visible spectrophotometers generally contain photomultiplier tube as a detector.

SAQ 1

Fill in the blanks in the following:

i)   Intensity of the discharge lamp increases by replacing hydrogen with ....

ii)   Tungsten filament lamp is used between .... and   .... nm for visible region.

iii)   In prism spectrometer, band pass width changes with ....

SAQ 2

What are the detectors for IR spectrometer ? Give their basic principle.

....

....

....

....

9.3   SAMPLE HANDLING TECHNIQUES

All the instruments would require some kind of a container to hold the sample. The first and the foremost characteristic of a container is that it should be transparent to

the region in which the spectrum is to be recorded. Secondly, when a spectrum of a sample in solution is to be recorded, the containers or the cells must be made of such a material which is inert to the solvent. The thickness of cell must be uniform. The surface facing the incident radiation must be flat. These are some of the other criteria which must be kept in mind. We shall now discuss various types of cells used for different regions of spectrum.

The Microwave Region

A rectangular tube of copper or silver known as waveguide is used to keep the sample for the microwave region. The tube is closed at both ends by thin mica windows. Holes are made in the tube for introduction of the sample as well as for evacuation of air. The beam direction can be fixed across the tube and hence the waveguide is made of metallic conductor with a rectangular shape.

The Infrared Region

Glass cells cannot be used for the infrared region, since the glass absorbs strongly at most of the frequencies in this region. NaCl and KBr are some of the salts which are transparent in this region of the spectrum. Hence, the cells are constructed from these salts. The NaCl cells are most commonly used for routine work in the region $4000\text{-}650^{-1}$. These are cheaper than KBr cells. Below 650 cm^{-1}, we must use KBr cells since NaCl absorbs in this region. Depending upon the phase – solid, liquid or gas – the sampling techniques change.

i) Sampling of Gases : The gas samples are contained in a cell approximately 10 cm long with sodium chloride windows at either end. It is kept across the path of infrared beam. These cells are used for gases at a pressure of 1 atm. or greater. For gases at low pressures specially designed cells are used. Since the area provided in the spectrometers is limited, the path length of the beam can be increased by repeated reflections within the cell by means of mirrors.

ii) Sampling of Liquids : For liquid samples, cells with fixed path lengths and variable path lengths are both commercially available. The liquid sample thickness should be between 0.01 to 0.05 mm which would give transmittance between 20-70 percent. The cells of this thickness are made of sodium chloride or potassium bromide rectangular plates sealed by gaskets and clamped together. A drop of liquid is pressed between NaCl/KBr plates which are put in a cell holder and scanned. For solutions, two matched cells are generally employed, one of which contains the solution and the other is filled with pure solvent and scanned through a double beam spectrometer. However, it is difficult to obtain a fully matched pair of cells since the cell material is easily affected by moisture. Under these circumstances, a careful selection of solvents is made such that they are transparent in the desired region of spectrum. The influence of a particular solvent on the solute must be carefully examined before its use.

iii) Sampling of Solids : There are basically two different techniques for handling of a solid sample. One which is most commonly employed is known as **nujol mull technique.** In this case the sample is finely ground to a paste in a small amount of mineral oil (nujol) or hexachlorobutadiene. It forms a fine suspension or mull of the sample in the oil. The mull is pressed between two NaCl/KBr plates to give a thin film of the sample. The two plates are clamped in a holder with open windows on both sides and the whole assembly is kept in the path of the infrared beam. Two spectra of the sample are recorded separately, one with a nujol mull and the other with a hexachlorobutadiene mull. Though hexachlorobutadiene absorbs at a number of frequencies in the infrared region, it is transparent in all those regions where nujol absorbs. Hence, by the combined study of the two spectra, we can get all the frequencies at which the sample absorbs.

The second technique is known as **pellet technique.** In this case a small amount of sample is mixed and ground with about hundred times its weight of potassium bromide. The mixture is transferred to an evacuable die to remove the moisture and then a high pressure is applied to yield a transparent pellet. It is put in a suitable holder and the whole assembly is placed in the line of the infrared beam. The holder may be even a thick folded paper with open slits. A blank KBr pellet of almost the same dimensions is placed in the path of the beam. The results with this technique are not easily reproducible. The resolution, however, is better as compared with the nujol mull method.

Raman Spectra

The type of cell for Raman spectrum varies with the amount of sample used, and the intensity of the source. When the quantity of the sample is small, a **multitraversal** tube is used where the incident beam is allowed to undergo a series of reflections with the help of mirrors before it emerges from the tube. The sample cells are larger for gases as compared to the ones used for liquids.

The usual length of the cylindrical tube may be between 20-30 cm and the diameter 1 to 2 cm with flat ends. The source is usually a mercury discharge lamp. However, when the source is a laser beam, the sample holders are of much smaller capacity of about 1ml and are made of quartz.

U.V. and Visible Region

A good quality glass or quartz can transmit radiations down to 200 nm. Hence, for routine work in the uv and visible region, quartz cells are most commonly employed. Alkali fluorides and clacium fluoride are transparent upto about 100 nm and as such these are used for specific samples where the desired absorption occurs below 200 nm. The thickness of the cell is usually 1 cm and rectangular in shape. They are normally supplied as matched pair.

9.4   MICROWAVE SPECTROMETER

The microwave spectrometer is shown in the form of a block diagram in Fig. 9.3. As shown in the figure, the source of monochromatic radiations in the microwave region is a Klystron whose emission frequency can be varied over a range. Since the frequency depends upon the applied voltage, by varying the voltage we can scan the whole region of microwave spectrum. Moreover, we have already learnt that Klystron emits radiations of narrow frequency range and so we do not need a monochromator in this case.
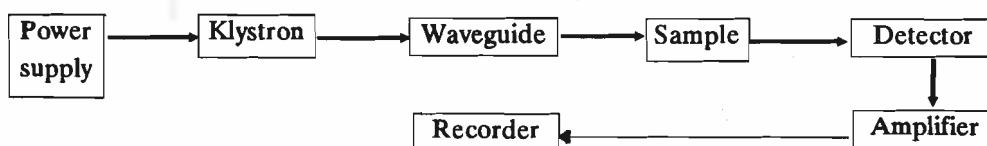

Fig. 9.3 : Block diagram of a microwave spectrometer.

The radiations are made to pass through a waveguide containing the sample in the gaseous state. After passing through the sample, the radiations fall on the detector. A quartz crystal acts as a detector which converts the radiations into electrical signals which are subsequently amplified. The amplified signal is connected to a pen-and-ink recorder. The functional details of various parts have already been discussed in previous sections.

9.5   INFRARED SPECTROMETER

There are two kinds of infrared spectrometers available: Single beam and double beam. A block diagram of the single beam spectrometer is given in Fig. 9.4.
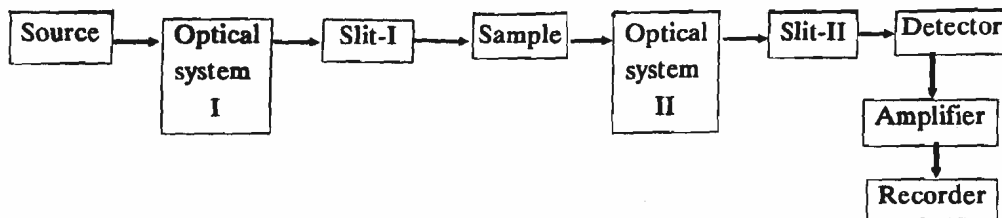
Fig. 9.4 : Block diagram of a single beam infrared spectrometer.

The optical system-I consists of a set of collimating mirror placed near the source. A parabolic mirror is used to produce parallel light rays. Slit-I regulates the amout of incident radiation reaching the sample. The radiations after passing through the sample are analyzed using optical system-II. Optical system II consists of a set of prism or grating, littron mirror and a spherical mirror. The spherical mirror is employed to focus the radiation on to the detector.

Knowing the original intensity and the intensity of radiation after passing through the sample as measured by the detector, you can find out how much radiation has been absorbed. Though the construction of a single beam spectrometer is cheaper and easier than a double beam spectrometer, it is associated with some inherent problems. First, since the intensity of emission of the radiation is not constant throughout the region of spectrum, it must be continuously balanced by varying the slit width which cannot be easily achieved. Secondly, water vapours and CO_2 present in the atmosphere also absorb in certain regions of the spectrum. This absorbance must be subtracted from the spectrum with the help of a blank-run. This 'back ground' spectrum must be repeated with each sample since the percentage of water vapours in the atmosphere is variable. Even this would not solve our problem if our sample shows characteristic absorbance at those frequencies where H_2O or CO_2 absorbs. Hence, these must be completely removed by some means before a spectrum is recorded. Again it cannot be done easily and completely. Finally if the spectrum of the sample is to be recorded in solution, it would show the absorbance peaks due to the solvent. All these problems are taken care of satisfactorily in a double beam spectrometer.

Littron Mirror: A plane mirror is placed behind the prism at a suitable angle. When a beam of light passes through the prism, it is reflected back by the mirror. Thus the beam passes through the prism two times thereby doubling the dispersion produced. It is known as double-pass system. We can improve the resolution further if the beam is returned one more time through the prism. This would make a total of four passes. It also reduces the scattered radiation to negligible amount.

An optical system is used to:
* select the proper frequency of radiation
* guide the radiation in the specified direction
* obtain a good spectrum

Double beam Spectrometer : In the double beam instrument, a plane mirror is placed in front of the source which splits the beam into two equivalent half beams. The two beams are focussed by separate concave mirror systems one passing through the sample while the other reference beam is left empty or allowed to pass through the solvent. A shutter-comb is placed in the path of the reference beam to reduce its intensity such that the two beams are again balanced. The two half beams after recombination with the help of mirror system reach the detector. The signal from the detector is amplified and fed to the recording system. The roles of prism (grating), littron mirror etc. remain the same as in the single beam instrument. Thus the spectrum recorded on the chart paper gives the relative transmittance of the sample.

SAQ 3

State the name of the instrument useful in studying the IR spectra in the solution phase.

9.6 RAMAN SPECTROMETER

A block diagram of a Raman spectrometer is shown in Fig. 9.5.
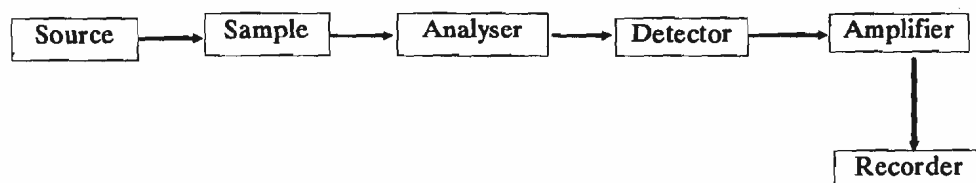

Fig. 9.5 : Block diagram of a Raman spectrometer.

The sample is irradiated with an intense beam of monochromatic light and the scattered radiations are collected at right angles to the incident beam. These are then passed on to the analyser, detector, amplifier and recorder sequentially. Raman intensities are approximately 0.01 percent of the incident light and therefore incident light must be very intense. This is achieved by surrounding the sample tube with four to eight tubular mercury arc lamps. These arcs generate a good amount of heat and hence the Raman tube is protected from the heat by means of a water jacket through which tap water is circulated. Selection of useful lines in the mercury arc lamp is done by placing suitable liquid filters between the source and the sample tube. A cross-sectional diagram of the whole set-up is shown in Fig. 9.6.
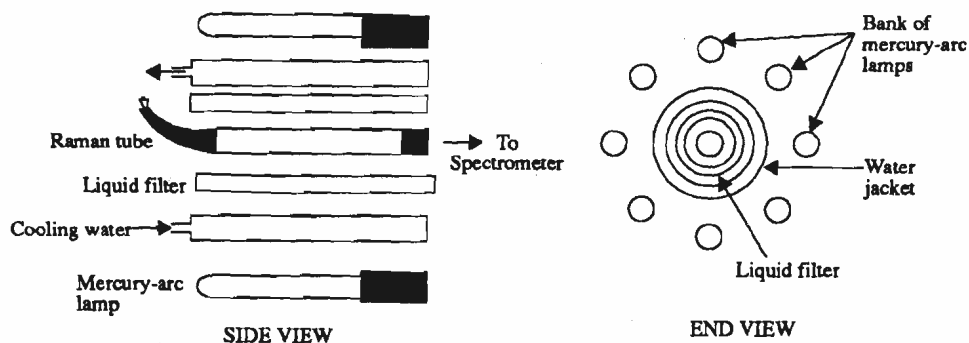

Fig. 9.6 : Arrangement of sample tube and Raman excitation source.

The introduction of laser source, which gives narrow, intense and monochromatic beam, has simplified the arrangement drastically. The laser beam is directly focussed on to the sample. The sample container in this case is a rectangular quartz tube approximately 2 cm in length and 0.5 cm^2 in cross-section with suitably located openings for transferring the solution.

The scattered light after passing through the sample is focussed at the front slit of the spectrometer with the help of two prisms and lenses. The beam from the entrance slit is allowed to fall on two monochromators with the help of spherical mirrors. The gratings are rotated linearly in wave numbers and the wave number setting is read on a counter. The beam then passes through an exit slit to a rotating mirror. The function of the rotating mirror is to direct the beam to two photomultiplier tubes alternately. This arrangement avoids the loss in energy. The signals from the two photomultiplier tubes are combined. Another reference phototube collects a portion of the exciting radiation through an alternative optical path. The two signals from the reference and the Raman beam are amplified and compared. The use of a double monochromator reduces the effect of scattering by dust particles in the sample.

SAQ 4

What is the function of the rotating mirror in Raman spectrometer ?

....

....

9.7 ELECTRONIC (VISIBLE AND ULTRAVIOLET) SPECTROMETER

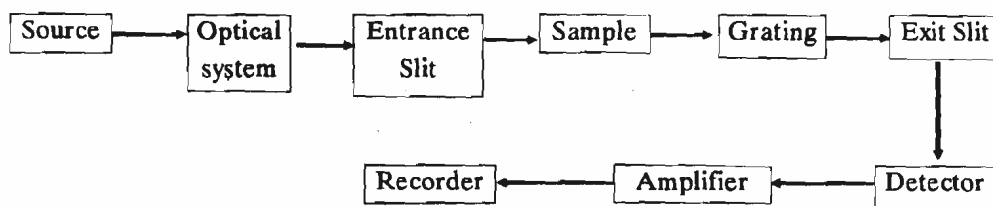The basic features of a single beam u.v. - visible spectrometer are shown in Fig. 9.7.

Fig. 9.7 : Schematic diagram of a visible and uv spectrometer.

The radiation from a suitable source is focussed on an entrance slit with the help of lens system. In the single beam spectrometer the beam passes through the sample and falls on a prism or grating which is mounted on a rotating table. After dispersion from the prism or grating, the radiation of the desired wavelength passes through the exit slit and on to a detector. The signal from the detector is amplified and fed to a recorder. In a double beam spectrometer. The beam is split into two equivalent half-beams with the help of lens systems. One part of the beam passes through the sample and the other through the reference cell which contains the solvent. Two parts of the beam emerging out from the sample and reference cells are focussed on to a detector which records the difference in transmittance of the two beams. The signal from the detector is fed into an amplifier. The amplifier commonly employed is a photomultiplier tube. The signal transmitted by the amplifier enters the recorder. The recorder consists of a pen and a chart paper whose movement is synchronised with the movement of the grating. Thus the chart paper plots a graph between the wavelength and absorbance (or transmittance).

The only difference between the u.v. and visible spectrophotometers lies in the choice of the radiation source. For visible region, we use tungsten filament lamp which is useful in the region of 350-800 nm. For ultraviolet region covering the range from 150 to 350 nm, a hydrogen lamp or deuterium lamp is used, which is basically a discharge tube containing hydrogen (or deuterium) gas under pressure. The pressure of the gas is kept high in order to obtain a continuous spectrum otherwise a line spectrum would be obtained. There are a number of other types of discharge tubes available in the market but the one described above is the most commonly used.

Thus we can record the spectrum from say 150 to 800 nm by the same spectrohotometer just by changing the source from hydrogen lamp to tungsten filament lamp. As stated earlier, the electronic spectra can be recorded either on a photographic plate or on a chart paper with the help of a photomultiplier tube as a detector. For any short lived species a photographic plate is more useful since it can record the whole spectrum in a fraction of a second. No detector can operate at such a fast speed. Even unstable species giving very weak signals can be recorded on a photographic plate by increasing the exposure time. These signals can be easily missed by a photomultiplier tube. However, the greatest disadvantage with the photographic plate is its limited resolving power besides being expensive.

Once the spectrum is recorded — which is basically a plot between absorbance (or transmittance) and the wavelength — it can be analysed to get useful information.

9.8 FLUORESCENCE AND PHOSPHORESCENCE SPECTROMETER

The instrument for measuring fluorescence are known as fluorimeters by the British and fluorometer by the Americans. They are further classified as filter fluorometers and fluorescence spectrometer. The difference between the two lies in the way the exciting radiations and the fluorescence (emission) radiations are selected.

The basic components of a filter fluorometer are shown in a block diagram form in the Fig. 9.8.
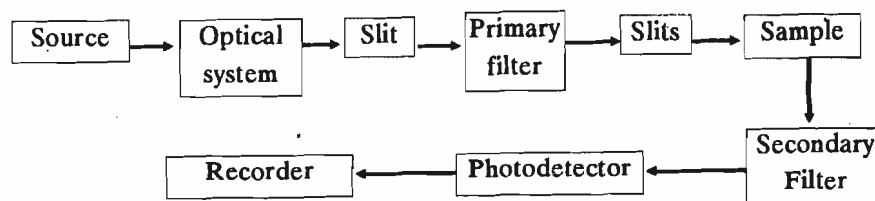

Fig.9.8: Block diagram of a fluorometer.

The source of excitation is usually a mercury discharge lamp. The principal lines of this occur at 366, 405, 436, 546 and 578 nm. We can select any of these exciting lines with the help of a primary filter. The beam after passing through the sample passes through a secondary filter and falls on the photocell placed at right angles to the incident beam in order that it may not be affected by primary radiation. Proper optical system and secondary filters are to be used to absorb the primary radiation and transmit the fluorescent radiation. The intensity of the fluorescence is measured with reference to some standard substance.

In the fluorescence spectrometer, we get rid of the filters by using two monochromators — usually gratings. Thus we can selectively utilise the wave-length of the exciting radiation as well as the fluorescence peaks. Further improvement is made by making use of a beam splitter. A portion of the beam is reflected directly to a monitoring photomultiplier tube and the other portion after passing through sample is detected by fluorescence photomultiplier tube in the usual fashion. The output from the two photomultiplier tubes are fed into a radiation recorder. Thus, we can obtain a true excitation spectrum.

Phosphorescence Spectrometer: Phosphorescence spectrometers are essentially very similar to fluorescence spectrometers. There are however, two basic differences. In order to minimize all the other degradation processes through collision except the phosphorescence transitions, we maintain the sample at liquid nitrogen temperature. Secondly, the substance under study may give both phosphorescence and fluorescence spectrum. Since we want to record only the phosphorescence spectrum, we introduce a device known as phosphoroscope. It introduces a delay between the time when the sample is irradiated and when the phosphorescence is observed. Two commonly employed phosphoroscopes are rotating disk or rotating drum type.

Rotating disk phosphoroscope consists of two slotted disks mounted on a shaft driven by a variable speed motor. The disks are so arranged that the openings in one are in line with the unslotted portion of the other. The sample is placed between the two disks. When the disks are rotated, the sample gets illuminated and then darkened. When it is dark, the phosphorescence passes through the second disk, and can be recorded in the usual manner. In the rotating drum phosphoroscope, the sample is surrounded by a hollow drum having equally spaced slits. The drum is rotated by a variable speed motor. When a slit is in line with exciting radiation, the sample is illuminated and then it gets darkened. The phosphorescence radiation passes through the other slit at right angles to the exciting radiation and then on to the monochromator. The common solvent used for the phosphorescence studies is a mixture of ethyl ether, isopentene and ethanol. At liquid nitrogen temperature, it forms a clear rigid glass.

9.9 SIGNAL TO NOISE RATIO AND RESOLVING POWER

The quality of spectrum would depend on the nature of the substance, type of spectrometer, and the sample handling technique. However, there are a couple of

things which if properly handled can yield better spectrum. These are discussed under the heading signal to noise (S/N) ratio and resolving power. As we shall see they are interrelated and indirectly controlled to a certain extent by the slit width of the monochromator.

S/N Ratio: It is a recognised fact that all electronic devices, whether it is a detector or an amplifier, produce fake electronic signals. These singals are non-uniform and random in nature. Such signals are called 'noise' and are inherent weakness of any electronic device. The main reason for the noise is not too difficult to understand. The electrons which are the signal (charge) carriers are not confined to narrow energy value of the signal but spread over a range of energy values due to thermal motion and hence the false signals.

If the noise of the instrument is low in comparison with the signal due to absorption of the sample, it does not interfere and we can neglect it. However, if the absorption due to the sample is very weak it would be lost in the noise of the instrument. Even with sensitive detectors, the signals can be identified easily only if their intensity is three or four times that of the noise.

Resolving Power: We have stated earlier that the electronic spectra never occur at a single frequency. It is always spread over a range of frequencies. Now if there are two absorption peaks very near to each other, we shall be recording the total abssorption due to the two peaks as the radiations pass across the slit. To a certain extent, we can resolve the two peaks if the width of the slit is narrowed but too much resolution will cause unnecessary noise superimposed upon the signal. On the other hand, too little resolution depresses the peak heights and the separation of the bands is less well defined. Obviously, we can operate only with an optimum band width.

The resolution of the bands is also determined by the scan speed, size and the dispersing characteristics of grating or prism, optical design of the instrument etc. We are not going to discuss these factors here.

9.10 SUMMARY

In this unit, we have studied the different sources of radiation and the detectors used for the various spectroscopic regions. We have also analysed the reasons for using different kinds of materials and their limitations. Sample handling techniques also vary in different regions of the spectrum and these have also been discussed briefly. Next, we discussed the working of spectrometers concentrating mainly on the variations in the optical systems of different regions. The role of monochromators and filters has also been indicated. We defined the terms, signal to noise ratio (S/N ratio), slit width and the resolving power. Throughout the text, we have emphasized the point that this discussion should give you a brief idea of instrumentation, so that you may not consider any instrument as a black magic box in which you insert your sample and out comes the result!

9.11 TERMINAL QUESTIONS

1) What do you understand by the term "band pass width" ?

2) What are the sources of radiation for the following spectrophotometers ?

   i) IR   ii) Raman   iii) UV

3) What is the function of Littron mirror in IR spectrophotometer ?

4) What are the differences between phosphorescence and fluorescence spectrometers ?

5) Draw block diagram of a spectrometer ?

9.12 ANSWERS

Self Assessment Questions

1. i) Deuterium
    ii) 350 nm; 800 nm
    iii) Wave length

2. Golay cell, bolometer and thermocouple are the detectors for IR
    spectrophotometer. Their basic principles are as follows:

    Golay Cell: Radiation heats up the gas, causing change in pressure within cell.
    These changes are recorded.

    Bolometer and thermocouple work by photoconductivity phenomenon.

3. Double beam spectrophotometer

4. The function of the rotating mirror is to direct the beam to two photomultiplier
    tubes alternately.

Terminal Questions

1) The range of wavelengths between two points at which the transmittance is one
    half of the maximum transmittance is known as band pass width.

2) i) Nernst glower and Globar filament

    ii) Mercury discharge lamp.

    iii) Hydrogen or deuterium discharge lamp.

3) It is used for improving the resolution.

4) Unlike fluorescence spectrometers, phosphorescence spectrometers make use
    of liquid nitrogen temperature and a device known as phosphoroscope.

5) Please see Fig. 9.1.

Further Reading

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