No amount of experimentation can prove me right, a single experiment may, at any time, prove me wrong.

..... Albert Einstein
INTRODUCTION

In order to study the spectral phenomena, one requires a device for separating electromagnetic radiation into its component frequencies. The form of the device naturally depends on the spectral region to be studied - ultra-violet, visible, infrared or microwave - as well as the nature of the phenomenon under investigation - absorption, reflection or emission.

A device which separates radiation into constituent frequencies and presents them for visual observation is called a spectroscope; if it also permits a measurement of frequency then it is called a spectrometer. If it gives the relative amount of energy associated with each wavelength, it is known as spectrophotometer. Generally these spectrophotometers consist of a source, wavelength selector, detector and recording system as chief components. In the case of emission
spectroscopy, the sample itself is the emitter of radiation and acts as a source. For the study of absorption or reflection properties, an arrangement is made for mounting and exposing the sample to the radiation from the source.

In this chapter, a general description of the UV-VIS-NIR and IR spectrophotometers and EPR & Mössbauer spectrometers is given along with their principles. The details of the specific instruments with their design and function, employed in the present investigation are described.

UV-VIS-NIR SPECTROPHOTOMETER

Spectrophotometers are sensitive instruments through which one can measure the intensities of the bands or spectral lines which correspond to the presence of a particular element or ion in the sample. Any spectrophotometer contains five components. They are:
1. a stable source of radiant energy;
2. a wavelength selector that permits the isolation of a restricted wavelength region;
3. a transparent container for holding the sample;
4. a radiation detector or transducer that converts radiant energy into electrical signal; and
5. a signal processor and readout system.

To get linear relation between optical signal and concentration, wavelength selectors are made by filters and monochromators. Filters are primarily used for visible radiation whereas monochromators are used for UV-VIS-NIR and IR regions also. In a monochromator, light is admitted through an entrance slit and is collimated with a lens or mirror. It is then dispersed by means of a prism or grating. Any portion of the resulting light can be focussed on an exit slit, again with a lens or mirror. Quartz or fused silica is required in UV (below 350 nm) region. These, as well as glasses can be employed in visible region and crystalline NaCl, CaF$_2$ and KBr are used as sample containers in infrared region. In the present investigation, to record the optical absorption spectra in UV-VIS-NIR region, Hitachi U-3400 Spectrophotometer is employed.
Hitachi U-3400 Spectrophotometer

This spectrophotometer is the well advanced computer controlled instrument with an accuracy of ±0.2 nm in UV-VIS region and 1 nm in NIR range. The optical alignment of the spectrophotometer is shown in Fig.2.1. Deuterium (D2) lamp is used as a source of radiation in UV-VIS region and iodine tungsten lamp (W1) is employed in NIR region.

The light from the source is reflected by the concave mirror M1 which is then chopped into regular pulses by the chopper CH. This beam passes through the slit S1 and is directed to the prism P by the toroidal mirror M2 and concave mirror M3. The dispersed light beam is focussed onto the second monochromator (S2) by the mirrors M3, M4 and M5. The light is then reflected onto the gratings G1 and G2 with the help of the concave mirror M6 which again gets reflected by M6 & M7 and passes through the rotating mirror M8 which splits the beam into two paths, one passes through the sample and the other through the reference in the sample compartment. These two beams are directed onto the detectors with the help of plane mirrors M12 & M13 and M14, M15 & M16 toroidal mirrors. The detectors, photomultiplier tube (R 928) {UV-VIS} and PbS {NIR} are used to measure the difference in intensities of the sample and the reference beams. The measured optical absorbance/transmittance intensity is plotted on the screen of the computer with respect to the wavelength and the spectrum is recorded with the help of the printer attached to the system.

INFRARED SPECTROPHOTOMETER

The block diagram delineating the essential components of a double beam spectrophotometer is given in Fig.2.2. This double beam system compares the radiant energy transmitted by the unknown sample to that transmitted through a known reference. The comparison of this infrared energy is made in the photometer. In order to determine the spectral variation of this comparison, the energy from the photometer is dispersed by the monochromator so that only a narrow spectral region is transmitted to the detector at any time. The amplifier operates on the signal from the detector so as to present the sample-to-reference comparison from the photometer on the ordinate of the recorder. The abscissa of the recorder is coupled
M1 Concave mirror
M2 Toroidal mirror
M3 Concave mirror
M4 Plane mirror
M5 Plane mirror
M6 Concave mirror
M7 Cylindrical mirror
M8 Rotating mirror
CH Mechanical chopper
M9 Cylindrical mirror
M10 Plane mirror
M11 Cylindrical mirror
M12 Plane mirror
M13 Plane mirror
M14 Toroidal mirror
M15 Toroidal mirror
M16 Toroidal mirror
P Prism

S1 1st monochromator slit
S2 2nd monochromator entrance slit
S3 2nd monochromator exit slit
PMT Detector for UV-VIS (R928)
PbS Detector for near infrared ray
G1 Plane grating 1440 lines/mm (190~850 nm)
G2 Plane grating 600 lines/mm (800~2600 nm)

Fig.2.1. HITACHI U-3400 UV-VIS-NIR spectrophotometer.
Fig. 2.2. Block diagram of a double beam IR spectrophotometer.
to the monochromator so that the recorder will plot this information as a function of wave number in the spectrum.

To record the IR spectrum of a solid sample, the KBr-pellet technique is now being employed widely. But normally the accuracy of this technique is very much less than that of solution technique because of the non-homogeneous distribution of the sample in the pellet. So, care is taken in the preparation of pellets. KBr is mixed with a small quantity of sample and they are ground together to maintain homogeneity. Then, from this, 300 mg is weighed and transferred into the die and the pellet is obtained by means of hydraulic press with a pressure of 50 kN (Fig.2.3).

The principle of IR spectrophotometer is similar to that of UV-VIS-NIR spectrophotometer. Here, the source, sample holder, detector and optical elements are made up of suitable materials to record the spectrum in the infrared region. In the present study Pye Unicam SP3-300 Infrared Spectrophotometer is used to record the spectrum.

Pye Unicam SP3-300 Infrared Spectrophotometer

This spectrophotometer is a double beam instrument operating in the infrared region of the electromagnetic spectrum. A simplified schematic diagram of the instrument is shown in Fig.2.4. As shown in the figure, there are three types of systems namely, (1) a radiation linkage indicated by dashed lines; (2) a mechanical linkage shown by broken solid lines; and (3) an electrical linkage shown by solid lines. Here, a thin bar of electrically conducting ceramic material is used as a radiation source. It is supplied with 15.5 VAC at 2.0 A from a secondary winding of the transformer in the electronic unit and its operating temperature is in the region of 1223 K. The mounting for cells and other sample accessories has three positions for optimization of sample efficiency. The cells are made up of rock salt.

The detector is a Mullard l-alanine doped triglycine sulphate detector, the element of which is protected by caesium iodide window. The window is coated with a non-hygroscopic material which provides protection from fogging by atmospheric humidity. This instrument gives an accuracy of ±4 cm\(^{-1}\) in the region 4000 to 2000 cm\(^{-1}\) and ±2 cm\(^{-1}\) in the region 2000 to 200 cm\(^{-1}\).
Fig. 2.3. Hydraulic press.
Fig. 2.4. Schematic diagram of a Pye Unicam SP2-300 infrared spectrophotometer.
MÖSSBAUER SPECTROMETER

General Features of Mössbauer Spectrometer

In comparison to many spectroscopic experiments, the basic Mössbauer equipment is rather simple and inexpensive. The block diagram of a typical Mössbauer spectrometer is shown in Fig.2.5. It consists of a radio active source such as $^{57}$Co to emit low energy Mössbauer $\gamma$-rays, a $\gamma$-ray detector associated with amplifying and sorting equipment and a multichannel analyser as data storing device.

The Mössbauer spectrum is a record of the transmission of resonant $\gamma$-rays through an absorber as a function of the Doppler velocity with respect to the source. A cyclic movement is imposed on the source to give a small range of photon energies by deliberate use of the Doppler effect.

The amplitude of movement of the source should be small compared with the distance between the source and the absorber. The output from the detector which will respond only to the Mössbauer radiation, is fed to a recording device which is synchronized with the movement of the source. So the photons emitted during each small interval of time are detected and recorded in a particular channel of the recorder. Thus after a period of time, the recorder contains a spectrum of the number of photons reaching the detector, having passed through the absorber, as a function of the mean velocity of movement of the source in each of a large number of velocity intervals. The sample should be located fairly close to the source so that the probability of recording photons that have suffered a small angle Mössbauer scattering event is kept low. In the present study, the Mössbauer spectrometer supplied by ECIL, India was used. A brief description of the instrument is given below.

ECIL Mössbauer Spectrometer

In this instrument, $^{57}$Co in Ruthenium matrix with 10 mCi activity has been used as the source of gamma rays. The proportional counter filled with Krypton is used as the detector. This detector has a resolution of 13 to 16 percent for 14.4 keV gamma rays. The sample under study is finely ground and is sandwiched between the two aluminium foils of 2.5 cm diameter. This will act as an uniform
Fig. 2.5. Block diagram of a typical Mössbauer spectrometer.
absorber with randomly oriented crystallites. In the case of small amount of sample whose recovery is essential, a special perspex holder with two thin windows have been built. This absorber is placed between the source and the detector in a single axis using optical bench. The block diagram of ECIL spectrometer is shown in Fig.2.6.

This spectrometer consists of an electromechanical system for giving the Doppler motion, which can be operated in a constant acceleration mode having the range of velocities 0 to 90 mm s\(^{-1}\) in one cycle. Proportional counter is given a high potential difference of the order of 1800 V. A pre-amplifier is used for impedance matching besides the linear amplifier employed for the amplification of the pulse. The signals through the single channel analyser are fed to the multichannel analyser operating in time mode with 512 channels. The time for each channel to record the events is set at \(2 \times 10^4\) s. The stored counts are displayed on the screen. When sufficient data is stored the spectrum is recorded with the help of a printer. Hence, the output gives both the spectrum as well as the number of counts stored in each channel.

The calibration of Mössbauer spectrum is done by taking the spectrum of iron foil supplied by Radio Chemical Centre, Amersham, England as reference. The distance between the detector and the source is kept more than 15 cm to avoid solid angle effects.

**ESR SPECTROMETER**

The essential features of any ESR spectrometer are:

1. a source of microwave radiation of constant frequency and variable amplitude,
2. a sample cell and a means of transmitting the radiation energy to the sample cell,
3. a homogeneous but variable magnetic field,
4. a detection system, and
5. a recorder or an oscilloscope.

Most of the spectrometers employ radiation of frequency about 9000 MHz or 3 cm wavelength. This corresponds to the microwave X-band and the magnetic field needed for the samples with \(g = 2\) is about 3300 Gauss. The radiation source,
Fig. 2.6.  Schematic diagram of ECIL Mössbauer spectrometer.
wave guide, resonant cavity to place the sample under observation and the crystal
detector to detect the ESR signal are the main components and the block diagram of
the simplest form of ESR spectrometer is shown in Fig.2.7.

The purpose of the resonant cavity is to concentrate energy on to the sample
by multiple reflections of the travelling microwave from the two end walls. The
absorption of energy by the sample may be seen by direct observation of the current
in crystal detector while slowly varying the field. As the field approaches the value
corresponding to resonance, power is absorbed by the sample so that the power
transmitted through the cavity to the crystal detector is reduced. In the present study,
the EPR data was recorded in a polycrystalline form. A well powdered sample was
taken in an EPR quartz tube and the spectra were measured by inserting the tube
into the EPR cavity. As some of the samples contain iron as paramagnetic impurity,
all the spectra were recorded in quartz tubes, as iron is known to exist as an impurity
in glass tubes.

A standard sample, DPPH (Diphenyl picryl hydrazyl) with g value 2.0036
was used. From the resonance condition $h\nu = g\beta B$, and from the field position of
DPPH, the g value for the sample was calculated by using the formula,

$$g_{\text{sample}} = \frac{2.0036 \times B_{\text{DPPH}}}{B_{\text{sample}}}.$$

In the present study, Varian E-112 ESR Spectrometer operating at both
X- and Q-bands having a 100 kHz field modulation with phase sensitive detection
was used. The block diagram of E-112 ESR spectrometer is shown in Fig.2.8.

The E-112 EPR spectrometer consists of 1200 W field regulated power supply
for a 12 inch magnet. The magnetic field can be varied linearly from 0 to 6000 G by
adjusting the input to the power supply. The microwave source consists of a +640V
Klystron beam and -400V for the reflector both of which get the power from the
Klystron power supply. The workable frequency range is 8.8 to 9.6 GHz. The
microwave resonant cavity of rectangular shape operates in TE$_{102}$ mode. At the
resonance condition a signal was observed due to a change in the impedance of the
cavity. The first derivative spectrum is obtained by 100 kHz sweep generator which
provides a small modulation at the sample.

A 100 kHz signal detector, 100 kHz signal amplifier, oscilloscope and an X-Y
recorder forms the detection system. The central magnetic field for a sample can be
fixed at any desired position and the scan range can be varied in different steps.
Fig. 2.7. Block diagram of the simplest form of a ESR spectrometer.
Fig. 2.8. Block diagram of Varian E-112 EPR spectrometer.