CHAPTER – II

INSTRUMENTATION AND SAMPLE HANDLING
TECHNIQUES OF INFRARED AND
RAMAN SPECTROSCOPY

ABSTRACT

The experimental techniques of Fourier transform infrared and Raman spectrographs and techniques involved in handling the samples are briefly explained. Advantages of Fourier transform spectrometers are also discussed.
CHAPTER – II

INSTRUMENTATION AND SAMPLE HANDLING
TECHNIQUES OF INFRARED AND RAMAN SPECTROSCOPY

2.1 INTRODUCTION

The infrared (IR) and Raman spectroscopy generally yield similar types of information. IR and Raman spectroscopic techniques from it early beginning continues to be a complementary fertile research tool in the hands of physicists and chemists. Often it is necessary to use several instrumental techniques to obtain the information required to solve an analytical problem. Analytical instrumentation place an important role in the production and evaluation of new products. In recent years, Fourier transform (FT) spectroscopy techniques enjoy the advantages over the conventional IR and Raman spectroscopy due to the very intensive interest created by offering some unique features. The ultimate performance of any infrared spectrometer is determined by measuring its signal-to-noise ratio (SNR). This is best achieved by FT-IR spectrometers. The improved SNRs available with FT-IR make it to become the instrument of choice for obtaining IR spectra. Frequency precision, good spectral subtractions and high resolution are difficult to achieve with conventional Raman spectroscopy. Hence a new technique, in which the Raman module is an accessory to an FT-IR spectrometer, called FT-Raman spectroscopy. FT-IR and FT-Raman technique has been found to be useful in increasing the spectral sensitivity and thus yielding new information about the atomic or molecular species, or the functional group that exist in the sample.
Modern spectrometers are generally attached with sophisticated computers and high energy sources like lasers, which permit spectrum storage and retrieval, scale expansion, repetitive scanning, spectral comparison, spectral simulation, automatic control of slit etc. Often these are under the control of a microprocessor and microcomputers. Accessories such as beam condensers, reflectance units, polarizers and microcells can usually be added to extend versatility or accuracy. In this chapter the instrumentation and sample handling techniques of FT-IR and FT-Raman spectrometers are presented.

The IR and Raman spectroscopic techniques are based on different principles. The intensity of the infrared spectrum depends on the magnitude of the dipole moment change whereas the Raman intensity is dependent on the polarizability of the vibrating atom and their bonds. Hence the appearance of Raman band normally differs from the corresponding IR band. However the position the bands are usually in good agreement. The IR and Raman methods are used to study the materials existing in various states. The molecular vibrational frequencies obtained by these methods have been used in molecular mechanics and they yield considerable information about the interatomic forces in various molecules [56].

2.2 FOURIER TRANSFORM INFRARED SPECTROMETER

The discovery of the fast Fourier transform algorithm and the concurrent introduction of sophisticated computers permitted the new generation of infrared instrumentation called Fourier transform infrared spectrometer. The Fourier transform infrared spectrographs have replaced the conventional infrared spectrographs. A FT-IR spectrometer consists of two parts: (a) an optical system which uses an interferometer and (b) a dedicated computer which stores data, performs computations
on data and plots the spectra. A schematic diagram of the essential components of a
FT spectrometer based on Michelson interferometer is shown in Fig. 2.1. It consists of
two perpendicular mirrors; one of which is a stationary mirror and other a movable
mirror which can be displaced perpendicularly to the fixed mirror at a constant
velocity. Between these two mirrors the beam splitter is set at 45° from the initial
position of the movable mirror. A parallel beam of radiation from an infrared source
is passed to the mirrors through the beam splitter. The beam splitter reflects about half
of the beam to the fixed mirror which reflects it back to the beam splitter and
transmits the other half to the movable mirror which reflects it back to the beam
splitter. The returning beams are again split and mixed about half going back to
source and half passing through the sample compartment. The composition of the
beam splitter depends on the spectral region of interest. For example in the mid-
infrared region (4000–400 cm\(^{-1}\)), a beam splitter of germanium coated on KBr plate
(substrate) is often used. Germanium reflects the radiation while KBr transmits most
of the desirable radiation. In the far infrared region, germanium coated on CSI (800–
200 cm\(^{-1}\)) or germanium coated on Mylar (polyethylene terephthalate) (650–10 cm\(^{-1}\))
are used as beam splitters. A thin film of the beam splitter material is coated on an
optically flat substrate.

The return beams from both the mirrors along the same path length as their
incident path are recombined into a single beam at the beam splitter. The path length
of one of the return beams is changed in order to create phase difference to cause an
interference pattern. The recombined radiation is then directed through the sample and
focused on to the detector. The detector measures the amount of energy at discrete
intervals of mirror movement.
Fig. 2.1: Optical arrangements of Fourier Transform infrared spectrophotometer
The movable mirror can be moved in a range of say ± 5 cm. The mirror velocities from 5 to 0.05 cm\(^{-1}\) are used. Interferometer instruments need detectors with response times short enough to detect and transmit rapid changes to the recorder. The detector used in conjunction with rapid scanning interferometers in the mid-infrared region at room temperature is triglycine sulfate with KBr windows as pyroelectric bolometer. It has a high response time. Other most common detectors used such as thermocouples, bolometers and Golay detectors have short response time. The design of the Michelson interferometer is such as to make measurement in any infrared region possible by simply changing the beam splitter and the detector.

2.2.1 Instrumentation

(a) Introduction

The basic components of an infrared spectrometer are shown in Fig. 2.2. A source provides radiation over the entire range of the infrared spectrum. The monochromator disperses the light and then selects a narrow wave number range. The detector measures the energy and transforms it into an electric signal. This signal is further amplified and registered by the recorder.

With recent improvements in instrumentation, the infrared region of the electromagnetic spectrum is now considered to cover the range from approximately 12500 to 10 cm\(^{-1}\) (1000–0.8 µm). It is generally subdivided into three sections: near infrared (12500–4000 cm\(^{-1}\)), mid infrared region (4000–400 cm\(^{-1}\)) and the far infrared (400–10 cm\(^{-1}\)). The mid infrared region is the one of the most commonly used standard laboratory investigations as it covers almost all the vibrational and rotational
on data and plots the spectra. A schematic diagram of the essential components of a FT spectrometer based on Michelson interferometer is shown in Fig. 2.1. It consists of two perpendicular mirrors; one of which is a stationary mirror and other a movable mirror which can be displaced perpendicularly to the fixed mirror at a constant velocity. Between these two mirrors the beam splitter is set at 45° from the initial position of the movable mirror. A parallel beam of radiation from an infrared source is passed to the mirrors through the beam splitter. The beam splitter reflects about half of the beam to the fixed mirror which reflects it back to the beam splitter and transmits the other half to the movable mirror which reflects it back to the beam splitter. The returning beams are again split and mixed about half going back to source and half passing through the sample compartment. The composition of the beam splitter depends on the spectral region of interest. For example in the mid-infrared region (4000–400 cm\(^{-1}\)), a beam splitter of germanium coated on KBr plate (substrate) is often used. Germanium reflects the radiation while KBr transmits most of the desirable radiation. In the far infrared region, germanium coated on CSI (800–200 cm\(^{-1}\)) or germanium coated on Mylar (polyethylene terephthalete) (650–10 cm\(^{-1}\)) are used as beam splitters. A thin film of the beam splitter material is coated on an optically flat substrate.

The return beams from both the mirrors along the same path length as their incident path are recombined into a single beam at the beam splitter. The path length of one of the return beams is changed in order to create phase difference to cause an interference pattern. The recomined radiation is then directed through the sample and focused on to the detector. The detector measures the amount of energy at discrete intervals of mirror movement.
Modern spectrometers are generally attached with sophisticated computers and high energy sources like lasers, which permit spectrum storage and retrieval, scale expansion, repetitive scanning, spectral comparison, spectral simulation, automatic control of slit etc. Often these are under the control of a microprocessor and microcomputers. Accessories such as beam condensers, reflectance units, polarizers and microcells can usually be added to extend versatility or accuracy. In this chapter the instrumentation and sample handling techniques of FT-IR and FT-Raman spectrometers are presented.

The IR and Raman spectroscopic techniques are based on different principles. The intensity of the infrared spectrum depends on the magnitude of the dipole moment change where as the Raman intensity is dependent on the polarizability of the vibrating atom and their bonds. Hence the appearance of Raman band normally differs from the corresponding IR band. However the position the bands are usually in good agreement. The IR and Raman methods are used to study the materials existing in various states. The molecular vibrational frequencies obtained by these methods have been used in molecular mechanics and they yield considerable information about the interatomic forces in various molecules [56].

2.2 FOURIER TRANSFORM INFRARED SPECTROMETER

The discovery of the fast Fourier transform algorithm and the concurrent introduction of sophisticated computers permitted the new generation of infrared instrumentation called Fourier transform infrared spectrometer. The Fourier transform infrared spectrographs have replaced the conventional infrared spectrographs. A FT-IR spectrometer consists of two parts: (a) an optical system which uses an interferometer and (b) a dedicated computer which stores data, performs computations
on data and plots the spectra. A schematic diagram of the essential components of a FT spectrometer based on Michelson interferometer is shown in Fig. 2.1. It consists of two perpendicular mirrors; one of which is a stationary mirror and other a movable mirror which can be displaced perpendicularly to the fixed mirror at a constant velocity. Between these two mirrors the beam splitter is set at 45° from the initial position of the movable mirror. A parallel beam of radiation from an infrared source is passed to the mirrors through the beam splitter. The beam splitter reflects about half of the beam to the fixed mirror which reflects it back to the beam splitter and transmits the other half to the movable mirror which reflects it back to the beam splitter. The returning beams are again split and mixed about half going back to source and half passing through the sample compartment. The composition of the beam splitter depends on the spectral region of interest. For example in the mid-infrared region (4000–400 cm\(^{-1}\)), a beam splitter of germanium coated on KBr plate (substrate) is often used. Germanium reflects the radiation while KBr transmits most of the desirable radiation. In the far infrared region, germanium coated on CSI (800–200 cm\(^{-1}\)) or germanium coated on Mylar (polyethylene terephthalete) (650–10 cm\(^{-1}\)) are used as beam splitters. A thin film of the beam splitter material is coated on an optically flat substrate.

The return beams from both the mirrors along the same path length as their incident path are recombined into a single beam at the beam splitter. The path length of one of the return beams is changed in order to create phase difference to cause an interference pattern. The recombined radiation is then directed through the sample and focused on to the detector. The detector measures the amount of energy at discrete intervals of mirror movement.
The movable mirror can be moved in a range of say \(\pm 5\) cm. The mirror velocities from 5 to 0.05 cm\(^{-1}\) are used. Interferometer instruments need detectors with response times short enough to detect and transmit rapid changes to the recorder. The detector used in conjunction with rapid scanning interferometers in the mid-infrared region at room temperature is triglycine sulfate with KBr windows as pyroelectric bolometer. It has a high response time. Other most common detectors used such as thermocouples, bolometers and Golay detectors have short response time. The design of the Michelson interferometer is such as to make measurement in any infrared region possible by simply changing the beam splitter and the detector.

### 2.2.1 Instrumentation

#### (a) Introduction

The basic components of an infrared spectrometer are shown in Fig. 2.2. A source provides radiation over the entire range of the infrared spectrum. The monochromator disperses the light and then selects a narrow wave number range. The detector measures the energy and transforms it into an electric signal. This signal is further amplified and registered by the recorder.

With recent improvements in instrumentation, the infrared region of the electromagnetic spectrum is now considered to cover the range from approximately 12500 to 10 cm\(^{-1}\) (1000–0.8 \(\mu\)m). It is generally subdivided into three sections: near infrared (12500–4000 cm\(^{-1}\)), mid infrared region (4000–400 cm\(^{-1}\)) and the far infrared (400–10 cm\(^{-1}\)). The mid infrared region is the one of the most commonly used standard laboratory investigations as it covers almost all the vibrational and rotational
transitions. The FT-IR spectra of most of the samples were recorded in mid and far IR regions and are used for the present investigation [57–60].

**Fig. 2.2 : Block diagram of major units in an infrared spectrometer**

(b) **Source**

Infrared radiation is produced by electrically heating a source, usually a Nernst filament or a Globar to 1800–1000°C. The Nernst filament is fabricated from a binder and oxides of thorium, cerium, zirconium and yttrium. The Globar is a small rod of silicon carbide usually 5 cm in length and 0.5 cm in diameter. The maximum radiation for the Globar occurs in the 5500–5000 cm⁻¹ region. Nichrome wire, carbon arc, rhodium wire and tungsten filament lamp are also used as light source.

In a commercial infrared spectrometer either a nichrome wire or a platinum filament contained in a ceramic tube is commonly used as infrared source for the range 4000–400 cm⁻¹.

(c) **Monochromator**

A monochromator is a means of separating wavelengths of the source radiation. The monochromator is used to separate polychromatic radiation into a suitable monochromatic form [60]. This is achieved by means of prisms or diffraction
Materials for prism construction, which are found most suitable in the infrared region are; Glass–SiO₂ (300 µ to 2 µ (5000 cm⁻¹)), Quartz (800 µ to 3 µ (12500 to 3300 cm⁻¹)), Lithium fluoride (600 µ to 6 µ (1670 cm⁻¹)), Calcium fluoride (200 µ to 9 µ (1100 cm⁻¹)), Sodium chloride–NaCl (200 µ to 14.5 µ (625 cm⁻¹)), Potassium bromide–KBr (25 to 10 µ (400 cm⁻¹)) and Cesium iodide–CsI (38 to 10 µ (260 cm⁻¹)).

An ideal prism instrument would contain large number of prisms made from different optical materials, so that each could be used in sequence in its effective region. High resolution prism instruments contain combination of SiO₂, NaCl and KBr prisms. Low-cost instruments use a NaCl prism over the full range. They give highest resolution in the vital finger-print region.

A monochromator thus carries out three functions: (i) it disperses the radiation according to its wave number components (ii) it restricts the radiation falling on the detector into a narrow wave number range, and (iii) it maintains the energy incident on the detector to an approximately constant level when no sample is present throughout the wave number range of the instrument. Some instruments use a double monochromator. That is, the exit slit of the first monochromator serves as the entrance slit for the second monochromator. As a result, the spectra obtained with spectrophotometers having double monochromator have higher resolution.

(d) Detectors

Detectors used in infrared spectrophotometers usually convert the thermal radiant energy into electrical energy, which can subsequently be plotted on a chart recorder. Two Types of the detectors are commonly used:

i. The heating effect of the radiation (Thermal detector)
Photoconductivity (Photon detector)

1. **Thermal Detectors**, in which the infrared radiation produces a heating effect that alters some physical property of the detector.

2. **Photon Detectors**, which use the quantum effects of the infrared radiation to change the electrical properties of a semiconductor.

1. **Thermal Detectors**

   The detector mostly produces an electrical signal which is proportional to the intensity of the incident radiation over the whole spectral range of the instrument. The most desirable features of the detectors are the closeness with which they approach the behaviour of a black body, high sensitivity, high speed and robustness.

   The infrared detectors may be selective or non-selective. The selective detectors are those whose response is markedly dependent upon the wavelength of the incident radiation. Examples of this type are photocells, photographic plates, photoconductive cells and infrared phosphors. The non-selective detectors are those whose response is directly proportional to incident energy but relatively independent of wavelength. Common examples include thermocouples, bolometers and pneumatic cell. Recent detectors, fabricated from crystals are known as pyroelectrics and take less time than other thermal detector. Hence with these crystals, radiation can be chopped at a higher rate. However, these are more expensive and not widely employed.

2. **Photon Detector**

   The more sensitive infrared detectors rely on a quantum interaction between the incident photons and a semiconductor—the result producing electrons and holes. This is the internal photoeffect. A sufficiently energetic photon that strikes an electron
in the detector can raise that electron from a nonconducting state into a conducting state. As conductors, electrons contribute to the current flow in one of two ways, depending on the configuration of the semiconductor. These are referred to as photovoltaic or photoconductive cell.

**Photoconductive cells** commonly used are indium antimonide (InSb) or Hg–Cd–Te (MCT), which have high sensitivity and very quick response time in infrared detection. These detectors operate at liquid nitrogen temperature which reduces noise. The radiant energy falling on the detector is converted into measurable electrical energy.

**Photovoltaic cells** are essentially electrical resistors, which decrease in resistance in relation to the intensity of light striking their surface and are characterized by greater sensitivity and rapidity of response. They are constructed from a thin layer (0.1 µ) of semiconductor, like lead sulphide and lead tin telluride. These detectors extend spectral sensitivity up to 6 and 3.5 µ respectively [59].

**(e) Amplifiers and Recorders**

The radiant energy received by the detector is converted into measurable electrical signal and is amplified by the amplifiers. The amplified signal is registered by a recorder or a plotter. The recorder is driven with a speed which is synchronized with that of a monochromator, so that, the pen moving across the chart, records the transmittance of the sample as a function of the wavenumber.

**(f) Beam Splitter**

Beam splitter are constructed by transparent materials with refractive indices such that approximately 50% of the radiation is reflected and 50% is transmitted. A widely used material for the far-infrared region is a thin film of mylar sandwiched
between two plates of a low refractive index solid. Thin films of germanium or silicon deposited on cesium iodide or bromide, sodium chloride or potassium bromide are satisfactory for the mid-infrared region.

2.3 SAMPLE HANDLING TECHNIQUES IN INFRARED SPECTROMETER

Sample handling is considered as an important technique in infrared spectroscopy. There are various methods of sample preparation to enable almost any type of sample to be examined.

Some significant problems arise when trying to construct sample containers for vibrational spectrometry, because every material has some vibrational absorption. The material that has a minimum interference in the regions of interest is used as sample. The material of choice for IR spectroscopy is a solid potassium bromide plate. Such plates are used in a number of ways. Polyethylene pellets are used for recording the far IR spectra.

a) Solids

Solids are sampled in a wide variety of ways. If the sample is soluble, it may be dissolved and handled as for a liquid. Solid samples for which no solvent is suitable can be prepared for analysis by incorporating them into a pressed pellet of alkali halide, usually potassium bromide. Sample is mixed with a weighted amount of powdered potassium bromide and the mixture is admitted to a pressure of several tones in a die, to produce a highly transparent plate or disc which can be inserted into the spectrophotometer.
The use of KBr eliminates the problems of additional bands due to mulling agent. KBr does not absorb infrared light in the region 15–2.5 μm and a complete spectrum of the sample is obtained.

Solid samples have also been examined in the form of a thin layer deposited by sublimation or solvent evaporation on the surface of a salt plate. Another method, called mulling has also been developed, in which the powdered sample is mixed to form a paste with little heavy paraffin oil. The mull is sandwiched between salt plates for measurement. Mulls are formed by grinding 5 to 2 mg of finely powered sample in the presence of one or two drops of a heavy hydrocarbon oil called Nujol [57–60].

b) Liquids

In most instances the spectra of liquids are measured in either a demountable type cell or in fixed thickness or sealed cells. The spectra of pure samples can be measured as very thin films squeezed between two alkali halide windows of a demountable cell. This technique can produce a film of thickness 0.01 mm or less. This method is most useful for qualitative work only because the sample thickness cannot be controlled. Liquid cells consist of two alkali halide windows usually NaCl or KBr, separated by a spacer of suitable thickness made of Teflon or lead which limits the volume of the cell [57–60].

c) Gases

Absorption spectra of gases can be measured in a wide variety of gas cells ranging from a few centimeters to several meters that can be directly placed in the path of the infrared beam. The end walls of the cell are usually made of sodium chloride which is transparent to infrared. The low frequency vibrational changes in the gaseous phase often split the high frequency vibrational bands [61].
d) **Solvents**

Solvents of good infrared transparency over a convenient frequency range are available and the spectra of the sample dissolved in carbon tetrachloride and carbon disulphide provide the complete range. Chloroform is considered to be an important solvent and is frequently used because it shows absorptions though it is less symmetric molecule than carbon tetrachloride and carbon disulphide.

### 2.4 ADVANTAGES OF FOURIER TRANSFORM TECHNIQUE

The main advantages of FT spectroscopy are the greater ease and speed of measurement. The entire spectrum can be recorded within few seconds using sophisticated computers. Recent developments in FT-IR spectrometers have thus led to higher resolution, total wavelength coverage, higher accuracy in frequency and intensity measurements. It can also be used in the characterization of all kinds of samples. In FT-IR method, all the source energy passes through the instrument and the resolving power is constant over the entire spectrum. The signal to noise ratio is also improved [62]. The smoothening of peaks and the vertical and horizontal expansion of selective region is also possible.

### 2.5 FOURIER TRANSFORM RAMAN SPECTROMETER

The Raman spectroscopy is made sophisticated with the advent of gas lasers and computers. The advantages of lasers are their high intensity, high monochromaticity, narrow band width, high resolution and coherence. From the time of invention of Raman Effect, both IR and Raman spectra of chemical compounds have been effectively used for the determination of molecular structure and also for the quick identification of the presence of the characteristic group frequencies in the
compound as discussed [63–65]. In order that for a molecular vibration to be Raman active there must be a change in the polarizability of the molecule.

An important advantage of Raman spectra over infrared lies in the fact that water does not cause interference; indeed, Raman spectra can be obtained from aqueous solutions. In addition, glass or quartz cells can be employed, thus avoiding the inconvenience of working with sodium chloride or other atmospherically unstable window materials. Raman spectra are acquired by irradiating a sample with a powerful laser source of visible or near-infrared monochromatic radiation. A major advantage of FT-Raman over conventional dispersive Raman spectroscopy is its ability to render spectra that are generally free of fluorescence interference. FT-Raman enjoys the wavelength precision of FT-IR so that spectra may be co-added, resulting in a rapid improvement in signal-noise ratio (SNR) performance. In this study, the spectral data were recorded on BRUKER IFS-66V, FT-IR with FRA-106 FT-Raman spectrophotometer and the block diagram of the instruments is shown in Fig. 2.3.

2.5.1 Instrumentation

(a) Introduction

In Raman spectrometer the sample is irradiated with monochromatic light and the scattered light is observed at right angles to the incident radiation Raman spectrometer consists of sources, a sample holder, a monochromator and a detector. Fig. 2.4 represents schematic diagram of a Raman spectrometer.
Fig. 2.3: Block Diagram of FT-Raman Spectrometer
(b) **Source**

The sources used in modern Raman spectroscopy are nearly always lasers because their high intensity is necessary to produce Raman scattering of sufficient intensity to be measured with a reasonable signal to-noise ratio. Five of the most common lasers along with their wavelength (nm) used for Raman spectroscopy are; Argon ion (514.5 or 488 nm), Krypton ion (647.1 or 530.9 nm), Helium/Neon (632.8 nm), Diode laser (830 or 782 nm) and Nd:YAG (1064 nm). Because the intensity of Raman scattering varies as the fourth power of the frequency, argon and krypton ion sources that emit in the blue and green region of the spectrum have an advantage over the other sources. Diode and Nd:YAG laser which emit near-infrared radiation are used as powerful excitation sources. Near-infrared sources have two major advantages over shorter wavelength lasers. The first is that they can be operated at much higher power (upto 50W) without causing photo decomposition of the sample. The second is that they are not energetic enough to populate a significant number of fluorescence...
producing excited electronic energy states in most molecules. Consequently, fluorescence is generally much less intense or nonexistent with these lasers. The Nd:YAG line at 1064 nm is particularly effective in eliminating fluorescence. The two lines of the diode array laser at 830 nm and 782 nm also markedly reduce fluorescence in most cases.

The laser radiation is directed to the sample by means of a lens and a parabolic mirror and the scattered light from the sample is collected and passed to a beam splitter and to the moving mirrors. It is then passed through a series of dielectric filters and focused onto a liquid nitrogen cooled detector.

(c) **Filter**

Liquid filters are placed between the source and the samples tube. Different filters are used for different excitation radiation. Filters made of quartz glass or nickel oxide glass is used for getting monochromatic radiations. The functions of filters are;

- To isolate a single exciting line
- To remove high energy radiation that might cause photo decomposition or fluorescence.
- To remove the continuous spectrum in the region occupied by the Raman lines.

(d) **Monochromator**

In the monochromator, both lenses and mirrors have been used. Most Raman spectrometers use a diffraction grating as the dispersing element. A grating instrument has a wide aperture and a medium dispersion. A double monochromator is used to avoid stray light problem from scattering by dust particles in the sample.
(e) Detector

Raman spectrum can be photographed with an ordinary spectrograph. Basically there are two different ways to detect and record Raman lines. The easiest way is together the scattered light emerging through a glass window at the end of the Raman sample tube. It is passed through a prism or grating and then focused on a photographic plate. The plate is then developed and both the line frequencies and intensities can be measured using external equipments. Modern spectrometers which have photo multiplier tubes are direct measurements and facilitate automatic scanning of a spectrum. The spectrum produced by the monochromatic is passed through a slit which allows a narrow wavelength region to pass through which is focused on to a photo multiplier type detector. This detector employs an amplifier and a recorder. It directly provides the Raman Spectrum.

2.6 SAMPLE HANDLING TECHNIQUES IN RAMAN SPECTROMETER

Sample handling techniques for Raman spectroscopic measurements is simpler than for infrared spectroscopy because glass can be used for windows, lenses and other optical components instead of the more fragile and atmospherically less stable crystalline halides. In addition, the laser source is easily focused on a small sample area and the emitted radiation efficiently focused on slit. Consequently very small samples can be investigated. In fact, a common sample holder for non absorbing liquid sample is a glass melting-point capillary.

a) Solids

The Raman spectra of solids as polycrystalline material or as a single crystal can be recorded. No medium such as null, KBr or solvent is needed. A few milligrams of the solid samples are required. Solid can be packed into a capillary tube as a
powder. The crystal can be mounted in a goniometer on a glass or silica fibre. The spectra can be measured for different orientation of the crystal. For a single crystal, the Raman spectrum varies depending on the direction of the crystal axis, when polarized light is used as incident radiation. Raman spectra of adsorbed species can be recorded at different temperatures and pressures.

b) Liquids

The spectrum of a liquid can be recorded as neat or in solution. Ordinarily about 0.3 ml of a liquid may be required. The sample could be taken in glass or silica containers or capillaries. The spectra can be measured directly from the reaction vessel. Water is a good solvent for recording the Raman spectra. Water absorbs strongly in the infrared but it gives a poor Raman scattering. Raman spectroscopy is thus a valuable tool for studying water soluble biological materials.

c) Gases

The Raman spectra of gases are generally weaker than those of liquids or solids and hence may require cells of larger path length. The gas may be filled in a glass or silica tube of 2 to 1 cm diameter. If the resolving power of the instrument is good and if the molecule has sufficiently low moment of inertia, the rotational fine structure may be observed on either side of the Rayleigh line. Generally a broad band contour may be observed.

The main advantages of Raman spectroscopy is that it may be used for a wide variety of sizes and forms of the sample. Samples in gas, liquid and solid states can be examined easily.
2.7 ADVANTAGES OF RAMAN SPECTROSCOPY

The linear relationship of intensity versus concentration in the Raman technique makes identification of major components of a mixture easier than in infrared, where intensity is logarithmically related to concentration. Raman intensities are directly proportional to the concentration of the active species. In this respect, Raman spectroscopy more closely resembles fluorescence than absorption, where the concentration intensity relationship is logarithmic.

Analysis of multi component mixtures—especially the conjugated systems, dienes, styrenes, cyclic paraffins etc., where the infrared spectra are often very similar, is simpler with Raman spectroscopy. Raman spectroscopy has a great advantages over infrared for the study of aqueous solutions, because infrared is not readily adaptable to the study of aqueous solutions. Raman spectroscopy can be readily employed for the analysis of organic compounds that carry polar groups but differ in skeleton structure.