EXPERIMENTAL ASPECTS

3.1 INTRODUCTION:

In this chapter, we present a brief discussion of the experimental techniques and the instruments used to obtain the Raman spectra, viscosity and refractive index of molecules taken under study.

Raman scattering is inherently a weak phenomenon. Only a small fraction of photons are scattered by the sample and it leads to weak signals (≈0.001% of the excitation source). The weak signals can be amplified with good signal to noise ratio by increasing the measurement time and improving its experimental techniques. In a standard Raman experiment, highly intense monochromatic radiation is focused onto the sample. The scattered light is collected by the assembling optics and is directed to a dispersive system typically using a double monochromator which selects the scattered light of particular frequency range. At the exit port of the monochromator, the Raman spectrum is displayed in the form of a series of faint lines. The signals are detected and amplified by a photomultiplier tube and finally recorded by a DATAMATE using DM-3000 software. The schematic block diagram of Laser Raman set-up used to record the Raman spectrum is shown in Fig. 3.1.1.

With the advancement of technologies, more precise and sophisticated Raman spectrometer, namely Micro-Raman spectrometer has been developed. Such Raman spectrometer is able to measure Raman spectra from microscopic samples quickly, easily and non-destructively. This Raman system is durable, easy to use and highly sensitive. It uses highly sophisticated software to operate.
Fig. 3.1.1: Block diagram of the laser Raman set-up.
In the present work, Micro-Raman spectrometer (Renishaw RM1000) manufactured by Renishaw Plc. has been used for Raman scattering measurements. Fig. 3.1.2 shows the schematic diagram of the micro Raman set-up used for our experimentation.

![Schematic diagram of Micro Raman set-up.](image)

**Fig. 3.1.2:** Schematic diagram of Micro Raman set-up.

The main parts of Renishaw system consists of a laser, a system unit, a microscope and a peltier cooled CCD camera. The system unit is equipped with a grating of 2400 grooves/mm. Laser beam of wavelength 514.5nm from an Ar⁺ laser (spectra model 165 Ar⁺) is brought through different mirrors and microscope objective to the sample. The scattered signal as well as Rayleigh line scattered from the sample is collected at 180° geometry. The collected signal contains both the Rayleigh line and
Raman scattered signal. The intensity of Rayleigh line is very high and needs to remove for recording good quality Raman spectra. In order to remove Rayleigh line at 514.5nm, the signal collected at 180° geometry is passed through Rayleigh line filter which allows only Raman scattered signal through it. The Raman scattered signal is then made to incident on grating where it is dispersed. The dispersed discrete wavelength in Raman signal now travels in different directions. The dispersed signal from grating focused on the lens of the detector CCD. The charged coupled device (CCD) camera has rectangular two dimensional arrays of pixels that convert the light falling to each pixel into a charge, which is proportional to the integrated light intensity. Data acquisition was then obtained from the computer using Renishaw software. All components of spectrometer are controlled in a synchronized manner by using software GRAMS-32.

3.2 SOURCE OF EXCITATION [1]:

The spectra physics model 165 Ar⁺ laser is used as an excitation source for recording the Raman spectra. The specification of Spectra Physics model 165 Ar⁺ laser is presented below:

- Noise, Current control RMS, 10 Hz – 2 MHz: 1%
- Noise, light control RMS, 10 Hz – 20 MHz: 0.2%
- Frequency stability: 60 MHz/°C
- Beam Diameter: 1.25 mm
- Beam Divergence (full angle): 0.69 mrad
  - W/ prism: 1.05 + 0.003 meter
- Cavity configuration: long radius, output, flat high reflector
- Cavity length w/o prism: 1 + 0.003 meter
- Folded cavity: N/A
- Polarization: Vertical
- Mode-spacing w/o prism: 149.6-150.5 MHz
  - W/ prism: 142.5-143.3 MHz
- Folded cavity: N/A

The spectra Physics model 165 Ar⁺ laser is a continuous wave (CW) laser available in the ultra violet (UV) to deep red range. It has been engineered with
optimum combination of size, stability, convenience, versatility and reliability. It mainly consists of a laser head and an exciter (spectra physics model 265). The laser head was designed to a minimum size and weigh consisting of a field-proven Beryllium oxide (BeO) plasma tube closed at each end by the Brewster angle windows, a solenoid and an optical resonator. The optical resonator is formed by a spherical reflector (mirror) at the output end, together with a prism assisted by a flat reflecting mirror at the back end. The prism is placed in the optical path of the resonator in such a way that it selects the correct wavelength. The plasma tube is placed exactly along the central line of the mirror. External thumb wheel controls are making available for the selection of correct wavelength of the emitted radiation and for changing the intra-cavity aperture. The polarized light emitted from the laser source can be changed to any desired plane by means of the half-wave ($\lambda/2$) plate.

The spectra physics model 265 Exciter is conservatively designed to be a reliable, trouble-free, long-life supply. It contains all the necessary electric and electronic circuits in order to create, sustain and monitor the ionic discharge in the plasma tube. It also monitors and controls the output power and regulates the solenoid current of the 165 Ar$^+$ laser head. The 265 Exciter runs on 230 volts three phase power line, which is provided by a power transformer supplied with a three phase 400 volts stabilized power from the main line. The input stabilization was achieved with the help of three single-phase 8.3 KVA (each) Nelco voltage stabilizers connected in the star (Y) configuration. Both the 165 Ar$^+$ laser and the 265 exciter are continuously cooled by flowing chilled de-ionized distilled water at a constant temperature of 15$^0$C and at a pressure of 40 PSIG from the Neslab HX-500 (air cooled) water chilled plant.

**3.3 OPTICS AROUND THE SAMPLE [2]:**

The laser light is filtered by a laser filter before it enters the focusing system. The laser filter is a small grating monochromator, which allows the correct excitation wavelength to pass through and blocks weaker non-lasing lines from the laser plasma. Therefore, it can provide a clean Raman spectrum uncluttered by the laser-plasma lines, especially for a strong scattering sample.
The filtered laser beam is deflected upward through 90° by a mirror and is focused onto the sample to a spot of diameter of around 10 μm by the fused silicon-condensing lens. Scattered radiation from the sample passes through a polarization analyzer, a device based on birefringence and total reflection or on dichroism. The polarization analyzer provides direct information regarding the state of polarization of the observed plasma band and transmits light of a particular polarization depending on the orientation of the polarizer. The scattered radiation from the sample is collected by an ellipsoidal mirror, which ascertains a large solid angle about the focal volume and hence collects the optimum amount of scattered light. Fig. 3.3.1 shows the optical diagram of the light scattering systems of Raman instrument.

**Fig. 3.3.1:** Optical diagram of the light scattering system of Raman instruments.
3.4 THE SPECTROMETER: SPEX RAMALOG MODEL 1403 DOUBLE MONOCHROMATOR:

Spectrometer basically separates the spatially scattered photons from the sample based on the wavenumber. The light dispersing process is repeated by linking two single monochromators to form a double monochromator. The double monochromator separates the Raman photons from the overwhelming number of Rayleigh photons.

SPEX Ramalog 1403 double monochromator provided with a water-cooled photomultiplier tube RCA C-31034-02 has been used to record the Raman spectra. The SPEX Ramalog 1403 double monochromator equipped with 1800 grooves/mm holographic gratings is f/7.8 instrument with a spectral coverage from $3.1 \times 10^4$ cm$^{-1}$ to $1.1 \times 10^4$ cm$^{-1}$. A resolution of 0.15 cm$^{-1}$ and a spectral repeatability of ± 0.2 cm$^{-1}$ having accuracy of ± 1 cm$^{-1}$ in the 10,000 cm$^{-1}$ range can be achieved by this instrument. The gratings are mounted on a modified Czerny-Turner mount as shown in Fig. 3.4.1.

![Czerny mount of gratings for the SPEX model 1403 Ramalog.](image)

**Fig. 3.4.1:** Czerny mount of gratings for the SPEX model 1403 Ramalog.
The fundamental grating equation [3] as applied to Czerny- Turner mount is

\[ d(\sin \alpha + \sin \beta) = l \lambda \]  

(3.4.1)

where, \( l = \) order, \( \lambda = \) wavelength, \( d = \) grating spacing, \( \alpha = \) angle of incidence and \( \beta = \) angle of diffraction.

In case of 1403 instrument, substituting \( \alpha = \theta + \phi \) and \( \beta = \theta - \phi \), equation (3.4.1) can be written as

\[ d \sin \theta \cos \phi = l \lambda \]  

(3.4.2)

where, \( \phi = 10^0 \), hence \( \cos \phi = 0.984 \).

\( \theta = \) grating rotation measured from zero (Fig.3.4.1) and \( \phi \) represents the constant angle, which depends on the design of the instrument.

The 1800 grooves/mm holographic gratings disperse the scattered radiation focussed onto the entrance slit of the spectrometer. Nearly monochromatic radiation of frequency \( \nu \) for a particular tuning of the spectrometer reaches the exit slit of the double monochromator by the grating mirror combination.

The theoretical resolving power \( R_T \) is given by

\[ R_T = \frac{\lambda}{\Delta \lambda} = \frac{\nu}{\Delta \nu} = 2 \sin \theta \cos \phi \frac{W}{\lambda} = 1 N \]  

(3.4.3)

where, \( \lambda = \) wavelength

\( \nu = \) wavenumber

\( N = \) total number of grating grooves

\( W = \) width of grating ruling and

\( l = \) order of diffraction.

**Factors influencing resolution:**

**Source:** Resolution depends linearly on the grating width (i.e. optical path difference).

The dispersing power of a grating/spectrometer pair can usually be considered constant in terms of wavelength. However, Raman spectra use an energy related unit (Raman shift or wavenumber in \( \text{cm}^{-1} \)) which means that the spectral resolution decreases as the laser excitation is changed from infra-red to visible to ultra-violet wavelengths.

Resolution gets worse if the source illuminates less than the full width of the grating. Therefore, the source or condensing lens should fully illuminate the collimating mirror.

This can usually be checked visually by opening the spectrometer or, in the case of
energy outside the visible spectrum, by making certain that throughput is reduced when the edges of the collimating mirror are obstructed.

**Slit height:** Instrumental resolution diminished with the increase in slit height. As the height of the slits is increased, the ends of the exit slit begin to pass portions of adjoining wavelengths.

**Slit width:** Spectral bandpass is a function of the reciprocal linear dispersion, which, in turn depends on the wavelength, the grating constant, the focal length of the instrument and the spectral order.

### 3.5 COLLECTION OF SCATTERED RADIATION:

A standard sampling platform is supplied with the SPEX 1459 illuminator. The Raman liquid cell of 1 ml capacity with 1431 M holder was used for holding the sample. The sample is illuminated with laser radiation and then the laser focus control is adjusted until the brightest image is observed at the sample. The image of the sample-scattered radiation is deflected on the target. An elliptical collection mirror (f/1.4) images the scattered radiation on the entrance slit of the spectrometer. The image is centered on the cross wires with the lateral adjustments and focus adjustment are turned until the sharpest image is achieved. By rotating the swing away mirror counter clockwise, the sample-scattered radiation is allowed to pass into the spectrometer. The signal is now peaked photo-electrically between the focus and lateral adjustments until the signal from the detector is maximized. In order to increase the scattering and collection efficiency, spherical mirrors may be mounted above and behind the sample in the 1459 illuminator. Both mirrors increase the amount of scattered radiation that reaches the spectrometer entrance slit and therefore increase the signal from the detector. Two optical elements may be interposed in the beam, an analyzer and a scrambler, before it reaches the entrance slit. The scrambler is employed in front of the entrance slit of the monochromator to depolarize the radiation. It is a wedge of birefringence materials. The two components of polarized light passing through it will be thrown out of phase as with a \( \lambda/2 \) plate. The laser output is polarized perpendicularly, whereas the Raman radiation from the sample is depolarized. The analyzer interposed in
pathway may transmit the light either perpendicularly polarized or parallel polarized, depending on the orientation of the analyzer.

3.6 PHOTON COUNTING DETECTION [2]:

Photon counting detection system consists of a RCA C31034-02, II-stage QUANTACON type photomultiplier tube (PMT) with S-20 response in the photon-counting mode. SPEX DATAMATE DM 3000 software were used for recording the spectra and for the acquisition of the data. The central processing unit (CPU) of the DATAMATE is an 8-bit microprocessor based ROM. The data can be processed in real time to subtract away background, take ratios, integrate or convert to logarithm for absorption states. DATAMATE photon counting results are presented in counts/sec. The DATAMATE also supplies high voltage (0-2000volts D.C. –ve) to the PMT. The high voltage is CPU selectable in 10 volts increment. The output current is variable from 0-2 mA. The linearity is better than 0.01% over full range. The noise level is 0.015% peak to peak at full load. The input in photon counting – DAM mode is –ve going pulse 0.1mV amplitude or greater. The gain of the amplifier is 400 and the rise time is 10 ns. The pulse pair resolution is less than 25 ns. The maximum count rate for photon counting is 25X10^6 Hz. The linearity and accuracy of the output data (Y-axis) is 0.3% full scale and resolution is one part in 4000.

3.7 THE PHOTOMULTIPLIER TUBE:

RCA C-31034-02 photomultiplier tube was used for obtaining the Raman Spectral data. This photomultiplier tube consists of a gallium arsenide chip placed at its photocathode, an ultraviolet transmitting glass window and an inline copper beryllium dynode structure consisting of eleven dynodes. It is designed specifically for use at reduced temperatures upto -300 C. The photomultiplier tube having an almost linear, absolute, responsivity 3000Å wavelength range operates for a current gain of 10^6 with a maximum dark pulse summation of 12cps. The raw data is obtained from the output of the preamplifier (pc Dam) of gain 400. The anode of the PMT is the input of the pc Dam. The high voltage of 1750 volts required for operating the PMT is supplied by the DATAMATE with a stability of +0.002% after 30 minutes of warm up.
3.8 THE CHARGED-COUPLED DEVICE [4, 5]:

The charged-coupled device (CCD) is in many respects close to being the ideal detector for Raman microscopy. It is an electronic replacement for photographic plate used by Raman. The CCD has advantages other than quantum efficiency over the photographic plate. The CCD detector and arrays are essentially large area silicon devices constructed such that the sensing area is divided into a two-dimensional matrix of pixels (shown in Fig. 3.8.1). Each pixel is an individual detection element, but combination of pixels, or binning is also possible.

![Fig. 3.8.1: CCD readout registers.](image)

The spectrum is spread out in the horizontal direction and each pixel corresponds to Raman scattered light of different frequency. The dark border in the figure represents the area on the CCD where the desired spectral information is recorded. Both the photographic plate and the CCD have the capability of recording a large section of a Raman spectrum simultaneously, with the diffraction grating in a fixed
position. With a photomultiplier, by comparison, only a single point in the spectrum is recorded at a time.

The signal from the CCD is processed, amplified and converted to digital data points by electronics in the Detector controller. The data is then passed from the Detector Controller to the memory of the computer. This allows the software running in the host PC to access it rapidly for further processing and display.

3.9 SAMPLING TECHNIQUES:

A laser beam, being a narrow and unidirectional, entity, can be manipulated in a variety of sample cell configurations thus providing considerable ingenuity in exercising the design and use of sample cells. A substantial advantage stemming from the geometric simplicity of the Raman experiment is that samples may be examined in any physical states and shapes. For liquid samples, which we have used more frequently, a cell consisting of around 1 cm path length is adequate, provided the cell bottom is transparent. In order to minimize the amount of scattered light from the interface reaching the spectrometer, the cell should be topped around the meniscus.

3.10 MEASUREMENT OF DEPOLARIZATION RATIO (DR) [6]:

There are two methods for measuring the depolarization ratios. In one method the polarization analyzer is inserted in the beam path after the sample (between the sample and spectrometers) and in other method a polarization rotator is inserted before the sample (shown in Fig. 3.10.1). More accurate results are obtained by the latter method. Since the laser beam is nearly 100% polarized and efficient rotation with a half-wave plate or an optically active rotator produces an almost ideal source for the measurement of depolarization ratios. A half wave plate or an optically active rotator has the property of rotating the sense of polarization of an incident radiation about its direction of propagation.

The principle of measurement of the DR by the first method is illustrated in Fig. 3.10.2. For obtain the DR, the method is generally to make two successive scans between which for instance either the polarization of the incident light or the orientation
of the analyzer is changed in order to obtain the two intensities \( I_{\parallel} (= I_{VV}) \) and \( I_{\perp} (= I_{VH}) \) from which the DR is calculated.

The mathematical expression used to determine the DR is given by

\[
\rho = \frac{I_{\perp}}{I_{\parallel}}
\]

(3.10.1)

\[ 
(\text{3.10.1})
\]

Fig. 3.10.1: Two methods of measuring depolarization ratio.

The intensities of isotropic and anisotropic components of Raman band can be obtained by using the following standard relationship

\[
I_{iso} (v) = I_{VV} (v) - \frac{4}{3} I_{VH} (v)
\]

(3.10.2) and

\[
I_{aniso} (v) = I_{VH} (v)
\]

(3.10.3)

where, \( I_{VV} (= I_{\parallel}) \) and \( I_{VH} (= I_{\perp}) \) are the polarized and depolarized Raman components.
Fig. 3.10.2: Measurement of depolarization ratio. $I_{\|}$ and $I_{\perp}$ are the intensity of the scattered light component with its electric vector parallel and perpendicular to that of incident beam.

3.11 MEASUREMENT OF REFRACTIVE INDEX [7]:

Optical properties determination is one of the most important characterizations to study the solute-solvent interaction. The optical property related to the refractive index can be measured by using refractometers. In the present study, an Abbe’s refractometer from Mittal enterprises was used to measure the refractive indices. The refractive indices (n) of the prepared liquid binary mixtures at different concentration at constant temperature were measured by smearing two or three drops of the liquid.
mixture in between the two split portions of the prism. The uncertainty in the measurement of the refractive index was 0.0005. Experimental setup and optical layout of Abbe’s refractometer is shown in Fig. 3.11.1.

Fig. 3.11.1: Experimental setup and optical layout of Abbe’s refractometer.
3.12 MEASUREMENT OF VISCOSITY [8]:

Viscosity of liquid plays an important role in molecular dynamics study. Ostwald viscometer was used to measure the coefficient of viscosity of the liquid mixtures. The image of the Ostwald viscometer is shown in Fig. 3.12.1. Specific gravity bottle of 25ml was used to measure the density of the liquid. The viscosity of the liquid mixture was determined by comparing with that of water. The formula used to determine viscosity of the liquid mixture is given by

\[
\eta_i = \frac{\rho_i t_i}{\rho_w t_w} \eta_w
\]

(3.12.1)

where, \( \rho_i \) and \( \rho_w \) are the densities of the binary mixture and water respectively, \( \eta_w \) is the viscosity of water, \( t_i \) and \( t_w \) are the time of flow of the binary mixture and water respectively.

![Fig. 3.12.1: Ostwald viscometer](image-url)
3.13 REFERENCES:


