Basic idea: In this chapter, the methods of sample purifications and preparations, experimental techniques and instrumental details for Raman, IR, electronic absorption and emission spectroscopy have been discussed briefly.

SEC.1 INTRODUCTION

Extensive works have been carried out to study various properties of some molecules containing two aromatic rings in the ground and excited electronic states using different spectroscopic techniques. These techniques include electronic absorption and emission spectroscopy and Raman scattering. Electronic absorption spectra of the molecules have been studied in different solvents at room temperature. In order to get a thorough picture of various photophysical processes of the molecules, their luminescence spectra have been investigated at liquid nitrogen temperature which include studies on excitation spectra, life time measurements, determination of the polarization characteristics of different emission bands etc. The vibrational signatures of the molecules have been acquired from detailed studies of their infrared and Raman spectra (including their polarization characteristics). Besides, Raman excitation profiles (REPs) of different Raman bands have been critically analyzed to investigate some intricate properties of the molecules in their ground and excited electronic states. In this chapter we have briefly described various experimental methods including sample procurement, purification and preparation.
SEC.2 CHEMICALS, SAMPLE PREPARATION AND PURIFICATION

2A. CHEMICALS
Di-phenyl-methane (DPM) is supplied by Lancaster, UK with purity grade 99%+. Benzophenone (BP) and Di-pyridyl-ketone (DPK) are supplied by Aldrich Chemical Company, USA with purity grade 99%. All the chemicals are used as such for Raman, infrared and absorption spectroscopic studies. Spectroscopic grade solvents such as acetonitrile, carbon tetrachloride, chloroform, cyclohexane and methanol were purchased from S.L.R, India and have been used as received for the same spectroscopic studies.

2B. PURIFICATION
For emission experiments, benzophenone and dipyridyl-ketone are recrystallized from ethyl alcohol before use. Spectroscopic grade solvents, ethyl alcohol (EtOH) and methyl cyclohexane (MCH), supplied by E. Merck, Germany are distilled under reduced pressure and tested for residual impurity emission at a sensitivity level at least one order of magnitude greater than that used for recording the emission spectra of the compounds under investigation [1]. No impurity emissions from the solvents are found.

2C. SAMPLE PREPARATION
Concentrations of the solutions were varied from $10^{-6}$ to 1M for recording the electronic absorption spectra of DPM and from $10^{-6}$ to $10^{-2}$M for recording the same for BP and DPK. Concentrations of the solutes in the solutions were maintained around $5 \times 10^{-3}$ m dm$^{-3}$ for all emission measurements in BP and DPK. The Glassy forms of the freshly prepared solutions of BP and DPK in EtOH and MCH at 77K are obtained by rapidly immersing the sample tubes into liquid nitrogen. This technique of forming glassy matrixes by rapid cooling is well known and have been used previously both for EtOH and also for MCH solvents [2,3].

As Ordinary Raman spectroscopy is not suitable for vibrational studies at low concentration for weak scatterer, the concentration of the solution was maintained around 1M for recording the Raman spectra of DPM and BP whereas in case of DPK it was varied from $10^{-3}$M to 1M. Chloroform and carbon tetrachloride are chosen as the solvents because of the following reasons: (i) all samples, studied in the present work, are readily dissolved in both the solvents even at higher concentration; (ii) in order to test
consistency of experimental observation, these weakly polar and non-polar solvents, respectively, are preferred; (iii) no intense Raman line of CHCl₃ and CCl₄ appears in the frequency range of the fundamentals, whose REPs have been studied; (iv) the Raman wavenumbers, 667 cm⁻¹ of CHCl₃ and 461 cm⁻¹ of CCl₄ have been conveniently used as internal standards and (v) no strong Raman bands of the samples overlap with these reference lines. Otherwise, the intensities of the reference lines would have led to erroneous results in the measurement of the REPs. Attempt has been made to measure the REPs in the polar solvent methanol also. But the solvent band at 1032 cm⁻¹ (generally used as internal standard) overlaps with the solute bands in this region so profoundly that the idea of measuring REPs in this solvent is left undone.

SEC.3 MEASUREMENT OF ABSORPTION SPECTRA
The electronic absorption spectra in the range from 900 to 190 nm are recorded by UNICAM 500 UV-Visible spectrophotometer. This spectrophotometer has a tungsten light source for the visible range of the spectrum (900 to 340 nm) and a deuterium source for the ultraviolet range of the spectrum (340 to 190 nm). The resolution of the spectrometer is 1 to 2 nm for the sharp bands and slightly less for the broader ones. The samples are taken in a quartz cell of path length 1 cm. During the course of the emission studies, electronic absorption spectra of DPK and BP are taken with Shimadzu UV-VIS 2101PC spectrophotometer. The resolution of this spectrophotometer is 1 nm. A schematic diagram of the UNICAM 500 UV-Visible spectrophotometer is shown in the figure-2.1.
FIGURE 2.1 → A Schematic diagram of the UNICAM UV-VIS Spectrophotometer
SEC.4 MEASUREMENT OF EMISSION SPECTRA

The emission spectra are recorded with F-4500 fluorescence spectrophotometer (Hitachi), that is equipped with a 150 watt high pressure xenon lamp which serves as the exciting light source. The light emitted from the luminescent sample is scanned through the emission monochromator and is then detected by the photomultiplier tube R446F of Hamamatsu Corporation, Japan and recorded on a PC floppy or hard drive. A schematic diagram of the emission spectrophotometer is shown in the figure-2.2. The resolution of each of the absorption and emission instruments is 1 nm. The corrected excitation spectra are recorded with the accessories attached to the fluorescence spectrophotometer. Quantum yields are measured using benzophenone (BP) in ethanol as standard [3]. The anisotropies (r) of the phosphorescence spectra are measured with the help of UV-VIS polarizer accessories including a UV linear dichroic polarizer (wave length range 230 – 700nm), purchased from oriel instruments, USA. The anisotropies are determined from the following relation:

\[ r = \frac{I_{EE} - I_{EB} \cdot G}{I_{EE} + 2I_{EB} \cdot G} \text{, where } G = \frac{I_{BE}}{I_{BB}} \] ........................ (1)

Here \( I_{EE} \) and \( I_{EB} \) are the intensities of parallel and perpendicular polarized emissions with vertically polarized excitation and \( I_{BE} \) and \( I_{BB} \) are the intensities of perpendicular and parallel polarized emissions when excited with horizontally polarized light. G is the instrumental correction factor (which determines the polarization characteristics of the photometric system). This correction is made for any change in the sensitivity of the emission channel for the vertically and horizontally polarized components.

The life time is determined by recording the decay of different phosphorescence peaks after the exciting radiation (within the envelope of the \(^1\text{L}_a\)-band) being withdrawn when the phosphorescence intensity achieves a steady state. The goodness of fit has been assessed with the help of statistical parameters \( \chi^2 \) and correlation coefficients.
SEC.5 MEASUREMENT OF INFRARED SPECTRA
The infrared spectra of the pure samples were taken in thin films on a previously calibrated Perkin-Elmer Model 783 infrared spectrophotometer. The resolution of the infrared bands is about 2 cm\(^{-1}\) for sharp bands and slightly less for the broader ones.

SEC.6 RAMAN SPECTRAL MEASUREMENT
Raman spectroscopy is an ideal tool for chemical analysis due to its unique advantages over other analytical techniques. It is a method of obtaining the fingerprint spectrum of materials, requiring no special sample preparation. Despite the fact that Raman spectroscopy has so many advantages, it still is not in widespread use. The main reason is the high cost, typically associated with the Raman analyzer systems. Therefore, better-
resolution and lower-cost Raman systems are key to increase and enable greater acceptance and usage of Raman spectroscopy [4].

The necessary components for the observation of Raman spectra are: (a) source of monochromatic radiation, (b) an appropriate device to mount the sample illuminated optimally and to collect efficiently the scattered light by light gathering mirrors, (c) a dispersive system and (d) a detection device.

The factors governing the intensity and resolution of the scattered radiation are primarily guided by the Raman instrumentation. The Raman scattered intensity from a sample is proportional to the fourth power of the scattered frequency, the intensity of the exciting radiation, amount of the sample (i.e. number of scattering centers in the interaction path of the incident radiation) and most crucial among all, the scattering cross-section. Out of these factors, first two are the characteristics of exciting source, whereas, third and fourth ones are basically determined by the geometry of illumination and nature of the sample, respectively. Ideally, for good Raman spectra to be observed, optimum concentrated sample should be illuminated by an intense monochromatic source with frequency as high as possible towards blue region. For non-resonance Raman scattering, the excitation frequency does not match with any electronic transition band of the sample. Resonance excitation may cause a very intense fluorescence from the sample and the Raman signal may be buried in the background.

In the presence of the entire Rayleigh scattered light, it is very difficult to observe the Raman shift below $50\text{cm}^{-1}$ [5], even with most efficient monochromatic systems in the case of liquid molecules. The well-defined polarized laser beam may be used to decrease Rayleigh scattering in the direction of observation. In fact, it can be decreased to an appreciably low value by observing the scattered light in a direction perpendicular to the incident laser beam and the plane of the polarization of incident beam should be perpendicular to the plane of scattering. So, a 90° scattering geometry should be used to record the Raman spectra along with their polarization measurements.

The advantage of using laser as an exciting source is many-fold, such as, availability of several exciting lines, (usually having small bandwidth, less than $0.1\text{cm}^{-1}$), well-defined polarization properties and controllable high intensity. These factors together greatly facilitate the Raman instrumentation. There are so many lasers, which are commonly...
used in the Raman experiments. However, the Ar⁺-ion laser is one of the most frequently used lasers for recording the normal Raman spectra and has been used as excitation source in all the experiments in the present work also. Under normal conditions, a given laser line consists of a number of longitudinal cavity modes of slightly varying wavenumbers, which form an envelope. By appropriate mode selection optical device, very narrow laser line width can be achieved, which is important for the high-resolution study. For example, the Ar⁺ laser at 514.5 nm normally has a line width of ~0.15 cm⁻¹, whereas, by mode selection, a line width of 0.001 cm⁻¹ can be achieved [6].

Raman scattering being an essentially weak process as one out of a million incident photons, in normal case, is expected to be scattered, one needs an effective dispersive device with high light gathering optics and a very sensitive detection device to record Raman spectrum. Single, double, double-pass tandem and triple monochromators are now available as good dispersing system. Both photographic and photoelectric techniques are used, but PMT (photomultiplier tube) is still in common use. Another technique using photodiode arrays (PDAs), which is in a new electronic version of the photographic technique, has also been used in the last five to ten years. Another very sensitive detection device, which has come up in last five years, is the CCD (charge coupled device). The PMT detection is used in scanning mode, whereas, PDAs and CCDs are used in multi-channel mode. Combining the advantages of both multi-channel technique (using PDAs and CCDs) and scanning technique, scanning multi-channel (SMT) technique has been introduced most recently in the field of Raman Spectroscopy by Kiefer and co-workers [7,8].

In the present work, however we have used a Spex double monochromator (Model 1401) equipped with a cooled photomultiplier tube (Model R 928/7, Hamamatsu Photonics, Japan) and photon counting system. Samples are taken in a quartz cell and are illuminated by different laser radiations available from a Spectra Physics Ar⁺ laser (Model 165 of Spectra Physics). PC 32 GB is used for monochromator control, data acquisition and analysis. A schematic diagram of the Raman set up is shown in figure-2.3. Brief description of the instrument used is given in the following section.
6A. GENERAL EXPERIMENTAL SET UP

The Raman spectra are recorded on a Spex Ramalog spectrometer, whose details are given below. A 2 watt Spectra Physics Ar-ion laser model (model 165 of Spectra Physics) is used as excitation source. The Spex Ramalog spectrometer consists of a sample mounting compartment, a 1401 double monochromator system, thermoelectrically chilled photomultiplier tube and a PC (32GB) for performing the spectrometer control, data acquisition and analysis.

As illustrated in figures-2.3 and 2.4, the laser beam is focused into the sample from below. As shown in the figure-2.4, the beam is reflected in vertical direction with the help of a mirror (M5). During the entire process, the power of the laser incident at the sample reduces approximately to one third of initial laser power. The light is then collimated at the samples with the help of lens \( L_1 \). \( L_1 \) is a fused silica condensing lens of small focal length which can focus a laser beam of diameter 1.5 mm to a spot of about 10 \( \mu \text{m} \) diameter. The scattered beam from samples is collected using a usual 90° scattering geometry and is made to fall on the entrance slit of the double monochromator with the help of an elliptical mirror (M8) and a plane mirror (M9). After passing through an optical path shown in the figure (2.4) in the monochromator, the dispersed light reaches the PMT for detection. As the monochromator is scanned, the scattered light falls into the PMT and a signal proportional to the intensity of scattered light is produced and detected.
The resolution of the spectrometer, in the first place is a linear function of the width of the grating. Thus for better resolution, as much width of the grating as possible should be illuminated. The entrance slit ($S_4$) to some extent and the exit slit ($S_7$) to very large extent govern the resolution of the spectrometer, whereas two middle slits ($S_5$ & $S_6$) are used to reduce the stray radiations which helps in reducing the background intensity and hence improving the quality of the spectrum.
FIGURE 2.4 → A schematic optical diagram of Spex 1403 Double Monochromator with Sample Illuminator

6B. SPECTRA PHYSICS Ar⁺ LASER (model 165 of Spectra Physics)
The Ar⁺ laser (model 165 of Spectra Physics), used in the present set of experiment, is a 2-watt (all wavelengths) CW laser. This whole system consists of the laser head and an exciter (model 265) from Spex. The head contains plasma tube, solenoid and optical resonator. The plasma tube is made up of beryllium oxide (BeO) which provides a number of advantages; such as: high terminal conductivity, strength, structural stability etc. The tube is terminated at each end by fused silica Brewster’s angle windows. The necessary magnetic field generated by a solenoid surrounding the plasma tube keeps the electron away from the walls of the tube and ultimately helps to achieve a stronger
population inversion. The magnetic field also causes Zeeman splitting of the laser lines. However the split lines are elliptically polarised and Brewster's angle windows take care of them by allowing the laser oscillation only to such lines which are polarised very near to the vertical direction and discarding those polarized in the other directions. The whole plasma tube is mounted in an optical cavity resonator, which is formed by a spherical reflector at the output end and a prism assisted by a flat mirror at the high reflector end. The flat mirror is used to select the wavelength. The resonator assembly is strongly held against quartz rods with springs. Aperture adjusting wheel is provided for changing the intra cavity aperture.

The Spectra Physics model 265 exciter is fully equipped with the necessary electronic circuits to create, sustain and regulate the ion discharge in the plasma tube and to control the output power from the laser by simultaneously regulating the solenoid current. An arrangement is provided to have a desired constant output optical power when operated in 'light control' mode. The 265 exciter is fed with a stabilized three phases 380 V (phase to phase) power line. This unit requires cooling of the transistor pass bank in the exciter, the solenoid and the BeO plasma tube, which is achieved by circulating distilled and deionized water at $15^\circ C$ at 40 PSI from water chiller plant from Neslab model HX-500.

As mentioned earlier the laser operates at a number of wavelengths. Excitation is effected with some prominent radiation at 514.5, 501.7, 496.5, 488.0, 476.5 and 457.9 nm at the blue green region of the electromagnetic spectrum. Three different excitation processes [9], held in argon ion laser are shown below:-

\[
\begin{align*}
(a) & \quad Ar + e(fast) \rightarrow Ar^+ + e(slow) + e(slow) \\
(b) & \quad Ar^+ + e(fast) \rightarrow Ar^{+*} + e(slow) \\
(c) & \quad Ar + e(fast) \rightarrow Ar^{+*} + e(slow) + e(slow)
\end{align*}
\]
6C. SAMPLE CHAMBER (ILLUMINATOR)

Schematic diagram of the sample chamber is shown in figure-2.4. The laser line is focused at the center of the 1-cm quartz cell (containing the samples) through its bottom face. The laser beam is focused to produce a beam of much smaller diameter, which extends over a short length before beginning to diverge again. The region in which the beam is concentrated is called the focal cylinder. As the area of the focused beam is about $10^3$ times the area of the unfocused beam, the irradiance at the sample is increased by a factor of about $10^3$. If high irradiance is harmful to the sample, focused beam is not used. The sample is placed in such a way that it is illuminated well and the scattered radiations are collected effectively. A lens is used to collect the scattered radiation for further dispensation. Additional concave mirrors, $M_6$ and $M_7$ placed opposite to the monochromator side and on the top of the cell respectively are used to increase the observed intensity of the scattered light by 8 to 10 times. Filters and optical devices such as polarizer and analyzer may be inserted in the path of incident and scattered laser beam respectively. Moreover, the elliptical mirror $M_8$ and the plane mirror $M_9$ send the collected scattered light into the monochromator.

6D. SPEX DOUBLE MONOCHROMATOR (MODEL 1401)

Since Raman scattered intensities are too low compared to the excitation radiation, utmost care must be taken to minimize the stray radiation. The use of double monochromator equipped with two intermediate slits (figure-2.4) reduces the stray radiation considerably. For historical reasons, the instrument for Raman spectroscopy may be divided into the two classes depending upon the final method of recording spectra. Prisms were generally used in photographic instruments in earlier days (like 50's and 60's), whereas, gratings are used as dispersing system in modern photoelectric instruments, mostly, after the advent of lasers. The speed of an instrument based on photoelectric detection depends upon the total energy incident on the detector [5]:

$$E_\lambda = B_\lambda T_\lambda A D (\Delta \lambda)^2 \left( \frac{h}{f} \right)$$  

...............(2)
where $B_\lambda$ is source brightness, $T_\lambda$ is a function of the optical system, $A$ is area of the limiting aperture, $\Delta \lambda$ is the spectral slit width, $D$ is the angular dispersion and $f$ is the focal length of collimators. The position is governed by the fundamental grating equation,

$$m\lambda = d(Sin\alpha + Sin\beta) \tag{3}$$

where, $m$ is spectral order number, $\lambda$ is wavelength, $d$ is grating spacing, $\alpha$ is angle of incidence and $\beta$ is angle of diffraction. For simplicity, equation-3 may be expressed as,

$$m\lambda = 2d Sin\theta Cos\varphi \tag{4}$$

such that $\alpha = (\theta + \varphi)$ and $\beta = (\theta - \varphi)$. Again $\theta$ is grating rotation angle measured from zero and $\varphi$ is $10^\circ$. [$Cos\varphi = 0.984$ (manufacturer's supplied values)].

There are two shortcomings, which are generally associated with the grating spectrometers. One of them is the overlapping of different orders of different wavelengths. In a Raman spectrometer, however, this problem is avoided due to the fact that entire Raman spectrum is spread about $3500 \text{ cm}^{-1}$ on the Stokes side of the exciting frequency and hence the overlapping of different orders are avoided. The transmission factor or the efficiency of a grating varies with the polarization of the incident radiation [10,11]. This effect causes problems in obtaining Raman polarization data. A polarization scrambler consists of a quartz or calcite wedge, which rotates the plane of polarization of a given wavelength by different amounts for each point on the slit. Thus the net effect is the change of the incident light with definite polarization into the light of mixed polarizations.

Spectral purity is the most important factor of any monochromator system used in Raman spectroscopy. It is basically its ability to distinguish a narrow wavenumber band between $\nu$ and $\nu + \delta\nu$, to which it is set, from the other wavenumbers. The ability of a monochromator to distinguish lines of comparable intensity depends essentially upon the factors like resolution, dispersion power and slit width. The optical ray diagram and schematics of the spex 1403 double monochromator has been shown in the figure-2.4. It covers a spectral range from $31000 \text{ cm}^{-1}$ to $11000 \text{ cm}^{-1}$ with an accuracy of $\pm 1 \text{ cm}^{-1}$ in the visible region. The spectral repeatability is $\pm 0.2 \text{ cm}^{-1}$ and the aperture is $f/7.8$. The holographic type grating in this instrument has 1800 grooves/mm and it is mounted on a modified Czerny-Turner mount.
6E. PHOTOMULTIPLIER TUBE (MODEL 928-7)

In a Raman spectrometer, the photoelectric detection is achieved with a special kind of photocell called photomultiplier tube (PMT). The essential components of the PMT are a photosensitive cathode of low work function and dynodes with the property to emit more secondary electrons that received in the incident electron bombardment. Photons falling on the photocathode, depending upon its quantum efficiency, get the electrons released from the cathode and these electrons are accelerated to different dynodes one after another, which results in the multiplication of number of electrons at every dynode. The total gain of a PMT may be represented as $\delta^n$, where $\delta$ is the secondary gain and $n$ is the number of dynodes. The electron multiplying process makes the PMT a suitable device for the detection of the low-level light signal. A schematic diagram of the PMT is given in figure 2.5.

Along with the signal electrons, there may be additional electrons randomly (thermally) emitted from the photo-cathode and dynodes. These electrons will also be multiplied and will contribute as a noise to the main signal. Even with no signal, due to these thermally emitted electrons in the PMT, the value of current or voltage developed is not insignificant and constitutes the dark noise of the detecting device.

![Schematic diagram of PMT](image)

**FIGURE 2.5** → A schematic diagram of the PMT
The photomultiplier tube (model 928-7 Hamamatsu Photonics, Japan) that responds to Raman scattered radiation over the full scan range, has been used in the experiments of the present work. The PMT is cooled by thermoelectric cryostat. Circulation of cold water at 15°C cools the PMT housing. The dark current of a properly cooled PMT is quite small and therefore allows the observation of even a very weak Raman band. The PMT associated with the photon counting system in conjunction with a computer drive facilitates the recording of the Raman spectra. The tube has a high quantum efficiency and uniform sensitivity over the range 400-800 nm, which is the usual range for detection of scattered Raman radiation. By properly cooling the PMT, selecting an appropriate time constant (1 sec), and using a slow scan speed (0.5 cm⁻¹/sec), the Raman spectra with a reasonably good signal to noise ratio are recorded in the present work.

6F. DATA ACQUISITION SYSTEM

A 32-GBPC performs the spectrometer control and data acquisition. The inbuilt software helps one to do frequency and intensity range expansion or reduction. Microcal origin 16 bit program is also employed to analyse the spectrum. The background-corrected spectra are presented without any smoothing. Spectral data can be stored in a floppy disc.

6G. SCANNING OF RAMAN SPECTRA

There are number of difficulties associated with recording Raman spectra of coloured samples under resonance conditions. These include: (a) optimization of the sample to minimize reabsorption of the scattered light by the sample and at the same time allowing the scattering to be maximum; (b) the local heating of the sample due to absorption of exciting light which may give rise to thermal lens effect and also lead to thermal decomposition of the sample and (c) the strong background due to fluorescence from impurities in the compound or in the solvents or intrinsic fluorescence from the sample itself.

The first point can be taken care of by using samples of different concentrations until a good quality spectrum is obtained. To avoid local heating effect Kiefer and Bernstein [12,13] had developed a technique, which involves continuous rotation of the sample with respect to the laser beam. In this case, as the sample rotates continuously, the small
portion of the sample from which light scattering takes place due to laser irradiation remains in the laser beam only for a short period of time. Again a fresh sample replaces previous one due to continuous movement of the solution. Thereby this process reduces the local heating and thermal decomposition. To reduce the fluorescence background, Raman spectra can be measured in solid form in KBr pallet. However to obtain vibrational information from solution, it is always better to get rid of impurities from compounds and solvents.

To record Raman spectra of liquid solution, 1-2 ml solution of the respective sample at appropriate concentration is taken in a cylindrical quartz cell and positioned in a proper mount. The laser beam of selected wavelength is then made to strike the bottom of the cell very near to its perimeter. In this way self-absorption in the scattered light is minimized. The spectra are routinely calibrated with known Raman lines of solvents (CHCl₃ & CCl₄). To minimize any damage of the sample and degradation of the solute due to its prolonged exposure to laser radiation, the laser power is kept at a low value (20mw) for all excitations. The slit widths of the monochromators are adjusted to obtain reasonably good spectra. Other spectral parameters such as integration time (1 sec), wavenumber increment (0.5cm⁻¹), scanning speed etc. are adjusted from time to time to optimize signal to noise ratio. For weak Raman signals, the spectra are averaged 4-5 times with the help of Datamate.

6H. POLARIZATION MEASUREMENT

The different techniques, which are used for polarization measurement [5] in the Raman spectrum, may be divided into the three categories. In the first one, natural unpolarized incident radiation is used and the scattered radiation is analyzed in terms of its polarization. In the second one, polarized incident radiation is used but no analysis of scattered radiation is made in terms of polarization. In the third and final one, the incident radiation is polarized and analyses of scattered radiation in terms of polarization are done. Out of the above three techniques, it is the last one that is commonly employed nowadays. In this technique, the incident polarization is kept fixed and the Raman spectra are recorded twice for scattered polarizations parallel and perpendicular to that of the incident radiation which are achieved by properly rotating the analyzer by 90°. Since Ar⁺
laser line is polarized in the vertical direction, the later arrangement is used in the polarization measurements in order to record $I_{||}$ and $I_{\perp}$ components. Thus in order to study the character of polarization of Raman lines of a compound in the liquid state, the arrangement is slightly modified by introducing an analyzer in the path of scattered radiation.

Bringing the instrumental set up to an appropriate condition for the polarization measurements, test runs are taken with CCl$_4$ by scanning the (150-550) cm$^{-1}$ range for both the parallel ($I_{||}$) and perpendicular ($I_{\perp}$) components of the Raman radiation (where $||$ and $\perp$ directions are with respect to the scattering plane). During the test runs, the Raman spectra are recorded with a data step size 0.5 cm$^{-1}$, integration time of 0.5 sec and slit settings at 400:200:200:400 $\mu$M. The polarization of the incident laser line has been carefully adjusted to produce the depolarization ratios $[I_{\perp}/(I_{||} \times \frac{1}{4})]$ of the Raman bands of CCl$_4$ appropriately in the $90^\circ$ scattering geometry. Then $I_{||}$ and $I_{\perp}$ components of Raman radiation of the samples are subsequently recorded without altering the slit settings.

61. RELATIVE INTENSITY CALCULATION

For the measurement of the Raman excitation profiles, the Raman intensity of each band is normalized relative to that for the excitation wavelength at 514.5nm and also the excitation frequency dependence of the intensity of the solvent band, used as internal standard, has been taken into consideration. The relative intensity of a Raman line of wavenumber $\tilde{\nu}$ corresponding to a excitation radiation of wavenumber $\tilde{\nu}_{exc}$ is given by,

$$I_{rel}(\tilde{\nu}, \tilde{\nu}_{exc}) = I(\tilde{\nu}, \tilde{\nu}_{exc}) / I(\tilde{\nu}_{IS}, \tilde{\nu}_{514.5})$$

$$= [I(\tilde{\nu}, \tilde{\nu}_{exc}) / I(\tilde{\nu}_{IS}, \tilde{\nu}_{exc})] \times [I(\tilde{\nu}_{IS}, \tilde{\nu}_{exc}) / I(\tilde{\nu}_{IS}, \tilde{\nu}_{514.5})]$$

$$= [I(\tilde{\nu}, \tilde{\nu}_{exc}) / I(\tilde{\nu}_{IS}, \tilde{\nu}_{exc})] \times ([\tilde{\nu}_{exc} - \tilde{\nu}_{IS}] / (\tilde{\nu}_{514.5} - \tilde{\nu}_{IS}))^3$$

where, all the intensities (i.e. I's) are measured in terms of the number of photons per sec per scan. Thus $\tilde{\nu}^3$ dependence is taken instead of $\tilde{\nu}^4$. $\tilde{\nu}_{514.5}$ is the wavenumber of the excitation radiation of wavelength 514.5 nm and $\tilde{\nu}_{IS}$ is the wavenumber of the solvent band used as internal standard.
SEC. 7 REFERENCES