CHAPTER 2

EXPERIMENTAL DETAILS AND PROCEDURE

2.1 Introduction

In this chapter we describe the various experimental apparatus, arrangements and techniques employed in the studies which constitute the subject matter of the next four chapters. Infrared spectra were studied with a Leitz double beam prism spectrometer covering the range 10,000-420 cm^{-1} and a Polytec Fourier spectrometer operating over the range 20-650 cm^{-1}. Raman spectra were studied with a Cary-81 Raman spectrometer with modified external optics, employing photon counting, and a Spectra Physics He-Ne laser as the light source. A Perkin-Elmer DSC-2 differential scanning calorimeter was used in the thermal studies of phase transitions. A hot stage microscope was employed for the measurement of phase transition temperatures and the study of optical textures.

2.2 Infrared Spectrometers

(a) Near-infrared region

A Leitz Model 081 double beam prism spectrometer[1] employing interchangeable NaCl and KBr prisms was used to obtain spectra in the region 10,000 - 420 cm^{-1} (1 - 25 μm). The transmitted intensity of the sample is directly plotted on a chart whose ordinate is calibrated in percentage transmission. The spectrum is linear in wavelength. The spectral resolution is determined by a choice of slit programs.

(b) Far-infrared region

A Polytec Model FIR-30 Fourier spectrometer[2] was used to obtain spectra in the far-infrared region. This is an interferometric spectrometer operating on the principle of Fourier transform spectroscopy[3] and normally covers the spectral range 20 - 650 cm^{-1} by means of four separate beam splitters. The heart of the set-up (figure 2.1) is a Michelson interferometer with which an interferogram is recorded and Fourier transformed[3,4] in real time to yield the corresponding spectrum. The spectrum is plotted on a chart with percentage transmittance as ordinate and is linear in wavenumber. The real time Fourier transformation and other data processing is effected by an on-line Nova 1200 computer operated via a teletype terminal.

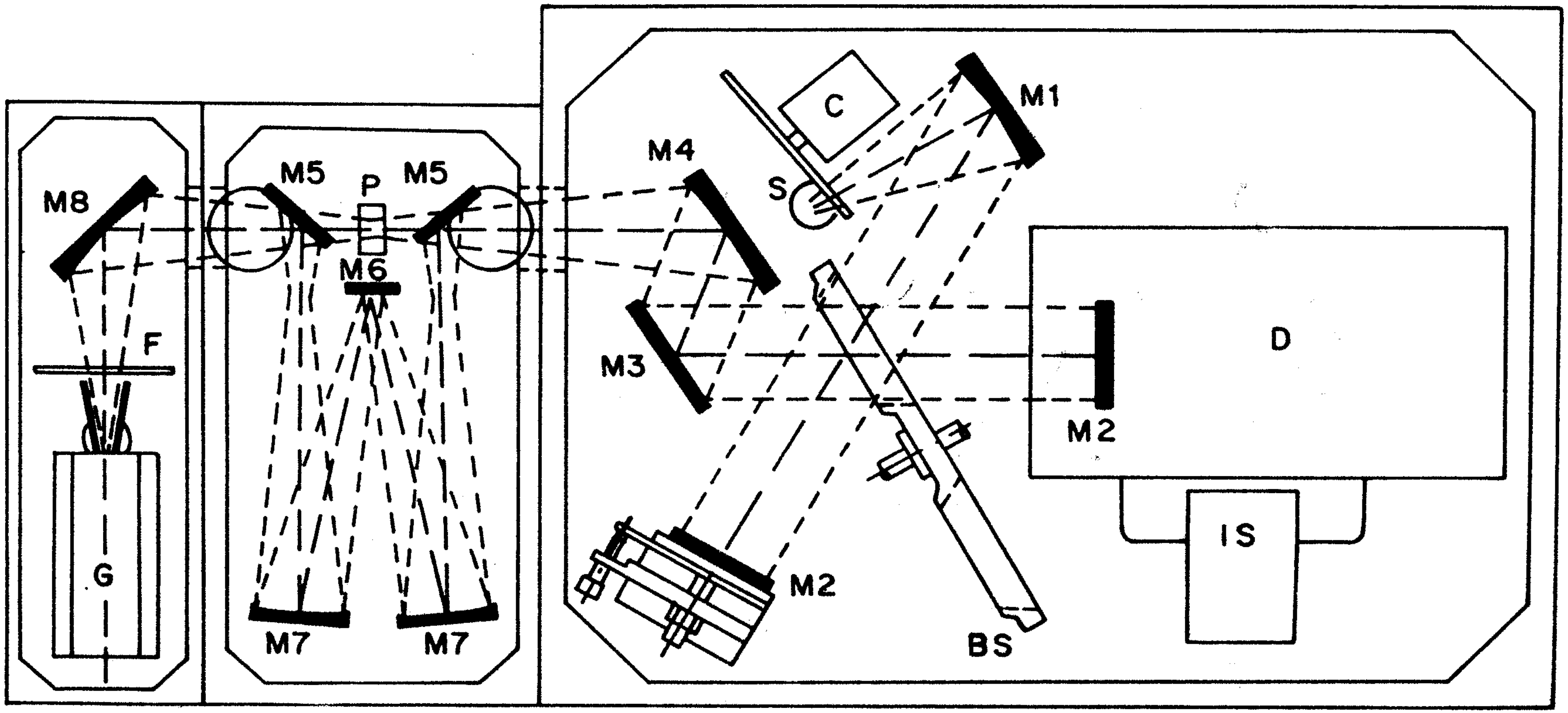
Since this spectrometer is a single beam instrument it is necessary to normalise the spectral data of a sample to those obtained from a separate reference scan with just the empty sample cell in place, keeping all other instrumental parameters unchanged.

Because of the multiplex and throughput advantages[3,5] inherent to this set-up, it is possible to obtain spectra with both good resolution and high

FIGURE 2.1

Schematic optical lay out of the Michelson interferometer system, sample chamber and detector of the Polytec FIR30 Fourier Spectrometer [Reproduced from Polytec Technical Bulletin No.1, 1972].

S	Source
C	Chopper
M2	Michelson Mirrors
M1,M3,M4,M5,M6,M7,M8	- Mirrors
BS	Beam splitter
D	Movable carriage
IS	Moiré fringe system
G	Golay detector
P	Sample in the transmission mode.


M8
F
G
M5
P
M5
M6
M7
M7
M4
M3
C
S
M1
D
M2
M2
BS
IS

signal-to-noise (S/N) ratio in the entire infrared region.

The spectral resolution $\Delta\nu$ of the spectrometer is given by[5]

$$\Delta\nu = \frac{1.21}{2L}$$

where L is the optical path difference between the fixed and movable mirrors in the Michelson interferometer. The resolution employed for the far-infrared spectra reported in this work ranges between 5 and 8 cm^{-1}.

2.3 Raman Spectrometer

A Cary Model 81 Raman spectrometer[6] with modified external optics was used to obtain Raman spectra. This employs a twin-grating, double monochromator for the spectral analysis of scattered radiation over the range of frequency shifts, ±4000 cm^{-1}. A Spectra Physics

Model 125 Helium-Neon Laser[7] was used as source for the excitation of Raman spectra.

Figure 2.2 is a block diagram of the modified Cary-81 external optics set-up. Plane polarised radiation from the He-Ne laser, at a wavelength of 632.8 a, passes through an interference filter F which [redacted]es the plasma lines o[redacted] [redacted] laser. XI#& —— to the sample $ via surface #&&=—— M_1, M_2, M_3 and a short focuss lens L_1. am —— radiation from the sample is collected by lens L_2 and focussed on to the entrance slit of the monochromator by means of a second lens L_3. For polarisation studies, a circular sheet polariser mounted on a rotating holder can be placed between L_2 and L_3.

The analysed radiation is incident on a cooled photomultiplier tube via the exit slit of the monochromator. The output of the photomultiplier is processed by a photon counting system and plotted on a strip chart recorder against the Raman frequency shift.

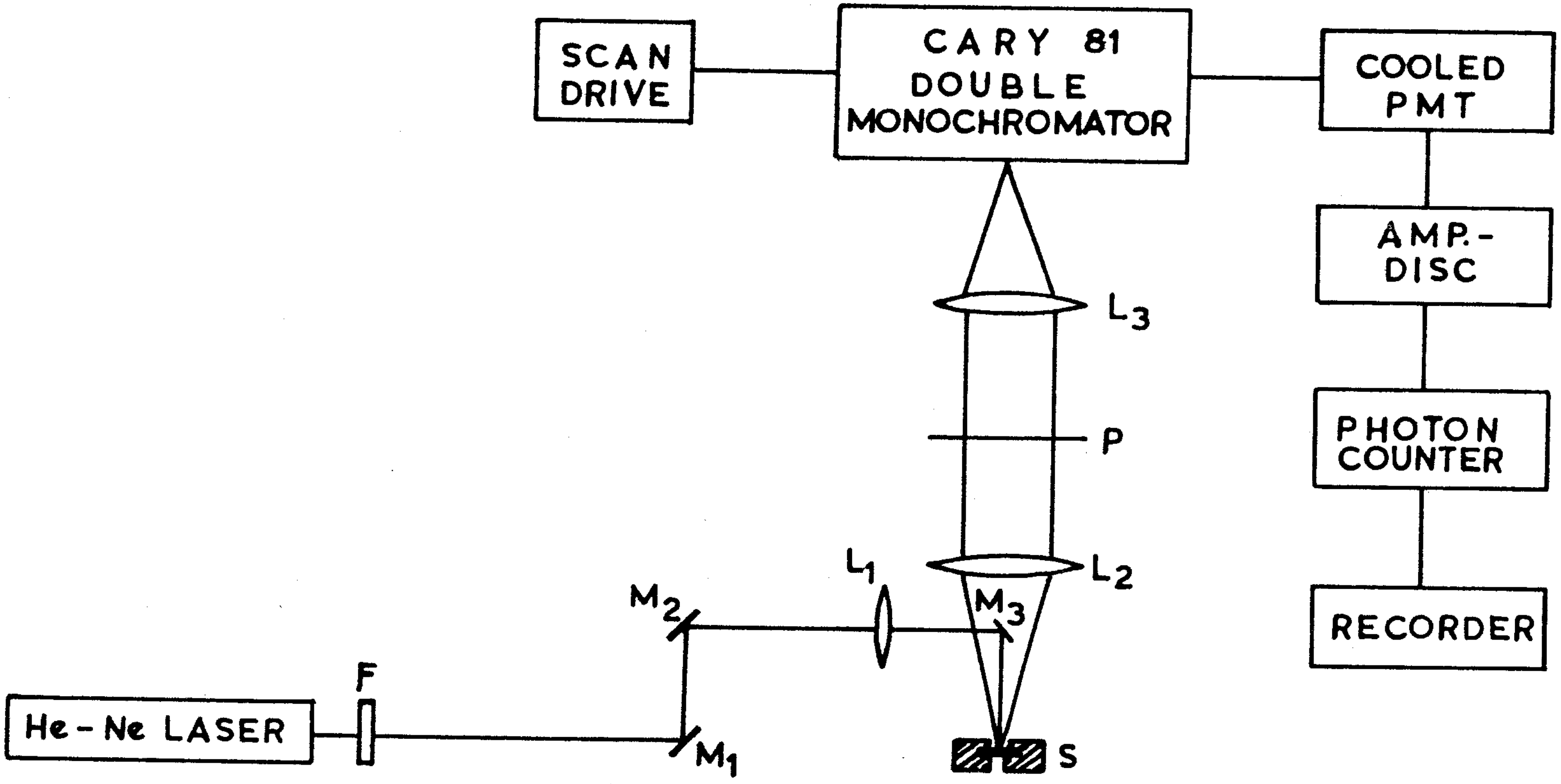


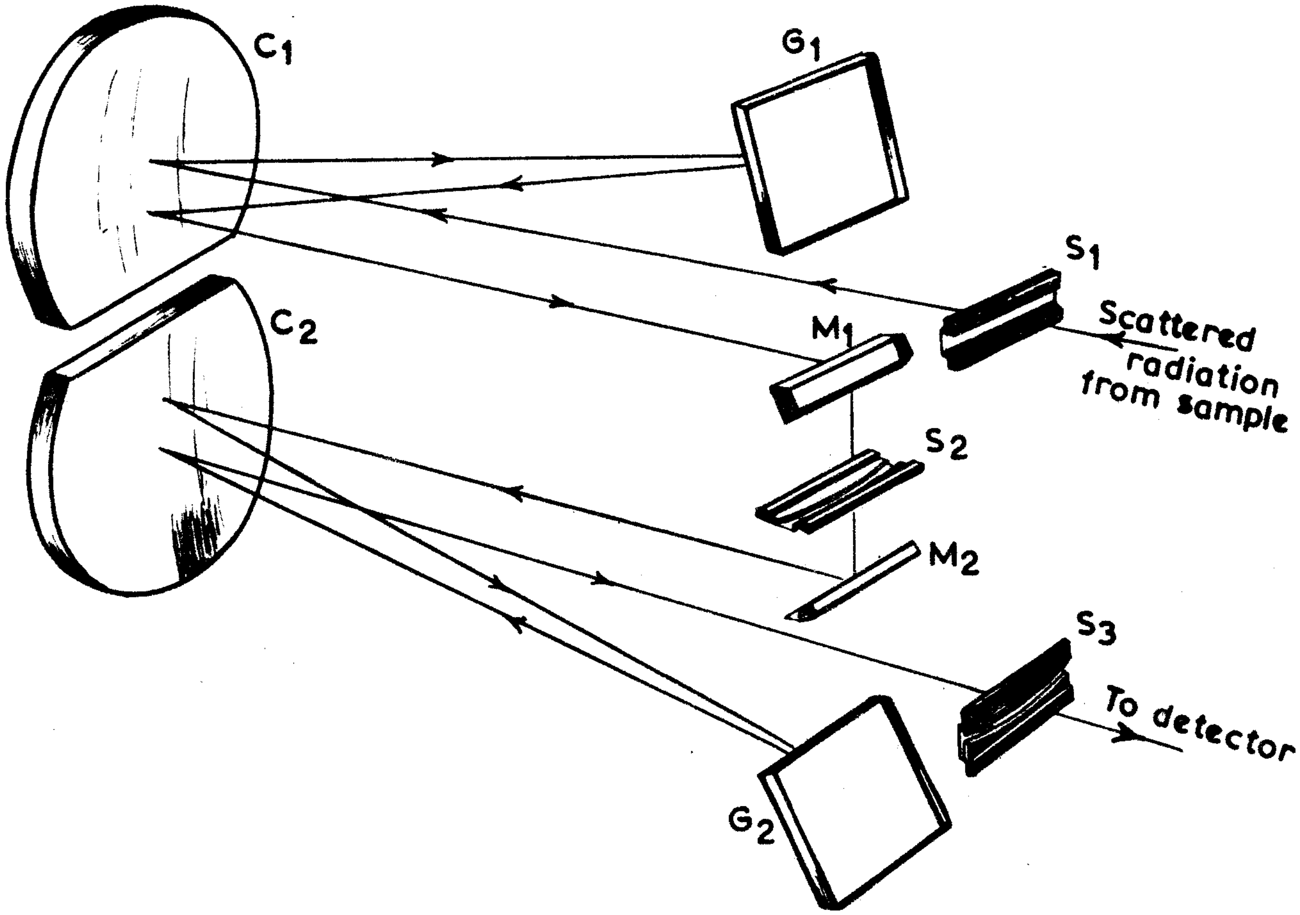
FIGURE 2.2

Block diagram of Cary 81 modified external optics and detector set up.

M_1, M_2, M_3 - MIRRORS
L_1, L_2, L_3 - LENSES
S - SAMPLE CELL
P - POLARISER
F - INTERFERENCE FILTER

Figure 2.2 depicts the back-scattering geometry. It could be easily modified to give a right-angle scattering geometry. In the back-scattering mode the mirror M_3 had to be extremely small so as to maximise the amount of scattered radiation collected by L_2. It was mounted on a pin-head and about 1.5 mm x 1.5 mm in size.

Figure 2.3 shows the lay out of the optical components in the Cary-81 double monochromator. The two collimating mirrors C_1 and C_2 are off-axis spherical mirrors mounted in a Littrow arrangement. The focal length of the monochromator is 1000 mm and its aperture 100 mm x 100 mm. This gives its optics a power of $\sim f/9$. The entrance, intermediate and exit slits are simultaneously variable in width over the range 0 - 1.5 mm (0 - 15 cm^{-1} at 625 nm) and their length fixed at 25 mm. The gratings are ruled 1200 lines per mm and blazed for 500 nm in the first order.



S_1 — ENTRANCE SLIT
S_2 — INTERMEDIATE SLIT
S_3 — EXIT SLIT
C_1, C_2 — COLLIMATING MIRRORS
G_1, G_2 — GRATINGS
M_1, M_2 — MIRRORS

FIGURE 2.3

Diagram of Cary 81 Double Monochromator (Adapted from Cary Model 81 Laser Raman Spectrophotometer Bulletin 181, 1968).

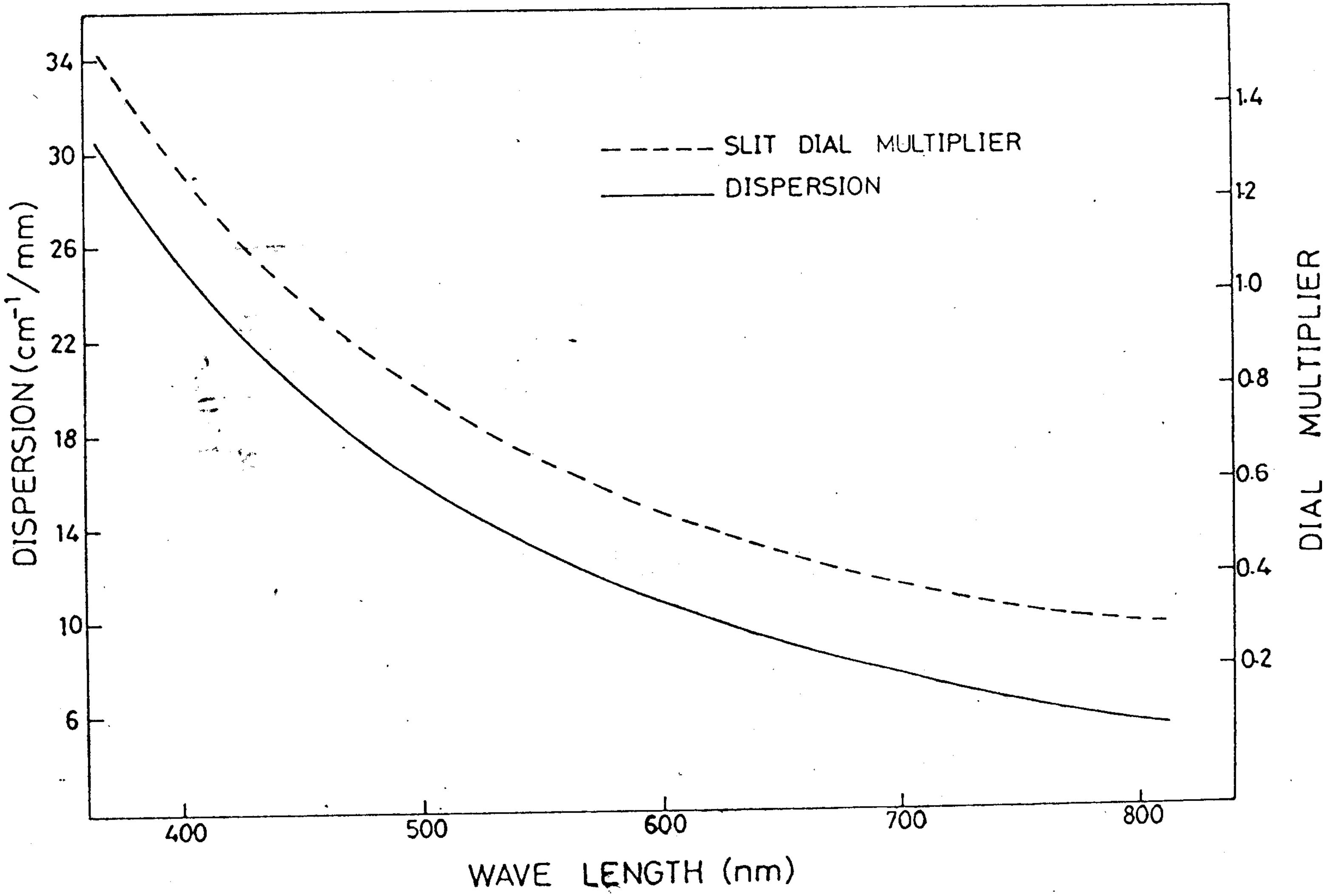
The spectrum is scanned by rotating the two gratings in unison. A linear wave number scale for the scan drive is achieved by employing a cosecant grating drive mechanism. A frequency accuracy of 0.5 cm^{-1} and a reproducibility of 0.1 cm^{-1} are achieved. The wavelength scan mechanism is driven by a synchronous motor through a three-stage gear shift mechanism. Any one of fourteen scan speeds, from 0.25 to 500 cm^{-1}/min, can be employed. The spectrometer gives a maximum resolution of 0.5 cm^{-1} at 632.8 nm.

The wavelength calibration was checked using the known wavelengths of spectral lines from a mercury capillary source in conjunction with the He-Ne laser wavelength.

The dispersion of the monochromator as a function of the wavelength is shown in figure 2.4. The slit dial graduation is 20 cm^{-1} per mm of slit

FIGURE 2.4

Dispersion of the Cary 81 Double Monochromator as a function of the wavelength. The corresponding slit dial multiplication factor is also shown. Slit dial graduation = 20 cm^{-1}/mm.


SLIT DIAL MULTIPLIER
DISPERSION
DISPERSION (cm^{-1}/mm)
34
30
26
22
18
14
10
6
DIAL MULTIPLIER
1.4
1.2
1.0
0.8
0.6
0.4
0.2
400
500
600
700
800
WAVE LENGTH (nm)

width at 450 nm wavelength. At this wavelength the dispersion is 20 cm^{-1}/mm. At any other wavelength the dial reading has to be multiplied by the ratio of the dispersion at that wavelength to the dispersion at 450 nm, to get the actual spectral slit width. This slit dial multiplication factor is also shown in the figure as a function of the wavelength.

While scanning a spectral feature, a limit to the scan speed is set by the spectral slit width employed, the time constant of the photon counter electronics and the recorder pen traverse speed. For a high fidelity, distortion-free recording of the true spectral feature, the time constant is chosen to be typically a quarter of the time spent in scanning the spectral slit width. Thus

$$\text{Max. scan speed} \approx \frac{\text{spectral slit width}}{(4 \times \text{time constant})} .$$

Because of the ruled gratings employed, the monochromator has an unequal response for the two different polarizations (parallel and perpendicular to the slit) of the scattered radiation. The response function is dependent both on the slit width employed and the wavelength of the spectral feature being studied. To determine this, polychromatic light from a small incandescent source, placed at the position of the sample, was analysed by the monochromator after passage through a polariser. The intensities corresponding to the two polarizations of the scattered radiation were measured at the desired frequency (~ 2225 cm^{-1} for the studies reported in this work) and slit width. The ratio of the two intensities, vertical to the horizontal, was used as a correction factor to scale up the depolarization ratios measured.

Table 2.1 gives the monochromator response function at different slit widths corresponding to a Raman frequency shift of 2225 cm^{-1}.

Table 2.1

Cary-81 double monochromator response function at different slit widths corresponding to a Raman frequency shift of 2225 cm^{-1}

Slit width cm^{-1}	Response function $I_{\perp} / I_{\parallel}$
0.8	5.00
1.0	4.77
1.5	4.58
2.0	4.55
4.0	4.44
6.0	4.37
8.0	4.30
9.0	4.25
10.0	4.18
12.0	3.97
15.0	3.84

An RCA 8852 photomultiplier tube (PMT) was used to detect the analysed radiation from the monochromator. It was placed inside a thermoelectrically refrigerated chamber and maintained at about 40 degrees below ambient temperature to reduce the PMT dark noise to acceptable levels. A photon counting set-up consisting of a PAR Model 1120 Amplifier-Discriminator[8] and a PAR Model 1105 Data Converter[8] was employed to process the PMT output.

A Spex DPC-2 Digital Photometer[9] in its photon-counting mode was also employed in the measurements of Raman depolarization ratios discussed in chapter 6. The nature of the digital averaging technique employed in this instrument enabled the determination of integrated intensity of the $- C \equiv N$ Raman bands in the Raman spectra of 7CB and 8 OCB (see chapter 6).

2.4 Differential Scanning Calorimeter

The calorimetric data reported in chapter 5 were obtained with a Perkin-Elmer Model DSC-2

Differential Scanning Calorimeter[10] which combines high calorimetric sensitivity with excellent baseline linearity and repeatability.[11] The sample temperature can be varied between two preset limits at a precisely controlled preset rate with a digital programmer. The thermogram is plotted on a strip chart recorder with a choice of eight full scale sensitivities ranging from 20 to 0.1 mcal/sec.

2.5 Hot Stage Microscopy

Phase transition temperatures were measured to an accuracy of ± 0.2 K using a hot stage microscope. The samples were filled in open-ended flat capillary tubes. The transitions were monitored visually under the microscope. The texture photographs reproduced in chapter 5 were also made with this set-up. For this, the sample was taken in the form of a thin film sandwiched between two glass plates.

2.6 Sample Cells and Sample Preparation

Except for the Raman spectra of ethyl-p-azoxy-benzoate (EPAB) reported in chapter 4, all other vibrational spectra required temperature and phase dependent studies with or without preferential alignment of molecules in the liquid crystalline phase. This called for specially designed sample cells with windows possessing high transmission as well as good thermal and mechanical ruggedness. We now describe the various cells employed, the cell windows and the mode of sample preparation and confinement in each.

(a) Near-infrared studies

NaCl was the window material used in this region. Plates of NaCl, about 50 mm x 25 mm x 5 am in size, were cut from commercially available blanks. They were ground and polished employing a technique[12] perfected earlier in our laboratory. This yields a reasonably flat, scratch-free surface of high ψ —— quality.

Liquid crystal samples were prepared by allowing the mesophase to flow between the windows by capillary action so that a bubble-free thin film was obtained. For materials which are in the solid phase at room temperature, the windows were first heated over a hot plate to a temperature high enough to melt the material. Samples were generally prepared in the nematic phase since many liquid crystalline compounds tend to decompose at higher temperatures in the isotropic liquid phase. The thickness of the sample was set by a mylar spacer of known thickness separating the windows all along their edges. Thicknesses of up to ~ 25 μm were employed.

Homeotropically aligned samples of 7CB and 8 OCB required for the near-infrared dichroic measurements reported in chapter 6 were prepared between specially treated NaCl windows. The window surfaces were first polished and then rubbed in a random manner on a piece of chamois leather. The resultant surfactant coating gave excellent homeotropic alignment not only in the nematic phase of 7CB and 8 OCB but also in the smectic A phase of 8 OCB upon cooling slowly from the aligned nematic phase. The alignment was checked under a polarising microscope.

Solid samples were prepared by cooling the liquid crystalline film between NaCl windows slowly till it solidified. This gives a polycrystalline sample in which the crystallite size keeps the unwanted scattering of radiation reasonably low. Nevertheless the scattering effects of such samples were considerable in the region 5000 - 3000 cm^{-1} as seen from a pronounced baseline slope.

The sample cell was heated to the desired temperature using a variable temperature copper oven[12] shown in figure 2.5. The oven, holding the sample cell in a vertical position, could be placed in the path of the sample beam inside the Leitz double beam spectrometer.

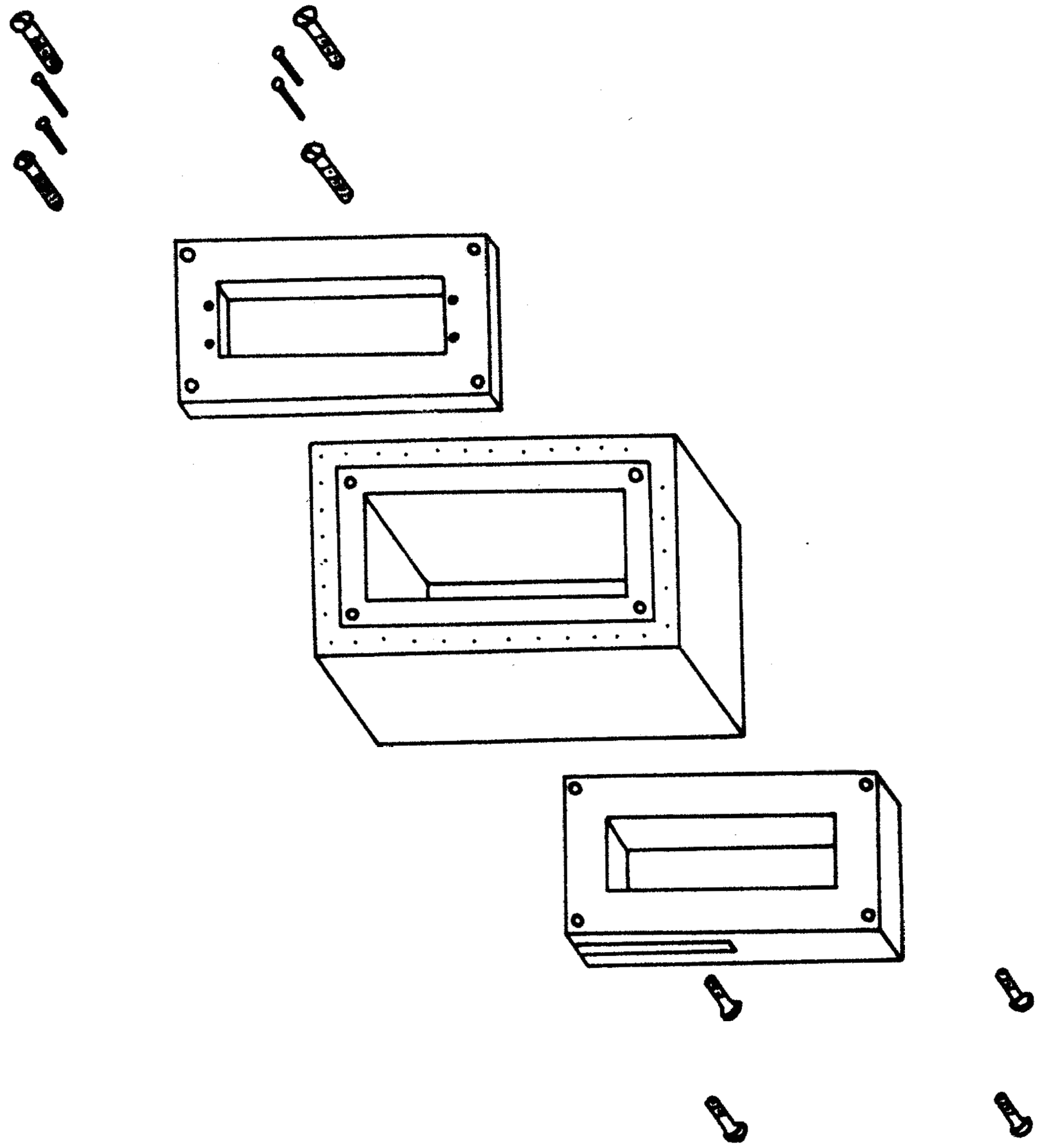


FIGURE 2.5

Exploded view of the sample cell and oven used in the infrared measurements [Reproduced from J.R.Fernandes, Ph.D. Thesis, 1978].

(b) Far-infrared studies

Alpha-quartz windows with polished surfaces were used in the range 20 – 250 cm^{-1}.

In the interferometer of the Polytec spectrometer, the radiation is partially polarised W a result of reflection from the beam splitter. The vertical polarisation is ~ 1.6 times as intense as the horizontal polarisation. Alpha-quartz has a strong absorption band at 128 cm^{-1} which is also polarised in a plane normal to the C-axis. To minimise the effects of this absorption, the windows were cut with principal axes lying in the plane and the C-axis was kept along the vertical whenever unpolarised spectra were obtained.

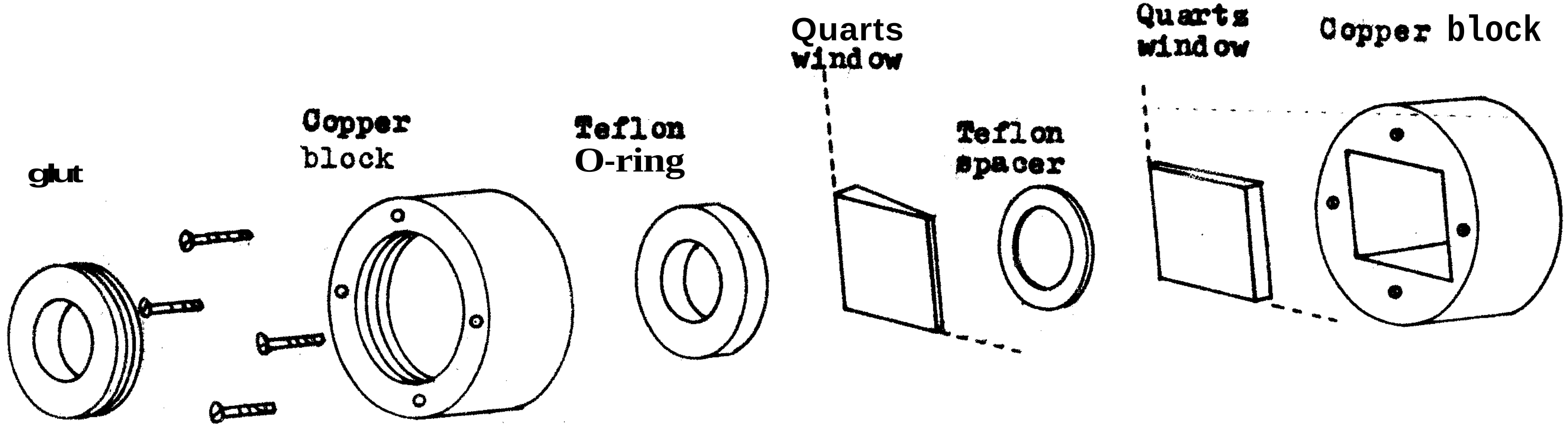
Circular alpha-quartz windows of diameter 25 mm and thickness 1.2 mm were used for confining randomly oriented samples. To eliminate interference effects, the windows were wedged at an angle of ~ 1°. The effective sample aperture was 15 mm which is also the diameter of the beam when it is imaged at the position of the sample.

For the dichroic spectra of PAA reported in chapter 3, 25 mm x 25 mm square alpha-quartz windows cut with the c-axis lying parallel to one edge were used. They were rubbed parallel to the c-axis and the nematic liquid crystal was allowed to flow between them along the direction of rubbing. The resultant sample was aligned homogeneously (to the degree the alignment was achievable) parallel to the c-axis.

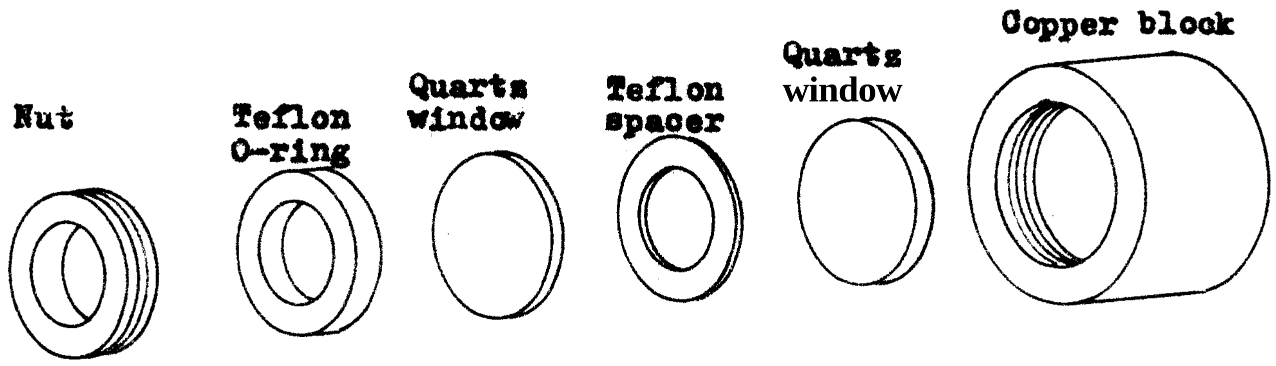
As noted earlier, the radiation from the interferometer is partially polarised, with the vertical component of the electric vector being more intense. To exploit this feature and obtain spectra with better signal-to-noise ratios, vertically polarised radiation was used in the dichroic study of PAA. The sample cell was rotated so that the c-axis of the window pair and hence the direction of alignment of the sample, was kept either parallel or perpendicular to the electric vector of the incident radiation. This procedure also ensured that possible birefringence effects arising from the alpha-quartz windows were greatly minimised.

Since the sample chamber of the FIR spectrometer is maintained in vacuum the spacer between the sample cell windows should be able to contain fluid samples even in high vacuum. Spacers punched out of a teflon tape of thickness ~ 110 µm were found best suited for this purpose.

For temperature dependence studies, the far-infrared cell windows were contained in a copper block as shown in figure 2 A continuously threaded nut facilitates an effective sealing of the cell to keep the sample confined within it even in high vacuum. The whole assembly is placed inside a variable temperature cell with vacuum-sealed lead wires for its



A. Dichroic measurements



B. General measurements

FIGURE 2.6: Exploded view of the sample cell and mounting assembly used in the far-infrared measurements [Reproduced from J.R.Fernandes, Ph.D.Thesis, 1978].

variable temperature controller (Model TC-30) and thermocouple. The desired temperature can be preset and is achieved within 10 - 15 minutes.

(c) Raman studies

The Raman spectra of EPAB reported in chapter 4 were obtained at room temperature with finely powdered sample taken in a capillary tube. The right-angle scattering geometry was employed.

The Raman depolarisation ratios which constitute the raw data for the measurements of order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ reported in chapter 6 required thin aligned samples of the liquid crystalline material in different orientations witch respect to the polarisation of the incident radiation (see figure 6.2, chapter 6). The sample was confined between a pair of optically flat, polished, fused quartz windows of 10 mm x 10 mm x 1.2 mm size. A mylar spacer of ~ 100 µm thickness was used. Homogeneous alignment was obtained by vacuum coating the window surfaces with a very thin layer of silicon oxide at an angle of ~ 30° to the surface. Homeotropic alignment was obtained by evaporating from the surfaces a dilute solution of cetyl trimethyl ammonium bromide in chloroform and then gently rubbing the coated surface randomly with A wad of tissue paper so as to remove any visible traces of the surfactant. The aligned sample was prepared by letting the nematic fluid flow between the windows which were preheated' to the required temperature. Both modes of alignment were checked between crossed polarisers under a microscope.

The fused quartz windows holding the sample were placed in a specially designed copper block as shown in figure 2.7. The teflon O-ring and the continuously threaded nut facilitate application of a gentle pressure on the sample cell so that the sample is well confined. A copper screw can be turned inside the nut so that the small front surface mirror at the tip of the screw

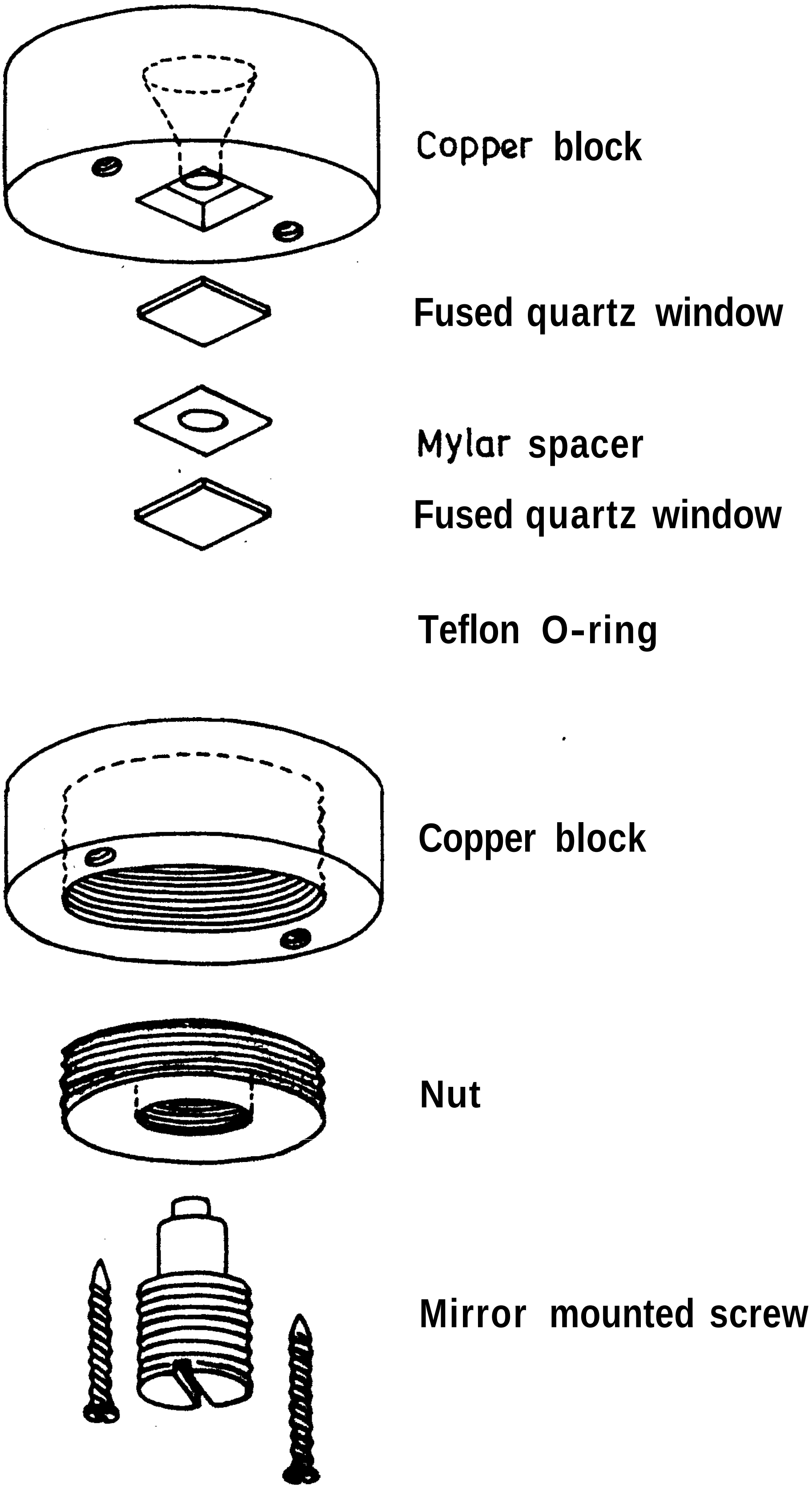


FIGURE 2.7: Exploded view of sample cell and mounting assembly used in Raman measurements.

barely touches the quartz window surface. This enables a double passage for the incident laser light through the sample, thus substantially increasing the intensity of the Raman scattered radiation. The sample had a circular cross-section of diameter ~ 6 mm. The illuminated area however was much smaller. The entire assembly was placed inside a variable temperature cell made up of a cylindrical copper block wound on the outside with nichrome wire and insulated from the metal by a strip of mica. The heater assembly was surrounded by a metal jacket, the intervening space having been filled with plaster of paris for thermal insulation. This was in turn imbedded in a cylindrical block of aluminium mounted on a thick horizontal strip of bakelite for thermal insulation between the sample oven and the base of the external optics compartment.

To change the direction of molecular alignment in the homogeneously aligned sample with respect to the polarisation of the incident laser light, it was found convenient to rotate the entire sample chamber within the outer cylindrical copper block.

2.7 Temperature control and measurement

(a) Infrared studies

The infrared sample cell has a large sectional area of the windows, thus giving rise to a thermal gradient across the sample. The sample temperature at the centre was lower (by about 0.2 K at say 350°K) than that at the edges in contact with the oven. The temperatures quoted for all the infrared measurements are estimated mean values.

A calibrated chromel-alumel thermocouple was used to measure the temperature. A thermal lag whose magnitude increased with temperature was always found between the sample and the thermocouple. A correction for this lag was determined in the vicinity of the liquid crystal - isotropic liquid transition

T_c, by monitoring the transition through the accompanying spectral changes wherever these were significant. Using the value of T_c determined previously from thermal microscopy, the correction to the measured T_c could be determined. This correction was 1 - 1.5 K for the range of T_c values encountered in our studies. The corrected temperatures are estimated to be accurate to within ±0.5 K.

(b) Far-infrared studies

The control and measurement of temperature in the far-infrared cells were accomplished using a pre-calibrated copper-constantan thermocouple in conjunction with a temperature controller. At least 15 minutes were allowed for the sample to attain thermal equilibrium after the controller indicated that the preset temperature had been attained. The temperatures measured are accurate to within ± 1 °K and temperature fluctuations were within 0.5 K.

(c) Raman studies

Control and stability of the sample temperature in the Raman spectral studies were achieved in a manner similar to that in the infrared studies. Because of the small exposed area of the sample cell windows there was no detectable thermal gradient in the sample. However, there was a thermal lag of ~0.5 K between the sample and the chromel-alumel thermocouple. This was determined and corrected for in a manner similar to that employed for the near-infrared cell. The temperatures reported are accurate to within ± 0.25 K.

2.8 Sample Purity

The compounds of the PAA Series used in the near and far-infrared studies (chapters 5 and 3) were obtained from Eastman Kodak Co. and were purified further by column chromatography followed by recrystallisation in an analar grade solvent and finally vacuum dried.

EPAB was also obtained from Eastman Kodak Co. and was used without further purification.

The nematic-isotropic transition temperature is usually a sensitive measure of the purity of liquid crystalline compounds[13] and this property was used to ascertain the purity of the samples used. The transition temperatures of all the samples agreed with the values reported in the literature well within acceptable limits. Whenever necessary, the transition temperatures were rechecked after an experiment to ensure that it had not degraded during the experiment.

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