

CHAPTER 2

EXPERIMENTAL APPARATUS AND PROCEDURE

2.1 Introduction

Infrared spectra can be obtained using either dispersive spectrometers or interferometers. Conventional spectrometers equipped with incandescent sources and a prism or grating as the dispersive element are generally adequate *for* most applications in the range $10,000\text{--}400\text{ cm}^{-1}$. At lower frequencies, the intensity available from such sources becomes quite weak. Hence in the far-infrared region, dispersive spectrometers generally yield spectra with rather poor signal-to-noise (S/N) ratio. This problem is especially severe when spectra with high resolution are needed.

It is now well known that this limitation can be overcome to a considerable extent by the technique of Fourier transform spectroscopy.¹ The Michelson interferometer is the basic component of an infrared Fourier spectrometer. Thanks to the multiplex and throughput advantages inherent to the Michelson interferometer, it has now become possible to obtain superior spectra with both good resolution and S/N ratio in the entire infrared region. It is also worth noting some other advantages

which arise due to the basic principle of Fourier transform spectroscopy itself:

- i The problem of stray radiation is largely avoided as one relies only on *the* intensity modulations generated by the interferometer for obtaining the spectrum.
- ii Overlapping of radiation from different regions of the spectrum, as encountered with the different orders of diffraction produced by a grating, is eliminated.
- iii Path differences in the interferometer can be controlled and measured to very good accuracy; this in turn leads to excellent frequency accuracy in the spectrum. The often substantial calibration errors that are characteristic of dispersive spectrometers are thus automatically reduced.

Extensive discussions on the theory and practice of Fourier transform spectroscopy are available in the literature.¹⁻³ The practical aspects relevant to our equipment will be briefly dealt with in the course of the following description of the two infrared spectrometers used in this work.

2.2 Spectrometers

(a) Leitz double beam prism spectrometer ⁴ (Leitz Model 081): This is a conventional double beam dispersive spectrometer equipped with interchangeable NaCl and KBr prisms. The former covers the range $10,000-667\text{ cm}^{-1}$ while the latter is used in the range $769-420\text{ cm}^{-1}$. The optical and electronic layout of the instrument is shown in Fig. 2.1. The source of radiation is a Nernst glower. The incoming beam is divided into two equal parts, as is characteristic of any double beam spectrometer, and the two beams are chopped and transmitted alternately by the rotating semicircular mirror M4. After being focussed on the entrance slit S1 by the field lens L, the radiation is first collimated, than dispersed by the Littrow system comprising of the prism P and mirror LM, and finally focussed on the exit slit S2 of the monochromator. It is then deflected by M6 on do the collecting mirror C3 which focusses the radiation on a vacuum thermocouple T.

The wavelength is scanned by rotating the Littrow mirror. Automatic scanning is facilitated by the motor TM. The slits S1 and S2 are coupled to the Littrow mirror, and their width varied according to a preset slit program so as to keep the energy falling on the detector constant throughout the spectral range. The deflectox mirror M6 is arranged so that *for* frequencies lass than 735 cm^{-1} ,

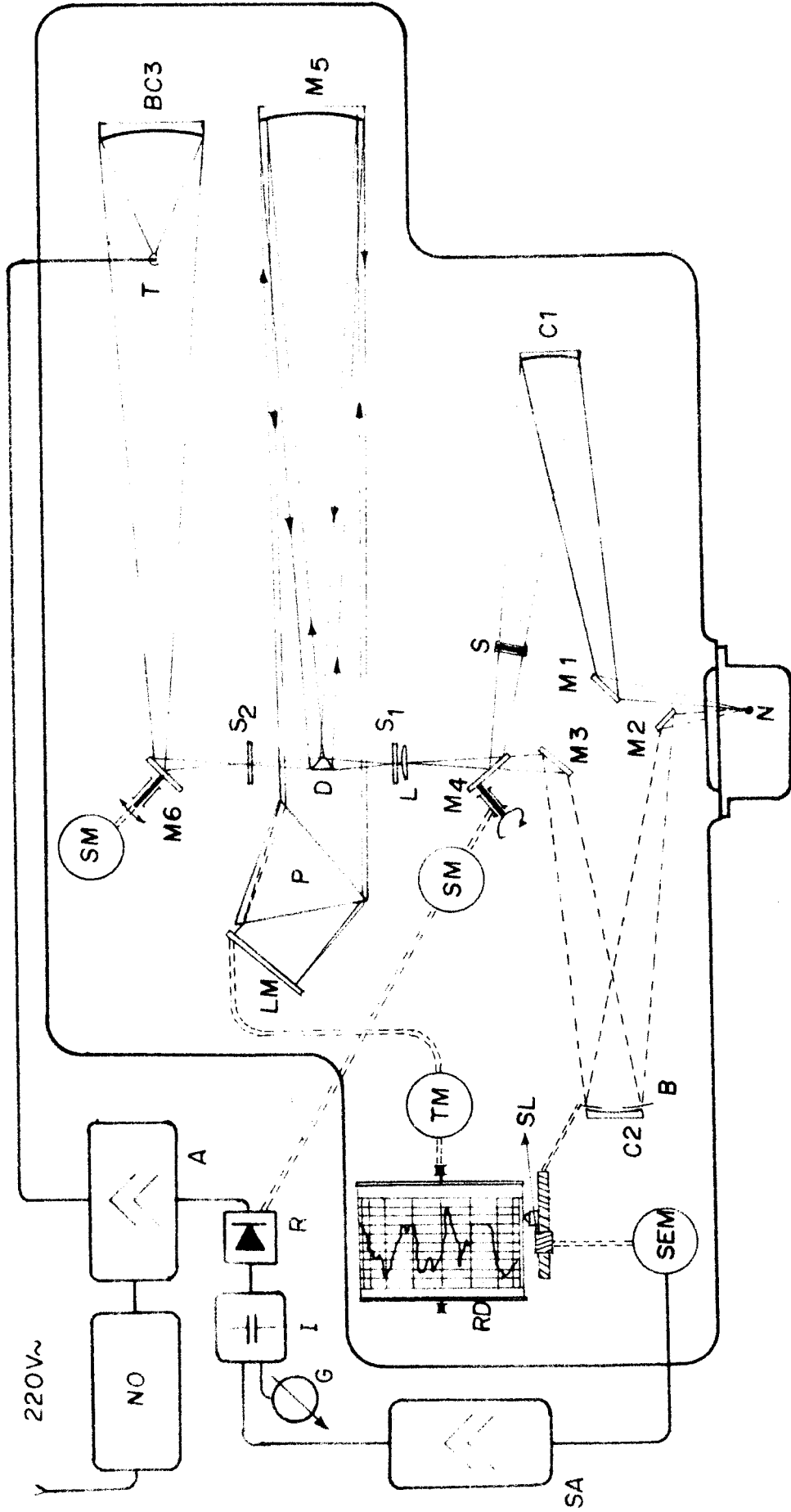


Figure 2.1: Schematic diagram of the electronic and optical lay-out of the Leitz Model O81 Prism Spectrograph. [Reproduced from Infrared Spectrograph Operational Manual, Ernst Leitz GmbH, West Germany.]

the polished reflecting surface is automatically replaced by a matted glass surface using the change over motor CM. This serves to eliminate scattered radiation of shorter wavelengths.

When the two beams of light are of unequal intensity, say, due to absorption by the sample S at any given wavelength, the detector generates a difference signal at the chopping frequency. This signal is amplified by A which is tuned to the chopping frequency. It is then rectified by R which is phase-locked to the rotating mirror M4. The rectified signal is smoothed using a variable time constant and is displayed on the galvanometer G. The direction of deflection of the galvanometer needle depends on which beam has the greater intensity, and when the two beams are of equal intensity, there is no deflection*. The signal is also fed to the servoamplifier SA which determines the directionality of the signal and triggers the servomotor SEM. This drives the diaphragm B in front of the mirror C2 so as to increase or decrease the aperture of C2 and thereby equalise the intensity in the two beams. The extent of opening of the diaphragm is determined by the attenuation in the sample beam. By means of a stylus SL coupled to the servomotor, the transmitted intensity of the sample is directly plotted on a chart* whose ordinate is calibrated in percentage transmission. The chart drum RD

is coupled to the wavelength drive. The latter can be operated at different scan speeds. The wavelength scale on the chart, which is linear in wavelength, could also be expanded by a factor of 3 using a system of gears, when necessary, to facilitate accurate measurement of lineshapes.

The sample cell is placed at S. A reference cell may also be placed in the reference beam after M3 in order to compensate for absorption due to the cell windows or the solvent employed.

The spectral resolution as a function of wavelength for the slit program used in all our measurements is shown in Fig. 2.2.

(b) Far-infrared Fourier spectrometer⁵ (Polytec Model FIR-30): This instrument normally operate@ over the range 20-650 cm^{-1} . It is centered around a Michelson interferometer wherein the path difference is varied by driving the movable mirror in a slow, continuous manner. In order to optimize the intensity transmitted by the beam splitter over the entire usable range, a choice of four beam splitters with overlapping spectral ranges is available.

The schematic optical Layout is shown in Fig. 2.3.

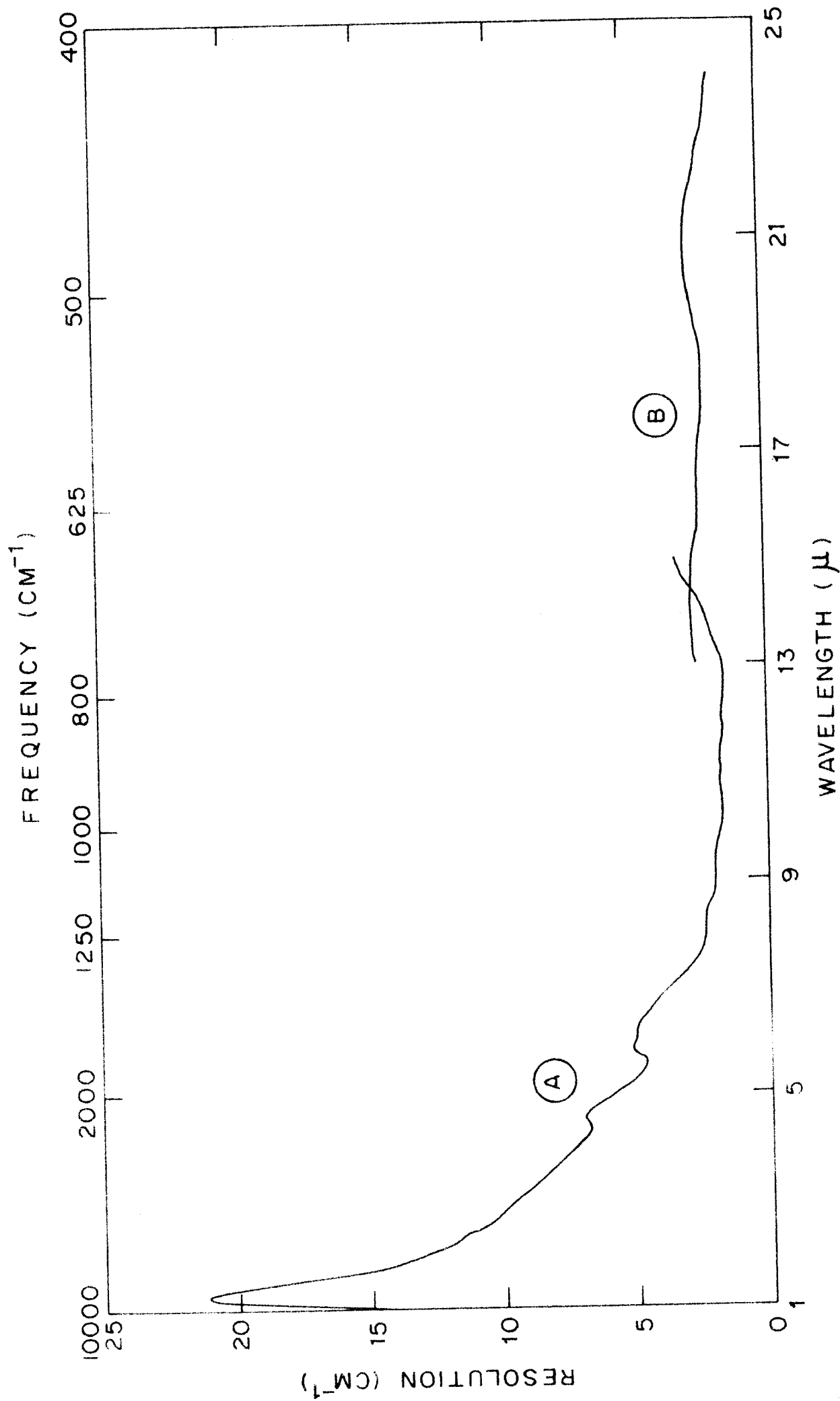


Figure 2.2: Spectral resolution of the Leitz Infrared Spectrograph as a function of wavelength in the two spectral ranges used. (A) NaCl prism (slit program 3), (B) KBr prism (slit program 5).

The source of radiation S is a high pressure mercury arc lamp and the radiation is chopped by the chopper C. M1 is an off-axis paraboloidal mirror which collimates the beam and directs it on the beam splitter BS at an angle of incidence close to 30° . Of the two Michelson mirrors M2, one is the fixed mirror; the other one is mounted on a movable carriage D, the displacement of which is monitored by a Moiré fringe system IS. The recombined beam enters the sample chamber via the plane mirror M3 and an off-axis paraboloidal condenser M4. After passing through the sample placed at P, it is focussed by the toroidal mirror M8 on to the Golay detector G. A suitable filter F is placed in front of the Golay detector in order to eliminate any unwanted high frequency radiation. The mirrors M5 and M7, which are not used in transmission measurements, may be swung into the optical path for measuring reflectivities of samples placed at M6.

The beam splitter consists of four prestretched polyethylene terephthalate films of different thicknesses mounted on a support frame. Corresponding to any given beam splitter a separate high frequency cut-off filter is positioned in front of the detector. For a given cut-off frequency, ^{the} interferogram data must be sampled at least at twice the cut-off frequency, in accordance with the sampling theorem. The beam splitter thicknesses, their

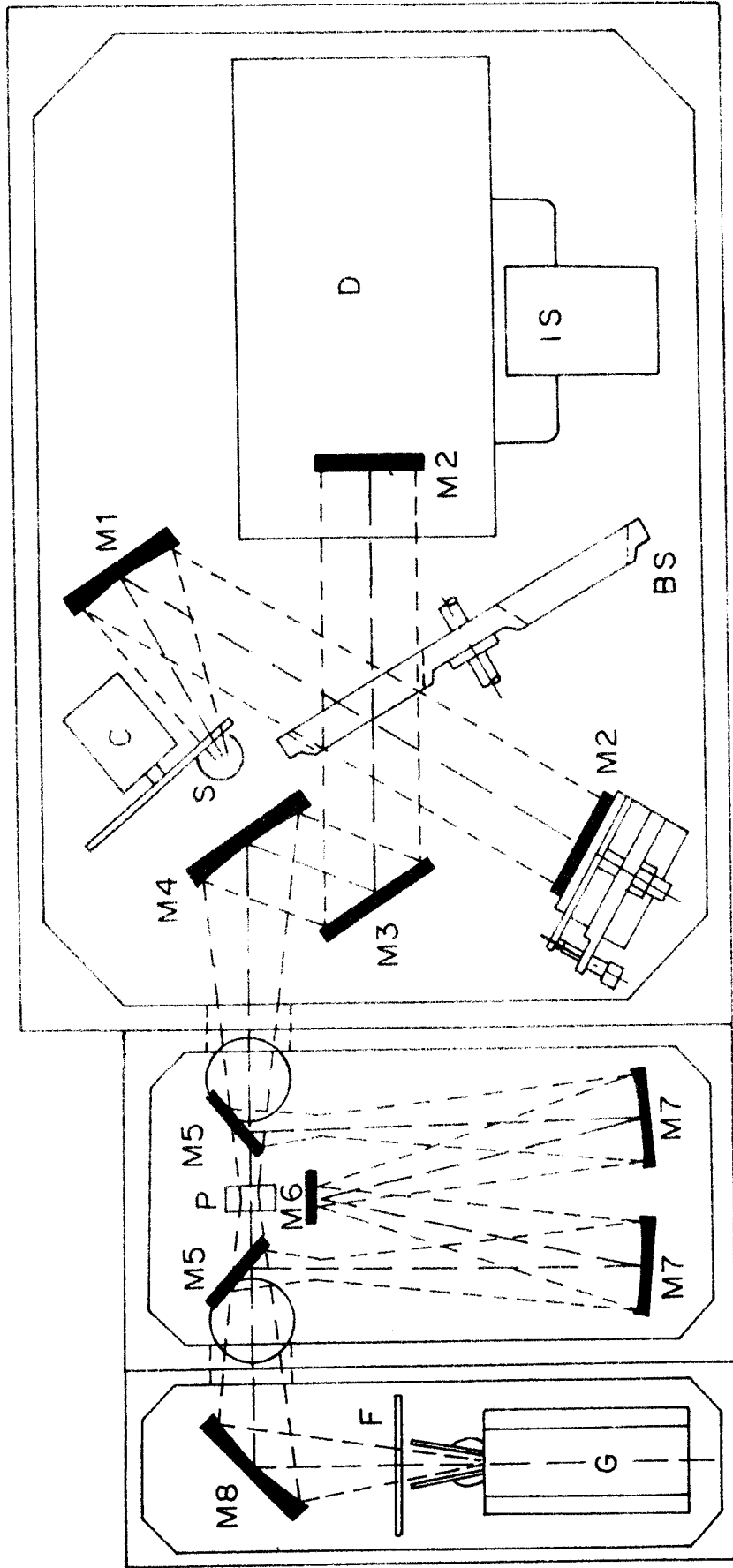


Figure 2.3: Schematic optical layout of the Michelson interferometer system of the Polytec
 FIR 30 Fourier spectrometer. [Reproduced from Polytec Technical Bulletin. No.1, 1972]

transmission ranges, out-off filter characteristics and the corresponding sampling intervals are given in Table 2.1.

Table 2.1

| Spectral Range No. | Effective Wavenumber range (cm^{-1}) | Beam Splitter thickness (μm) | Low pass filter combination | Sampling Interval (μm) |
|--------------------|---|---|--|-------------------------------------|
| 1 | 200-650 | 2.5 | black polyethylene | 5 |
| 2 | 50-450 | 6 | black polyethylene + 2 mm clear polyethylene | 5 |
| 3 | 20-180 | 15 | black polyethylene + 3 mm teflon | 10 |
| 4 | 20-55 | 50 | black polyethylene + 2 mm crystal quarta | 20 |

All four beam splitters are mounted on a common wheel which can be rotated by an attached motor. Using external controls, it is thus possible to position any beam splitter in the path of the radiation. A similar arrangement facilitates the selection and positioning of the corresponding filter in front of the detector*

In order to eliminate the absorption due to atmospheric water vapour, the interferometer, sample and detector chambers are all evacuated by a rotary pump. The

resultant vacuum is typically between 100 to 200 millitorr.

The detection and data processing systems are shown schematically in Fig, 2.4. The detector output is amplified and synchronously rectified, the reference signal being generated at the chopper by a photocell arrangement. It is then smoothed to give an analog DC signal proportional to the interferogram intensity. The signal is also digitized by an analogue-to-digital (A/D) convertor which is triggered by the Moire fringe system at preselected intervals in optical path difference. This digitized interferogram is Fourier transformed in real time by a dedicated NOVA 1200 minicomputer. The evolving spectrum could be displayed on a storage oscilloscope and the final spectrum plotted on a strip chart recorder. It is also possible to obtain a record of the interferogram data on punched paper tape using a model ASR 33 teletype.

The entire system operates effectively as a single beam spectrometer. A conventional double beam spectrum can, however, be obtained by normalizing the spectral data of a sample to that obtained from a separate reference scan with the empty cell in place.

(i) Resolution and apodization: All the spectra were computed without the use of any apodizing function. This

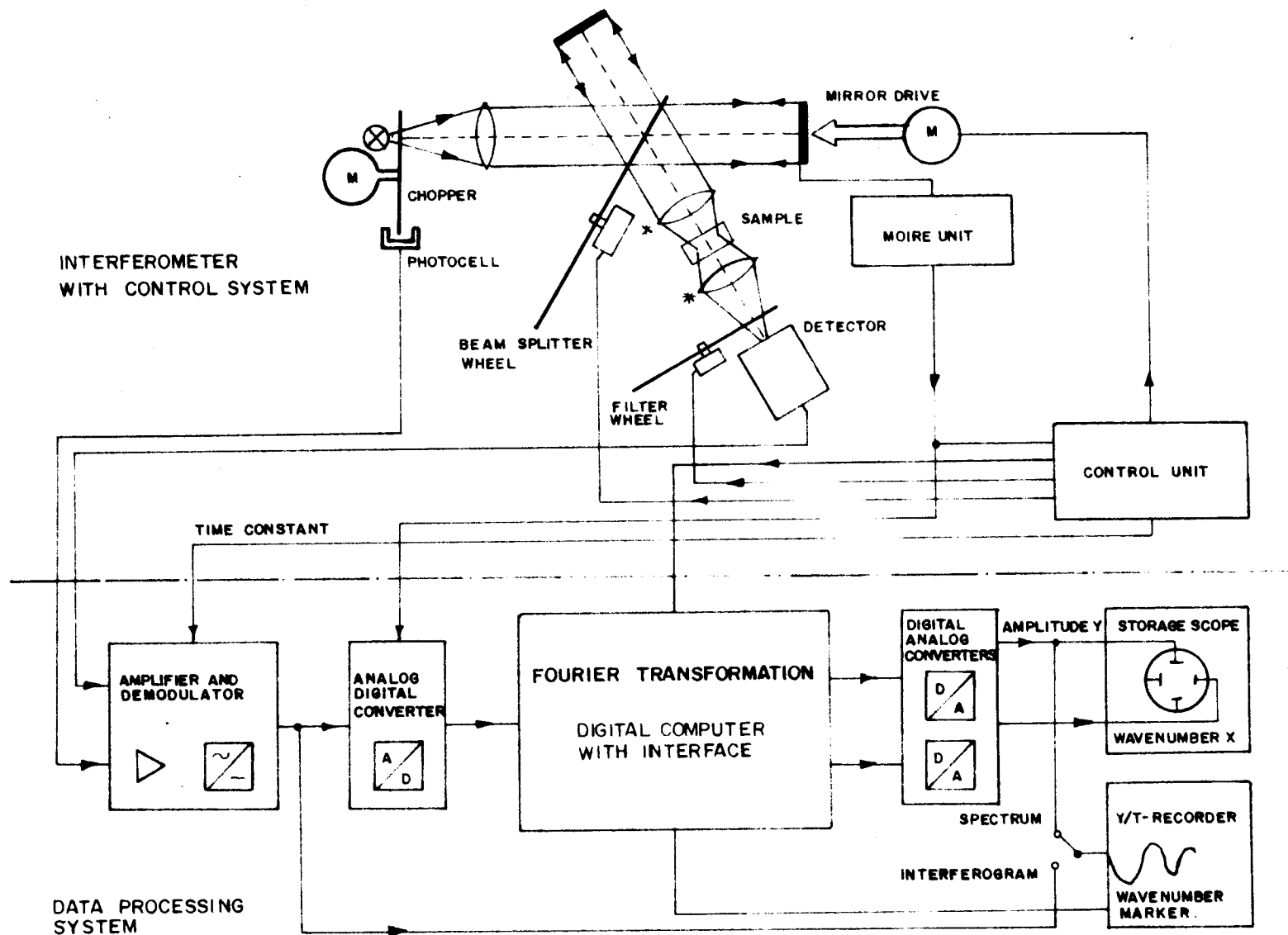


Figure 2.4: Block diagram of the electronic control and data processing system of the Polytec FIR 30 Fourier spectrometer. For simplicity, lens-type optics have been drawn in for the interferometer. [Reproduced from Polytec Technical Bulletin, No.1, 1972]

was because in all the samples studied here, the absorption bands were usually broad enough to render any apodization unnecessary. The spectral resolution, $\Delta \nu$ in cm^{-1} , corresponding to an optical path difference of L cms is hence given by¹

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

Typically, the resolution employed for most of the spectra varied between 2.5 and 6 cm^{-1} .

(ii) Correction for phase error: As the interferogram is, in principle, symmetric about the central peak, a one-sided scan is sufficient for computing the spectrum. However, this presumes that the first data point exactly coincides with the actual peak of the interferogram. In practice, this is almost never the case and this is the origin of the phase error. The Polytec interferometer is provided with an externally operated mechanical adjustment of the fixed mirror to compensate for this. This permits the user to actually shift the peak of the interferogram within a small range until it coincides nearly exactly with one of the points of the grid where the Moiré fringe system gives a the trigger signal for digitizing the data. When this adjustment is satisfactorily completed, the two data points on either side of the peak should be of almost equal intensity. The actual experiment is always commenced after: the mechanical phase correction is carried out

in this manner. Any residual phase error is then corrected by the computer itself. This is done by fitting the apparent peak intensity and the two data points on either side of it to a parabola; the resultant fit determines the necessary phase and intensity correction to the apparent; peak of the interferogram.

As the phase correction is carried out in real time, it is necessary to scan the interferogram on only one side, except for a very short stretch on the other aide to facilitate the phase correction procedure.

(iii) Computer and soft ware: The Nova 1200 computer executes the necessary phase correction, Fourier transformation of the interferogram data in real time and calculation of double beam spectra. Input data required for spectral computations are fed to the computer via the teletype. The computer controls all input and output operations concerning interferogram and spectral data. The requisite program for all these operations is available on paper tape as a standard accessory to the spectrometer.

2.3 Preparation of samples

Of specific interest in the study of vibrational spectra of liquid crystals in their various phases is the temperature dependence of the spectra. It is therefore necessary to be able to confine liquid crystals in

appropriate sample cells, whose temperature may be varied and controlled to the required precision.

Samples were prepared in a sandwich configuration, between two windows separated by a spacer. The windows are chosen so that they have good transmission in the frequency region to be studied. Mylar spacers were used for near infrared studies. For the far-infrared region, as the sample chamber has to be evacuated, it is necessary to have a spacer which is able to contain even fluid samples under high vacuum. It was found that spacers cut out of teflon tape were ideal for this purpose.

Liquid crystal samples were prepared by allowing the mesophase to flow between the windows by capillary action, so that a bubble free film was obtained. For substances which are solids at room temperature, the windows were first heated to the melting point of the material. Since the materials may decompose at higher temperatures, samples were generally prepared in the nematic phase,

Homeotropically aligned samples for near infrared measurements were prepared between specially treated NaCl windows. The windows were first polished as described further below. The polished surfaces were then rubbed in a random manner on chamois leather. Our experience shows that the resultant surfactant coating imparted by chamois leather favours the homeotropic alignment of many smectic A

and nematic liquid crystals. The nematic liquid crystal was allowed to flow between the surfaces treated in such a manner. Samples prepared following this procedure showed good extinction under crossed polaroids. On cooling below the nematic-smectic A transition the samples continued to maintain their alignment in the smectic A phase also.

Solid samples could be prepared by either of two methods. In one, the sample in the liquid crystalline phase is cooled slowly till it solidifies. This gives a polycrystalline sample where the crystallite size is typically large enough to reduce the scattering of radiation. The scattering effects of samples prepared in this manner are however considerable in the very high frequency range of $10000-4000 \text{ cm}^{-1}$.

In the other method, the sample is prepared using finely ground powder which is subsequently sieved to eliminate particles larger than $\sim 40 \mu$. A fairly uniform layer of the powder is then sandwiched between the windows. This method yields satisfactory far infrared spectra at frequencies below 200 cm^{-1} . The scattering losses are minimized in this case because the typical particle size is smaller than the wavelength of the radiation,

For near infrared studies spacer thicknesses up to 25μ were used. Samples with a thickness less than $\sim 3 \mu$

could be prepared without using any spacer. For far infrared studies, the spacer thickness was between 50-100 μ .

2.4 Cell windows

For temperature dependent studies, the cell windows must possess high transmission as well as good thermal and mechanical ruggedness. No single material is available which has uniformly good transmission over the entire infrared region. It was however possible to cover the region of 10000-20 cm^{-1} with four different materials.

NaCl transmits from the visible region down to about 670 cm^{-1} while KBr is transparent down to 400 cm^{-1} . Together they cover the entire spectral range offered by the Leitz spectrometer. NaCl is generally preferred as it is thermally and mechanically more rugged and it was therefore used in all the measurements in the near infrared region from 10000 to 670 cm^{-1} .

Platen of NaCl, 53 x 28 x 5 mm in size, were cut from commercially available blanks.⁴ After preliminary grinding using a slurry of fine grade carborundum (#600) in a saturated solution of NaCl in distilled water, they were polished on chamois leather which was held taut on a glass plate. Red rouge was used as the polishing agent and a saturated solution of NaCl in distilled water served

as the lubricant. This method yields reasonably flat, scratch-free windows. The surface quality was checked by observing the quality of a reflected image. A well polished surface shows a sharp image of the object over the entire area. The method of polishing KBr windows was identical except that a saturated solution of KBr in distilled water was used as the lubricant during both grinding and polishing.

Diamond windows were used in the range $250-650 \text{ cm}^{-1}$. They were approximately circular in shape with a diameter of about 15 mm and their surfaces were already polished when obtained. An effective sample aperture of 10 mm diameter was attainable with these windows,

alpha-quartz windows were used in the range $20-250 \text{ cm}^{-1}$. Their surfaces were already polished when initially obtained. For randomly oriented specimens, circular windows of 25 mm diameter and a thickness of 1.2 mm at the centre were used. To eliminate interference effects, the windows were wedged at an angle of 1° . As a result of reflection from the beam splitter, the radiation from the interferometer is partially polarized, the vertical polarization being ~ 1.6 times more intense than the horizontal polarization. alpha-quartz has an absorption band at 128 cm^{-1} which is polarized in a plane normal to the c-axis. To minimise the effects of this absorption,

the windows were cut with the two principal axes lying in the plane and the c-axis was kept along the vertical whenever unpolarized spectra were obtained. The effective sample aperture was 15 mm. This is also the diameter of the beam when it is imaged at the position of the sample.

2.5 Far infrared dichroic studies

Dichroism measurements in the range $30-250 \text{ cm}^{-1}$ were carried out on homogeneously aligned samples using a wire grid polarizer.⁷ Hitherto no polarization studies on oriented liquid crystals have been reported in the far infrared region. The major difficulties encountered in this regard are the reduction in available energy with the use of a polarizer and the lack of adequate choice in window materials, which can facilitate the preparation of oriented samples at higher temperatures as well as permit a visual check of the alignment under a polarizing microscope. α -quartz windows are normally employed in the range below 250 cm^{-1} and here again the birefringence of the windows can pose added problems unless due precautions are taken. The square α -quartz windows used in this study were cut with the c-axis lying parallel to one edge. 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

homogeneously aligned parallel to the c-axis. The degree of alignment could be checked under a polarizing microscope provided the incoming light was polarized along either of the two principal axes of the windows. It was found that the degree of alignment in the nematic phase was not quite uniform over the entire sample. On cooling to the smectic A phase, the alignment deteriorated noticeably, although an overall tendency towards alignment along the original direction was still apparent.

As already noted, the radiation from the interferometer is partially polarized with the vertical component of the electric vector being more intense. To exploit this feature and obtain spectra with better signal-to-noise ratio, vertically polarized radiation was used in all the measurements. The sample cell was rotated so that the direction of alignment of the sample and hence the c-axis of the windows were all kept either parallel or perpendicular to the electric vector of the incident radiation. This procedure ensured that possible birefringence effects arising from the a-quartz windows were greatly minimized in our dichroic measurements.

2.6 Temperature variation and control

The sample cell were heated using a variable temperature copper oven.

The oven used in the near infrared measurements

is shown in Fig. 2.5, It consists of a rectangular copper frame around which nichrome wire is wound, the copper frame being insulated with a thin sheet of mica. This assembly is surrounded by an asbestos frame, the intervening space being filled with plaster of Paris in order to reduce heat losses. On the open sides of this frame, copper sheets with rectangular openings are fixed as shown in the figure. One sheet is fixed permanently to the frame, and a groove cut into its side facilitates the mounting of the cell on an insulating stand* The other sheet is fixed by means of removable screws. Continuously threaded holes near the inner perimeter of this sheet enables four screws to be brought into contact with the windows. Thus the pressure on the windows, and hence the thickness of fluid samples could be varied over a small range,

The temperature of the samples was varied by changing the voltage applied to the nichrome heating element. The temperature stabilises by convective and radiative exchange of heat with the surroundings and it was found that about 90 minutes were required for a given temperature to stabilize after the corresponding voltage was set. The fluctuations in the temperature were less than 0.1°C . The large cross sectional area of the windows, only the edges of which are in contact with the oven, gives rise to a thermal gradient across the sample. The

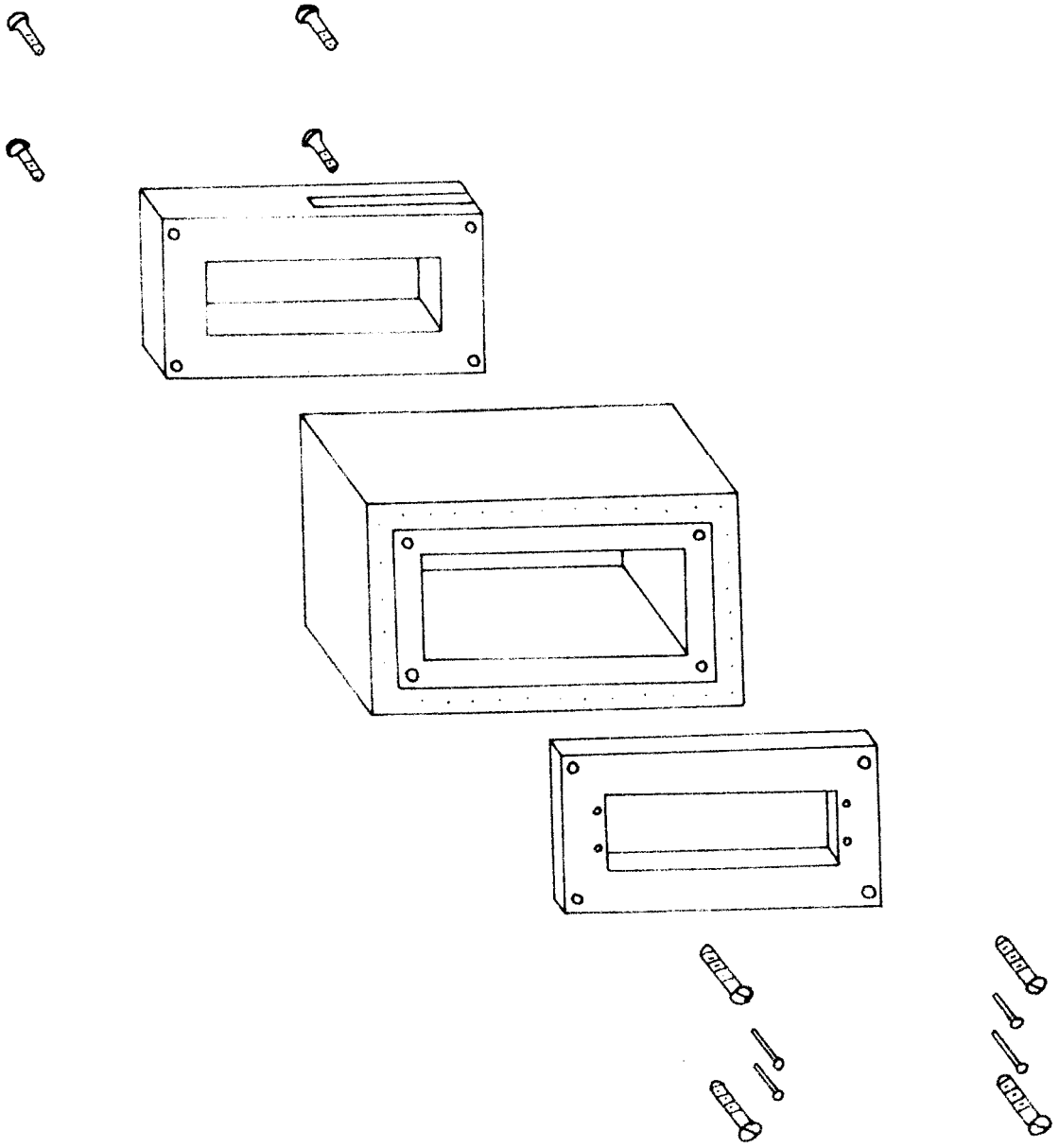
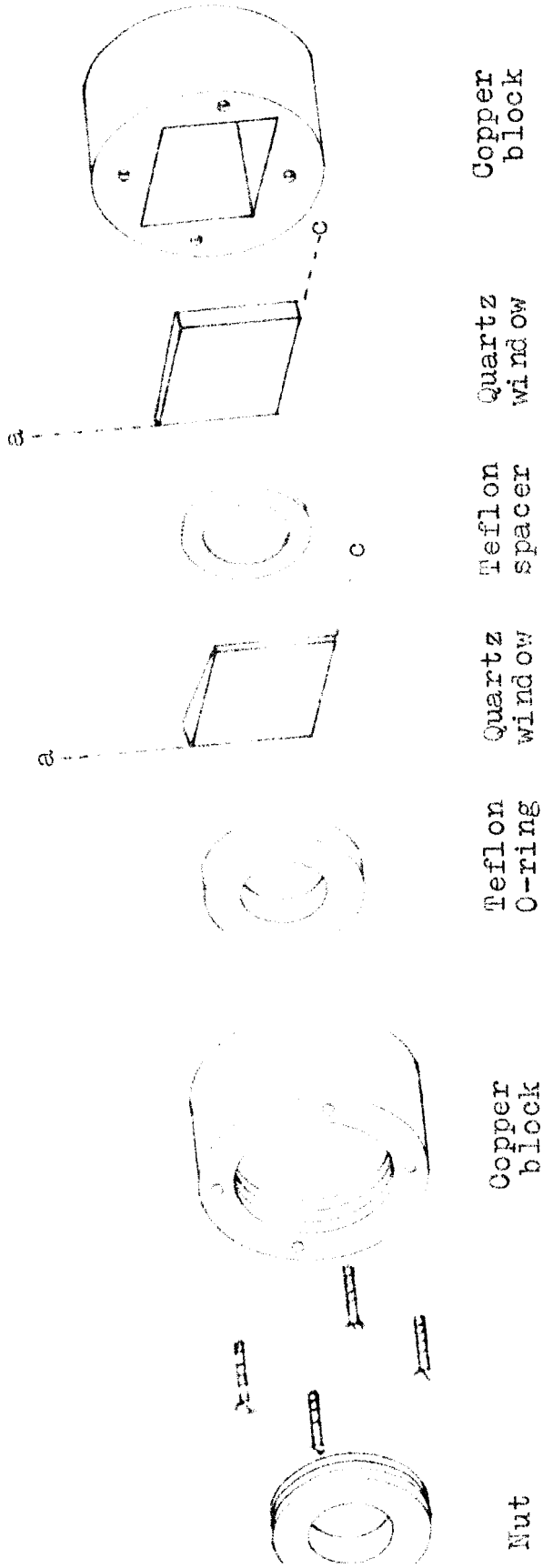


Figure 2.5: Exploded view of the oven used in the near infrared measurements.

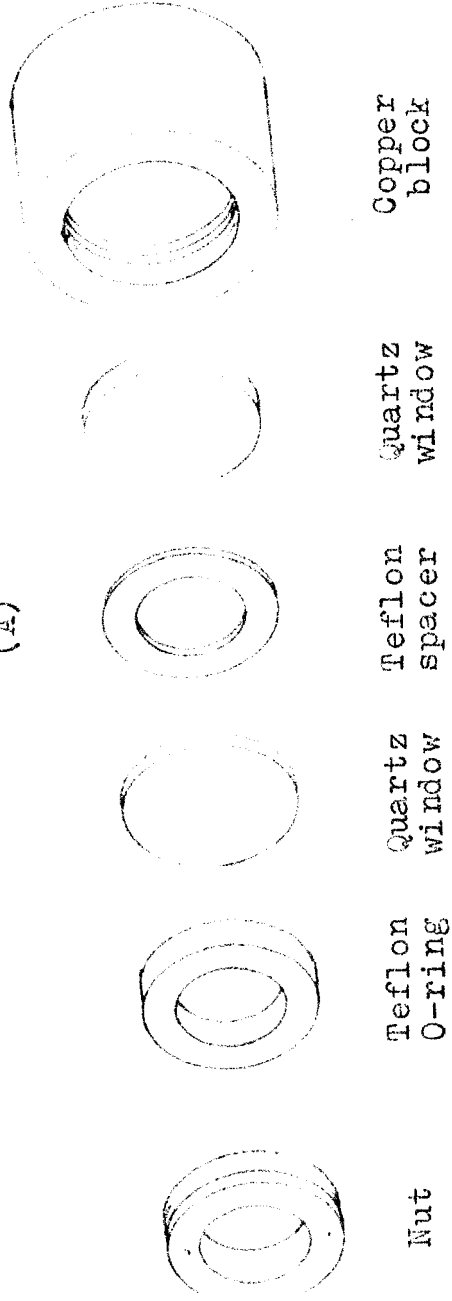
temperature difference between the centre and the outer edge of the sample was found to be $\sim 0.2^{\circ}\text{C}$. The temperature quoted for all the measurements is hence the mean of the temperature at the centre and that at the edge,

A copper-constantan thermocouple was used to measure the temperature. The thermo e.m.f. was measured using a vernier potentiometer and a mirror galvanometer (OSAW). A thermal lag was noticeable between the sample and the thermocouple. The magnitude of this lag increases with increasing temperature and it was not always reproducible. Hence the appropriate correction for the lag in the vicinity of the respective liquid crystal-isotropic transition temperature, T_c , was determined during each measurement. This was done by monitoring the liquid crystal-isotropic transition through the accompanying spectral changes. Using the value of T_c determined from thermal microscopy as the standard, the correction to the measured T_c could be determined. The correction was usually within ~ 1 or 2°C for the range of T_c values encountered in our studies. The measured temperatures are estimated to be accurate within $\pm 0.5^{\circ}\text{C}$.

For far infrared studies, the windows were mounted in a copper block shown in Fig. 2.6. A continuously threaded nut facilitates the application of pressure on the windows, so that the sample is held securely within the spacer and not leaked into the sample chamber when it



(A)



(B)

Figure 2.6: Exploded view of the sample cell and copper mounting assembly used in the far-infrared measurements. (A) Dichroism measurements (B) General measurements.

is evacuated. This assembly is mounted in a VTH 30 variable temperature cell⁵. The control and measurement of temperature were accomplished using a calibrated copper-constantan thermocouple in conjunction with a TC 30 temperature controller.⁵ The temperature measurements are accurate to within $\pm 1^\circ\text{C}$ and fluctuations are within 0.5°C . Before measurements were commenced, about fifteen minutes were normally allowed for the sample to attain thermal equilibrium after the controller indicated the desired temperature.

2.7 Purification of samples

CBOOA⁸ obtained from Eastman Kodak Co. was recrystallized in AnalaR grade n-heptane following the procedure of Gladis.⁹ The samples were dried in vacuum. Another batch of the same material was recrystallized using the same procedure from methanol.

The other liquid crystals were prepared in our Chemistry Laboratory and were used without further purification.

Commercial grade p-nitrotoluene, which was used in the solute dichroism studies, was recrystallized in ethanol after the solution in ethanol was boiled with activated charcoal and filtered. Pale yellow crystals were obtained.

2.8 Thermal microscopy

The nematic-isotropic transition temperature is usually a sensitive measure of the purity of liquid crystals,¹⁰ and this property was used to ascertain the purity of the specimens used. The transition temperatures were measured using a hot stage microscope¹¹ and are accurate to within $\pm 0.2^\circ\text{C}$. The samples were normally filled in open-ended Plat capillary tubes except in the case of TBBA, where, owing to the possibility of decomposition in the presence of atmospheric oxygen, the capillaries were sealed under vacuum.

The temperatures of the other transitions were also measured by this technique. The smectic C-smectic A transition in TBBA could not be observed visually and was detected using differential scanning calorimetry.

2.9 Differential Scanning Calorimetry (DSC)

DSC experiments were carried out; using Perkin-Elmer differential scanning calorimeters,¹² Models DSC-1B and DSC-2. About 5 mg of the sample was crimped in an aluminium sample pan with a cover. Data were obtained during both the heating and cooling cycles and the sample chamber was continually flushed with dry nitrogen during the experiments.

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