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**Effect of Electric Field on the Polarised Infrared
Spectra of Smectic Liquid Crystals**

Ph.D Thesis

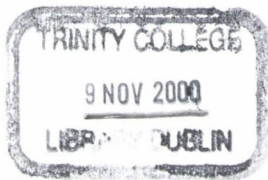
**Presented to the faculty of Engineering, Trinity College, in fulfillment
of the requirements for the degree of Doctor of Philosophy**

By

Mohammad Mehdi Jamshidi

**Department of Electronic and Electrical Engineering,
University of Dublin, Trinity College, Dublin 2, Ireland**

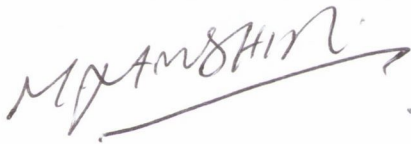
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Declaration

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A handwritten signature in dark ink, appearing to read 'M. Jamshidi', with a long horizontal stroke extending to the right.

Mohammad Mehdi Jamshidi

Dedication

To my wife, children and brothers and sisters who always supported and encouraged me to complete my Doctoral study. I appreciate them all so much.

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Abstract

In this research Fourier Transform Infrared Spectroscopy has been used to investigate the effect of the polarised infrared beam and the electric field on the orientational behaviour of the ferroelectric and antiferroelectric liquid crystals. For this, infrared spectra are measured as a function of the polariser angle as the bias voltage to liquid crystal cells was altered. The most significant absorption bands have been assigned for the materials under investigation. The characteristics of the absorbance profiles and their rotational motions for the various molecular groups were studied in details. For the antiferroelectric material the rotation of the C = O groups round the long molecular axis are biased. The degree of orientation is defined in terms of the dichroic ratio (D_r). The apparent tilt angle is found from the average values of the polarisation angle for maximum absorbance ($\Omega_{\max}$) as the sense of the electric field is altered across the liquid crystal cells. The dependencies of the dichroic ratio and the apparent tilt angle to the applied field for different molecular function are investigated and results are discussed. In terms of the antiferroelectric material, some comparisons of the characteristics in different smectic phase have been made. This was followed using polarising microscope and the presentation of the results of induced polarisation measurements. The reorientation of the molecular groups in each phase has been observed by the application of the electric field for both compounds. This was followed by the interpretation and discussion of the molecular structure related to the various stage of the helix unwinding process for different molecular groups in different phases. For the antiferroelectric material the biasing angle and the biasing parameters of the C = O groups for the studied phases have been found and the results are presented and compared. The method of calculations has been described. Finally, FTIR spectroscopy has been found to be an efficient technique for investigation of the rotational bias and the orientational behaviour of the various parts of the molecules in liquid crystal cells.

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Chapter 1

Introduction to Liquid Crystals (LC)

1.1. Background

The existence of liquid crystals can be traced back to 1888 [1]. The foundation of physics of liquid crystals was laid in the 1920's, but their properties were not clarified until the second half of this century. In 1958, the importance of liquid crystals was brought to attention by F.C. Frank at a discussion of the Faraday Society. Since then scientists have come to the valid conclusion that quantitative experimental work on liquid crystals offers direct information about the molecular interactions in condensed phases [2]. P.G. de Gennes was awarded the Nobel Prize for his contribution to this area of science. His book, *The Physics of Liquid Crystals* [3], which was published in 1975 has given an excellent account of the subject. In the last few years a vast amount of research activity has grown in this field, due to the realisation that liquid crystals have many applications of which the most important one is flat panel displays.

1.2. Definition of Liquid Crystals

We are all aware of the fact that, the matter exists either as a solid, liquid or a gas. Consider water, which is in the liquid state at normal temperature, but when heated above 100 °C, becomes vapour (gas state). If cooled below 0 °C, it changes to ice (solid state) and may exist as crystalline or amorphous. This classification of the state of matter is valid as far as the constituent molecules are more or less spherical. In the case of the longitudinal or disk shape molecules, it is possible to obtain a liquid crystal state, which exists between the liquid and the crystalline phases. The term liquid crystal signifies a state of aggregation that is intermediate between the crystalline solid and the amorphous liquid. In normal liquids, the centre of the mass of molecules is randomly distributed. Therefore there is no long range positional order, and the long axes of molecules has no preferable orientation, thus when a physical property is measured in different directions, the same value is obtained. This form represents isotropic liquids. In contrast to it, the crystalline state, has a three-dimensional positional order which is fixed. In the liquid crystal state, a substance is strongly anisotropic in some of its properties and yet exhibits a certain degree of fluidity, which in some cases may be comparable to that of an ordinary liquid. The first observation of liquid crystalline of mesomorphic behaviour was made towards the end of the last century by Reinitzer [1] and Lehmann [4]. Several thousands of organic compounds are now known to form liquid crystals [5]. An essential requirement for mesomorphism to occur is that the molecule must be highly geometrically anisotropic in shape, like a rod or a disk. Depending on the detailed molecular structure, the system may pass

through one or more mesophases before it is transformed into the isotropic liquid. Transition to these intermediate states may be brought about by purely thermal processes (thermotropic mesomorphism) or by the influence of solvents (lyotropic mesomorphism). In this work thermal process was used for the phase transition process.

1.3. Liquid Crystal Phases

If a substance is cooled down from its isotropic phase, it can go through some successive liquid crystalline phases before reaching the crystalline state. The vast majority of thermotropic liquid crystals are composed of rod-like molecules. They are broadly classified by Friedel [6] into three types: nematic, cholesteric and smectic. In simple form, the molecules of these types can be considered as being long and of elliptical shape with the axis (long molecular axis) coinciding with the major axis of the ellipse, see Fig. 1.1.

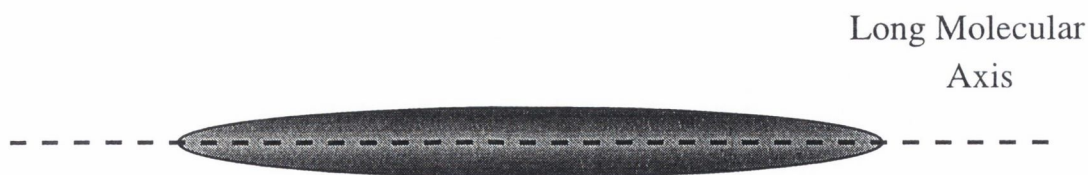


Figure 1.1. Representation of general form of a simple rod-like liquid crystal molecule.

1.3.1. Nematic and Cholesteric phases

The nematic phase (N) is the first phase observed as cooling takes place from the isotropic phase. The molecules in this phase tend to align nearly parallel to each other forming a long range orientational order. The direction of orientation is called the director, shown by a unit vector n , see Fig. 1.2. The long axis of a single molecule deviates from the average direction n by the effect of the thermal fluctuations. The long range orientational order can be measured by the quantity called order parameter (S), first introduced by Tsvetkov [7]:

$$S = \frac{1}{2} \langle 3 \cos^2 \Theta - 1 \rangle \quad (1.1)$$

In the above relation, Θ represents the angle between the long molecular axis of a single molecule and the director n . For perfectly parallel alignment $S = 1$, while for random orientation $S = 0$. In the nematic phase, S has an intermediate value which is strongly temperature dependent.

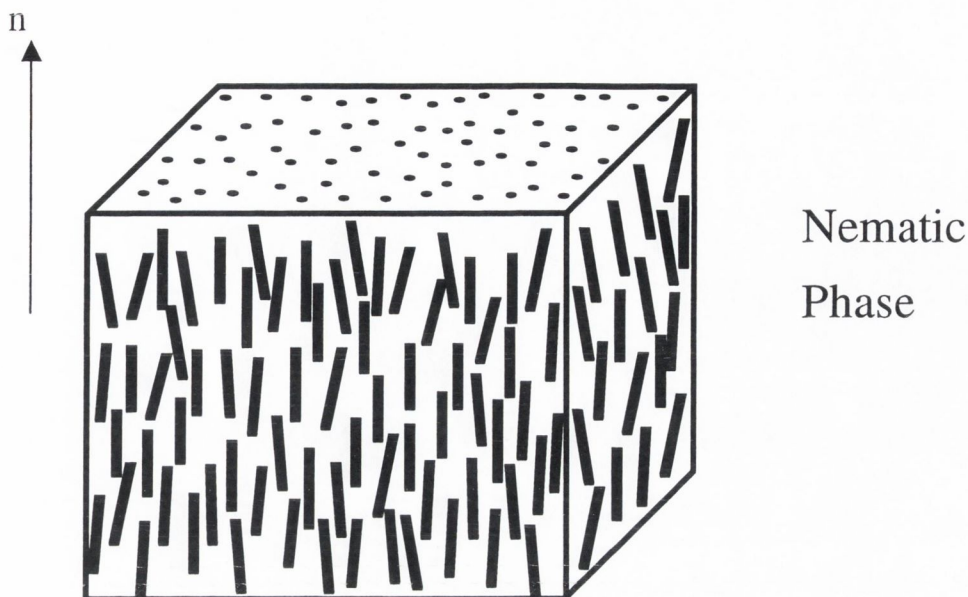
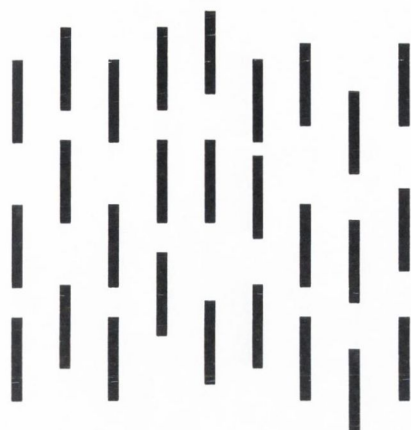


Figure 1.2. The side and top views of nematic phase. As seen unit vector n is parallel to the average orientation of molecules.

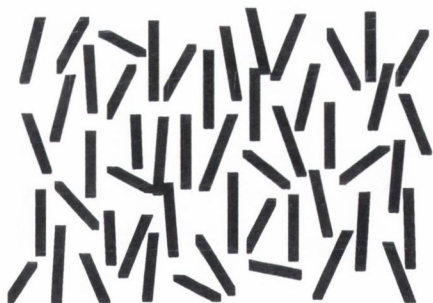
If we consider one dimensional view of molecular orientation, the following arrangement can be expected. In the nematic phase, the molecules possess freedom to move from one position to another and there is no long range positional order of the centres of mass of the molecules. Normally, the molecules can rotate along the long and short molecular axes. Fig. 1.3 illustrates a general molecular arrangement in the crystalline, nematic and isotropic phases.



Crystal
Phase



Nematic
Phase



Isotropic
Phase

Figure 1.3. Schematic representation of molecular order in the crystalline, nematic and isotropic phases.

In the nematic phase, the components of different macroscopic properties in the plane perpendicular to the director n are degenerate. Therefore this is a uniaxial phase. Furthermore it is important to mention that, the nematic phase (N) is used widely in the manufacturing of liquid crystal displays (LCD). In cholesteric phase (N^*), the constituent molecules are chiral (lack of mirror symmetry). Thus we get a nematic phase that the director n adopts a helical configuration. This phase is known as a chiral nematic or a cholesteric phase. Fig. 1.4 shows a cholesteric liquid crystal phase with the helical structure.

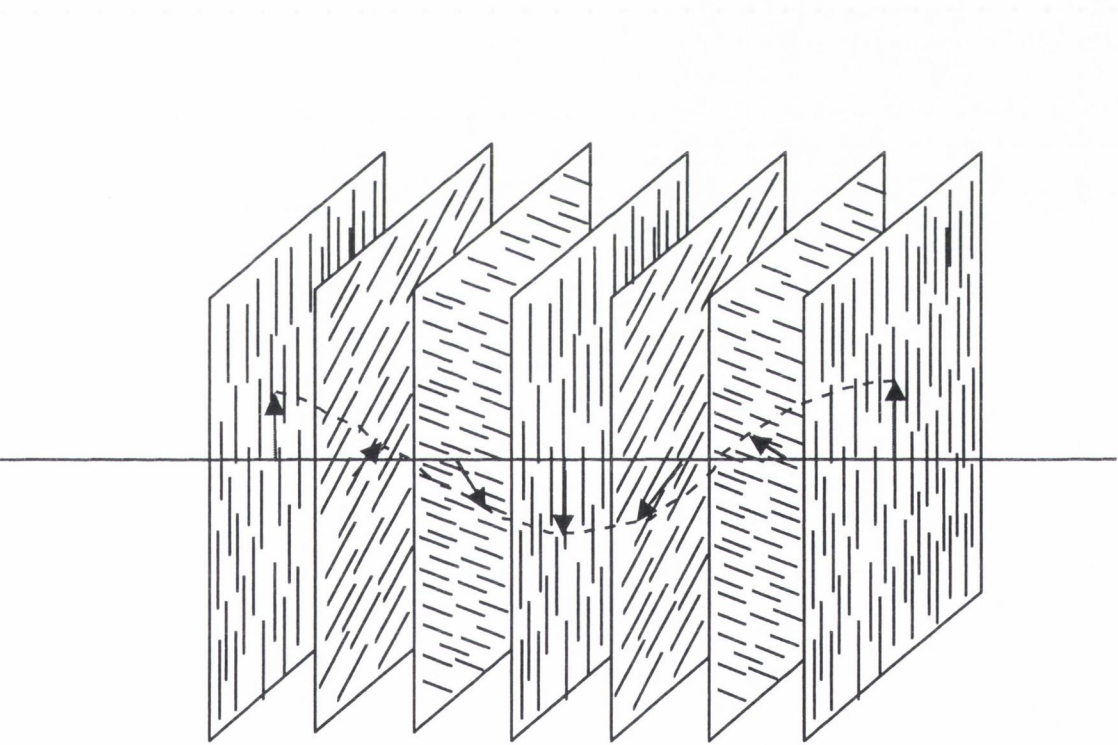


Figure 1.4. Schematic representation of the helical structure in the cholesteric (chiral nematic) liquid crystal phase.

1.3.2. Smectic A and Smectic C phases

As the cooling process continues from nematic phase, we may come to obtain smectic A (SmA) or smectic C (SmC) phases.

Smectic liquid crystals have stratified structure but a variety of molecular arrangements are possible within each stratification. In smectic phases, molecules are situated in layers. In smectic A phase, the molecules are upright in each layer with their long molecular axis perpendicular to the plane of the layers. In smectic C phase, the molecules are tilted with respect to the layer normal, making an angle Θ . The position of the molecules are randomly distributed within each layer and has a two dimensional long range order. In both smectic A and C it is possible for the molecules to reorient around their long and short axes. General structures of both smectic A and C phases can be noticed in Fig. 1.5.

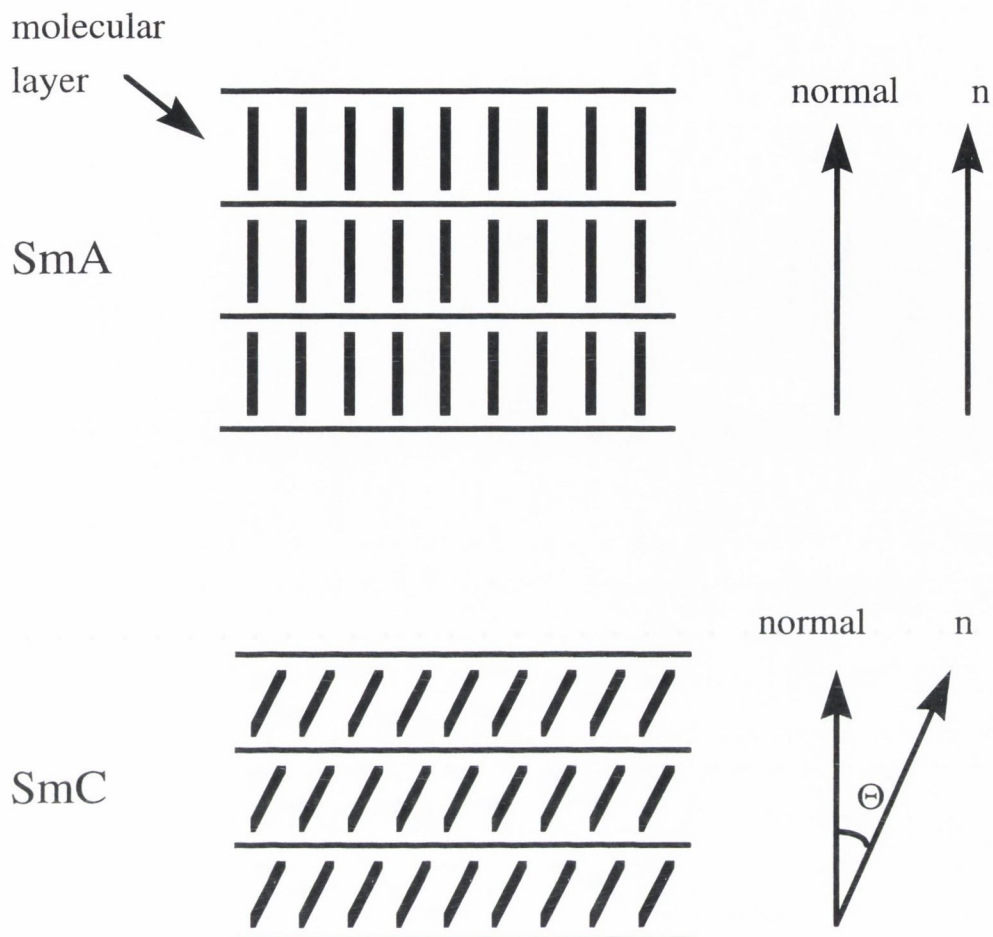


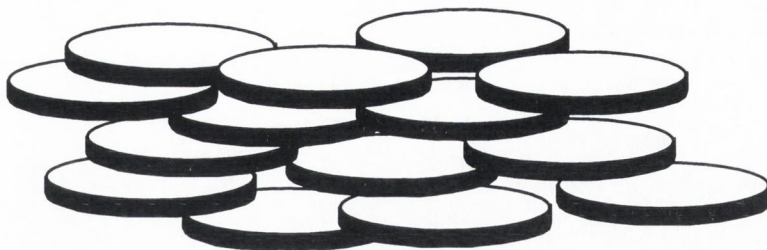
Figure 1.5. Schematic view of the structure of Smectic A and Smectic C phases.

In Smectic phases, the interlayer attractions are weak as compared with lateral forces between molecules and in consequence the layers are able to slide over one another relatively easily [2]. Hence this mesophase has fluid properties, though it is considerably more viscous than the nematic phase. Over a dozen or more other distinct smectic modifications have been identified [8,9]. Some of these have three dimensional long range positional order as in a crystal, though with very weak interlay forces, hence their have energetically weak interlayer ordering. In this case, there is a higher correlation in molecular position between the successive layers.

1.3.3. Liquid Crystals with Discotic Phase or Disk-like Molecules

There are generally referred to liquid crystals which contain discotic phase in between crystalline and the isotropic phases. These were first identified in 1977 [10]. Since then a large number of discotic compounds have been synthesised and a variety of discotic mesophases discovered [11]. Structurally, most of them fall into two distinct categories, the columnar and the nematic. The columnar phase in its simplest form consists of discs stacked on top of each other periodically to form liquid-like columns. The different columns can constitute a two dimensional lattice. A various number of such structures have been identified: hexagonal, rectangular, tilted, etc. The nematic phase has an orientationally ordered arrangement of the discs without any long range transitional order. Fig. 1.6 displays these arrangements.

Nematic



Columnar



Figure 1.6. The schematic arrangement of columnar and nematic phase of the disk-like molecules.

1.3.4. Details of SmC Structure

As stated previously, in smectic phases the molecules are randomly distributed within every layer. The molecular reorientation is uniaxial in SmA but is biaxial in SmC phase. this biaxiality can be described by considering a single molecule in a plane of symmetry within three dimensional co-ordinates, see Fig. 1.7.

In this structure, the tilt angle Θ is directly dependent on the layer thickness whereas the azimuthal angle φ is not. Consequently, at any given temperatures,

the amplitude of the oscillations of the director $\mathbf{n}$ are small compared with those of the φ oscillation.

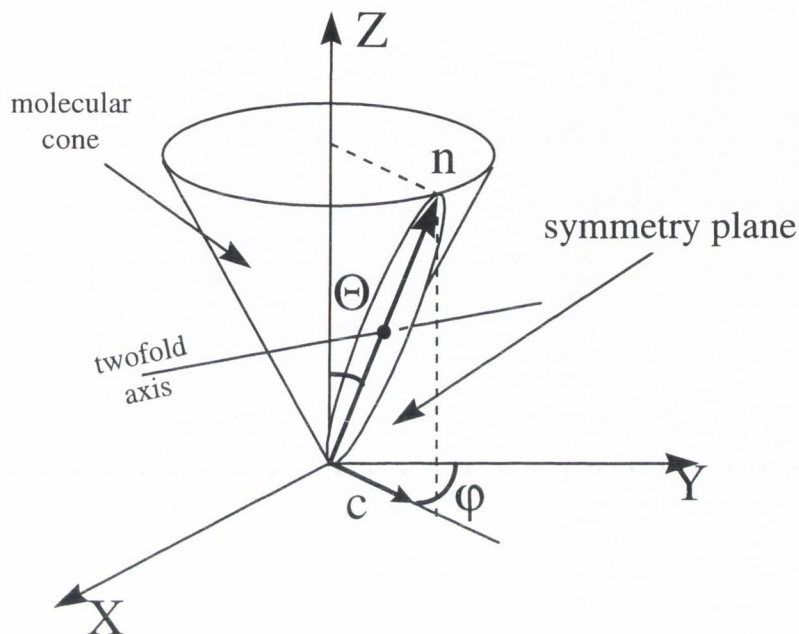


Figure 1.7. Schematic diagram of liquid crystal molecule in SmC phase.

In this case, the uniaxial symmetry about the mean molecular director disappears, and there exists only a plane of symmetry. Due to this and also anisotropic polarisation field effect, SmC is optically biaxial. The optic axial angle is generally quite small ($\sim 10^\circ$).

SmC is often followed by the SmA at a high temperatures, and in such a case tilt angle decreases to zero with the gradual rise of temperature. If the SmC - SmA transition is of second order the tilt Θ decrease is smooth, whereas if it is of first order Θ drops abruptly to zero at the transition point.

Experimentally, only second order SmC - SmA transitions have been observed. Some compounds exhibit transition from SmC to the isotropic phase.

Interestingly, a slight increase of Θ with increasing temperature has been reported for two such compounds [12].

1.4. Ferroelectric Liquid Crystals

1.4.1. Chiral Smectic C Phase (SmC*)

The Greek word chiral can be defined as mirror asymmetry. Two hands are the mirror images of each other but are asymmetric to mirror reflection. A molecule is called chiral which has asymmetrical mirror reflections. The helical structure in the cholesteric or chiral nematic is a direct consequence of the chirality of constituent molecules. These types of molecules can show strong optical activity. The effect of chirality in the SmC* phase is manifest in the existence of the spontaneous polarisation associated within each layer. Therefore such smectic layers have ferroelectric properties. An interesting modification of SmC is the SmC* phase, which has a twist axis normal to the layers. The possibility of such a structure being formed by the addition of optically active molecules to the ordinary SmC was envisaged by Saupe [13], but the first identification of this chiral phase in pure optically active compound was made by Helfrich and Oh [14]. As far as the light propagation along the twist axis is concerned, SmC* is identical to the cholesteric, but at oblique incidence some additional features may be expected [15,16]. Fig. 1.8 displays the ferroelectric SmC* phase with helicoidal and unwound structures.

In SmA phase molecules are perpendicular to smectic layers, and since there is no head to tail ordering (the director being apolar) there is no polarisation normal to the layers.

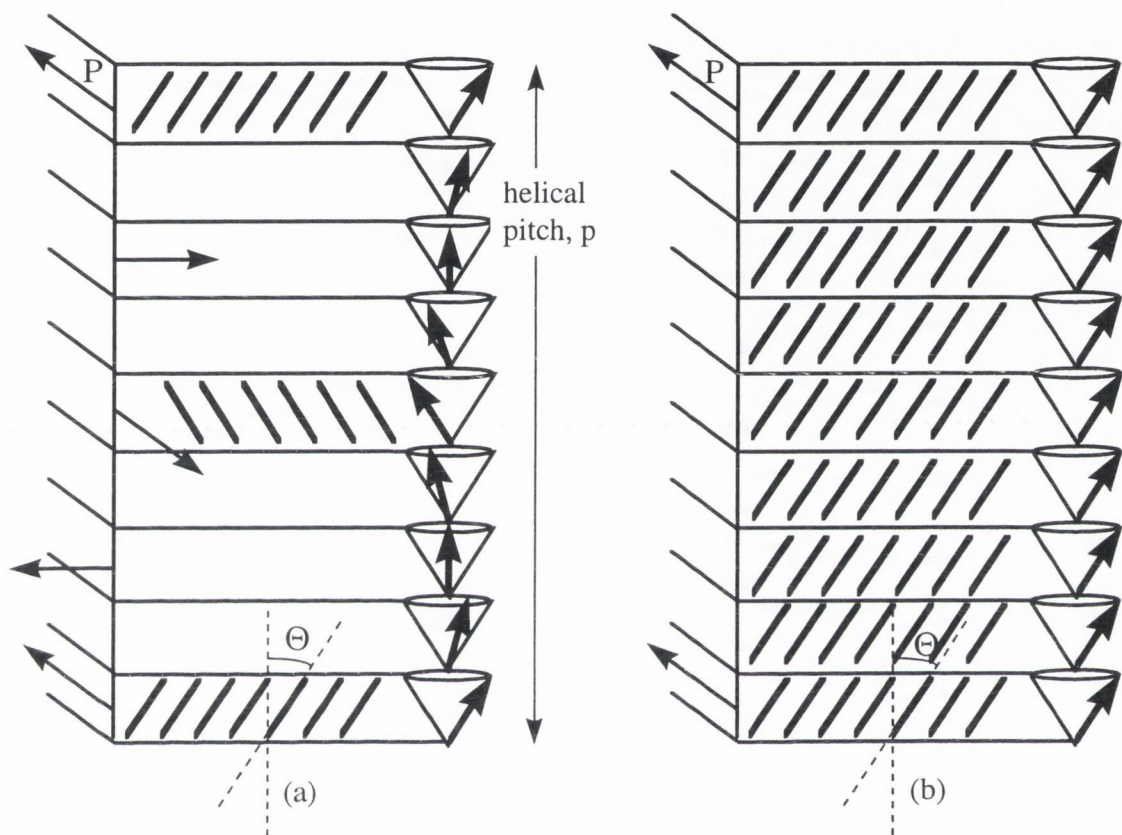


Figure 1.8. (a) Representation of helicoidal structure of the ferroelectric SmC* phase, (b) helix unwound by an electric field applied normal to helical axis.

Furthermore, even if the molecules themselves are chiral, there is equal probability of their assuming any orientation about their long molecular axis. Therefore, the transverse component of the dipole moment is averaged out and there is no net polarisation parallel to the layers.

The molecules are tilted in SmC* phase, and their rotation about their long axis is biased. Hence the transverse dipole moment spends longer time in some

directions than others. Consider the arrangements as shown in Fig. 1.7 again. The symmetry plane of the ordinary SmC is now absent because the molecules are chiral. If XY plane is assumed to be a surface layer, then the only symmetry element that remains is a twofold axis parallel to the layer plane and perpendicular to the long molecular director. This allows the existence of a permanent dipole moment parallel to this axis and perpendicular to the molecular director n .

From this description we can infer that in SmC*, each layer is spontaneously polarised. Since the structure has a twist about the layer normal, the tilt and the polarisation direction rotate from one layer to the next (see figure 1.8(a)). This implies that there is a constant bend around the helical axis, which gives rise to a flexoelectric contribution to the polarisation. The first demonstration of SmC* phase with ferroelectric properties was made by Meyer et al [17] in 1975. It must be mentioned that, the transition from SmA to SmC* phase is driven by intermolecular forces responsible for the tilted smectic phase and not by the dipole-dipole (ferroelectric) coupling. In ferroelectric liquid crystals, the primary order parameter is the tilt angle (Θ) and not the polarisation (P) as in crystalline materials.

1.4.2. Bookshelf Geometry, Surface Stabilised Liquid Crystals and Chevron Structure

Due to the existence of helix in the SmC*, its utilisation for electro-optic application was not possible for years. Clark and Lagerwall [18] introduced the

method to unwind the helix and obtain macroscopic polarisation. They used sufficiently thin $\sim 4\mu\text{m}$ layers depends on the material, and imposed surface forces to stabilise the molecules in what is called bookshelf geometry, thus preventing the development of helix. Such a structure is known as surface stabilised ferroelectric liquid crystal (SSFLC). In SSFLC, the diameter of the helical pitch is greater than the cell thickness and the smectic layers standing perpendicular to the windows of the cell. In this arrangement, when the polarity of the applied electric field is reversed, the molecules are reoriented by rotating around the surface of the cone. Thereby moving through an angle equal to twice that of the tilt angle. The spontaneous polarisation in this case is antiparallel to each other. See Fig. 1.9.

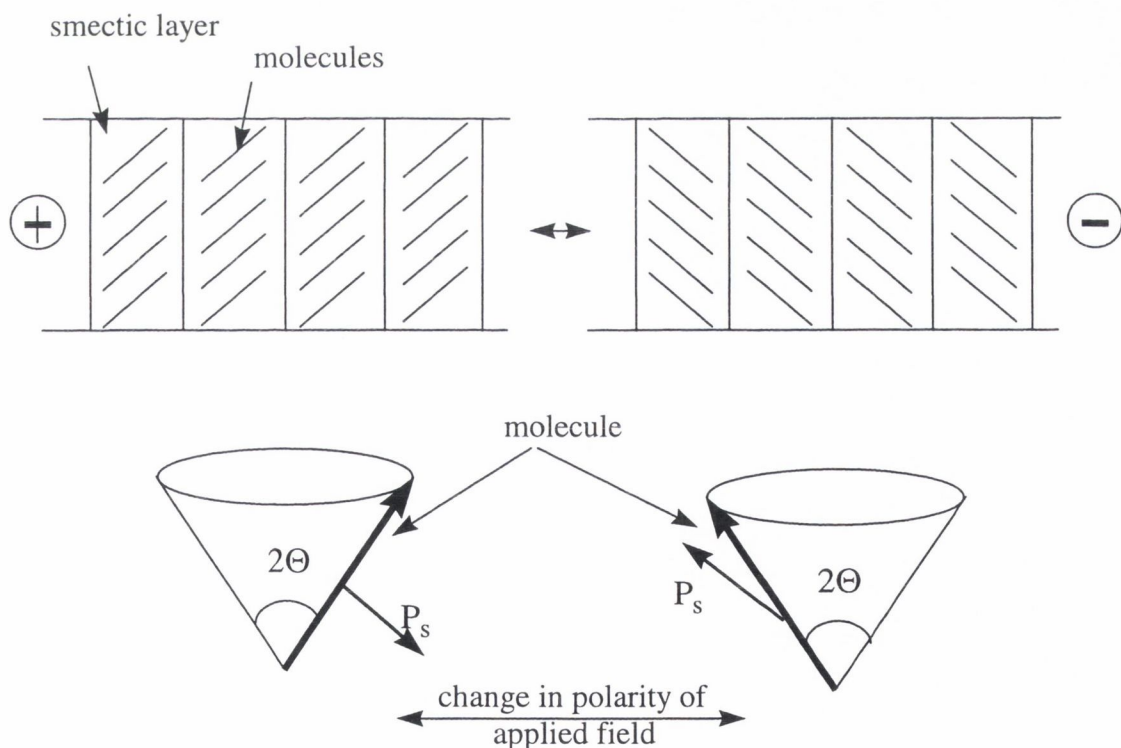


Figure 1.9. The effect produced in SSFLC cell when the polarity of the field is reversed.

The molecules are reoriented through an angle equal to twice the tilt angle. The polarisation directions are opposite to each other and perpendicular to the plane of the page.

The advantage of the SSFLC device is that the switch on and switch off times are just a few tens of microseconds, about 1000 times faster than the twisted nematic device. For a given cell thickness, the material parameters that determine the switching speed are the polarisation and the viscosity. However, in practice, it is found that the molecules adopt a chevron type of structure [19] rather than the bookshelf structure. In this case, the mechanism of reorientation from one stable state to the other on reversing the voltage is a complex one which involves the formation of defects [19]. Fig. 1.10 shows the simple form of a cell with a chevron structure.

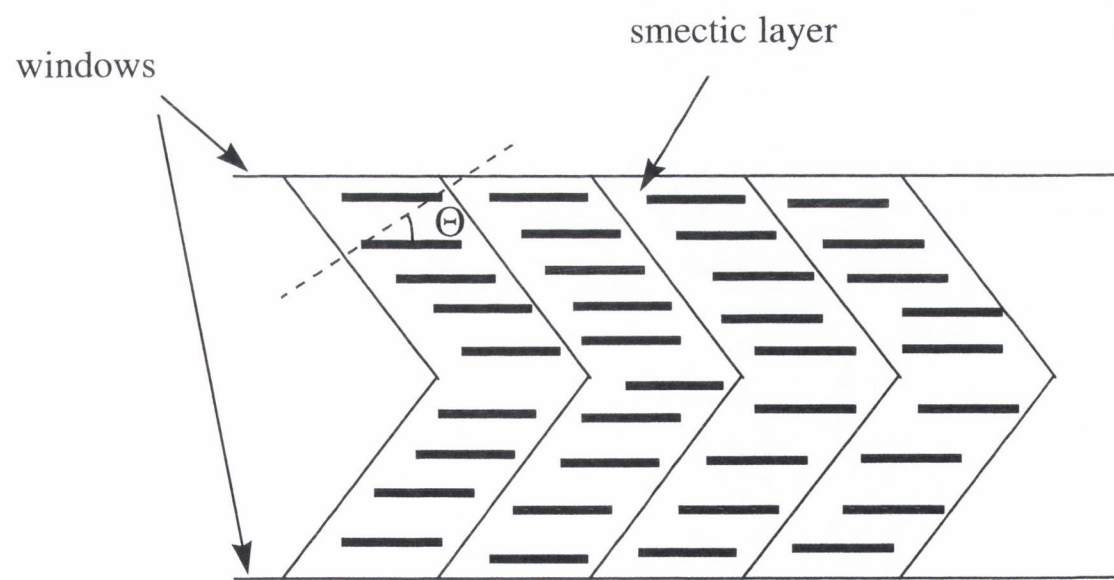


Figure 1.10. Schematic diagram of chevron structure in the liquid crystal cell.

As can be seen, in chevron structure molecules make an angle Θ with the smectic layer normal but lie parallel to the windows. This form can also occur in transition between SmA to SmC*. Apparent angle in chevron is small in comparison with that of the bookshelf geometry.

1.4.3. Antiferroelectric Liquid Crystals

Antiferroelectric liquid crystals have so far been found in materials where the degree of chirality is relatively high, for example in materials where the chiral centre is close to the rigid aromatic core of the molecule or where the peripheral aliphatic chain is relatively long. In these materials, the motion of the chiral centre about the long axis of the molecule is damped, and therefore the degree of chirality is increased. The increase in chirality in closely related systems is manifest in a shortening of the pitch length of the helix in chiral phases and a substantial increase in the spontaneous polarisation. [20].

In the antiferroelectric chiral smectic phase SmC_A*, the molecules in the neighbouring layers tilt in almost the same direction but in the opposite sense. Therefore, the spontaneous polarisation in the neighbouring layers point in the opposite sense of the direction perpendicular to the tilting plane, thereby cancelling each other. There is as yet no net spontaneous polarisation. As in SmC*, chirality induces a slight precession from layer to layer in tilting and hence in-plane spontaneous polarisation. This leads to a formation of the helicoidal structure with the axis parallel to the smectic layer normal [21]. This helicoidal

pitch is much larger than the smectic layer spacing, i.e. $p/d \approx 10^3$ where p is the length of the pitch and d is the thickness of smectic layer. Fig. 1.11 displays a typical characteristics of this phase in comparison with SmC^* phase.

If the antiferroelectric phase is subjected to DC voltage, the layer ordering will break up, and the molecules will be poled in one direction depending on the polarity of the applied electric field in order to give a ferroelectric phase.

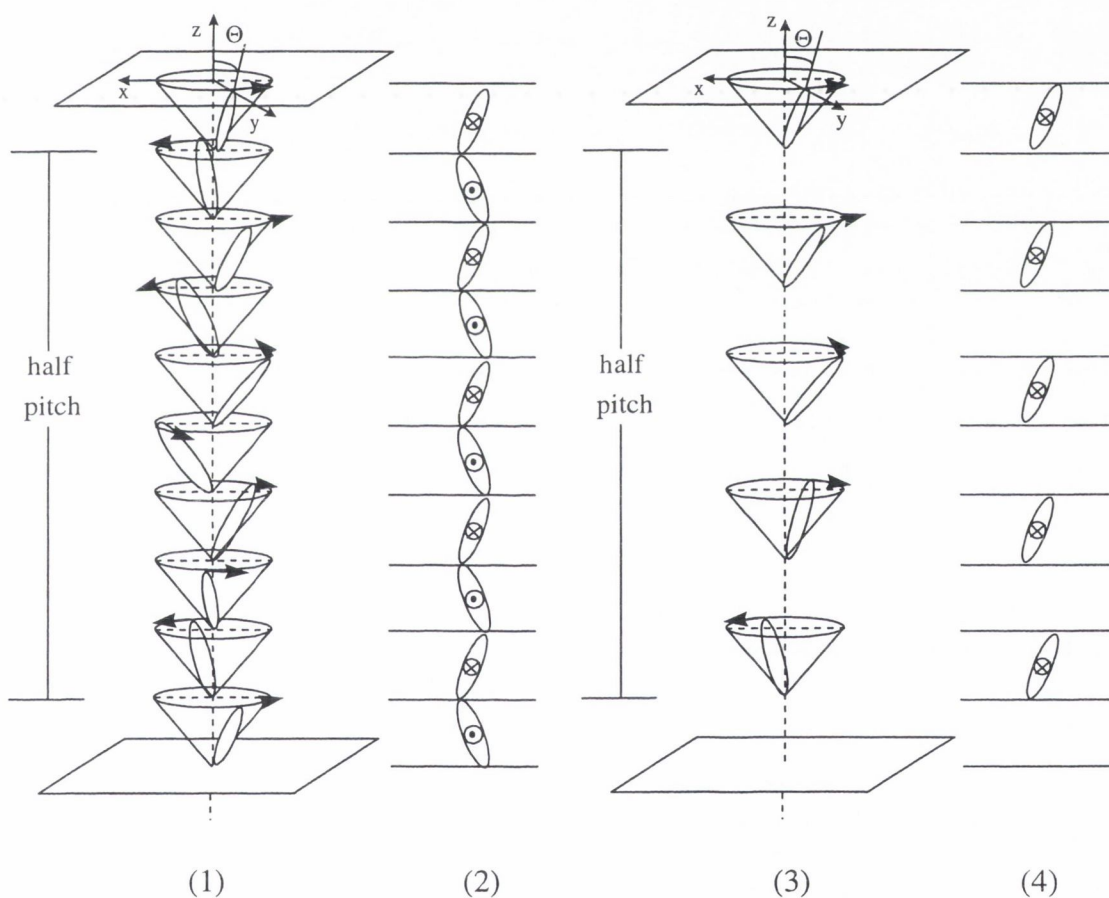


Figure 1.11. Schematic illustration of (1) - antiferroelectric helicoidal, (2) - antiferroelectric unwound, (3) - ferroelectric helicoidal and (4) - ferroelectric unwound structures.

Switching from the antiferroelectric to the ferroelectric phase is associated with a sharp threshold field. This behaviour is different from the switching in a conventional ferroelectric liquid crystalline phase, where the process appears to be continuous, i.e. switching occurs without a threshold field in cases where the switching states are not surface stabilised. The presence of a threshold field to switching is useful in display applications that rely on the multiplexing of a large number of pixels in order to operate.

The switching process can be investigated by measuring the apparent tilt angle as a function of the applied voltage. No change in the apparent tilt angle occurs for low voltages, and at a critical field the structure of the phase changes from being antiferroelectric to ferroelectric. At this point, tilt angle increases substantially, and reaches the full tilt angle of the Smectic C* phase.

There is a degree of hysteresis when the voltage cycles up and down or the polarity is reversed as shown in fig. 1.12.

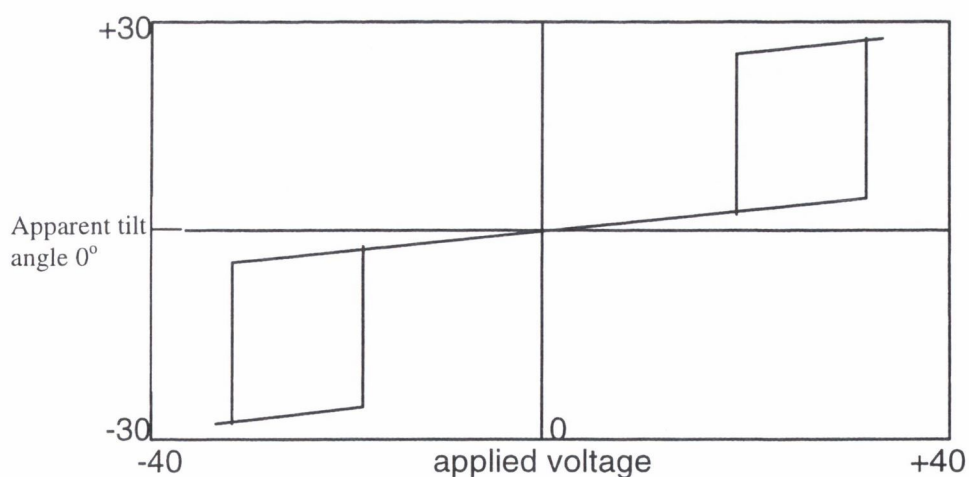


Figure 1.12. Typical graph of hysteresis effect when switching from an antiferroelectric state to SmC* liquid crystal.

Unlike the structure of the normal SmC* phase which is repeated for each 360° rotation of the helix, the helical structure of the antiferroelectric phase is repeated for every 180° rotation. Therefore, the pitch appears to change quite dramatically as the temperature is altered.

1.5. Application of Liquid Crystals

Due to the various applications, liquid crystals are very interesting and important materials [22, 23]. Some of these applications are as follows:

Liquid crystal display (LCD) – This ranges from simple digital displays for watches etc., through computer and television screens, up to large-area video wall panels. Liquid crystal devices have the potential for most displays. This is because the devices are more compact, have lower power consumption and are more rugged than conventional display units containing cathode ray tube. They also do not emit any radiation and are therefore more suitable for applications where people sit in front of a display for a long duration (e.g. computer screen). However, considerable research on a global basis is aimed at developing a much wider range of liquid crystal displays.

Liquid crystal display devices work by virtue of the interaction between the liquid crystal material and the light. The materials are anisotropic (meaning they have differing optical properties in different directions), this allows them to influence the polarisation of light (that is the direction in which the electric field of the light oscillates) which can be used to determine the amount of light transmitted through

a device. In this respect, the materials are crystalline. Because the materials also have liquid behaviour, the molecules can be rearranged by the application of an electric field, allowing control of the optical properties and hence control of the light transmitted by devices [24].

Liquid Crystal Thermometers - The chiral nematic (cholesteric) liquid crystals reflect light of wavelength equal to the pitch. Due to the dependence of pitch on temperature, the colour reflected also is dependent on temperature. Hence, liquid crystals make it possible to accurately gauge temperature just by looking at the colour of the thermometer. By mixing different compounds, a device for practically any temperature range can be manufactured. LC thermometers have important applications in medicine and other industries. Special liquid crystal devices can be attached to the skin to show a map of temperatures. This is useful because often physical problems, such as tumours, have a different temperature distribution than the surrounding tissue. Liquid crystal temperature sensors can also be used to find bad connections on a circuit board or show the temperature of a running machine by detecting the characteristic higher temperature.

Optical Imaging - In this technology, a liquid crystal cell is placed between two layers of photoconductor. Light is applied to the photoconductor, which increase the material's conductivity. This causes an electric field to develop in the liquid crystal corresponding to the intensity of the light. The electric pattern can be transmitted by an electrode, which enables the image to be recorded. This technology is still being developed and is one of the most promising areas of liquid crystals research.

Other Liquid Crystal Applications - Liquid crystals have a multitude of other uses. They are used for non-destructive mechanical testing of materials under stress. This technology is also used for the visualisation of RF (radio frequency) waves in waveguides. They are used in medical applications where, for example, transient pressure transmitted by a walking foot on the ground is measured. Low molar mass (LMM) liquid crystals have applications including erasable optical disks, full colour “electronic slides” for computer-aided drawing (CAD), and light modulators for colour electronic imaging [24].

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Chapter 2

Introduction to Fourier Transform Infrared Spectroscopy and Molecular Vibrations

2.1. Definition

Infrared Spectroscopy is the study of the interaction of infrared light with matter. The light wave moves through space in a plane perpendicular to the planes containing the electric and magnetic waves. It is the electric part of light, called the electric vector, that interacts with molecules. The amplitude of the electric vector changes over time and has the form of a sine wave, as shown in Figure 2.1. The *wavelength* (λ) of a light wave is the distance between adjacent crests or troughs. The *wavenumber* of a light wave is defined as the reciprocal of the wavelength

$$\tilde{\nu} = 1/\lambda \quad (2.1)$$

where $\tilde{\nu}$ is wavenumber. If λ is measured in cm, then $\tilde{\nu}$ is reported as cm^{-1} .

Wavenumbers are the units typically used in infrared spectroscopy.

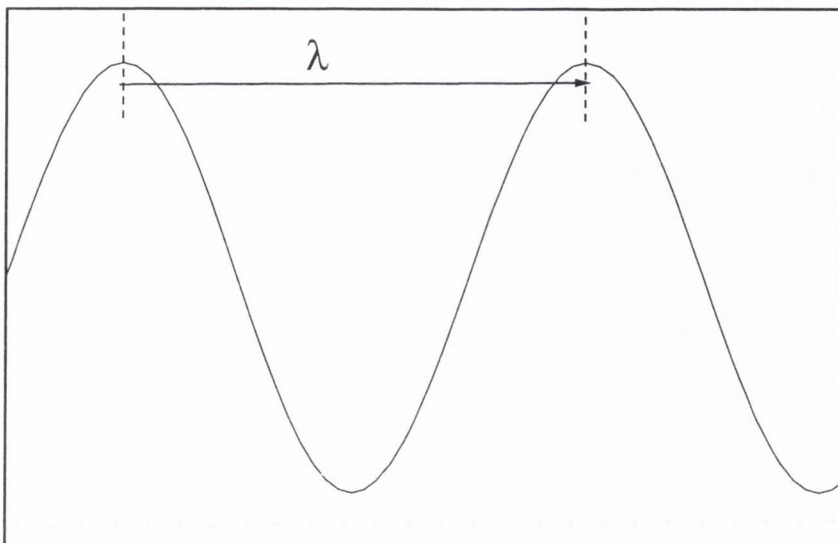


Figure 2.1. The distance between two consecutive crests in the wave.

The wavenumber of a light wave is directly proportional to energy as follows:

$$E = h c \tilde{\nu} \quad (2.2)$$

where:

E = Light energy

c = The speed of light (3×10^8 meters/second)

h = Planck's constant (6.63×10^{-34} Joule-second)

$\tilde{\nu}$ = Wavenumber

Thus, high wavenumber light has more energy than low wavenumber light.

The infrared range is normally divided into three regions as follows [1]:

Near-infrared between 13,300 to 4,000 cm^{-1} or 0.75 to 2.5 μm ,

Mid-infrared between 4,000 to 400 cm^{-1} or 2.5 to 25 μm ,

Far-infrared between 400 to 10 cm^{-1} or 25 to 1,000 μm .

All measurements carried out for the purpose of this thesis are in the mid-infrared range. Mid-infrared represents the fundamental vibrational region and is the most useful area for analytical spectroscopy. Calcium Fluoride windows used for our measurements are capable to exhibit the transmission for frequencies higher than 1,000 cm^{-1} . Hence, all the spectra were recorded between 3,600 to 1,000 cm^{-1} . Fig. 2.2 shows the typical infrared spectra of a liquid crystal cell with CaF_2 windows.

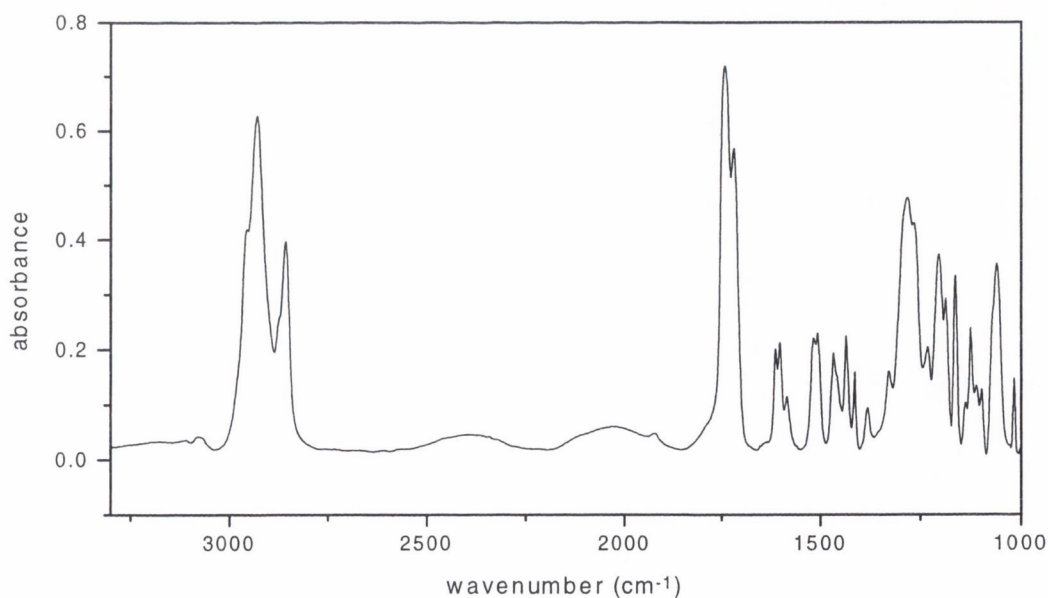


Figure 2.2. Example of an infrared spectra of a liquid crystal.

When infrared radiation interacts with matter it can be absorbed, causing the chemical bonds in the material to vibrate. The presence of chemical bonds in a material is a necessary condition for infrared absorbance to occur. Chemical structural fragments within molecules, known as *functional groups*, tend to absorb infrared radiation in the same wavenumber range regardless of the structure of the rest of the molecule that the functional group is in. For instance, the stretching vibrations of a carbonyl group occurs at $\sim 1700\text{ cm}^{-1}$ in ketones, aldehydes, and carboxylic acids. This means there is a correlation between the wavenumber at which a molecule absorbs infrared radiation and its structure. This correlation allows the structure of unknown molecules to be identified from the infrared spectrum. This is what makes infrared spectroscopy a useful tool for chemical analysis [2].

A plot of the measured infrared radiation intensity versus wavenumber is known as an *infrared spectrum*. In Figure 2.2 can be seen that, the infrared spectra is plotted with high wavenumber on the left and low wavenumber on the right. This means that as a spectrum is read from left to right one is looking from high energy to low energy. Note in Figure 2.2 that the Y axis is in absorbance, and that the X axis scale is in wavenumber. The upward pointing peaks represent wavenumbers at which the sample absorbed infrared radiation. The Y axis can also be plotted in transmittance, in which case the peaks would point down and represent wavenumbers where the sample transmitted less infrared radiation. Regardless of the Y axis units, it is the wavenumber (X axis) positions of these peaks that correlates with molecular structure. For instance, generally the peaks in the region of $2900\text{-}2800\text{ cm}^{-1}$ represent the vibrations for CH_2 and CH_3 groups in liquid crystals. In addition to

chemical structures, infrared spectra can provide quantitative information as well, such as the concentration of a molecule in a sample. The basis of all quantitative analyses in FTIR is Beer's law, which relates concentration to absorbance, and has the following form [2]:

$$A = \epsilon l c \quad (2.3)$$

Where A = Absorbance,

ϵ = Absorptivity

l = Pathlength (micrometer)

c = Concentration (mole/liter)

The absorbance is measured as a peak height, peak height ratio, peak area, or peak area ratio from the FTIR spectrum. The absorptivity is the proportionality constant between concentration and absorbance. It changes from molecule to molecule, and from wavenumber to wavenumber for a given molecule. For example, the absorptivity of acetone at 1700 cm^{-1} is different than the absorptivity for acetone at 1690 cm^{-1} . However, for a given molecule and wavenumber, the absorptivity is a fundamental physical property of the molecule. For example, the absorptivity of acetone at 1700 cm^{-1} is as invariant as its boiling point or molecular weight. The units of ϵ are usually given in $(\text{concentration} \times \text{path length})^{-1}$, so the absorptivity cancels the units of the other two variables in Beer's law, making absorbance a unitless quantity. The width of an infrared band gives information about the strength

and nature of the molecular interactions. Thus, an infrared spectrum provides a great deal of information about a sample.

The absorbance is linearly proportional to concentration as stated in Beer's law, but transmittance is not. Transmittance is defined in the following equation:

$$T = I / I_o \quad (2.4)$$

Where T is transmittance, I is light intensity with the sample in the beam and I_o is light intensity with no sample in the beam.

In FT-IR, I_o is the background spectrum, and I is the single beam spectrum.

Absorbance is defined as:

$$A = \log_{10} I_o / I \quad (2.5)$$

From equation (2.4)

$$I / T = I_o / I \quad (2.6)$$

Hence,

$$A = \log_{10} I / T \quad (2.7)$$

Equation (2.7) represents the relationship between absorbance and transmittance in FT-IR spectroscopy.

2.2. Brief History of FTIR

The development of FTIR would have been impossible without the use of the Michelson interferometer. This optical device was invented in 1880 by Albert Abraham Michelson [3, 4]. He was awarded the Nobel Prize in Physics in 1907 for accurately measuring wavelengths of light using his interferometer.

The major advance in this area was made by J.W. Cooley and J.W. Tukey, then at Bell Labs, who invented what is known as the "Fast Fourier Transform" (FFT), or "Cooley-Tukey Algorithm" [5]. This algorithm quickly performs Fourier transforms on a computer, and is still the basis for the transformation routines used in commercial FTIRs. The marriage of the FFT algorithm and minicomputers was the breakthrough that made FTIR possible.

The first commercially available FTIRs were manufactured by the Digilab subsidiary of Bock Engineering in Cambridge, Massachusetts during the late 1960s [6, 7]. The efforts of Peter Griffiths, Raul Curbelo, L. Mertz and others made this possible. These instruments incorporated many features we now take for granted in an FTIR: the use of an air bearing driven Michelson interferometer, a He-Ne reference laser used to track mirror position and act as a wavelength standard, and a minicomputer running the Cooley-Tukey algorithm. These instruments made possible the acquisition of quality, high resolution data in a short period of time, and established the advantages of FTIR over previous means of obtaining infrared spectra. Since the 1960s many other companies have begun manufacturing and

selling FTIRs in the United States. The mid-1970s saw the entry of Nicolet Instruments of Madison, Wisconsin into the FTIR business, who quickly became one of the largest FTIR manufacturers. The early 1980s saw the entry of Bio-Rad, instrument company, a giant Perkin-Elmer Corp. of Norwalk and others coming into the FTIR in conjunction with microcomputers and packages for analyzing infrared spectra. Presently various programs and computerized techniques are available for an analysis of the FTIR data. Gram Research is one of the most advanced and popular computer packages, which is also used in this research for the analysis of infrared spectra [8].

Today FTIRs have moved from the research lab, to the quality control lab, and on to the factory floor for on-line analysis, enabling environmental sensing to be done routinely. The general trend will be to apply FTIR to more and more problems that impact our everyday lives, through reducing air pollution and enhancing medical diagnoses.

2.3. The Advantages and Limitations of FTIR

The ultimate performance of any infrared spectrometer is determined by measuring its signal-to-noise ratio (SNR). SNR is calculated by measuring the peak height of a feature in an infrared spectrum (such as a sample absorbance peak), and ratioing it to the level of noise at some baseline point nearby in the spectrum. Noise is usually observed as random fluctuations in the spectrum above and below the baseline. An example of an isolated peak and associated baseline noise is seen in Figure 2.3. For this peak, the signal is 0.45 absorbance units at 2228 cm^{-1} , and the noise is 0.025 absorbance units at 2196 cm^{-1} . The SNR for the spectrum in this region would be $(0.45/0.025)$ or 18.

For a given sample and set of conditions, an instrument with a high SNR will be more sensitive, be applicable to more kinds of samples, and allow absorbances to be measured more accurately than an instrument with a low SNR. Signal-to noise ratio is also used to determine whether or not a spectral feature is real. A spectral feature's intensity must be 3 times that of the noise to be considered real. If a spectral feature is less than 3 times as intense as the noise, it should be ignored.

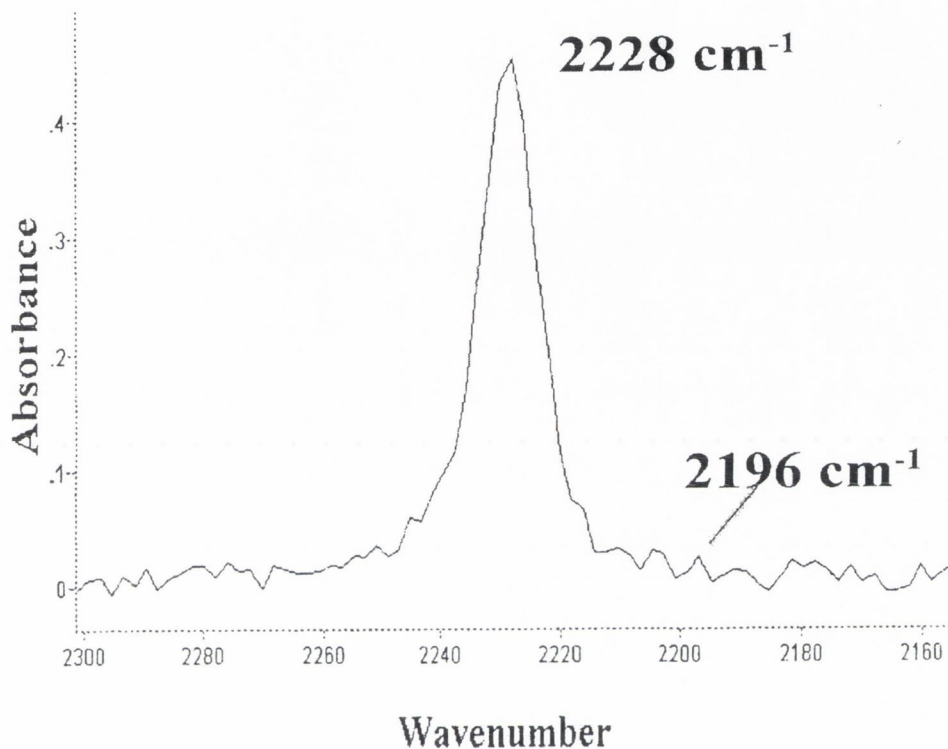


Figure 2.3. An isolated peak and associated baseline noise. The signal measured at 2228 cm^{-1} is 0.45 and the noise measured at 2196 cm^{-1} is 0.025. The SNR for this spectrum in this region is $(0.45/0.025)$ or 18.

For a constant resolution, the SNR is related to the number of scans added together as follows:

$$\text{SNR} \propto (N)^{1/2} \quad (2.8)$$

where N is the number of scans added together, and $\propto$ stands for proportionality.

Despite the many advantages of FTIR for molecular group investigation, there are

limitations on what is achievable with infrared spectroscopy in general, and there is one specific limitation of FTIR in particular. A general limitation of infrared spectroscopy is that it cannot detect atoms or monatomic ions. Single atomic entities contain no chemical bonds, do not possess vibrational motion, and hence do not absorb infrared radiation. In general, it is impossible for an infrared spectrometer to measure the level of an element in a substance, unless the element is present as part of a molecule whose spectrum can be detected. Also, the noble gases such as helium and argon cannot be detected because they exist as individual molecules. Another class of substances that do not absorb infrared radiation are homonuclear diatomic molecules. These are molecules comprised of two identical atoms, such as N_2 and O_2 . Homonuclear diatomic molecules do not possess infrared spectra due to their symmetry. N_2 and O_2 are very abundant in the atmosphere, and if they absorbed infrared radiation all the radiation in the spectrometer would be absorbed by the atmosphere before it got to the sample [2].

Another limitation of infrared spectroscopy is its use in analyzing some complex mixtures. These samples give rise to complex spectra, whose interpretation is difficult because it is hard to know which bands are from which molecules in a sample. A specific limitation of FTIR spectrometers is that, FTIR is a single beam technique. This means that the background spectrum, which measures the contribution of the instrument and the environment to the spectrum, is measured at a different point in time than the spectrum of the sample. *Ideally*, the instrumental and environmental contributions to the spectrum are eliminated by ratioing the sample spectrum to the background spectrum. However, if something in the instrument or

the environment changes between when the sample and background spectra are obtained, spectral artifacts can appear in the sample spectrum. Common examples include water vapor and carbon dioxide peaks. These artifacts can be misinterpreted, or may mask sample absorbances. Artifacts do not always appear in sample spectra, but one should know where they may show up to avoid misassigning them.

2.4. Selection rules and intensity

Molecular spectra and the form they take depends on the type of the transition. The underlying classical idea is that, for the molecule to be able to interact with the electromagnetic field and absorb or create a photon of frequency ($\tilde{\nu}$), it must possess at least transiently, a dipole oscillating at that frequency. This transient dipole is expressed quantum mechanically in terms of the transition dipole moment. The intensity of the transition (I) is proportional to the square of the transition dipole moment, i.e. $I \propto |P_i|^2$. Hence, if the transition moment is only non-zero, it can contribute to the spectrum [9].

In the case of rotational transitions, the transition moment is zero unless the molecule has a permanent dipole (i.e. unless it is polar). The classical basis of this rule is that a polar molecule appears to possess a fluctuating dipole when rotating.

In the case of vibrational transitions, the transition moment is zero unless the electric dipole moment of the molecule changes during the vibration. The classical basis is that the vibrating molecule shakes the electromagnetic field into oscillation if its dipole changes as it vibrates [9]. Note that, the molecule need not have a permanent dipole. The rule requires only a change, possibly from zero.

2.5. Typical vibrations for Diatomic Molecule

Consider a simple molecule with two atoms such as sodium chloride (NaCl). If m_1 and m_2 are the masses for Na and Cl atoms respectively, then the potential energy V of the molecule depends on the interatomic distance r . In the equilibrium system when $r = r_0$ a function $V(r)$ has a minimum value. In this case potential energy $V(r)$ near the equilibrium state can be expressed by a Taylor's series theorem.

$$V(r) = V(r_0) + \left[\frac{\partial V}{\partial r} \right]_{r=r_0} (r - r_0) + \frac{1}{2} \left[\frac{\partial^2 V}{\partial r^2} \right]_{r=r_0} (r - r_0)^2 \quad (2.9)$$

If $V(r_0)$ is eliminated from the above series then the energy of the equilibrium state can be zero. Note that, function $V(r)$ is at minimum if $r = r_0$. Therefore,

$$\left[\frac{\partial V}{\partial r} \right]_{r=r_0} = 0 \quad (2.10)$$

For small vibrational frequencies the higher terms with powers of 3, 4, etc. are neglected. This is called a harmonic approximation. Terms with higher power (3, 4, etc) are called inharmonic, hence $V(r)$ can be written as:

$$V(r) = \frac{1}{2} \left[\frac{\partial^2 V}{\partial r^2} \right]_{r=r_0} (r - r_0)^2 \quad (2.11)$$

where

$$\left[\frac{\partial^2 V}{\partial r^2} \right]_{r=r_0} = k \quad (2.12)$$

k = Force constant.

As before wavenumber is defined as $\tilde{\nu} = \frac{1}{\lambda}$ where λ is a wavelength and is measured in cm. The frequency of vibrations is proportional to $\tilde{\nu}$.

$$f = \frac{c}{\lambda} = \tilde{\nu} c \quad (2.13)$$

where c = speed of light

The result is given by [10]:

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{m}} \quad (2.14)$$

where $m = m_1 m_2 / m_1 + m_2$, is a reduced mass. $\tilde{\nu}$ provides results for a certain

frequency or intensity of a vibration for diatomic molecule. The position of vibrations for the more complex molecules is complicated to calculate and requires advanced numerical methods. Nevertheless, today various PC programs are available to calculate the spectrum of a complex molecule with its chemical formula as an input data [11]. In this thesis Gram Research program version 368 is used for the analysis of the peak intensities belonging to molecular vibrations of the ferroelectric and antiferroelectric liquid crystal materials.

Analysis of infrared spectrum shows that, for lines (absorption spectrum of a vibration during the transition of a molecule from one oscillation level to another) and bands (the set of lines), the shape can be approximated by Gauss and Lorentz functions. The measurements of the line or a band profile have also shown that the line or a band exhibits neither the shape of a pure Lorentz nor Gaussian functions. The reason for the line and a band being mixture of the two shapes is due to (1) the effects of interatomic and intermolecular interactions and (2) the Doppler effect of vibrating atoms and natural vibration damping. i.e. Lorentz (due to 1) and Gaussian (due to 2). Gram Research program for bandfit is capable of fitting the bands with the individual function or mixture of both. The Lorentz function is also known as Cauchy function.

The Lorentz and Gaussian functions are described by the following formula:

Lorentz function

General formula
$$L(\tilde{\nu}) = \frac{a}{b^2 + \tilde{\nu}^2} \quad (2.15)$$

Normalised hight $L(\tilde{v}) = \frac{b^2}{b^2 + \tilde{v}^2} \quad (2.16)$

Normalised area $L(\tilde{v}) = \frac{b^2}{\pi(b^2 + \tilde{v}^2)} \quad (2.17)$

Where $2b$ is the width of a line at half of its maximum height $\frac{a}{b^2}$ and $\tilde{v}$ is measured from the maximum of $L(\tilde{v})$.

Gaussian function

General formula $G(\tilde{v}) = \frac{a}{b^2} \exp\left[-\frac{\tilde{v}^2 (\ln 2)}{b^2}\right] \quad (2.18)$

Normalised height $G(\tilde{v}) = \exp\left[-\frac{\tilde{v}^2 (\ln 2)}{b^2}\right] \quad (2.19)$

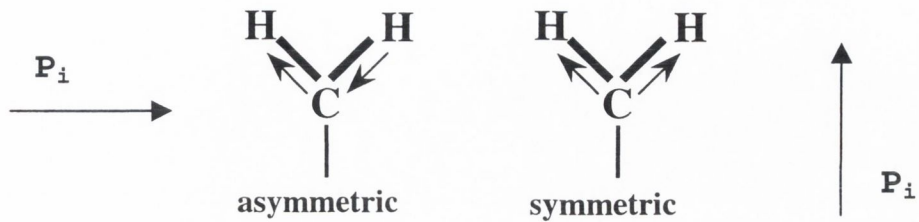
Normalised area $G(\tilde{v}) = \frac{\sqrt{\ln 2}}{b\sqrt{\pi}} \exp\left[-\frac{\tilde{v}^2 (\ln 2)}{b^2}\right] \quad (2.20)$

The symbols used for Gaussian function have the similar meaning as for the Lorentz function. Note that, these formulas are considered as a foundation for band fitting procedure.

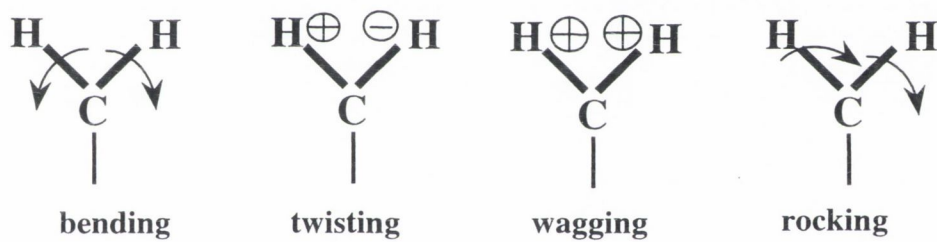
2.6. Vibrations of Liquid Crystal molecules due to Infrared beam

Ferroelectric and antiferroelectric liquid crystals investigated in this thesis contain rod like molecules. Various type of LC molecules are described in the early chapter. Rod like LC molecules consist of molecular core and a tail. Generally molecular core contains phenyl rings and carbonyl groups. Molecular tail contains CH_2 (methylene) and CH_3 (methyl) groups. The transition dipole moment (P_i) of an individual molecular group interacts with an incoming infrared beam and its average position decides about an absorbance of the line for a certain vibration. The change of dipole moments parallel and perpendicular to the axis of the any molecular group give rise to the parallel and perpendicular bands in the spectra respectively. Maximum and minimum absorbances are also obtained when peak intensities belonging to parallel and perpendicular bands are analysed respectively. Figure 2.4 shows the possible vibrations for CH_2 and CH_3 groups.

Stretching vibrations for CH₂ group



Bending or deformation vibrations for CH₂ group



Bending or deformation vibrations for CH₃ group

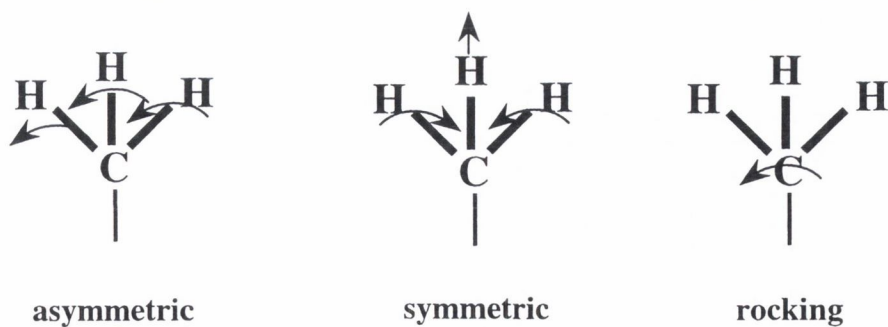


Figure 2.4. Some possible vibrations for CH₂ and CH₃ groups.

Vibrations for CH₂ and CH₃ groups occur at various frequencies. Their approximate values are shown in Table 2.1.

Approximate wavenumber (cm ⁻¹)	Group assignments
2950	CH ₃ asymmetric stretching vibration
2930	CH ₂ asymmetric stretching vibration
2870	CH ₃ symmetric stretching vibration
2850	CH ₂ symmetric stretching vibration
1468	CH ₂ scissoring deformation
1460	CH ₃ asymmetric deformation
1380	CH ₃ symmetric deformation
1350, 1180	CH ₂ twisting deformation
1300	CH ₂ wagging deformation
1140, 1130	CH ₃ rocking deformation
720	CH ₂ rocking deformation

Table 2.1. Vibrational frequencies for CH₂ and CH₃ groups.

The frequency of vibrations listed in Table 2.1 can vary by about ± 15 cm⁻¹ depending on the substituent groups. In addition to CH₂ and CH₃ symmetric and asymmetric stretching vibrations, phenyl (C – C) stretching vibrations at the frequency of 1602 cm⁻¹ and the carbonyl (C = O) stretching vibrations for the core and chiral at frequencies of 1743 and 1719 cm⁻¹ are investigated for this study. Generally

connection of the various groups to the phenyl rings can alter its frequency of vibrations by about $\pm 10 \text{ cm}^{-1}$ [10]. Other vibrational frequencies for phenyl rings and the carbonyl groups can be observed using the published infrared data [12-15].

2.7. References

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Chapter3

How Fourier Transform Infrared operates

3.1. The infrared spectrometer

Figure 3.1 illustrates the Michelson interferometer, which is the central part of any FTIR spectrometer.

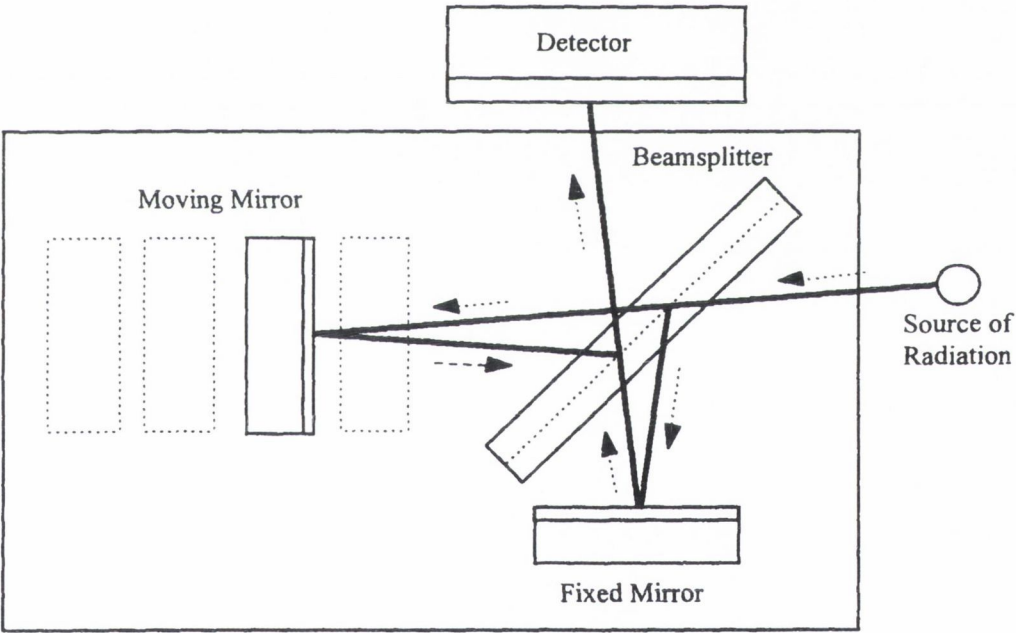


Figure 3.1. Michelson Interferometer

The interferometer contains a fixed mirror, a movable mirror, and a beamsplitter. The beamsplitter transmits half of the incident radiation to the moving mirror and reflects the other half to the fixed mirror. The two beams are reflected back by these mirrors to the beamsplitter, where they recombine.

When the fixed mirror and moving mirror are equidistant from the beamsplitter, the amplitudes of all frequencies are in phase and recombine constructively. This position of zero path difference (zpd), or zero retardation, is where the interferogram centerburst occurs. As the moving mirror is moved away from the beamsplitter (retarded), an optical path difference is generated. As the position of the moving mirror changes, the two beams travel different distances within the interferometer before recombining. A pattern of constructive and destructive interference is generated based on the position of the moving mirror and the frequency of the retardation. Thus, the intensity of the radiation varies in a complicated pattern, as a function of the mirror movement, and the output beam is a result of modulation by the interferometer. This modulated output beam is then directed through the sample compartment to the detector. At the detector it generates a continuous electrical signal called an *interferogram* [1].

The moving mirror is driven at a constant velocity by a linear motor under computer control to vary the optical path difference. A beam from a He-Ne laser, operating at 632.8 nanometers, is also passed through the interferometer to its own detector, where it generates a reference signal, which enables the spectrometer electronics to sample the interferogram at precise intervals. The computer converts the interferogram into a single-beam spectrum by Fourier transformation. The single-beam background spectrum is the spectrum of the source modified by the transmission characteristics of the beamsplitter and the response characteristics of the detector. Most grating instruments (dispersive) are double beam spectrometers, which measure the spectrum of the radiation that passes through the sample and automatically ratio it to the spectrum of the source. This

results in a transmission spectrum directly. FTIR instruments, however, first collect the spectrum of the source (single-beam background spectrum), and store it on disk. Then the sample is inserted in the instrument. The single-beam spectrum of the source, modified by the absorption due to the sample, is collected and ratioed against the single-beam background spectrum to obtain the desired transmission spectrum.

The optical retardation is equal to twice the difference between the distance of the moving mirror and the distance of the fixed mirror from the beamsplitter.

Resolution is the smallest frequency separation for which two distinct spectral lines of equal intensity can be distinguished.

Apodization is a method to control the line shape. This does cause some decrease in resolution. Generally two types of apodization are employed (1) Triangular: with lower resolution, used for liquid and solid phase sample and (2) Boxcar: with high resolution, used for gas phase sample.

In FTIR spectroscopy a quantitative relationship exists relating signal to noise ratio (SNR), resolution, number of scans, and measurement time. This is shown as [2]:

$$\text{SNR} \propto (N)^{1/2} \propto (T_m)^{1/2} \quad (3.1)$$

Where N is the number of scans and T_m is the measurement time (mirror moving time). For example, if a spectrum is collected at 4cm^{-1} resolution using 16 scans it will have twice the signal to noise ratio as a 4cm^{-1} spectrum using 4 scans.

The signal to noise ratio of a spectrum is also related to the resolution. For a

given number of scans the signal to noise ratio increases as the resolution decreases. A spectrum at the resolution of 8 cm^{-1} has twice the signal to noise ratio as a spectrum obtained with an equal number of scans but at a resolution of 4 cm^{-1} . Hence, the analysis is related to the time and resolution is:

$$T_m \propto 1/\text{Resolution} \quad (3.2)$$

3.2. FTS-60A System Hardware

Figure 3.2 shows the FTS-60A spectrometer with the main operating components attached to it. The Bio-Rad FTS-60A spectrometer features a dynamically aligned interferometer with the capability of spectral range changes through interchangeable beamsplitters. The changing of beamsplitters is facilitated through an autoalignment program. Two detectors, DTGS and an MCT can be used with this spectrometer. The later detector must be cooled by nitrogen. The DTGS detector does not need cooling but its operation in scanning the spectrum is few times slower. The MTC detector must be filled approximately half an hour before scanning, to stabilise the temperature. Note that, every 5 to 6 hours the detector has to be refilled with liquid nitrogen. To keep the interferometer alignment stable, the MTC detector must be filled slowly and gently. Otherwise the alignment needs to be performed again by removing the sample. Afterward, measurements should be repeated. The FTS-60A spectrometer incorporates dynamic interferometer alignment in a high throughput 60° Michelson interferometer.

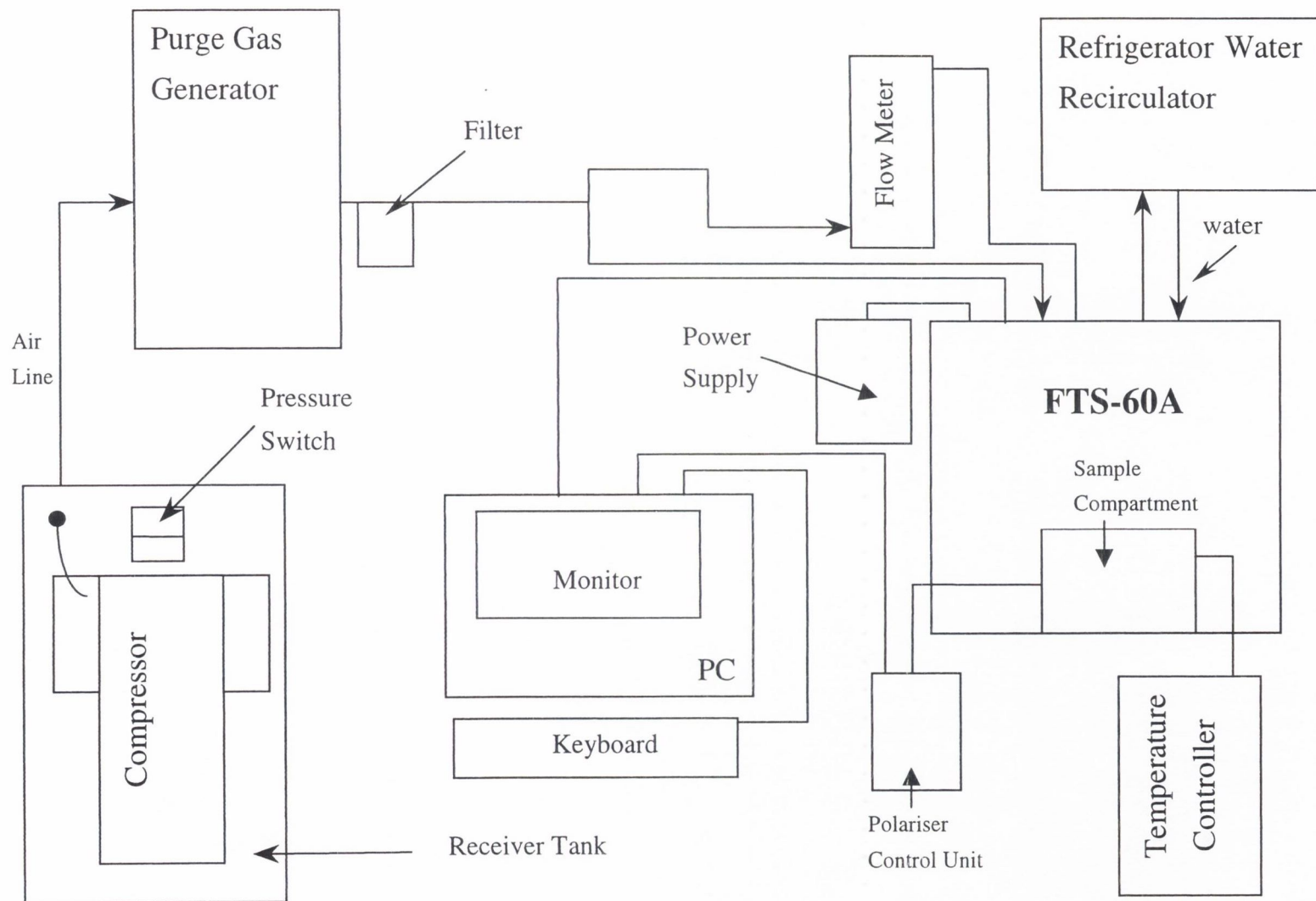


Figure 3.2. The FTS-60A system with external components.

The proprietary dynamic alignment system uses multiple reference laser beams for precise mirror tracking and accurate alignment. The spectrometer optical head is equipped with dual source and dual detector capability, i.e. with Far and Mid infrared source Mercury Arc Lamp. The Mid infrared region is obscured by intensive water vapour absorption. Due to this, an efficient system for purging is necessary. The external components attached to the FTS-60A spectrometer shown in Fig. 3.2 are briefly described as follows:

Air bearing and purge requirements – Purging is vital as it extracts the humidity out of the spectrometer and keeping the detector and the measuring compartment continuously dry with a constant flow. Also *in the air bearing* of the interferometer, the shaft attached to the moving mirror is surrounded with a cushion of this dry clean air upon which it floats.

It is noted that, a reliable hardware design arrangement and installations of the purging devices were performed by the *author*. For this, a GAST double piston dry runner compressor is installed on the 25 liter receiver tank with the pressure switch. Compressed air with 4 bar pressure and free pulsation is supplied from the tank to the Whatman Purge Gas Generator and after purification circulates through the spectrometer with the flow of 7.5 liter per minute. It is noteworthy to mention that, *air bearings* are somewhat sensitive to vibrations, which can cause the shaft attached to the moving mirror to bounce around and contact the housing. This leads to errors in the measurement of the interferogram. Fig. 3.3 shows the example of a moving mirror with an air bearing. Mechanical bearing is also used in some interferometers, but due to bearing friction they are not as sensitive in

comparison with interferometers containing air bearing [3].

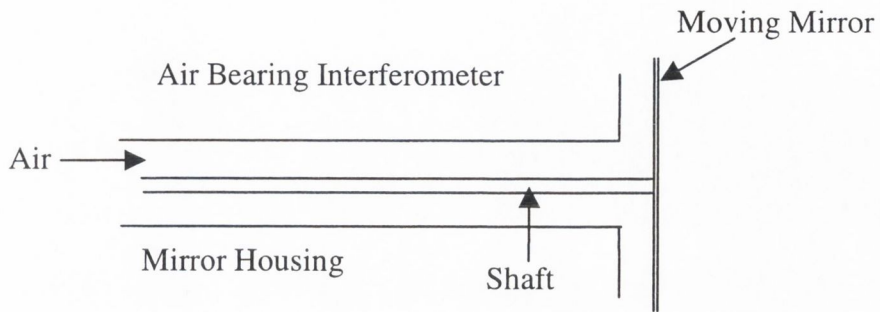


Figure 3.3. Moving mirror with air bearing mechanism.

Source Cooling – To cool the IR source, a supply of non-corrosive cooling water is required. For this, a closed cycle Bio-Rad Refrigerated Recirculator model E4860 is used to circulate the water at the temperature of 20° C and the flow of 1 liter per minute through the spectrometer chamber by the connector pipes of half an inch thickness.

Power Supply – This is a separate module from the spectrometer and supplies power to the spectrometer via a cable. The power module is internally fused to protect it against most common surges and transients.

PC – This is used to execute the data and controls the various functions of the spectrometer.

Temperature Controller – The Oxford Intelligent temperature controller (ITC4) is used to control and keep the temperature of the liquid crystal sample constant during measurements. ITC4 temperature controller is programmable and working on the base of the Zilog Z80A, 8-bit microprocessor. The thermocouple and the heater which are attached to the sample are connected to one of the I/O 9-way D-socket on the rear panel of the ITC4. The information about the temperature of the sample goes to the controller, and the controller alters the voltage on the output connected to the heater. It is important to keep the lid of the measuring compartment closed during measurements. Otherwise, about 30 minutes is needed for the purging and the sample temperature to stabilise again.

In order to avoid the overshooting and stabilise the temperature in the high temperature region some important parameters should be set on the controller.

The most appropriate experimental parameters are as follows [4]:

INT = 4.0 (Integral Action Time in minutes)

DERIV = 0.0 (Derivative Action Time in minutes)

PROP = 0.8 for temperatures < 370 K

PROP = 1.0 for temperatures between 370 and 400 K

PROP = 1.4 for temperatures > 400 K

PROP indicates the proportional band as a percentage of the input span.

The most appropriate time step for the liquid crystal sample to sweep the temperature from one value to another is 1 K/1 minute. When the required phase temperature is reached, approximately half an hour is needed before measurements can be made. Otherwise, phase pretransitional effects may influence the results.

Polariser Rotator – The degree of the angle of polariser rotation is automatically controlled by a computer. For this, a stepper motor that rotates the polariser is connected through the control unit to a PC. The capability of a rotational step by this device is 2 degree.

In FTIR once an interferogram is measured, it is digitized using analog to digital converter (ADC). The purpose of the ADC is to turn the signal from volts or analog signal into a series of base 2 numbers (a digital signal), the language that a computer understands. To eliminate detector saturation, the amount of infrared energy reaching the detector must be reduced. One way to do this is to place an aperture in the beam. Second way is by placing a neutral density filter in the beam to attenuate it. With FTS-60A spectrometer, metal mesh is used for this purpose. Number of metal meshes in the beam can control the amount of infrared radiation reaching the detector.

3.3. References

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2. P. Griffiths and J. de Haseth, *Fourier Transform Infrared spectroscopy*, Wiley, New York, 1986.
3. B. C. Smith, *Fundamental of Fourier Transform Infrared Spectroscopy*, CRC Press, 1996.
4. Instruction Manual for *Oxford Intelligent Temperature Controller* (ITC4).

Chapter 4

System Software and Spectra Manipulation

4.1. Introduction

General theory of infrared spectroscopy states that a molecule may absorb infrared radiation of the appropriate frequency to excite it from one vibrational or rotational level to another. When a beam of infrared energy, covering a broad frequency range, passes through a sample, the energy at certain frequencies is absorbed by the sample. A graph of energy absorbed versus frequency is the absorption spectrum of the sample. The spectrum is a characteristic of the particular molecule and its molecular motions.

4.2. How an Interferogram changes to a Spectrum

According to the theorem developed by Fourier, any mathematical function with an (x, y plot) can be expressed as a sum of sinusoidal waves. An interferogram is simply a large number of sinusoidal signals added together, each of which contains information about the wavenumber of a given infrared peak and amplitude information about the peak intensity at that wavenumber. The Fourier Transform

simply calculates the infrared spectrum from the summed sinusoidal waves in the interferogram. The practical aspect of this definition is such that, the interferogram is a plot of infrared intensity versus optical path difference, which can be measured in centimeter [1].

4.3. FTS-60A System Software

Win-IR Version 4 software package supplied by Bio-Rad Digilab was used to produce the sample spectra. For this, it was necessary to install special electronic boards on the spectrometer and on the PC attached to it. The purpose of the installation was to convert the analog signals produced by the spectrometer directly to digital signals for the execution of data by a PC.

For calculating the absorbance, the integrated absorbance for the separated peaks and the peak positions, *Win-IR Version 4* is identical to *Gram Research Version 386*, which is used in this research. The instruction and operating manuals for these computer packages clearly describe their usage. Nevertheless, some of the features for the manipulation and analysis of the infrared spectra will be detailed at a later stage in this chapter. In order to plot the maximum absorbance ($A_{\max}$), maximum polarisation angle ($\Omega_{\max}$) and the dichroic ratio ($A_{\max}/A_{\min}$) against the applied voltage to the sample, *Origin Version 378* software package was used. Note that, the

above computer packages can be run on the Microsoft Windows 95 operating system.

4.4. Obtaining an IR Spectrum

To obtain a spectrum characteristic of the sample, all effects and features of the spectrometer (*instrument function*) must be eliminated. The instrument function varies from spectrometer to spectrometer. It depends upon the output of the source, efficiency of the beamsplitter, reflective losses of the optics, atmospheric absorbances in the beam path, and response of the detector and pre-amplifier.

The instrument function is removed by first recording a background spectrum (that is, a spectrum with no sample), then measuring a sample spectrum, and finally dividing one by the other. This procedure can be described as follows:

1. Collect a background interferogram.
2. The background interferogram is Fourier transformed into a background single beam spectrum.
3. The sample is inserted into the beam in the measuring compartment. The sample interferogram is collected.
4. The sample interferogram is Fourier transformed into a sample single beam spectrum.
5. Next, to obtain the desired ratioed spectrum:

(a). To produce a % transmittance spectrum, the sample single beam spectrum is divided by the background single beam spectrum, and displayed and/or plotted from 0 to 100%.

$$\%T = (Sample\ single\ beam\ spectrum / Background\ spectrum) * 100 \tag{4.1}$$

(b). To produce an absorbance spectrum, the logarithm (base 10) of the reciprocal of the transmittance spectrum is computed.

$$A = \log_{10} (1/T) \tag{4.2}$$

$$\text{where } T = \frac{Sample}{Background} \tag{4.3}$$

Using *Win-IR Version 4* software [2], one can combine the above steps as follows:
 First take a background spectrum. A single command will collect the interferogram and compute the single beam spectrum.
 Second insert the sample, and select the type of spectrum required (for example % transmittance or absorbance). A single command will collect the interferogram, compute the single beam spectrum, and produce the desired spectrum.
 The typical transmittance and absorbance spectrum are shown in Fig. 4.1 and Fig. 4.2 respectively.

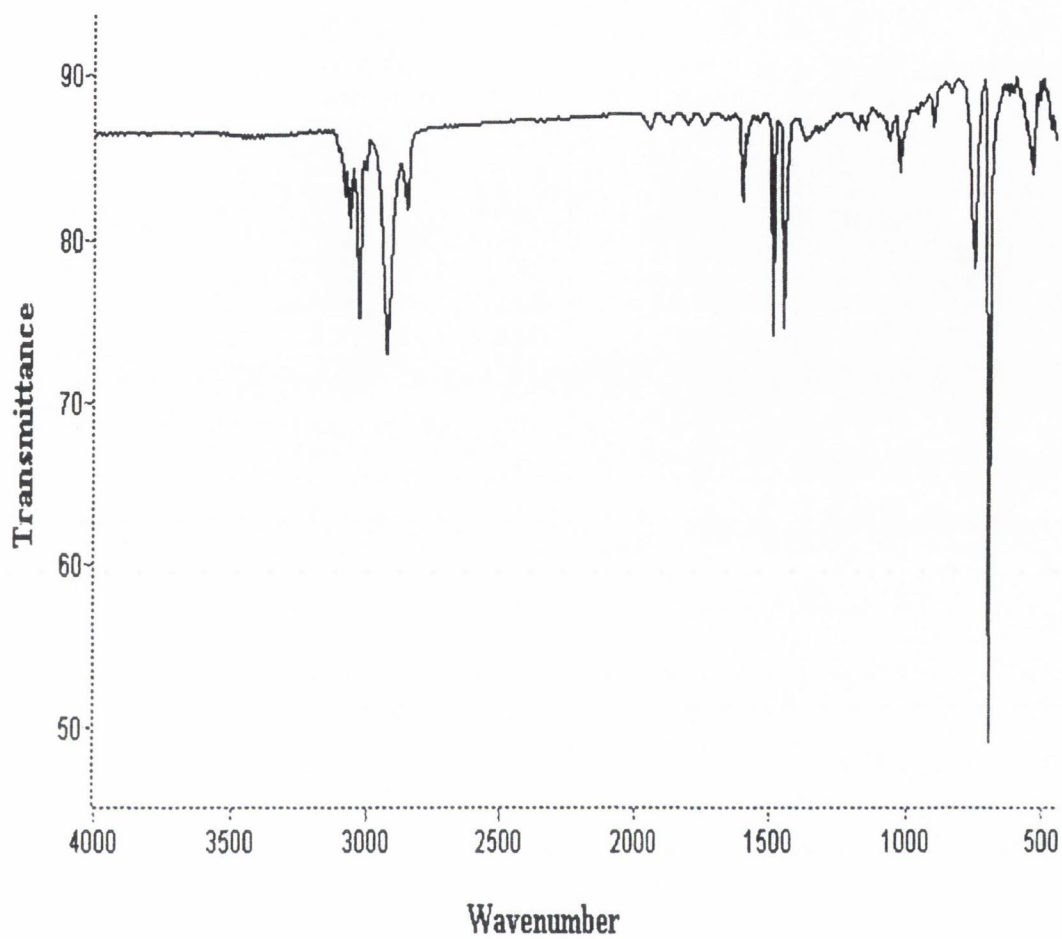


Figure 4.1. An example of a transmittance spectrum. The graph shows percentage transmittance and the frequency scale from 500 cm^{-1} to 4000 cm^{-1} .

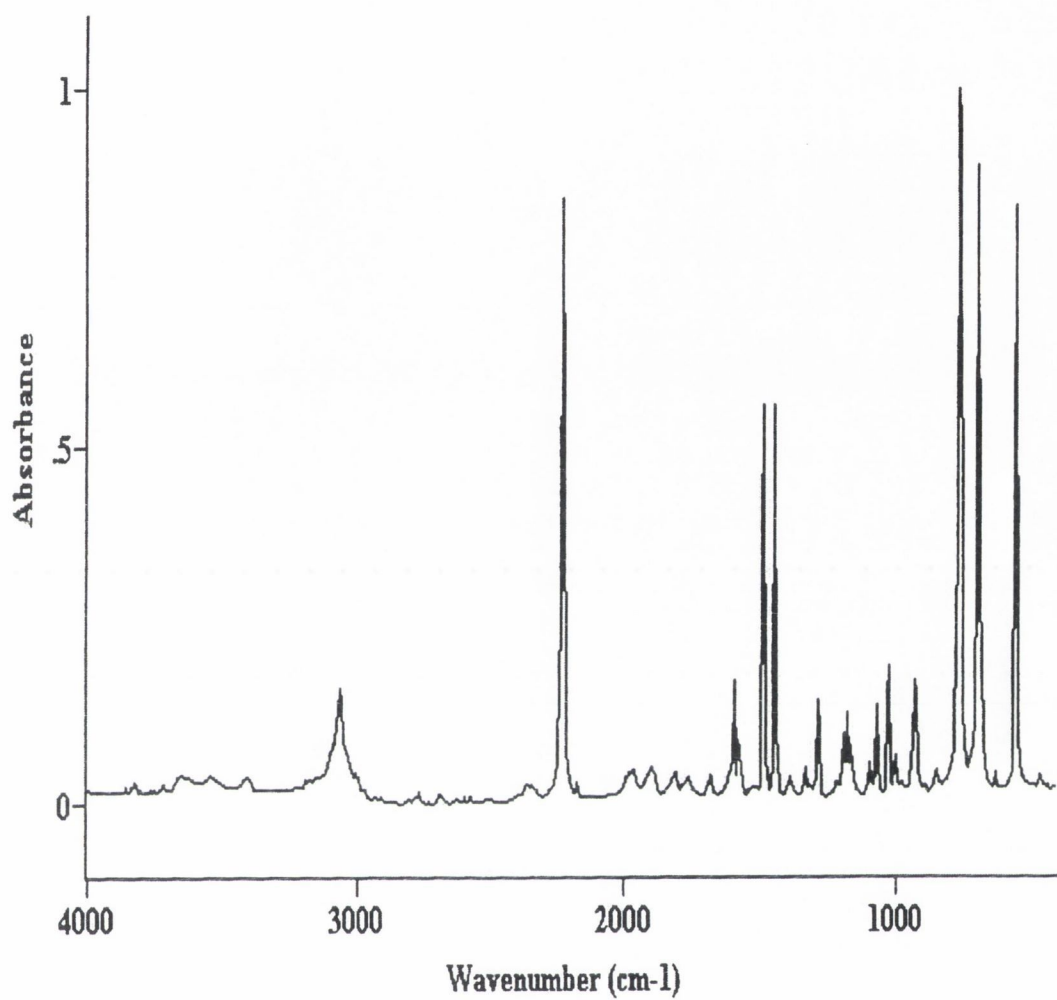


Figure 4.2. An example of an absorbance spectrum. The intensity scale is from zero to one and the frequency scale is from 500 cm^{-1} to 4000 cm^{-1} .

4.5. Spectra Manipulation

For this thesis, the manipulation of absorbance spectra is performed using *Gram Research Version 386* software package [3]. This procedure involves altering or performing a calculation on the original spectrum received from the instrument. The purpose of manipulating a spectrum is to enhance its appearance, or extract more information by interpretation of certain parameters, characteristics or behaviour. If spectral manipulations are not performed properly they can add artifacts to a spectrum, or completely destroy the integrity of the data [4].

In this research, peak intensities of different frequency of the absorbance spectra (maximum absorbance) for various polarisation angles and voltages are calculated. For this, when a particular absorbance spectra is selected as an active file in Gram Research program, one can use the applications of *Arithmetic Menu* of the program to fit the required bands (whether the bands are overlapped or not). In this way, the fitted values of peak intensities are calculated.

The Arithmetic Menu Applications provide a library of the common operations performed on the scientific data. They can be selected directly from the Arithmetic Menu. Clicking the OK button after performing an arithmetic application will first confirm if you wish to keep the results. Some of the important commands when using these applications for fitting are as follows:

“Add New” retains the original data and creates a temporary copy of the new data in the memory. Use File / Save to save the new data.

“*Replace*” replaces the original file with the new data. Use file / Save or Save As to save the results.

“*Discard*” retains only the original data and is similar to the *Cancel* button.

The standard Arithmetic Menu Applications for the fitting of the absorbance spectra in this investigation in the order of usage are as follows:

1. ***Zap*** – This is used to truncate the trace or spectra to a specific region (i.e. selects a particular section of the spectra or band at certain frequencies).

2. ***Baseline*** – This application performs baseline correction of a data file using one of three possible methods: Two point level, Multiple point level, and Auto level. These methods differ in how the baseline is defined.

The simplest method “Two point level” which is used in this work performs a linear, two-point baseline correction.

The “Multi-point” method allows multiple point baseline correction. This method is similar to the Two-point method.

The “Auto level” method performs baseline correction without any user interaction, making it the easiest method to use. It automatically fits the best straight baseline to the *non-peak* areas of the data. Note that, this method is optimized for use with absorbance data only and not the transmittance data.

When the baseline correction procedure is completed, the base of the spectra or a band will coincide with the frequency axis of the spectra. The next step is to go to “Offset”.

3. ***Offset*** – This adds or subtracts a constant *offset* to the current data file. This has the effect of simply sliding the trace up or down along the Y-axis. To locate the

minimum point in the data after baseline correction and set it to a Y value of zero, click the Zero minimum button. The trace is shifted such that the Y-value of the minimum point of the absorbance spectra becomes zero. At this time, the selected part of the spectra with the corrected baseline on zero is ready for the *Curve Fit* application.

4. ***Curve Fit*** – Curve Fit is a powerful application that models or fits a number of ideal peaks to a complex set of overlapping peaks. Curve Fit is also commonly referred to as peak deconvolution, peak fitting, or curve fitting. GRAMS/386 Curve Fit is a complete, fast and flexible application. Capabilities of this application include:

Fits Gaussian, Lorentzian, mixed Gaussian-Lorentzian, Log Normal, Pearson VII, Voigt, and exponentially modified Gaussian line shapes.

Fits a baseline using an offset, linear, quadratic or cubic model.

Peak parameters may be optionally locked or constrained.

The number of peaks fit and the size of the data to fit are constrained only by available memory. Literally hundreds of peaks can be fit over thousands of data points.

An advanced AutoFind peak picker automatically estimates the initial number of peaks and their positions.

An interactive peak selector is provided for fast, flexible selection of initial parameters by real time visual inspection of the peaks and the residual trace.

Flexible statistics and graphic reporting.

CurveFit is based on the original algorithm of non-linear peak fitting as described by Marquardt and also known as the Levenberg-Marquardt method [5]. Curve fitting can be extremely useful for determining the exact peak positions, widths, heights, and areas of a set of overlapping peaks. It is less useful for determining the exact number of peaks except, in an indirect fashion by examining the residual error of the fit for a different number of fitted peaks.

Curve fitting can be a frequently misused and misunderstood mathematical processing technique and the results should be carefully scrutinized. This is not the fault of the technique itself but rather that of the scientist employing the tool. Curve fitting requires the use of non-linear fitting techniques and, as such, must proceed to a solution iteratively from a set of trial values.

Assume that a measurement is made (usually spectroscopic or chromatographic) whereby the peaks are poorly resolved. The analyst needs to resolve the peaks and determine accurately the number of peaks, the positions, and the areas. For some types of measurements, it may be possible to improve the resolution to assist in these calculations. In others, it may be impractical or impossible. This measurement may be a candidate for the application of curve fitting, provided the following information is obtainable.

1. An accurate determination of the number of peaks.
2. Knowledge of the true peak shapes (e.g., Gaussian, Lorentzian, etc.).
3. An approximate estimate of the peak parameters (e.g., width, height, etc.).

These initial estimates are entered into the Curve Fit program. The program then adjusts these starting values to obtain the "best" fit of the sum of the calculated peaks to that of the measured peaks. The goodness-of-fit in this case is described as follows [3]:

$$\chi^2 = \frac{\sum_{i=0}^n \left(\frac{Actual_i - Calculated_i}{RMSNoise} \right)^2}{(n - f)} \quad (4.4)$$

The *Actual* and *Calculated* values are the measured and calculated data, respectively. The *RMS Noise* is the estimated Root Mean Squared noise in the *Actual data* over the fitted region. The variable n is the number of data points in the fitted region and f is the total number of variables from all the peak and baseline functions. Thus, $(n - f)$ is the number of degrees of freedom.

Fig. 4.3 shows the example of a fitted band using Gram Research Version 386. The fitted value of each peak in the overlapped band is shown. In this way the best value of absorbance for any vibrational band at the certain polarisation angle and the applied voltage is obtained. The data values of these absorbances were transferred to *Microcal Origin Version 378* [6] and the polar plots with 0° to 360° polarisation angle were constructed for each value of the applied voltage to the Liquid Crystal cell.

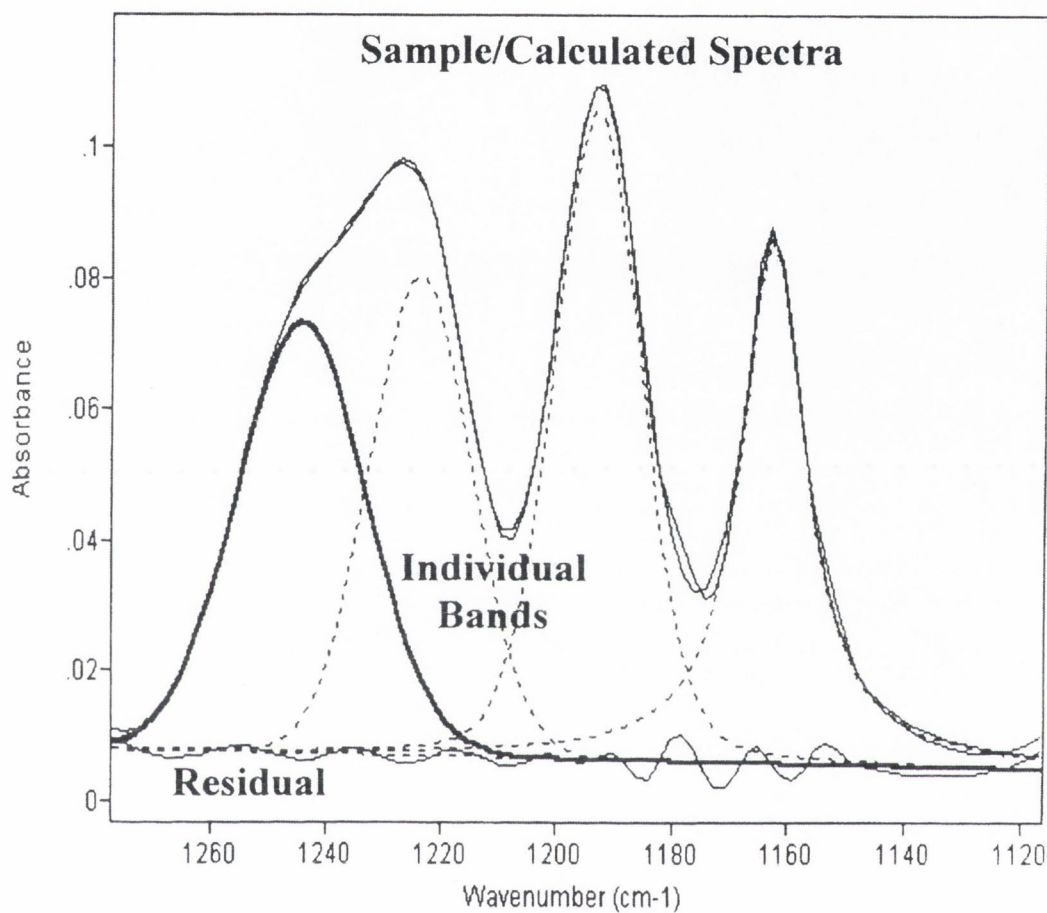


Figure 4.3. An example of the results of a curvefit. The sample spectrum and the calculated spectrum are almost perfect overlaps as seen in the top of the display. The middle shows the bands that make up the calculated spectrum, and the bottom shows the residual.

The absorbance profiles from the polar plots of the required vibrational bands for various DC applied voltage are fitted to equation (4.5) [7,8] and the values of maximum absorbance ($A_{\max}$), minimum absorbance ($A_{\min}$) and maximum polarisation angle ($\Omega_{\max}$) are calculated. For this, the fitting procedure in *Microcal Origin* is used.

$$A(\Omega) = -\log (10^{-A_{\max}} + (10^{-A_{\min}} - 10^{-A_{\max}}) \sin^2(\Omega - \Omega_{\max})) \quad (4.5)$$

In equation (4.5), Ω is the angle of polarisation, $A_{\max}$ and $A_{\min}$ are related to parallel and perpendicular absorbances respectively and $\Omega_{\max}$ is the polarisation angle at which $A_{\max}$ is obtained.

In this thesis characteristics of several molecular groups in various smectic phases of two liquid crystal samples are substantially investigated using Polarised Fourier Transform Infrared Spectroscopy.

These are as follows:

- (a). SmC* and SmA* phases of a ferroelectric liquid crystal mixture.
- (b). SmC_A*, SmC_γ*, SmC* and SmA* phases of an antiferroelectric liquid crystal.

The experimental procedures, detailed discussions and the findings of these investigations are presented in chapter 5 and chapter 6.

4.6. References

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2. User Instructions for *Win-IR Version 4* software package for operating FTS-60A spectrometer.
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Chapter 5

Influence of Bias Voltage on the Orientation of Core Carbonyl and Phenyl Groups of a Ferroelectric Liquid Crystal Mixture

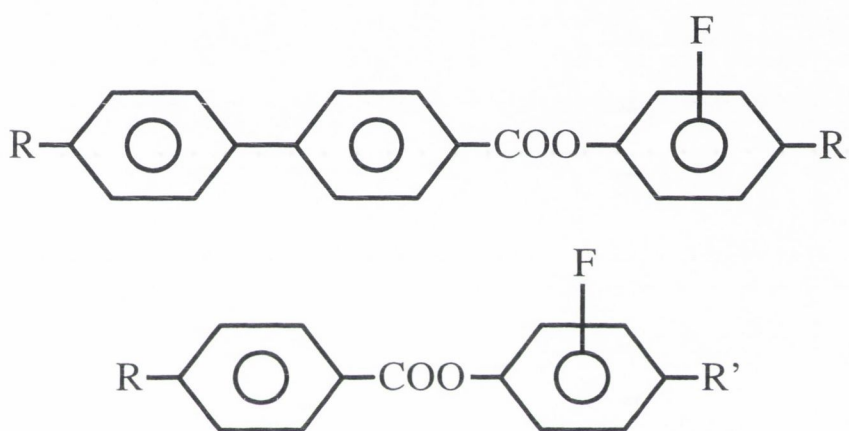
5.1. Introduction

In this chapter Fourier Transform Infrared Spectroscopy is used to find the effect of the applied bias voltage on the orientational behaviour of core carbonyl ($C=O$) and phenyl ring ($C-C$) bands with stretching vibrations at 1737 cm^{-1} and 160 cm^{-1} , respectively. Infrared measurements at normal incidence are carried out as a function of the polarisation angle for which the bias voltage is altered across the cell. The effect of bias voltage on the dichroic ratio for the phenyl ring is observed whereas carbonyl group is found not to exhibit dramatic variation in the dichroic ratio. The degree of orientation is expressed in terms of the dichroic ratio as a function of the bias voltage which, shows a difference in the pattern for phenyl band as the polarity of the field is altered across the cell. The angle between the smectic layer normal and the direction to absorbance maximum (A_{max}) together with their absorbance profiles of both carbonyl and phenyl groups rotate with different degree with respect to the zero axis of the polariser as the polarity of the applied bias voltage is altered. The absorbance profiles of each stretching band are studied and their characteristics in relation to the orientation of the molecules are discussed. The apparent tilt angle for each molecular group is also found and their

values as a function of the applied electric field are given. FTIR spectroscopy is an efficient technique for investigating the orientational behaviour of the various parts of the molecules in a liquid crystal cell [1,2]. It is known that in a bookshelf geometry the direction of the long molecular axis is fixed relative to the smectic layer normal by the application of a constant electric field. This voltage across the cell causes distortion and an eventual unwinding of the helicoidal structure. However the molecular director can be switched to a new but opposite sense when the sign of the applied field is altered. In this arrangement the molecular director is parallel to the plane of the cell windows [3]. The intermolecular interactions can influence the frequency and the shape of the vibrational bands under investigation. This leads to a better understanding of the molecular behaviour for switching in SmC*. Furthermore, absorption profiles obtained from these selected bands as a function of the polariser rotation angle together with their rotational motion can be studied in greater details. Generally for chiral materials the origin of ferroelectricity lies in the average biased rotation of the molecules about their long axis. The biased rotation and the permanent dipole moment located near the chiral center gives rise to the spontaneous polarisation. Note that, for this material due to the low percentage of the dopant the effect of chirality is considerably low and also the location of the chiral center in the structural formula is not known. For this study we focus our attention on the characteristics of the phenyl and the core carbonyl groups.

5.2. Experimental

The material (SCE8) used in this investigation is a commercial ferroelectric liquid crystal mixture manufactured by Merck Ltd [4]. The structural formula and the phase transition temperatures in °C are as follows:



This material is a mixture of two components and two substituents R and R'. One component is a chiral dopant with ~ 5% and the other is a matrix which is not chiral. R and R' represent the alkyl chains in the molecules. R represents heptyloxy, octyloxy and dodecyl chains in the ratio 1.9, 2.7 and 1.0. R' represents pentyl, heptyl and octyloxy chains in the ratio 3.75, 1.0 and 1.25 respectively. Precise molecular structure is not available due to the manufacturer regulations.

Sample was aligned between the two transparent CaF_2 windows with inner surfaces coated with conductive indium tin oxide (ITO). For planar alignment ITO surfaces were spin coated with polyvinyl alcohol (PVA) and after drying, the surfaces were rubbed in antiparallel directions on a velvet rail. In this way the surfaces become grooved and hence, during the cell filling with liquid crystal, molecules will lie approximately along the direction of the grooves. Mylar spacer of thickness $6\mu\text{m}$ was used between the two CaF_2 windows for obtaining a fixed sample thickness. The cell was filled at a temperature above the isotropic phase, i.e. $>100^\circ\text{C}$, and examined for the alignment using polarising microscope. The structure of the cells used in this study is shown in Fig. 5.1(a).

Measurements were carried out by recording the polarised IR spectra as a function of the polarisation angle for different DC voltages across the cell in SmC^* phase. No electric field was applied for carrying out measurements in SmA^* phase. For this investigation the absorption peaks at 1737 cm^{-1} for the core carbonyl stretching ($\text{C}=\text{O}$) and at 1605 cm^{-1} for phenyl ring stretching ($\text{C}-\text{C}$) vibrations have been analysed. The polarisation angle is fixed to be zero when the axis of the polariser is parallel to the smectic layer normal. A Bio-Rad FTS60A spectrometer with a 2cm^{-1} resolution with an averaging over 16 scans is used. The wire grid polariser is rotated with a computer controlled device with a capability of a rotational step by 2 degrees.

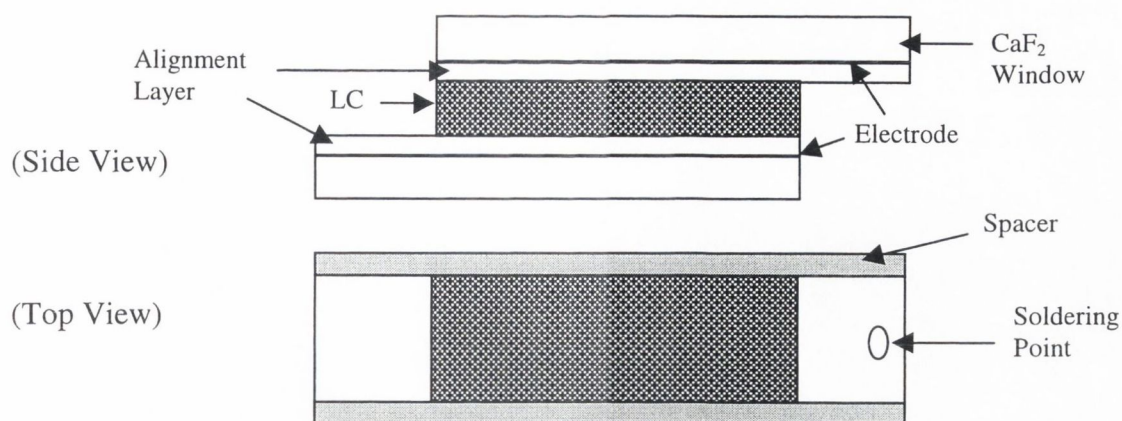


Figure 5.1(a). Structure of the experimental cell.

5.3. Results and Discussion

Fig. 5.1(b) illustrates the absorbance versus frequency for two vibrational bands that have been investigated. The angle of polarisation for 0° and 90° represents parallel and perpendicular spectra with respect to the smectic layer normal.

The selected bands correspond to the molecular vibrations of the core carbonyl (C=O) at the frequency of 1737 cm^{-1} and the phenyl (C-C) vibrations at frequency of 1605 cm^{-1} .

The polarisation angle is defined as the angle between the layer normal and the electric vector of the infrared beam. In SmA* phase the long molecular axis is essentially parallel to the smectic layer normal and therefore lies along the rubbing direction of the cell windows. Fig. 5.1(b) displays the differences between absorbance peaks at 0° and 90° polarisation angles which represent a higher degree

of orientation for the phenyl rather than for the core carbonyl group in SmC* phase at an applied voltage of +12V. The small shift of frequency between peak positions for core carbonyl group seen in Fig. 5.1(b) can be addressed to the existence of dopant in the compound.

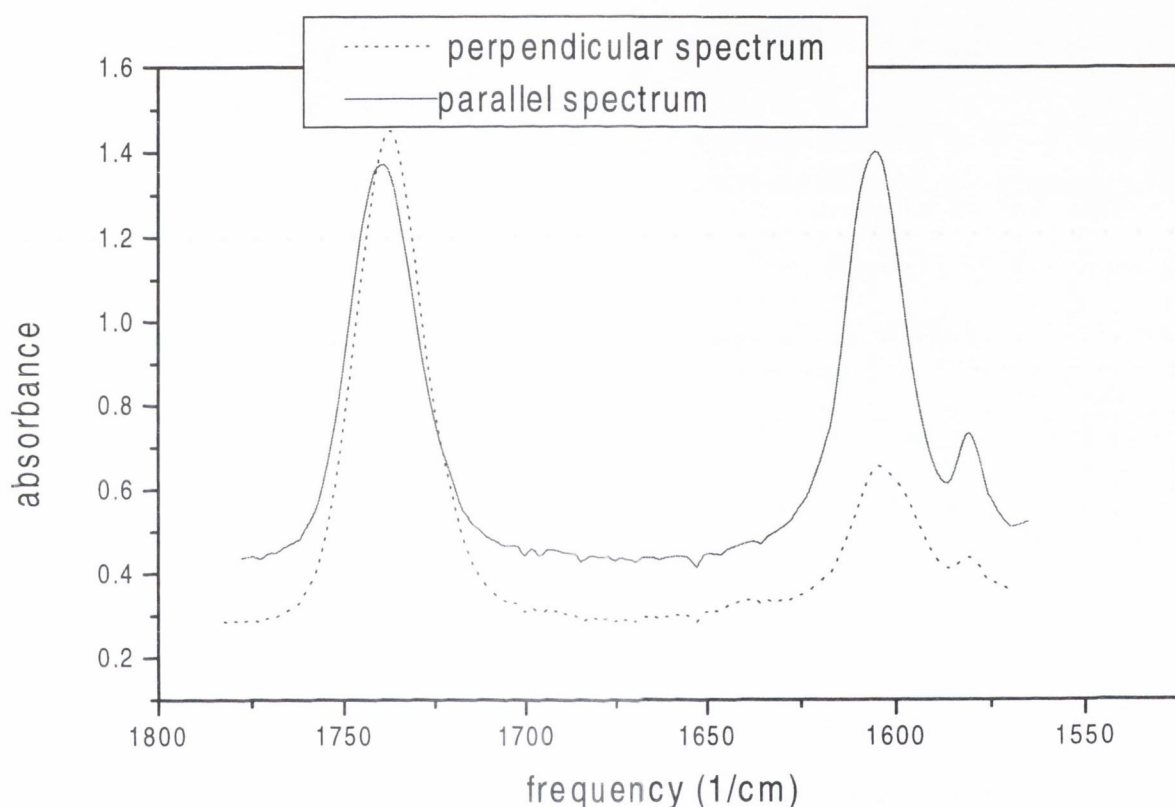


Figure 5.1(b). Absorbance as a function of vibrational frequency (cm^{-1}) for which DC applied voltage across the cell is +12V. Plot shows two absorption band intensities at 1737 cm^{-1} (C=O) and 1605 cm^{-1} (C-C) for two polarisation angles, dash line $\Omega = 90^\circ$ and full line $\Omega = 0^\circ$.

Polar plots of the absorbance profiles $A(\Omega)$ for the two bands in SmC* phase with bias voltage at +12 and -12V are shown in Figure 5.2. It is noted that, in SmA* phase the maximum absorbance ($A_{\max}$) for the phenyl ring profile occurs when the apparent tilt angle is approximately 0° or 180° , whereas for the core carbonyl profile $A_{\max}$ is situated at 90° or 270° .

The molecular orientation is expressed in terms of the average direction of the molecular director. If this director is not collinear with the transition dipole moment then $A_{\max}$ does not occur for which the apparent tilt angle has a zero value [5].

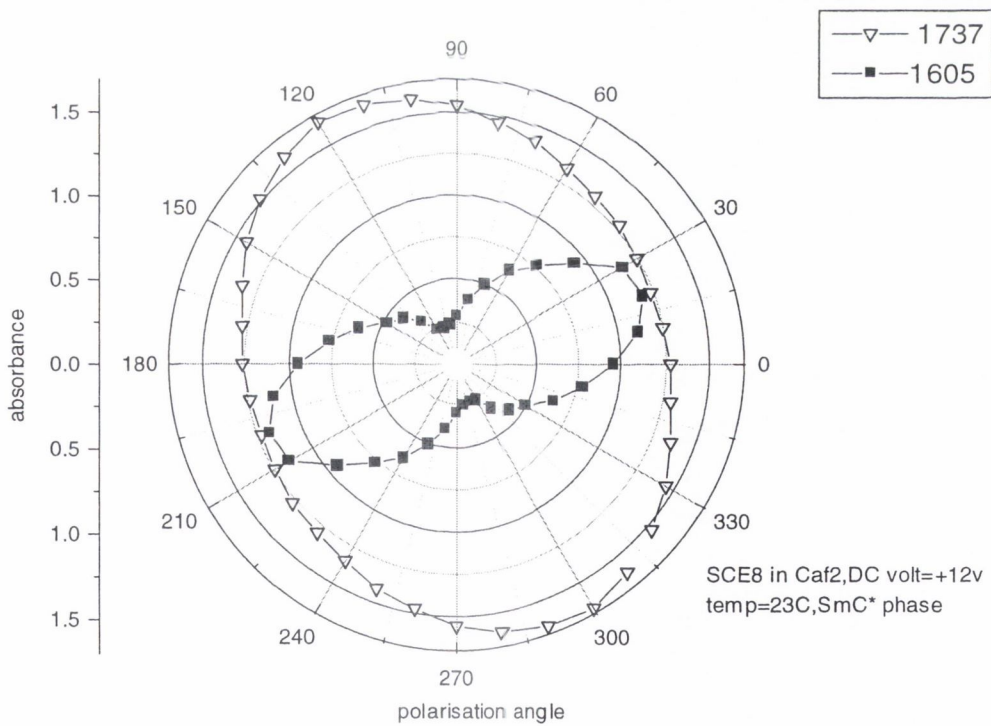
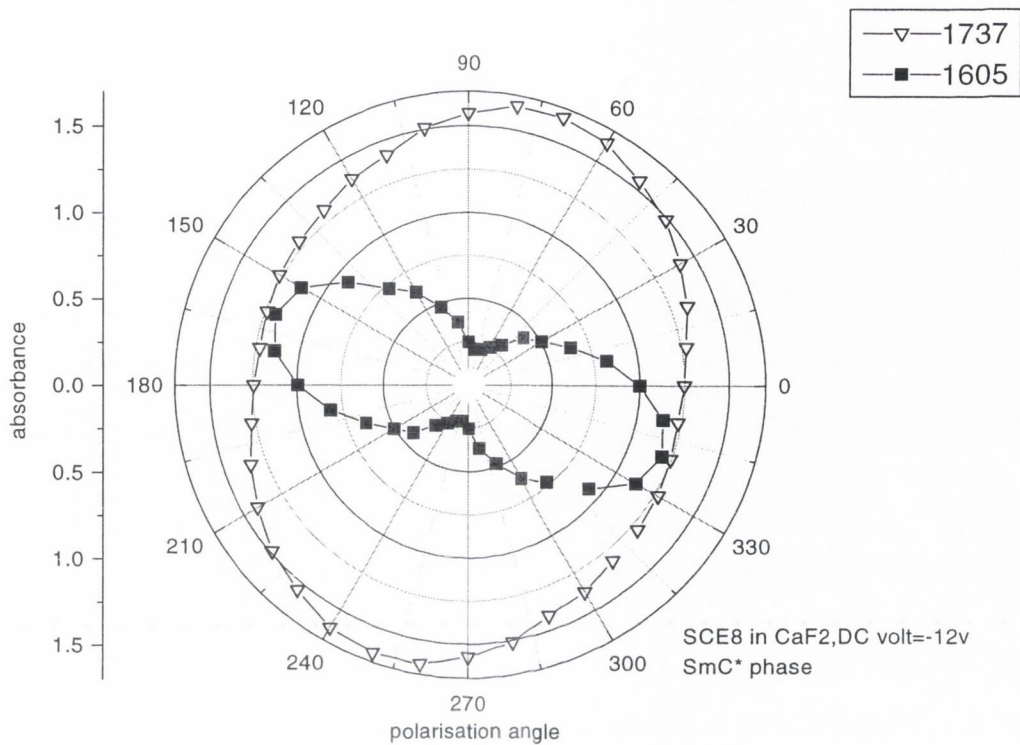


Figure 5.2. Absorbance profiles in SmC* phase with the applied field of -12V (top) and +12V (bottom).

In SmC* phase, we find that both phenyl and core carbonyl profiles show angular changes with bias voltage. The direction of the angular motion is the same for both profiles for any sign of the applied electric field. Fig. 5.3 clearly shows that both profiles rotate with smaller polarisation angles when the sign of the applied bias voltage is negative. The angle of rotation is approximately equivalent to the optical tilt angle with respect to the polarisation axis. Furthermore, we notice that, the value of the apparent tilt angle for these absorbance profiles does not change in the same manner as the polarity of the bias field changes with respect to zero voltage position. This can be due to the effect of the hysteresis within the cell, see Fig. 5.3.

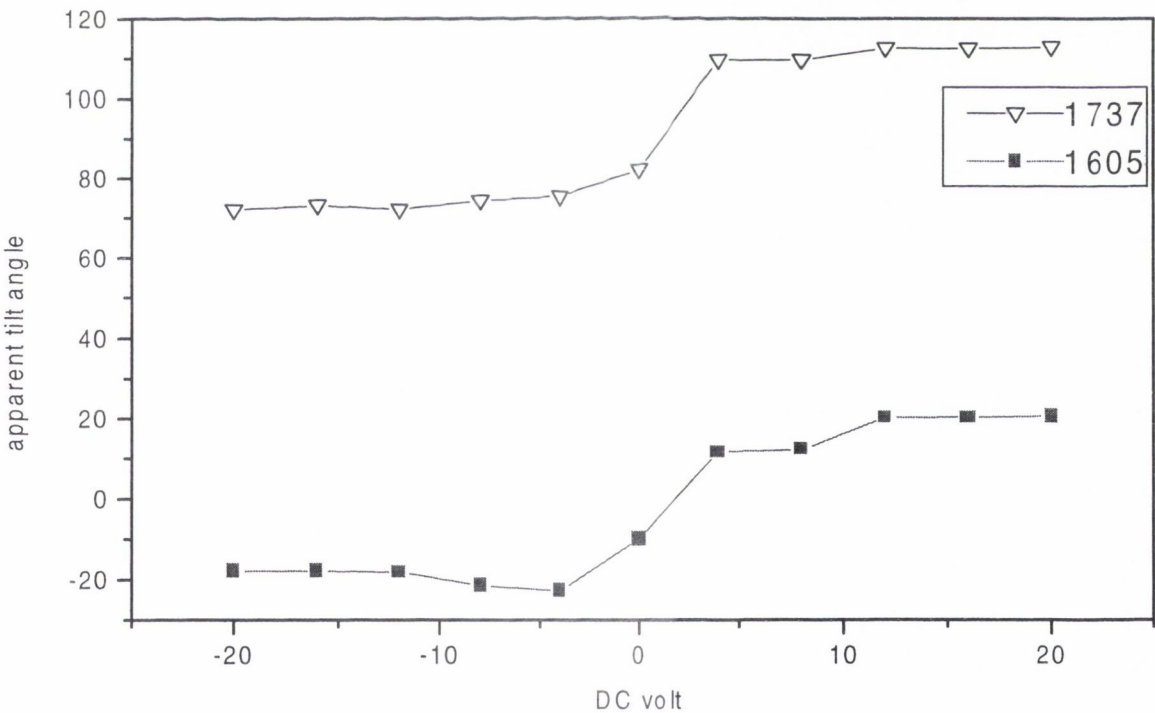


Figure 5.3. Voltage dependence of apparent tilt angle for core carbonyl and phenyl groups.

The dependence of the tilt angle on the applied voltage in the range of -12 to +12V is shown in Fig. 5.4. In this range of voltages the unwinding of the helical structure in FLC takes place [6]. However for both polarity of voltages >12V, the helix has been completely unwound and the tilt angle is the same.

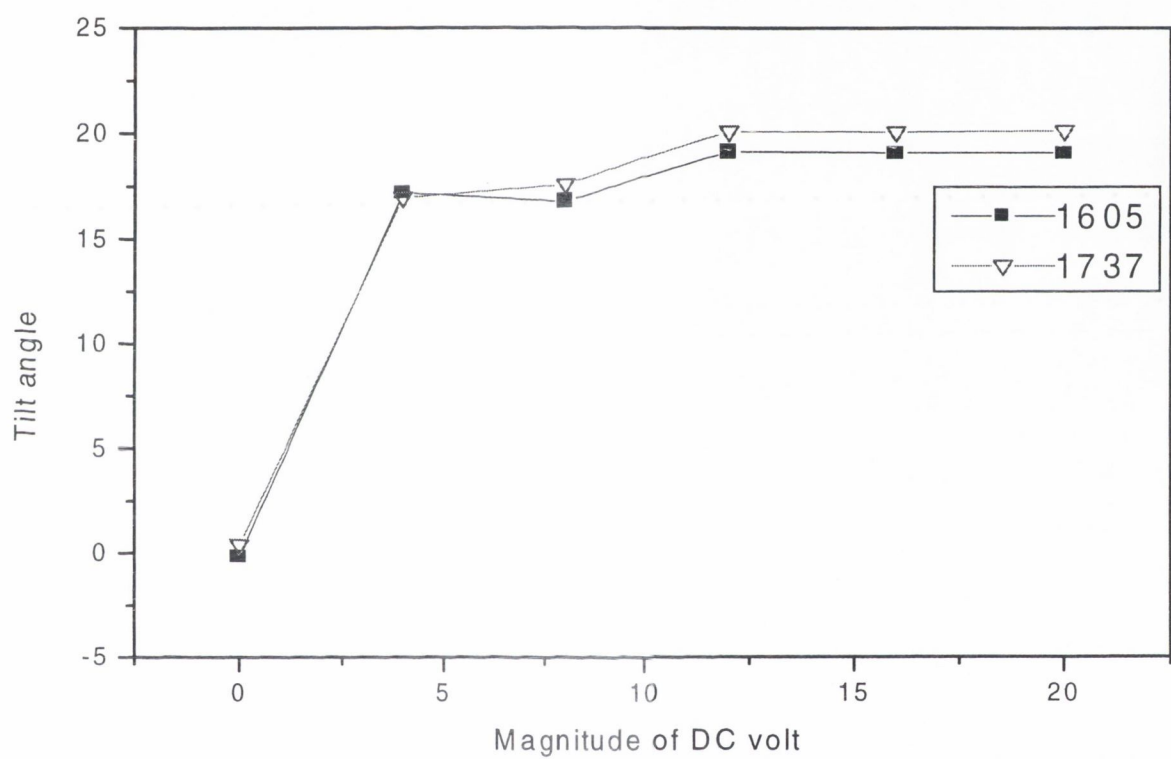


Figure 5.4. Tilt angle as a function of the magnitude of applied voltage for core carbonyl and phenyl groups.

Jang et al [2] show that the variation of the absorbance profile for various bands depends on the degree of bias and on the polar angle of the transition dipole moment with respect to the molecular axis.

The absorbance as a function of the angle of polarisation is given by the following formula [2, 7]:

$$A(\Omega) = -\log(10^{-A_{\max}} + (10^{-A_{\min}} - 10^{-A_{\max}}) \sin^2(\Omega - \Omega_{\max})) \quad (5.1)$$

In equation (5.1), $A_{\max}$ and $A_{\min}$ are obtained when the electric vector of the polarised infrared beam is parallel and perpendicular to the transition dipole moment respectively, Ω is the angle of polarisation and $\Omega_{\max}$ is the polarisation angle to the direction at which $A_{\max}$ occurs.

The dichroic ratio (D_r) for a single absorbance profile can simply be defined as:

$$D_r = A_{\max} / A_{\min} \quad (5.2)$$

In this investigation the absorbance profiles of the core carbonyl (C=O) and phenyl ring (C-C) for various biased applied voltages are fitted to equation (5.1) and the values of $A_{\max}$, $A_{\min}$ and $\Omega_{\max}$ are obtained.

Table 5.1 shows the angular shift ($\Delta\Omega_{\max}$) of the maximum absorbance for various voltages across the cell for the phenyl and the core carbonyl bands.

Fig. 5.3 also shows the variation of angular shift ($\Delta\Omega_{\max}$) as the bias voltage across the cell increases from -20 to +20V. Figure 5.4 displays the change in tilt angle

obtained, from the values of Ω_{max} as the polarity of the applied voltage changes at any particular value for both phenyl (C-C) and core carbonyl (C=O) groups.

DC	-20	-16	-12	-8	-4	0	+4	+8	+12	+16	+20
volts											
C-C	-18°	-18°	-18.2°	-21.5°	-22.7°	-9.96°	11.66°	12°	20.1°	20.2°	20.2°
phenyl											
C=O	72.14°	72.23°	72.3°	74.48°	75.6°	82.44°	109.5°	109.6°	112.5°	112.4°	112.4°
core											

Table 5.1. Angular shift ($\Delta\Omega_{\text{max}}$) for various applied voltages for the phenyl and the carbonyl groups.

Figure 5.5 shows dichroic ratio versus biased voltage. It can be seen that D_r of phenyl ring is dependent on the applied electric field in the range of -12 to +12V and is different in its response to fields of different polarities (ie $D_r=4.16$ at 0 voltage, 4.44 at +12V and 4.61 at -12V DC). From this we can infer that prior to the completion of unwinding process by the application of DC field, the molecular orientation is dependent to the degree to which the helix is disturbed. Once the helix is unwound, the orientation stays constant for both positive and negative voltages, therefore the value of dichroic ratio stays unaffected at higher voltages [6]. For a thinner cell of thickness 4 μ m, distortion of the helix at the same voltage can be stronger.

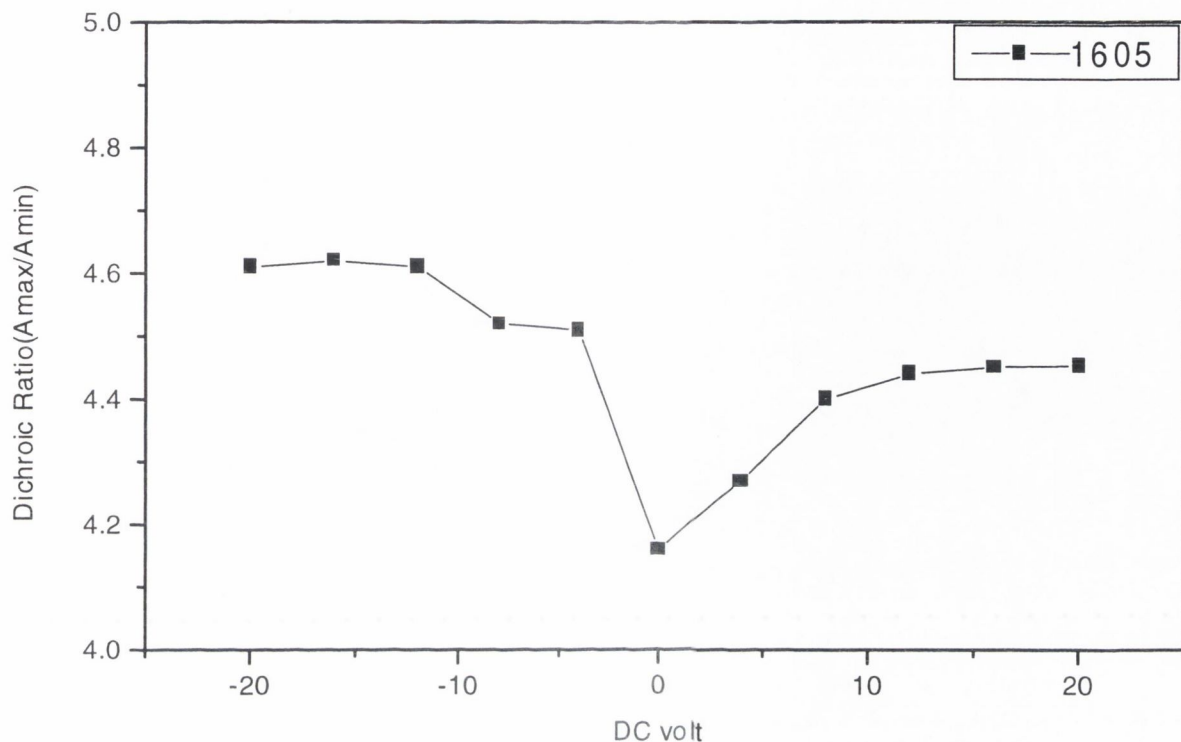


Figure 5.5. Dichroic ratio as a function of applied voltage for phenyl band (C – C).

The surface effect tends to align the molecules on the surface better than in the bulk for a thinner sample. Therefore surface effect also plays a vital role in fixing the position of the molecular director [8].

Fig. 5.6 shows that D_r for the core carbonyl group has a low value ≈ 1.33 in comparison with the phenyl ring and is nearly independent of the bias voltage, see Figs. 5.5 and 5.6. This indicates that orientation of the core carbonyl group does not change dramatically by the application of electric field. However, for both groups, the rotation of absorbance profile show differences with respect to zero polarisation axis when positive and negative field is applied. As mentioned before

this phenomena can be due to the existence of hysteresis when the polarity of the field is altered.

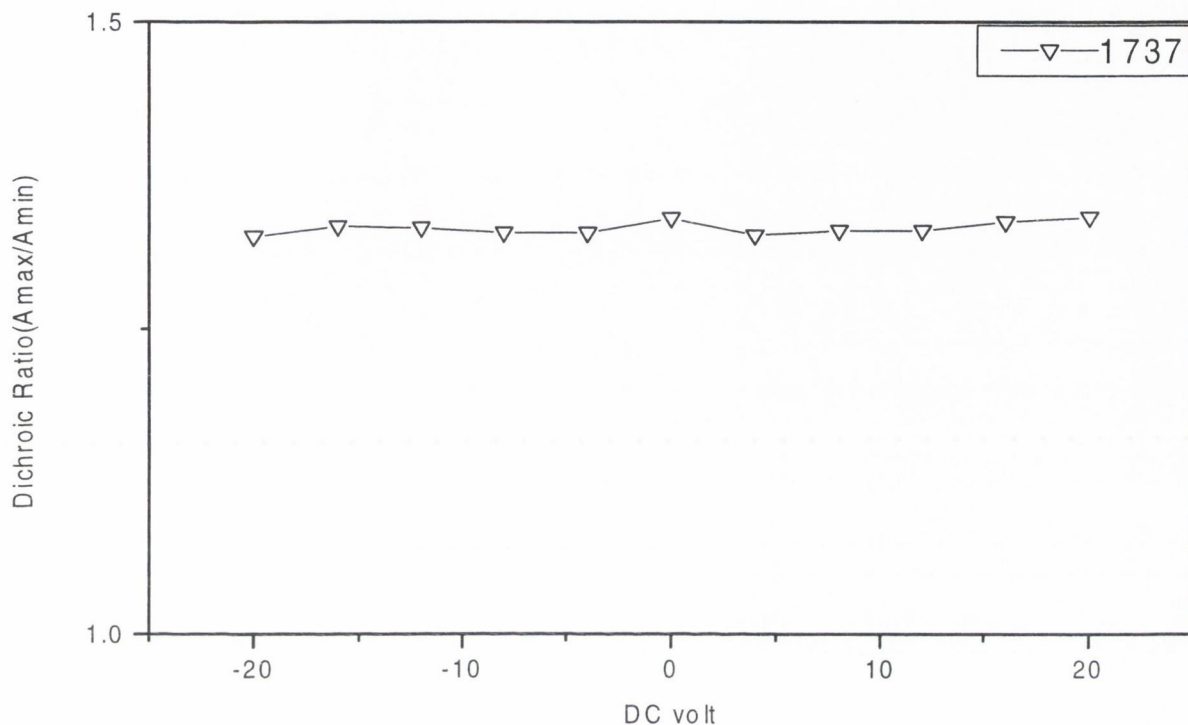


Figure 5.6. Dichroic ratio as a function of applied voltage for core carbonyl band (C = O).

Using a polarising microscope, the cell shows strips with the applied field at saturated values. This is a consequence of a bookshelf structure present in the cell [9]. We found that the dichroic ratio is dependent on the difference between the values of A_{max} and A_{min} and ultimately on the shape of the absorbance profile.

Fig. 5.7 shows the dichroic ratio versus bias voltage for CH_2 asymmetric vibration at 2926 cm^{-1} and CH_2 symmetric vibration at 2856 cm^{-1} . From this figure, it is evident that for voltages greater than 8V, the dichroic ratio stays nearly constant.

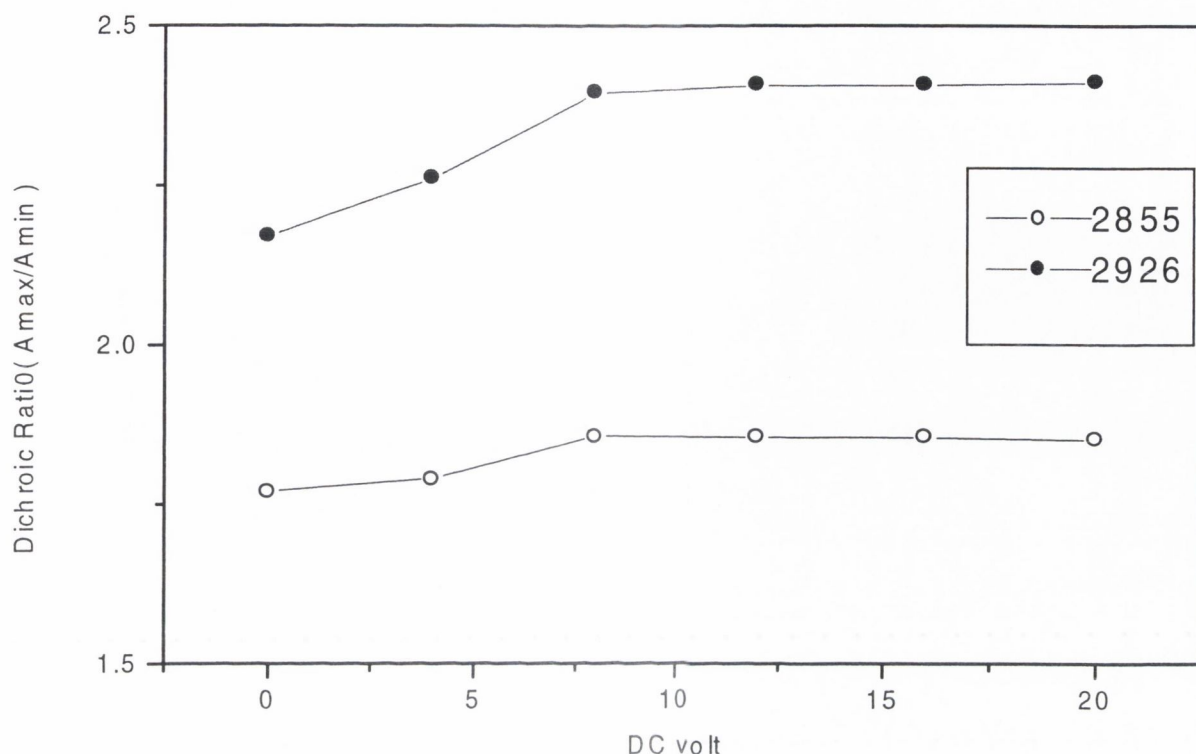


Figure 5.7. Dichroic ratio as a function of applied DC voltage for CH_2 symmetric vibration at 2855 cm^{-1} and CH_2 asymmetric vibration at 2926 cm^{-1} .

Fig. 5.8 displays apparent tilt angle versus bias voltage. From this we can confirm that prior to the application of the bias voltage, the apparent tilt angle for phenyl group was found to be -9.96° with respect to the axis of the polarisation. This indicates that the helix was already disturbed due to the surface stabilization of the liquid crystal cell and possibly due to the hysteresis effect. For the cell, the helical pitch is large in comparison with the thickness of the cell.

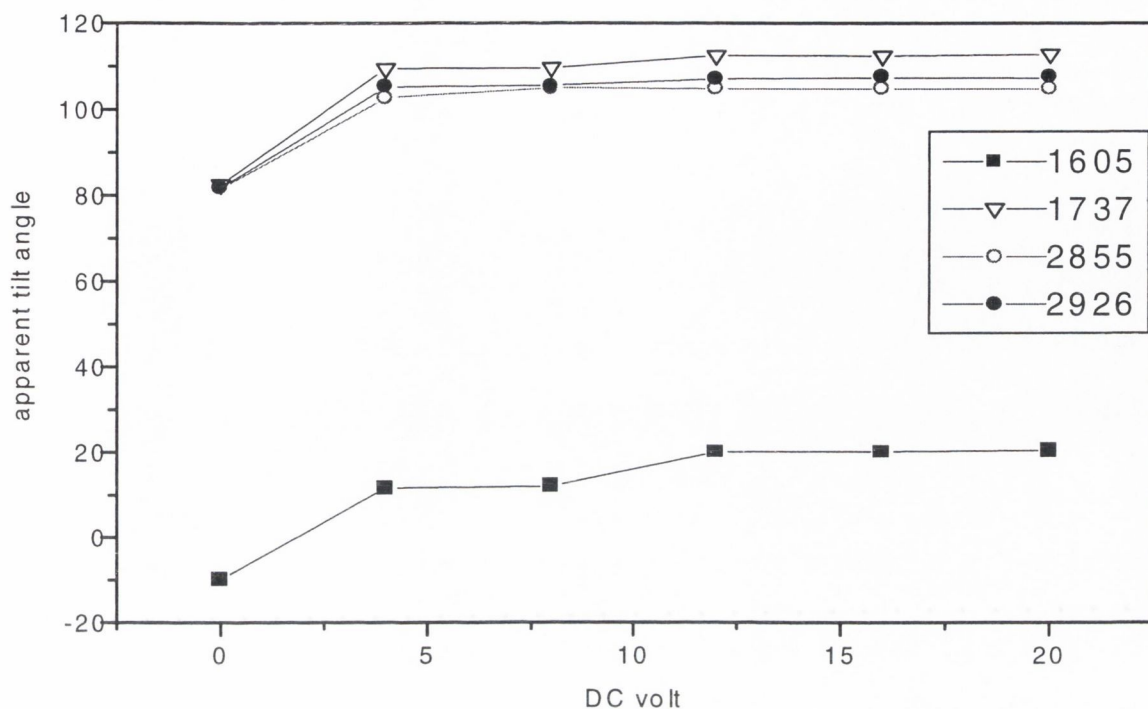


Figure 5.8. Apparent tilt angle as a function of applied voltage for phenyl, core carbonyl and CH_2 groups.

Fig. 5.8 also shows the higher magnitude of apparent tilt angle versus bias voltage for phenyl group rather than for CH_2 group. Thus, angle of rotation around the Z axis for phenyl group is larger than for CH_2 group. From the correlation between the dependencies of dichroic ratio and the apparent tilt angle on the applied field for phenyl and core carbonyl groups, the following summary is drawn.

5.4. Summary

IR spectroscopy is found to be an efficient technique for investigation of the localized orientation of the various molecular segments. We find that for chiral smectic C (SmC*) the rotation of the both phenyl (C - C) and core carbonyl (C = O) absorbance profiles are unidirectional as the value of the applied voltage is altered across the cell. The angular rotation is also different with respect to the polarisation axis as the polarity of the field changes in the range of -12V to $+12\text{V}$. The hysteresis effect was found to be the reason for this angular difference. Values obtained for the dichroic ratio under the applied biased voltage with two different polarities indicate that the orientation of the molecules depend on the degree to which the helix is disturbed by this voltage. At higher voltages when the helix is completely unwound, molecules exhibit symmetrical orientation with respect to the zero volt position. The surface stabilized liquid crystalline cell is one of the main causes for the disturbance of the helix prior to the application of bias voltage across the area of the cell. In general hysteresis effect can also give a non-zero value in the apparent tilt angle with voltage. A further increase in the dichroic ratio with the application of bias voltage for phenyl group associates with a deformation of the helix and a presence of the chevron structure in the cell. As the applied field of both polarities reaches to saturated values, the helix is unwound and the chevron structure is converted into a bookshelf structure. At this time the molecules are tilted within their smectic layers and making a maximum apparent tilt angle with respect to the layer normal. The direction of the tilt

depends on the polarity of the applied field. At this stage the spontaneous polarisation (P_s) reaches to its maximum value.

5.5. References

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Chapter 6

Orientational Behaviour and Rotational Bias in SmC^* , SmC_A^* and SmC_γ^* Phases of an Antiferroelectric Liquid Crystal

6.1. Introduction

This chapter investigates the behaviour of several absorbance peaks in SmC^* , SmC_A^* and SmC_γ^* phases of an antiferroelectric liquid crystal material using polarised infrared spectroscopy. To explain the molecular orientation and the rotational bias, infrared absorbances are studied as a function of polariser rotation angle at various applied voltages across the homogeneously aligned cell. Three dimensional arrangement is considered for investigating the rotational bias of the C = O groups around the long molecular axis. The extent of the biasing is found from the analysis of the azimuthal distribution function of the transition dipole moments in the plane at right angles to the molecular director. Distortion and the eventual unwinding process of the helical structure are observed as the applied field is increased to the saturated values. The apparent tilt angle is found as the absorbance profiles of the various peaks rotate clockwise and anticlockwise with the sign of the applied field. The findings of each vibrational band for the three smectic phases are discussed. The stretching peaks under the influence of electric field are quantitatively analysed and the biasing parameters of the transition dipole

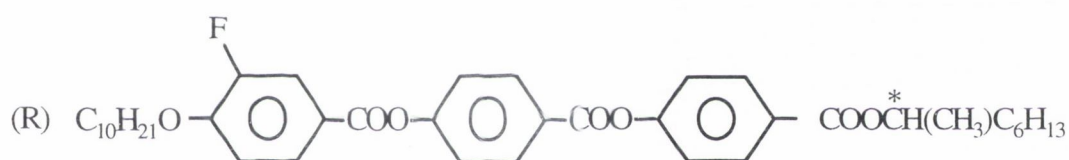
moments belonging to the (C = O) groups for each phase are calculated and compared.

It is noteworthy to mention that, the frequency and the shape of the vibrational bands can also be effected by the intermolecular interaction [1]. For the three smectic phases the rotational bias of the permanent dipoles situated near the chiral centre is the cause for the appearance of ferroelectricity and antiferroelectricity and for producing the spontaneous polarisation. However, the intermolecular interactions and spontaneous polarisation are different for each case as the apparent tilt angle varies [2,3]. Through a detailed analysis of the absorbance profiles, the behavioural characteristic of each band under the influence of the applied field is interpreted for the three smectic phases. Our quantitative investigations suggest that, the values of the biasing parameters of the orientational distribution of the C = O groups can be different in different phases.

6.2. Experimental

An antiferroelectric liquid crystal material ((R)-2-methylheptyloxycarbonylphenyl 4-[(4-decyloxy-3-fluoro)benzoyloxy]benzoate) with acronym (R)-10 F BBB C8 was used in this experiment. It's phase transition temperature in °C and the structural formula are as follows:

SmC_A* 103 SmC_γ* 104.5 SmC* 114.4 SmA* 126 Iso



Homogeneously aligned sample was prepared between the two optically polished transparent CaF₂ windows with the same approach as explained in chapter 5. The cell was filled at a temperature above the isotropic phase, i.e. > 126°C, using the capillary effect. The cell was then examined for the alignment using polarising microscope.

Measurements were carried out by recording polarised IR spectra as a function of the polarisation angle for different DC voltages across the cell in SmC_A*, SmC_γ* and SmC* phases.

The basic experimental arrangement is as follows:

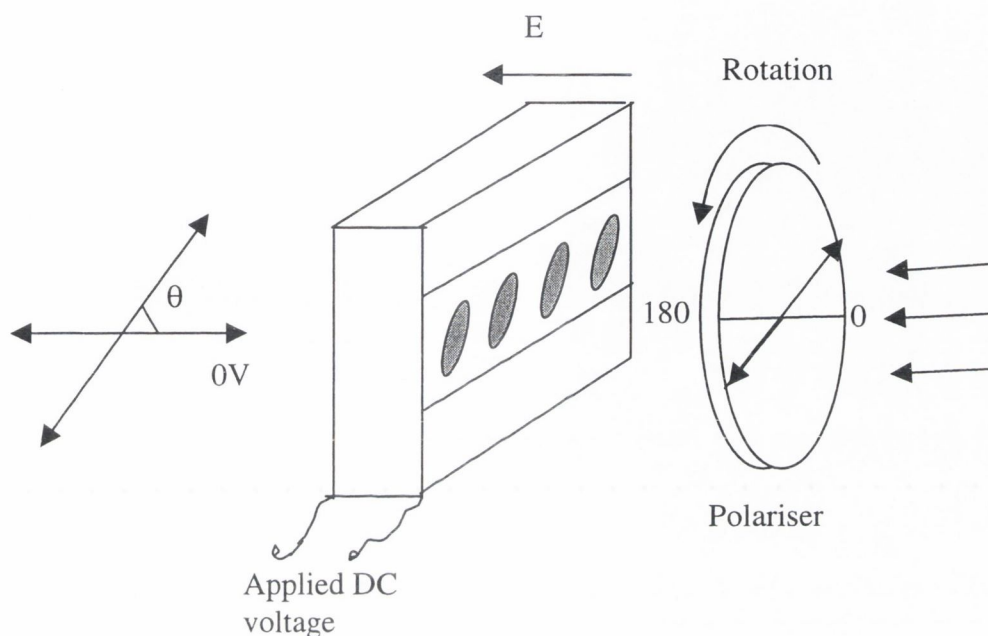


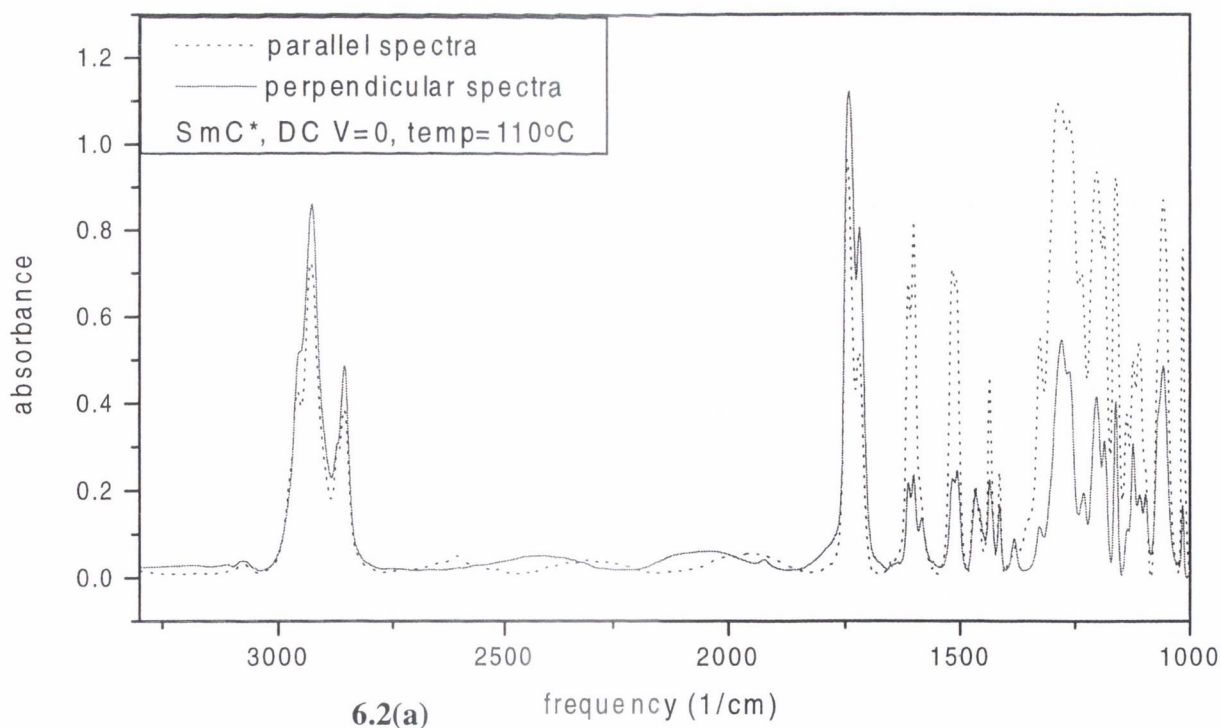
Figure 6.1. Basic experimental arrangement for infrared measurements. The sample is at normal incidence. The polariser is rotated for every value of the applied voltage to the cell.

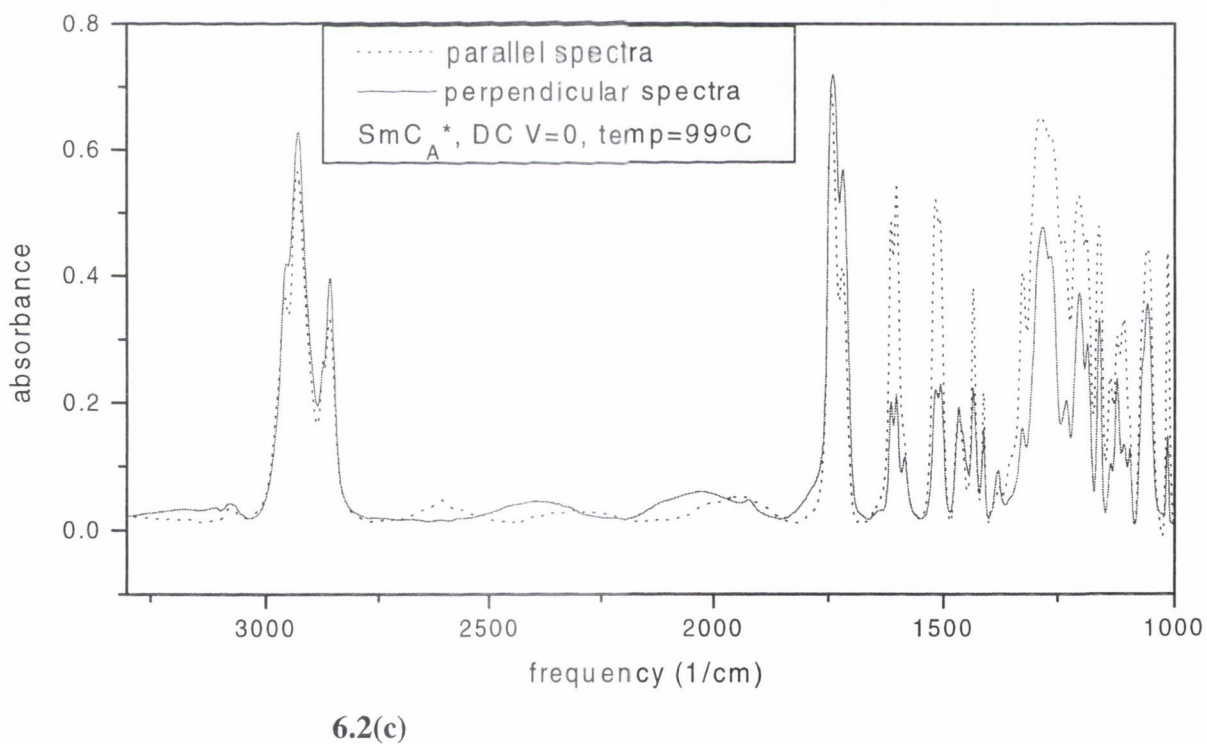
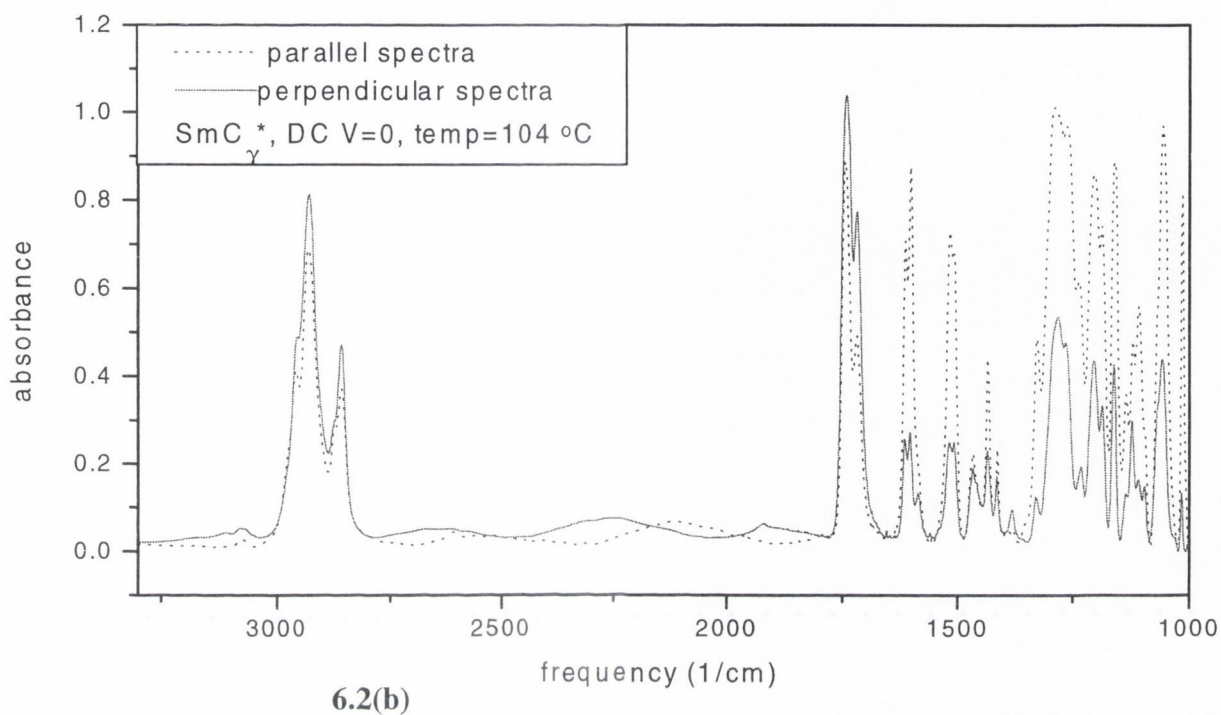
For this investigation the absorption peaks related to C – C phenyl, C = O chiral, C = O core, CH₂ symmetric, CH₂ asymmetric and CH₃ asymmetric stretching vibrations have been analysed. The polarisation angle is fixed to be zero when the axis of the polariser is parallel to the smectic layer normal. As before Bio-Rad FTS60A spectrometer with a 2cm⁻¹ resolution with an averaging over 16 scans is used. The sample phase temperature was set and held constant to an accuracy of 0.1 °C using Oxford intelligent temperature controller (ITC4). The wire grid polariser is rotated with a same computer-controlled device used for the

experiment in chapter 5. Measurements of the induced microscopic polarisation were also carried out and the results are presented and discussed.

6.3. Results and Discussion

Figures 6.2 (a), (b) and (c) represent absorbance spectra belonging to SmC^* , SmC_γ^* and SmC_A^* phases. Parallel and perpendicular spectra are obtained when the polarisation angle between the electric vector of the infrared beam and the layer normal is 0° and 90° respectively. Generally the molecular director represents the average direction of the molecular orientations. Therefore the director should coincide with the average direction of the long molecular axis. This direction lies along the average direction of the transition dipole moment for those, which are approximately parallel to the long molecular axis. For such a transition moment, the maximum absorbance is obtained when the electric vector of the incident beam is at 0° polarisation angle.





Figures 6.2 (a), (b) and (c). Parallel and perpendicular absorbance spectra for SmC^* , SmC_γ^* and SmC_A^* phases.

The degree of orientation is expressed in terms of dichroic ratio obtained from the absorbance profiles at any particular value of the applied bias voltage to the cell. From Figs. 6.2(a), (b) and (c), the differences between absorbance peaks in parallel and perpendicular spectras show the highest value for the phenyl ring (C – C) stretching vibration at the frequency of 1602 cm^{-1} for the three phases. Hence, the dichroic ratio at zero voltage for the three smectic phases for the phenyl group is higher than for the rest of the molecular segments studied in this investigation. The difference between the absorption band intensities at 0° and 90° polarisation angles is due to the change in the transition dipole moment related to the particular part of the molecule. The infrared absorption for a single molecule is proportional to $(\mathbf{E} \cdot \mathbf{p}_i)^2$ where $\mathbf{E}$ is the electric vector of the incident infrared beam and $\mathbf{p}_i$ is the transition dipole moment vector which corresponds to a particular vibration of molecules.

$\mathbf{p}_i$ is defined as:

$$\mathbf{p}_i = d \mu_i / dq_i \quad (6.1)$$

In (6.1) μ_i is the change of position of the dipole and q_i is the normal co-ordinate of the i^{th} mode. IR spectroscopy gives the possibility of studying the rotational bias and the orientational distribution of dipoles ($\mathbf{p}_i$) for those parts of the molecule where the molecular vibrations are localized. This contrasts with other techniques where the molecular orientation as a whole is investigated [1].

The value of absorbance as a function of the angle of polarisation is given by the following formula [2]:

$$A(\Omega) = -\log (10^{-A_{\max}} + (10^{-A_{\min}} - 10^{-A_{\max}}) \sin^2 (\Omega - \Omega_{\max})) \quad (6.2)$$

In equation (6.2) $A_{\max}$ and $A_{\min}$ are the maximum and minimum values of absorbance where the electric vector of the polarised infrared beam is parallel and perpendicular to the transition dipole moment respectively, Ω is the polarisation angle and $\Omega_{\max}$ is the angle at which a maximum absorbance is obtained.

In this chapter, the absorbance profiles obtained from circular graphs for the various molecular groups are fitted to equation (6.2) and the values of $A_{\max}$, $A_{\min}$ and $\Omega_{\max}$ are obtained for different bias voltages. In order to obtain the degree of orientation for an absorbance profile, the dichroic ratio (D_r) is found by defining:

$$D_r = A_{\max} / A_{\min} \quad (6.3)$$

The polarisation angle is expressed as the angle between the electric vector of the infrared radiation and the smectic layer normal. For a homogeneously aligned cell of 10 F BBB C8 in SmA* phase, the molecular director essentially coincides with the layer normal and therefore is parallel with the rubbing direction of the cell windows.

Figure 6.3(a) is a view of the circular graph for SmA* phase, showing the absorbance as a function of the polarisation angle. This Figure clearly describes the polarisation dependence of the absorbance peaks. For a single absorbance profile, a distance from the centre represents the absorbance at its polarisation angle (Ω). It can also be seen that in SmA* phase the maximum absorbance ($A_{\max}$) for the phenyl ring profile at the frequency of 1602 cm^{-1} occurs when the apparent tilt angle is close to 0° or 180° .

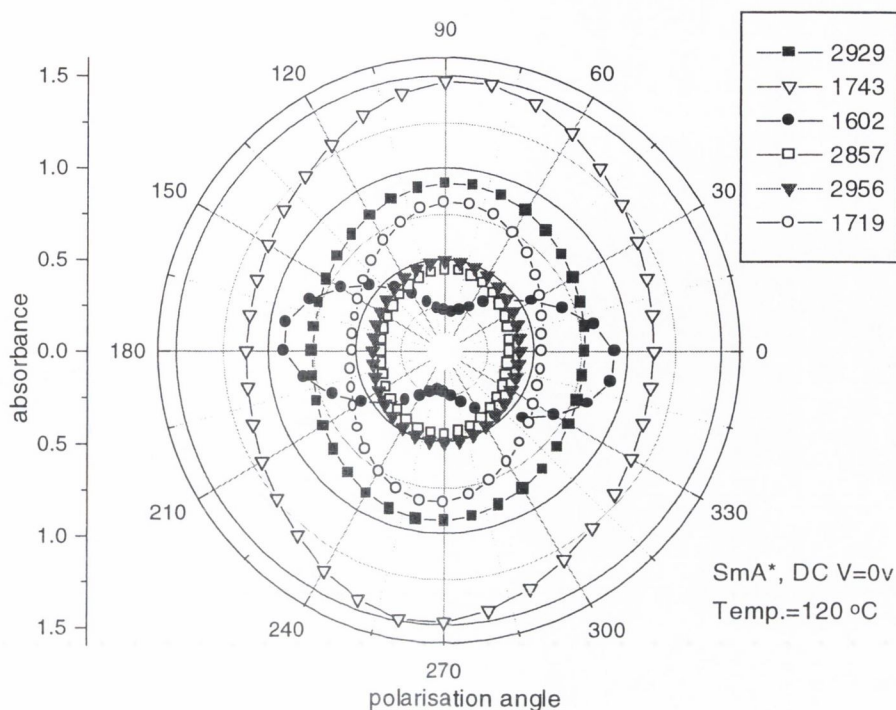


Figure 6.3(a). Polar graph showing absorbance profiles in SmA* phase.

The small value of $\Omega_{\max}$ seen for the phenyl band in SmA* phase can be due to the positioning of the cell for measurements or the rubbing direction not being parallel with the smectic layer normal. Although the transition moments responsible for the C = O peak at the frequency of 1743 cm^{-1} may not be perpendicular to the molecular long axis, the absorbance maximum appears at approximately 90° or 270° because of the free rotation and the head and tail equivalence of the molecule [3]. Absorbance profiles belonging to the rest of vibrational bands studied are almost collinear with the direction of the core carbonyl profile. (with not more than a 2° differences). In SmA* phase the phenyl ring profile shows a large dichroic ratio of $Dr = 4.32$, whereas dichroic ratios for the other profiles varies between 1.2° to 1.55° . This result indicates that the average stretching direction of

the phenyl band coincides with the long molecular axis. It is noted that higher dichroic ratio indicates the higher polarisation dependence of absorbance. We can also infer that the transition moments responsible for the CH₂ vibrational bands at 2929 and 2857 cm⁻¹ are perpendicular to the alkyl chain C - C bond. CH₃ asymmetric stretching band located at the end of flexible carbon chain has an isotropic character, therefore it may rotate and fluctuate randomly [3].

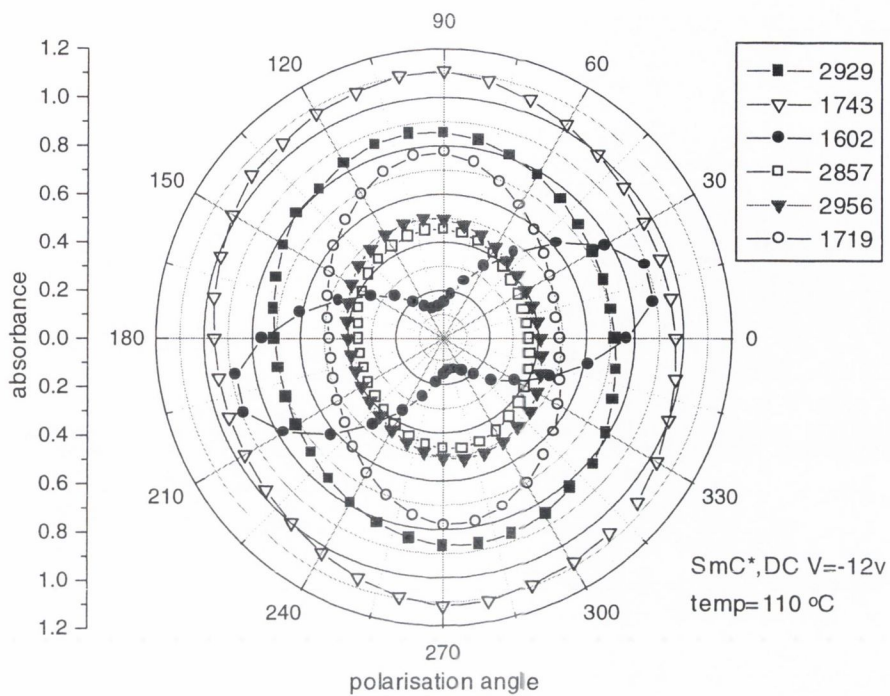
We focus our attention on the peaks related to phenyl and core carbonyl stretching vibrations for the behaviour of the molecular core, and on the peaks which can provide information about the molecular chain. These are chiral carbonyl, CH₂ symmetric, CH₂ asymmetric and CH₃ asymmetric stretching vibrations connected to the chiral centre. It is noted that the C = O stretching peaks due to two carbonyls in the core and chiral parts are not separated because of the inductive effect [4,5] of CH₃ in the chiral parts.

Using the published infrared data [6-9], The assignments of selected absorption bands are given in Table 6.1.

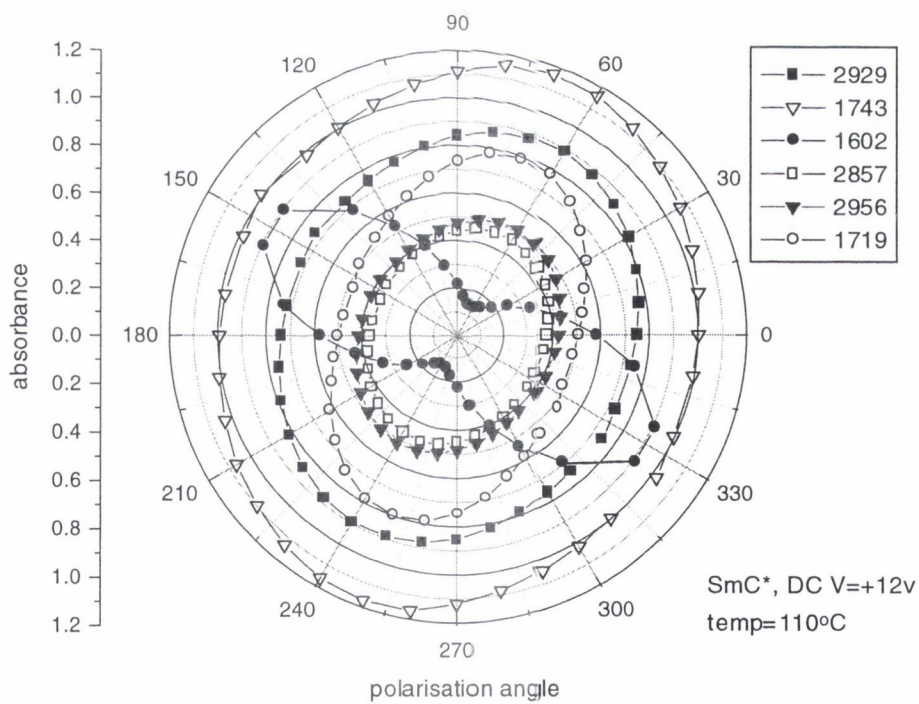
Wavenumber (cm ⁻¹)	Assignments
2956	CH ₃ asymmetric stretching vibration
2929	CH ₂ asymmetric stretching vibration
2857	CH ₂ symmetric stretching vibration
1743	C=O stretching vibration (core)
1719	C=O stretching vibration (chiral)
1602	C-C stretching vibration (phenyl)

Table 6.1. Assignments of absorption bands intensities for IR spectra.

Figs. 6.3(b) and (c) display the absorbance profiles $A(\Omega)$ for the six selected vibrational bands shown in Table 6.1 as a function of the polarisation rotation angle for SmC*. It can be seen that the applied electric field of +12V and -12V to the sample can rotate the absorbance profiles through approximately the optical tilt angle clockwise and anticlockwise. The sense of rotation depends on the polarity of the electric field. A similar rotation of the absorbance profiles is observed in SmC_γ* and SmC_A* phases. Application of an electric field greater than the threshold can transform the system from SmC_A* to the induced ferroelectric (F(+)) and F(-) states [2,10].



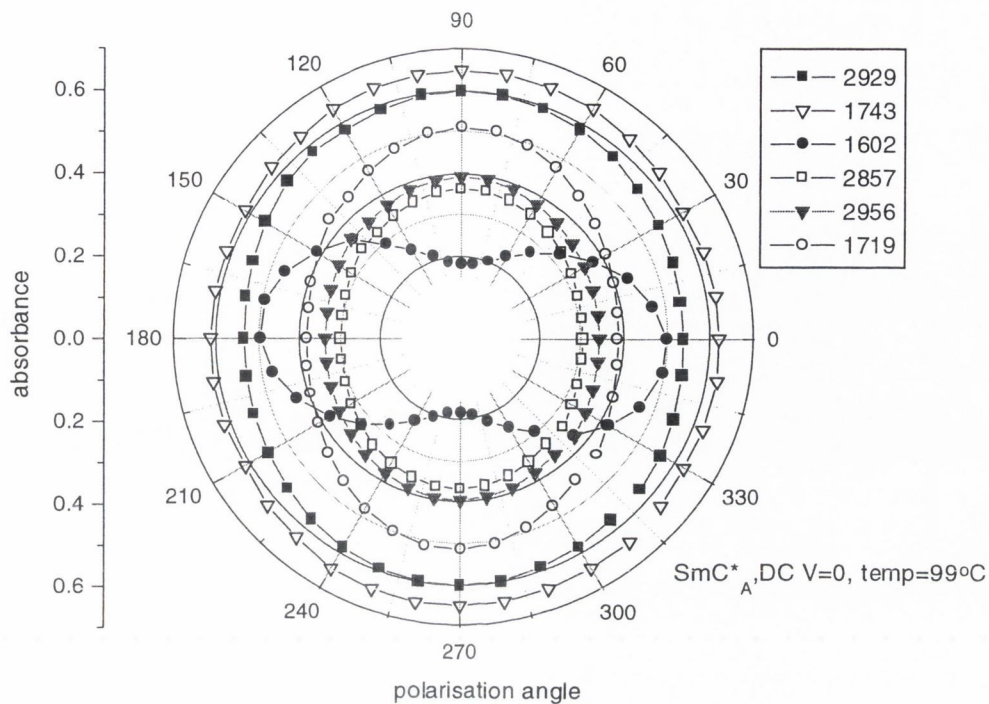
6.3(b)



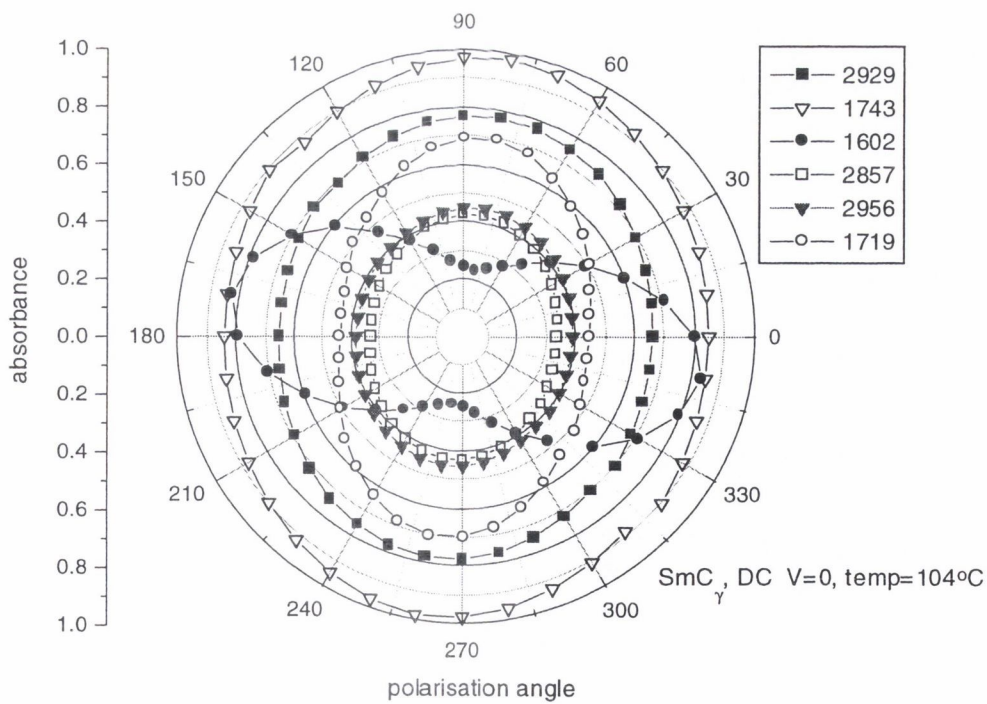
6.3(c)

Figures 6.3(b) and (c). Rotational motions of absorbance profiles in SmC* phase.

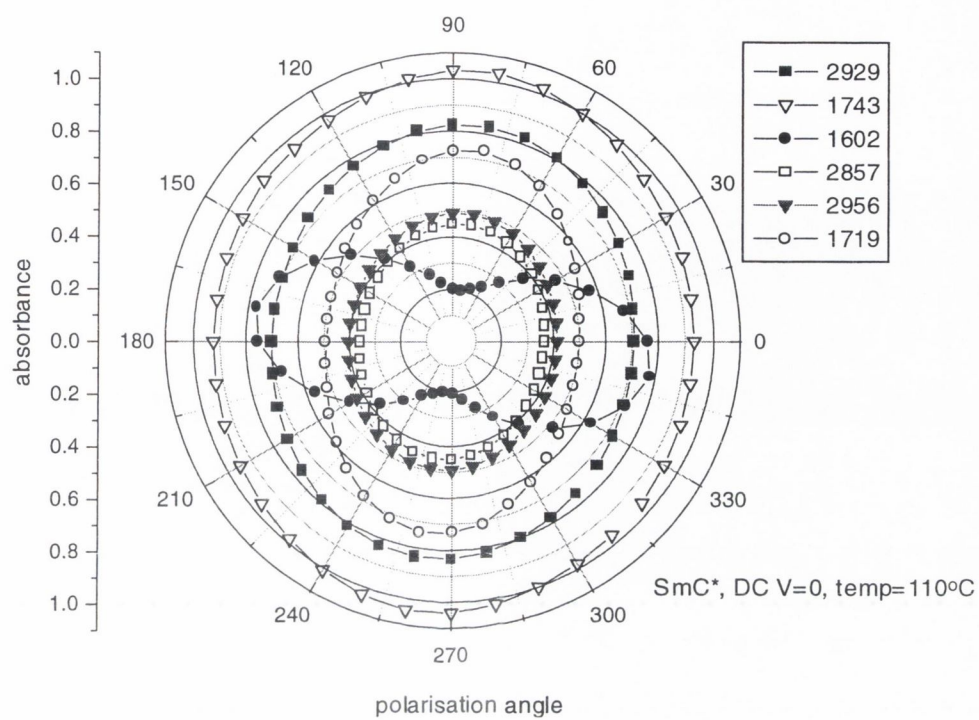
Figs. 6.4(a), (b) and (c) show the absorbance as a function of the polarisation angle at zero voltage for the six representative peaks shown in Table 6.1. For the three smectic phases at zero voltage, The angle for $A_{\max}$ of the stretching bands listed in Table 6.1 appear in the same direction as in SmA^* phase. Due to the helical structure in SmC_A^* phase the maximum absorbances of the phenyl stretching band, core carbonyl, chiral carbonyl and CH_2 stretching bands decrease in comparison with SmA^* phase. However, for CH_3 asymmetric vibrational band no dramatic change in $A_{\max}$ is observed. It is noted that dichroic ratios of the core carbonyl, chiral carbonyl and the alkyl chain with CH_2 peaks and CH_3 asymmetric peak are also small in comparison with the phenyl stretching band for the three phases. Nevertheless, the value of the apparent tilt angle for the phenyl (C - C) profile at zero voltage display the largest deviation from the zero polarisation angle in SmC_γ^* and the smallest in SmC_A^* respectively, see Figs. 6.4(a), (b) and (c). The variation of $A_{\max}$, $A_{\min}$ and the shape of the absorbance profiles at zero voltage for the three smectic phases confirm that, the absorbance is also dependent on the phase temperature. For comparative study of the orientational and rotational behaviour of the molecules in three smectic phases, we consider the six vibrational bands listed in Table 6.1. For each vibrational band of a common frequency, the voltage dependencies of dichroic ratio (D_r), apparent tilt angle ($\Omega_{\max}$) and the maximum absorbance ($A_{\max}$) are investigated in SmC_A^* , SmC_γ^* and SmC^* phases.



6.4(a)



6.4(b)



6.4(c)

Figures 6.4(a), (b) and (c). Absorbance profiles in SmC_A^* , SmC_γ^* and SmC^* phases in the absence of electric field.

The voltage dependencies of the dichroic ratio (D_r) and the apparent tilt angle for the phenyl group for the three smectic phases are shown in Figs. 6.5 and 6.6 respectively. The beginning of the curves show the unwinding of helix for each smectic phase before the application of the external field to the cell. The molecules are tilted out of the YZ plane. This is possibly due to the surface interaction and the weak spontaneous polarisation (P_s).

In SmC_A^* the voltage dependencies of dichroic ratio and apparent tilt angle for the phenyl band have the similar shape. On applying the external voltage below the threshold the values of dichroic ratio and apparent tilt angle remain almost unchanged. The slow rise in apparent tilt angle is for the reason that a coupling of δP (average polarization) of SmC_A^* phase with E (electric field) is just sufficient to distort the periodic unit of a two layer structure [11,12,13]. If the two directors were exactly at 180° , $\delta P = 0$ and hence distortion of the 2-layer repeat unit cannot occur. On reaching the threshold voltage (~ 17 V) the SmC_A^* phase goes directly into unwound SmC^* phase and this corresponds to the jumps in the dichroic ratio and the apparent tilt angle. For the field below the threshold, the long helix is unwound and the apparent tilt angle show a small rise and at threshold apparent tilt angle abruptly rises to a saturated value when the helix is totally unwound. The dichroic ratio (D_r) depends on the orientation of the molecules and the order parameter. It is interesting to note that D_r for SmC_A^* phase decreases with an increase in voltage before the threshold. This decrease is interpreted in the first unwinding of the long helix and the rotation of the tilt plane away from the YZ plane. Furthermore, D_r for the SmC_A^* has the lowest value at start. This is

possibly due to the fact that, the directors in the plane of the glass plate make an angle of $2 \times$ the tilt angle.

The results for the SmC_γ^* are even more intriguing. For a low field of $\sim 3.5\text{V}$ an abrupt increase in apparent tilt angle is followed by a slow increase. We note that the helix of the 3 layers repeat unit [11,12,13] is just unwound such that the resulting directors reach to a state where the average tilt is $1/3$ of its final value. The slow rise in the angle implies that the average angle of the **C** directors (projection of the molecular director on the smectic layers) of a periodic unit of 3 layers are initially distorted from an angle of 120° but with an increase in voltage, the **C** directors of neighboring layers collapse. A threshold field of $\sim 5\text{V}/6\ \mu\text{m}$ makes the conversion into a helical SmC^* phase. This is almost completely unwound for a field of $10\text{V}/6\ \mu\text{m}$. For SmC_γ^* phase D_r first increases slightly and then decreases. The first increase is connected with the distortion of the long helix and the decrease is connected with making the structure planar as in the Ising model [14]. Then at a field of $5\text{V}/6\ \mu\text{m}$, the 3 layer repeat unit breaks up leading first to a field induced helical SmC^* phase followed by a complete unwinding of the helix and conversion to a stable tilted structure (stripped) SmC^* phase. This represents the transition from ferri to ferroelectric phase. The spontaneous polarisation (P_s) reaches the maximum value at this point.

For the sample in the helical state of SmC^* phase, an increase in voltage unwinds the helix with the result that the position of the average director first increases abruptly and then saturates. For SmC^* phase D_r first increases slightly then abruptly to a large value as the helix is unwound. This then decreases with increase in voltage. The decrease may be connected to the appearance of the

stripped-bookshelf structure where the chevron structure is modulated along an axis, which is at right angles to the layer normal and this modulation being parallel to the plane of the electrodes. Note that, up to $\sim 6\text{V}$ for the first sharp increase in the dichroic ratio and the apparent tilt angle the molecules preferably lie in the YZ plane. We also infer that, from $\sim 6\text{V}$ to 10V , the interaction due to the dielectric anisotropy ($\Delta\epsilon$) becomes comparable with the infrared absorption ($E.P_i$). Hence, the molecules start tilting out of the YZ plane and the dichroic ratio decreases. When the dichroic ratio and the apparent tilt angle approach saturation the helix is completely unwound and the stripped texture appears [15].

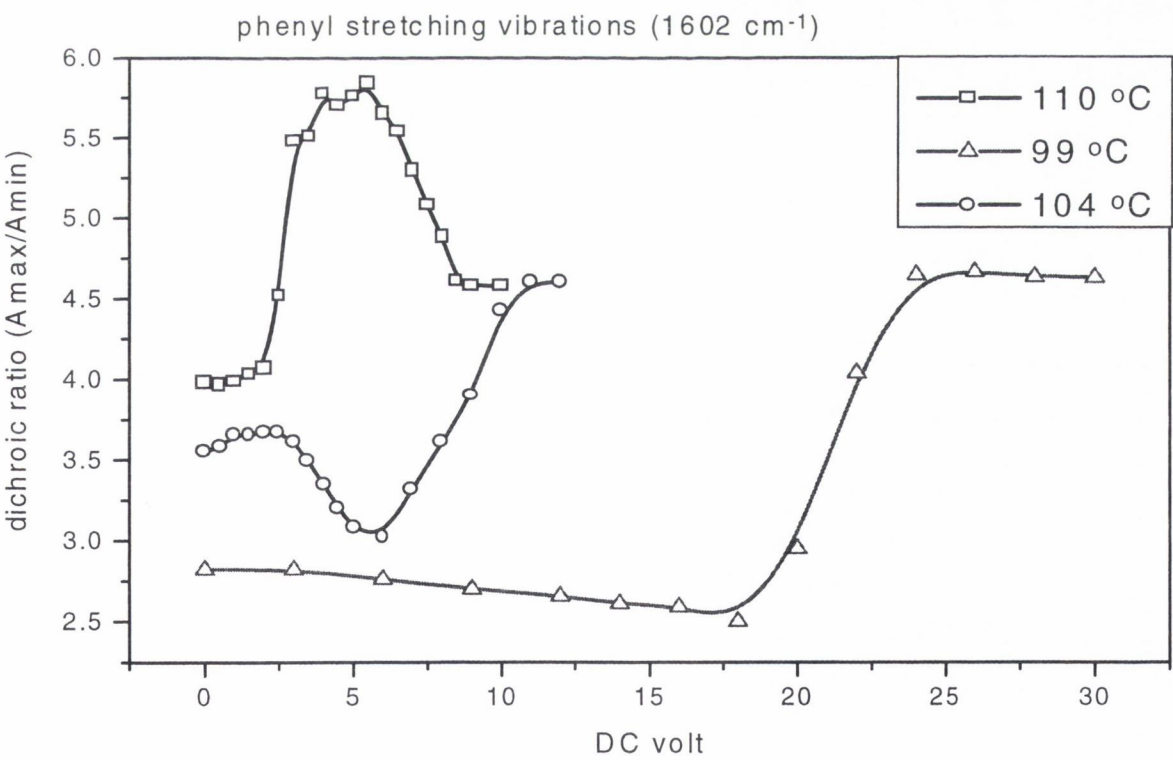


Figure 6.5. Dichroic ratio as a function of applied voltage for phenyl band (C – C) for three smectic phases.

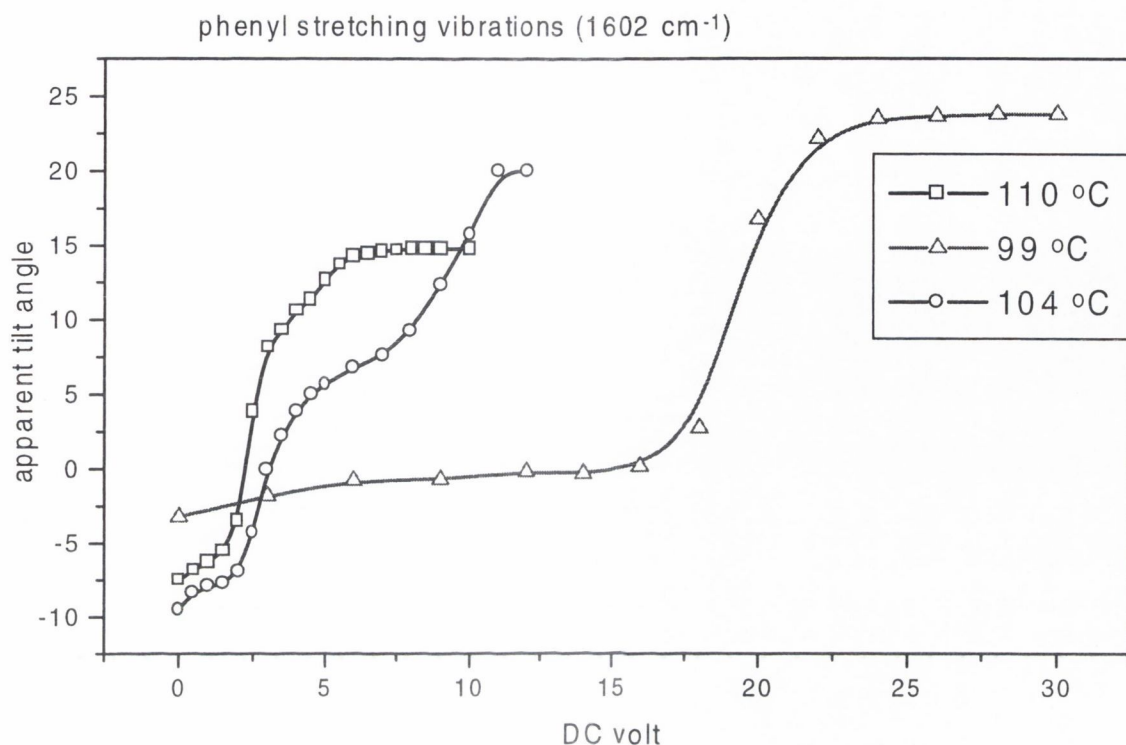


Figure 6.6. Voltage dependence of apparent tilt angle for phenyl band for three smectic phases.

We note that, in SmC_A^* , the molecules in the neighbouring layers tilt in almost the same direction but in the opposite sense. The spontaneous polarisation in the neighbouring layers point in the opposite sense of the direction perpendicular to the tilting plane, thereby cancelling each other. There is, as yet, no net spontaneous polarisation. As in SmC^* phase, chirality induces a slight precession from layer to layer in the tilting and hence the in-plane spontaneous polarisation leading to the formation of a helical structure with the axis parallel to the smectic layer normal [16].

Induced polarisation measurements represent the average characteristics of the liquid crystal molecules in the various phases. To confirm our results shown in

Fig. 6.6, macroscopic polarisation measurements are carried out for the three smectic phases. In this way square wave signal with the frequency of 52 Hz is applied to the cell in which the voltage is increased from 0V to 5V for SmC^* and SmC_γ^* and from 0V to 14V for SmC_A^* phase.

Fig. 6.7 shows the voltage dependence of the normalised induced polarisation for SmC^* , SmC_γ^* and SmC_A^* phases respectively. From this Fig. it is evident that, in SmC^* phase application of the electric field disturbs the helical structure and induces non zero polarisation. Thereafter by increasing the external field, polarisation reaches its maximum value where the helix is completely unwound. In SmC_γ^* phase application of the external field initially disturbs and then unwinds the ferroelectric helix until polarisation reaches almost 1/3 of the spontaneous polarisation. Further increase in the voltage induces the transition from SmC_γ^* to SmC^* phase. At this stage spontaneous polarisation is at a maximum [16].

In SmC_A^* phase, an initial increase of the external field does not produce any changes in polarisation, until voltage reaches the threshold $\sim 9\text{V}$. At this stage the helix starts unwinding and transition from SmC_A^* to SmC^* phase is induced. In other words antiferroelectric ordering is destroyed and ferroelectric ordering starts to form. The behaviour of the angle of maximum absorbance in the corresponding smectic phases (Fig. 6.6) are very similar to the optical switching angle and the induced polarisation. In terms of SmC_γ^* phase, there exists a field induced state with the field induced angle about 1/3 of the maximum saturated value. This fact supports the Ising [14] structure of ferroelectric SmC_γ^* phase.

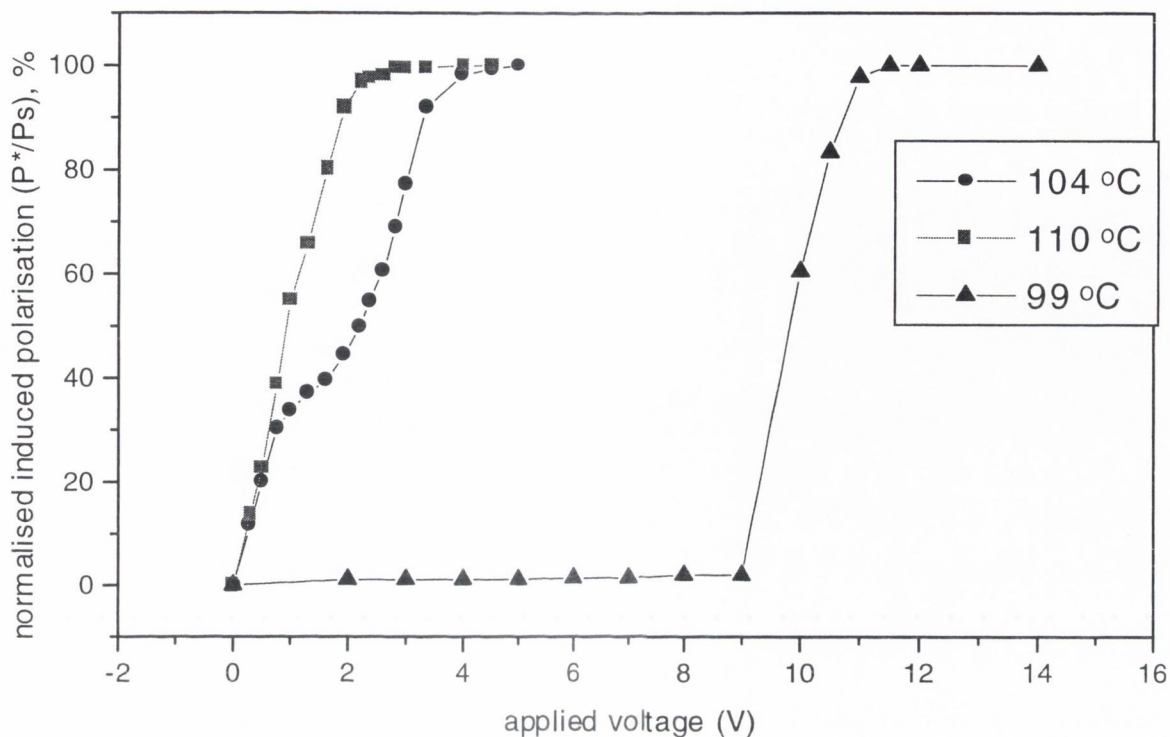


Figure 6.7. Voltage dependence of normalised induced polarisation for three smectic phases.

Fig. 6.8 shows maximum absorbance ($A_{\max}$) versus bias voltage for the phenyl group in SmC^* , SmC_γ^* and SmC_A^* phases. As can be seen, the change in $A_{\max}$ is lowest for SmC_A^* phase. Although, for the three smectic phases the variation of $A_{\max}$ is approximately similar in shape with respect to the applied bias voltage despite having different slopes.

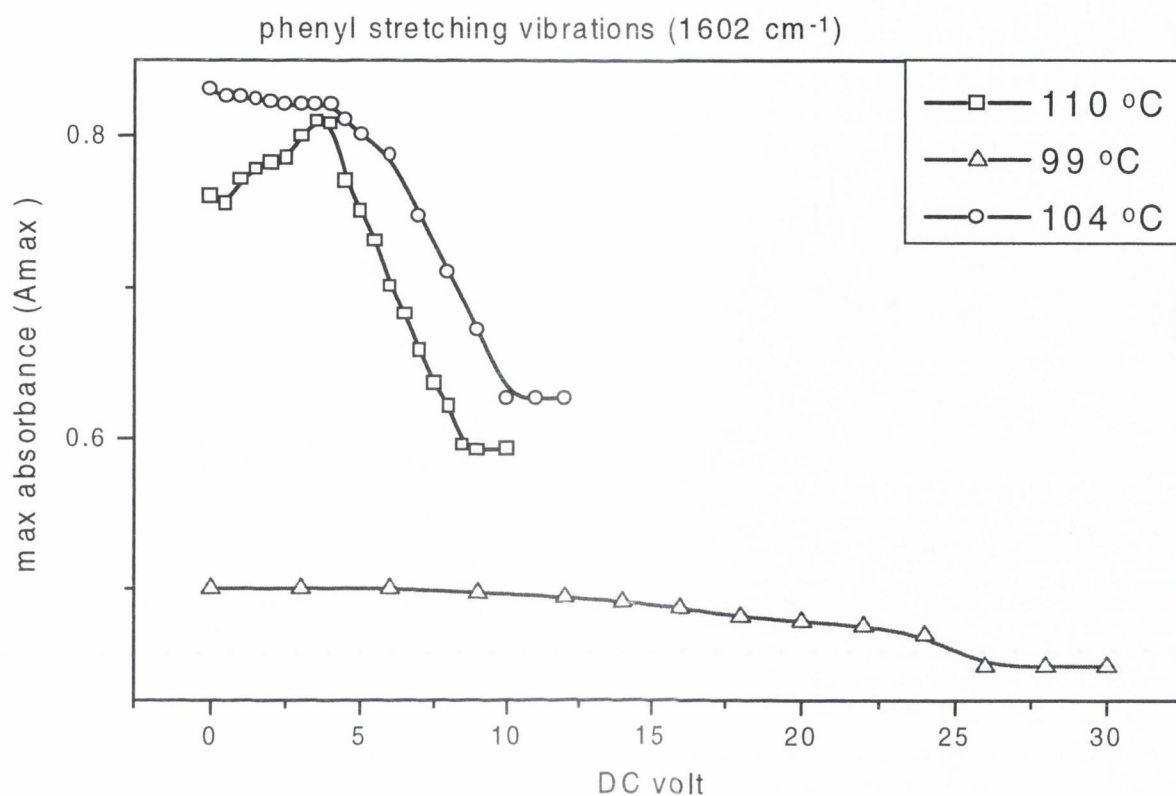


Figure 6.8. Voltage dependence of maximum absorbance for phenyl band for three smectic phases.

Figs. 6.9 and 6.10 show the voltage dependencies of D_r and apparent tilt angle for core carbonyl group for the three smectic phases. For this part of the ester group it is evident that D_r is quite low for the three smectic phases when compared with the phenyl group. For apparent tilt angle versus applied field the trend of the curve for each phase is almost similar to the ones for the phenyl group. D_r for each phase for the phenyl group has almost the same value at saturation but it varies for the $C=O$ core group. The beginning of the curves show the unwinding of the helix, possibly due to the surface interaction effect.

For SmC_γ^* phase up to 3.5V dichroism is independent of the applied field and the apparent tilt angle is small. In the region between 3.5V to 10V dichroic ratio decreases abruptly. The helix is unwinding until D_r saturates and the apparent tilt angle approaches maximum. At this time the helix is completely unwound.

For SmC^* phase we observe a maximum increase in D_r at 4V and sharp decrease at $\sim 7\text{V}$ before saturation is obtained. It is evident that the increase in the apparent tilt angle with the applied field in various stages corresponds with the fluctuation of the dichroic ratio from some maximum to minimum values before saturation. At voltages higher than 8V when the helix is totally unwound both dichroism and the apparent tilt angle saturate. The core carbonyl group is expected to lie in the molecular tilt plane [16,17].

For SmC_A^* phase up to 14V one can notice that the increase in the apparent tilt angle is very small or almost negligible. A further increase in the applied voltage unwinds the helix until D_r eventually saturates and the maximum apparent tilt angle is obtained. At this stage $\text{C} = \text{O}$ core group also appear to lie in the tilt plane.

Note that, the dichroic ratio for each smectic phase does not show any structured pattern and they are quite different from the ones for the phenyl group. However, the apparent tilt angle for each smectic phase is smaller than for the phenyl group. This can indicate that the rotation of the $\text{C} = \text{O}$ core group for each smectic phase around the long molecular axis is biased. We note that, the polarisation dependence of the $\text{C} = \text{O}$ peak absorbance depends not only on the degree of biasing but on the spatial position of the $\text{C} = \text{O}$ group [3]. It is also true that the

C = O core group rotation is biased for the same reason that the angular dependence of the C = O core peak is not symmetric with respect to the director. Furthermore, the orientational distribution of the core carbonyl group may be mirror symmetric with respect to the tilting plane, though biased. Although absorbance dichroism measurements alone cannot decide the existence or nonexistence of this mirror symmetry, it is expected that the core C = O group, which is distantly separated from the chiral centre, scarcely contributes to the spontaneous polarisation [3,16]. We also add that, for the antiferroelectric phase the C = O core group does not produce the in-layer spontaneous polarisation in the middle of the smectic layer because of the head and tail equivalence and the mirror symmetry with respect to the tilt plane [17,18].

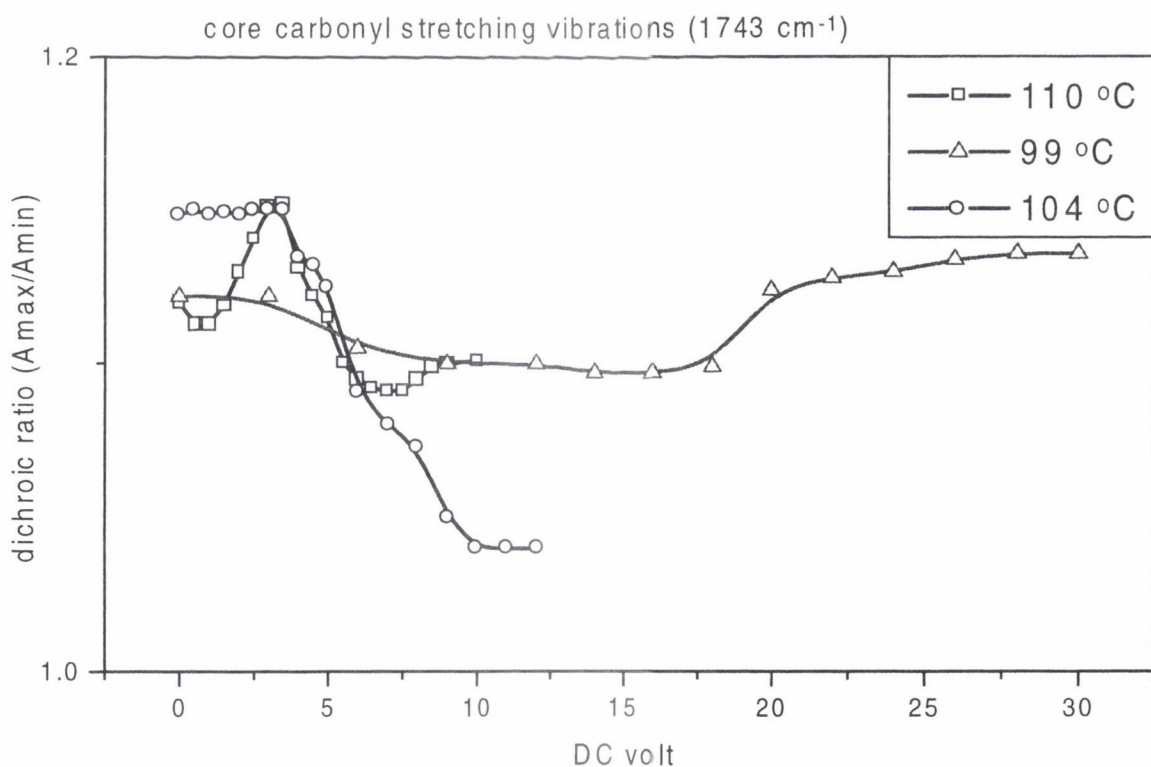


Figure 6.9. Voltage dependence of dichroic ratio for core carbonyl band for three smectic phases.

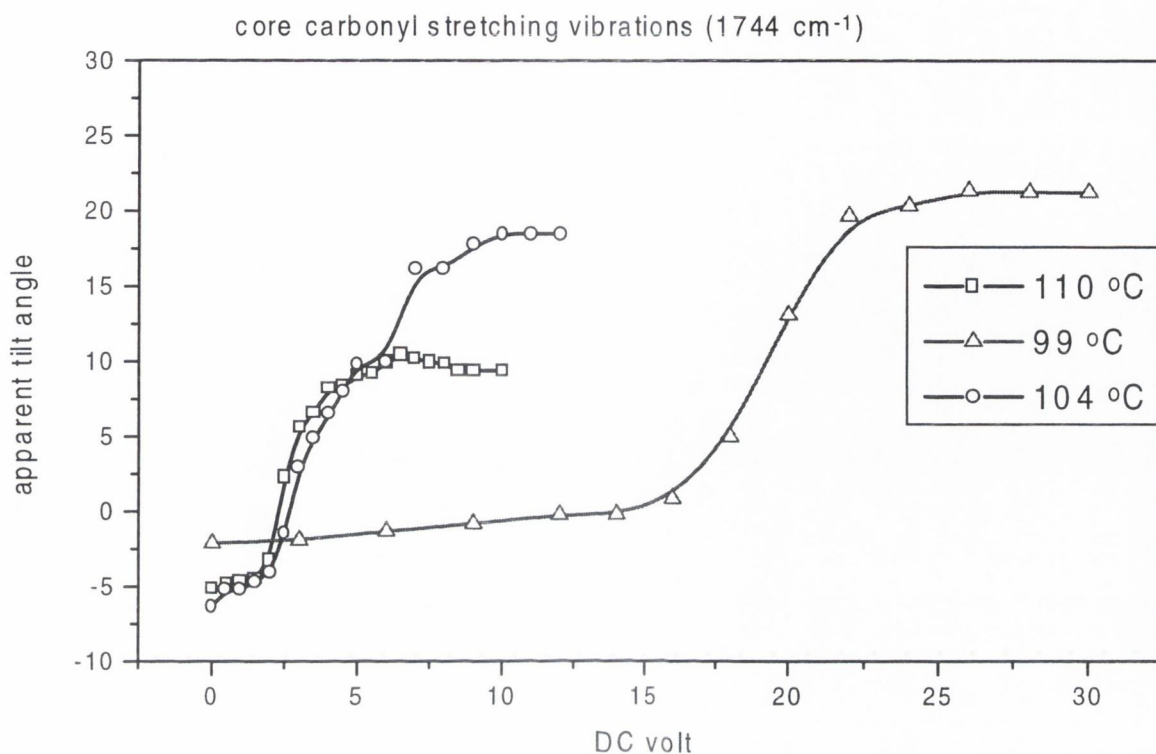


Figure 6.10. Voltage dependence of apparent tilt angle for core carbonyl for three smectic phases.

Fig. 6.11 shows that maximum absorbance ($A_{\max}$) for SmC_A^* phase has a lowest value for the core carbonyl band, and in comparison with SmC^* and SmC_γ^* is nearly independent of the applied field. This states the fact that, the small voltage dependency of the dichroic ratio for SmC_A^* phase shown in Fig. 6.9 is due to the variation of $A_{\min}$ in their absorbance profiles. Moreover, from Fig. 6.11, it is noticeable that, the variation of $A_{\max}$ with respect to the bias voltage for SmC^* and SmC_γ^* phases is almost identical. However, $A_{\max}$ shows higher value for SmC^* phase.

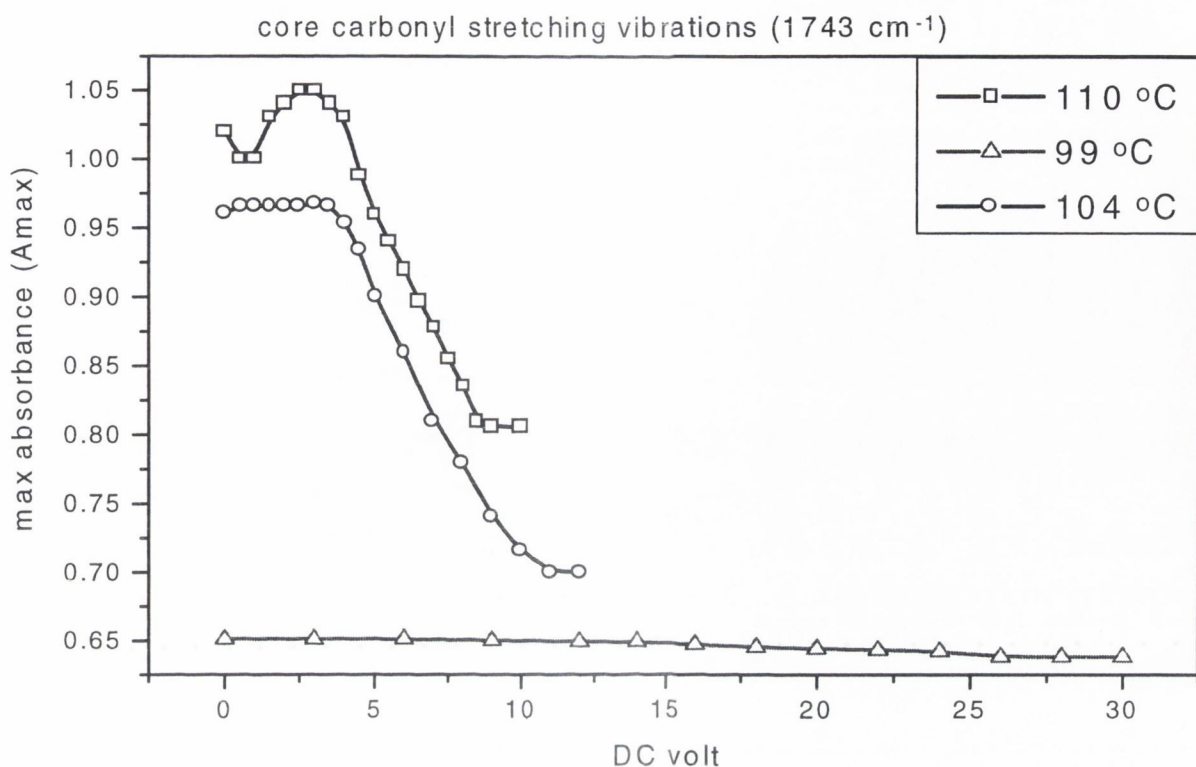


Figure 6.11. Voltage dependence of maximum absorbance for core carbonyl band for three smectic phases.

Fig. 6.12 shows the voltage dependence of the maximum absorbance ($A_{\max}$) for chiral carbon stretching vibrations at the frequency of 1719 cm^{-1} for the three smectic phases. As seen, the variation in $A_{\max}$ is almost identical for SmC^* and SmC_γ^* phases whereas, for SmC_A^* , the maximum absorbance stays constant up to 16V and thereafter continues to decrease until the applied field approaches higher than threshold value.

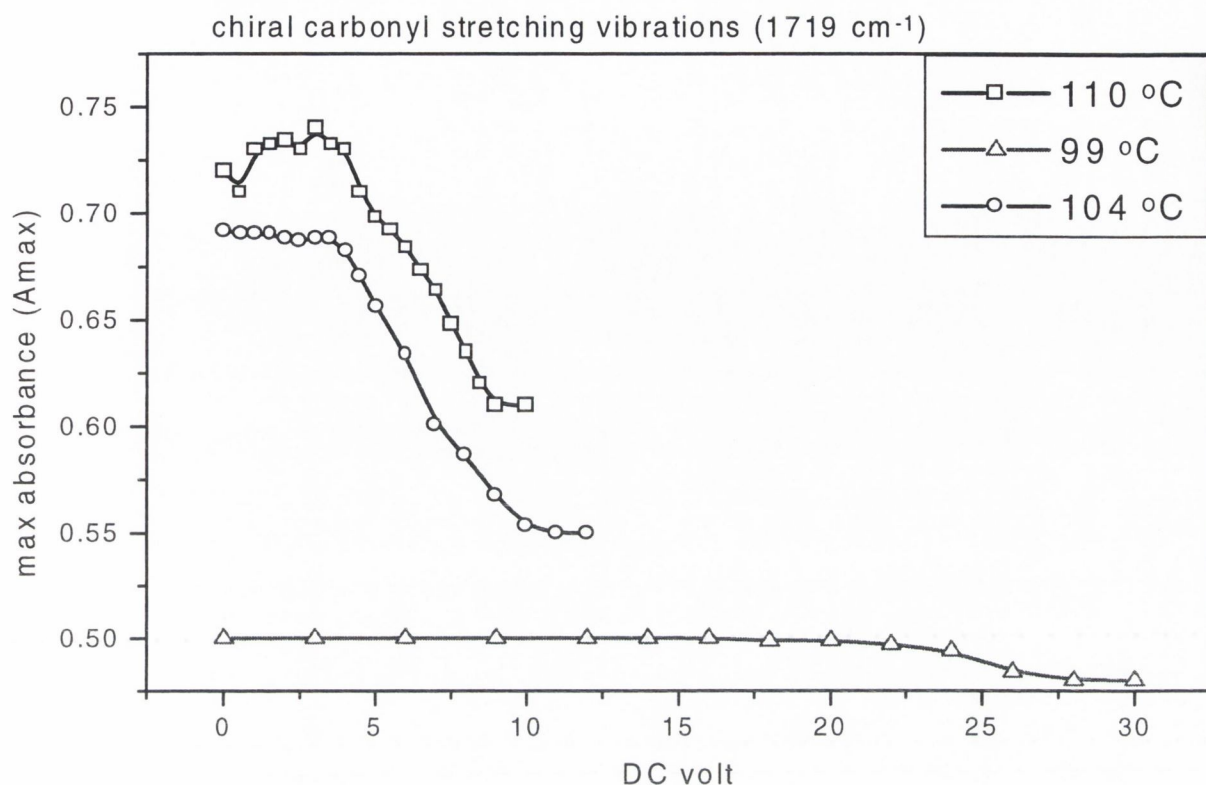


Figure 6.12. Voltage dependence of maximum absorbance for chiral carbonyl band for three smectic phases.

Figs. 6.13 and 6.14 present the voltage dependencies of D_r and apparent tilt angle for the $C=O$ chiral group for the three smectic phases. The start of the curves up to $\sim 2.5V$ correspond to the unwinding of the helix. The degree of orientation is pretty low compare with the phenyl group for each smectic phase.

For SmC^* phase in the region of $2.5V$ to $4V$ a small increase is observed in the dichroic ratio and the apparent tilt angle. As the voltage increases to $\sim 8V$ dichroism decreases sharply to saturation and the apparent tilt angle rises to maximum where the helix is completely unwound. At this time $C=O$ chiral group would take a considerably upright position with respect to the tilt plane

[17]. For SmC_γ^* phase up to 4V we notice a minor decrease in D_r and a small rise in the apparent tilt angle. The helix is unwinding. Between 4V and 10V an abrupt decrease in D_r is observed whereas the apparent tilt angle sharply rises to saturation. The core chiral group is mostly expected to be out of the tilt plane. The helix is totally unwound at this stage.

In SmC_A^* phase the unwinding of the helix is a slow process. Both D_r and the apparent tilt angle increase uniformly with the applied field and show a constant slope up to $\sim 16\text{V}$. From the threshold of 16V to 22V unwinding of the helix is more intense as both dichroism and the apparent tilt angle jump to saturation. Now the helix is completely unwound. Note that in SmC_A^* phase the $\text{C}=\text{O}$ chiral group has a tendency to lie in the molecular tilt plane [18].

Our experimental results show similarity for the voltage dependence of the apparent tilt angle for the phenyl and the chiral carbonyl groups for the three smectic phases, see Fig. 6.6 and 6.14. However, each phase shows a smaller angular dependence and different dichroic behaviour when compared with the phenyl group. This can indicate that the rotation of the $\text{C}=\text{O}$ chiral group for each phase is biased in a specific direction with respect to the average direction of the long molecular axis [16,19].

By considering these results one can infer that, the possible orientation belonging to the $\text{C}=\text{O}$ group is not exactly in the direction of the polar symmetry axis (C_2). However, due to the molecular head and tail equivalence, the spontaneous polarisation appears along the two-fold axis for each smectic phase.

Note that, the biasing parameters and the biasing angles of the rotation for $\text{C}=\text{O}$ core and chiral groups for the three smectic phases are calculated and the results

are given in the later stage of this chapter, see Table 6.3. For these calculations the polar angle β (the angle between the phenyl dipole and the long molecular axis) is taken to be zero. Table 6.2 present the values of the apparent tilt angle for each molecular group for each smectic phase investigated in this research. Note that, due to the position of the C = O chiral group with respect to the tilt plane in SmC_A^* and SmC^* phases, the in-layer spontaneous polarisation parallel to the tilt plane exist at smectic layer boundaries in SmC_A^* phase [18].

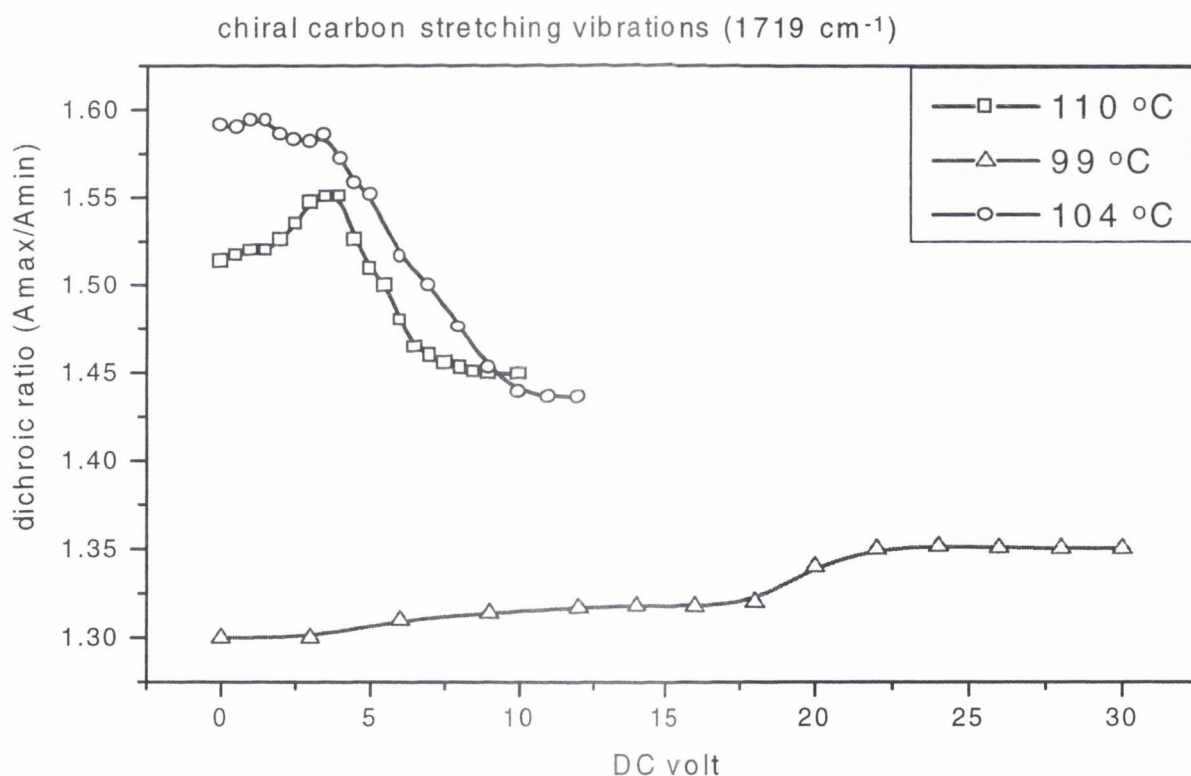


Figure 6.13. Voltage dependence of dichroic ratio for chiral carbonyl band for three smectic phases.

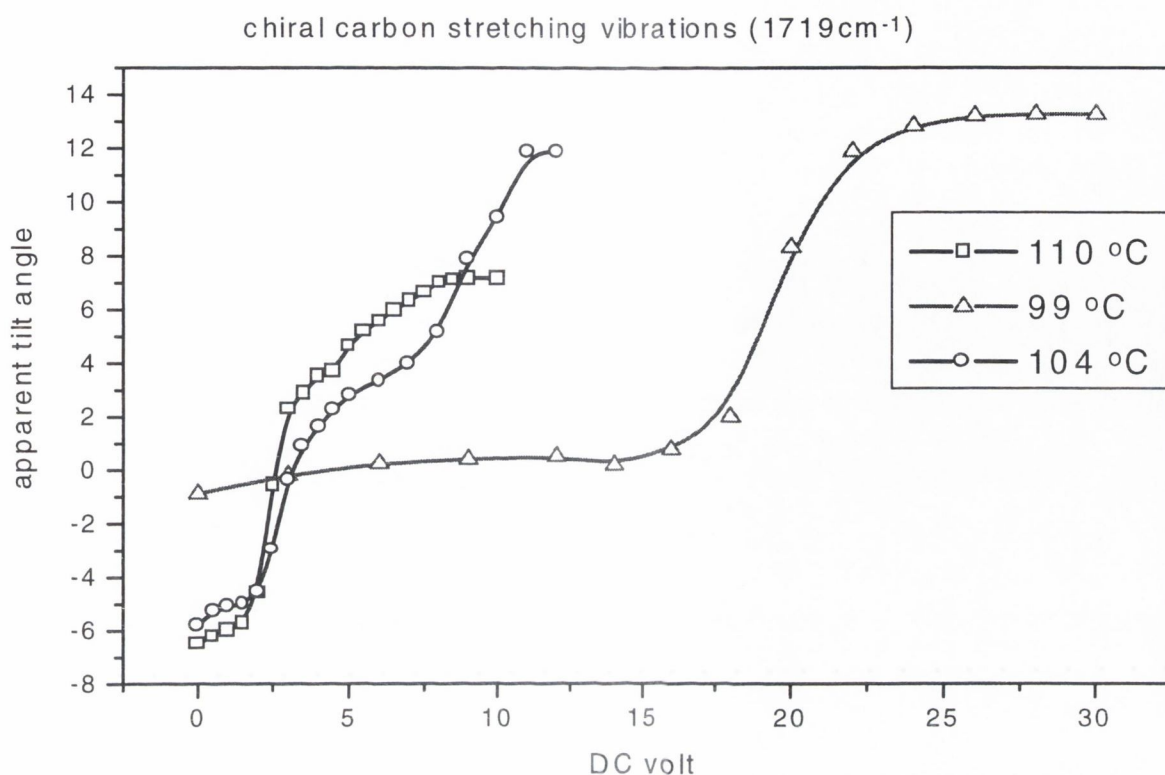


Figure 6.14. Voltage dependence of apparent tilt angle for chiral carbonyl band for three smectic phases.

Despite the low values of the dichroic ratio for the chiral group, the transverse permanent dipoles located near the chiral carbon give rise to the appearance of ferroelectricity and antiferroelectricity. In both cases, rotation of the molecule around the long molecular axis is biased so the chiral part is averagely oriented along a particular direction to produce spontaneous polarisation. However, in ferroelectric and antiferroelectric phases, the intermolecular interactions are different. In ferroelectric SmC^* phase, dispersion forces between the transverse permanent dipoles are the most probable reason for the molecular tilt and the ferroelectric ordering [20,21]. In SmC_A^* phase, direct interactions between the permanent dipoles in the adjacent layers is the cause for the existence of

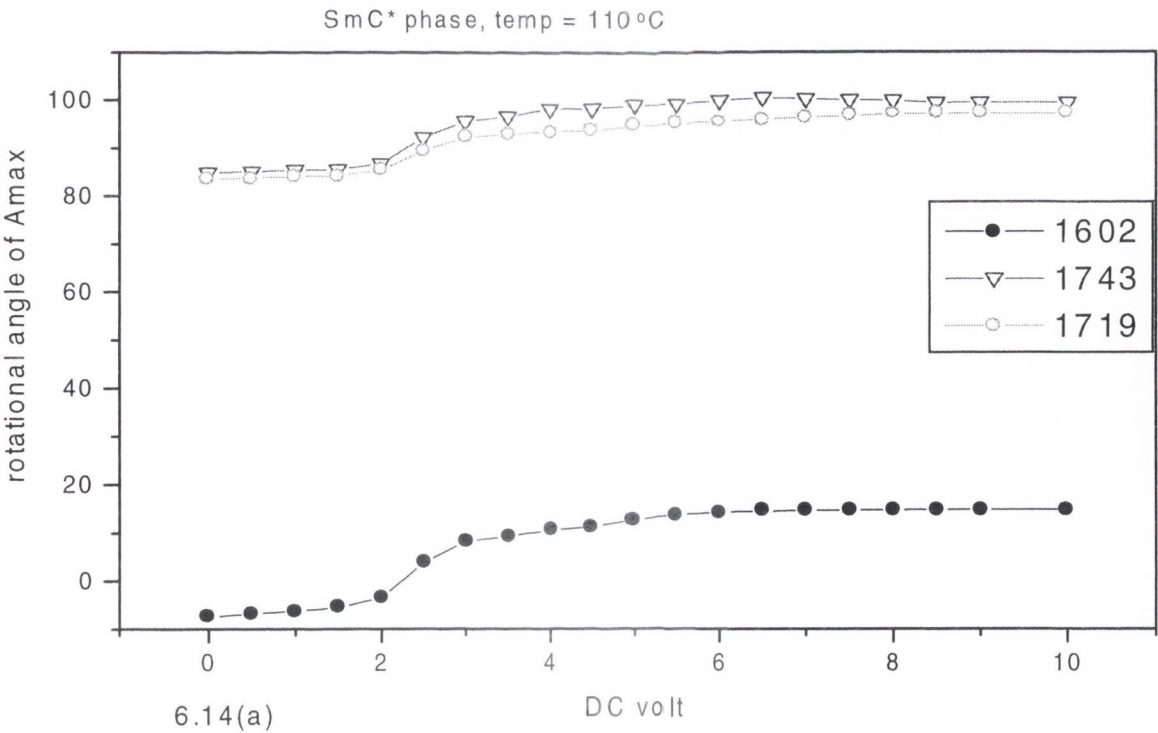
antiferroelectricity [22]. Due to various type of interactions in antiferroelectric liquid crystals, the angle of rotational biasing is expected to be different in SmC_A^* to that in SmC^* phase. For the carbonyl group near the chiral centre, this has been confirmed using infrared spectroscopy [3,10,18]. These facts can state the reasons for the differences of voltage dependencies of dichroic ratios and the apparent tilt angle which is found for the common vibrational bands investigated among SmC_A^* , SmC_γ^* and SmC^* phases in this study.

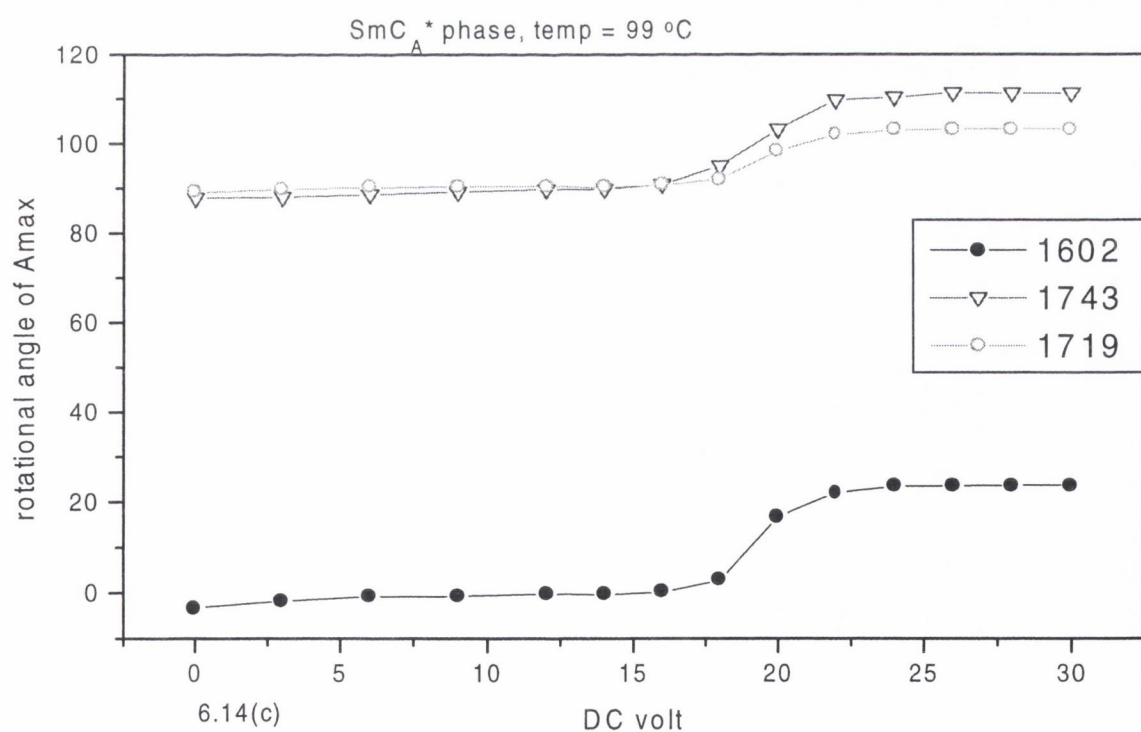
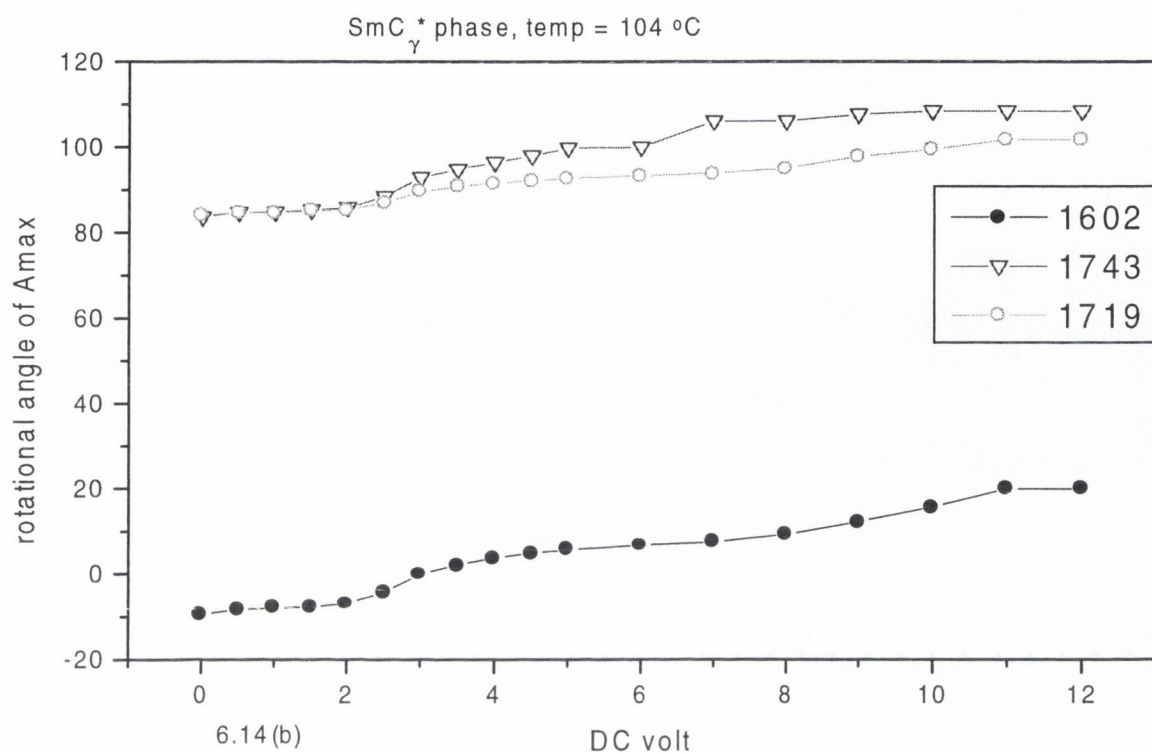
It is noted that, the vibrational frequency is related to the force constant (k) and the reduced mass of vibration (m). This can be expressed by the following relation [1]:

$$\tilde{\nu} \sim \sqrt{\frac{\langle k \rangle}{m}} \quad (6.4)$$

In (6.4), $\tilde{\nu}$ is the frequency of vibrations. $\langle k \rangle$ is the average value of the intermolecular interactions and depends on the balance between the attractive and repulsive forces. For attractive forces being larger than repulsive ones, $\langle k \rangle$ is small and vibrational frequency ($\tilde{\nu}$) decreases. The opposite is also true when attractive forces are smaller than repulsive ones. We observe small shifts of vibrational frequency ($\tilde{\nu}$) of some common bands for (C - C) phenyl, (C = O) core carbonyl and (C = O) chiral carbonyl stretching vibrations between the three smectic phases. Considering (6.4), this may well be due to intermolecular interactions and ultimately the difference in molecular orientation in different phases.

Figs. 6.14(a), (b) and (c) show the voltage dependencies of the rotational angle of $A_{\max}$ for phenyl, core and chiral carbonyl groups for each smectic phase. It is evident that, the absorption profiles belonging to the three molecular segments rotate at the same direction with the same polarity of the applied voltage for each smectic phase. $A_{\max}$ at zero volt for phenyl, core and chiral carbonyl groups for SmC^* phase is observed at the angles -7.5° , 84.85° and 83.5° respectively. For SmC_γ^* phase these values are -8.43° , 83.72° and 84.2° and for SmC_A^* phase they are -3.23° , 87.9° and 88.12° . These values show that the absorption profiles of the $C = O$ group for each smectic phase are not exactly perpendicular to the absorption profile of the phenyl group. The angular differences for $A_{\max}$ between the phenyl group and the $C = O$ groups for each phase varies as the applied field increases. However, the most probable orientation of the $C = O$ group is not normal to the tilt plane and they have a biased rotational motion around the molecular axis [10].





Figures 6.14(a), (b) and (c). Voltage dependencies of rotational angle of $A_{\max}$ for phenyl, core and chiral carbonyl groups for SmC^* , SmC_γ^* and SmC_A^* phases.

Figs. 6.15, 6.18 and 6.21 show the dichroic ratio, Figs. 6.16, 6.19 and 6.22 show the apparent tilt angle and Figs. 6.17, 6.20 and 6.23 show the maximum absorbance voltage dependencies for CH_2 and CH_3 groups for the three smectic phases. These results show similarity with the ones shown for the phenyl group in Figs. 6.5, 6.6 and 6.8.

In SmA^* phase due to the large volume of smectic layers the molecular tail containing CH_2 and CH_3 groups rotates with random free motion. Therefore, the orientation of the tail does not correlate with the orientation of the molecular core. However, in tilted smectic phases the volume of the layers decrease. Hence, the rotational motion and the orientational behaviour of the tail begin to correlate more with the orientation of the rigid core due to this decrease in volume. Of course in SmC_A^* phase due to the larger tilt angle this correlation is most predominant among the three smectic phases. Due to these facts we can state that, the behaviour of the infrared absorption peaks for CH_2 and CH_3 groups have close similarity with the peaks related to the core of the molecule.

The values of the apparent tilt angle in Table 6.2 show that the asymmetric CH_3 group rotates with the larger angle around the Z axis than CH_2 groups for each smectic phase. Possibly, this is due to the isotropic character of the CH_3 asymmetric vibration band, as this group is located at the end of the flexible carbon chain [3]. These results show that the dichroic ratios for CH_2 and CH_3 groups do not change dramatically with the application of the electric field. They are also of low values in comparison to those for the core for the three smectic phases. This confirms that the alkyl chain of the molecules is considerably disordered [16,19]. This behaviour is either due to their flexibility or due to the

existence of several conformations of the molecule in which the chain lies in different position [1]. Moreover, when the polarity of the applied field is reversed, the alkyl chain rotates to a lesser extent than the core, implying that the average alkyl chain axis does not coincide with the average direction of the long molecular axis [19].

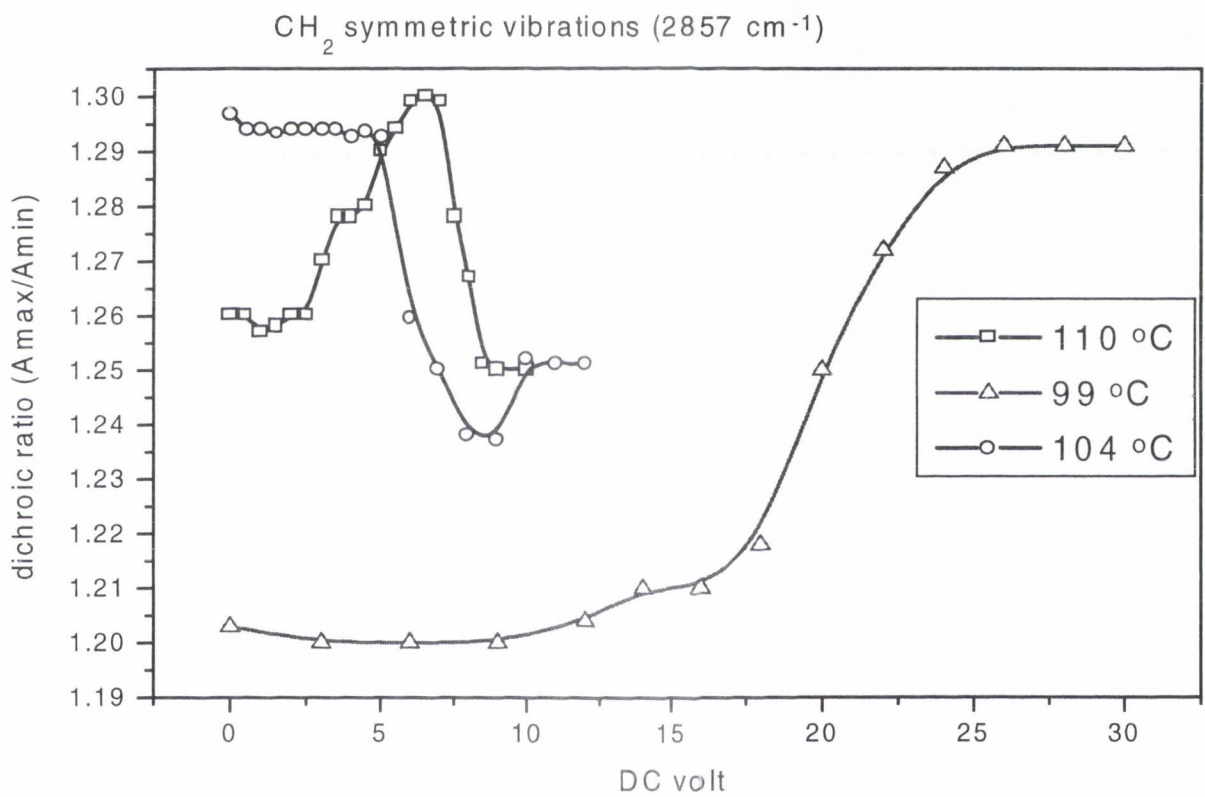


Figure 6.15. Voltage dependence of dichroic ratio for CH_2 symmetric vibrations for three smectic phases.

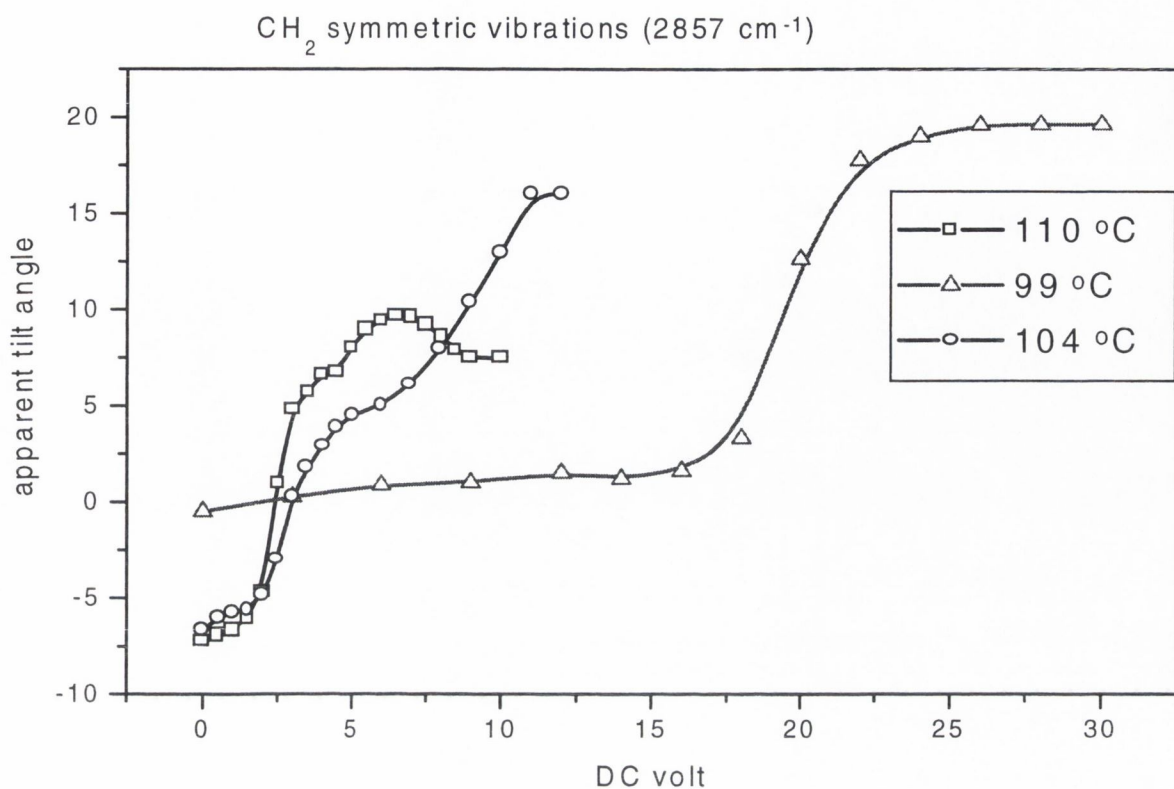


Figure 6.16. Voltage dependence of apparent tilt angle for CH_2 symmetric vibrations for three smectic phases.

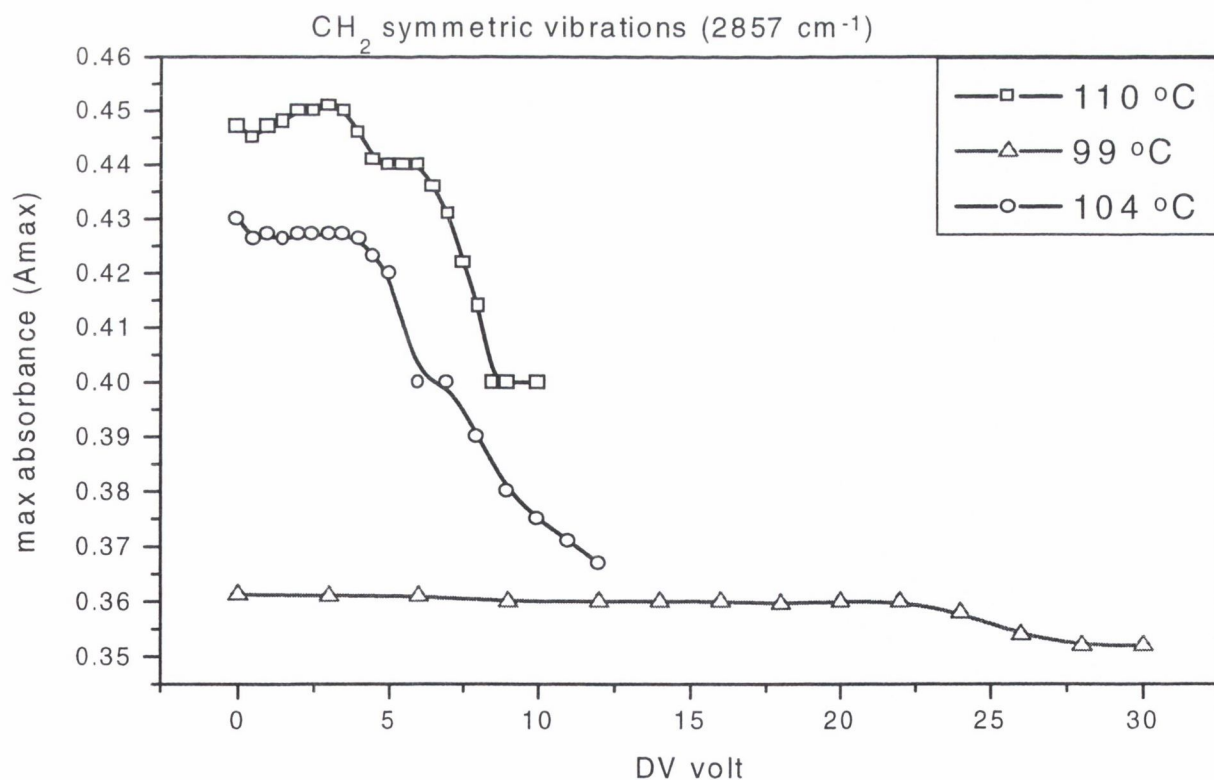


Figure 6.17. Voltage dependence of maximum absorbance for CH_2 symmetric vibrations for three smectic phases.

CH₂ asymmetric vibrations (2929 cm⁻¹)

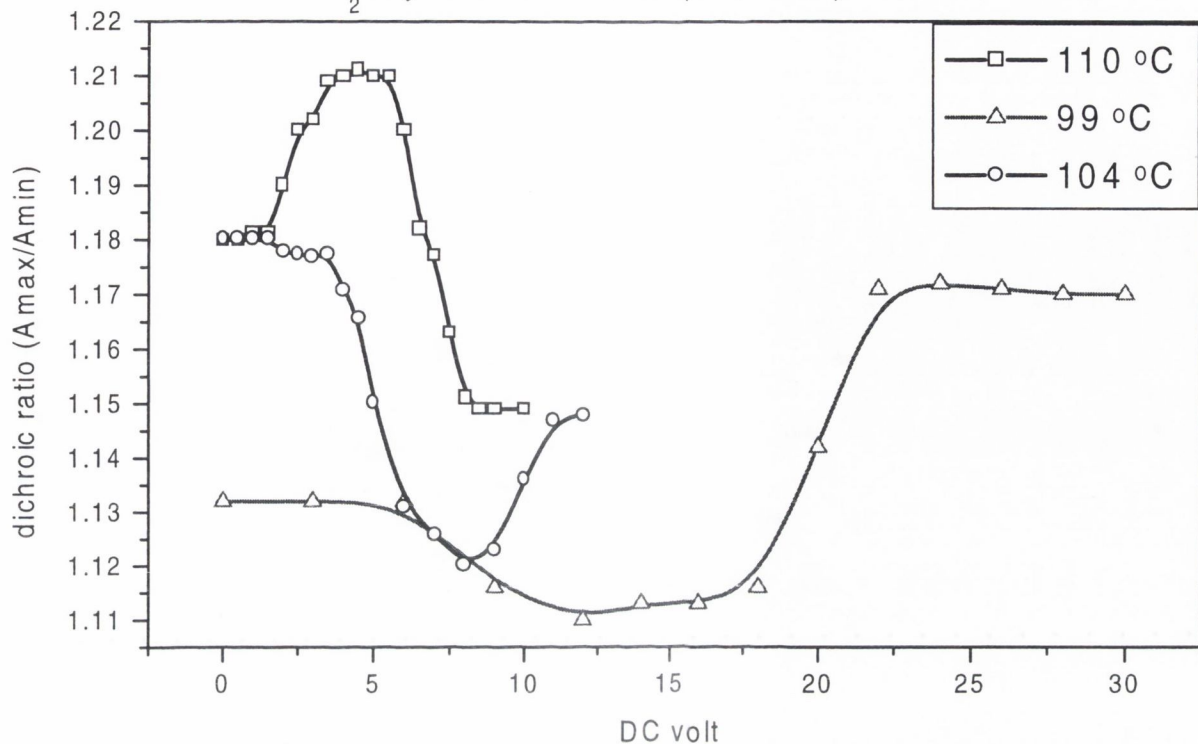


Figure 6.18. Voltage dependence of dichroic ratio for CH₂ asymmetric vibrations for three smectic phases.

CH₂ asymmetric vibrations (2929 cm⁻¹)

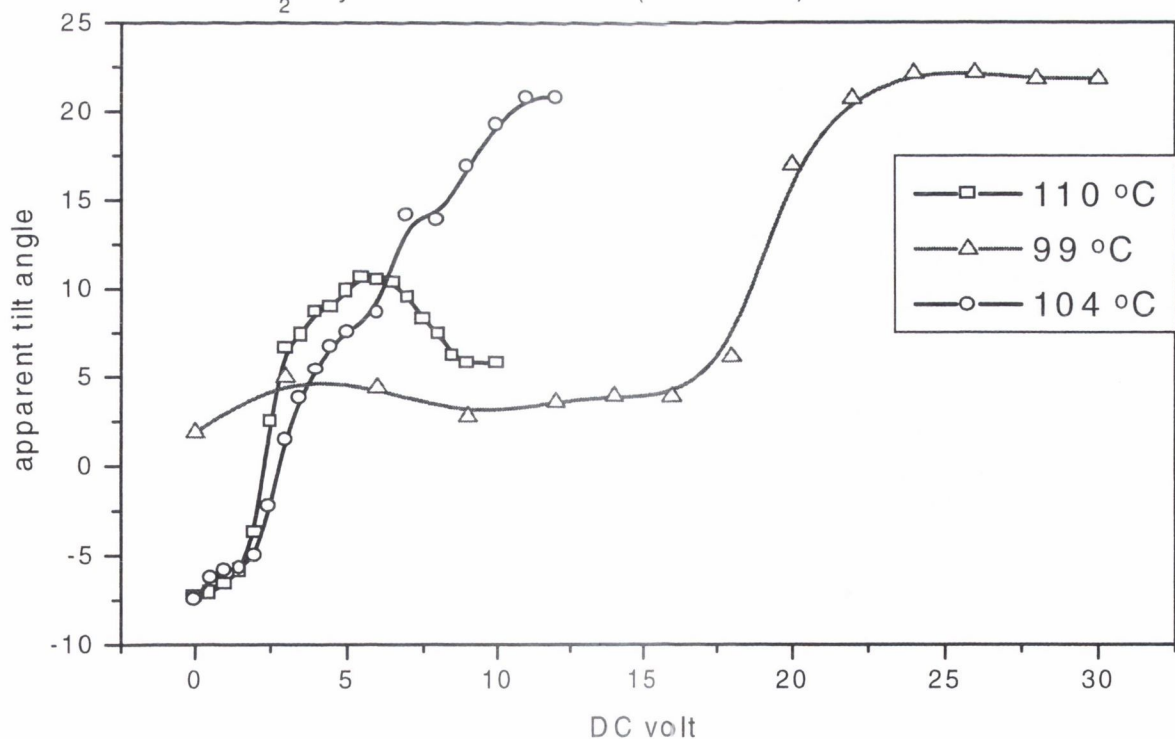


Figure 6.19. Voltage dependence of apparent tilt angle for CH₂ asymmetric vibrations for three smectic phases.

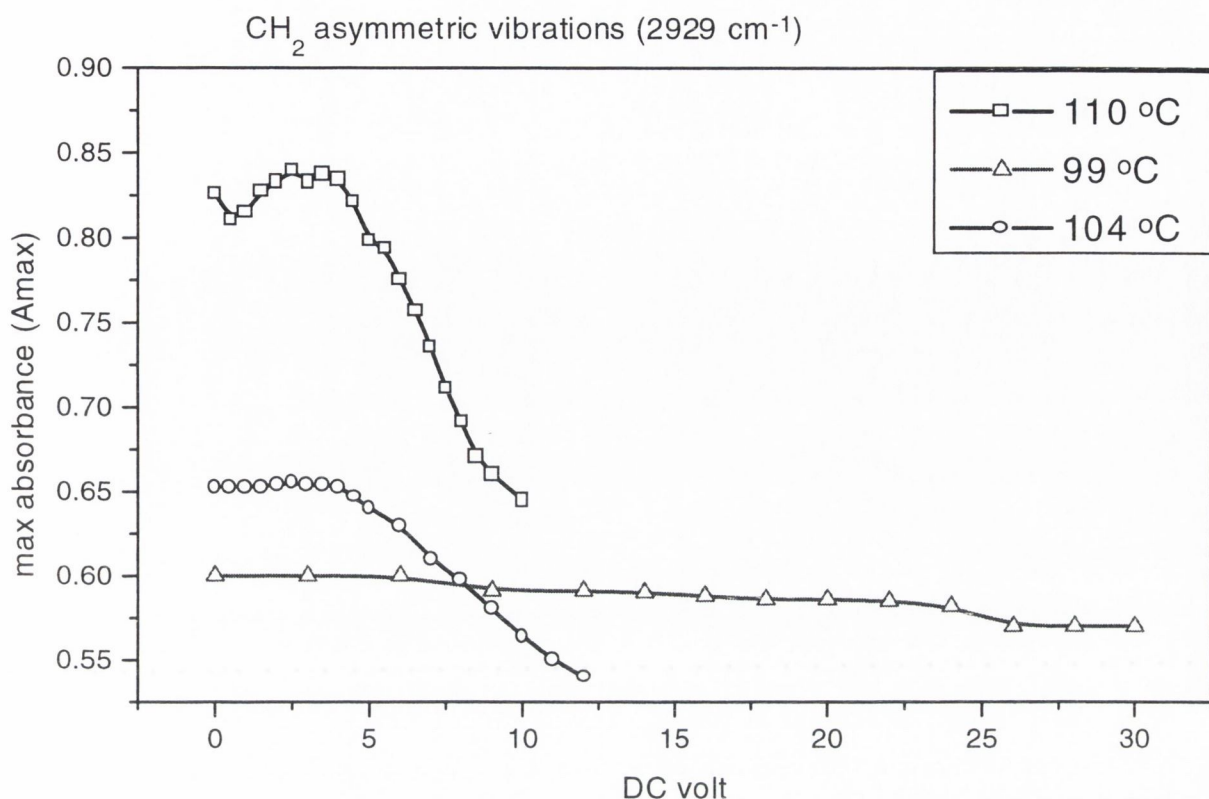


Figure 6.20. Voltage dependence of maximum absorbance for CH_2 asymmetric vibrations for three smectic phases.

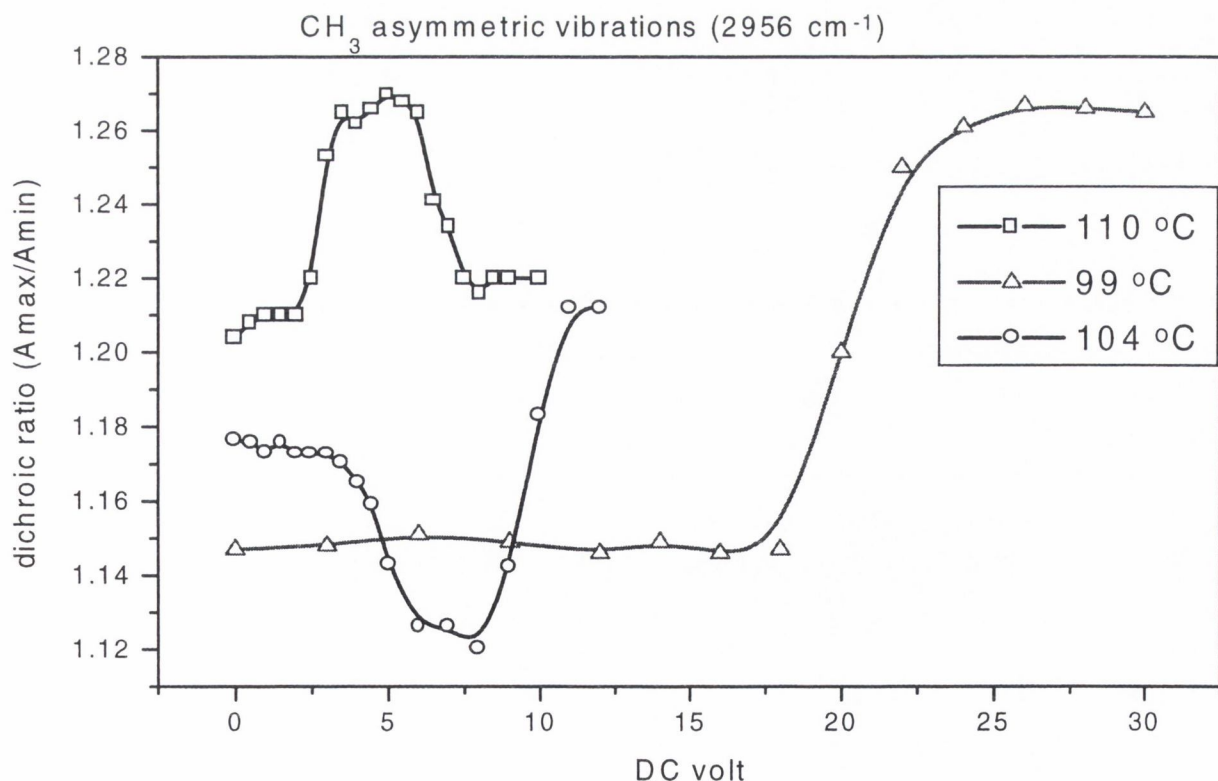


Figure 6.21. Voltage dependence of dichroic ratio for CH_3 asymmetric vibrations for three smectic phases.

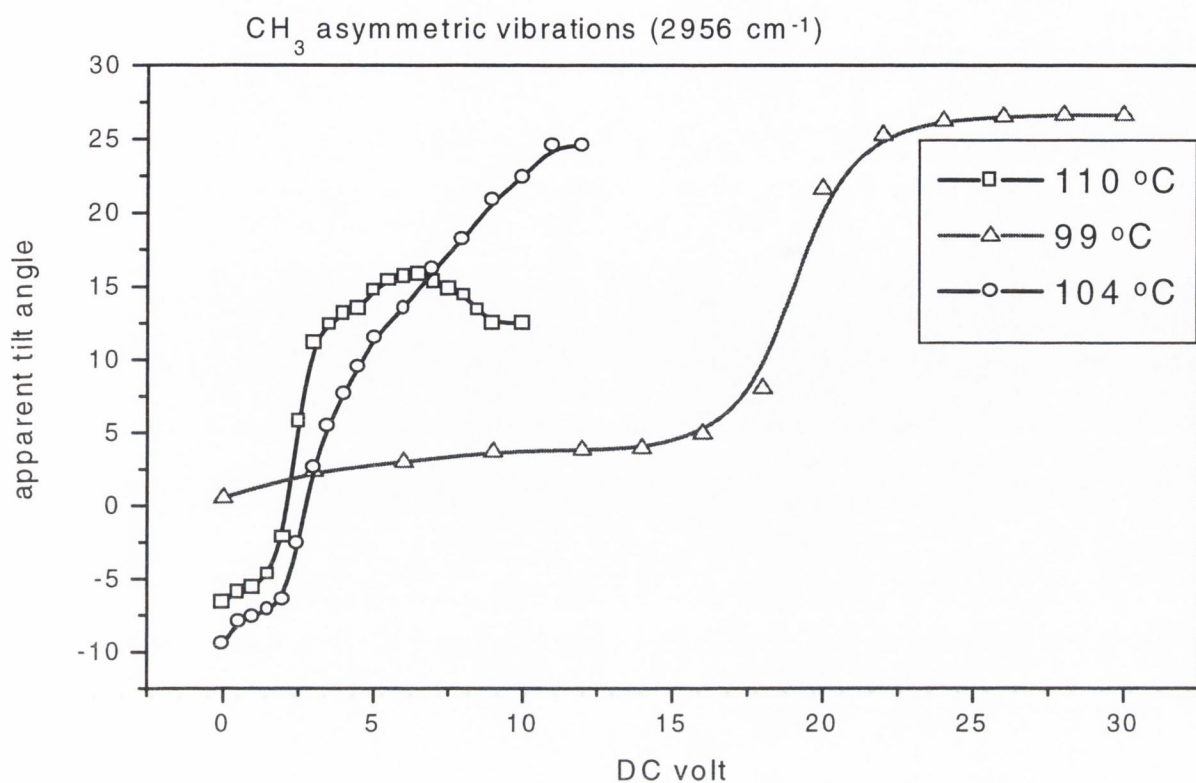


Figure 6.22. Voltage dependence of apparent tilt angle for CH_3 asymmetric vibrations for three smectic phases.

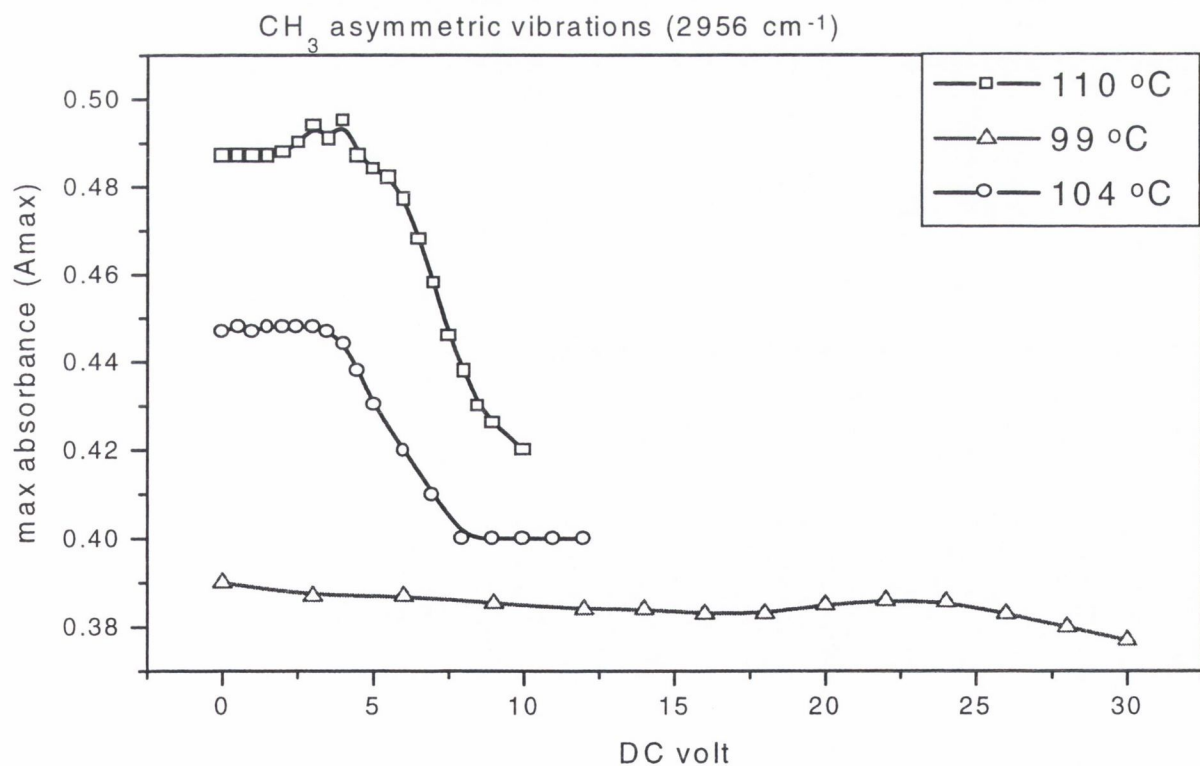
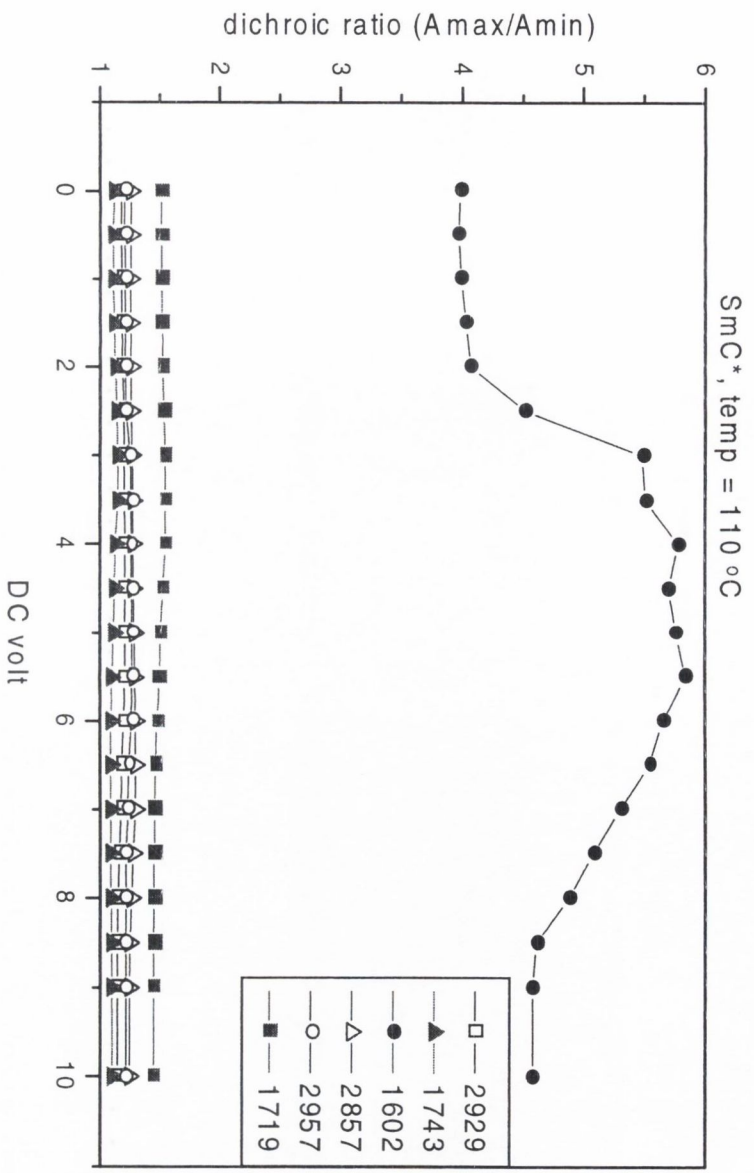


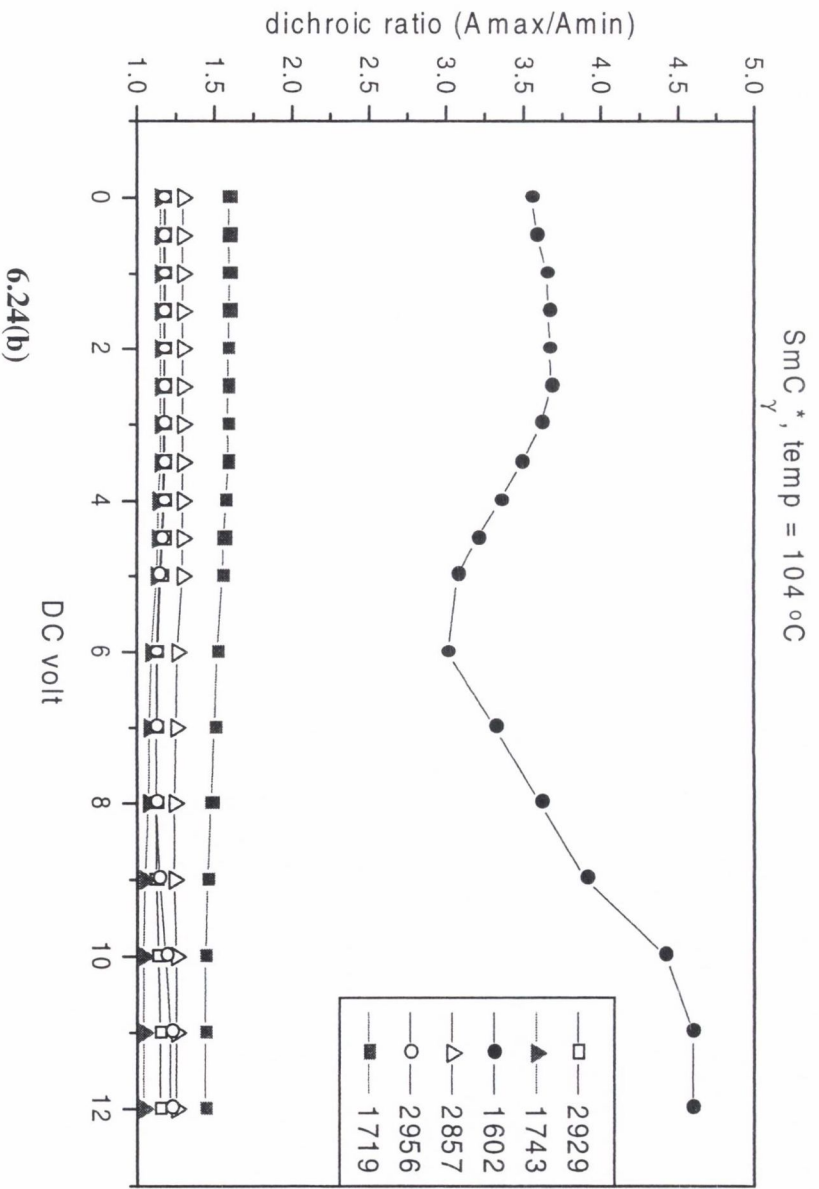
Figure 6.23. Voltage dependence of maximum absorbance for CH_3 asymmetric vibrations for three smectic phases.

6.3.1. Observation of the individual smectic phase in terms of D_r , $\Omega_{\max}$ and $A_{\max}$

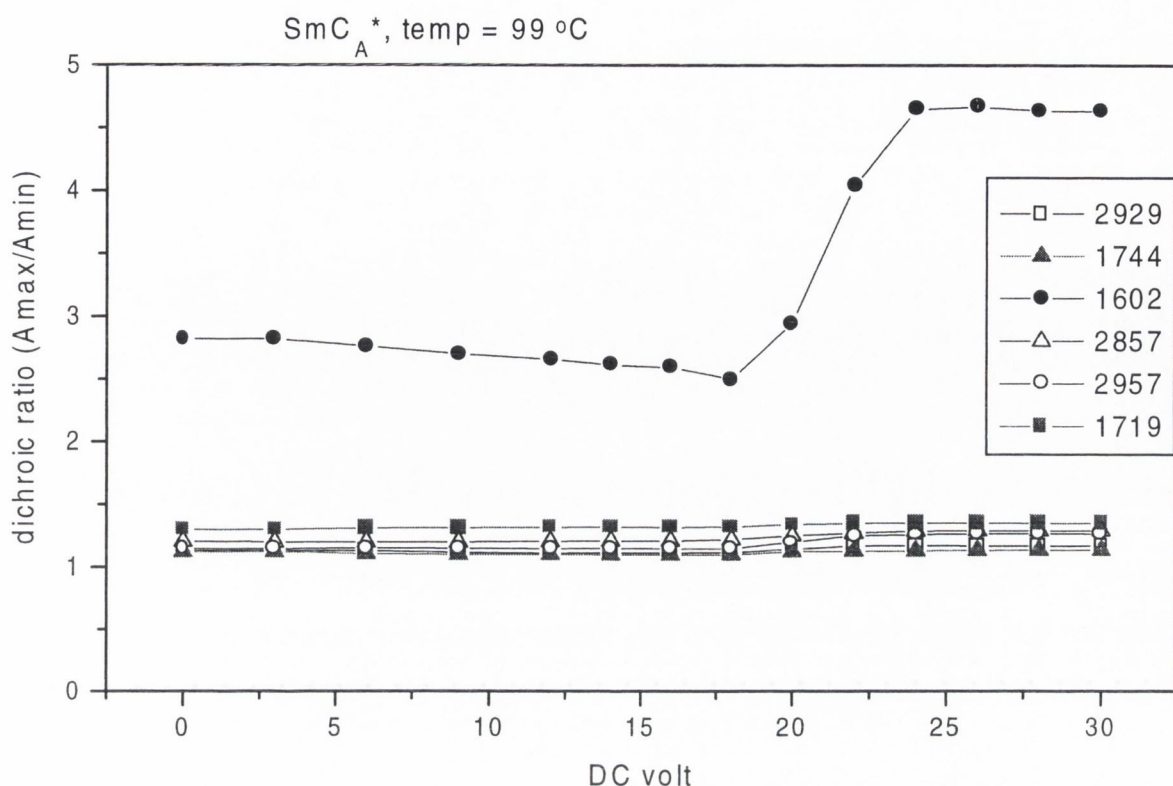
In this part of the chapter a brief explanation of each smectic phase is given. Figs. 6.24(a), (b) and (c) illustrate the dichroic ratio versus DC voltage for SmC^* , SmC_γ^* and SmC_A^* phases for phenyl, core carbonyl, chiral carbonyl and the vibrational bands CH_2 and CH_3 belonging to the alkyl chain of the molecule. As can be seen, the dichroic ratio of the phenyl ring has the largest dependencies on the applied field for the three smectic phases. These Figs. also indicate that, the dichroic ratio for each phase for phenyl group go through some primary and intermediate changes prior to reaching a constant value at their saturated voltages. This confirms that, prior to the completion of the unwinding process by the application of bias voltage, the molecular orientation for each phase is dependent to the degree to which the helix is disturbed. Once the saturated voltage for each phase is reached, the helix is completely unwound and the orientation stays constant. Therefore the value of dichroic ratio for each smectic phase stays unaffected at higher voltages [15]. For a cell thinner than $6\mu\text{m}$ thickness, distortion of the helix at the same voltages can be more intense for each phase. The surface effect tends to align the molecules on the surface better than in the bulk for a thinner sample. Thus, the importance of the surface effect comes in fixing the molecular position [23].



6.24(a)



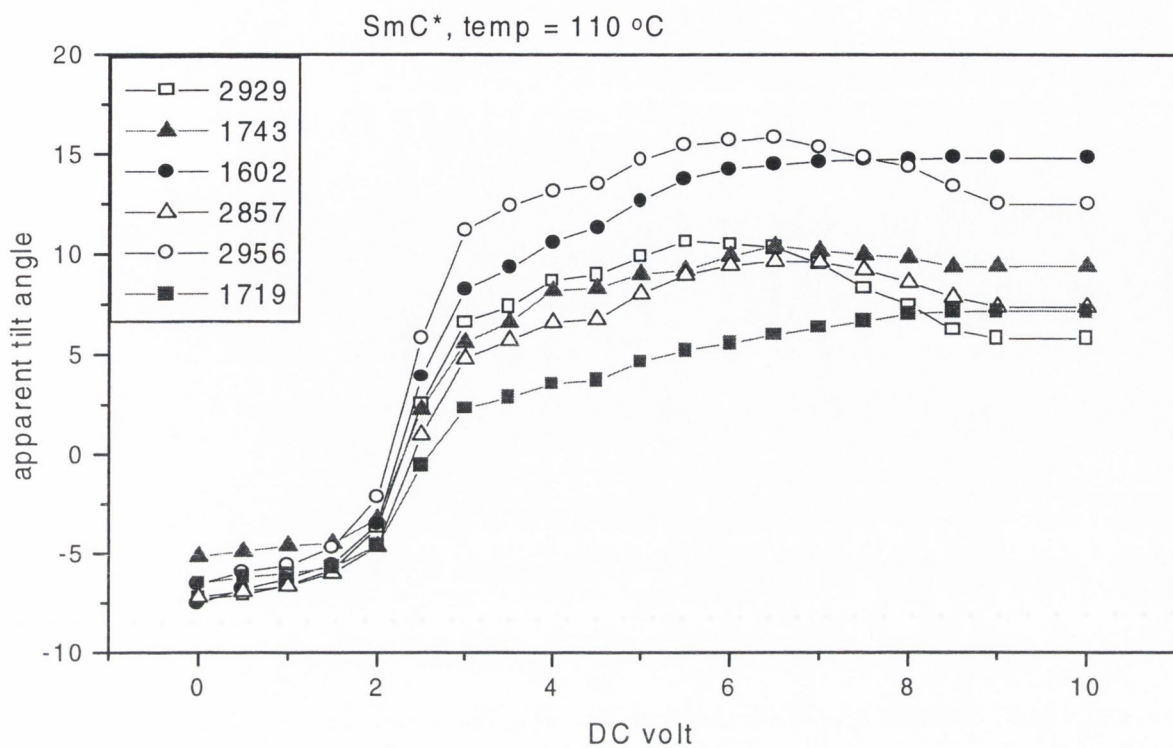
6.24(b)



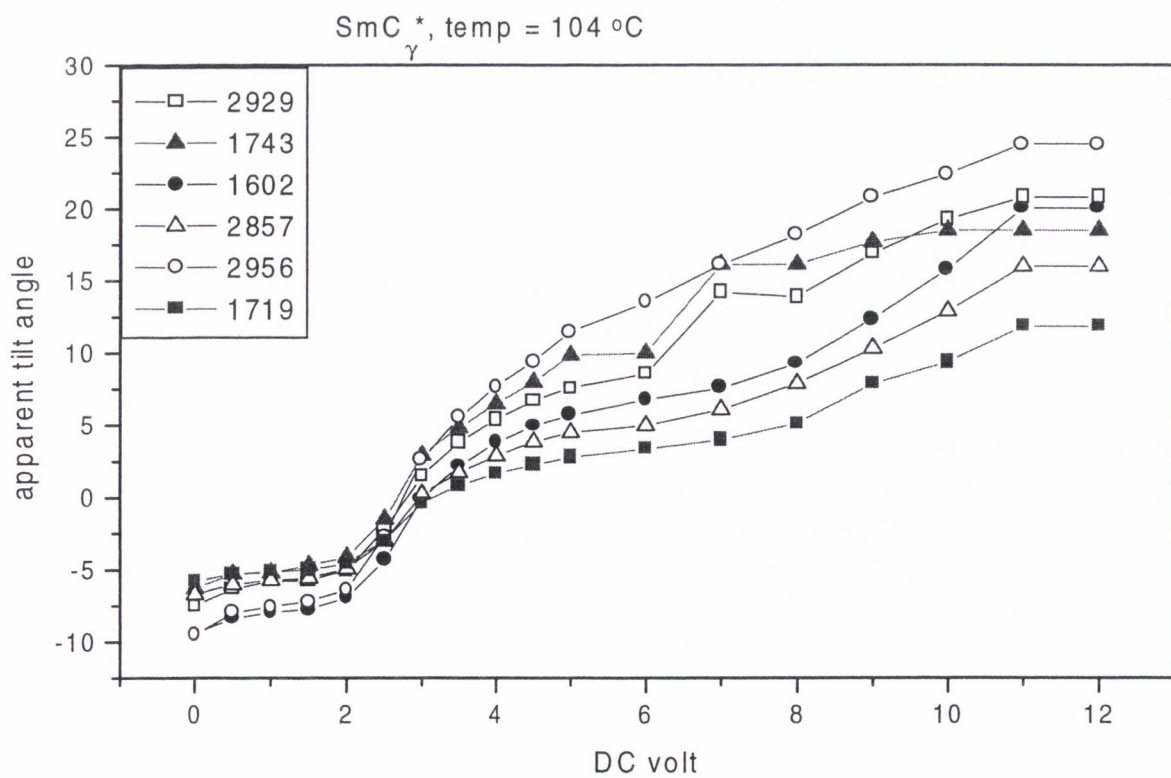
6.24(c)

Figures 6.24(a), (b) and (c). Voltage dependencies of dichroic ratio for six stretching vibrational bands investigated for SmC^* , SmC_γ^* and SmC_A^* phases

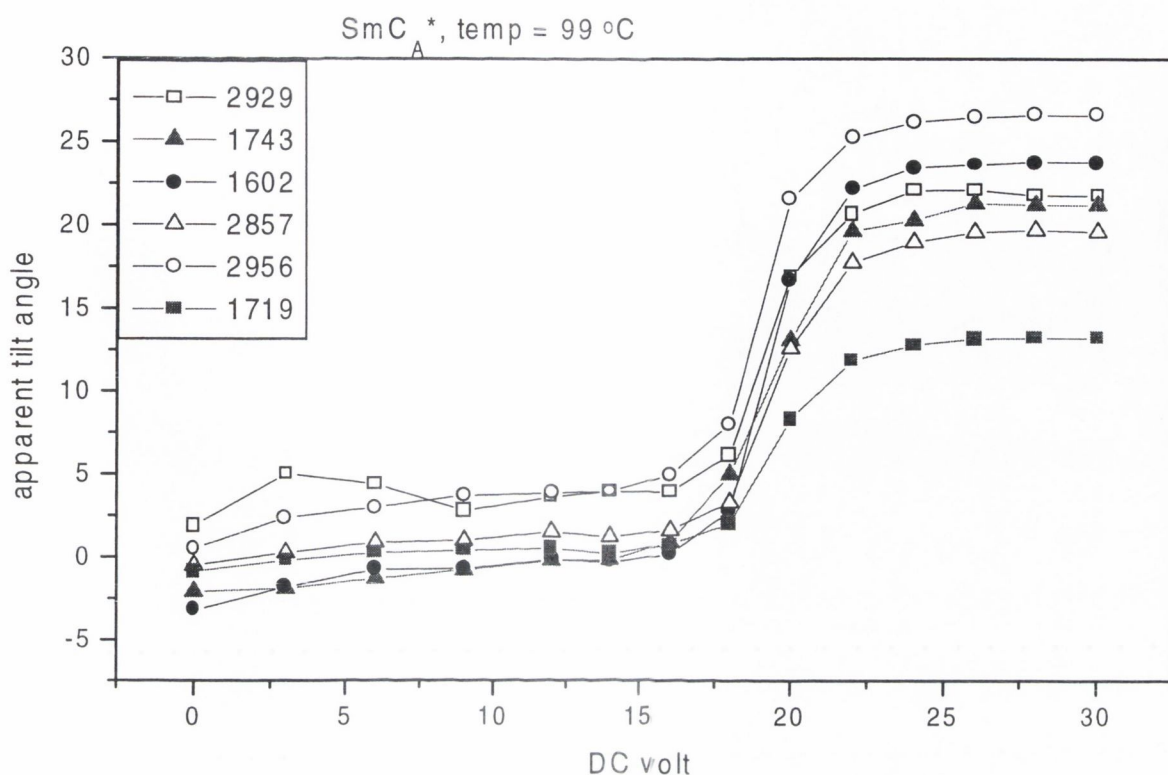
Figs. 6.25(a), (b) and (c) show the apparent tilt angles versus DC voltage for SmC^* , SmC_γ^* and SmC_A^* phases for phenyl, core carbonyl, chiral carbonyl and the vibrational bands CH_2 and CH_3 belonging to the alkyl chain of the molecule. From these Figs. it is evident that, at the saturated voltages, when the helix is completely unwound for each phase, the apparent tilt angle for the core of the molecule gives the largest value for the phenyl group. The value of the apparent tilt angle for the core carbonyl and chiral carbonyl groups follow consecutively. Therefore we can infer that, the phenyl group rotates with the larger angle with respect to Z axis than the rest of the groups in the core of the molecule for each phase.



6.25(a)



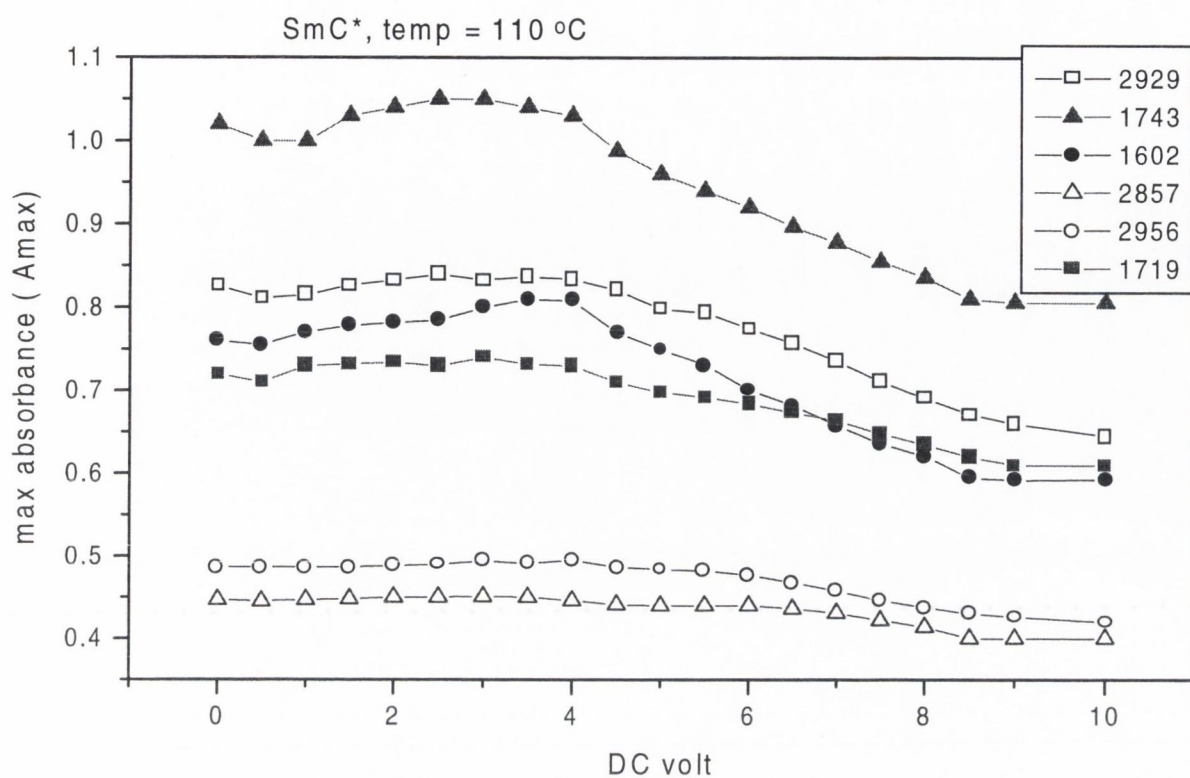
6.25(b)



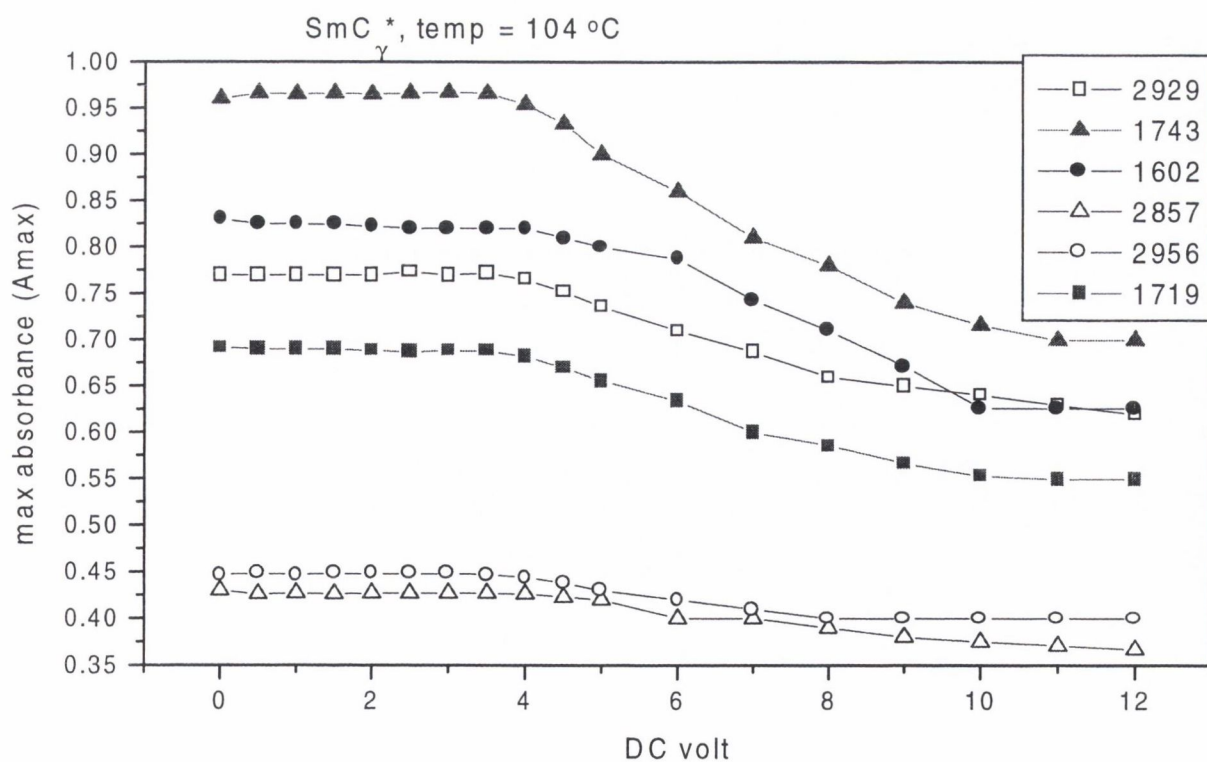
6.25(c)

Figures 6.25(a), (b) and (c). Voltage dependencies of apparent tilt angle for six stretching vibrational bands investigated for SmC^* , SmC_γ^* and SmC_A^* phases

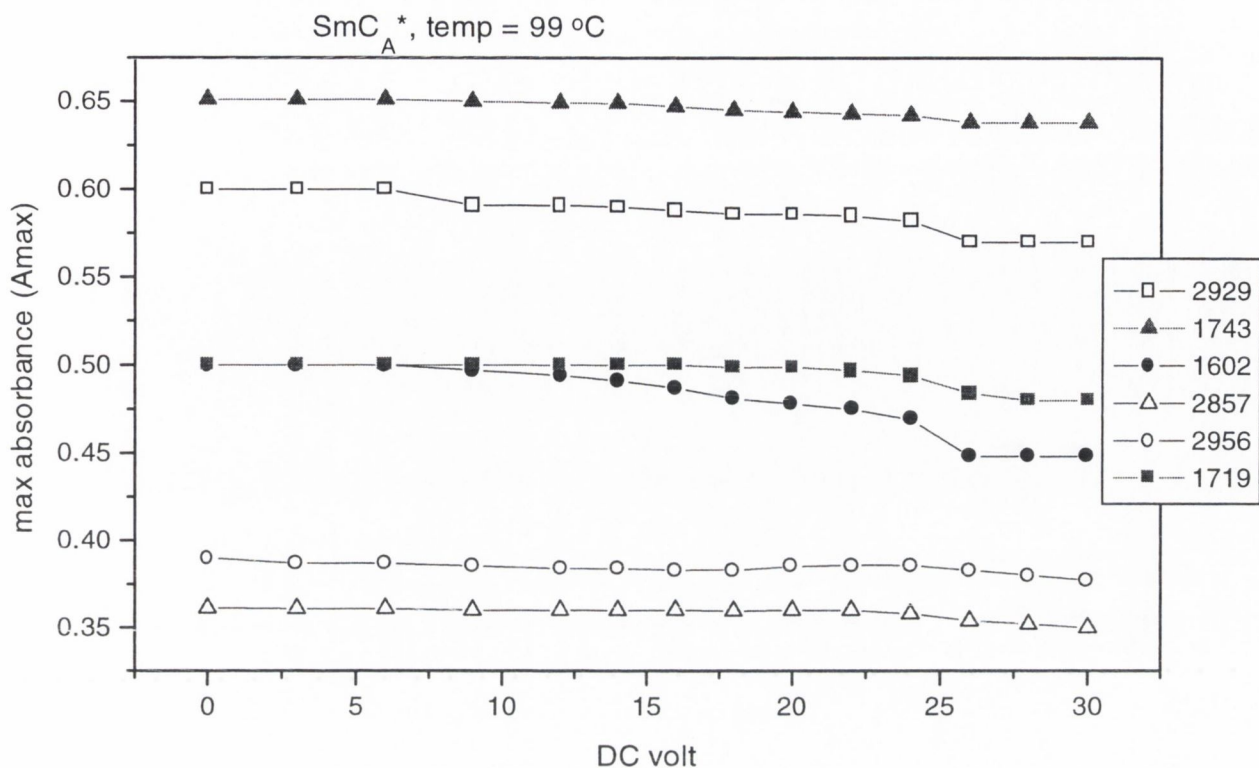
Figs. 6.26(a), (b) and (c) show how the absorbance maximum ($A_{\max}$) behaves with the applied voltage for the six peaks investigated for SmC^* , SmC_γ^* and SmC_A^* phases. From these plots, it is clear that, the dependence of $A_{\max}$ on the applied field for the six peaks are higher for SmC^* and SmC_γ^* than for SmC_A^* phase. One can also see that, the effect of the applied field on $A_{\max}$ is continuous for each peak in SmC^* phase, whereas the applied field influences the $A_{\max}$ at some intermediate stage for each peak in SmC_γ^* phase. The change on the absorbance maximum in SmC_A^* phase for each peak can be observed in the vicinity of the threshold voltage.



6.26(a)



6.26(b)



6.26(c)

Figures 6.26(a), (b) and (c). Voltage dependencies of $A_{\max}$ for six stretching vibrational bands investigated for SmC^{*}, SmC_γ^{*} and SmC_A^{*} phases

Table 6.2 shows the mean angular shift $\Delta\Omega_{\max}$ (deg) of peak profiles at the saturated voltages for which the helix is completely unwound for each smectic phase.

Band Freq. (cm ⁻¹)	Phenyl 1602	C=O chiral 1719	C=O core 1743	CH ₂ sym 2857	CH ₂ asym 2929	CH ₃ asym 2956
Temp. =99°C SmC _A [*]	29.1	18.76	26.2	24.92	26.2	30.8
Temp. =104°C SmC _γ [*]	25.3	17.36	23.6	21.3	25.9	28.7
Temp. =110°C SmC [*]	20.1	12.68	15.3	12.8	11.12	16.71

Table 6.2. Mean angular shift for six peaks for SmC_A^{*}, SmC_γ^{*} and SmC^{*} phases.

Table 6.2 shows that, in each smectic phase, the maximum value of tilt angle obtained is for the phenyl ring (C - C) stretching vibrations (1602 cm^{-1}). These values are confirmed with the electro-optic measurements of the tilt angle for each phase. The tilt angle for most other bands except the carbonyl group is approximately 5° lower than for the phenyl ring. This molecular behaviour can be explained in terms of a steric model where the spontaneous polarisation direction is fixed by spatial configuration of the chiral centre and the dipole moments associated with it [2,10]. Hence, for tilted molecules the rigid aromatic core may lie with a larger angle than the rest of the molecule in the smectic plane.

To describe the rotational orientation distribution of the C = O core and C = O chiral groups Fig. 6.27 is used. This Fig. shows the orientational distribution of a transition dipole moment in a molecular system. z is the long molecular axis, β is the polar angle measured between z and the transition dipole moment and γ displays the azimuthal angle measured from the normal to the tilt plane.

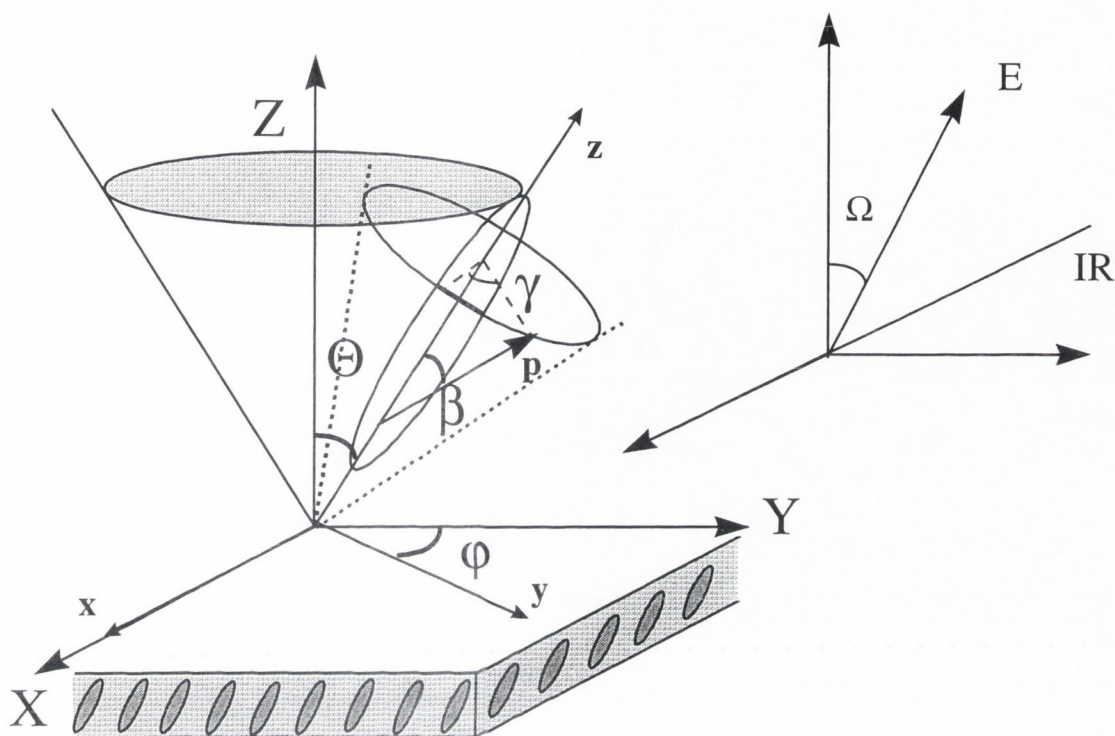


Figure 6.27. Co-ordinate system used for calculating of biasing parameters for (C = O) core and chiral groups. (X,Y,Z) represents the laboratory frame and (x,y,z) shows the molecular frame. Z is a normal to smectic layer and z is the long axis of the molecule. x coincides with X and the direction of the infrared propagation. β is the polar angle between the transition dipole moment (P) and the molecular long axis (z), and γ is its azimuthal angle.

6.3.2. Calculations of the biasing parameters for (C = O) core and chiral carbonyl groups

To calculate the rotational bias parameters for the (C = O) groups, similar simulation techniques to those presented in [10, 24] is used. Note that, the calculations are performed for SmC_A^* , SmC_γ^* and SmC^* phases.

$A_{\max}$ and $A_{\min}$ can be related to the main components in the laboratory frame as follows:

$$\begin{aligned} A_Z &= A_{\max} \cos^2(\Omega_{\max}) + A_{\min} \sin^2(\Omega_{\max}), \\ A_Y &= A_{\max} \sin^2(\Omega_{\max}) + A_{\min} \cos^2(\Omega_{\max}), \\ A_{YZ} &= (A_{\max} - A_{\min}) \sin(\Omega_{\max}) \cos(\Omega_{\max}) \end{aligned} \quad (6.5)$$

For each smectic phase the absorbances A_Z , A_Y and A_{YZ} in the laboratory frame can be described in terms of $\langle \sin\gamma \rangle$ and $\langle \sin^2\gamma \rangle$ as follows [10]:

$$\begin{aligned} A_Z &= k\{\cos^2\beta \langle \cos^2\theta \rangle - 2\sin\beta \cos\beta \langle \sin\theta \cos\theta \rangle \langle \sin\gamma \rangle + \sin^2\beta \langle \sin^2\theta \rangle \langle \sin^2\gamma \rangle\}, \\ A_Y &= k\{\cos^2\beta \langle \sin^2\theta \rangle + 2\sin\beta \cos\beta \langle \sin\theta \cos\theta \rangle \langle \sin\gamma \rangle + \sin^2\beta \langle \cos^2\theta \rangle \langle \sin^2\gamma \rangle\}, \\ A_{YZ} &= k\{\langle \sin\theta \cos\theta \rangle (\cos^2\beta - \sin^2\beta \langle \sin^2\gamma \rangle) + \sin\beta \cos\beta (\langle \cos^2\theta \rangle - \langle \sin^2\theta \rangle) \langle \sin\gamma \rangle\} \end{aligned} \quad (6.6)$$

The azimuthal distribution functions of the transition dipole moments around the long axis of the molecule for phenyl (C - C) and core carbonyl (C = O) stretching bands can be approximated in terms of $\langle \sin\gamma \rangle$ and $\langle \sin^2\gamma \rangle$ are as follows [10]:

$$f(\gamma) = 1/2\pi + a_1 \cos(\gamma - \gamma_0) + a_2 \cos 2(\gamma - \gamma_0),$$

$$\langle \sin \gamma \rangle = \int_0^{2\pi} \sin \gamma f(\gamma) d\gamma = \pi a_1 \sin \gamma_0,$$

$$\langle \sin^2 \gamma \rangle = \int_0^{2\pi} \sin^2 \gamma f(\gamma) d\gamma = 1/2(1 - \pi a_2 \cos 2\gamma_0) \quad (6.7)$$

In this material both C = O profiles rotate in the same direction as the phenyl profile for each smectic phase, but their angles are lower than the phenyl profile. It is found by comparison with the optical tilt measurements that the phenyl stretching transition dipole moment nearly coincides with the molecular long axis [3]. For this reason an asymmetry of the C = O absorbance profiles with respect to the phenyl profile clearly shows that the rotation of the C = O group round the long molecular axis is biased.

In the formula (6.7) γ_0 is the angle of biasing, and a_1 , a_2 are the biasing factors.

In this investigation, values of A_Z , A_Y and A_{YZ} for each stretching band are calculated from equations (6.5) using $A_{\max}$, $A_{\min}$ and $\Omega_{\max}$ belonging to their related absorbance profiles at the applied voltage which the helix is completely unwound for each smectic phase. The constant k in sets of equations (6.6) for both phenyl (C - C) and (C = O) stretching bands is obtained from the absorbance components in SmA* phase using equations (6.6). If we assume that molecules have free rotation around their long axis in SmA* phase, then transition dipole is distributed around the long molecular axis in a uniform manner [3,10]. In this case the values of $\langle \sin \gamma \rangle = 0$ and $\langle \sin^2 \gamma \rangle = 0.5$ can be expected. In order to obtain the biasing parameters of the (C = O) stretching bands for each phase, we have taken the polar angle of the transition dipole moment of the phenyl ring to be zero ($\beta \equiv 0$).

The averages $\langle \cos^2\theta \rangle$ and $\langle \sin\theta \cos\theta \rangle$ can be found by using bands for which the transition dipole moments are well defined in the molecular system of coordinates. We have calculated these averages for the phenyl ring (C - C) stretching band using equations (6.6). We note that θ describes the orientation of the molecular long axis (z axis) relative to the director in the laboratory frame, thus the averages $\langle \cos^2\theta \rangle$ and $\langle \sin\theta \cos\theta \rangle$ provide information about the distributions of the molecular long axes with respect to the director [2,10].

The polar angle β of the (C = O) group transition dipole moments with respect to the phenyl ring has been reported $\sim 60^\circ$ in accordance with X-ray analysis and molecular orbital calculations [25, 26]. Hence, for these calculations $\beta \cong 60^\circ$ was taken as an initial value. For (C = O) core and chiral stretching bands the best values found for β from the fitted profiles are 68.7° and 59.4° respectively. These values are kept constant for the three smectic phases.

By having the values of k , $\langle \cos^2\theta \rangle$ and $\langle \sin\theta \cos\theta \rangle$, we use equations (6.6) to obtain $\langle \sin^2\gamma \rangle$ and $\langle \sin\gamma \rangle$ for the core and the chiral groups. In equations (6.7) one can see that for $a_2 = 0$ the value of $\langle \sin^2\gamma \rangle = 0.5$ can be obtained. As for smectic phases this is not a case, a_2 and a_1 are altered from zero to a desired value to fit a set of equations (6.7). Thus γ_0 is also found.

The results of the calculations are given in table 6.3 in terms of biasing factors a_1 and a_2 , biasing angle γ_0 and the averages $\langle \sin\gamma \rangle$ and $\langle \sin^2\gamma \rangle$. Note that, the unique solution for γ_0 , a_1 and a_2 can not be obtained.

phase	band	$\langle \sin^2 \gamma \rangle$	$\langle \sin \gamma \rangle$	$ \gamma_0 $	a_1	a_2
SmC _A *	1743cm ⁻¹	0.495	0.120	38.6°	0.045	0.021
	1719cm ⁻¹	0.486	0.108	44.3°	0.055	0.031
SmC _γ *	1743cm ⁻¹	0.504	0.108	41°	0.046	0.027
	1719cm ⁻¹	0.494	0.105	47.7°	0.051	0.049
SmC*	1743cm ⁻¹	0.504	0.125	40.7°	0.060	0.031
	1719cm ⁻¹	0.479	0.109	49°	0.065	0.019
SmA*		0.50	0			

Table 6.3. Biasing parameters for (C = O) core and chiral groups for the three smectic phases.

In Table 6.3 any new value for the biasing angle (γ_0) depends on the values of a_1 and a_2 . Nevertheless, due to the biased rotation, the C = O groups spend more time around $\pm \gamma_0$ and $\pm (\gamma_0+180)$ depending on the polarity of the applied voltage. It is noted that, the difference in the biasing angles can correspond to the torsional angles between the components of the core [2]. However, the overall distribution for all molecules is generally a linear combination of $[f(\gamma) + f(-\gamma)]/2$ and $[f(\pi + \gamma) + f(\pi - \gamma)]/2$. For the positive polarisation the first term is predominant while for the negative polarisation the second term is [2,10]. From the results of the calculation one can notice that, (C = O) chiral

group rotates with a larger biasing angle than (C = O) core group for each phase. They also indicate that, the spontaneous polarisation for each smectic phase is different.

6.4. Summary

Polarised IR spectroscopy is found to be a useful technique for analysing the molecular behaviour in smectic phases of antiferroelectric liquid crystals. It is found that, due to surface interactions the helix for each smectic phase was already disturbed before the application of the electric field to the cell. At the saturated voltages, the dichroic ratio (D_r) of the phenyl band (C – C) stretching vibrations is almost the same for the three smectic phases. The transition from ferri to ferroelectric phase is also clear from the helix unwinding in SmC_γ^* phase by exhibiting devil's staircase. We have supported these results with the induced polarisation measurements using electro-optic facilities. A similarity of the apparent tilt angle ($\Delta\Omega_{\text{max}}$) and D_r voltage dependencies for phenyl group for SmC_A^* phase is also another interesting point. The absorbance profiles influenced by the applied voltage show that, the biased rotation exists for the three smectic phases. The shape of these profiles depends on the degree of biasing and on the polar angle of the transition dipole moment with respect to the long axis of the molecule. The rotation of the profiles are also found to be unidirectional for all the stretching bands in each smectic phase as the polarity of the applied voltage is altered. From the variation of the biasing angle (γ_0) for both the (C = O) core and chiral groups for each smectic phase it is clear that, the application of the electric field not only unwinds the helix but influences the extent of the biasing at saturated voltages. Despite a lower value of $\Delta\Omega_{\text{max}}$ for chiral carbonyl group, the biasing angle (γ_0) for each smectic phase shows a larger value for the chiral part

rather than for the carbonyl part. Therefore, the rotation of the chiral carbonyl group for each smectic phase is more biased than the core carbonyl group with respect to the long molecular axis. Our results show that, the possible orientation of the dipoles belonging to the (C = O) groups is not exactly in the direction of the polar symmetry axis (C_2). However, due to the molecular head and tail equivalence, the spontaneous polarisation appears along the two-fold axis for each phase. The biasing parameters and the biasing angles of the rotation for both (C = O) core and chiral groups for SmC_A^* , SmC_γ^* and SmC^* phases are found and the results are presented. The behaviour of the molecular tail containing CH₂ and CH₃ groups show the similar pattern as the phenyl group for the three smectic phases. This is found to be due to the restriction in volume of the smectic layers for the tilted smectic phases which, the tail displays almost similar orientation to the molecular core.

6.5. References

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Chapter 7

Conclusions and Recommendations for future work

7.1. Conclusions

The orientational behaviour of a ferroelectric liquid crystal mixture and an antiferroelectric liquid crystal material in various smectic phases for several molecular groups have been investigated under the external electric field using polarised FTIR spectroscopy. The electric field dependencies of the dichroic ratio and the apparent tilt angle for the stretching bands of the phenyl group and the C = O core group in chapter 5 and phenyl, C = O core and chiral, CH₂ and CH₃ groups for the various smectic phases in chapter 6 are investigated. In chapter 6, from the quantitative analysis, the extent of the biasing angle of rotation of the C = O groups around the long molecular axis for the smectic phases are found and the values are given. Using the polarised infrared beam and the application of electric field with different polarity to the cell, the absorbance profiles show the unidirectional rotation with the polarity of the field for the molecular segments. For the antiferroelectric material the biased rotation of the C = O groups around the long molecular axis exist for the three smectic phases.

It was also found that the surface interactions of the cell and the hysteresis effect are the reasons for the initial orientation of the molecules. The results show that, the helical structures in the cells under investigation were already disturbed before the application of the electric field to the cells. This was due to the surface

interactions where the pitch of the helical structure is comparable with the thickness of the cells and also due to the possible existence of the hysteresis. Values obtained for dichroic ratio under the applied electric field show that the orientation of the molecules depends on the degree to which the helix is disturbed by this field. At saturated voltages, when the helix is completely unwound, it was found that the molecular orientation is uniform and symmetrical with respect to the zero volt position. From the variation of the biasing angle (γ_0) for the C = O groups for the three smectic phases it is found that, the application of the electric field not only unwinds the helix but has an effect on the extent of the biasing at saturated voltages.

It is noted that, the polarising microscopy can give information about the average characteristics (molecular long-range order) of liquid crystals, whereas FTIR spectroscopy can provide us with a quantitative information about the various parts of the molecule and the short-range order.

For the antiferroelectric material used in this study, it was found that the changes in the apparent tilt angle with the application of the electric field imply that, the field induced phase transition occurs from helicoidal SmC* or SmC $_{\gamma}$ * or SmC $_A$ * to an unwound and uniform SmC* phase. As a result of this unwinding the absorbance is brought to approximately the same value as in SmA* phase. It is also found that, peaks related to CH₂, CH₃ and C = O groups rotate by a lower angle than the phenyl peak and finally the absorbance profiles are not entirely symmetric with respect to the apparent tilt angle of the phenyl peak. It is important to note that such behaviour of the absorbance profiles clearly suggests the biased rotation of the molecules around the long molecular axis. For the three

phases for the C = O groups the biasing parameters and the biasing angles are calculated for the antiferroelectric material used in this investigation and the results are discussed. The exact methodology for the calculation used is clearly explained. The results of the biasing for SmC_A*, SmC_γ* and SmC* phases in chapter 6 are also compared. From this comparison it is found that, the biasing angle (γ_0) and the biasing parameters for the C = O chiral group is larger than for the C = O core group whereas, the apparent tilt angle for the C = O chiral group is smaller than for the C = O core group in each smectic phase. This can confirm the more intensive biasing for the chiral group with respect to the long molecular axis. In chapter 6 it is confirmed that the intermolecular interaction is different for different smectic phases as the frequency and the shape of the vibrational bands change differently by the applied field in each phase. The results show that the permanent dipoles near the chiral centre have different biased rotation in each smectic phase. This leads to a variation of ferroelectricity and antiferroelectricity and also an existence of the spontaneous polarisation in each phase. As mentioned, the orientation of the dipoles related to the C = O groups do not completely coincide with the direction of the polar symmetry axis (C₂). For all that, because of the molecular head and tail equivalence, the emergence of the spontaneous polarisation occurs along the two-fold axis for each phase.

Many measurement techniques such as microscopic, conoscopy, apparent tilt angle and X-ray diffraction have been employed to investigate and determine the structure of ferroelectric phases. However, all of these techniques are indirect and their results sometimes contradict each other as they support various structural models. Therefore, up to now the question of the exact molecular structure of

liquid crystals with ferrielectric phases is still open. In this research infrared spectroscopy has been employed to study the structural behaviour of the molecular segments of a ferrielectric phase and its transformation to a ferroelectric phase and results are interpreted and discussed.

7.2. Recommendations for future work

Due to the surface interactions of the liquid crystal cells used in this research, the helical structure in the cells were disturbed before the application of the electric field to the cell. For future investigations this problem can be remedied by constructing cells with thickness $> 6\mu\text{m}$, i.e. ~ 7 or $8\mu\text{m}$ or using liquid crystal materials with their helix being of a smaller pitch. CaF_2 windows used for the cell construction were not capable of showing the frequencies of absorbance below 1000 cm^{-1} (wave numbers). Therefore, It was not possible to investigate the perpendicular vibrations of the phenyl ring ($\text{C} - \text{C}$) around 760 cm^{-1} which is vital for the calculation of biased rotation of the molecule as a whole. Using windows such as ZnSe for the cell makes it possible to obtain this vibrational frequency. In order to use the Oxford Temperature Controller more efficiently, its RS232 port should be connected to a PC and controlled with special software. This would be a great assistance to study the structural behaviour of the molecular groups and the biasing parameters of subphases such as SmC_{α}^* , FiLC_1 , FiLC_2 and AF in antiferroelectric liquid crystals by optimum control of these phases temperature. It would also be interesting to use the power of infrared

spectroscopy in order to perform precise investigation of a new elector-optic effect so called V-Shape switching. This effect is very useful for the new type of liquid crystal displays. It is noted that, physics and the structure of this effect is still under discussions.

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Appendix

In this section, the derivation of the formula (1),

$$A(\Omega) = -\log(10^{-A_{\max}} + (10^{-A_{\min}} - 10^{-A_{\max}}) \sin^2(\Omega - \Omega_{\max})) \quad (1)$$

used in chapter 5 and chapter 6 of this thesis is shown. As described before in equation (1), $A(\Omega)$ is the absorbance as a function of the angle of polarisation, $A_{\max}$ and $A_{\min}$ are obtained when the electric vector of the polarised infrared beam is parallel and perpendicular to the transition dipole moment respectively, Ω is the angle of polarisation and $\Omega_{\max}$ is the angle at which $A_{\max}$ is obtained. In SmA* phase $\Omega_{\max}$ is normally zero.

The infrared absorption due to a single molecule is proportional to $(\mathbf{E} \cdot \mathbf{p})^2$ where $\mathbf{E}$ is the local electric field and $\mathbf{p} = \partial\mu / \partial q$ is the transition dipole moment of a vibrational mode characterized by the normal coordinate q . It is noted that, the field acting on a particular vibrating mode E^{LOC} is different from $\mathbf{E}$ by a factor called the local-field correction factor [1, 2]. For these calculations the absorption spectrum are considered at IR wavelengths where, especially for certain bands, dichroism in absorbance is significant. For simplicity, the local field anisotropy is assumed to be negligibly small [3, 4]. To describe this procedure, let's consider a diagram shown in Fig. 1.

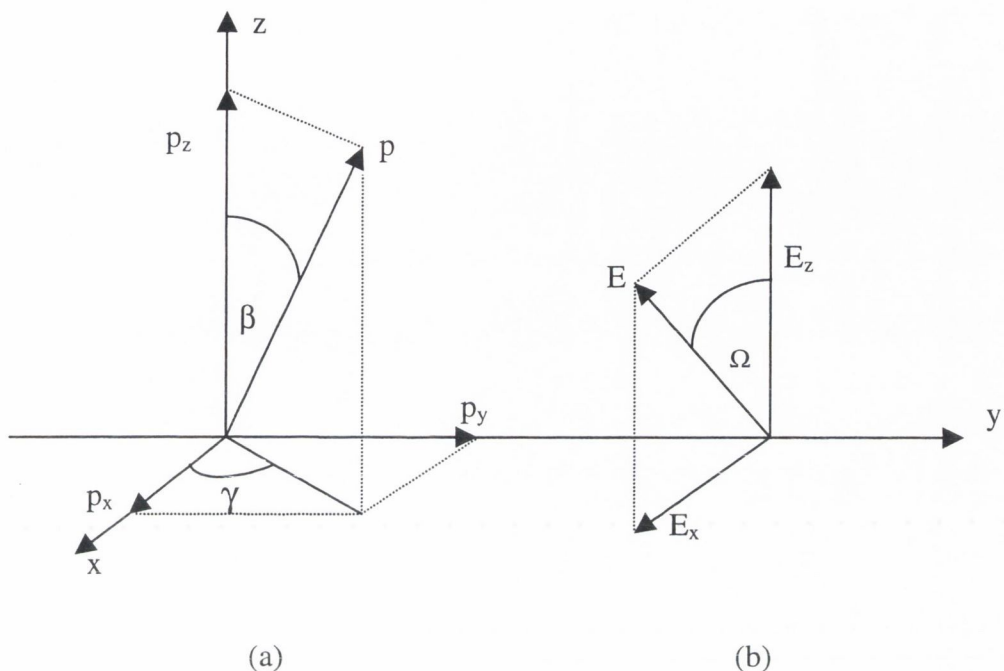


Figure 1. (a) Orientation of the vibrational transition dipole moment p in the laboratory frame with the z axis parallel to the optical axis of the sample, (b) Electric field orientation in the laboratory frame; Ω is the angle of polarization.

The electric field of the incident beam is assumed to lie in the x - z plane as shown in Fig. 1, making an angle Ω with the z direction. z axis is chosen to coincide with the director of the homogeneously aligned sample. At a distance y from the incident plane, the angle α , is determined by the x and z components of the electric field E_x , E_z :

$$\tan \alpha(\Omega, u) = \frac{|E_x(u)|}{|E_z(u)|} \quad (2)$$

where u is a dimensionless variable ($u = y/d$), normalized by the total thickness of the sample d ; u varies between 0 and 1. Due to the IR dichroism, the amplitudes of the two field components are continuously reduced in magnitude while passing through the sample. Following the definition of the absorbance, we have

$$E_x^2(u) = 10^{-uA_{\min}} \cdot E_x^2(0) \quad (3)$$

$$E_z^2(u) = 10^{-uA_{\max}} \cdot E_z^2(0) \quad (4)$$

For this study, relative variations in the phase part of the electric field for the two directions are neglected. It is known that molecular modes of vibrations in liquids and those in liquid crystals are uncorrelated with each other. Hence, variation brought about by the phase will not affect the intensity of the beam. Using equations (2), (3) and (4), we get

$$\begin{aligned} \tan^2 \alpha(\Omega, u) &= \left[\frac{E_x^2(u)}{E_z^2(u)} \right] = 10^{-u(A_{\min} - A_{\max})} \cdot \frac{E_x^2(0)}{E_z^2(0)} \\ &= \tan^2 \Omega \times 10^{-u(A_{\min} - A_{\max})} \end{aligned} \quad (5)$$

If $A_{\min} \neq A_{\max}$, then α is dependent on u , and differs from the incident angle Ω . Next we calculate [5] the absorption due to an arbitrarily oriented

transition dipole $\mathbf{p}$ ($p \sin \beta \cos \gamma$, $p \sin \beta \sin \gamma$, $p \cos \beta$) and normalize it to the total absorption; angles β and γ are defined in Fig. 1 (a).

$$\begin{aligned} \frac{(E(\Omega,u) \cdot p)^2}{(|E(\Omega,u)| \cdot |p|)^2} &= \frac{1}{3} + \frac{2}{3} P_2(\cos \beta) + \\ &+ \left[\frac{1}{2} \sin^2 \beta \cos 2\gamma - P_2(\cos \beta) \right] \sin^2 \alpha(\Omega,u) + \\ &+ \frac{1}{2} \sin 2\beta \cos \gamma \sin 2\alpha(\Omega,u) \end{aligned} \tag{6}$$

where the angle $\alpha(\Omega,u)$ is given by equation (5) and $P_2(\cos \beta) = 3/2 \cos^2 \beta - 1/2$ is the second-order Legendre polynomial.

In order to obtain the absorption coefficient of a thin layer situated at a distance u from the incident plane, we multiply the absorption of a single dipole by its distribution function $F(\beta,\gamma)$, given for the case of the symmetry of the SmC* phase [6]:

$$\begin{aligned} F(\beta,\gamma) &= \frac{1}{4\pi} [1 + 3A \sin \beta \sin \gamma + 5BP_2(\cos \beta) \\ &+ \frac{15}{4} C \sin 2\beta \cos \gamma + \frac{15}{4} D \sin^2 \beta \cos 2\gamma] + \dots \end{aligned} \tag{7}$$

and integrate over all values of the angles β and γ . The coefficient A measures the polar order. B is the second order parameter, $\langle P_2 \rangle$, often simply called P_2 and this

pertains to the order relative to the z axis. C and D are the parameters connected with the quadrupolar order. The absorption of the layer $\Delta A(\Omega, u)$ relative to the absorption of the disordered or isotropic sample is then given by

$$\frac{\Delta A(\Omega, u)}{A_{iso}} = \left[1 + 2B + \left(\frac{3}{2}D - 3B \right) \sin^2 \alpha(\Omega, u) + \frac{3}{2}C \sin 2\alpha(\Omega, u) \right] \Delta u \quad (8)$$

On using the trigonometric identities,

$$\sin^2 \alpha = \frac{\tan^2 \alpha}{1 + \tan^2 \alpha}, \quad \sin 2\alpha = \frac{2 \tan \alpha}{1 + \tan^2 \alpha}$$

and equation (5), the angle α in equation (8) can be expressed in terms of Ω . On integrating over the limits 0 to 1 for u , the total absorption of the sample is calculated to be as follows:

$$\begin{aligned} \frac{A(\Omega)}{A_{iso}} = & 1 + 2B + \frac{\left(\frac{3}{2}D - 3B \right)}{(A_{max} - A_{min}) \ln 10} \times \log \left[\frac{1 + \tan^2 \Omega \times 10^{(A_{max} - A_{min})}}{1 + \tan^2 \Omega} \right] + \\ & + \frac{6C}{(A_{max} - A_{min}) \log 10} \times \left[\tan^{-1}(\tan \Omega) \times 10^{0.5(A_{max} - A_{min})} - \tan^{-1}(\tan \Omega) \right] \end{aligned} \quad (9)$$

Equation (9) is a general formula depicting the absorption suffered by an incident IR beam polarized at an angle Ω , in passing through an anisotropic medium. For $\Omega=0$, equation (9) reduces to

$$\frac{A_{\max}}{A_{iso}} = 1 + 2B \quad (10)$$

and for $\Omega = 90^\circ$, equation (8) becomes

$$\frac{A_{\min}}{A_{iso}} = 1 - B + \frac{3}{2}D \quad (11)$$

Equations (10) and (11) are the same as those derived previously by Zgonik *et al.* [6]. Equation (9) predicts an altered dependence of the absorbance caused by the anisotropy in the absorbance (dichroism).

The order parameter B (or $\langle P_2 \rangle$) can be calculated from the measured values of $A_{\max}$ and $A_{\min}$. On knowing B , D can be calculated from $A_{\min}$ and A_{iso} . For $D = 0$, $\langle P_2 \rangle$ can be calculated from $A_{\max}$ and $A_{\min}$ for the liquid crystal phase.

Liquid crystals in their smectic and nematic phases can be regarded as approximately uniaxial: for these cases the coefficients $C = D = 0$. For a uniaxial LC, equation (9) reduces to

$$\frac{A(\Omega)}{A_{iso}} = 1 + B \left(2 - \frac{3}{A_{\max} - A_{\min}} \cdot \log \left[\frac{1 + \tan^2 \Omega \cdot 10^{(A_{\max} - A_{\min})}}{1 + \tan^2 \Omega} \right] \right) \quad (12)$$

The expression for the orientational order parameter (B) and the absorbance in isotropic phase (A_{iso}) are given as follows:

$$B = \frac{A_{\max} - A_{\min}}{A_{\max} + 2A_{\min}}, \quad A_{iso} = \frac{A_{\max} + 2A_{\min}}{3}$$

Substituting for A_{iso} and B in equation (12), we obtain

$$\begin{aligned} A(\Omega) &= \frac{A_{\max} + 2A_{\min}}{3} \left(1 + \frac{A_{\max} - A_{\min}}{A_{\max} + 2A_{\min}} \left\{ 2 - \frac{3}{A_{\max} - A_{\min}} \times \right. \right. \\ &\quad \left. \left. \log \left[\frac{10^{A_{\max}} (10^{-A_{\max}} + \frac{\sin^2 \Omega}{\cos^2 \Omega} \cdot 10^{-A_{\min}})}{1 + \frac{\sin^2 \Omega}{\cos^2 \Omega}} \right] \right\} \right) \\ &= A_{\max} - \log \left[\frac{\frac{10^{A_{\max}}}{\cos^2 \Omega} (10^{-A_{\max}} \cos^2 \Omega + 10^{-A_{\min}} \sin^2 \Omega)}{\frac{1}{\cos^2 \Omega}} \right] \end{aligned} \quad (13)$$

By simplifying equation (13) one can result the following equation

$$A(\Omega) = -\log(10^{-A_{\max}} \cos^2 \Omega + 10^{-A_{\min}} \sin^2 \Omega) \quad (14)$$

As $\cos^2 \Omega = 1 - \sin^2 \Omega$, the equation (14) becomes

$$A(\Omega) = -\log(10^{-A_{\max}} + (10^{-A_{\min}} - 10^{-A_{\max}}) \sin^2 (\Omega)) \quad (15)$$

Equation (15) is valid for SmA* phase. For tilted smectic phases this equation changes to

$$A(\Omega) = -\log(10^{-A_{\max}} + (10^{-A_{\min}} - 10^{-A_{\max}}) \sin^2(\Omega - \Omega_{\max}))$$

The main reference for this appendix is

A.Kocot, R.Wrzalik and J.K.Vij, *Liquid Crystals*, Vol., 21, No.1, 147-151(1996),

where references 1, 2, 3, 4, 5 and 6 are included.