Fourier transform infrared ATR and transmission study of the response of liquid crystalline 5CB to electric excitation

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Abstract. Attenuated total reflection and transmission results on the electric perturbation of liquid crystalline 5CB between orienting walls are compared. In the interface between a wall and the bulk a depth dependent average orientation of the director is observed in the presence of ac fields. In this transition region the dynamic behaviour of the liquid crystal shows a faster and qualitatively different response from the bulk. Near the orienting wall the effect of the field perpendicular to the wall depends on the field direction as indicated by the observation of a large response component at the ac frequency.

1. Introduction

Modern FTIR is a versatile technique offering a broad range of exciting and fruitful applications. Now that step-scan is a routine scanning method, the time evolution of numerous processes can be followed on a molecular scale. Individual functional groups can be monitored and their time dependent behaviour can be studied. Increasing the experimental effort from routine to high level, the time scale may be diminished from the millisecond and the microsecond to the nanosecond range.

In addition to the usual transmission techniques, attenuated total reflection (ATR) offers the possibility of depth profiling. The present report addresses comparison of the response of liquid crystalline 5CB to electric fields as observed with transmission and ATR.

The IR-observed response of liquid crystals to the application of electric fields has been discussed in a number of papers, a selection of which is cited in the references. In frequency domain work, the amplitude and phase of the response to a monochromatic ac excitation is studied [1, 3, 7]. In time domain studies the time-resolved response of a sample to an excitation in the form of a pulse or a burst is obtained [2–6]. Because IR is a technique that probes functional groups in molecules, considerable attention has been directed at the question of whether a phase lag between the rigid 'head' and the flexible 'tail' of 5CB was indicated by the results in the frequency domain and the time domain.

In a recent frequency domain study [7] no intramolecular phase differences were found. Also, it was observed that the major response of nematic liquid crystalline 5CB to an ac excitation at frequency ν occurs at twice the excitation frequency, i.e. 2ν. This is typical for a material in which the dynamic unit that couples to the field has no permanent dipole. Coupling of the ac field to the induced moment then leads to oscillations at 2ν. The molecules in 5CB possess a large permanent dipole moment. The dynamic

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unit observed with IR in the millisecond range is, therefore, not the single molecule. A consistent interpretation could be developed in terms of a locally defined director and a local polarizability, which is an averaged property, i.e. averaged over molecular motions fast with respect to the millisecond time scale of the experiment. This is in accordance with the absence of intramolecular phase differences in the experimental observations. A maximum in the response divided by the square of the field amplitude is expected from this model if the response is obtained as a function of the field amplitude. In a subsequent study the occurrence of the maximum at the expected average orientation of the director was found [8]. Also, the time-resolved trace of the CN absorption of 5CB was obtained while the sample was submitted to an ac excitation. In this way the response at 2ν could be directly shown. In a subsequent study [9] the decrease of the oscillation amplitude of the director with increasing excitation frequency, as observed from the time-resolved response, was explained qualitatively. Comparison of the time-resolved responses of the head and the tail of 5CB confirmed the absence of intramolecular phase differences in the millisecond time domain. NMR [10] work on 5CB, slowed down by the presence of 5.4 wt% of a block copolymer, indicates that the same conclusion is valid in this composite system.

In the present report the following features of the response of liquid crystalline 5CB to electric excitation are discussed.

First it is demonstrated that the experimental ATR setup easily discriminates between isotropic (liquid mesitylene) and anisotropic (5CB) systems.

Next it is shown that the average director orientation in the presence of an electric field depends on the distance to the orienting wall. This is seen by comparing the response of IR–ATR signals from absorptions at different wavelengths.

Then the observation, in transmission, of two relaxation regimes in the response of 5CB to bursts of sufficient amplitude is studied. This phenomenon was taken to indicate that 5CB molecules close to the orienting wall relax significantly faster than in the bulk of the sample [11]. Results of ellipsometric experiments in the visible region [12] and theoretical modelling [13] are in accordance with this picture. Presently, comparison of transmission and ATR observation of the time-resolved response of the same IR absorption shows that the relaxation in an interface layer of at least half a micron is much faster than in the bulk.

Finally the time-resolved oscillations of liquid crystalline 5CB are investigated with the transmission and ATR techniques. It is found that the dynamic behaviour of 5CB in the interface is the source of the observation of the response at the excitation frequency that is often observed in transmission experiments in addition to the main response at twice this frequency. The origin of this single frequency response which is best observed with a low frequency excitation plus a dc offset [9] has not been discussed before as far as we know, even though, but for one exception, all 2D–IR work has been done with this component of the response (see the discussion in [7]).

2. Experiment

Commercially available 5CB, 4-pentyl-4′-cyanobiphenyl (Merck), was used.

In the transmission experiments the sample was placed between Ge windows coated with poly-vinylalcohol (PVA) that was gently rubbed with cloth to obtain orienting surfaces. The Ge windows also served as electrodes for the application of electric fields. A path length of 8 microns was used.

In the ATR experiments, a Ge hemisphere was used as internal reflection element and electrode; the other electrode was the Cu film of a print plate. Again both electrodes were

coated with PVA and rubbed with cloth. The ATR cell was Harrick's 'Seagull', equipped with a Ge hemispherical internal reflection element which allows convenient setting of the angle of incidence of the IR beam.

In step-scanning, the optical path difference is not changed continuously in time but stepwise; i.e. each path difference used is maintained for a time interval Δt, which may be chosen. During this interval the basic time dependence of the signal, necessary to drive the detector efficiently, is induced by oscillation of the static mirror (phase modulation). A second type of time dependence is created by manipulation of the sample: this is the experiment. The experiment is cyclical and it is duplicated at every optical retardation. This time dependence is registered by storage of the demodulated signal in a number of consecutive channels. The signals in the channels with the same 'number' but at different optical retardations form the interferogram for this instant of the experiment.

A Bio-Rad FTS60A spectrometer with MCT detector was used in step-scan mode. Phase modulation was at 16 kHz; Win-IR Pro software from Bio-Rad does not permit phase modulation in step-scan and step-scan–TRS modes but the 16 kHz fixed mirror dither is always present in step-scan modes. A wire-grid polarizer was positioned between the source and the sample. The phase-modulated IR signals were demodulated with a SR830 lock-in amplifier from Stanford Research Systems. The electric field applied to the sample was obtained from an HM8130 signal generator from HAMEG. At each optical retardation an excitation and relaxation of the sample was executed while collecting the detector signal at (usually) 2 ms intervals. Standard software was used to obtain the interferograms from this data set.

3. Results and discussion

The absorption spectra of liquid crystalline 5CB for two polarization directions, parallel and perpendicular with respect to the rubbing direction of the coating, are shown in figure 1. Assignments of IR bands are collected in table 1. The dichroism of the IR bands associated with the rigid part of 5CB (i.e. CN-stretch, phenyl CC stretch etc) is very much larger than the dichroism of bands associated with the flexible pentyl moiety. This is due to the bond angles in the pentyl chain and the small dichroic effect indicates that in the ordered nematic state a number of conformations are accessible for this chain.

Table 1. Assignment of IR bands of 5CB ([1, 3, 4]).

| Assignment	Wavenumber
Phenyl CH stretch	3026
Pentyl CH_3 asym. stretch	2956
Pentyl CH_2 asym. stretch	2929
Pentyl CH_3 sym. stretch	2870
Pentyl CH_2 sym. stretch	2857
CN stretch	2226
Phenyl CC stretch	1606
Phenyl CC stretch	1494
Pentyl CH deformation	1460
Pentyl CH deformation	1397
Pentyl CH deformation	1378
Biphenyl CC	1285
Phenyl CH in plane deformation	1006
Phenyl CH wag	833
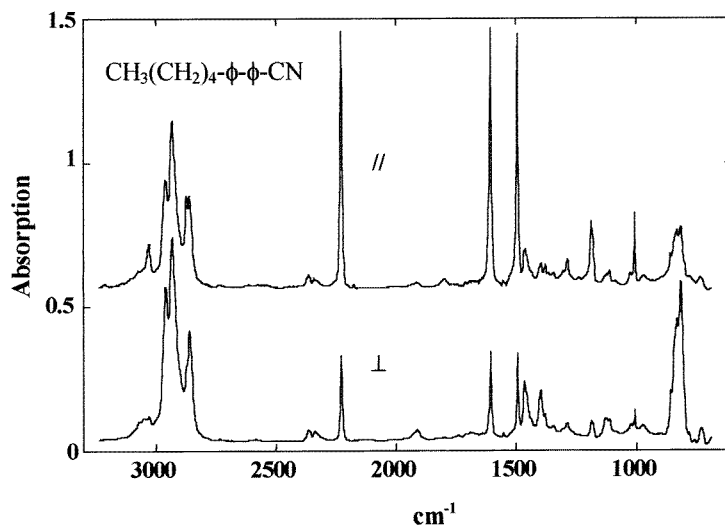
Figure 1. Absorption spectra of 5CB. Polarization parallel (upper) and perpendicular (lower) to the rubbing direction of the window coating.

Figures 2 and 3 show the different behaviours of the TE and TM modes in isotropic and anisotropic systems. In an isotropic liquid such as mesitylene the ATR signals obtained for the two modes exhibit the same dependence on the estimated effective thickness in clear contrast with the results for 5CB. In the 5CB experiment, the electric vector for the TE mode is parallel to the rubbing direction of the coating of the electrodes which is also the direction of the director of the liquid crystal and of the transition moments of the IR bands used in figure 3. Both bands are associated with the rigid 'head' of 5CB. With the TM mode two directions are probed, both perpendicular to TE and, in the present setup, the director: one direction is parallel to the surface of the Ge internal reflection element (IRE) and the other is perpendicular to this surface. At equal effective thickness the ATR signal from the TM mode is therefore expected to be smaller than the TE signal, in accordance with the observation. The effective thickness values were estimated with the equation discussed by Harrick [14] which is probably a reasonable approximation for weak absorption bands (absorption coefficient $<10^4$ cm^{-1}).

Figures 4 and 5 compare the ATR and transmission responses of liquid crystalline 5CB to applied ac voltages of increasing amplitude. In the ATR experiment the TE mode was observed, so only a single polarization direction was involved that was parallel to the rubbing direction. The IR beam polarization was also parallel to the rubbing direction in the transmission experiment. The experiments were free running, i.e. while each ac voltage was applied a sufficient number of normal scans were collected to obtain the average response over several periods of the voltage. In a previous investigation it was found [9] that the amplitude of the director oscillations around its average orientation are very small for 100 Hz ac anyway. In the transmission experiment the total sample thickness of about 8 microns contributes to the absorption and it is seen that the relative change of the absorption due to the orientation of the director in the electric field is insensitive to the wavelength of the IR band observed. In the ATR experiment the effective sample thickness varies from an estimated 0.45 microns for the band at 2226 cm^{-1} to 0.95 microns for the band at 1006 cm^{-1}. The dependence of the ATR response from the wavenumber of the IR band
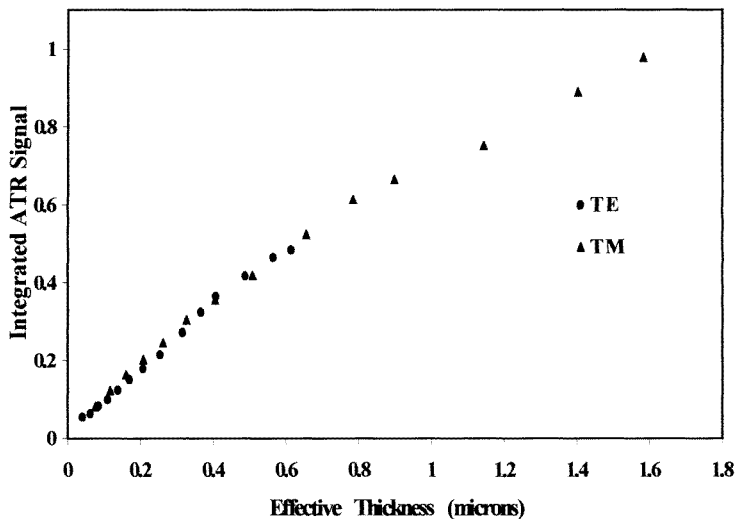
Figure 2. ATR. TE and TM modes of the 1607 cm^{-1} band of mesitylene. ATR signal is $-\log(R/R^0)$, where R^0 is the internal reflection spectrum of the empty cell. For this isotropic liquid the two modes show the same dependence of the effective thickness.
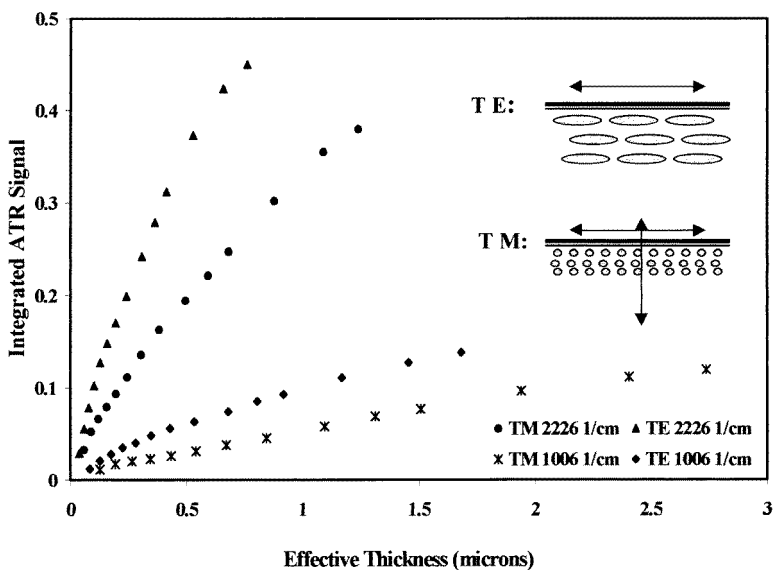

Figure 3. ATR of homogeneous planar 5CB. The rubbing direction is perpendicular to the plane of incidence. The angle of incidence was varied from 29 to 80°. The anisotropy of the sample shows up clearly in the different dependences of the TE and TM modes on the estimated effective thickness.

shows that a region of the sample is probed where the director orientation changes in the presence of an electric field with increasing distance from the orienting wall. Close to the wall the effect of the electric field is small but deeper into the sample the director follows the field. Thus with ATR it is possible to probe the behaviour of the liquid crystal within
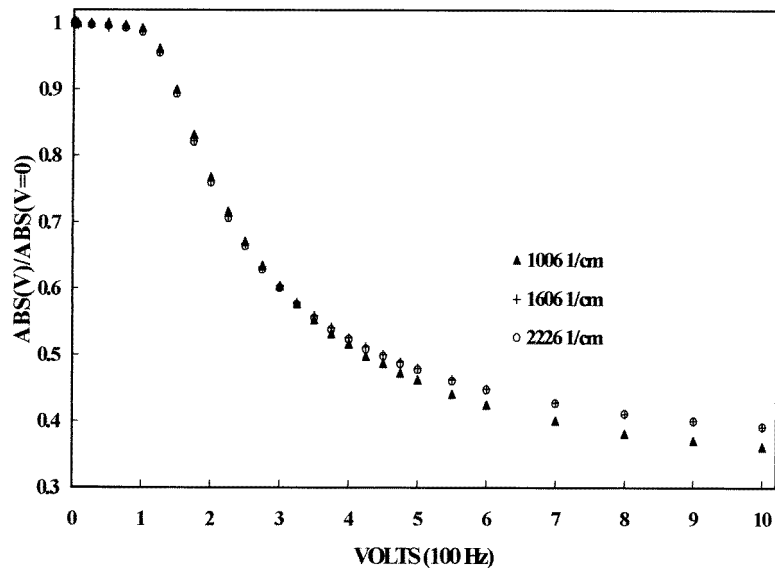
Figure 4. Transmission experiment. Normalized absorption against voltage for different IR bands of liquid crystalline 5CB. IR beam polarization was parallel to the rubbing direction of the window coating.
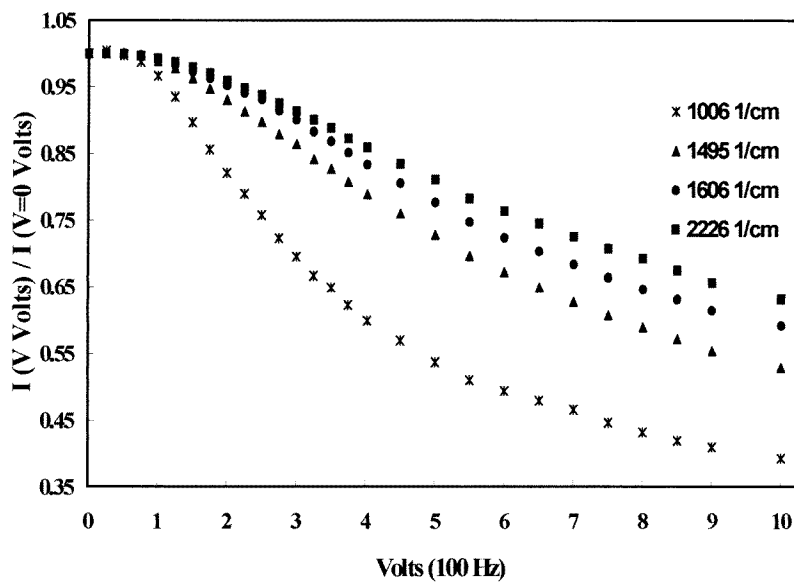

Figure 5. ATR experiment. Normalized ATR signal against voltage of different IR bands of liquid crystalline 5CB. IR beam polarization was parallel to rubbing direction and perpendicular to the plane of incidence. The angle of incidence was 30°. Sampling depth increases with IR wavelength in ATR.

a coherence length from the wall [15].

Next, it is of course of interest to examine the dynamic behaviour of the director near the wall. To this end figures 6 and 7 compare the response of the liquid crystal to a 30 ms

ac burst of 10 V amplitude at 1 kHz. In accordance with previous work [11] two decay regimes are observed after a steep initial build-up of the response. The first, fast, decay has been interpreted as the relaxation of molecules close to the orienting wall [11]. Recently this was confirmed by ellipsometric experiments in the visible region [12] and the response curve could be reproduced theoretically using Frank's elastic continuum model for liquid crystals [13]. The fast relaxing layer was estimated with this theory to be 80 nm thick. Figure 7 shows that for an estimated effective thickness of 0.4–0.7 microns the director relaxation is very fast. This is directly observed from the CN-stretch mode located in the rigid part of the 5CB molecules. More extensive ATR experiments should show how far from the orienting wall the fast decay changes into the slow decay found in the long time tail of the transmission experiments.
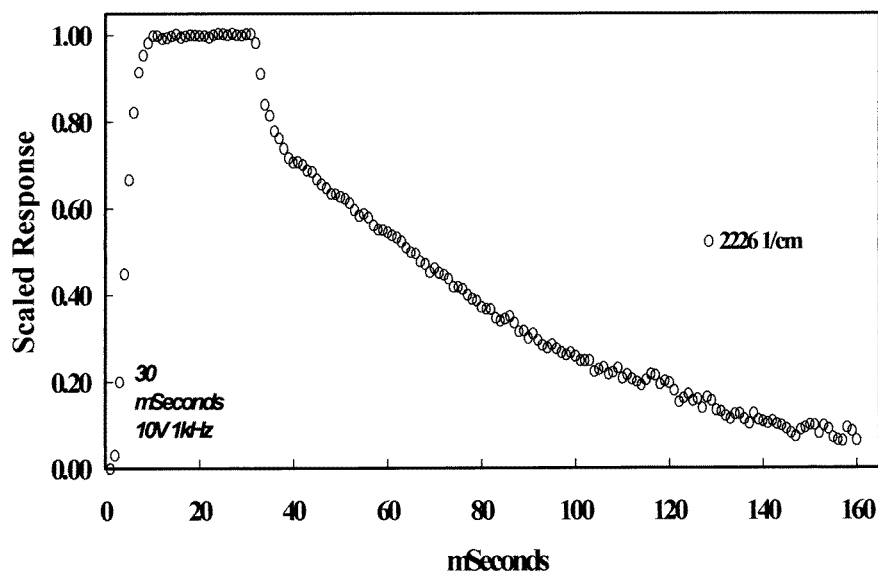

Figure 6. Transmission experiment. Response of liquid crystalline 5CB to an ac voltage burst of 10 V amplitude at 1 kHz during 30 ms. The polarization of the IR beam was parallel to the rubbing direction. A fast and a slow relaxation regime are obtained.

In figures 8 and 9 the oscillation of the liquid crystal is followed during excitation with a 5 Hz voltage and for different amplitudes. In these experiments the spectrometer was used in the step-scan TRS mode: the excitation is repeated at each stationary value of the optical retardation of the interferometer while the detector signal is stored with a chosen time resolution. In the present experiments, the excitation–observation cycle was: |40 ms:0 volts|960 ms:V volts 5 Hz|. Observation at a time resolution of 2 ms started simultaneously with excitation. In the ATR experiments the voltage was set to zero before the end of the excitation interval to allow the collection of a background spectrum. The transmission experiments yield signals that are typical for a director oscillation at twice the excitation frequency v:

$$\text{Abs} \sim \cos^2[\theta_{av} + \theta_{amp} \sin^2(2\pi vt)] \tag{1}$$

with θ_{av} the average angle of the director and the polarization of the IR beam. The second term in the argument of the cosine represents the time dependent coupling of the ac field with
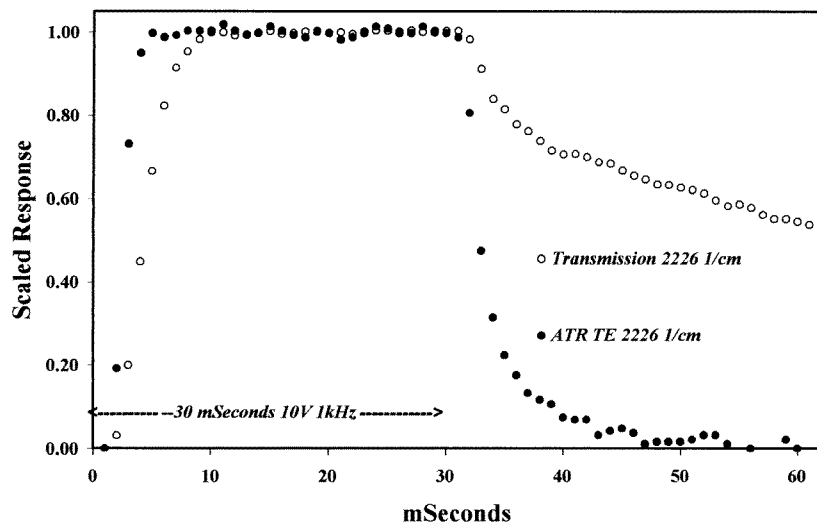
Figure 7. Response of liquid crystalline 5CB to a burst of 10 V at 1 kHz as observed in transmission and with ATR. In both experiments the IR beam polarization was parallel to the rubbing direction of the orienting coating which was also the direction of the TE mode in ATR. The angle of incidence in the ATR setup was 30°. This is equivalent to an estimated effective thickness of 0.43–0.66 microns for the observed CN-stretch absorption at 2226 cm^{-1}, depending on the director orientation.

the induced dipole moment. The amplitude, θ_{amp}, of the director oscillation is proportional to the square of the field strength [7]. The change in the shape of the signal with increasing voltage shows an increase of θ_{av} from somewhat below 45° to values considerably above 45° as evidenced by the flat appearance of the lower excursions of the oscillation at higher voltages. The absence of splitting of the lower excursions shows that even at high voltage $\theta_{av} + \theta_{amp}$ does not exceed 90°: the liquid crystal is highly damped, as may also be directly seen from the absence of free oscillations after cutting off the driving voltage. The nearly symmetric shape of the response curve at very low voltage shows that it derives from regions in the sample where θ_{av} is not too far below 45° i.e. well removed from the orienting walls. A director oscillation at the frequency ν itself would generate a symmetric signal at 2ν for θ_{av} equal to zero, but with increasing θ_{av} the signal would have a large amplitude at the single frequency and a small component at 2ν. As concluded earlier, the main oscillation of the director is at twice the excitation frequency [8]. Still, careful inspection of figure 8 shows the presence of a very small component at the single frequency in the observed response. Its origin will be discussed below.

The ATR version of the time-resolved registration of the liquid crystal oscillation, shown in figure 9, reveals that the dynamic behaviour near the orienting wall is different from the resultant observed in a transmission experiment. At low ac voltage the main response has the same period as the excitation. With increasing voltage the component at 2ν increases and at high voltage the responses of the ATR and transmission experiments are similar. The response at ν derives from the fact that the nematic liquid crystal is not a structureless object with cylindrical symmetry at all time scales; its symmetry is the resultant of averaging over the fast molecular motion of the constituting dipolar 5CB molecules. Close to the wall where its orienting tendency successfully competes with the electric field, the effect of the two half-periods of the ac field are not equivalent: the dipoles are stimulated to rotate to the
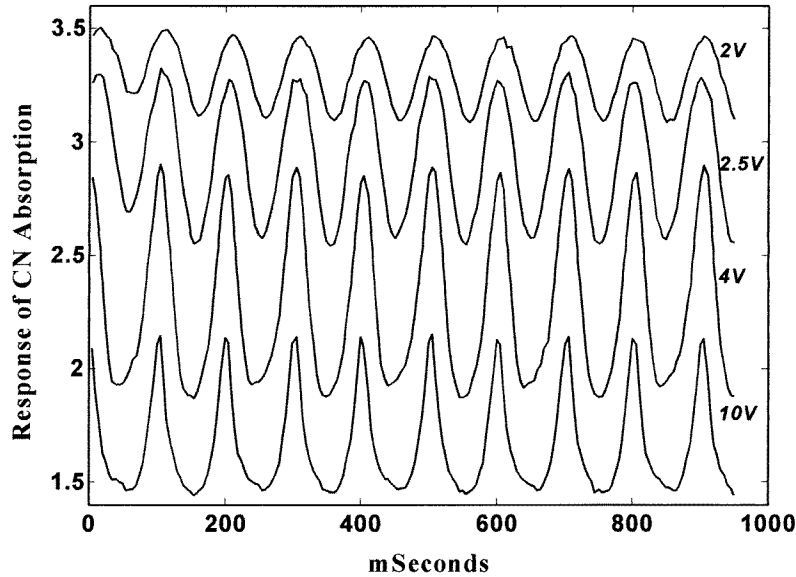
Figure 8. Transmission experiment. Response of liquid crystalline 5CB to different sinusoidal voltage amplitudes at 5 Hz. IR beam polarization was parallel to the rubbing direction of the orienting coating. The shape of the response changes as the average angle of the director and the windows increases.
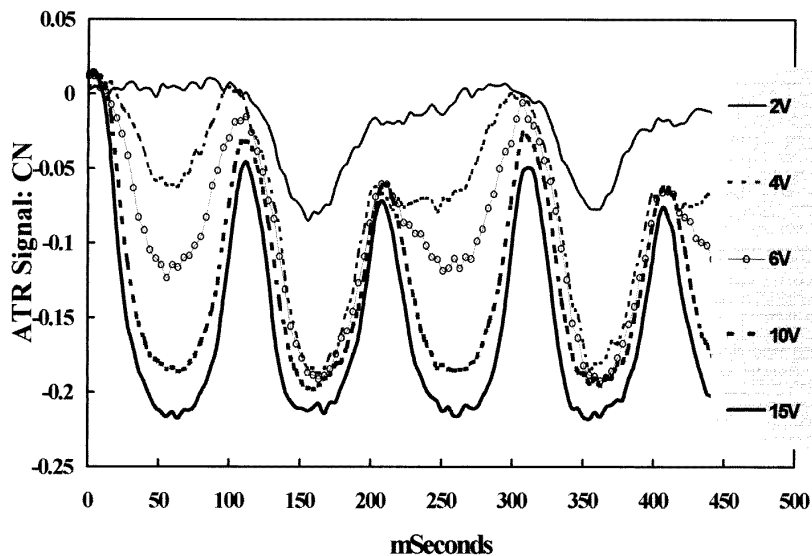

Figure 9. ATR TE mode. Response of liquid crystalline 5CB to different sinusoidal voltage amplitudes at 5 Hz. IR beam polarization was parallel to the rubbing direction of the orienting coating and to the TE mode.

wall or away from it, depending from the field direction in the half-period considered. Thus, for the region within a coherence length from the wall the induced dipole has a different amplitude in two consecutive half-periods of the ac voltage. Coupling the induced dipole

with the field then yields an unequal response of the system for the two half-periods, just as observed in the ATR experiment at low ac voltages. The coherence length is expected to be proportional to the inverse square of the field strength [15] which is consistent with the increasing symmetry of the response in two adjacent half-periods of the ac voltage with increasing amplitude, as observed in figure 9. Now, in a transmission experiment two opposing orienting walls are observed. The effect of the two walls on the induced dipole moment is of course similar but with a phase difference equal to π. Therefore, a departure from a pure 2ν response is expected only if the coherence length for the two walls is different. This may occur easily because of the somewhat artisanal manner of obtaining the orienting layer: rubbing a polymer coating with cloth. For the same reason the results shown in figure 9 depend somewhat on the particular sample: the practically pure signal at 2ν may appear at considerably higher voltage. The relative magnitude of a signal with frequency ν from a transmission experiment may be used as a measure of the equivalence of the two orienting walls involved.

4. Conclusions

ATR offers an inexpensive and fruitful extension of FTIR studies of liquid crystals. Both static and dynamic experiments reveal features of the behaviour of the liquid crystal near the orienting wall that are unobserved with the usual transmission techniques. The dynamic response of 5CB within a coherence length from the orienting coating reflects the broken symmetry in this region, as shown by the occurrence of a mode with a large amplitude at the exciting ac frequency. Depth profiling in the range where the director orientation changes from parallel with the wall into parallel with the field is a distinct possibility.

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