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FT-IR study of liquid crystal molecules on alignment layers

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Alignment control at the molecular level is crucial for realizing high-performance LCDs. In particular, the structure of the interface between the liquid crystal and the alignment layer must be clarified. By utilizing RAS (reflection–absorption spectroscopy), a highly sensitive FT-IR spectroscopic technique, we have obtained the following information about the orientation of liquid crystal molecules; (1) the cyano group in a liquid crystal molecule behaves like an electron donor with respect to an SiO layer, but like an electron acceptor with respect to a polyimide layer; (2) with the use of polarized IR spectroscopy, it was discovered that the liquid crystal 8CB is aligned with a slant away from the aligning direction, regardless of the type of alignment layer. The angle between the molecular short axis within the plane of the core and the surface normal was found to be smaller on polyimide layers than on SiO layers.

1. Introduction

Alignment control at the molecular level is crucial for realizing high-performance liquid crystal display devices. In particular, clarifying the structure of the interface between the liquid crystal and the alignment layer is an important issue. It has been hypothesized that liquid crystal molecules are aligned by rubbed polyimide films because of their surface morphology, characterized by the presence of microgrooves, or the intermolecular interaction between the liquid crystal molecules and the stretched polymers. In the case of obliquely evaporated SiO layers, there is a supposition that molecular alignment is brought about by the oblique column shape of the SiO films, but this mechanism has not been elucidated.

There have been numerous reports about alignment layers or liquid crystals, but reports about the LC-alignment layer interface are sparse [1]. In this report, observations using FT-IR spectroscopy of 4′-octyl-4-cyanobiphenyl (8CB; structure **1** shown in figure 1) on the surface of an SiO layer are described, and the structure of the LC molecules at the interface is discussed.

2. Experimental

2.1. *Liquid crystal materials*

Samples of 8CB (structure **1**) and 5CB (structure **2**) were purchased from E. Merck. 8CB undergoes phase transitions at 21·0°C (crystal–smectic A), 30·2°C (smectic A–nematic), and 37·1°C (nematic–isotropic). 5CB undergoes phase transitions at 23·7°C (crystalline–nematic) and 33·7°C (nematic–isotropic). DSC (differential scanning calorimetry) was used to determine these phase transition temperatures.

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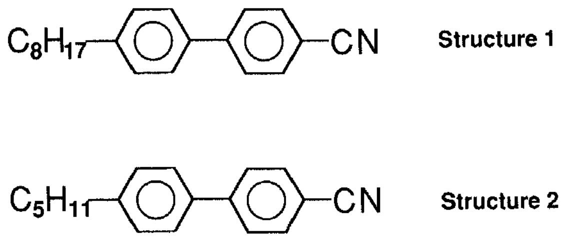


Figure 1. Molecular structures of 8CB and 5CB.

2.2. *The alignment layers*

There are two main kinds of alignment layer for aligning liquid crystal molecules. One is the SiO obliquely evaporated alignment layer in which SiO particulates are evaporated in oblique pillars on to the substrate. Another is the rubbed alignment layer obtained by subjecting substrates coated by a thin polymer film to rubbing with velvet cloth.

SiO obliquely evaporated alignment layers were deposited under a pressure of $1{\cdot}07 \times 10^{-3}$ Pa on to the ITO electrodes. The evaporation angle was 85° relative to the electrode surface normal. The thicknesses of the SiO obliquely evaporated layers were about 60 nm. The SiO layers were annealed at 300°C for 1 hour in order to achieve a stable molecular orientation.

Rubbed alignment layers were fabricated from two kinds of polyimide–U-Wanis A (0·67 wt% conc.) from Ube Industries Ltd. and Sun Ever 721 (3·5 wt% conc.) from Nissan Chemical Industries Ltd. These were spincast at 1000 revolutions per minute for 4 s followed by 3500 revolutions per minute for 30 s. Thicknesses of both films were 60 nm. U-Wanis A films were annealed at 130°C for 20 min and at 220°C for 1 h; Sun Ever 721 films were annealed at 80°C for 15 min and at 240°C for 1 h. Both polyimide films were rubbed five times.

2.3. *Sample structure*

For RAS (reflection–absorption spectroscopy), an FT-IR spectroscopic method, glass substrates with dimensions of $26 \times 35 \times 1{\cdot}1$ mm were used. Thin aluminium films of thickness 200 nm were deposited under pressure of $2{\cdot}0 \times 10^{-3}$ Pa on the substrates. The alignment layers on the aluminium films were about 60 nm thick. The liquid crystal/chloroform solution that had been prepared previously was spincast on the alignment layers by rotation of the substrates at 3000 revolutions per minute for 4 s, followed by 2000 revolutions per minute for 15 s.

FT-IR measurements were made on the smectic A phase of 8CB at room temperature (26°C). This measurement was carried out after the orientation of the liquid crystal molecules had been improved by heating the sample from room temperature to 60°C (isotropic phase) and then gradually cooling down to room temperature. The sample set-up is shown in figure 2.

2.4. *FT-IR measurements*

Infrared spectra were monitored with Perkin–Elmer Corp. FT-IR model 1600 and 1800 specrometers equipped with DTGS detectors. RAS (reflection–absorption spectroscopy) measurements were made at room temperature (26°C). The spectra were obtained after 500 accumulations and the resolution was 2 cm^{-1}. The sample chamber was purged by nitrogen gas prior to measurements.

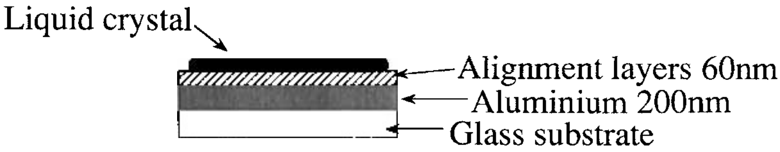


Figure 2. The set-up of the sample.

3. Results and discussion

3.1. *The thickness of thin films of 8CB molecules on SiO obliquely evaporated layers*

In order to obtain information about the interface between the liquid crystals and the alignment layers, we conducted RAS measurements on 8CB films of varying thicknesses. The samples were prepared as follows; 8CB was dissolved in chloroform and the solution was dripped on to the substrate alignment layers on the aluminium films in the largest possible quantities that the surface tension would permit, and then spun. We then estimated the number of liquid crystal layers resulting from each concentration of solution as discussed below.

3.1.1. *Measurements of reference samples*

280 μl samples of 8CB/chloroform solutions of varying concentrations between 0·1 mol l^{-1} and 0·01 mol l^{-1} were dripped on to the glass substrates with dimensions of 26 × 38 mm, and the chloroform was evaporated very slowly. The temperatures of these substrates were initially increased up to 60°C (isotropic phase), and then they were gradually cooled down.

We then estimated the number of 8CB molecules from the volumes of the droplets and the 8CB concentration, and monitored the intensity of the absorbance band by RAS measurement with p-polarization. Thus, we obtained the calibration curve defining the relationship between the standard intensity of the CN stretching vibration band and the number of molecules for use in estimating the numbers or molecules on the substrates with the alignment layers on the aluminium films formed by spin casting.

3.1.2. *Measurement of samples*

The intensity of the CN stretching vibration band was measured by RAS for samples at all concentrations.

3.1.3. *Calculation of number of layers*

The calibration curve defining the relationship between intensity and number of molecules is shown in figure 3. Thus, it is possible to estimate the number of molecules at any concentration.

The 8CB molecule was calculated to have dimensions of 0·5 × 0·7 × 2·3 nm by a molecular orbital method, as shown in figure 4. We deduced the number of layers from the size of the 8CB molecules. If all the molecules stood straight up, the number of layers would be minimized. On the other hand, the maximum number of layers corresponds to all molecules lying parallel to the substrate. The calculated numbers of layers for each concentration is shown in figure 5. The number of layers is actually somewhere between the maximum and the minimum, because the 8CB molecules are expected to tilt.

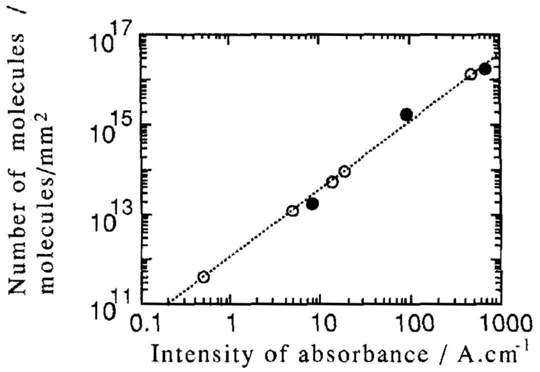


Figure 3. The calibration curve for the relationship between the intensity of the CN stretching vibration band and the number of molecules per unit area.

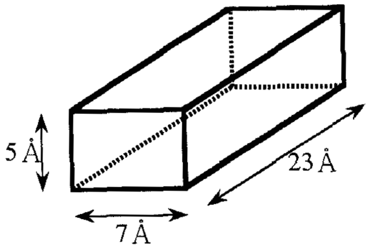


Figure 4. The dimensions of an 8CB molecule.

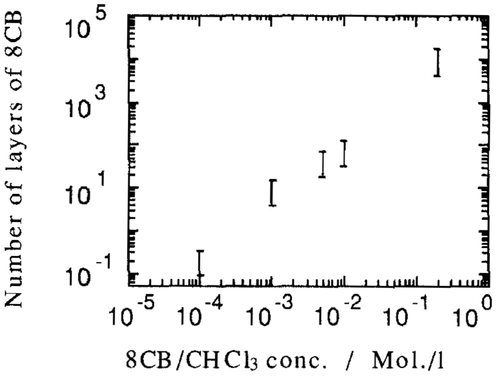


Figure 5. Relation between 8CB/CHCl$_3$ concentration and the number of layers of 8CB.

3.2. *The interaction between liquid crystal molecules and alignment layers at the interface*

3.2.1. *RAS measurements for 8CB on substrates with several kinds of alignment layer*

The RAS measurements were performed with p-polarization in order to clarify the interaction between liquid crystal molecules and alignment layers at the interface and to compare the dependence of the alignment layers on the substrates. Samples of 8CB in the smectic A phase were prepared on aluminium, on two kinds of polyimide alignment layers (U-Wanis A and Sun Ever 721) and on SiO obliquely evaporated layers. Samples of 5CB in the nematic phase were prepared similarly to 8CB on SiO obliquely evaporated layers. Thus, we compared 8CB in the smectic A phase to 5CB in the nematic phase.

A remarkable shift of the CN stretching vibration band was observed in all alignment layers (see figures 6–9). On SiO obliquely evaporated layers, the CN stretching vibration band is at 2227 cm^{-1} for more than 30 layers, and the CN band splits into two, one at 2227 cm^{-1} and the other at 2236 cm^{-1} for 20 layers. For fewer than 5 layers, the CN band shifts to a higher wavenumber of 2238 cm^{-1} (see figure 6). Similarly, for the nematic phase on SiO obliquely evaporated layers, the CN band shifts to higher wavenumber (see figure 7) with decreasing concentration.

On rubbed alignment layers, the CN stretching vibration band is at 2227 cm^{-1} for more than 20 layers. For less than 5 layers, on Sun Ever 721, the CN band shifts to a lower wavenumber of 2225 cm^{-1} (see figures 8 and 9).

3.2.2. *FT-IR spectra of 8CB bulk*

To obtain information about shifts of the CN stretching vibration band, due not to the interactions among the liquid crystal molecules, but to the interaction between the liquid crystal molecules and the alignment layers, we monitored the FT-IR spectra of 8CB in the bulk state and made appropriate comparisons.

It is known by SHG measurements that molecules of the *n*CB series, where *n* is the length of alkyl chain, form loose dimers in the bulk [4]. Transmission spectra of 8CB involving dimer formation were monitored in the bulk state. The bulk samples were prepared by coating bare CaF_2 substrates with 8CB. Transmission measurements were also made on KBr tablets coated with 8CB. In both cases, the CN stretching vibration bands were observed at 2227 cm^{-1}.

From these results, interactions at the molecular level between liquid crystal molecules and alignment layers were confirmed. The CN band of 8CB molecules on the rubbed alignment layers (2225 cm^{-1}) is lower than the CN band for 8CB in the bulk (2227 cm^{-1}). Thus, the wavenumber of the CN band in the rubbed alignment layers was affected not only by liquid crystal molecules, but also by the alignment layers.

3.2.3. *FT-IR spectra of 8CB in the gas phase*

In order to establish the CN stretching vibration band of an isolated 8CB (or 5CB) molecule without any effect from other molecules, the FT-IR transmission spectra of 8CB and 5CB were monitored in the gas phase. Measurements were made with a JEOL JIR-6500 FT-IR spectrometer operating in the GC-IR mode. Spectra were accumulated 10 times with a resolution of 4 cm^{-1}. The atmosphere was He gas at 300°C.

In both cases, the CN stretching bands were observed at 2230 cm^{-1}. The frequency of molecular vibrations may become higher at 300°C than at room temperature, and the CN stretching vibration band may shift to lower wavenumber at 300°C than that at room temperature. However, the wavenumbers of all bands other than the CN stretching vibration band at 300°C are nearly equal to the wave numbers of the bands at room temperature. Thus, the CN band, without any effect from other molecules, was assumed to be at 2230 cm^{-1} at room temperature.

From these results, the CN band of 8CB molecules on SiO obliquely evaporated layers (2238 cm^{-1}) is shifted to a larger wavenumber than that of the CN band of 8CB unaffected by other molecules (2230 cm^{-1}). Thus, the CN stretching vibration band on an SiO obliquely evaporated layer is affected by the alignment layers, indicating interaction between the 8CB molecules and the SiO obliquely evaporated layers, with

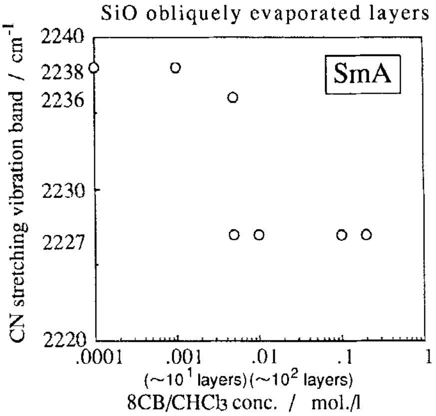


Figure 6. The shift of the CN stretching vibration band of 8CB on SiO films in the smectic phase with number of layers.

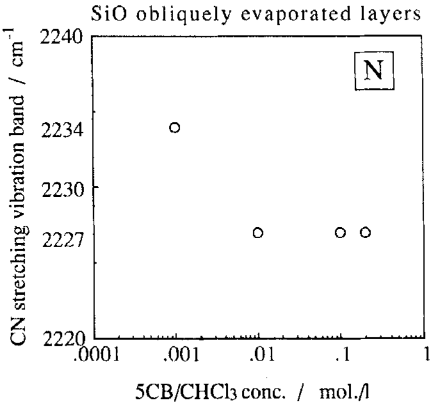


Figure 7. The shift of the CN stretching vibration band of 5CB on SiO films in the nematic phase with decreasing concentration.

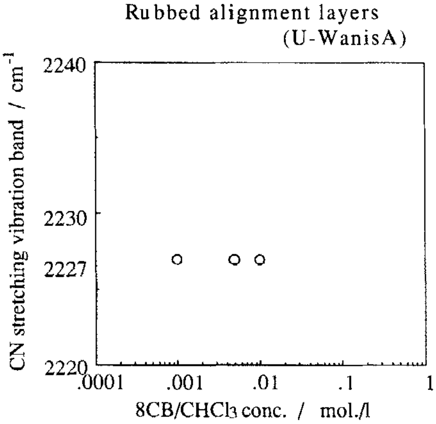


Figure 8. The shift of the CN stretching vibration band of 8CB on rubbed films (U-Wanis A).

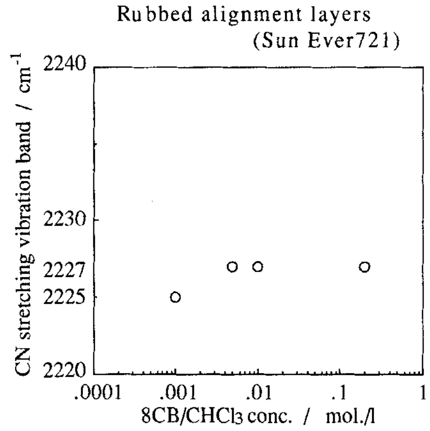


Figure 9. The shift of the CN stretching vibration band of 8CB on rubbed films (Sun Ever 721).

the cyano group acting unusually as an electron donor (assumed from molecular orbital treatment by the AM1 method). It is suggested that this anchoring force occurs in the nematic phase, because the CN band of 5CB shifts to a similar higher wavenumber.

3.2.4. *Molecular orbital method by AM1*

We compared the experimental results with calculations of the anticipated shifts in the CN stretching vibration frequencies when the cyano group is an election donor or acceptor.

After optimization of the electron density by using the MNDO (modified neglect of diatomic overlap) hamiltonian of the MOPAC method for the 8CB molecule, we calculated the electron density of the cyano group of one 8CB molecule using the AM1 method (see figures 10 and 11).

The highest occupied molecular orbital (HOMO) (see figure 10) is the 57th orbital of the cyano group. The CN stretching vibration shifts slightly to a lower wavenumber, because it is a weak antibonding molecular orbital. Thus the cyano group behaves like an electron acceptor in the case of 8CB on the polyimide films.

In the lowest unoccupied molecular orbital (LUMO) (see figure 11) is the 58th orbital of the cyano group, to which one electron is excited from the 57th orbital. The CN stretching vibration shows a significant shift to a higher wavenumber because it is a strongly bonding molecular orbital. Thus the cyano group behaves like an electron donor in the case of 8CB on the SiO films.

From the calculated results and the experimental results, it is deduced therefore that the cyano group behaves like an electron donor in the case 8CB on the SiO films, but plays the role of an electron acceptor in the case of 8CB on the polyimide films.

3.3. *8CB molecular orientational structure near the liquid crystal–alignment layer interface*

By means of RAS measurements, the molecular structure near the liquid crystal–alignment layer interface was investigated. In the RAS measurements, infrared light was polarized parallel or perpendicular to the surface normal. The polarized infrared light and alignment directions are shown schematically in figure 12. With s-polarized light, only vibrational modes of direction perpendicular to the substrate normal, i.e. spectra in a direction parallel to the orientation direction, can be observed. With p-polarized light, only vibrational modes of direction parallel to the substrate

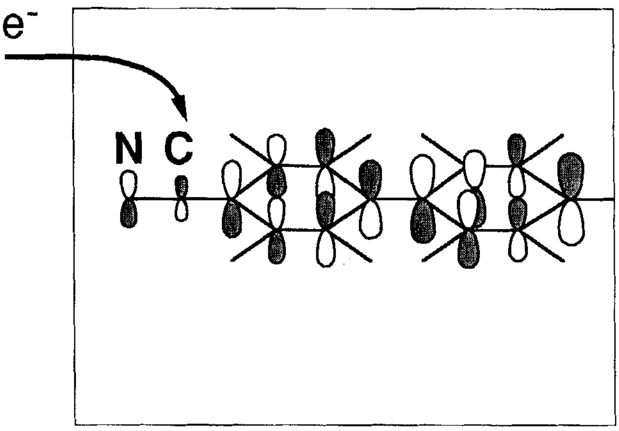


Figure 10. Electron density of the cyano group of the 8CB molecule in HOMO by AM1.

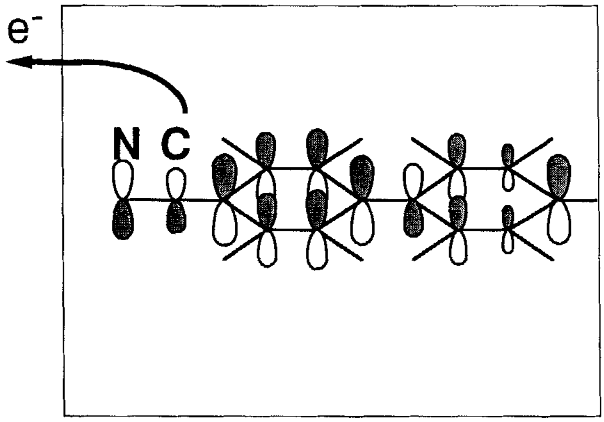
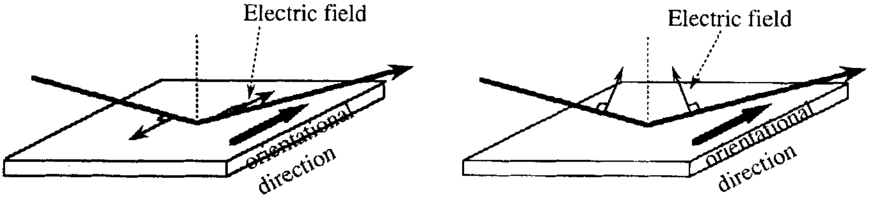


Figure 11. Electron density of the cyano group of the 8CB molecule in LUMO by AM1.

normal can be observed. Accordingly, if the spectra of RAS measurements (§ 3.2) were analysed, the liquid crystal molecular structure in the vicinity of the interface between the liquid crystal molecules and the alignment layers could be clarified. However, when experimental samples are in small quantities, RAS data for s-polarization are difficult to analyse, because band intensities are weakened by the interference of incident and reflected light at the interface. 8CB/chloroform (0·2 mol l^{-1}) solutions were spincast on each type of alignment layer; the calculated number of layers for this concentration



s-polarized light p-polarized light

Figure 12. Polarization and orientational direction in the RAS measurements.

The assignment of the bands obtained by RAS measurements on 10 000 layer samples of 8CB.

Wavenumber	Assignment of the bands
The shapes of band near 815 cm^{-1} [3]	*trans*-form of the alkyl chain: The bands are clearly distinguishable *gauche*-form: The bands are not clearly distinguishable
815 cm^{-1} [3]	CH out-of-plane deformation
1467 cm^{-1} [4]	CH_2 deformation (subcell packing): rhombic system: doublet bands ~ 1471 cm^{-1}, ~ 1462 cm^{-1} hexagonal system: single band ~ 1467 cm^{-1}
1915 cm^{-1} [3]	CH in-plane deformation
2227 cm^{-1} [3]	CN stretching

is about 10 000. RAS measurements were made, and the assignments for these spectra are shown in the table.

3.3.1. *The orientational structure of 8CB molecules on SiO obliquely evaporated layers*

The RA spectra of the 10 000 layer samples on SiO are shown in figure 13. Since the CN band is observed to shift to higher wavenumber than in the bulk state, the CN group is in contact with the faces of the alignment layers. Monitoring the extinction angle of the polarized light, the 8CB molecules were found to be aligned at a 45 degree slant away from the aligning direction. As shown in figure 15, the fact that the CN band and the CH out of plane deformation band are larger for p-polarization than s-polarization, and that the CH in-plane deformation is almost equivalent in area intensity indicate that the plane normal to the plane of the phenyl ring must be more parallel to the plane normal to the substrate than perpendicular [5]. From the shapes of the band near 815 cm^{-1} and doublet CH_2 deformation bands, the conformation of the hydrocarbon chain includes *gauche* conformations with orthorhombic subcell packing [3].

3.3.2. *The orientational structure of 8CB molecules on rubbed polyimide alignment layers (SunEver 721)*

The RA spectra of 10 000 layer samples on rubbed films are shown in figure 14. Since the CN band is observed to shift to a lower wavenumber than in the bulk state, the CN group is in contact with the alignment layer surfaces. Monitoring the extinction angle of the polarized light, the 8CB molecules were found again to be aligned at a 45 degree slant away from the aligning direction. Applying the same arguments as above, the plane normal to the plane of the phenyl ring must again be more parallel to the plane normal to the substrate than perpendicular as shown in figure 16 [5]. In particular the core part stands with a greater angle from the substrate faces on rubbed alignment layers than on SiO films. Similar conclusions to those above with respect to the hydrocarbon chain could be reached.

We have therefore investigated the liquid crystal molecular structures by conducting RAS measurements on films approximately 10 000 layers and comparing the spectra resulting from vertical and parallel polarizations. On both SiO obliquely evaporated layers and rubbed alignment layers, 8CB slants with respect to the alignment direction. Of particular note is the fact that the core part stands with a greater angle from the substrate faces on rubbed alignment layers than on SiO films.

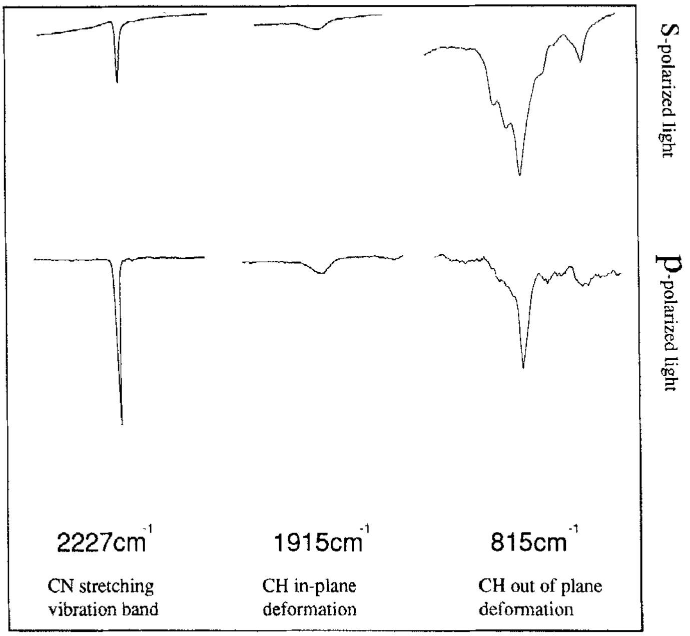


Figure 13. The RA spectra of 10000 layers on SiO films.

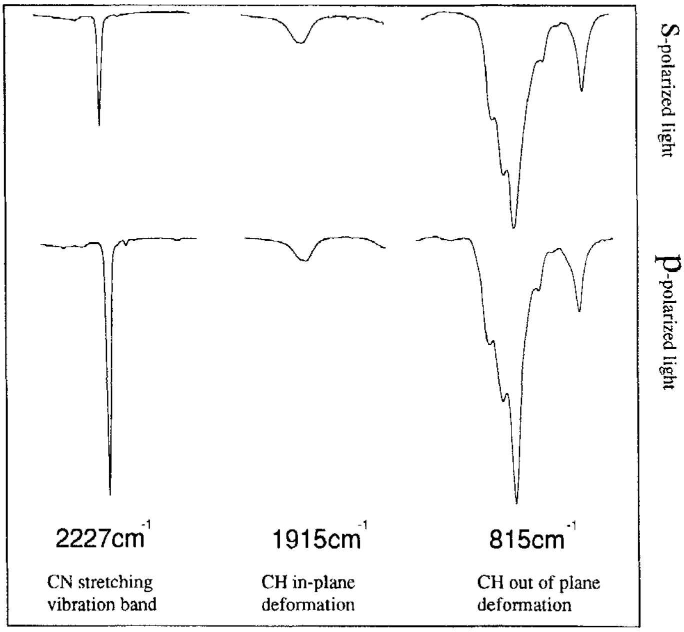


Figure 14. The RA spectra of 10000 layers on rubbed films (Sun Ever 721)

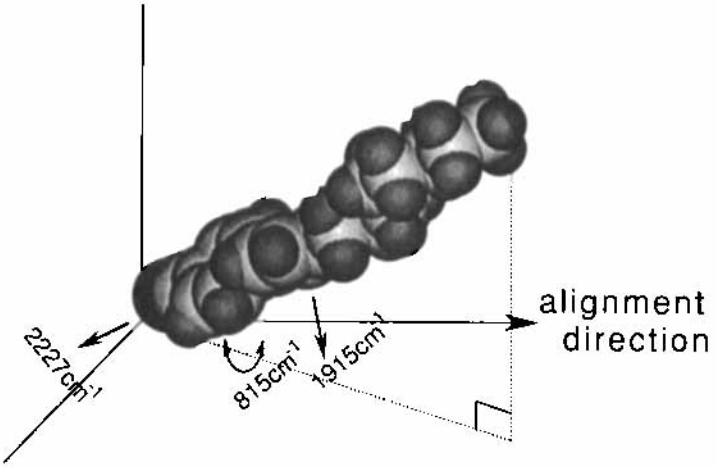


Figure 15. The orientational structure of 8CB on SiO films.

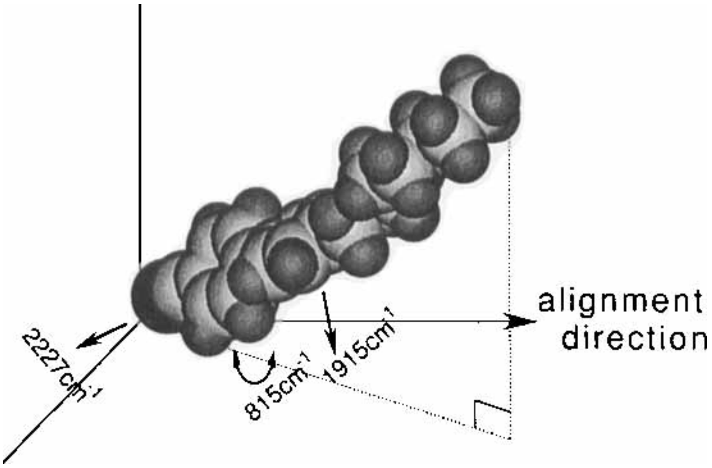


Figure 16. The orientational structure of 8CB on rubbed films.

4. Conclusions

In this study, we have achieved a better understanding of the state of liquid crystals at the liquid crystal–alignment layer interface as a result of RAS measurements on samples prepared by spincasting dilute liquid crystal solutions on to substrates coated with alignment layers.

(1) We have gained significant insight into the interaction between a liquid crystal film of thickness averaging less than one layer and the alignment layers, as a result of RAS measurements on samples prepared by spincasting dilute liquid crystal solutions on to thin metal films coated with alignment layers.

The cyano group in the liquid crystal molecules behaves like an electron donor with an SiO layer, but like an electron acceptor with a polyimide layer.

(2) We have conducted RAS measurements on 10 000 layer samples of liquid crystal molecules and clarified the alignment at the liquid crystal–alignment layer interface.

The 8CB molecule is aligned with a slant away from the aligning direction, regardless of the type of alignment layer, but the angle between the molecule short axis within the plane of the core and the surface normal was found to be smaller on the polyimide layers than on the SiO layers.

The RAS FT-IR method has been shown to be effective in determining the molecular orientational structure for scales of the order of several molecules, unlike other techniques which yield orientational structures only on a macroscopic scale.

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