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Hysteresis and ferroelectric liquid crystal displays

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One cause of the hysteresis in the voltage–transmittance curve is polarization in the alignment layers brought about by the spontaneous polarization of FLC molecules. The hysteresis was reduced by increasing the conductivity of the alignment layers. The structural changes on switching were examined by measuring time-resolved shifts of FT-IR peaks of selected groups. The shifts of selected groups in the IR peak can be attributed to changes in the local dielectric constants of the ambient environment during switching by molecular orbital calculations. The orientation on switching in the SmC* phase was found to be similar to that in the N* phase.

1. Introduction

Ferroelectric liquid crystals (FLC) which possess the memory effect enable passive matrix addressing of displays of a large number of lines [1, 2]. FLC displays have advantages such as fast response time and wide viewing angle. Because of their bistable limitation, they must have a grey-scale capability if they are to be applied to video displays. We have invented a new method for the analogue grey-scale response for FLC displays [3]. This new method involves a micro-domain texture and the addition of nanometer-scale particles into an FLC mixture, leading to a wide distribution of the threshold voltage within one pixel. This threshold-voltage distribution is caused by an increase of distribution in tilt angles of smectic layers with a micro-domain growth being pinned by the nanometer-scale particles [4].

The *image sticking* phenomenon is known to occur for all kinds of liquid crystal displays including FLC displays, and can easily be observed in still pictures and moving pictures with little action. This phenomenon is that an image displayed for a long time remains even after the following image appears. It has been reported that the occurrence of this phenomenon can be attributed to the presence of ions in FLC-display panels [5]. The presence of hysteresis in voltage–transmittance (*V–T*) curves was found in our FLC displays with the micro-domain texture. We have also found that the deterioration of the clarity of the display with the occurrence of the *image sticking* phenomenon and insufficient controllability of the grey-level response were caused by the presence of hysteresis. Even for conventional black and white FLC displays, the hysteresis in the *V–T* curves degrades the clarity of the display, and in particular, in analogue grey-scale FLC displays, this problem is crucial. We have been considering that there are seven separate factors which influence the hysteresis in *V–T* curves: (1) the sticking interaction between FLC molecules and the alignment layer caused by polarization, (2) the remaining elastic distortion of helices in the smectic C* phase, (3) the instability of the memory state [6], (4) the difference in process between nuclear growth and disappearance of FLC domains, (5) the amount of ions in the FLC mixture, (6) the amount of ions in the alignment layers, and (7) the asymmetry of the spontaneous polarization of FLC molecules in the applied electric field caused by the pre-tilt angle difference between the two substrates.

In this report, in order to realize analogue grey-scale FLC displays, we studied the mechanism of hysteresis in the *V–T* curves and found that the polarization in the alignment layers due to the spontaneous polarization of FLC molecules plays an important role in the mechanism. In order to accelerate depolarization in the alignment layers, we performed further experiments in which the conductivity of the alignment layers was increased. Time-resolved Fourier-transform-infrared (FT-IR) measurements were also performed, revealing the switching dynamics and the interaction of FLC molecules responsible for the occurrence of hysteresis during switching.

2. Experimental and computational details

The properties of the FLC mixture (FLC1) used in our experiments are shown in table 1. FLC1 was a mixture of seven kinds of molecules, all of which had a phenyl-pyrimidine skeleton. In particular, the spontaneous polarization of FLC1 was produced by the carbonyl

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Table 1. The properties of the ferroelectric liquid crystal FLC1.

Phase transition temperatures	I 115°C N* 105°C SmA 69°C SmC*
Melting point	-9°C
Spontaneous polarization	10·1 nC cm^{-2}
Latching pulse width	30·0 μs (under 25 V$_{p-p}$ μm^{-1})
Contrast ratio	>50

groups of chiral compounds. Surface-modified nanometer-scale particles were amorphous titanium dioxide obtained from Idemitsu Kosan Co., Ltd. Their average diameter was 17 nm. Nanometer-scale particles were added to the FLC1 mixture in the amount of 1 wt% and were dispersed homogeneously. The formation of SiO obliquely evaporated layers as alignment layers was performed as previously reported [7]. The angle between the SiO flux direction and surface normal of the substrate was set at 85°, and the temperature of the substrate was 100°C. Four different kinds of SiO film were fabricated by thermal annealing at 180°C, 200°C, 250°C and 300°C. The difference in the annealing temperature caused a difference in the ratio of silicon and oxygen atoms in the SiO alignment layers, as the annealing temperature is linear with the binding energy of the Si$_{2p}$ orbital [7]. Because the larger binding energy of the Si$_{2p}$ orbital leads to lower conductivity, this shows that conductivity can be controlled by changing the annealing temperature. SiO alignment layers were assembled in an antiparallel configuration in order to realize a tilted bookshelf geometry [8]. Sample cells used for the electro-optic measurements consisted of two indium–tin oxide (ITO) coated glass plates whose inside surface was coated with the four different kinds of SiO film, whereas the cells used for the time resolved FT-IR measurements consisted of two ITO-coated calcium difluoride plates with the four kinds of SiO film. The FLC1 mixture with nanometer-scale particles was injected into the space between the plates from the isotropic phase and gradually cooled to room temperature at a cooling rate of -5°C min^{-1}. The thickness of the FLC layers was 1·6 μm due to the presence of the SiO$_2$ spacers. In order to stabilize the micro-domain structure, an electric field treatment with a square waveform of 100 Hz under 20 V$_{p-p}$ μm^{-1} of voltage was applied to the cells for 2 s at room temperature after the injection.

Grey-scale properties were evaluated using the waveform shown in figure 1 [4]. The driving scheme applied consisted of bipolar reset and select pulses to ensure that there was no d.c. electric field which might have caused a degradation of the liquid crystal materials. In FLC cells, FLC molecules switch due to the interaction between the spontaneous polarization and applied electric field and are stable in the memory state. The reset pulse assured a reproducible grey-level response [9–11]. The grey level was determined by varying the amplitude of the bipolar select pulse. Electro-optic transmittance in the memory state was measured using a photomultiplier with crossed polarizers. The transmittance was plotted against the applied electric field to give the *V–T* curves.

Time resolved FT-IR spectroscopy measurements were performed using a Jeol JIR-6500 system composed of a time-resolved attachment and microscope unit [12] with the temperature controller. The resolution in time of this system is of the order of μs. Time-resolved IR spectra to clarify the FLC switching dynamics were measured with a select pulse of 25 V$_{p-p}$ μm^{-1} to ensure measurements starting from the latched state of FLC molecules, using the waveform shown in figure 1 at 30°C. The gate width was 5 μs and the interval time was 5 μs. One hundred interferograms were accumulated with a resolution of 2 cm^{-1}. The polarizer was set at 45° to the aligned direction.

The temperature dependence of the FT-IR spectra of/FLC1 on the calcium difluoride plate was monitored using the same system without the time-resolved attachment and polarizer. Thirty interferograms were accumulated with a resolution of 2 cm^{-1}.

Molecular orbital calculations were performed by using the program system Gaussian 94 DFT [13] on a Cray J916/12-4096 supercomputer. Either local density functional theory (LDFT) [14] or conventional *ab initio* molecular orbital theory was applied in the calculations with the correlation functional derived by Vosko *et al.* (VWN) [15] being used for the former, and for the latter, the Hartree–Fock (HF) approximation was applied. The basis set used was the 6–31 G* basis having a quality of double-ζ+polarization functions. Inclusion of the effect of dielectric constants of the ambient molecules was performed by applying the self-consistent isodensity polarized continuum model (SCI-PCM [16, 17]) which was originally used for calculations of solvated systems as implemented in the program Gaussian 94 DFT. The isodensity value for this model was set at 0·001. Geometries of molecules were fully optimized for all the calculations performed in this study.

3. Results and discussion

3.1. *Hysteresis in* V–T *curves and the relaxation of polarization in the alignment layers*

The *V–T* curves are shifted when the applied voltage is increased or decreased, as shown in figure 2, showing hysteresis. We note that the value of transmittance with a randomly applied voltage is located between values for the increased and decreased voltage. Consequently,

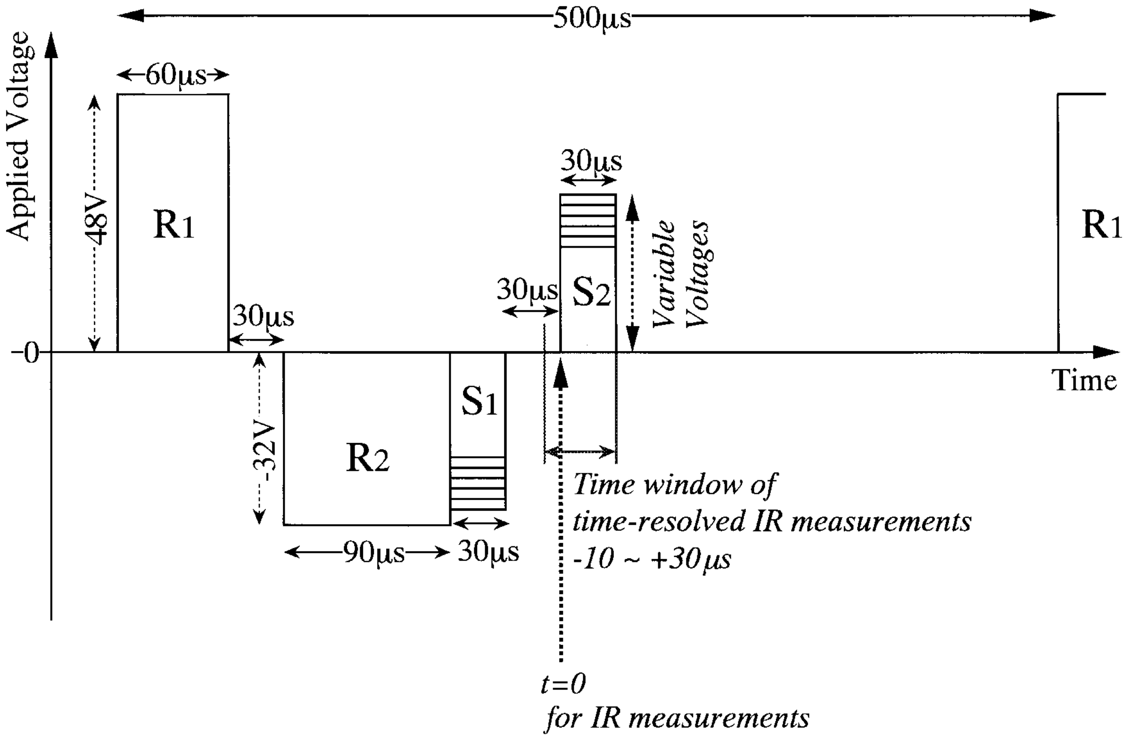

Figure 1. The driving scheme for grey-scale evaluation. For the *V–T* curve, the grey level is determined by a bipolar select pulse with variable amplitude. For time-resolved FT-IR spectra the select pulse is set at 25 $V_{p\text{-}p}$ μm^{-1}. The pulses denoted by R are reset pulses, and those denoted by S are select pulses.

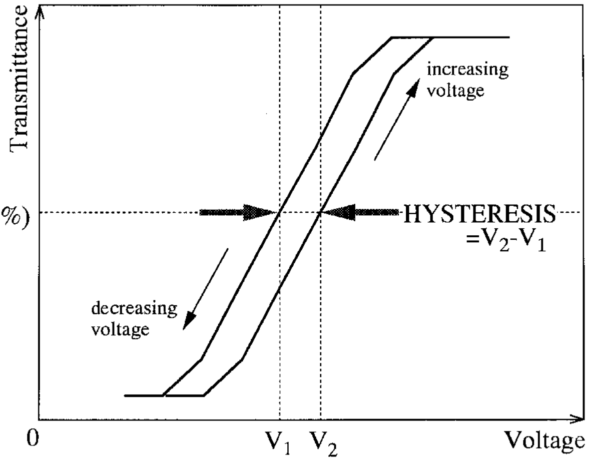

Figure 2. The shift in *V–T* curves with increasing and decreasing voltages.

the value of the transmittance cannot be determined by the applied voltage alone. Thus, the degree of this shift must be reduced significantly for full grey-scale control.

We studied the relaxation behaviour of polarization in the alignment layers, because this may be one of the factors which causes the hysteresis in the *V–T* curves. FLC molecules in the cell switch by spontaneous polarization reversal under an applied electric field. Their spontaneous polarization induces polarization in the alignment layers. FLC molecules and the alignment layer on the interface stick to each other. Because of this sticking, transmittance may change not only with the amplitude of the succeeding select pulse but also with the sticking. Moreover, this sticking leads to structural changes of the FLC system in the bulk, generating a reversed electric field to reduce the applied electric field. Thus, it can reasonably be assumed that polarization in the alignment layers causes hysteresis in the *V–T* curves, because of the sticking at the interface and revealing a reversed electric field.

In order to accelerate depolarization in the alignment layers, we increased the conductivity of the SiO layers. As the conductivity of the SiO layers is proportional to the degree of oxidation in the SiO layers, we have controlled the oxidation by changing the annealing temperature, as reported previously [7]. The *V–T* curves of the four different kinds of alignment layers, where the annealing temperatures were adjusted for each condition, were measured with increasing and decreasing voltage. The relationship between the annealing temperature and the hysteresis in the light of the shift of each *V–T* curve at a transmittance of 50 per cent is shown in figure 3. This figure shows that the *V–T* curves exhibit less shift with lower annealing temperatures. Because the

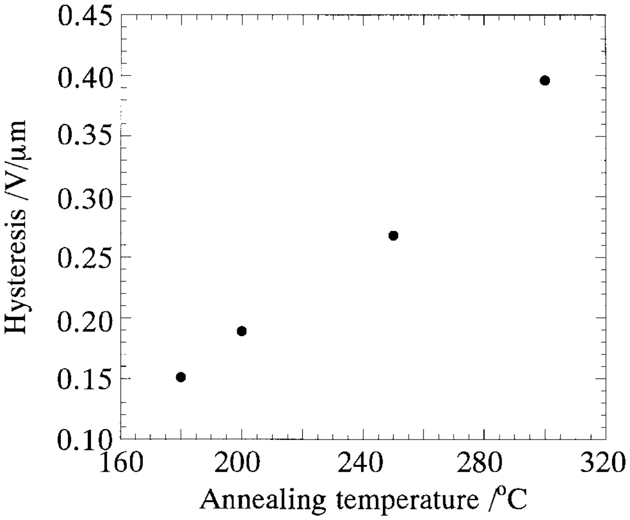

Figure 3. The relationship between the annealing temperature and the hysteresis at a transmittance of 50 per cent.

conductivity of the alignment layers becomes higher if the annealing temperature becomes lower, enhanced relaxation of polarization in the alignment layers due to the enhanced conductivity produces a smaller value of hysteresis in the *V–T* curves.

3.2. *Switching dynamics of FLC molecules*

In order to clarify the relationship between the structural changes of the FLC system in the bulk during switching and the relaxation of polarization in the alignment layers, time-resolved FT-IR spectra of the FLC1 mixture with the four kinds of alignment layers were monitored. The shifts in the IR absorption peak positions and heights of selected groups as a function of time were studied because these shifts are assumed to be related to the structural changes in the FLC system in the bulk due to the sticking between FLC molecules and alignment layers.

Time-resolved FT-IR spectra of the FLC1 mixture with the four different kinds of alignment layers were monitored. Figure 4 shows the time-resolved FT-IR spectra with the SiO alignment layer annealed at 200°C. The time window of time-resolved IR measurement is shown in figure 1. The shifts of peaks at around 1749 cm^{-1} and 1541 cm^{-1} were observed for all the alignment layers used. The former peak corresponds to the vibration of the carbonyl group which shows the spontaneous polarization, whereas the latter peak is considered to correspond to that of the C–N bonds of the pyrimidine skeleton which is along the molecular long axis [18].

The time-resolved change in the intensity of the carbonyl group cannot be investigated precisely, as the concentration of the chiral component is too low (5 wt %) for quantitative examination. In the FLC1 mixture without alignment layers only the peak at 1749 cm^{-1} was observed. The peak of the carbonyl group for all the alignment layers is located at 1749 cm^{-1} with no applied electric field. Table 2 shows the appearance and disappearance of the peaks for the carbonyl group during switching with an applied electric field. As shown in the table, the 1755 cm^{-1} peak with the alignment layer of the lower annealing temperature takes a shorter time to disappear. With the alignment layer annealed at 180°C, the peak at 1755 cm^{-1} appears again from 15 μs. Hence, the higher conductivity of the alignment layers causes a quicker disappearance of the peak at 1755 cm^{-1} and vice versa.

The peak attributable to the pyrimidine skeleton at 1541 cm^{-1} splits and a new peak appears at 1527 cm^{-1}

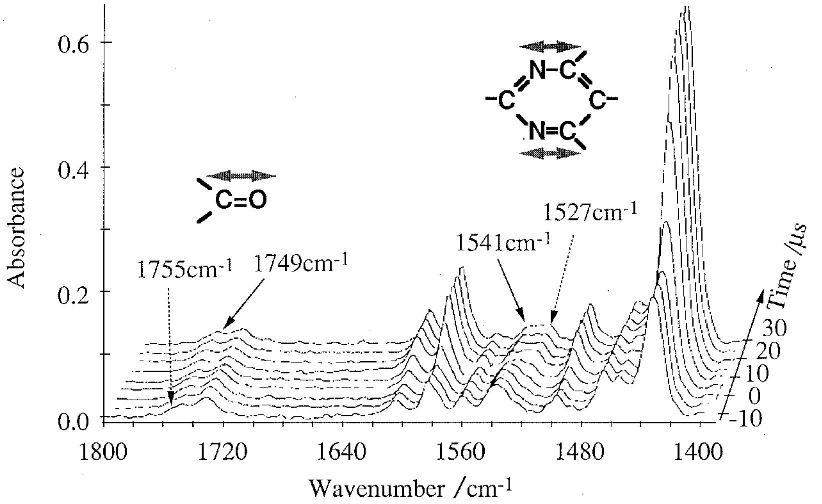

Figure 4. Time-resolved FT-IR spectra with the SiO alignment layer annealed at 200°C.

Table 2. Time-dependent behaviour of the peaks for the carbonyl groups with alignment layers made at different annealing temperatures.

Annealing temperature/°C	180		200		250		300	
Wavenumber of carbonyl group/cm^{-1}	1755	1749	1755	1749	1755	1749	1755	1749
30 µs	○	○		○		○		○
25 µs	○	○		○		○		○
20 µs	○	○		○		○		○
15 µs	○	○		○		○	○	○
10 µs		○		○	○	○	○	○
5 µs		○	○	○	○	○	○	○
0 µs		○	○	○	○	○	○	○
−5 µs	○	○	○	○	○	○	○	○
−10 µs	○	○	○	○	○	○	○	○

○: peak was observed.

by applying a select pulse during the switching. In the FLC1 mixture without alignment layers, only the peak at 1541 cm^{-1} was observed. With no applied electric field, the wavenumber of the C–N stretching band of the pyrimidine skeleton was 1541 cm^{-1} for all the alignment layers used. The intensity of the new peak at around 1527 cm^{-1} of the pyrimidine skeleton obtained by the Gaussian curve-fitting method was plotted against time for all the alignment layers used, as shown in figure 5. The IR spectra of the alignment layers at lower annealing temperatures show a lower intensity of the peak at 1527 cm^{-1} and faster switching speed. Higher conductivity of the alignment layers reduces the degree of sticking at the interface, resulting in the reduction of the reversed electric field. The reversed electric field is considered to lower an effective electric field in the cells. Therefore, an electric field is applied effectively to an FLC cell, and FLC molecules can be switched faster. Figure 6 shows the relationship between the degree of hysteresis in *V–T* curves at a transmittance of 50 per cent and a maximum intensity of the peak at 1527 cm^{-1}. This result shows that the intensity of the peak at 1527 cm^{-1} is linear in the degree of hysteresis in the *V–T* curves. The IR spectra of the alignment layers at higher annealing temperatures already show a higher intensity of the peak at 1527 cm^{-1} before the select pulse being applied. We should remark that in the regions of the lower conductivity of the SiO films, the relaxation time of depolarization seems to be longer.

The difference in behaviour between the carbonyl group and the pyrimidine skeleton is noteworthy. For the carbonyl group, the new peak at 1755 cm^{-1} remained at 0 µs and disappeared under the positive select pulse

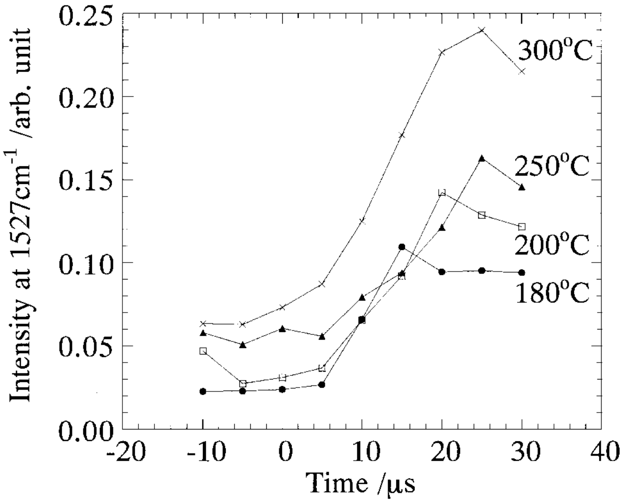

Figure 5. The time-resolved intensity of the peak at 1527 cm^{-1} for the pyrimidine skeleton during switching.

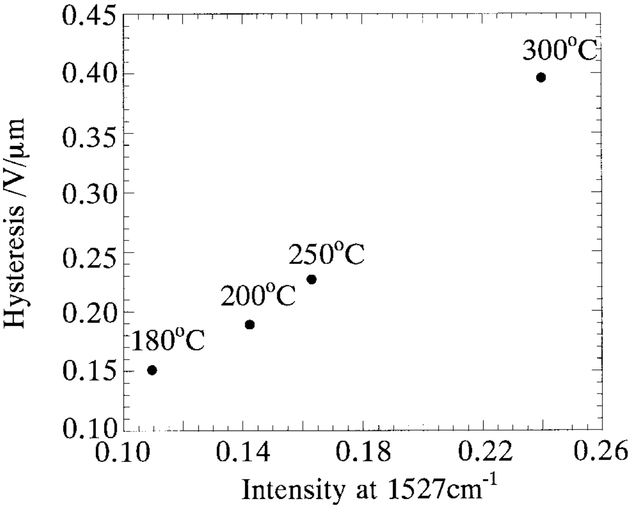

Figure 6. The relationship between the hysteresis at a transmittance of 50 per cent and the maximum intensity of the peak at 1527 cm^{-1}.

(S2), as shown in table 2. As mentioned above, the peak of the carbonyl group for all the alignment layers was located at 1749 cm^{-1} with no applied electric field. The new peak of the carbonyl group at 1755 cm^{-1} was generated by a negative electric field such as the reset pulse (R2) and/or the select pulse (S1) in figure 1. For the pyrimidine skeleton, the new peak at 1527 cm^{-1} started increasing from the midpoint of the positive select pulse (S2) in figure 1. The new peak of the pyrimidine skeleton was generated by a positive electric field.

3.3. *Simulation of the interaction of FLC molecules*

In order to determine the reason for the shifts in the IR peaks, we performed further theoretical molecular orbital calculations. There are two possible causes of the shifts in the vibrational frequencies. The shift might be caused by the distortion of liquid crystal molecules induced by applying the electric field or it might be caused by the changes in the local environment of the liquid crystal molecules.

We first performed theoretical calculations of the applied electric field-strength dependence of the vibrational frequencies of a molecule. The model molecule that we chose was acetone, which corresponds to the carbonyl group present in FLC1. The carbonyl group exhibits the largest dipole moment of all the groups present in FLC1, so that the effect of the applied electric field on the vibrational frequencies was most enhanced for this group. The HF method was applied to the calculations and the results are shown in table 3 for the vibration of the C=O bond in the gas phase. As is clearly shown in table 3, there was essentially no dependence of the C=O vibrational frequency on the field strength. For example, in the case of field strength of ~50 V μm^{-1}, which corresponds to the strength often applied experimentally in a liquid crystal cell, the calculated value was essentially the same as that without the applied field, with a difference of only 0·4 cm^{-1}. Thus, it can be concluded that the distortion of liquid crystal molecules does not account for the size of the shifts observed experimentally.

DFT calculated results using the SCI-PCM method are shown in figure 7. As shown in the figure, the C=O vibrational frequency in acetone becomes smaller with an increase in dielectric constant. For a pyrimidine molecule, the symmetric vibrational mode (A) for the ring shows the same tendency as that for the C=O vibration in acetone, whereas the frequency for the antisymmetric mode (A′) is essentially independent of the dielectric constant. This result shows that IR peaks can shift by 10–20 cm^{-1} when this is induced by a local change in the dielectric constants of the ambient environment. It should be noted that this range of the shift agrees with the experimental shift observed in our FLC system caused by the changes in orientation. If we compare the calculated results with the experimental results described above, it can further be suggested that the local dielectric constants around the carbonyl groups become lower during switching than those in the memory states with no applied electric field, whereas those around the pyrimidine rings become higher.

Table 3. The calculated dependence of the fundamental vibrational frequency of acetone on the applied electric field.

Electric field/V μm^{-1}	Fundamental calculated vibrational frequency/cm^{-1}
0	2017·9
5·14	2017·9
$5{\cdot}14\times10^1$	2018·3
$5{\cdot}14\times10^2$	2021·0

3.4. *Model of the orientation of FLC molecules on switching*

Thus, it is suggested that the shifts of the IR peaks can be attributed to the change in the local dielectric constant around the carbonyl and pyrimidine groups of FLC molecules. This further suggests that groups of FLC molecules adjacent to the carbonyl and pyrimidine groups change during switching. One of the most probable structural changes, which would account for the change in the local dielectric constants, is the rearrangement of the FLC molecules along the molecular axis from the smectic C* state to a state similar to that of the N* phase. Therefore, the temperature dependence of the IR spectra of the FLC1 mixture without alignment layers was monitored. For the peak of the carbonyl group in FLC1, a shift to a higher wavenumber is observed in the SmA, N* and isotropic phases rather than in the SmC* and crystalline phases, whereas for the peak for the pyrimidine skeleton in FLC1, a shift to lower wavenumber is observed, as shown in figure 8. These results show that the degree of wavenumber shift on switching in the SmA, N* and isotropic phases is identical. As mentioned above, the wavenumber shift under an electric field is as small as ~0·4 cm^{-1}. Thus, it is concluded that the orientation on switching in the SmC* phase is similar to that in states such as the N* phase.

4. Summary

Hysteresis in the voltage–transmittance curves is a critical problem in ferroelectric liquid crystal displays, particularly in analogue grey-scale displays. We have found that one of the causes of the hysteresis in *V–T* curves is the polarization in the alignment layers brought about by the spontaneous polarization of FLC molecules. It is generally understood that FLC molecules

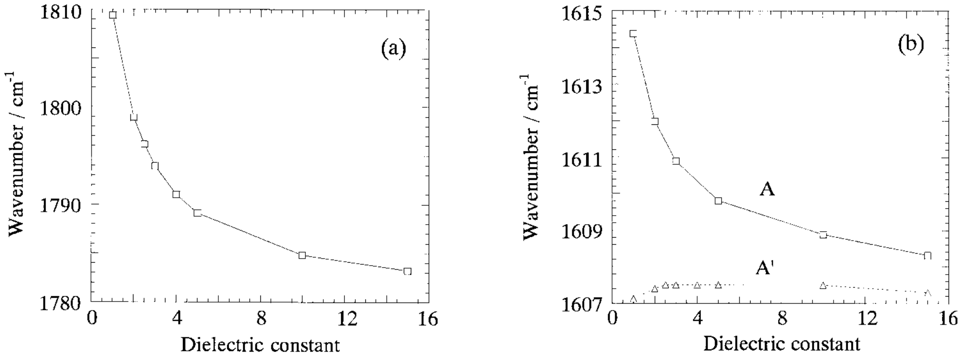

Figure 7. Calculated dependence of vibrational frequency (*a*) of the carbonyl group in acetone and (*b*) of the pyrimidine ring in pyrimidine on the dielectric constant of the ambient molecules.

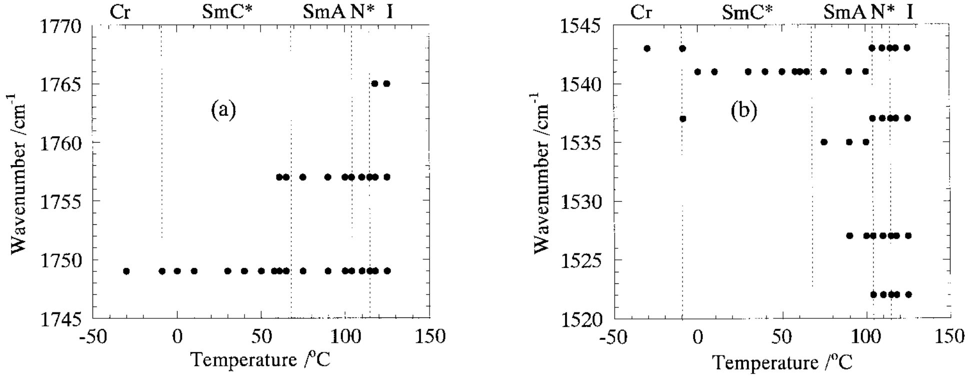

Figure 8. Temperature dependence of the wavenumber of the peak of (*a*) the carbonyl group and (*b*) pyrimidine skeleton in FLC1.

and the alignment layer on the interface stick to each other.

We further demonstrated that the degree of hysteresis can be reduced by accelerating depolarization in the alignment layers by controlling their conductivity. The sticking at the interface leads to structural changes of the FLC system in the bulk. The structural changes in the bulk on switching were examined by measuring time-resolved shifts of FT-IR peaks of the carbonyl group and pyrimidine skeleton in relation to the conductivity of the alignment layers.

We found that the intensity of the shifted peak of the pyrimidine skeleton when an electric field is applied corresponds to the degree of hysteresis and is reduced by high conductivity of the alignment layers. Moreover, the results of theoretical molecular orbital calculations indicated that the shifts of the carbonyl group and pyrimidine skeleton in the IR peak can be attributed to changes in the local dielectric constants of the ambient environment during switching. By observation of the temperature dependence of the IR spectra, the orientation on switching in the SmC* phase was concluded to be similar to that in states such as the N* phase.

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