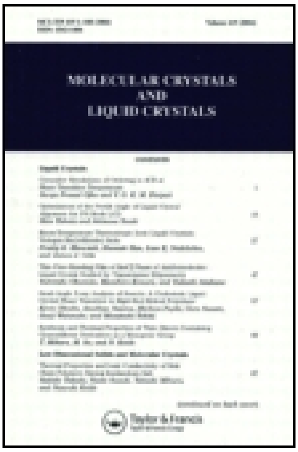

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One- and Two-Dimensional ET-IR Time-Resolved Spectroscopy of Liquid Crystals

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ONE- AND TWO-DIMENSIONAL FT-IR TIME-RESOLVED SPECTROSCOPY OF LIQUID CRYSTALS

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ABSTRACT This paper reports the application of FT-IR time-resolved spectroscopy (TRS) to the study of liquid crystal reorientation dynamics. One- and Two-dimensional FT-IR TRS experiments carried out for nematic 5CB liquid crystals have revealed new information about sub-molecular mechanisms of the electric-field induced reorientational transition. The major conclusion derived from this study includes: (1) 1D FT-IR TRS with microsecond time resolution has been successful to follow the real-time transition dynamics of each individual functional group within the molecule; (2) 1D TRS experiments at high fields show that the 5CB molecules in the anchoring layer undergo fast reorientational switching motion; (3) 2D FT-IR TRS, capable of analyzing temporal correlations between motions of different sub-molecular segments, has shown that a flexible terminal chain of 5CB undergoes a fast local motion in addition to the rotational relaxation motion of the entire molecule.

INTRODUCTION

FT-IR time-resolved spectroscopy (FT-IR TRS) with simultaneous temporal and spectral resolution has emerged as a powerful technique to elucidate dynamic, spectral information concerning both structural and orientational transitions of molecules in transient systems.[1]

The output from one-dimensional FT-IR TRS (1D TRS) is a stack of time-resolved spectra; the structural and orientational changes of the sample can be analyzed in terms of temporal changes of the time-resolved spectra. For example, in a step-scan FT-IR spectrometer we used in this study (Bio-Rad FTS60A/896), the spectra can be collected at time intervals as fast as 5 μs, and this sampling interval can be increased up to 30 s at 5-μs steps. In two-dimensional TRS (2D TRS), a frequency correlation analysis is applied to time-resolved spectra to yield a spectrum defined by two independent infrared wavenumbers. Thus, by expanding infrared absorption peaks over the second frequency domain, information about dynamic orientational correlation between different parts of the molecule can be obtained. In addition to this capability of analyzing dynamic behavior of sub-molecular units, 2D TRS has additional advantages including, for example, deconvolution of overlapped absorption bands and unambiguous band assignment through correlation analyses of interacting transition dipole moments.

In this paper we describe some representative FT-IR TRS results obtained for a nematic 4-pentyl-4'cyanobiphenyl (5CB) liquid crystal and illustrate its potential applicability to the study of a variety of time-dependent phenomena exhibited by liquid crystals.

EXPERIMENTAL

Fundamentals of 1D and 2D FT-IR TRS and experimental details have been described elsewhere.[1] The 5CB sample was sandwiched between two germanium plates separated by PET spacers. If the cell needs to be transparent in the visible region (for infrared microscope experiments with visual monitoring, for example), CaF_2 or BaF_2 plates coated with a conductive layer can be used instead of the germanium windows. The liquid crystal sample was injected into this cell along the rubbing direction so that the molecules align predominantly parallel to the rubbing direction (the homogeneous orientation). When a sufficiently high electric field is applied normal through the cell windows, the 5CB molecules undergo a transition to the homeotropic orientation in which the molecules are oriented parallel to the field direction. To analyze the dynamics of this homogeneous-to-homeotropic transition, 1D and 2D TRS experiments were carried out using a Bio-Rad FTS60A/896 FT-IR spectrometer equipped with a DC-MCT detector.

RESULTS OF 1D TRS EXPERIMENTS

Figure 1 shows a stack of 1D TRS spectra of 5CB measured during its homogeneous-homeotropic transition. The experiment was carried out at 1-ms time resolution, while the spectra in Figure 1 are shown at 4-ms intervals for visual purposes. The C≡N stretching band (2226 cm^{-1}) and the two phenyl C-C stretching bands (1606 and 1494 cm^{-1}), all polarized parallel to the cyanobiphenyl para-axis, decrease their intensity as the transition takes place and gradually recover the original intensity after the removal of the field. On the other hand, the phenyl C-H wagging band at 833 cm^{-1} increases its intensity in the transition region, in accord with the fact that its transition dipole moment is oriented perpendicular to the long molecular axis.

The functional group profile curve (i.e., intensity vs. time plot) constructed from the time-resolved spectra can provide a clear insight into the dynamic response of each individual absorption band. Figures 2 and 3 show an example of

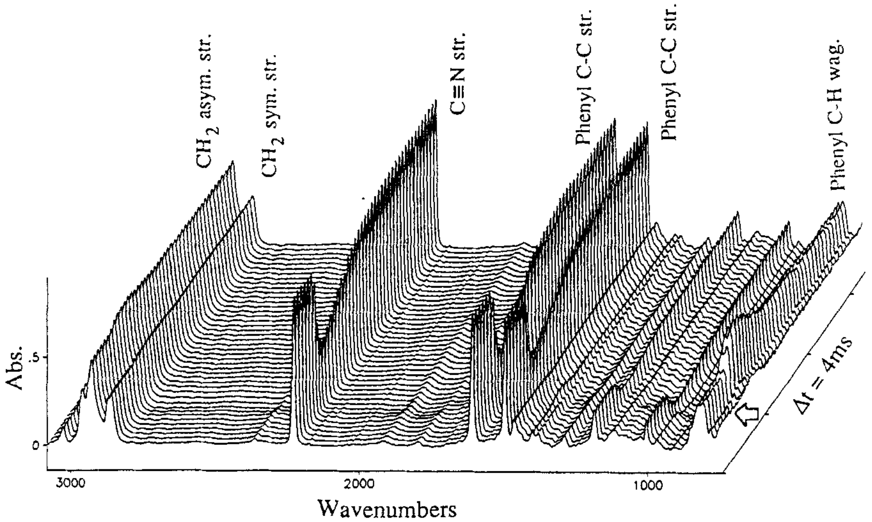
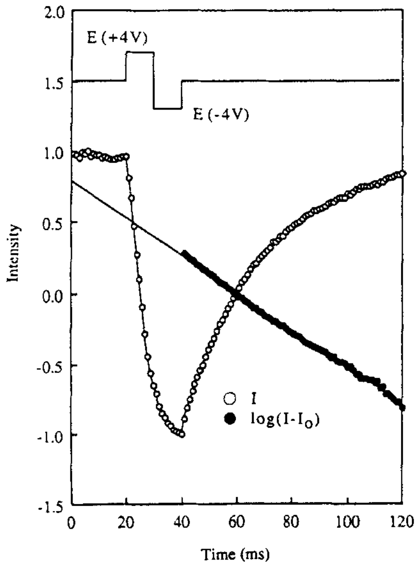


Figure 1 A stack of 1D time-resolved, polarized absorption spectra of 5CB measured during its electric-field induced homogeneous-homeotropic transition.



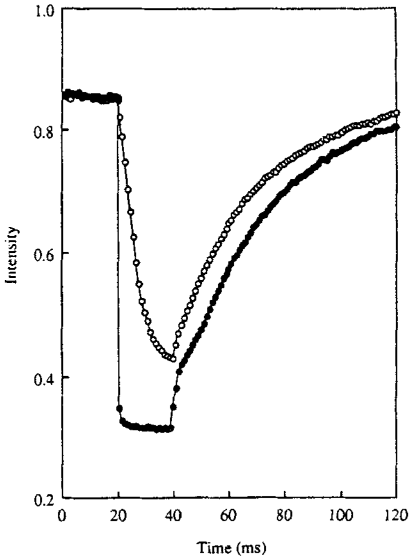


Figure 2 Plot of the integrated peak intensity of the C≡N stretching band (○), its logarithmic plot (●) and the applied electric field (—).

Figure 3 Plot of the integrated peak intensity of the C≡N stretching band; (○) E = 4 V and (●) E = 20 V.

such analysis, where the integrated peak intensity of the C≡N stretching band is plotted against time. It is evident in Figure 2 that the transition curve at low field (E = 4 V) consists of slow rise (~20 ms) and slow decay (~100 ms) processes. A semi-logarithmic plot of the decay curve gives a straight line, i.e., the orientational decay at low fields can be described by a rotational relaxation motion of the molecule as a whole. However, when the applied field strength is increased (E = 20V), the transition curve becomes more complicated. From comparison of the two transition curves observed at 4 and 20 V in Figure 3 we find that: (1) the rise process becomes faster (1-2 ms) at a higher field, (2) the decay curve at 20 V consists of two components, (3) the slower one of which has the same relaxation time as that observed in the low-field transition curve, and (4) this slow relaxation process starts when the polarized light intensity is decreased to the maximum value of the low-field transition curve. It should be emphasized again that the fast decay component appears only when a high external field is applied. Thus, we can conclude that this new component is associated with the motion of the molecules in less mobile state, i.e., those strongly anchored to the substrate surfaces and consequently requiring a higher torque for reorientation. Based on this mechanism, the origin of the fast rise process can also be interpreted. Since the strength of applied pulse filed is sufficiently high, the molecules in the anchoring layer are expected to be immediately peeled off from the substrate upon field application. This reorganization in the anchoring layer structure should act to accelerate the reorientation of bulk molecules into the homeotropic structure. Schematic illustrations of low- and high-field homeotropic structures are given in Figure 4.

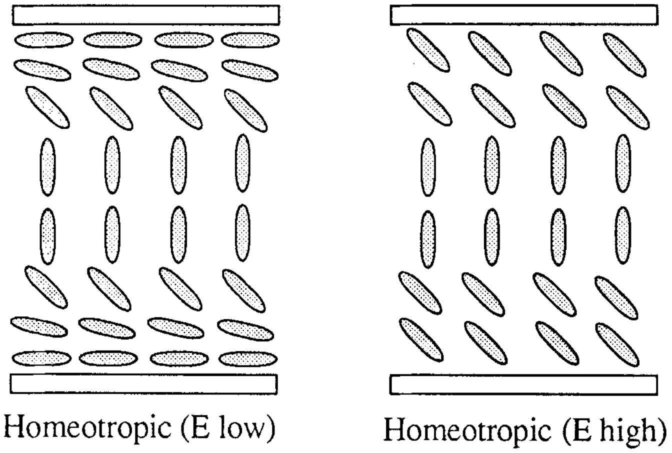


Figure 4 Schematic illustration of the homeotropic structure formed when low (left) and high (right) external electric field is applied.

RESULTS OF 2D TRS EXPERIMENTS

2D IR Spectra in the Cyanobiphenyl Absorption Region

To enhance dynamic spectral analysis of liquid crystals, we employed 2D IR frequency correlation analysis. Figure 5 shows the synchronous 2D IR correlation spectrum of 5CB including the region of the the C≡N and the phenyl C-C stretching bands (1450 - 2300 cm^{-1}). All these absorption bands, arising from the cyanobiphenyl group of the 5CB molecule, show correlation peaks both at the diagonal positions (autopeaks) and at the off-diagonal positions (cross peaks). For a pair of absorption bands, the two autopeaks and the two cross peaks can be connected by a correlation square. The signs of the autopeaks are always positive and, in this example, the signs of the cross peaks are also positive. The appearance of an intense, positive cross peak indicates that the time-dependent variations of the two transition dipoles responsible for generating the absorption bands are strongly coupled, or, in phase with each other. Thus, the above observation concludes that the cyanobiphenyl core of the 5CB molecule reorients as a unit in response to the applied electric field. In accordance with this, the corresponding asynchronous 2D IR spectrum shows no correlation peaks in this region. (Note that an asynchronous correlation peak appears only when the two transition dipoles reorient out of phase with each other.)

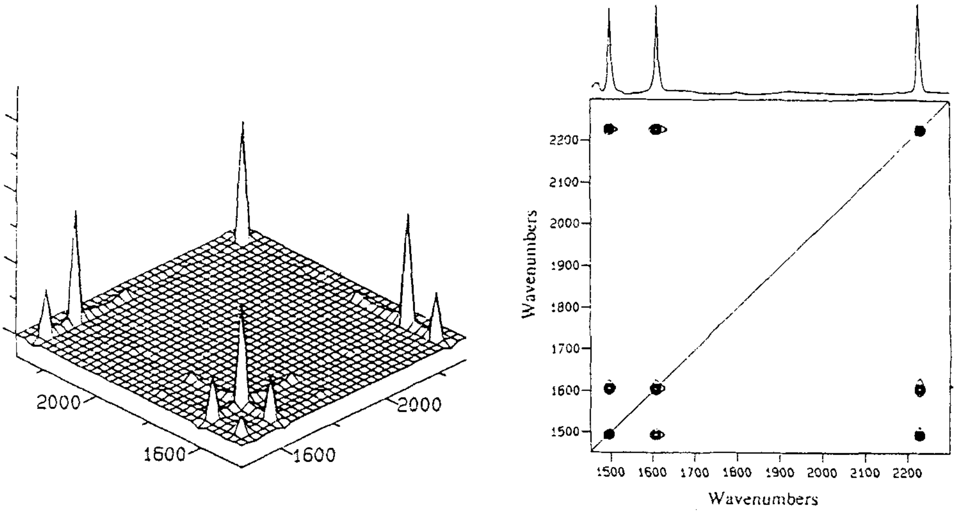


Figure 5 Synchronous 2D FT-IR frequency correlation spectrum of 5CB in the region of the C≡N and the phenyl C-C stretching bands (left: wire-mesh 3D plotting, right: contour 2D plotting).

2D IR Spectra in the C-H Region

The spectrum in the C-H region consists of a superposition of several different absorption bands. Some of them are associated with the phenyl C-H groups and others are with the C-H groups in the terminal pentyl chain. We will demonstrate in this section that the transition dipole moments responsible for generating these different C-H absorption bands reorient in different directions and exhibit different temporal responses to the external perturbation.

In Figure 6 we show a synchronous 2D IR correlation spectrum of 5CB in the C-H region. Each one of the five major absorption bands in the normal spectrum shows an autopeak at the diagonal. Three of these absorption bands (2857, 2929 and 2956 cm^{-1}) generate cross peaks with positive signs at the off-diagonal positions (group A). The remaining two absorption bands (2870 and 3026 cm^{-1}: group B) show also positive cross peaks. However, the cross peaks appearing between a pair of absorption bands that belong to different groups have always negative signs (these cross peaks are indicated by shaded contours). The appearance of negative correlation peaks indicates that the reorientation direction of one transition dipole moment is orthogonal to that of the other transition moment. It is clear therefore that the two sets of absorption bands, categorized into groups A and B, must have different origins (A: alkyl C-H, B: phenyl C-H).

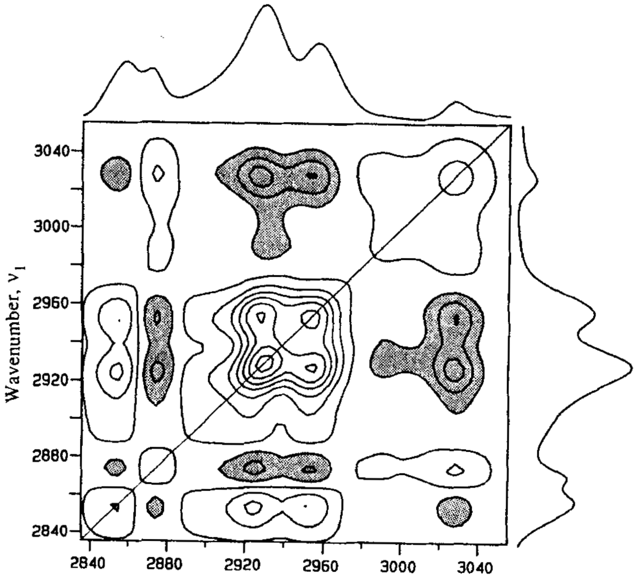


Figure 6 Synchronous 2D FT-IR frequency correlation spectrum of 5CB in the C-H stretching region. The shaded area represents a negative intensity region.

Figure 7 shows an asynchronous 2D IR correlation spectrum in the same region. First, it should be noted that, in contrast to the fact that the corresponding asynchronous spectrum in the cyanobiphenyl region does not show any cross correlation peaks, this asynchronous spectrum in the C-H region exhibits a number of cross peaks with different signs. It is important to point out here that the asynchronous cross correlation peaks appear when the motions of the two transition moments located at different molecular sites are decoupled, or out of phase with each other. For example, the band at ν_1 = 3026 cm^{-1}, attributable to the phenyl C-H stretching vibrations, shows cross peaks with the bands at ν_2 = 2956, 2929 and 2857 cm^{-1} — the latter two of which have been assigned to the asymmetric (2929 cm^{-1}) and symmetric (2857 cm^{-1}) CH_2 stretching vibrations. Thus, it is evident that the C-H groups attached to a rigid cyanobiphenyl core have different reorientational behavior from that of the C-H groups in a flexible pentyl chain. The sign of these cross peaks is positive, while the sign of the corresponding peaks in the synchronous spectrum in Figure 6 is negative. According to the rules of 2D IR frequency correlation analysis, we can conclude that the transition dipole moments giving rise to the pentyl C-H stretching bands reorient faster than those responsible for the phenyl C-H stretching bands. This result implies that a flexible alkyl

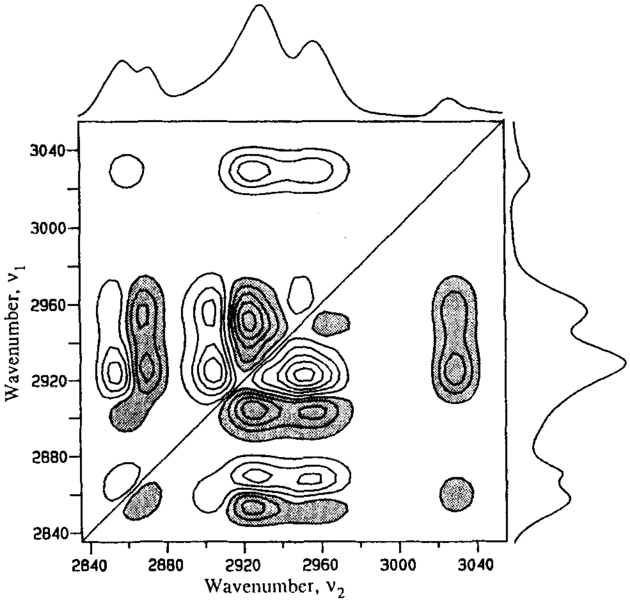


Figure 7 Asynchronous 2D FT-IR frequency correlation spectrum of 5CB in the C-H stretching region. The shaded area represents a negative intensity region.

chain appended to the rigid cyanobiphenyl core undergoes a fast local motion in addition to a much slower rotational relaxation of the 5CB molecule as a whole, when the external field is removed (Note that there were no detectable differences in the rise process; see Figure 1).

CONCLUSION

In this paper we reported the results of 1D and 2D FT-IR TRS analysis of reorientation transition of 5CB liquid crystals under the influence of an external electric field. Some important conclusions obtained here are as follows:

1) 1D FT-IR TRS with microsecond time resolution has been able to follow the real-time transition dynamics of each individual functional group in the 5CB molecule, providing information concerning the submolecular mechanism of the field-induced transition of liquid crystals.

2) 1D TRS experiment has shown that the 5CB molecules in the anchoring layer undergo a fast reorientational motion when a sufficiently high electric field is applied. This reorganization in the anchoring layer structure would accelerate the reorientational motion of the bulk molecules, and thus the response speed of 5CB becomes faster as the field strength is increased.

3) The capability of 2D FT-IR TRS of resolving spatial and temporal correlations of reorientational motions of different segmental units has been demonstrated. The 2D IR analysis of 5CB has shown that a flexible chain appended to a rigid mesogenic core undergoes a fast local motion in addition to the rotational relaxation of the entire molecule.

These observations should be important not only in understanding the submolecular mechanism of the filed-induced liquid crystal transition but also in design and fabrication of display devices utilizing electro-optical effects of liquid crystals. The fact that it has simultaneous "temporal" and "spectral" resolution is the key advantage of FT-IR TRS, and this technique can be applied to the study of a variety of time-dependent phenomena exhibited by liquid crystals.

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