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# Electric field-induced component dynamics in a binary liquid crystal mixture studied using two-dimensional Raman scattering

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The intermolecular interactions in a mixed, binary liquid crystal system are probed using two-dimensional Raman scattering. The sample is a 50/50 by weight blend of 4-pentyl-(4-cyanophenyl)cyclohexane (PCH5) and 4-methoxybenzylidene-4-butylaniline (MBBA). The response of the Raman anisotropy of the individual components to step voltages is identical. Furthermore, cross correlation analysis of oscillatory electric field experiments shows only synchronous reorientation between the two constituents. Since neat MBBA aligns perpendicular and neat PCH5 aligns parallel to the applied field, the data imply strong intermolecular interactions. Additionally, as previously observed for PCH5, frequency sweep experiments indicate that the flexible parts of the molecules can reorient independently of the rigid cores.

## 1. Introduction

Recent spectroscopic studies of the electric field-induced reorientation of 4-pentyl-(4-cyanophenyl)cyclohexane (PCH5) [1] and 4-pentyl-4-cyanobiphenyl (5CB) [2, 3] demonstrate that there are interesting intramolecular motions in liquid crystals subjected to an external electric field. Also of interest are the intermolecular motions in mixed liquid crystalline systems. Most industrial liquid crystal applications utilize mixtures in order to tailor physical properties [4]. Often the primary objective is to extend the temperature range of the liquid crystalline state or to tailor optical anisotropies and response times. Simple mixing rules have been successful in predicting transition temperatures, birefringence, and bulk order parameters in many multicomponent systems. However, it is known that the order parameters of the individual components within a mixture can significantly differ [5]. Therefore, it is expected that the components within such systems may display markedly different time-dependent responses in the presence of external fields.

Due to inherent chemical specificity, two-dimensional vibrational spectroscopies are well suited for studying the component dynamics and interspecies interactions in mixed liquid crystal systems. There has been only one 2D IR study on a multicomponent nematic monodomain: Sasaki and coworkers [6] investigated the electric field-induced reorientation dynamics of an eleven component

nematic mixture. The asynchronous spectrum contained cross peaks which suggest that different time-dependent responses may exist within the system. However, since the different components have common bond vibrations, it is uncertain whether the asynchronous intensity arises due to the non-cooperative motions of different components or due to non-cooperative intramolecular motions.

The two-dimensional Raman (2S Raman) study presented in this paper investigates a simpler binary nematic system. The liquid crystal PCH5, whose submolecular dynamics were recently investigated using 2D Raman [1], is mixed with 4-methoxybenzylidene-4-butylaniline (MBBA). MBBA and PCH5 differ significantly in dielectric anisotropy: whereas PCH5 possesses a positive dielectric anisotropy, MBBA possesses a slightly negative dielectric anisotropy. This leads to a tendency for neat PCH5 to align parallel and neat MBBA to align perpendicular to the applied electric field. Therefore, one might expect asynchronous motions within the blend due to the opposing electric torques. However, for the step and oscillatory amplitudes applied ( $<5$  V), the results show that PCH5 and MBBA reorient cooperatively with each other. The two components display synchronous dynamics over three decades of frequency. Thus, the intermolecular attractions are greater than the opposing electric torques on the two components. Additionally, confirming earlier findings for PCH5 [1], the data indicate non-cooperative intramolecular motions at frequencies that are faster than the bulk reorientation times.

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## 2. Two-dimensional Raman scattering

A comprehensive discussion of 2D Raman has been given elsewhere [7], and a brief discussion of the technique is presented here. The measure of interest is the *Raman anisotropy*, which is related to components of the derived polarizability tensor,  $\alpha'_{ij}$ , as follows:

$$\Gamma(v) = \langle \alpha'_{xx}{}^2 \rangle - \langle \alpha'_{zz}{}^2 \rangle. \quad (1)$$

Here,  $x$  is the preferred orientation direction of the material, light propagates along the  $y$ -axis, and the angled brackets refer to an average about the distribution function describing molecular orientation. For normalization, the  $R_{dc}$  component of the Raman scattered intensity is also collected and is related to the derived polarizability tensor as follows:

$$R_{dc} = \frac{1}{8} \{ \langle \alpha'_{xx}{}^2 + \alpha'_{zz}{}^2 + 2\alpha'_{zx}{}^2 \rangle \}. \quad (2)$$

Archer *et al.* [8] have demonstrated that, for a system of rigid rods with the orientation of molecular axes given by unit vectors  $u_i$ , the Raman anisotropy is of the form

$$\Gamma(v) = \gamma_1(v) (\langle u_x^2 \rangle - \langle u_z^2 \rangle) - \gamma_2(v) (\langle u_x^4 \rangle - \langle u_z^4 \rangle) \quad (3)$$

where  $\gamma_1$  and  $\gamma_2$  are constants particular to vibration  $v$ . Thus,  $\Gamma(v)$  is linearly related to the difference in the second and fourth moments of the orientation distribution function in the preferred and perpendicular directions within the plane normal to the propagation of light.  $\Gamma(v) = 0$  for isotropic systems and increases in magnitude monotonically with orientation in the preferred direction. Thus,  $\Gamma(v)$  can be used to quantify the orientation of individual components and submolecular orientation in complex systems using intrinsic bond vibrations as labels.

In addition to characterizing individual component orientation, 2D Raman provides for a measure of inter-species interactions. This is accomplished by cross correlating the dynamic Raman anisotropy arising from distinct constituents. The application of cross correlation analysis to spectroscopic measurements was first proposed by Noda [9, 10] in the development of two-dimensional infrared spectroscopy.

The application of a sinusoidal voltage,  $V = V^0 \sin(\omega t)$ , causes an oscillatory change in the moments of the orientation distribution function, and the Raman anisotropy becomes a dynamic Raman anisotropy,  $\tilde{\Gamma}$ . Since these nematic liquid crystals reorient equally for positive and negative voltages,  $\tilde{\Gamma}$  displays a response at twice the frequency of the applied electric field. Also, since liquid crystals are viscoelastic, the dynamic Raman anisotropy,  $\tilde{\Gamma}$ , responds out of phase with the field by a phase angle  $\delta$  and with amplitude  $\Gamma^0$ :

$$\tilde{\Gamma}(v) = \Gamma^0(v) \sin \{ 2\omega t + \delta(v) \}. \quad (4)$$

Equation (5) shows the limiting cross correlation of  $\tilde{\Gamma}$  emanating from the component containing bond vibration  $v_1$  and the component with bond vibration  $v_2$ :

$$\chi(\tau) = \lim_{\eta \rightarrow \infty} \frac{1}{\eta} \int_{-\eta/2}^{\eta/2} \tilde{\Gamma}(v_1, t) \tilde{\Gamma}(v_2, t + \tau) dt \quad (5)$$

where  $\tau$  is the correlation time. Substitution of equation (4) into equation (5) yields the solution:

$$\chi(\tau) = \Phi(v_1, v_2) \cos(2\omega\tau) + \Psi(v_1, v_2) \sin(2\omega\tau). \quad (6)$$

$\Phi(v_1, v_2)$  is the synchronous correlation intensity:

$$\Phi(v_1, v_2) = \frac{1}{2} \Gamma^0(v_1) \Gamma^0(v_2) \cos \{ \delta(v_1) - \delta(v_2) \} \quad (7)$$

and  $\Psi(v_1, v_2)$  is the asynchronous correlation intensity:

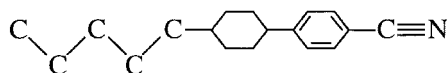
$$\Psi(v_1, v_2) = \frac{1}{2} \Gamma^0(v_1) \Gamma^0(v_2) \sin \{ \delta(v_1) - \delta(v_2) \}. \quad (8)$$

Since  $\Phi(v_1, v_2)$  is a maximum when  $\delta_1 = \delta_2$ , it is obvious that large values of the synchronous correlation intensity suggest simultaneous reorientation of the two components. On the other hand,  $\Psi(v_1, v_2)$  is a maximum when the two species lag the electric field exactly in quadrature with each other. Thus, large values of the asynchronous correlation imply independent reorientation of the two constituents.

## 3. Experimental

The components of the blend and their pertinent physical properties are shown in figure 1. The monodomain preparation and PCH5 material are the same as reported in the previous 2D Raman study [1] on PCH5. The sample of 4-methoxybenzylidene-4-butylaniline,

### PCH5



$$T_{CN} = 30 \text{ }^\circ\text{C}$$

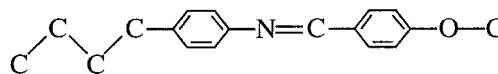
$$T_{NI} = 55 \text{ }^\circ\text{C}$$

$$\gamma_r = 110 \text{ cp}$$

$$\Delta\epsilon = 16.84$$

$$K_{11} = 9.6 \text{ E} - 12 \text{ N}$$

### MBBA



$$T_{CN} = 16 \text{ }^\circ\text{C}$$

$$T_{NI} = 46 \text{ }^\circ\text{C}$$

$$\gamma_r = 77 \text{ cp}$$

$$\Delta\epsilon = -0.7$$

$$K_{11} = 6.0 \text{ E} - 12 \text{ N}$$

Figure 1. Structures and physical properties of PCH5 and MBBA. The physical data for PCH5 at 20°C were obtained from EM industries; and properties of MBBA at 25°C were obtained from [4].

MBBA, was purchase from TCI America and was used without further purification. Efforts were made to reduce the hydrolysis [11] of this Schiff's base. Samples were stored with desiccant in a freezer and studies were performed within three weeks of delivery from the vendor. DSC experiments yielded a nematic to isotropic transition temperature of  $T_{NI} = 44^\circ\text{C}$  which indicates a relatively pure material [11].

A 50/50 by weight mixture was prepared at above the nematic–isotropic transition temperature of both components at  $60^\circ\text{C}$ . Miscibility was confirmed by optical microscopy and DSC. The DSC trace indicated a crystal to nematic transition below  $0^\circ\text{C}$  and exhibited a single peak characterizing the nematic to isotropic transition at  $T_{NI} = 47^\circ\text{C}$ .

The step and oscillatory electric field amplitudes applied were below the threshold for electrohydrodynamic structures that are known to occur in nematics with negative dielectric anisotropy and which are aligned perpendicular to the applied field [4]. Using polarizing microscopy, it was observed that MBBA exhibits a threshold of approximately 11 V for the appearance of striations or

Williams domains. The modulated structure became turbulent for steps above approximately 25 V. From the 50/50 MBBA/PCH5 mixture, circular domains appeared for steps of approximately 6 V. These may indicate electrohydrodynamic structures as seen for neat MBBA, or may be the result of electric field-induced phase separation. The sample became turbulent at about 20 V.

#### 4. Results and discussion

The spectra for  $125\ \mu\text{m}$  samples of PCH5 and MBBA are displayed in figure 2. The two components are combined 50/50 by weight, and the spectrum of the binary mixture is displayed in figure 3. The blend spectrum is a simple superposition of the spectra of the individual components. From figure 2 (a), it is seen that the motions of PCH5 can be monitored independently of MBBA using the symmetric cyano,  $\nu_s(\text{CN})$ , vibration giving rise to the peak at  $2226\ \text{cm}^{-1}$ . The spectrum for MBBA has been deciphered by Vergoten and Fleury [12] using Raman spectroscopy and normal coordinate analysis. The three peaks ( $1575$ ,  $1596$  and  $1626\ \text{cm}^{-1}$ ) shown in figure 2 (b) originate from the rigid core of MBBA. They result from the combination of the  $\text{C}=\text{N}$  and  $\phi-\text{N}$

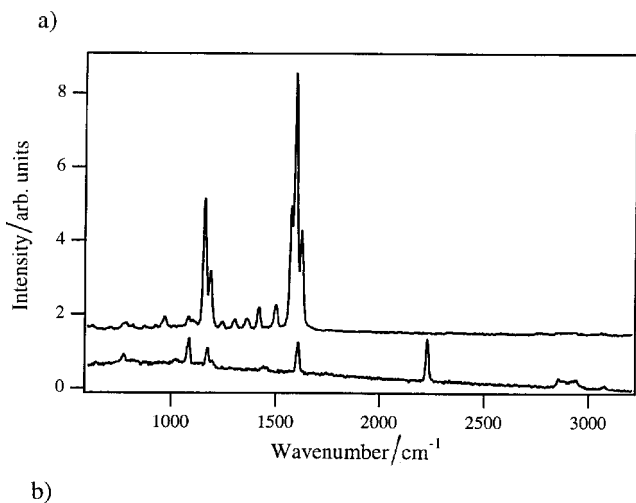


Figure 2. (a) Raman spectra of PCH5 and MBBA. The MBBA spectrum is offset above the PCH5 spectrum (b) Overlap of MBBA and PCH5 peaks around  $1600\ \text{cm}^{-1}$ .

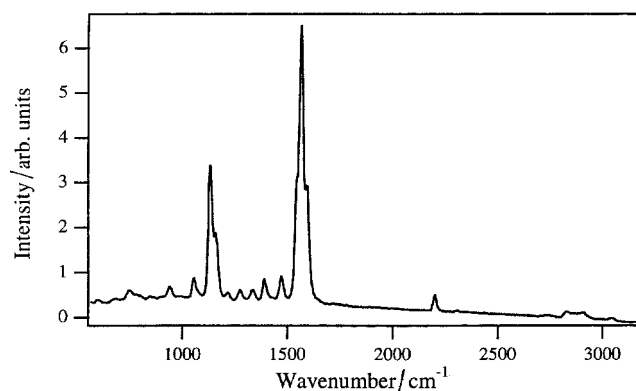


Figure 3. Raman spectrum of 50/50 MBBA/PCH5 mixture.

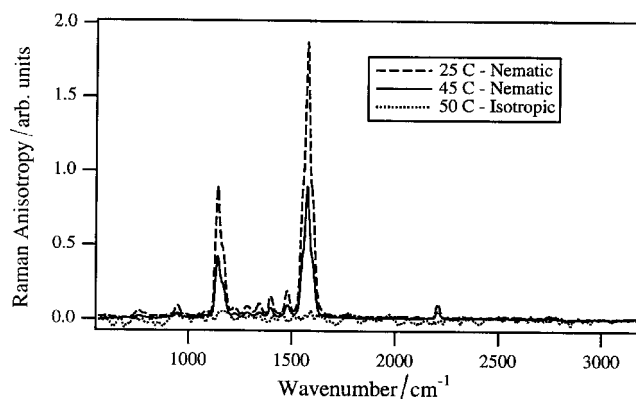


Figure 4. Raman anisotropy spectrum of 50/50 MBBA/PCH5 mixture.

stretching vibrations combined with multiple normal modes of the benzene rings. The peaks in this region are used to isolate the dynamics of MBBA even though there is a slight overlap with the  $\phi(\text{CC})$  band from PCH5. As seen in figure 2(b), the intensity from the MBBA peaks is substantially larger than from the PCH5

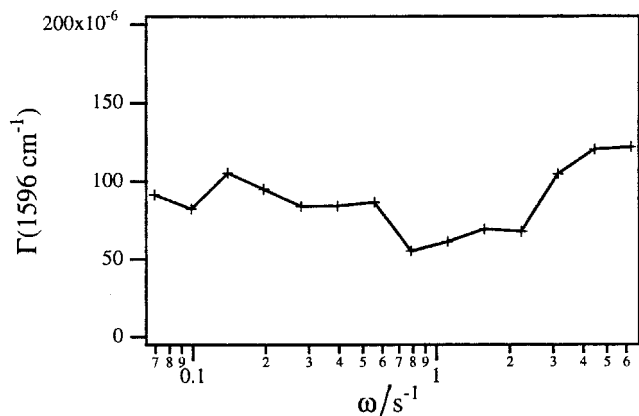
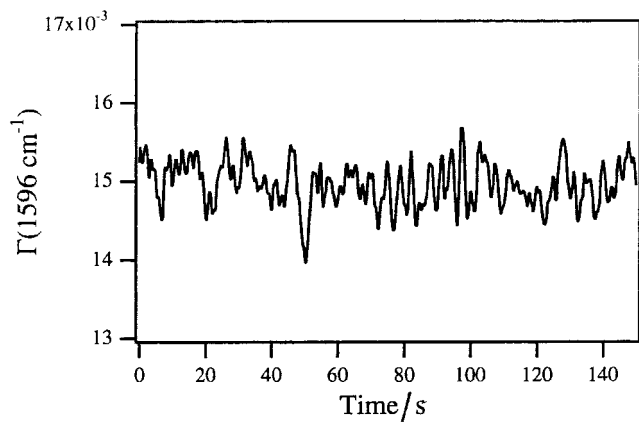
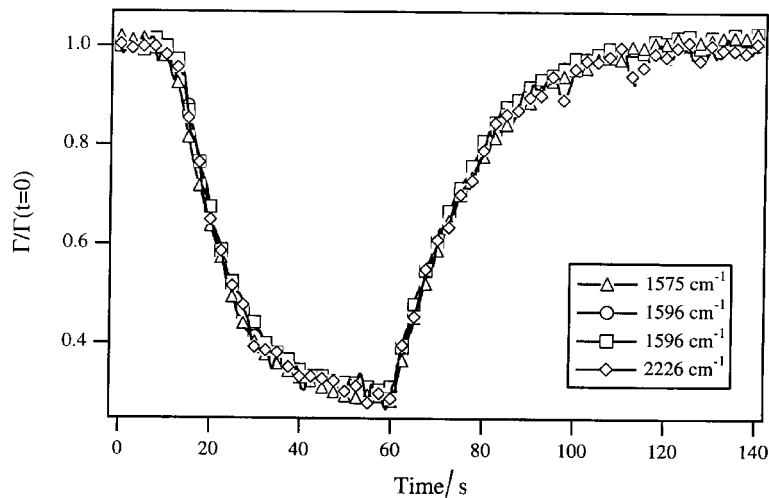


Figure 5. Response of MBBA to a 5 V step (above) and a 5 V amplitude oscillatory voltage (below) at 25°C.

Figure 6. Raman anisotropy signals, normalized by the no-field value, in response to a 4 V step electric field at time = 0 s; the field is turned off at time = 60 s. Markers denote every 10th data point.



peak. Also, there is only a slight overlap in the region between the 1596 and 1626  $\text{cm}^{-1}$  peaks.

Figure 4 displays the Raman anisotropy spectrum of the 50/50 mixture versus temperature. The 1575, 1596

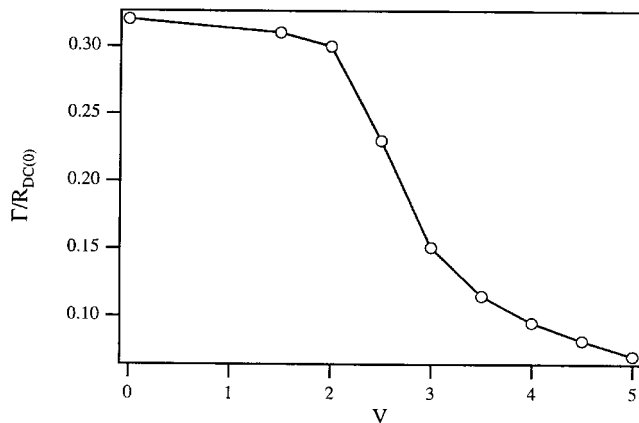


Figure 7. Steady state Raman anisotropy vs voltage for the  $\nu_s(\text{CN})$  vibration normalized by the  $R_{\text{dc}}$  component of the Raman intensity signal at zero field.

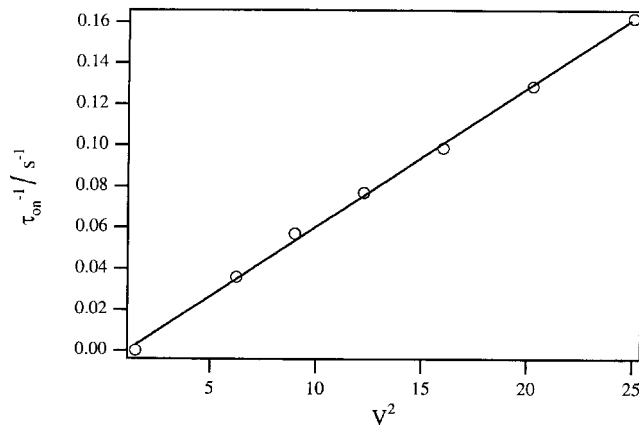


Figure 8.  $\tau_{\text{on}}^{-1}$  vs voltage for the  $\nu_s(\text{CN})$  vibration.

and  $1626\text{ cm}^{-1}$  peaks of MBBA give rise to a large Raman anisotropy, and the PCH5  $\nu_s(\text{CN})$  at  $2226\text{ cm}^{-1}$  is also resolvable. The CH profile associated with the

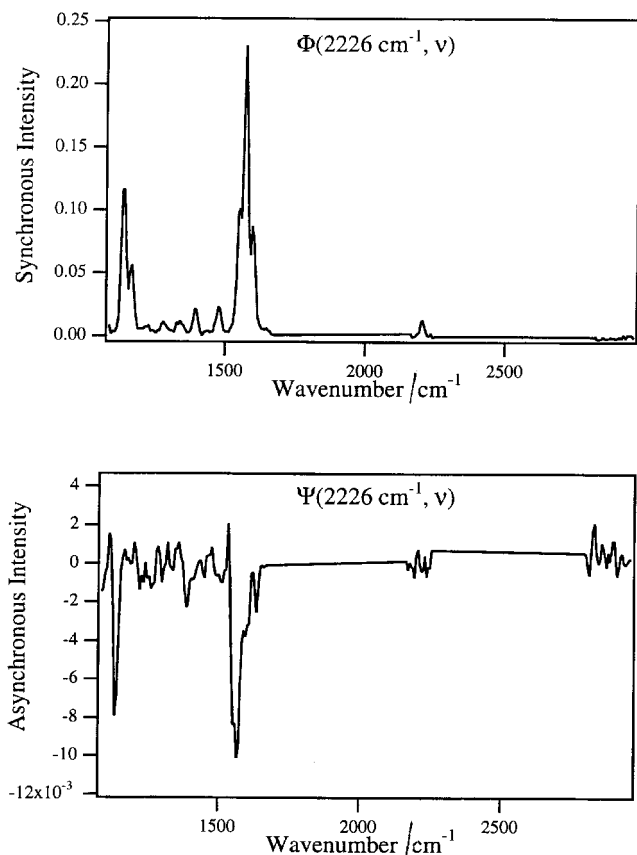


Figure 9. Synchronous and asynchronous intensity with respect to  $\nu_s(\text{CN})=2226\text{ cm}^{-1}$  subjected to a sinusoidal voltage of 5 V amplitude at 0.02 Hz at  $25^\circ\text{C}$ .

flexible alkyl chains in the  $2900\text{ cm}^{-1}$  region does not appear above the baseline. However, the monochromator was tuned to  $2857\text{ cm}^{-1}$  for the step and oscillatory experiments in an attempt to monitor the dynamic Raman anisotropy associated with the flexible tail of the molecules. As will be shown, the amplitude of the dynamic Raman anisotropy from the  $2857\text{ cm}^{-1}$  peak rises above the baseline at fast oscillatory frequencies.

Step and oscillatory electric field experiments were first performed on neat MBBA. Since the dielectric anisotropy of MBBA is negative ( $\Delta\varepsilon = -0.7$ ), MBBA prefers to align perpendicular to the electric field. The MBBA monodomain was prepared so that the molecules are initially perpendicular to the field direction; therefore, there should be no significant director realignment. As predicted, figure 5 shows that the Raman anisotropy associated with the  $1596\text{ cm}^{-1}$  peak does not respond to 5 V steps or to 5 V amplitude sinusoidal electric fields for various frequencies  $25^\circ\text{C}$ .

Step voltage experiments performed on the mixture indicate that the MBBA and PCH5 molecules reorient cooperatively for voltages below 5 V. Figure 6 displays the normalized response of the  $1575$ ,  $1596$  and  $1626\text{ cm}^{-1}$  peaks of MBBA and the  $2226\text{ cm}^{-1}$   $\nu_s(\text{CN})$  vibration of PCH5 to a 4 V step at 0 s and turned off at 60 s. The data in figure 6 are normalized by the no-field Raman anisotropy,  $\Gamma(t=0)$ . Also, the  $\nu_s(\text{CH}_2)$  vibration  $2857\text{ cm}^{-1}$  is not shown since it does not yield a signal above the noise in these step experiments. The data show no difference in the motion of the two molecules. Rather, both components orient in the direction preferred by PCH5 which has a dielectric anisotropy about 10 times the magnitude of  $\Delta\varepsilon$  for MBBA. Similarly to the response of PCH5 [1], all of the peaks exhibit an

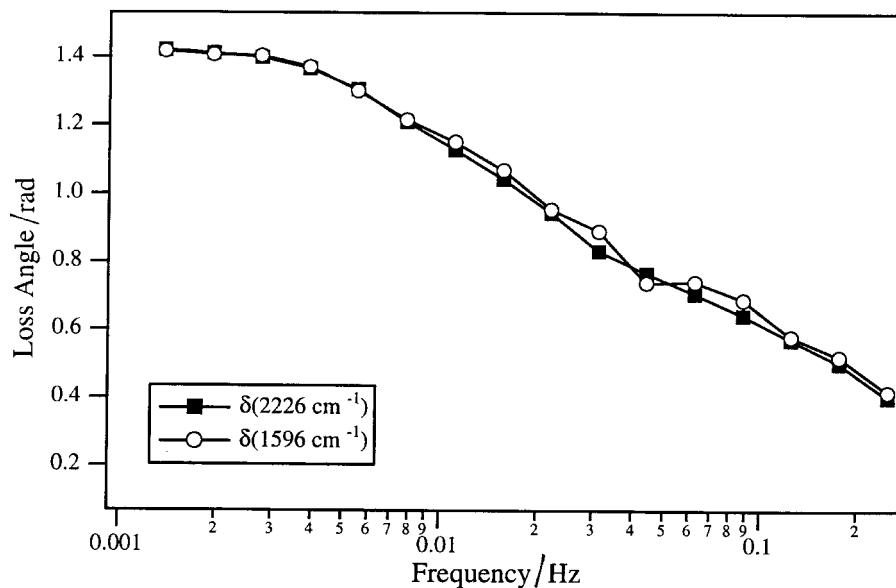


Figure 10. Loss angle vs frequency for the  $\nu_s(\text{CN})=2226\text{ cm}^{-1}$  vibration of PCH5 and the  $1596\text{ cm}^{-1}$  vibration of MBBA.

induction period after the field is turned on and relax immediately after the field is turned off at 60 s.

From the response of the  $\nu_s(\text{CN})$  vibration of PCH5, the bulk orientation changes were followed as a function of step voltage. Figure 7 displays the saturation value of the Raman anisotropy from the CN bond at 25°C. Comparing with previous results on PCH5 [1], it can be seen that the mixture has a threshold voltage similar to that of PCH5 of approximately 1.5 V. Also, the high voltage plateau is similar, but the initial no-field orientation is less than that of PCH5. By exponentially fitting the  $\nu_s(\text{CN})$  response after the induction period, the inverse of rise time constant is determined and

plotted in figure 8. The rise time constant is of the same order of magnitude but slightly larger than that of PCH5.

In order to investigate further the cooperative motions of MBBA and PCH5, the mixture was subjected to sinusoidally varying electric fields. Before acquiring data, the sample experienced many cycles of the oscillatory field until a steady state was achieved. The dynamic Raman anisotropy yields a signal at twice the frequency of the applied field. Fourier transforms are employed to analyse  $\Gamma(\nu)$  and determine the amplitude and phase with respect to the applied voltage. Since this study probes only two molecules, the cross correlation is plotted as a one dimensional, rather than two dimensional, function

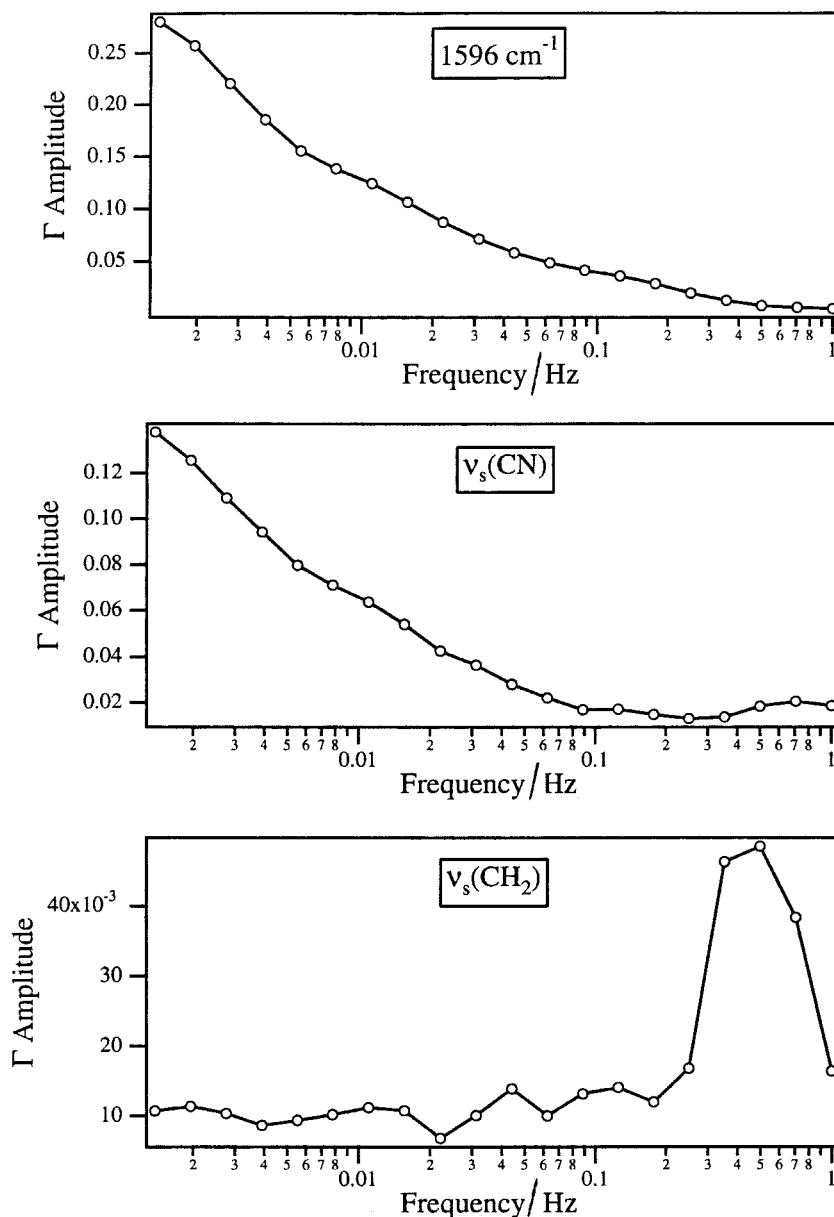


Figure 11. Raman anisotropy amplitude vs frequency in response to a 5 V amplitude sinusoidal electric field.

with respect to the PCH5  $\nu_s(\text{CN})$  vibration at  $2226\text{ cm}^{-1}$  for easier interpretation.

Figure 9 shows the cross correlation of the Raman anisotropy emanating from the various wavelengths. The synchronous intensity,  $\Phi(2226\text{ cm}^{-1}, \nu)$ , exhibits a large cross peak between the  $\nu_s(\text{CH})$  vibration from PCH5 and the rigid core vibrations from the MBBA molecules. This observation is in agreement with the results from the step experiments. The asynchronous intensity,  $\Psi(2226\text{ cm}^{-1}, \nu)$ , shows a cross peak between PCH5 and MBBA, but the asynchronous intensity is more than an order of magnitude less than the synchronous intensity. In order to probe further the possibility of non-cooperative motion between PCH5 and MBBA, the cross correlation was performed at various frequencies. These data demonstrate that the response of the mixture over three orders of frequency is highly synchronous. The asynchronous intensity as a function of frequency shows only fluctuations about zero. A difference in the phase angle between the two components is necessary for the presence of an asynchronous intensity. As shown in figure 10, the phase angles from the PCH5  $\nu_s(\text{CN})$  vibration and the MBBA  $1596\text{ cm}^{-1}$  vibration are identical. The other aspect of the cross correlation is the amplitude of the dynamic Raman anisotropy. Figure 11 displays the amplitude of the response vs frequency. At periodicities longer than the bulk reorientation times, PCH5 and MBBA exhibit large amplitude responses. As the perturbing frequency is increased, the rigid cores of the molecules can no longer reorient in the presence of the electric field and their motions are impeded. The situation is different for the  $\nu_s(\text{CN}_2)$  vibration that may be associated with both MBBA and PCH5. It is interesting that at the same time as the rigid cores become immobilized, the response from the  $\nu_s(\text{CH}_2)$  vibration is actually enhanced. In fact, at the low frequencies that are associated with cooperative motion between the molecules, the Raman anisotropy from the  $\nu_s(\text{CH}_2)$  vibration cannot be resolved above the noise level. Thus, as previously observed for PCH5 [1], the alkyl group can reorient independently of the rigid core in the presence of a quickly varying electric field.

## 5. Conclusions

The spectroscopic capabilities of two-dimensional Raman scattering have been used to monitor separately the dynamics of each component in a binary nematic mixture. Results from both step and oscillatory electric field experiments show that both MBBA and PCH5 reorient cooperatively. Since neat MBBA aligns perpendicular and neat PCH5 aligns parallel to an applied field, the experiments indicate strong intermolecular interactions between the two components. The results also show that at periodicities shorter than the bulk reorientation times, the flexible tail of the liquid crystal molecules can reorient independently of the rigid cores. Such dynamics have been observed for neat PCH5 and suggest that liquid crystals do not reorient as rigid rods at high frequencies.

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