

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230045545>

Raman investigation of the low-temperature phase transition in a liquid crystalline system: Terephthalidine-bis-heptylaniline (TB7A)

ARTICLE *in* JOURNAL OF RAMAN SPECTROSCOPY · SEPTEMBER 2002

Impact Factor: 2.67 · DOI: 10.1002/jrs.906

CITATIONS

13

READS

22

4 AUTHORS, INCLUDING:



Ranjan K Singh

Banaras Hindu University

71 PUBLICATIONS 506 CITATIONS

SEE PROFILE



Wolfgang Kiefer

University of Wuerzburg

878 PUBLICATIONS 9,837 CITATIONS

SEE PROFILE

Raman investigation of the low-temperature phase transition in a liquid crystalline system: terephthalidine-bis-heptylaniline (TB7A)

Ranjan K. Singh,^{1†} S. Schluecker,¹ B. P. Asthana^{2*} and W. Kiefer¹

¹ Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

² Department of Physics, Banaras Hindu University, Varanasi 221005, India

Received 18 June 2001; Accepted 7 June 2002

Raman spectra of terephthalidine-bis-heptylaniline (TB7A) were recorded in the region 1125–1225 cm⁻¹ from room temperature to 10 K at 18 different temperatures. The splitting of the ~1165 cm⁻¹ band, and the variation of the ratio of integrated intensities of the original band at ~1165 cm⁻¹ to the new component at 1170/1171 cm⁻¹ reveals a solid modification. The analysis of the temperature dependence of the linewidth was made using Rakov's relation. A logarithmic plot as a function of 1/T gives two straight lines with an abrupt discontinuity, which clearly exhibits a phase transition at about 210 K. The temperature dependence of the linewidth of the ~1165 cm⁻¹ band was used to characterize this transition. A relatively large variation (~3 cm⁻¹) of the linewidth on going from 250 to 10 K in TB7A having an odd ($n = 7$) number of carbon atoms in the alkyl tail compared with those observed (~1 cm⁻¹) in other homologues having an even ($n = 2$ or 10) number of carbon atoms in the alkyl tail is a clear demonstration of the even–odd effect. Copyright © 2002 John Wiley & Sons, Ltd.

INTRODUCTION

The pace of research in liquid crystals, after their discovery in the later part of the nineteenth century, remained slow until about 1960. The quest for technological applications of liquid crystals, however, triggered off rapid growth in research activity on its different aspects. The most widely used techniques¹ to investigate and characterize liquid crystalline phases and less investigated solid modifications in liquid crystalline systems at temperatures lower than the melting-point are nuclear magnetic resonance (NMR), x-ray diffractometry, neutron diffractometry, differential scanning calorimetry (DSC), differential thermal analysis (DTA)/thermogravimetric analysis (TGA), etc. However, the potential of Raman spectroscopy, which is a technique much more suited to understanding molecular dynamics, has not been fully exploited. At the transition point, certain obvious changes in spectral features, such as the appearance or disappearance of some Raman bands, are generally observed. In addition, a careful study of linewidth changes reflecting dynamic processes and shifts in peak positions and variations of integrated Raman intensities, which are

characteristic of static processes, help visualize the dynamics and molecular changes taking place at the transition point.^{2,3}

In supercooled liquid crystals, some spectroscopic studies^{4–14} on solid-state polymorphism have been reported, most of them being confined to the low-wavenumber region. Interestingly, in these studies,^{4–14} solid-phase polymorphism of only nematogens have been investigated and studies on supercooled smectogens are scarce. In recent work,¹⁵ a Raman study of supercooled terephthalidine-bis-decylaniline (TBDA) was made and a solid modification was reported at 47 K. Another system, terephthalidine-bis-butylaniline (TBBA), was investigated¹⁶ as early as 1976 to look for the low-temperature solid modifications through Raman measurements. A solid modification at 231 K was revealed by the variation of the peak position and linewidth with temperature for some lattice modes of TBBA. Fontana and Bini¹⁶ correctly pointed out that the measurement of the linewidths of the lattice modes cannot be performed precisely because of a relatively large background and weak Raman intensities. Some specific Raman modes are sensitive to order parameters^{2,17} in liquid crystalline systems. When these Raman-sensitive modes are sharp and strong, a precise analysis of linewidth variation can be made. Terephthalidine-bis-heptylaniline (TB7A), which belongs to the same homologous series as TBBA and TBDA and falls in between the two, in terms of alkyl chain length, is an interesting system to look for the solid modification. The

*Correspondence to: B. P. Asthana, Department of Physics, Banaras Hindu University, Varanasi 221005, India.
E-mail: bpasthana@rediffmail.com

Contract/grant sponsor: Alexander von Humboldt-Stiftung.

†Present address: Department of Physics, Rajendra College, Jai Prakash University, Chapra 841301, India.

chain length plays an important role for liquid crystal phase stabilization.^{2,12,13,15–17} In a recent comparative study¹⁸ of three systems of the same series, TBBA, TB7A and TBDA, where the Schiff-base core is the same, but the lengths of the alkyl chains are different, the importance of chain length was clearly pointed out. In the present work, we tried to look into the low-temperature dynamics of TB7A similar to that in TBDA.^{19,20} In order to understand the dynamics, we selected a representative band at $\sim 1165\text{ cm}^{-1}$, which clearly exhibits distinct spectral changes when the system undergoes a solid modification.

EXPERIMENTAL

Raman spectra were recorded using a Spex 1404 double monochromator (with a grating having $1800\text{ lines mm}^{-1}$) equipped with a charge-coupled device (CCD) detector. Radiation of 514.5 nm from an argon ion laser was used as the excitation source. The power on the sample was 5 mW . The sample of TB7A was kept in a capillary tube sealed at both ends. The later was kept in the sample compartment of a closed-cycle helium cryocooler. Vacuum of the order of 10^{-6} bar was achieved before cooling of the sample was started. The Raman scattered signal was collected in backscattering geometry using a microscope and focused on to the entrance slit of the spectrometer by a focusing lens. Commercially available software (MAPS V.20 from Photometrics) was used.

During all measurements, the entrance slit was kept constant at $100\text{ }\mu\text{m}$. Since the present study was aimed at analyzing precisely linewidth data, the instrumental slit function was also measured at the same slit setting to eliminate any effect of slit function on the measured linewidth. In order to measure the instrumental slit function, the laser beam was directed on to the slit of the spectrometer using a diffused reflector attenuating the laser intensity to a desired low level so as to permit the CCD to read the complete laser line profile without becoming saturated. The actual linewidth of the laser line was small and the width of the recorded laser line profile was obviously due to slit opening only. Thus the FWHM of the laser line profile, which turned out to be 0.72 cm^{-1} , was taken as the parameter S and was used to correct the measured linewidths for the instrumental slit function, similar to earlier studies.^{17–21} Some representative Raman spectra recorded in the region $1145\text{--}1205\text{ cm}^{-1}$ at seven different temperatures in the range $10\text{--}298\text{ K}$ are presented in Fig. 1.

RESULTS AND DISCUSSION

The structural formula of TB7A is shown in Fig. 2. X-ray studies^{20,22} on some systems of the terephthalidine-bis-alkylaniline (TBAA) series revealed that the compounds of TBAA homologous series crystallize in a c -centered monoclinic lattice with twofold symmetry along the b -axis and the molecular orientation along the c -axis. The length

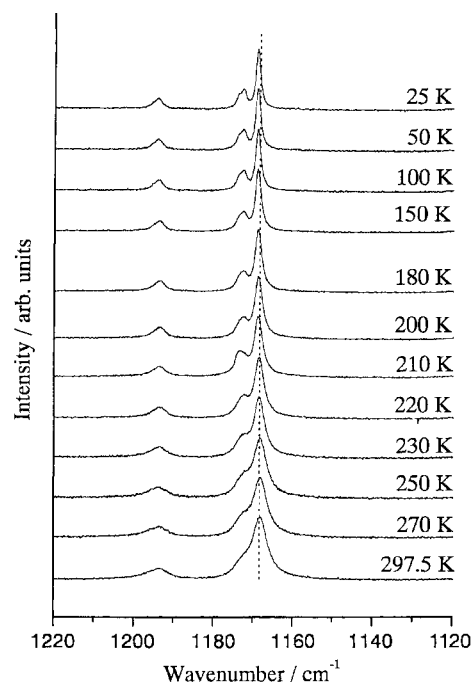


Figure 1. Raman spectra of TB7A in the region $1145\text{--}1205\text{ cm}^{-1}$ at 12 temperatures in the range $25\text{--}297.5\text{ K}$.

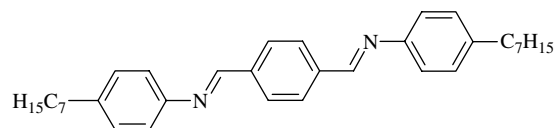
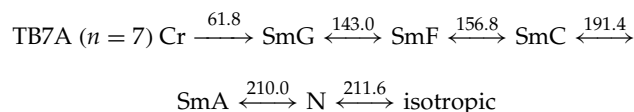


Figure 2. Molecular structure (schematic of the geometrical arrangement) of the atoms in the liquid crystalline system TB7A.

along the c -axis is approximately half of the molecular length. The phase diagram above room temperature which includes the liquid crystalline phase has been reported^{1,20} and is as follows:



However, the solid modification studied in this work has not been reported, to the best of our knowledge. From this configuration, it is clear that the molecular length stretches towards the c -axis and a layer is formed along the b -axis; the b -axis, apart from being a twofold axis, is also backbone staggered. Hence the most favorable configuration is that in which the ring planes are oriented along the $a\text{--}c$ plane. In such a situation, chains of the neighboring molecules will be close along the c -axis, but the rings of the two molecules belonging to different layers will be still closer along the b -axis.

The Raman spectra of TB7A as shown in Fig. 1 have certain striking features. The band at $\sim 1165\text{ cm}^{-1}$ has a distinct shoulder towards higher wavenumber at $\sim 1170\text{ cm}^{-1}$ at room temperature (298 K). On lowering the temperature, the shoulder starts to develop as a new band between 200 and 225 K. However, the development of this band is slow, as was the case with TBDA.¹² On lowering the temperature further, the new band also starts to show a shoulder at $\sim 1171\text{ cm}^{-1}$ around 175 K. At first glance, it may appear that splitting of the band, first into two and then into three bands, on lowering the temperature is simply due to line narrowing at lower temperatures leading to separation of two Raman line profiles which were overlapping at higher temperatures. Of course, on lowering the temperature, the reorientational contribution to the linewidth will reduce, leading to the band narrowing, which may be assumed to be more or less same for all bands. If this were the case, one might expect the intensity ratio of the main band to the new band to remain constant at all temperatures.

The measured spectra were analyzed at all temperatures using Spectra Calc. The observed spectra in the region $1160\text{--}1180\text{ cm}^{-1}$ were fitted to two profiles up to 200 K and to three profiles at and below 175 K. The integrated intensities of the different components were determined precisely at each temperature. The laser power, scattering geometry, sample position, position of the spectrometer grating and recording time were the same for all spectra. Since it is very difficult in Raman spectroscopy to measure absolute intensities, we calculated the ratio of integrated intensities of the 1165 and 1170 or/and 1171 cm^{-1} bands. In order to increase the accuracy in the intensity parameters, we concentrated only on single window spectra. The ratio of integrated intensities of the main band and the side band are plotted as a function of temperature in Fig. 3. The aforesaid

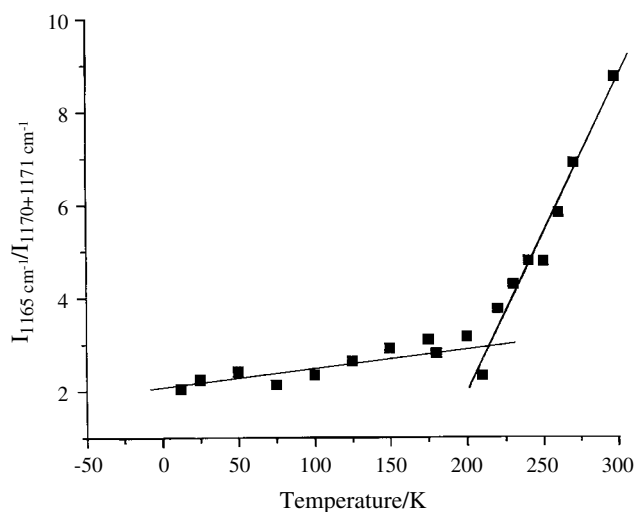


Figure 3. Ratio of the integrated intensity of the main band at $\sim 1165\text{ cm}^{-1}$ to the side band at $1170/1171\text{ cm}^{-1}$ plotted as a function of temperature (K).

intensity ratio drops drastically from 8.76 at 297.5 K to 3.76 at 220 K (see Table 1 and Fig. 3) and thereafter dips down to a minimum value at 210 K. The variation of the intensity ratio between 200 and 10 K is slow. The very rapid change in the intensity ratio between room temperature and 210 K and a much slower change between 200 to 10 K is unusual and cannot be explained as a simple narrowing effect of the spectral line.

In the intensity vs temperature plot, two aspects are worth considering: (i) the slope of the curve is different above 210 K to that below 200 K and (ii) a dip appears at 210 K. Both aspects signify a phase transition at 210 K. Furthermore, the different slopes in the two regions mentioned above also signify that it is a mixed-order transition. The experimental observations of Carabatos and Becker²³ indicates that on approaching the transition temperature T_C from above, the intensity of the reference mode is enhanced by increasing and fluctuating ordered clusters in the partially disordered phase. The intensities of the 1070 and/or 1071 cm^{-1} bands in the present study are increased with respect to the intensity of the main band at 1165 cm^{-1} band, which is in accordance with what Carabatos and Becker²³ observed. The variation of intensities of the modes associated with phenyl ring as a function of temperature has been used to determine the phase sequence in 10 FHBBM7*, where one phase, which was hitherto undetected by DSC, was detected in a Raman study²⁴ through intensity variations. Raman intensity has not only proved to be a reliable parameter for characterizing transitions in liquid crystalline materials,^{3–15} but has also been used to investigate and characterize phase transitions in liquid crystalline materials in several studies.^{18,24,25} The phase transitions have mostly been characterized by integrated intensity data, but we concentrated more on Raman linewidth data, which are obviously more precise, to investigate the transitions. However, the variations of integrated intensities were also analyzed and it also revealed fairly accurate information on transitions as reported in earlier studies.^{15–17} In some of our earlier studies^{15,17} on TBDA also, both linewidths and integrated intensities were used to characterize phase transitions in liquid crystalline materials.

In order to examine the phenomena leading to the drastic changes elaborated above, we determined precisely the linewidth changes of the ~ 1165 and $\sim 1191\text{ cm}^{-1}$ bands, which were recorded in a single window. These two bands are sufficiently strong with sharp peaks which enable one to measure the linewidth and peak position precisely. The linewidths were first obtained by fitting the measured profile in the $1130\text{--}1220\text{ cm}^{-1}$ range to three/four bands, as the case may be, using Spectra Calc, and were subsequently corrected for the instrumental slit function.²⁶ The corrected values of the linewidths are given in Table 1 for all the component bands. The linewidths thus obtained are fairly precise and may have an estimated error of $\sim 0.05\text{ cm}^{-1}$.

Table 1. Observed vibrational wavenumbers (cm⁻¹) and bandwidths of Raman bands (cm⁻¹) in the wavenumber region 1120–1220 cm⁻¹ at different temperatures

Temperature (K)	1165 cm ⁻¹ band		1170 cm ⁻¹ band		$I_{1165}/I_{1170+1171}$	1191 cm ⁻¹ band	
	ν	$(\Delta\nu_{1/2})_R$	ν	$(\Delta\nu_{1/2})_R$		ν	$(\Delta\nu_{1/2})_R$
297.5	1167.4	4.58	1172.0	4.51	8.76	1193.5	7.02
270	1167.4	4.25	1171.9	4.27	6.90	1193.5	6.48
260	1167.5	4.10	1171.8	4.46	5.83	1193.6	6.45
250	1167.5	3.95	1171.8	4.25	4.78	1193.5	6.13
240	1167.6	3.64	1172.0	3.97	4.79	1193.3	5.46
230	1167.7	3.30	1172.1	3.71	4.28	1193.3	5.30
220	1167.7	2.89	1172.1	3.44	3.76	1193.1	4.39
210	1168.0	2.61	1172.6	3.29	2.33	1193.2	4.14
200	1168.0	2.39	1172.2	3.13	3.16	1193.1	3.82
180	1168.0	2.08	1172.2	3.03	2.80	1193.2	3.49
175	1166.3	1.97	1169.8	1.81	3.10	1191.3	3.27
150	1166.5	1.73	1171.1	2.32	2.91	1191.4	3.00
			1170.0	1.70			
125	1166.7	1.55	1171.3	2.04	2.64	1191.8	2.78
			1170.2	1.58			
100	1166.7	1.48	1171.5	1.84	2.34	1191.8	2.73
			1170.2	1.54			
75	1166.8	1.36	1171.6	1.77	2.14	1192.0	2.59
			1170.3	1.43			
50	1166.8	1.36	1171.5	1.58	2.41	1192.0	2.59
			1170.3	1.43			
25	1166.8	1.26	1171.6	1.58	2.24	1192.0	2.51
			1170.3	1.33			
12	1166.8	1.13	1171.6	1.48	2.04	1192.1	2.38
			1170.3	1.23			
			1171.6	1.41			

The temperature dependence of the linewidths was examined in some detail using Rakov's relationship:²⁷

$$A = A_0 + B \exp(-C/kT) \quad (1)$$

where A is the corrected linewidth, T is the absolute temperature and k is the Boltzmann constant. The corrected linewidths were fitted to Eqn (1) in two different temperature ranges, 10–200 K and 210–297.5 K, for both Raman bands at ~ 1165 and ~ 1191 cm⁻¹. The values of the parameters A_0 , B and C were obtained in each case. Once these parameters are known, Eqn (1) can be written in a slightly different form as

$$\ln(A - A_0) = \ln B - C/kT \quad (2)$$

A plot of $\ln(A - A_0)$ vs $1/T$ for the two temperature ranges resulted into two almost parallel lines, as shown in Figs 4 and 5 for the Raman bands at ~ 1165 and ~ 1191 cm⁻¹, respectively. An abrupt discontinuity clearly exhibits a phase transition. The mid-points of the dotted lines in Figs 4 and 5 joining the two almost parallel straight lines corresponding

to two different ranges yield the value $1/T = 0.0476$, which gives the transition temperature as $T = 210.1$ K.

The variation of intensity ratio with temperature also shows a transition at the same temperature as above. It should be noted that a similar transition in TBDA has been reported¹⁵ at a much lower temperature, ~ 47 K, where a similar type of splitting was observed in the C–H out-of-plane wagging mode at ~ 975 cm⁻¹. In addition to this band, a band at ~ 1195 cm⁻¹ in TBDA (in this case at ~ 1191 cm⁻¹) also showed splitting, which was attributed to the ring–N bending mode. The band at ~ 975 cm⁻¹, which was used to characterize the low-temperature phase transition¹⁵ in TBDA, was fairly weak and a detailed study of the temperature dependence of the linewidth was not feasible. In the present study, since the characteristic band at ~ 1165 cm⁻¹ is very sharp and intense, its linewidth could be determined precisely and the temperature dependence shows a systematic variation. However, we consider that there may be a variation of about 2–3 K in the transition temperature.

One has to take into account an important aspect, namely that TBBA, TB7A and TBDA have same core and differ

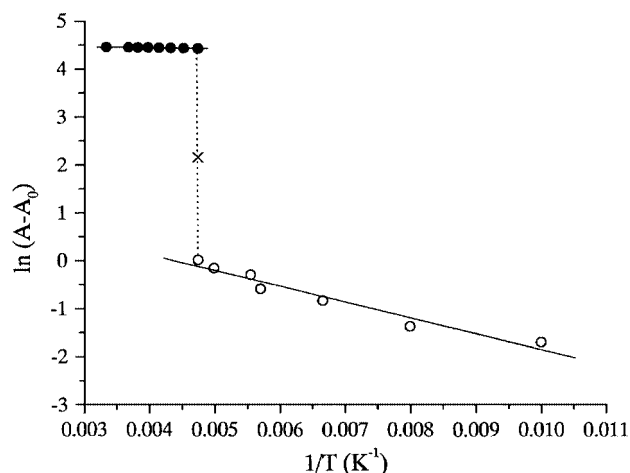


Figure 4. Plot of $\ln(A - A_0)$ vs $1/T$ for the Raman band at $\sim 1165 \text{ cm}^{-1}$. A is the corrected linewidth, and A_0 is the parameter obtained from the fitting of the linewidth data to Rakov's equation.²⁷

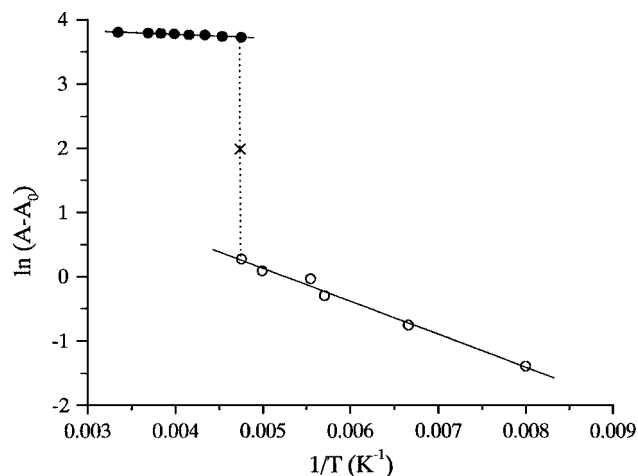


Figure 5. Same as in Fig. 4 for the Raman band at $\sim 1191 \text{ cm}^{-1}$.

only in the length of the alkyl chain. The role of the chain length in stabilizing liquid crystalline phases is significant. In TBBA, with only four C-atoms in the alkyl chain, a solid modification was reported¹⁶ at 231 K on the basis of linewidth variation with temperature for a low-wavenumber mode (at 260 cm^{-1}). In a more recent study,¹⁵ a solid modification was reported at 47 K in TBDA, with 10 C-atoms in the alkyl chain. In TB7A, with seven C-atoms in the alkyl chain i.e. between four and 10, the transition takes place at 210 K. The transitions in all the three homologues (TBBA, TB7A and TBDA) are essentially similar in nature, but they occur at different temperatures because of difference in alkyl chain length. In the case of the solid modification, an odd–even effect¹ does not seem to be operative as far as the transition temperature is concerned and the transition temperature decreases with increasing chain length.

The changes in linewidth with temperature can be explained by employing the concept of rotational Brownian motion. In molecular crystals there are two broadening mechanisms, namely anharmonic interactions and rotational Brownian motion. The first mechanism leads to a linear increase in linewidth with temperature, whereas the second mechanism, which is dependent on jump activation energy, leads to an exponential increase. The variation of linewidth of the 260 cm^{-1} band with temperature in the case of TBBA¹⁶ could be explained by taking into account the fact that in the low-temperature phase, TBBA molecules are fixed and intermolecular vibrations are increasingly damped by anharmonic coupling. As the transition temperature is approached, the rotational jump mechanism becomes active and triggers the transition and the linewidth increases rapidly at transition point. In the new phase the structure is changed and the rotational relaxation time stops decreasing exponentially but the hindered rotational motion still persists and the linewidth varies with temperature, but at a slower rate.

TBDA, which consists of a staggered core connected by Schiff base linkages and long saturated aliphatic chains on both sides of the core, assumes a metastable configuration of the phenyl rings, resulting in a decreased inter-planar spacing between different molecules and thereby increased steric hindrance in the low-temperature metastable phase. This phenomenon leads to a much closer molecular packing of TBDA molecules. As a result of increased interaction between the different molecules of the hexagonal packing, splitting of the Raman modes takes place.

The results for the linewidth variation can be viewed in the light of terminal moieties in a liquid crystalline material.¹ The effect of hydrocarbon terminal moieties, especially the number of the C-atoms in the alkyl chain is crucial in generation of specific types of liquid crystalline phase and the physical properties also depend on these moieties. The odd–even effect in the $\text{C}_n\text{H}_{2n+1}$ moiety is well known to affect the properties of liquid crystalline systems. In the present study, there was an opportunity to study this effect in detail since the n value in the moiety is even in TBBA and TBDA and odd in TB7A. The linewidth variation of the $\sim 1165 \text{ cm}^{-1}$ band varies from 3.5 to 2.5 cm^{-1} on going from 250 to 10 K in TBBA ($n = 4$), whereas in case of TB7A ($n = 7$) this variation is large, from 3.68 to 0.66 cm^{-1} in the same temperature range. It is pertinent to note that TBDA ($n = 10$) also showed a small variation in a manner similar to TBBA. This result is an obvious demonstration of the odd–even effect due to the number of C-atoms in the alkyl chain. The observed excitation profile in the pre-resonance region in TBBA, TB7A and TBDA also shows a similar effect where TBBA and TBDA behave alike and TB7A shows an abrupt enhancement.

Acknowledgements

One of us (R.K.S.) is grateful to the Alexander von Humboldt-Stiftung for a fellowship and B.P.A. thanks the AvH-Stiftung for

supporting his visits to the University of Würzburg. S.S. thanks the Stiftung Stipendien-Fonds des Verbandes der Chemischen Industrie and the Bundesministerium für Bildung und Forschung. The authors are grateful for support under the DST-DAAD Project Based Personnel Exchange program also. The authors are also grateful to Mr Sunil K. Srivastava for help in preparing the manuscript.

REFERENCES

- Gray GW. In *Physical Properties of Liquid Crystals*, Demus D, Goodby J, Gray GW, Spiess H-W, Vill V (eds). Wiley-VCH: Weinheim, 1999; 1.
- Nollman M, Etchegoin P. *Phys. Rev. E* 2000; **61**: 7235.
- Nollman M, Etchegoin P. *Phys. Rev. E* 2000; **61**: 5345.
- Cavarota F, Fontana MP, Kirov N. *Mol. Cryst. Liq. Cryst.* 1997; **34**: 241.
- Kirov N, Fontana MP, Cavarota F. *Mol. Cryst. Liq. Cryst.* 1979; **54**: 207.
- Kirov N, Cavarota F. *Spectrosc. Lett.* 1978; **11**: 589.
- Sciensinska E, Sciensinski J, Twardoski J, Janik JA. *Mol. Cryst. Liq. Cryst.* 1990; **27**: 125.
- Pogorelov VYe, Strela-Llopis IB. *Mol. Cryst. Liq. Cryst.* 1995; **265**: 237.
- Arendt P, Koswig HD, Reich P, Pilz W. In *Advances in Liquid Crystal Research and Application*, Bata L (ed.). Pergamon Press: Oxford, 1980; 341.
- Dolganov VK, Gal M, Kirov N, Rosta L, Sheka EF. *J. Mol. Struct.* 1984; **114**: 325.
- Jain PC, Kafle SRS. *Mol. Cryst. Liq. Cryst.* 1985; **29**: 199.
- Strela-Llopis I, Pogorelov V, Bukalo V, Astashkin Y. *Mol. Cryst. Liq. Cryst. Sci. Technol.* 1998; **320**: 45.
- Pogorelov V, Strela-Llopis I, Pinkevich I, Bukalo V. *Mol. Cryst. Liq. Cryst. Sci. Technol. A* 1997; **301**: 377.
- Ratchkevitch VS, Yakovenko SYE. *Liq. Cryst.* 1993; **15**: 591.
- Dash SK, Singh RK, Asthana BP, Alapati PR, Verma AL. *J. Raman Spectrosc.* 1999; **30**: 81.
- Fontana MP, Bini S. *Phys. Rev. A* 1976; **14**: 1555.
- Singh RK, Singh SC, Dash SK, Asthana BP, Verma AL. *J. Raman Spectrosc.* 2000; **31**: 543.
- Dash SK, Singh RK, Alapati PR, Verma AL. *Mol. Cryst. Liq. Cryst.* 1997; **319**: 147.
- Dash SK, Singh RK, Alapati PR, Verma AL. *J. Phys. Condens. Matter* 1997; **9**: 7809.
- Dash SK, Singh RK, Alapati PR, Verma AL. *Liq. Cryst.* 1998; **25**: 459.
- Tandon P, Neubert R, Wartewig S. *J. Mol. Struct.* 2000; **526**: 49.
- Doucet J, Levelut AM, Lambert M. *Phys. Rev. Lett.* 1972; **32**: 301.
- Carabatos C, Becker P. *J. Raman Spectrosc.* 1997; **28**: 663.
- Benattar JJ, Doucet J, Lambaert M, Levelut AM. *Phys. Rev. A* 1979; **20**: 2505.
- Shao Y, Zerda TW. *J. Phys. Chem. B* 1998; **102**: 3387.
- Singh RK, Singh SN, Asthana BP, Pathak CM. *J. Raman Spectrosc.* 1994; **25**: 423.
- Singh RK, Asthana BP, Bist HD. *Chem. Phys. Lett.* 1993; **209**: 390.