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M. Sidir[a]; R. Farhi[a]
[a] Laboratoire de Physique de la Matière Condensée, Université de Picadie Jules Verne 33, Amiens Cedex, France

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On the determination of orientational order parameters in liquid crystals from Raman scattering: CB9 revisited

by M. SIDIR and R. FARHI*
Laboratoire de Physique de la Matière Condensée,
Université de Picadie Jules Verne 33, rue Saint-Leu 80039 Amiens Cedex, France

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Orientational order parameters $\overline{P_2}$ and $\overline{P_4}$ have been determined for the nematic and smectic phases of CB9 (4-nonyl-4′-cyanobiphenyl) from Raman scattering intensity measurements. The derivations of $\overline{P_2}$ and $\overline{P_4}$ from Raman intensities have been made using uniaxial or biaxial Raman tensor assumptions, but the orientational distribution function is well peaked at $\beta = 0$ only when a uniaxial tensor is used. The opposite choice of a biaxial Raman tensor and its consequences are discussed. Negative values of $\overline{P_4}$ found in our study are shown not to affect seriously the orientational distribution. Furthermore, it is shown that such negative values, if not explained by microscopic theories, are allowed when a Landau-type phenomenological approach is used. Nevertheless, it is once more emphasized that local field effects should be taken into account.

1. Introduction

Nematic liquid crystals can be considered, as a first approximation, as sets of long molecules the long axes of which are, on average, parallel to a common direction **n**.

For a uniaxial liquid crystal system made of cylindrically shaped molecules, the probability density function $f(\alpha, \beta, \gamma)$ giving the orientational distribution of these molecules with respect to the director **n** depends only upon the Euler angle β and can be expanded in an even series of Legendre polynomials:

$$f(\beta) = 4\pi^2 f(\alpha, \beta, \gamma) = \sum_{L_{\text{even}}=0}^{\infty} \frac{2L+1}{2} \overline{P_L} P_L(\cos\beta) \qquad (1)$$

where $f(\beta)$ characterizes the orientation of the molecules through the moments of $\cos\beta$. It is obviously normalized to unity. For a completely disordered (isotropic) phase, $\overline{P_0} = 1$ and $\overline{P_{L\neq 0}} = 0$. On the contrary, $\overline{P_L} = 1$ for all L in a perfectly ordered phase. For the intermediate cases of nematic or smectic A liquid crystals, $\overline{P_2}$ is expected to be less than unity. Equation (1) shows that a perfect knowledge of $f(\beta)$ needs the determination of all the $\overline{P_L}$s. Unfortunately, most of the experimental techniques are limited to measurements of $\overline{P_2}$ only. Because Raman intensities are proportional to the square of the second rank, Raman tensor terms, their measurements give access to the mean fourth power of $\cos\beta$, i.e. to $\overline{P_4}$. Raman spectroscopy is thus expected to give a better approach to the orientational distribution function than other experiments.

Since the pioneering work of Jen *et al.* [1–3] about twenty years ago, several papers have been devoted to the determination of $\overline{P_2}$ and $\overline{P_4}$ orientational order parameters in nematic liquid crystals using Raman spectroscopy [4–9]. Nevertheless, some questions remain open as to the results obtained from this technique. More particularly, negative values are often found for $\overline{P_4}$, such that the maximum of the orientational distribution function is tipped away from $\beta = 0$ in the nematic phase.

Dalmolen *et al.* [10], suggested that such an anomalous behaviour for a nematic phase could be related to the head-to-tail dimerization of molecules such as the alkylcyanobiphenyls (CB*n*). Another explanation has been given by Luckhurst and Yeates [11] who introduced a potential for the molecules which is zero between β_0 and $-\beta_0$, and infinite beyond these angles. This interpretation was proposed by Constant and Decoster [8] in order to explain the negative values they found for $\overline{P_4}$. It should be noticed that the orientational order parameters determined for CB*n* by these last authors depend significantly upon the internal vibration (C≡N or C–C biphenyl link), the Raman intensity of which they studied. Their work included the smectic A phase, in which $\overline{P_2}$ and $\overline{P_4}$ parameters saturate. No jump of the $\overline{P_2}$ orientational order parameter was detected, in spite of the expected first order character of the nematic–smectic A transition for such compounds (see below and [12]).

Finally, most of the authors have used a biaxial Raman tensor in their calculation of $\overline{P_2}$ and $\overline{P_4}$ from Raman intensity ratios. At first sight, this choice does not seem to be justified, since the isotropic rotation of the molecules around their long axes restores a cylindrical symmetry, and is not consistent with the expansion of the orienta-

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* Author for correspondence.

tional distribution function in terms of Legendre polynomials rather than more general spherical harmonics.

The relations between the Raman intensities, the terms of the local Raman tensor and the Euler angles have been extensively developed in the paper by Jen *et al.* [2]. Because of the geometry of the CB*n* molecule, one of the principal axes of the Raman tensors for the C≡N and C–C link bonds vibrations is directed along the long axis of the core of the molecule. For a uniaxial medium constituted by cylindrical molecules, these relations reduce to

$$\left.\begin{aligned}
A^{-2}\langle\alpha_{xx}^2\rangle &= \frac{1}{9}+\frac{3B}{16}+\frac{D}{18}+\frac{11D^2}{288}\\
&\quad+\left(\frac{B}{8}-\frac{D}{6}-\frac{5D^2}{48}\right)\langle\cos^2\beta\rangle\\
&\quad+\left(\frac{3B}{16}+\frac{3D^2}{32}\right)\langle\cos^4\beta\rangle,\\
A^{-2}\langle\alpha_{xy}^2\rangle &= \frac{B}{16}+\frac{D^2}{32}+\left(\frac{3B}{8}-\frac{D^2}{16}\right)\langle\cos^2\beta\rangle\\
&\quad+\left(\frac{B}{16}+\frac{D^2}{32}\right)\langle\cos^4\beta\rangle,\\
A^{-2}\langle\alpha_{yz}^2\rangle &= \frac{B}{4}+\frac{D^2}{8}\langle\cos^2\beta\rangle-\left(\frac{B}{4}+\frac{D^2}{8}\right)\langle\cos^4\beta\rangle,\\
A^{-2}\langle\alpha_{zz}^2\rangle &= \frac{1}{9}+\frac{B}{2}-\frac{D}{9}+\frac{D^2}{36}\\
&\quad-\left(B-\frac{D}{3}+\frac{D^2}{6}\right)\langle\cos^2\beta\rangle\\
&\quad+\left(\frac{B}{2}+\frac{D^2}{4}\right)\langle\cos^4\beta\rangle,
\end{aligned}\right\}\qquad(2)$$

with

$$A=1+a+b,\quad B=\frac{(a-b)^2}{4A^2}\quad\text{and}\quad D=\frac{2-a-b}{A}.\qquad(3)$$

In the above relations, the local Raman tensor has been assumed to be biaxial:

$$\bar{\bar{\alpha}}=\alpha_0\begin{pmatrix} a & 0 & 0\\ 0 & b & 0\\ 0 & 0 & 1\end{pmatrix}.$$

Four experimental determinations are thus needed to determine unambiguously *a*, *b*, $\overline{P_2}$ and $\overline{P_4}$, and the four depolarization ratios:

$$R_1=C_n\frac{\langle\alpha_{yz}^2\rangle}{\langle\alpha_{zz}^2\rangle},\quad R_2=\frac{\langle\alpha_{zy}^2\rangle}{C_n\langle\alpha_{yy}^2\rangle},\quad R_3=\frac{\langle\alpha_{yx}^2\rangle}{\langle\alpha_{xx}^2\rangle}$$

and

$$R_{\text{iso}}=\frac{I_\perp}{I_\parallel}$$

are a good set of independent determinations for this purpose. C_n is a correction factor to the refractive indices of the glass plates and the liquid crystal.

If, in addition, the Raman tensor is uniaxial (i.e. $b=a$), *B* cancels in the relations (3) and only three independent experiments are needed at each temperature. Because the determination of R_3 is subject to large uncertainties due to the less strong intensities scattered in the (*xx*) and especially (*xy*) geometries, and needs the preparation of homeotropic samples, R_1, R_2 and R_{iso} should be preferred. Nevertheless, in order to compare the results obtained assuming a biaxial or uniaxial Raman tensor, the whole set of four intensity ratios has been determined in our study.

2. Experimental

We have focused our study on the 4-alkyl-4′-cyanobiphenyls (CB*n*) for which many results have been already obtained [4–6, 8–10] and more particularly on the $n=9$ homologue which exhibits a smectic A phase between 42·6 and $T_{\text{S}_\text{A}\text{N}}=47{\cdot}5°\text{C}$, and a transition from nematic to isotropic at $T_{\text{NI}}=49{\cdot}4°\text{C}$. The Raman spectra of the C≡N vibration ($\sim 2230\,\text{cm}^{-1}$) and the C–C biphenyl link vibration ($\sim 1290\,\text{cm}^{-1}$) were recorded using a Dilor Z 24 Raman spectrometer associated with a cooled photomultiplier. The exciting light was the 514·5 nm line of a Spectra Physics argon laser, the power of which was monitored at less than 20 mW at the sample. The polarization of the incident light was chosen using a half-wave plate, and the scattered light was analysed through a sheet of polarizer, followed by another half-wave plate in order to compensate the intensity variations due to the transfer function of the spectrometer. The scattered light was collected using a long focal length ($f=135\,\text{mm}$) collection lens. The slits of the triple monochromator were selected to obtain a resolution of $2\,\text{cm}^{-1}$, which is significantly smaller than the width of the Raman lines studied. The cells were placed in a Linkam hot-stage the temperature of which was controlled within ± 0·1 K. This hot stage was set in a horizontal position and a backward scattering geometry was obtained using an intermediate mirror tilted at 45° from the horizontal incident laser beam.

Planar alignment of the samples was obtained by unidirectional rubbing of the cleaned glass plates, and homeotropic alignment by coating the plates with HTAB. The alignments were controlled using polarizing microscopy before and after the runs.

Finally, because long wavelength director fluctuations in nematics may be very important [13], it seemed necessary to perform experiments for various thicknesses. Constant and Decoster [8], using a Raman microprobe, reported spurious effects on the incident and scattered light polarizations due to these fluctuations for thicknesses larger than 50 μm. On the contrary, Jen *et al.* [2], in their

Calculated parameters *a* and *b* (biaxial Raman tensor) and R_3 (uniaxial Raman tensor) for the nematic phase of CB9.

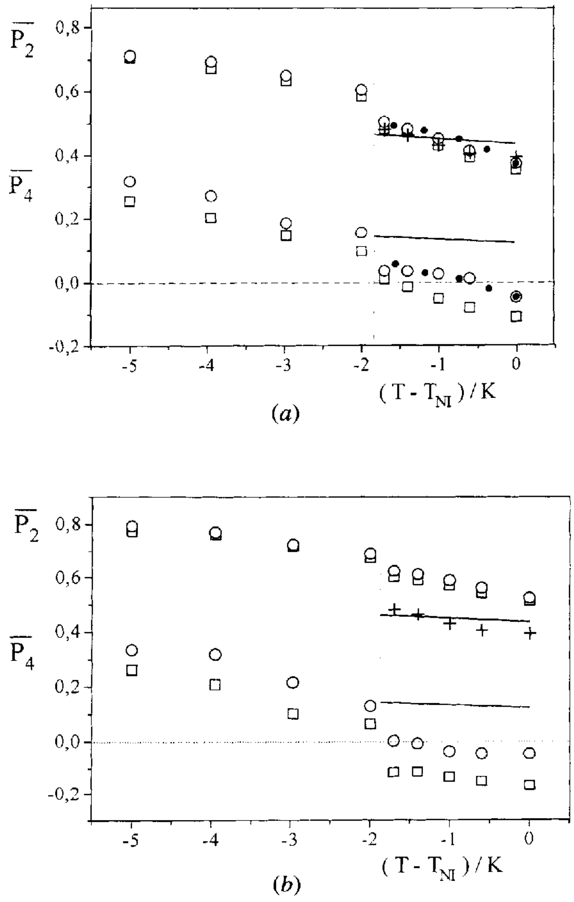
Bond	$T_{NI}-T$	*a*	*b*	$R_{3_{exp}}$	$R_{3(a=b=0{\cdot}055)}$
C≡N	0	− 0·10	0·24	0·31	0·22
	0·6	− 0·08	0·24	0·29	0·20
	1·0	− 0·09	0·25	0·30	0·18
	1·4	− 0·07	0·22	0·28	0·17
	1·7	− 0·10	0·23	0·31	0·17
C–C (biphenyl link)	0	− 0·03	0·08	0·30	0·25
	0·6	− 0·03	0·08	0·29	0·23
	1·0	− 0·04	0·07	0·28	0·22
	1·4	− 0·03	0·07	0·28	0·20
	1·7	− 0·03	0·07	0·28	0·20

measurements of the effects of thicknesses on R_1 and R_2, showed that these ratios very almost linearly until thicknesses of about 150 μm and tend to saturate above this value. Moreover, anchoring effects are suspected to play an increasing role in thin samples. Our experiments have been made for two different thicknesses (50 μm and 23 μm) which are expected to lie in the linear region, and results extrapolated to zero. A strong increase of the R_1 ratio for samples 50 μm thick has been observed for the nematic phase compared with that for the 23 μm cells, as observed previously [2].

3. Results

Integrated intensity ratios were corrected for the refractive indices factor C_n using the data given by Karat and Madhusudana [14]. Unfortunately, these authors did not report any value for the refractive index of CB9, but it can be seen from their work that no large variation is expected for C_n when going from the $n=8$ to the $n=9$ homologue. The calculation of a, b, $\overline{P_2}$, $\overline{P_4}$ from R_1, R_2, R_3 and R_{iso} for a biaxial tensor was done using the procedure given by Miyano [4]: using the set of R_1, R_2 and R_{iso} determined experimentally at each temperature, an infinite set of values for the couple (a, b) can be defined, from which R_3 is calculated and compared to the experimental result. In the case of a uniaxial Raman tensor a ($= b$) is determined from R_{iso}, and $\overline{P_2}$ and $\overline{P_4}$ are obtained in a straightforward way from R_1 and R_2. The measured values of R_{iso} were found to be 0·276 for the C≡N bond, in agreement with published data [2, 4, 9, 10], and 0·405 for the biphenyl link in the isotropic phase. We have reported in the table the results of our calculations of *a* and *b* at different temperatures in the nematic phase, together with calculated R_3 in the case of a uniaxial tensor for comparison with experimental determinations. Taking into account the experimental errors associated with the determination of R_3 (low ratios of intensities followed by an extrapolation to zero thickness), the disagreement between experimental and calculated values of R_3, at least for the C–C biphenyl link, is not very important and does not allow one to select unambiguously a biaxial rather than a uniaxial tensor. Furthermore, the biaxiality of the Raman tensor would be rather large in both cases, as already mentioned by Miyano [4]. Finally, this biaxiality does not seem to be consistent with the hypothesis of ergodicity and of cylindrical molecules constituting a uniaxial medium (Wigner matrices with $m = m' = 0$ [2]) which has been extensively used in all previous Raman studies (see next section). Consequently, these sets of data must be considered with some circumspection, since *a* and *b* are not obtained directly, and additional tests of coherence are needed, such as reported below.

We have plotted in figure 1 (*a*) and (*b*) the values obtained for $\overline{P_2}$ and $\overline{P_4}$ versus temperature in the case of uniaxial and biaxial Raman tensors, respectively, together with the data for $\overline{P_2}$ derived by Mitra [15] from the birefringence results of Bunning *et al.* [16], the results obtained by Dalmolen *et al.* [10] assuming a *biaxial*

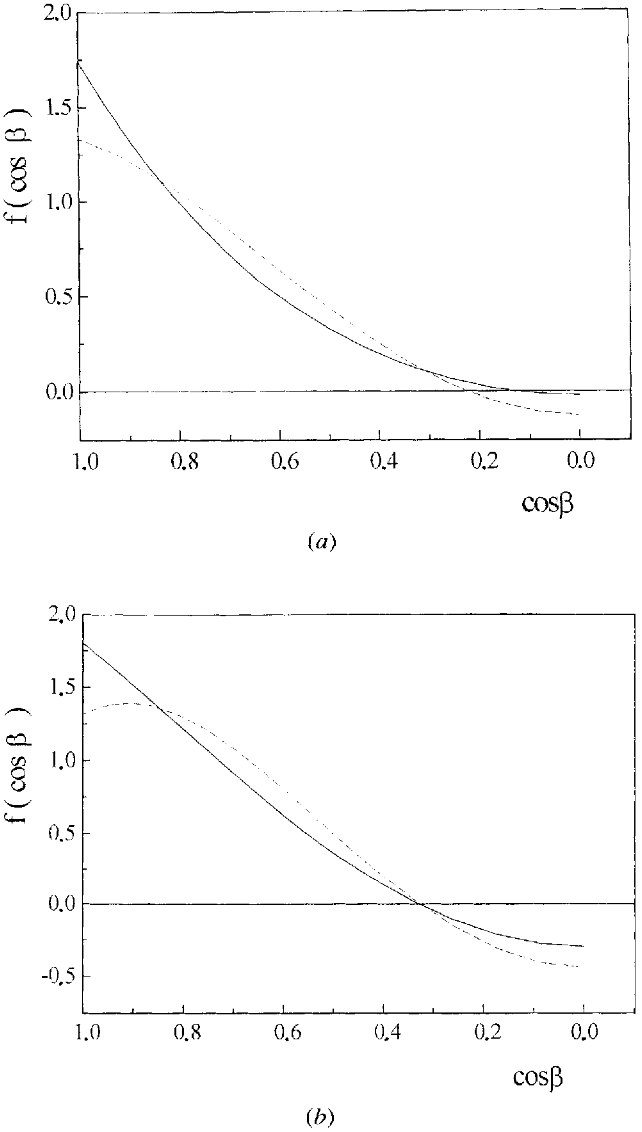


(*a*)

(*b*)

Figure 1. Orientational order parameters $\overline{P_2}$ and $\overline{P_4}$ as a function of temperature resulting from the use of a uniaxial (*a*) and a biaxial (*b*) Raman tensor: (○) our results for C–C biphenyl link and (□) C ≡ N vibrations; (+) results from Mitra [15, 16]; (●) results from Dalmolen *et al.* [10]; (——) Maier Saupe theory.

Raman tensor, and the predictions given by the Maier–Saupe (MS) theory [17]. It can be seen from these figures that our results for $\overline{P_2}$ are close to those given by Mitra [15] and deduced from the MS theory only if we consider a uniaxial Raman tensor. Furthermore, the values we have obtained are quite similar for $\overline{P_2}$ and do not differ so much for $\overline{P_4}$, whatever the vibration studied (C≡N or C–C biphenyl link). Finally, both figures show steps for $\overline{P_2}$ and $\overline{P_4}$ at the nematic to smectic A transition. These two last observations are not in agreement with what is reported by Constant and Decoster for CB8 [8]. It should be noticed that negative values have been found for $\overline{P_4}$ in the nematic phase, as already observed for CBn by many authors [4, 6, 8–10]. It can be easily seen that our pairs of $\overline{P_2}$, $\overline{P_4}$ values verify the Schwartz's inequality criterion [2].



(a)

(b)

Figure 2. Orientational distribution function $f(\cos\beta)$ at T_{NI}–$T = 1$ K (nematic phase) when a uniaxial (a) or a biaxial (b) Raman tensor is used: (——) C–C biphenyl link vibration (– – – –) C≡N vibration.

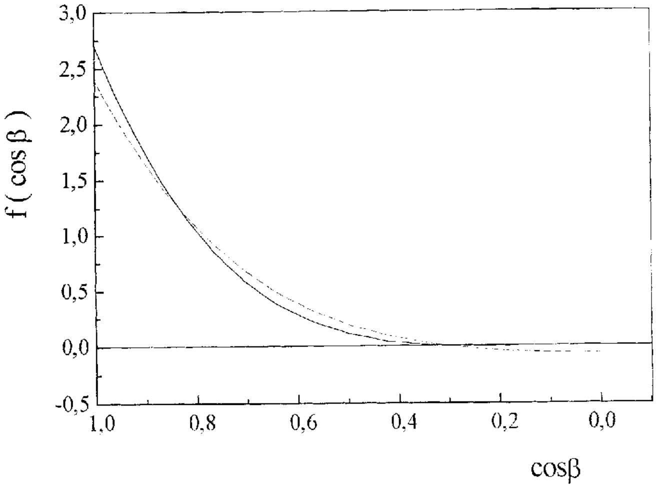


Figure 3. Orientational distribution function $f(\cos\beta)$ in the smectic A phase for T_{NI}–$T = 2$ K: (——) C–C biphenyl link vibration; (– – – –) C≡N vibration. Only a uniaxial Raman tensor has been considered.

The orientational distribution function $f(\beta)$ can be calculated from $\overline{P_2}$ and $\overline{P_4}$ data and equation (1) when neglecting higher order terms. The results are shown in figures 2 (a) and (b) for uniaxial and biaxial Raman tensors, respectively, at a temperature T such that T_{NI}–$T = 1$ K, i.e. in the nematic phase of CB9. If the Raman tensor is considered as uniaxial, this truncated distribution function is well peaked at $\beta = 0$, even if it looks flatter for the C≡N bond, hinting at more important fluctuations of this terminal part of the molecule. On the contrary, if a biaxial tensor is chosen for the calculations, $f(\beta)$ remains peaked at $\beta = 0$ for the C–C link bond, but is tipped away from $\beta = 0$ for the C≡N vibration. This is obviously related to the significantly negative values found for $\overline{P_4}$ in the latter case.

In the smectic A phase, the orientational distribution function is consistent with a far more ordered system, as can be seen from figure 3 where only a uniaxial Raman tensor has been considered.

4. Discussion

As already mentioned in the introduction to this work, most of the results aiming at the determination of orientational order parameters using Raman spectroscopy have been obtained assuming a biaxial Raman tensor for vibrations involving atoms of the core of the molecules. In a molecular frame attached to each molecule, this assumption is valid. As discussed by Miyano [4], a deviation from uniaxiality is expected for the C≡N bond, because of the interactions with the π orbitals of the benzene ring, and for the C–C biphenyl link, because the interplanar angle of the two benzene rings is not 90°. These considerations no longer hold for an isotropically rotating molecule. Hindered rotation has been considered by Jen *et al.* [2] in their original paper, by Miyano [4] and by Seeliger *et al.* [7]. Obviously an expansion involving Legendre polynomials $P_L(\cos\beta)$ is not sound in this case, and associated Legendre polynomials P_L^m should be used. This is equivalent to a renormalization of the $P_L(\cos\beta)$ and corresponding corrections have been calculated by the above mentioned authors [2,4,7]. Nevertheless, these corrections do not seem to improve significantly the results. Furthermore, a rather strong biaxiality of the Raman tensor has been found in some cases [4,7,8], and the need for the introduction of a biaxial Raman tensor in the calculations is neither clearly demonstrated nor physically supported. For instance, Miyano pointed out [4] that the use of an uniaxial tensor gives for CB5 results for $\overline{P}_2$ in fairly good agreement with those obtained from birefringence measurements. An attempt to estimate rotational diffusion times from a bandwidth analysis was found to be unsuccessful, since no additional broadening was observed, within experimental accuracy, when comparing polarized and depolarized spectra. Following Miyano [4], this could be explained either by very large relaxation times for rotation compared with translation or by uniaxial symmetry of the Raman tensor as well. A Raman study performed by Witko [18] on alkoxyazoxybenzenes gave rotational relaxation times of about 10^{-11} s and corresponding broadening near 1 cm^{-1}. Due to their molecular conformation, cyanobiphenyls are expected to be characterized by smaller or at least equal rotational relaxation times. No broadening has been observed either in careful Raman experiments on CB9 [19] or in quasi-elastic neutron scattering profiles of CB5 [20], which strongly suggests a uniaxial symmetry of the Raman tensor.

The comparison of our results obtained for a uniaxial (see figure 1 (*a*)) and a biaxial (see figure 1 (*b*)) Raman tensor shows that the former case only gives good agreement for $\overline{P}_2$ with the MS theory and with the results obtained from birefringence measurements [15, 16] and from Raman intensities assuming a *biaxial* tensor [10]. For a biaxial tensor, the discrepancy is far beyond the experimental uncertainties in the determination of $\overline{P}_2$. Furthermore, in the latter case, a maximum in $f(\cos\beta)$ is observed at about $\beta = 24°$ as far as the C≡N stretching vibration intensities are concerned. This 'anomalous' behaviour is clearly related to the strong negative values of $\overline{P}_4$. Our results show that a uniaxial tensor should be used for the calculation of orientational order parameters from Raman intensity measurements rather than a biaxial one. This results in a better agreement with previous determinations or calculations and is consistent with an isotropic rotation of molecules around their main axes.

Negative values of $\overline{P}_4$, which are also found from our data, even in the case of a uniaxial Raman tensor, have been extensively discussed previously [1,2,7,8,10]. It should be noticed first than many authors have compared their $\overline{P}_4$ values with those obtained from the MS theory, in which the potential is a function of $P_2(\cos\beta)$ only. We have also reported for information these positive theoretical values in figures 1 (*a*) and (*b*), but will not comment on the already debated discrepancy. Nevertheless, a self consistent approach using a potential including $P_4(\cos\beta)$ terms, as made by Humphries, James and Luckhurst [21], seems to be more appropriate for the determination of $\overline{P}_4$. Several explanations have been given for the negative experimental values of $\overline{P}_4$. An antiparallel association of CB9 molecules to give dimers has been suggested by Dalmolen *et al.* [10]. This dimerization would result in a tilt of the core of each molecule of the dimer by an angle β'_{D} with respect to the director. The 'sum rule' for Legendre polynomials gives

$$\overline{P}_L(\cos\beta)_{\mathrm{exp}} = P_L(\cos\beta'_{\mathrm{D}})\overline{P}_L(\cos\beta),$$

where the index 'exp' means 'experimentally determined'. Using the above formula, β'_{D} should be more than about 30° in order to obtain negative values for $\overline{P}_4(\cos\beta)_{\mathrm{exp}}$. This angle is significantly larger than the one calculated by these authors for CB9 molecules ($\sim 20°$) from space-filling molecular models. Nevertheless, this dimerization could give a qualitative explanation for the low and even negative values found for $\overline{P}_4$, but the tilt resulting from this molecular association should be detected by Raman experiments for the smectic phase too, and a variation in the optical contrast between crossed polarizers should be observed. Neither the tip from $\beta = 0$ (see figure 3) nor the optical contrast variation has been observed in our experiments. Furthermore, the orientational distribution function is well peaked at $\beta = 0$ even in the nematic phase, when a uniaxial Raman tensor is used (see figure 2 (*a*)).

Another model providing an explanation for the negative values of $\overline{P}_4$ has been proposed by Luckhurst and Yeates [11] and used by Constant and Decoster [8] to interpret their data. In this model, each molecule is restricted to move as a whole without exceeding a tilt angle of β_0, i.e. the single particle potential is finite (say $U(\beta) = 0$)) for $\beta < \beta_0$ and infinity for $\beta > \beta_0$. From straightforward statistical physics calculations, this potential results in an expression for $\overline{P}_2$ which depends only upon β_0, and in negative $\overline{P}_4$ values as long as $\overline{P}_2$ is less than 0·54, i.e. for β_0 larger than 49°. If this model provides a possible qualitative explanation for $\overline{P}_4 < 0$, its authors consider it as 'extreme', partly because it takes into account only repulsive forces. As a matter of fact, a MS potential which, in addition, is in agreement with our values for $\overline{P}_2$, or a higher-order potential such as that developed by Humphries *et al.* [21], seems to be more suitable.

Most of the questions arising above come from the fact that a $\overline{P}_4$ versus $\overline{P}_2$ representation calculated from the MS theory is nearly parabolic, and cannot consequently support negative values for $\overline{P}_4$. Actually, negative values are not forbidden provided they do not give way to any 'anomalous' behaviour, such as a systematic tilt from $\beta = 0$. For instance, within the frame of the classical Landau theory applied near the isotropic–nematic transition, a free energy of the form

$$F = \tfrac{1}{2}\alpha\bar{P}_2^2 + \tfrac{1}{3}\beta\bar{P}_2^3 + \tfrac{1}{4}\gamma\bar{P}_2^4 + \tfrac{1}{2}a\bar{P}_4^2 + \omega_1\bar{P}_2\bar{P}_4^2 + \omega_2\bar{P}_2^2\bar{P}_4 + \omega_3\bar{P}_2^2\bar{P}_4^2 + \omega_4\bar{P}_2^3\bar{P}_4 \qquad (4)$$

allows for negative $\overline{P}_4$ values. In this expression, $\alpha = \alpha_0(T - T_c), \beta < 0$, $\gamma > 0$ and $a > 0$. $\overline{P}_2$ is the primary order parameter and $\overline{P}_4$ is a secondary order parameter affected by the transition through the coupling terms, the invariance of which has been established using tensor symmetry analysis. Minimization of expression (4) with respect to $\overline{P}_4$ leads to

$$\overline{P}_4 = -\frac{\omega_2 + \omega_4\overline{P}_2}{a + 2\omega_1\overline{P}_2 + 2\omega_3\bar{P}_2^2}\,\bar{P}_2^2. \qquad (5)$$

A change of sign of $\overline{P}_4$ occurs when $\overline{P}_2 = -\omega_2/\omega_4$, provided $a + 2\omega_1\overline{P}_2 + 2\omega_3\bar{P}_2^2$ does not show any singular behaviour for $\overline{P}_2$ varying between 0 and 1. Our results for $\overline{P}_4$ versus $\overline{P}_2$ give $|\omega_4|/|\omega_2| \sim 2$ and $a \gg |\omega_1|, |\omega_3|$. This last inequality is equivalent to keeping in the free energy expansion coupling terms in which the powers of $\overline{P}_2$, $\overline{P}_4$ are smaller than those of the first four terms of expression (4) only. Except for some general considerations about the signs of the coefficients ω_1, ω_2, ω_3 and ω_4 with respect to a, other quantitative information cannot be obtained unless a good fit of the $\overline{P}_4$ versus $\overline{P}_2$ curve is obtained for the nematic phase. Due to the narrow range of temperature in which this phase occurs in CB9, such a fit is not realistic for this compound. Nevertheless, attempts to apply this phenonemological model to results for nematic phases of lower homologues of the CB*n*s [4, 6, 8] have given similar values for the coefficients in the expansion (4). On the contrary, these coefficients are quite different for other systems, like PCH-5 [7], for which only positive $\overline{P}_4$ values have been reported. Such differences between cyano compounds and other nematic liquid crystals have been pointed out previously [7, 13]. All these considerations will be developed elsewhere.

A jump in $\overline{P}_2$ and $\overline{P}_4$ order parameters is observed at the nematic–smectic A transition (see figures 1 (*a*) and (*b*)), which most probably reflects the first order character of this transition. According to McMillan's theory [12, 13] involving a coupling between the orientational and smectic order parameters, the transition from nematic to smectic phases is indeed expected to be first order in CB9, since $T_{S_AN}/T_{NI} > 0{\cdot}87$. It should be noticed that only a jump in $\overline{P}_2$ is predicted in McMillan's theory, since $\overline{P}_4$ is not explicitly introduced in the model. A complete form of the free energy which could account for both transitions from the isotropic to the nematic and to the smectic A phases should include $\overline{P}_2$, $\overline{P}_4$, the smectic order parameter and the invariant coupling terms. The tedious minimization of this free energy would not give more information than is already qualitatively given, more particularly because the physical meaning of the various coefficients in a Landau free energy expansion is not always straightforward. Nevertheless, it can be predicted from equations (4) and (5) that a jump in the $\overline{P}_4$ order parameter should be associated with any jump in $\overline{P}_2$, provided that the coupling between $\overline{P}_2$ and $\overline{P}_4$ is strong enough. This is indeed observed in figures 1 (*a*) and (*b*).

5. Summary and conclusion

Orientational order parameters $\overline{P}_2$ and $\overline{P}_4$ in the nematic and smectic A phases of CB9 have been determined using Raman spectroscopy, and the truncated distribution function $f(\beta)$ has been calculated from these order parameters, when using either a uniaxial or a biaxial Raman tensor.

The results obtained for $\overline{P}_2$ in the nematic phase of CB9 are in fairly good agreement with those obtained from other experiments or from the Maier–Saupe theory provided that a *uniaxial* Raman tensor is used to derive $\overline{P}_2$ and $\overline{P}_4$ from the Raman intensity ratios. The use of a biaxial tensor results in $\overline{P}_2$ significantly larger and showing discrepancies far beyond the experimental uncertainties. Furthermore, a biaxial tensor is not physically justified for a molecule rotating isotropically about its long axis. If a hindered rotation is considered, associated Legendre polynomials should be introduced rather than the $P_L(\cos\beta)$.

Some values found for $\overline{P}_4$ are slightly negative, even when a uniaxial Raman tensor is considered. Nevertheless, the orientational distribution function $f(\beta)$ derived from our values of $\overline{P}_2$ and $\overline{P}_4$ is in any case (C≡N or C–C biphenyl link vibration) unambiguously peaked at $\beta = 0$. Negative values of $\overline{P}_4$ have long been considered as a problem in the literature, most particularly because positive $\overline{P}_4$ are expected from the MS theory (in which the potential does not include any $L = 4$ or higher term). A phenomenological theory, such as the Landau-type expansion proposed in this work, allows negative $\overline{P}_4$ to occur.

Finally, a jump in $\overline{P}_2$ and $\overline{P}_4$ has been observed at the nematic–smectic A transition, as predicted by the McMillan theory for CB9 [12, 13].

An important point mentioned by most authors concerns the local field effects on the Raman tensor. Jen *et al.*

[1, 2], suggested that these could be taken into account by introducing a 'dressed' Raman tensor, i.e. corrected for the local field. This correction is expected to vary with temperature, but, in the case of CB9 in which the nematic phase extends over only about 2 K, the assumption of a constant local field correction is here probably valid. This is not necessarily true when going to the smectic phase and the jumps observed at the transition in $\overline{P_2}$ and $\overline{P_4}$ could be partly related to a variation in the local field.

Anyhow, and as already pointed out by Miyano [4] or Jen *et al.* [1, 2], local field effects must not be disregarded. A first attempt to deal with them has been made by Seeliger *et al.* [7]. These authors showed qualitatively that such effects could result in a lowering of experimentally determined $\overline{P_4}$ values and in discrepancies, depending upon the internal vibration studied. These behaviours have indeed been observed, to some extent, in our work, and hint that local field effects should not be underestimated. If they are not crucial in the case of CB*n*, they could affect the scattered Raman intensities in a far more significant way in other systems such as ferroelectric liquid crystals and related materials exhibiting a spontaneous polarization. Raman scattering from such compounds will be the subject of a forthcoming paper, in which local field effects will be considered in more detail.

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