Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Jadzyn, Jan , Czechowski, Grzegorz , Douali, Redouane and Legrand, Christian(1999) 'On the molecular interpretation of the dielectric relaxation of nematic liquid crystals', Liquid Crystals, 26: 11, 1591 — 1597

To link to this Article: DOI: 10.1080/026782999203571

URL: http://dx.doi.org/10.1080/026782999203571

LIQUID CRYSTALS, 1999, VOL. 26, NO. 11, 1591–1597

On the molecular interpretation of the dielectric relaxation of nematic liquid crystals

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(*Received 18 March 1999; accepted 31 May 1999*)

This paper presents the results of studies of the dielectric relaxation of nematic 6CHBT obtained for different values of the angle between the directions of the macroscopic orientation of the sample (director **n**) and the probing electric field **E**. Analysis of the evolution of the relaxation spectrum from $\varepsilon^*_{\parallel}(\omega)$ ($\mathbf{E}\parallel\mathbf{n}$) to $\varepsilon^*_{\perp}(\omega)$ ($\mathbf{E}\perp\mathbf{n}$) allows one to explain the hitherto existing inconsistency in the molecular interpretation of the spectra. A model of the molecular dynamics in the oriented nematics is proposed.

1. Introduction

Dielectric relaxation in liquids and liquid crystals can be observed after perturbation of the random distributed molecular dipoles, by an application of the electric field. A return of the system to an equilibrium state proceeds through all possible molecular movements. If a given type of movement is followed by a change of the projection of the molecular dipole moment on the direction of the probing electric field, and if the frequencies of the projection change and the field are coincident, then an absorption band appears in the dielectric relaxation spectrum. The large frequency range offered by dielectric spectroscopy makes this method very useful for studies of the dynamics of dipolar molecules both in dilute solutions and in complex polymer structures [1, 2].

Studies of the dielectric relaxation in nematic liquid crystals are of special interest and importance. The possibility of control of the molecular orientation in the whole nematic sample by an electric/magnetic field or by an appropriate preparation of the electrode surfaces gives an exceptional opportunity for studies of the molecular dynamics in relation to the directions of the principal axes of the nematogenic molecule. One could expect that in such advantageous circumstances the interpretation of the dielectric relaxation spectra is much more explicit and informative than in the case of isotropic liquids. Unfortunately, despite numerous papers devoted to dielectric relaxation in nematics [3–6], some basic problems concerning the interpretation of the experimental results are still not resolved. This mainly refers to the lack of consistency in the interpretation of the dielectric relaxation spectra obtained for two basic experimental arrangements—when the probing electric field **E** and the macroscopic molecular orientation, represented by the director **n**, are parallel $[(\varepsilon^*_{\parallel}(\omega)]$ or perpendicular $[\varepsilon^*_{\perp}(\omega)]$ to each other.

In this paper we present experimental results which make the interpretation of the dielectric relaxation spectra of nematics more clear and consistent.

2. Experimental

The nematic liquid crystal 4-(*trans*-4-*n*-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT, C_6H_{13}–CyHx–Bz–N=C=S) with the following sequence of phase transitions: Cr 12.7° N 43.1° I, was placed in a plane capacitor and oriented with the magnetic field **B** (1.2 T). The dielectric relaxation spectra were recorded for different values of the angle between the measuring electric field **E** (the direction of **E** is perpendicular to the surface of the capacitor electrodes) and the director **n** (the direction of **n** is determined by the orienting magnetic field vector **B**). The measurements were performed in the frequency range 1 MHz to 1 GHz using an HP 4191A Impedance Analyser, at three temperatures: 38, 40 and 42°C.

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Journal of Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online ©1999 Taylor & Francis Ltd
http://www.tandf.co.uk/JNLS/lct.htm
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3. Results and discussion

In the interpretation of dielectric relaxation spectra, the crucial point is the attribution of a given absorption band to a particular mode of the molecular movement. However, it is not rare that the spectrum obtained experimentally has a complex form and therefore it has to be resolved into elementary absorption bands. The procedure of resolution is, in general, not a simple matter and often a number of the elementary contributions are not self-evident. A general rule is that one proceeds by resolution of the experimental spectrum into as small a number of contributions as possible. Here, the argument is that each contribution introduces into the fitting procedure at least two parameters, so the greater number of contributions, the less unequivocal is the resolution of the spectrum. As we will see later, this rather intuitive rule can lead to erroneous conclusions. Besides, in some cases, one is dealing with the distribution of the relaxation times for a given reorientational process. Then, each elementary contribution introduces to the fitting procedure at least one additional parameter.

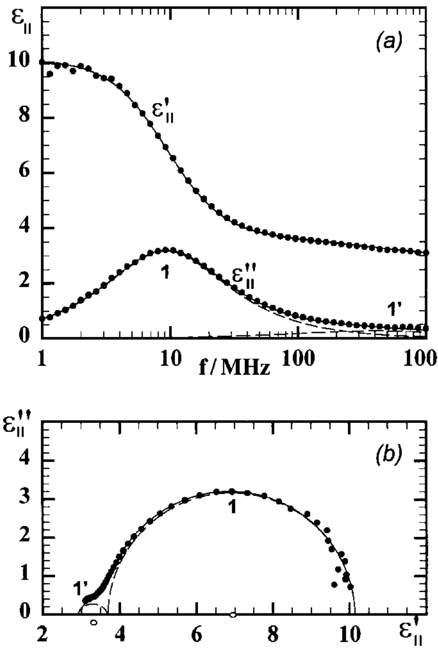

Figure 1. The frequency dependence (*a*) and the Cole–Cole plot (*b*) of the permittivity of nematic 6CHBT measured for **E**∥ **n**, at 40°C. The spectrum is resolved (as hitherto) into two elementary contributions 1 and 1′. It will be shown that the band 1′ is a sum of the two absorption bands (see figures 4 and 5).

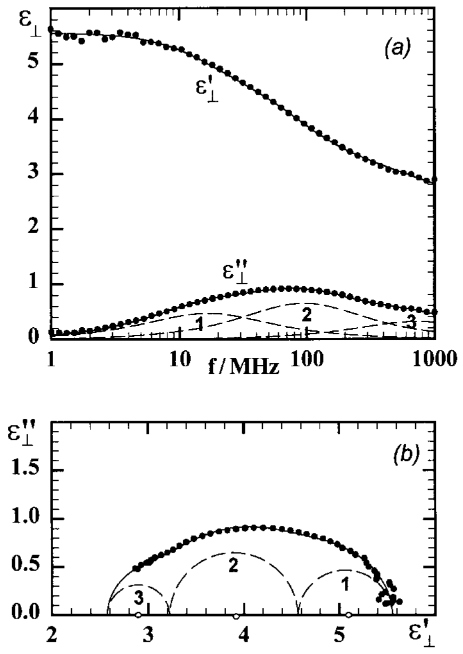

Figure 2. The frequency dependence (*a*) and the Cole–Cole plot (*b*) of the permittivity of nematic 6CHBT measured for **E**⊥ **n**, at 40°C. The spectrum is resolved into three elementary contributions.

Figures 1 and 2 present the dielectric relaxation spectra $\varepsilon^*_\parallel(\omega)$ and $\varepsilon^*_\perp(\omega)$ of 6CHBT. These are typical spectra for nematics with a positive dielectric anisotropy. In the figures the dashed lines represent the commonly used resolution of the experimental spectra into elementary contributions. The resolution was performed with the use of an empirical Cole–Cole formula [7]:

$$\begin{aligned}\varepsilon^*_a(\omega) &= \varepsilon'_a(\omega) - \mathrm{i}\varepsilon''_a(\omega)\\ &= \varepsilon_\infty + \sum_i \frac{A_i}{1+(\mathrm{i}\omega\tau_i)^{1-k_i}}, \quad (\mathrm{i}=\sqrt{-1}, a=\parallel, \perp)\end{aligned} \tag{1}$$

which takes into account the possibility of the distribution of the relaxation times. For the limiting value of the distribution parameter: $k_i = 0$, the i-th reorientational process is described by a single relaxation time (the Debye type process). A_i and τ_i denote, respectively, the dielectric strength and the relaxation time, and together with the k_i they are the adjustable parameters in the procedure of the fitting of equation (1) to the experimental spectrum. The ε_∞ denotes the high frequency value of the permittivity.

At first glance, the spectrum $\varepsilon^*_\parallel(\omega)$ seems to be much more simple than the spectrum $\varepsilon^*_\perp(\omega)$. When the probing electric field **E** is directed along the director **n**, one absorption band of the Debye type (band 1 in figure 1) strongly dominates in the spectrum. In the complex plane ($\varepsilon'_\parallel$, $\varepsilon''_\parallel$) this band is almost a perfect semicircle, figure 1 (*b*). There is no doubt that this absorption band is related to the molecular rotation around the short axis. The evidence for that is the experimentally observed dependence of the relaxation time $\tau_1^\parallel$ on the length of nematogenic molecules and on the temperature and viscosity of the medium [3, 4]. Besides, the high value of the dielectric strength of the band 1 is a consequence of the high amplitude of the change of the projection of the molecular dipole moment on the **E** direction. For molecules with a dipole moment directed, more or less, along the molecular long axis, as in the case of 6CHBT, such a dielectric strength may occur only on account of the rotation around molecular short axis.

The above molecular interpretation of the band 1, appearing in the low frequency region of the dielectric spectrum $\varepsilon^*_{\parallel}(\omega)$, is accepted in the literature without reserve. Unfortunately, it is the only point of agreement in this field. The molecular interpretation of the other dielectric absorption bands is a subject of incessant controversy.

For a full description of the $\varepsilon^*_{\parallel}(\omega)$ spectrum an absorption band (or bands) situated in the high frequency region of the spectrum must next be taken into account. This seems to be a reasonable assumption based on the existence of the one absorption band in the region. This band, designated in figure 1 as 1′, is usually attributed to molecular rotation around the long axis. However, due to the relatively small strength and other circumstances which will be discussed later, the values of the spectral parameters of the band 1′ (A'_1, τ'_1 and k'_1) obtained in different experiments are not very reproducible and, in the limiting case, one can find reports presenting the experimental spectrum $\varepsilon^*_{\parallel}(\omega)$ in a form of the Debye type band 1 only. Of course, if one is interested only in molecular rotation around the short axis, which undoubtedly yields the most important information about the molecular dynamics in the presence of the nematic potential, then the high frequency band 1′ can be ignored. Still, if one is interested in understanding all kinds of molecular motions in nematics, the band 1′ has to be analysed carefully, the more so if the dielectric strength of this band is of the same order of magnitude as the strength of the $\varepsilon^*_{\perp}(\omega)$ spectrum.

The values of the parameters corresponding to the resolution of the experimental spectrum $\varepsilon^*_{\parallel}(\omega)$ into two contributions using equation (1), are gathered in table 1.

Table 1. Parameters resulting from resolution of the dielectric spectra of nematic 6CHBT into two $\varepsilon^*_{\parallel}(\omega)$ and three $\varepsilon^*_{\perp}(\omega)$ elementary contributions by the use of equation (1).

Band	A_i	τ_i/ns	k_i
$\varepsilon^*_{\parallel}(\omega)$			
1	6.354	17.04	0.01
1′	0.70	0.60	0.10
$\varepsilon^*_{\perp}(\omega)$			
1	1.15	8.36	0.08
2	1.25	1.52	0.03
3	0.62	0.20	0.03

The resolution of the spectrum $\varepsilon^*_{\perp}(\omega)$ into elementary absorption bands can be performed—with reasonable agreement between the experimental values and the predictions of equation (1)—on the assumption of the existence of three contributions (figure 2). The values of the corresponding spectral parameters are gathered in table 1. As can be seen in figure 2, three absorption bands, all very close to Debye type ($k_i \approx 10^{-2}$, $i = 1, 2, 3$; see table 1), reproduce the experimental dependences $\varepsilon'_{\perp}(\omega)$ and $\varepsilon''_{\perp}(\omega)$ fairly well. As has been shown in many papers [8–12], such a resolution of the $\varepsilon^*_{\perp}(\omega)$ spectrum is also suitable for other nematics. The problem consists in the attribution of these bands to explicit molecular motions.

The theories of the dielectric relaxation in nematics predict four different relaxation times—two in $\varepsilon^*_{\parallel}(\omega)$ spectrum and two in $\varepsilon^*_{\perp}(\omega)$ spectrum—which should correspond to four different modes of the molecular motions [13–19]. Although several pictures have been proposed for a better understanding of these modes, there is no general consensus in the molecular interpretation of the $\varepsilon^*_{\perp}(\omega)$ spectrum.

The data gathered in table 1 show that for the resolutions presented in figures 1 and 2, there is no direct correspondence between the relaxation times appearing in the $\varepsilon^*_{\parallel}(\omega)$ and $\varepsilon^*_{\perp}(\omega)$ spectra. This fact can be taken as an argument in support of theory. Still, one can find that the low frequency bands in both spectra show some similarity with respect to the values of the relaxation times ($\tau^{\parallel}_1 = 17$ ns, $\tau^{\perp}_1 = 8.4$ ns) and the same concerns the high frequency bands ($\tau^{\parallel}_2 = 0.6$ ns, $\tau^{\perp}_2 = 0.2$ ns), which may suggest that their derivation is the same: molecular rotation around the short and long axes, respectively. The band 2, appearing in the $\varepsilon^*_{\perp}(\omega)$ spectrum, has no the counterpart in this scheme and presents many difficulties in the interpretation, see for example [11, 12].

One can recapitulate that despite numerous papers devoted to the studies of dielectric relaxation in nematics a molecular understanding of the phenomenon is far from satisfactory and the consistent and uniquevocal molecular interpretation of the $\varepsilon^*_{\parallel}(\omega)$ and $\varepsilon^*_{\perp}(\omega)$ spectra requires essential new experimental results.

We believe that the results presented in figure 3 are essential. In our simple experiment, a quasi-continuous evolution of the dielectric relaxation spectrum was recorded at every 10° angle step from $\varepsilon^*_{\parallel}(\omega)$ to $\varepsilon^*_{\perp}(\omega)$. The spectra are shown in 2-D and 3-D plots because each plot shows different features of the spectral evolution. The 2-D picture shows the existence of a point in the absorption spectra, which is not affected by the change in the angle $\alpha(\mathbf{E}, \mathbf{n})$ (‘isosbestic point’ at about 80 MHz). In the 3-D picture one can observe the evolution of the

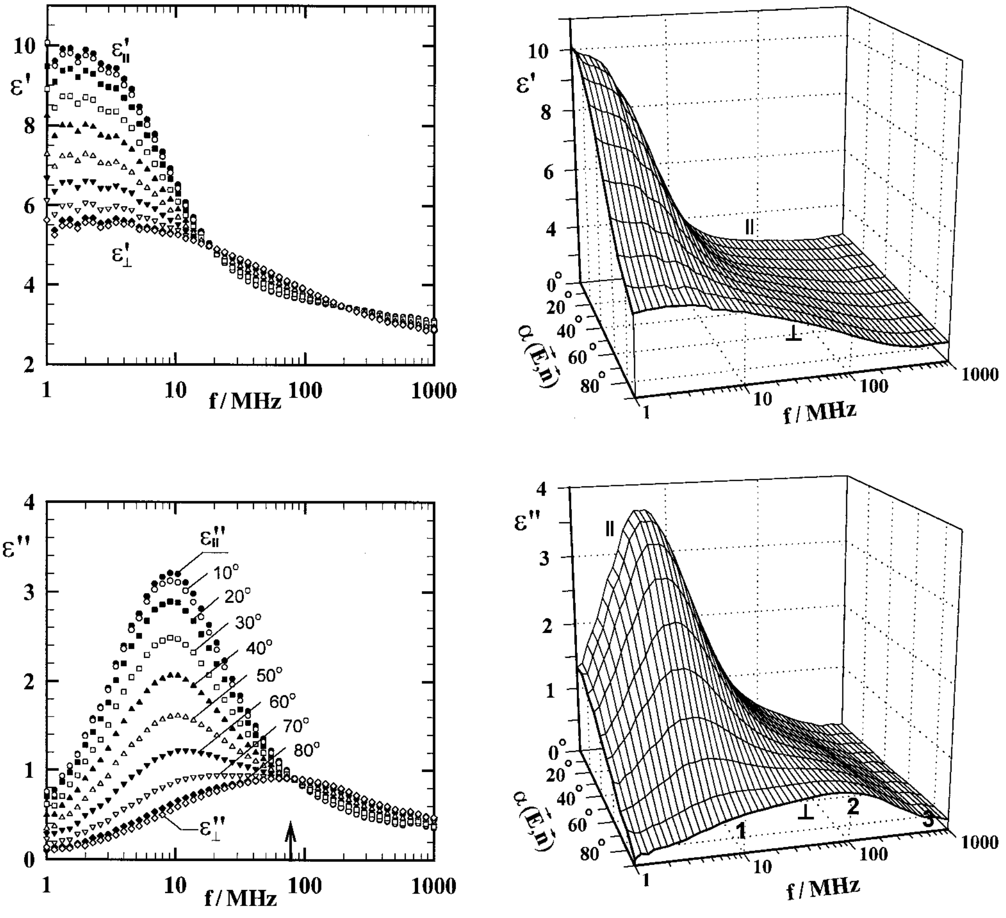

Figure 3. The evolution of the dielectric relaxation spectrum of nematic 6CHBT from $\varepsilon^*_{\parallel}(\omega)$ to $\varepsilon^*_{\perp}(\omega)$, at 40°C. The spectra were recorded for different values of the angle between the probing electric field **E** and the director **n**. The arrow at the bottom left on the plot of $\varepsilon''(f)$ indicates the frequency ($\sim 80\,\mathrm{MHz}$) at which the dielectric absorption is independent of the angle α ('isosbestic point').

positions and strengths of the bands due to the change in α; the most important observation concerns band 2.

The conclusion arising from the visual analysis of the spectra presented in figure 3 is the following: there are no sharp changes in either the frequency or the strength of the bands due to changes in the angle $\alpha(\mathbf{E}, \mathbf{n})$ from 0° to 90°.

The quantitative analysis of the spectra was performed using equation (1). The start-point was the spectrum $\varepsilon^*_{\perp}(\omega)$ ($\alpha = 90°$) composed of three elementary absorption

Table 2. Parameters resulting from resolution of the dielectric spectra of nematic 6CHBT into three contributions, equation (1). The spectra were recorded for different values of the angle α between the probing electric field **E** and director **n** (from **E**∥ **n** to **E**⊥ **n**).

α	A_1	τ_1/ns	k_1	A_2	τ_2/ns	k_2	A_3	τ_3/ns	k_3
0° (**E**∥ **n**)	6.507	17.34	0.02	0.33	1.15	0.01	0.52	0.16	0.01
10°	6.231	17.88	0.01	0.40	1.80	0.03	0.54	0.20	0.01
20°	5.872	17.66	0.02	0.42	1.38	0.02	0.54	0.19	0.01
30°	4.963	17.67	0.02	0.63	1.61	0.03	0.52	0.22	0.01
40°	4.107	17.33	0.02	0.80	1.60	0.03	0.56	0.19	0.03
50°	3.128	16.80	0.03	1.01	1.70	0.03	0.59	0.20	0.03
60°	2.233	15.96	0.03	1.17	1.85	0.04	0.64	0.23	0.03
70°	1.51	14.09	0.04	1.32	1.84	0.04	0.65	0.23	0.03
80°	1.24	10.02	0.08	1.21	1.62	0.02	0.67	0.22	0.03
90° (**E**⊥ **n**)	1.15	8.36	0.08	1.25	1.52	0.03	0.62	0.20	0.03

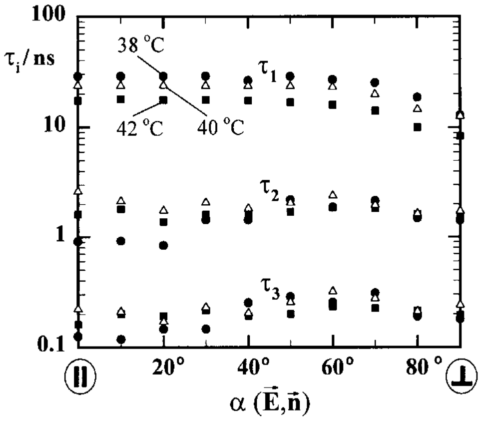

Figure 4. The angle α dependences of the relaxation times corresponding to the three elementary contributions to the dielectric relaxation spectra of nematic 6CHBT at 38, 40 and 42°C. The spectra evolve from $\varepsilon^*_{\|}(\omega)$ to $\varepsilon^*_{\perp}(\omega)$.

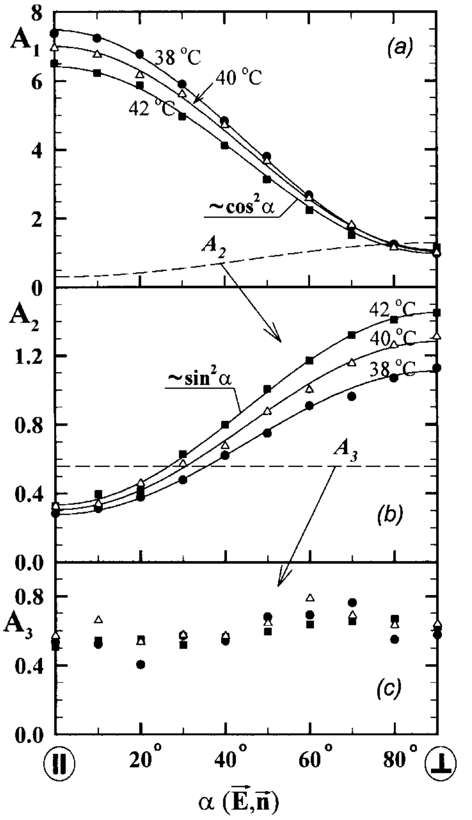

Figure 5. The angle α dependences of the strengths of the three elementary contributions to the dielectric relaxation spectra of nematic 6CHBT at 38, 40 and 42°C. The spectra evolve from $\varepsilon^*_{\|}(\omega)$ to $\varepsilon^*_{\perp}(\omega)$. The solid lines in (*a*) and (*b*) represent the functions $\cos^2\alpha$ and $\sin^2\alpha$, respectively.

bands (as in figure 2). Taking into account that the spectrum $\varepsilon^*_{\perp}(\omega)$ transforms into the $\varepsilon^*_{\|}(\omega)$ spectrum quite softly, we assumed the same procedure of resolution for the three absorption bands of all spectra, including, of course, the $\varepsilon^*_{\|}(\omega)$ spectrum. As a result, we obtained the dependences of the relaxation times τ_1, τ_2 and τ_3 (figure 4) and the strengths A_1, A_2 and A_3 (figure 5) of the elementary bands on the value of the angle $\alpha(\mathbf{E}, \mathbf{n})$. The numerical data concerning the resolutions are gathered in table 2.

The dielectric relaxation spectrum of nematic 6CHBT, recorded at any angle between the probing electric field **E** and the direction of the macroscopic order of the nematic sample **n**, can be considered as a sum of the *three elementary absorption bands*. The bands, situated at about 10 MHz, 100 MHz and 1 GHz, are, to a good approximation, of the Debye type ($k_i \approx 10^{-2}$, $i = 1, 2, 3$), and should correspond to the three modes of the motions of nematogenic molecules. The most important information enabling one to identify the modes, is contained in the angular dependences of the strengths of the bands (figure 5). Because the strength of an absorption band is proportional to the square of the amplitude of the projection of the moving dipole on the direction of the measuring field, the dependences of $A_i(\alpha)$ allow us to verify the possible modes of the molecular rotation with respect to the requirements presented in figure 5.

Our model of the molecular dynamics in oriented nematics is depicted in figure 6. The nematogen molecule rotates around the three axes of symmetry: two axes concern the molecule itself—molecular long and short axes, figure 6 (*a*) and 6 (*c*); the third axis is the director **n**, figure 6 (*b*). The molecular long and short axes are understood as the axes of minimum or maximum momentum of inertia, respectively. The molecular long axis l and the vector **n** form the angle Θ, which is a measure of the ordering in the nematic sample; the order parameter S is defined as mean value:

$$S = \frac{1}{2}\langle 3\cos^2\Theta - 1\rangle \tag{2}$$

The strength of the bands corresponding to two kinds of molecular movement, namely rotation around the short axis [strictly, it is the rotation around the axis perpendicular to the director **n**, figure 6 (*a*)] and rotation on the cone around the director **n** [figure 6 (*b*)], depend on the order parameter value. With decrease in S (increase of temperature) A_1 diminishes and A_2 grows, see figures 5 (*a*) and 5 (*b*), respectively.

It can be seen in figure 4 that the relaxation times depend rather weakly on the angle α. A tendency for acceleration of the movement around the molecular short axis (τ_1), observed for α approaching 90°, is probably due to the essential reduction of the dipole moment–electric field interaction in the configuration $\mathbf{E} \perp \mathbf{n}$.

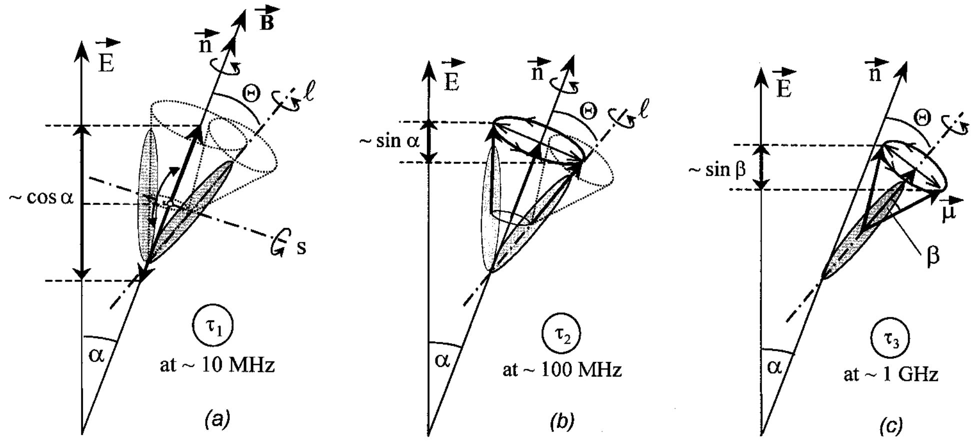

Figure 6. Sketches representing the possible molecular rotations around the symmetry axes in oriented nematics, causing an energy absorption in the different parts of the electromagnetic spectrum.

4. Conclusions

On the basis of the experimental results presented and from the analysis of the diagrams in figure 6, one can conclude the following.

For *perfect molecular alignment* in the nematic sample, the dielectric relaxation spectra, both $\varepsilon_{\parallel}^{*}(\omega)$ and $\varepsilon_{\perp}^{*}(\omega)$, should be composed of two elementary contributions. With respect to this point there is an agreement with theory.

The *band 3*, corresponding to the molecular rotation around the long axis, appears at ~ 1 GHz in both spectra $\varepsilon_{\parallel}^{*}(\omega)$ and $\varepsilon_{\perp}^{*}(\omega)$ at the same frequency ($\tau_3^{\parallel} = \tau_3^{\perp}$) and with approximately the same strengths ($A_3^{\parallel} = A_3^{\perp}$) (figures 4 and 5). The relaxation time τ_3 and the strength A_3 are rather insensitive to temperature changes. The strength A_3 is proportional to $\sin^2 \beta$, where β is the angle between the resultant dipole moment of the molecule and its long axis; for $\beta = 0$, $A_3 = 0$.

The *band 1*, corresponding to the molecular rotation around the short axis, appears at ~ 10 MHz only in the $\varepsilon_{\parallel}^{*}(\omega)$ spectrum; the *band 2*, corresponding to the molecular rotation on the cone around the director **n**, appears at ~ 100 MHz only in the $\varepsilon_{\perp}^{*}(\omega)$ spectrum. The relaxation time τ_1 has a relatively strong temperature dependence: with a decrease in temperature, the value of τ_1 increases (figure 4). As expected, the relaxation time τ_2 shows no significant temperature dependence.

The relation of the modes 1 and 2 to the director **n** brings about a coupling between these modes, see figures 6 (*a*) and 6 (*b*). The coupling is twofold and concerns the strengths of the bands 1 and 2, see figures 5 (*a*) and 5 (*b*). At a constant angle α, the strengths A_1 and A_2 show an opposite reaction to the temperature change, i.e. to the order parameter change; at constant temperature, the strengths show an opposite reaction to change in the angle α. The coupling between the modes 1 and 2 manifests itself in the absorption spectra presented in figure 3, as an 'isosbestic point' (well known in UV/VIS spectroscopy) at about 80 MHz.

Now, the important question is in what way does perfect molecular alignment occur in the nematic sample? The magnetic field arranges the nematogen molecules with respect to the 4,4′-axis of the phenyl ring or rings, and the electric field—with respect to the axis of the maximum electric polarizability (roughly, the direction of the resultant dipole moment of the molecule). In general, neither of the two axes coincides with the molecular long axis *l*. Even for structurally simple molecules like the *n*-alkylcyanobiphenyls, the angle β between the dipole moment (C≡N) (for the 4,4′-biphenylyl axis) and the long axis is about 15° [20]. For the molecular alignment due to a special surface preparation, the situation is much more uncertain.

In practice, perfect molecular alignment with respect to the molecular long axis can happen only by chance, as a result of two factors acting simultaneously—for example, the magnetic field and the anchoring forces at the electrode surface (chiefly in thin nematic samples). This means that the 'ideal' dielectric relaxation spectra, $\varepsilon_{\parallel}^{*}(\omega)$ and $\varepsilon_{\perp}^{*}(\omega)$, each composed of the two contributions, can occur only accidentally.

Figure 5 shows that due to the 'non-perfect' alignment of the 6CHBT molecules, the amplitude A_1 is not equal to zero for $\alpha = 90°$, and the amplitude A_2 is not equal to zero for $\alpha = 0°$. The situation can be additionally complicated by the well known effect of the preference of some nematogen molecules for planar or homeotropic self-ordering on some surfaces. Thus, it is quite possible that for a given nematic, one will obtain $A_1 \neq 0$ in the $\varepsilon_{\perp}^{*}(\omega)$ spectrum and simultaneously $A_2 = 0$ in the $\varepsilon_{\parallel}^{*}(\omega)$ spectrum: the appearances of band 1 in the $\varepsilon_{\perp}^{*}(\omega)$ spectrum and band 2 in the $\varepsilon_{\parallel}^{*}(\omega)$ spectrum should be considered as independent events.

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