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A proton spin relaxation study of ferroelectric liquid crystals

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A proton spin relaxation study of ferroelectric liquid crystals

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Here we present and analyse N.M.R. measurements of the Larmor frequency dependence (dispersion) of the longitudinal proton spin relaxation time, $T_1(\nu)$, for two chiral ferroelectric mesogens (Merck IS-1912 and DOBAMBC) in the isotropic, smectic A and smectic C* phases, making use of fast field cycling techniques. Although in the low frequency range the relaxation times of IS-1912 are much shorter than those of DOBAMBC, the form of the dispersion profiles is not basically different for the two materials. This reveals contributions by smectic order fluctuations, self-diffusion and molecular rotations. The order fluctuation term, which means relaxation by collective molecular reorientations, is clearly seen by characteristic dispersion profiles in the kHz regime ($T_1 \sim \nu^1$ or $T_1 \sim \nu^{1/2}$), which disappear in the isotropic phase. Our results do not indicate significant dissimilarities between the main relaxation processes in the S_C and S_C^* mesophases.

1. The problem

So far only a few N.M.R. relaxation studies of molecular reorientations in chiral ferroelectric liquid-crystalline mesophases exist [1, 2], and the results available do not reveal the unique fast switching modes obtainable by such systems [3, 4] in display devices. From numerous N.M.R. investigations of non-chiral thermotropic and lyotropic mesophases it is now well established, although some details are still hotly disputed, that the longitudinal proton spin relaxation time, T_1, is determined essentially by the dipolar couplings between neighbouring protons in the more rigid parts of the molecules. These dipolar magnetic interactions are modulated basically by three kinds of processes, namely (slow) collective motions as, for instance, order fluctuations of the director field and two (faster) non-collective diffusive motions, most probably self-diffusion and strongly hindered rotations about special molecular symmetry axes [5, 6]. The measurements of T_1 available for the S_C^* phase of DOBAMBC (4-*n*-decyloxybenzylidene-4′-amino-2-methylbutylcinnamate) [1, 2] do not allow a similarly detailed analysis. Qualitatively, it was concluded by Dong and Sandeman [1] and by Vilfan *et al.* [2] that in this case director fluctuations, i.e. the collective reorientations, with frequencies higher and with intensities stronger than those known for non-chiral S_C structures, as for instance in TBBA (terephtal-bis(4-*n*-butylaniline)) [6, 7], should be considered as the dominant relaxation contribution. However, because of some inconsistencies in the data, both papers emphasized the necessity of measurements over a broader Larmor frequency range than is feasible with standard high field N.M.R. spectrometers, in order to determine the form of the motional spectrum more exactly and reliably. Such experiments have recently become possible by modern fast field cycling devices [8, 9], which extend the conventional MHz spectroscopy to Larmor frequencies as low as only a few Hz, even in the presence of short relaxation times of the order of milliseconds, typical for liquid crystals at low fields [5, 6]. This work presents and analyses a systematic proton relaxation field cycling study of two ferroelectric mesogenic materials, namely the classical DOBAMBC [4] and the new Merck product IS-1912 (S-1-(2-methylbutyl)-c4(4′-*n*-heptyloxybiphenyl-4-yl)-*r*-1-cyclohexancarbonitrile (MBHBCHC)) [10]. The results are compared with observations by dielectric and optical mixing studies [3, 4].

2. Experimental techniques and results

DOBAMBC (mesophase transition temperatures from the literature:

$$\mathrm{I} \xrightarrow{117^\circ\mathrm{C}} \mathrm{S_A} \xrightarrow{93^\circ\mathrm{C}} \mathrm{S_C^*} \xrightarrow{61^\circ\mathrm{C}} \mathrm{S_H^*} \xrightarrow{50^\circ\mathrm{C}} \mathrm{C})$$

was synthesized by Levstik [2], IS-1912 (mesophase transition temperatures communicated by Merck:

$$\mathrm{I} \xrightarrow{131^\circ\mathrm{C}} \mathrm{Ch} \xrightarrow{112^\circ\mathrm{C}} \mathrm{S_A} \xrightarrow{107^\circ\mathrm{C}} \mathrm{S_C^*} \xrightarrow{66^\circ\mathrm{C}} \mathrm{C})$$

was obtained from Geelhaar [10]. The samples were degassed by the usual freeze–pump–thaw method and then sealed under vacuum in tubes (diameter 1 cm) suitable for the N.M.R. apparatus used. To measure the longitudinal proton relaxation time over a broad Larmor frequency range (100 Hz $\leqslant \nu \leqslant$ 84 MHz) we used two complementary instruments described previously: between 100 Hz and 9 MHz a home-built fast field cycling device [9, 11], and between 9 and 84 MHz a standard frequency adjustable pulsed spectrometer [9, 11]. No deviations from single exponential magnetization decay could be observed within the experimental error limits. All measurements were performed on cooling the samples, in the presence of a high magnetic field, from the isotropic to the considered chiral or non-chiral smectic state to obtain a well defined director orientation. For reasons that are not yet fully understood, the reproducibility of the DOBAMBC data at low frequencies was significantly poorer (± 15 per cent and sometimes worse) than that of IS-1912 (± 5 per cent).

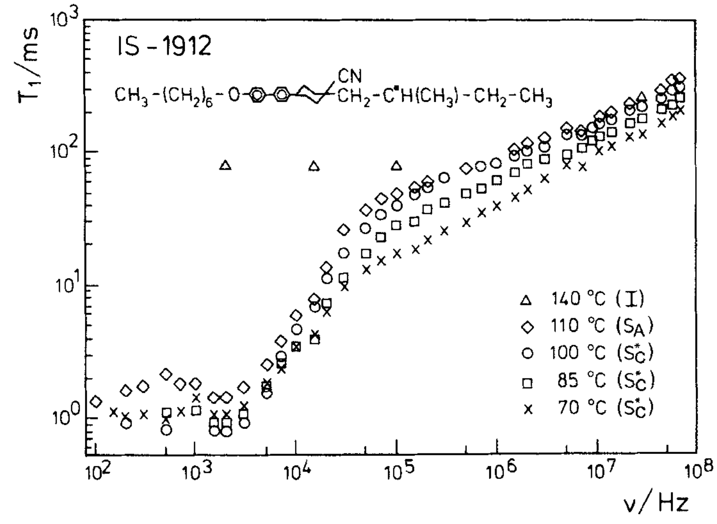

Figure 1. Larmor frequency dependence (dispersion) of the longitudinal proton spin relaxation time T_1 of IS-1912 at temperatures in the $\mathrm{S_C^*}$, $\mathrm{S_A}$ and isotropic phases.

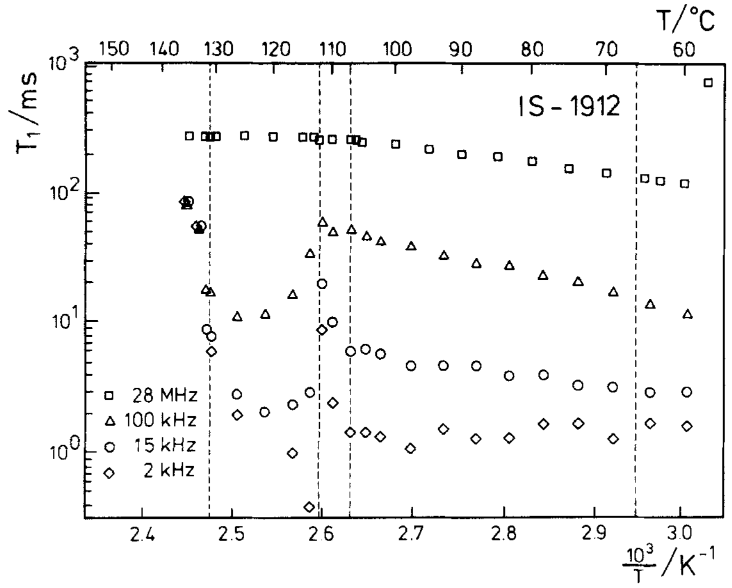

Figure 2. Temperature dependence of the longitudinal proton spin relaxation time, T_1, of IS-1912 at low, medium and high Larmor frequencies, ν.

We first consider the more transparent results obtained for IS-1912. Figure 1 illustrates the experimental dispersion profiles, $T_1(\nu)$, at five temperatures: one in the isotropic phase (I), one in the non-tilted non-chiral smectic phase (S_A) and three in the tilted chiral smectic state (S_C^*). Figure 2 shows the related temperature dependence, $T_1(T)$, at four selected Larmor frequencies more completely, including the cholesteric (Ch) mesophase. Overlooking some details, e.g. the complex behaviour in the cholesteric range, the findings are similar to the observations described in the literature [5–7] for other nematic or smectic liquid crystals. For the anisotropic liquids (S_A, S_C^*) two clearly separated frequency regimes always exist, namely a low one (I; 10^3 Hz $\lesssim \nu \lesssim 10^5$ Hz) with a strong frequency dependence and a high one (II; $\nu \gtrsim 10^5$ Hz) with a weak dependence on frequency. This indicates (at least) two different kinds of molecular reorientation with different timescales [9, 12, 13]. The characteristic feature of range I is an approximate $T_1 \sim \nu^1$ increase starting from a $T_1 \sim \nu^0$ plateau, which disappears completely in the isotropic liquid, whereas in range II the S_A–I transition has comparatively little effect on T_1. Hence, there can be no doubt that the typical mesogenic dynamics are effective relaxation mechanisms only at low frequencies. The separation into two regimes is also clearly seen in the $T_1(T)$ diagram by the different slopes of the Arrhenius plots at high and low frequencies. Furthermore, figure 2 reveals what is less obvious from figure 1, namely that the low frequency process has very different activation energies in the various mesophases. It is negligibly small for the S_C^* phase, but rather high for the S_A and Ch phases. In addition, in the cholesteric state $T_1(T)$ shows a minimum!

As illustrated by figure 3 and 4, the general properties of the T_1 measurements on DOBAMBC are not basically different from the IS-1912 data. However, in detail there exist significant distinctions, which make the diagrams look more complex. Again we can easily separate ranges I and II, and find almost the same transition frequency near 10^5 Hz, but compared with IS-1912 range I has a more intricate

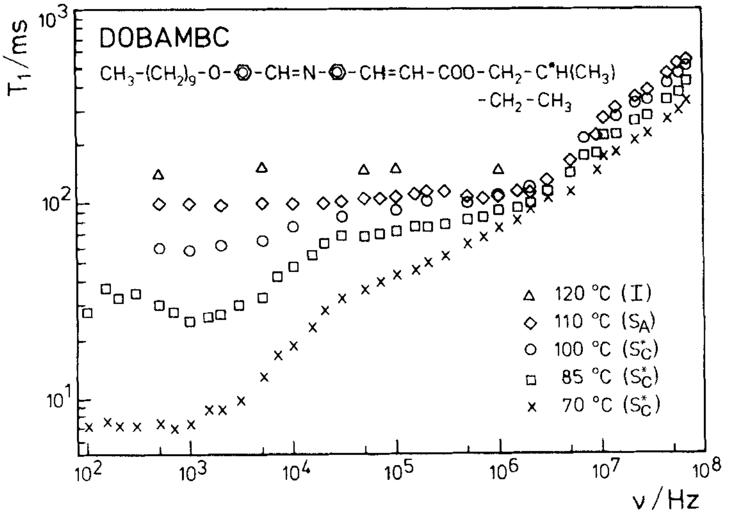

Figure 3. Larmor frequency dependence (dispersion) of the longitudinal proton spin relaxation time, T_1, of DOBAMBC at temperatures in the S_C^*, S_A and isotropic phases.

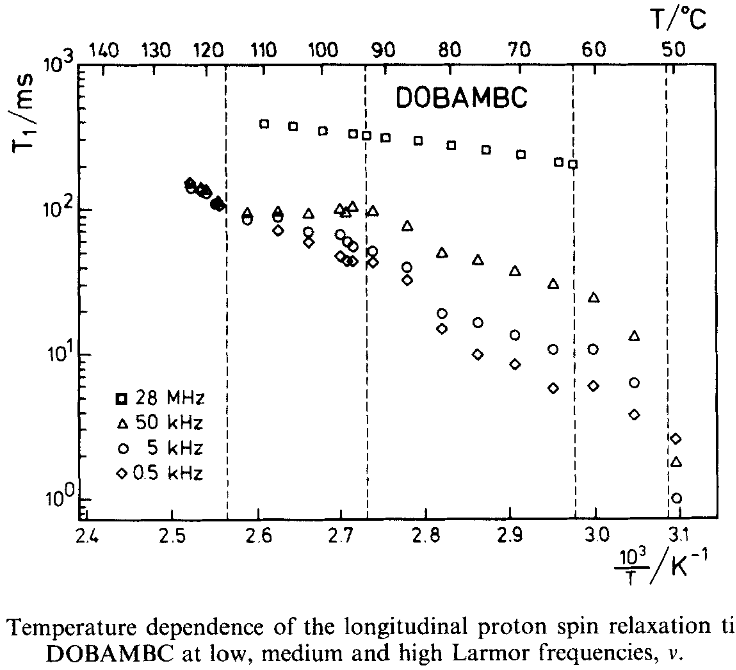

Figure 4. Temperature dependence of the longitudinal proton spin relaxation time, T_1, of DOBAMBC at low, medium and high Larmor frequencies, ν.

structure. Thus, T_1 does not decrease to comparably short times, because the slope of the dispersion step is smaller than in the preceding example ($T_1 \sim \nu^{0.6}$). However, the level of the low frequency plateau is strongly dependent on temperature, even in the S_C^* phase, so that the evolution of the range I dispersion profile between the anisotropic and the isotropic liquid crystal develops almost steadily and not discontinuously. Nevertheless, we emphasize that at least the second effect need not necessarily indicate a basic distinction between the collective molecular motions of the two materials, since to a minor degree it is also visible in the Merck compound. Obviously, additional dispersion measurements need to be carried out for the S_A phase in order to come to a decision. However, these require some improvements in the (absolute) temperature control of our apparatus because of the narrow stability interval. In range II the relaxation times are almost identical for both materials, particularly the data in the S_C^* range. We also note that in this high frequency regime our results are in excellent agreement with the previous N.M.R. work on DOBAMBC between 4 and 270 MHz [1, 2]. This is really astonishing in view of the comparatively large experimental scatter in range I, mentioned before.

3. Analysis and discussion

It has been established by numerous field cycling studies of non-chiral nematic and smectic liquid crystals [5–9] that the proton T_1 relaxation dispersion over more than six orders of magnitude, i.e. between Hz and MHz frequencies, can be interpreted remarkably well by a superposition of collective and individual molecular motions. These are generally easily distinguishable by characteristic exponents n in the $T_1 \sim \nu^n$ laws. Because of the qualitative parallelism between the new relaxation diagrams (see figures 1–4) and the previous results for other mesogens, we have tried a quantitative analysis in terms of models developed and examined before the interest in chiral ferroelectric mesogens. This means a combination of T_1 contributions arising from smectic order fluctuations (OF), self-diffusion (SD) and rotational diffusion (Rot) according to

$$\frac{1}{T_1} = \frac{1}{T_{1\mathrm{OF}}} + \frac{1}{T_{1\mathrm{SD}}} + \frac{1}{T_{1\mathrm{Rot}}}. \tag{1 a}$$

Cross-terms [14–16] have not been included, since such refinements cannot be checked critically at present without already knowing some of the underlying microscopic details (e.g. the self-diffusion constant and its temperature dependence), to reduce the number of model parameters. For the same reason only the simplest theories for the three mechanisms were considered, namely the results of Blinc *et al.* for $T_{1\mathrm{OF}}$ in a smectic ordering potential (undulation waves including a long and a short wave mode cutoff) [17], the Abragam–Pfeifer result for $T_{1\mathrm{SD}}$ (an isotropic approximation, acceptable since the diffusion anisotropy is known to be small) [12, 18], and a Bloembergen–Purcell–Pound approach for $T_{1\mathrm{Rot}}$ (making use of Woessner's interpretation in the limit of strongly anisotropic molecular reorientations) [13, 19]. On this basis the three individual relaxation rates can be written more explicitly, i.e. showing all of the relevant parameters, in the form [20]

$$(T_{1\mathrm{OF}})^{-1} = A\nu^{-1} f_{\mathrm{OF}}(\nu/\nu_{\mathrm{c\,low}}, \nu/\nu_{\mathrm{c\,high}}, \phi_{nH}), \tag{1 b}$$

$$(T_{1\mathrm{SD}})^{-1} = B\tau_{\mathrm{SD}} f_{\mathrm{SD}}(\nu, \tau_{\mathrm{SD}}), \tag{1 c}$$

$$(T_{1\mathrm{Rot}})^{-1} = C\tau_{\mathrm{Rot}} f_{\mathrm{Rot}}(\nu, \tau_{\mathrm{Rot}}), \tag{1 d}$$

where the notation is as follows: A, B and C are constants depending on the molecular geometry, ordering and viscoelasticity; $f_{\mathrm{OF}}(\nu)$, $f_{\mathrm{SD}}(\nu)$ and $f_{\mathrm{Rot}}(\nu)$ are spectral functions characteristic of the three kinds of molecular tumbling; $\nu_{\mathrm{c\,low}}$ and $\nu_{\mathrm{c\,high}}$ are the lowest and highest frequencies (cutoffs) of the collective mode spectrum, τ_{SD} and τ_{Rot} are the time constants of translational and rotational diffusion; and ϕ_{nH} is the angle between the director axis **n** and the magnetic field **H**, which in the S_C^* phase is the tilt angle

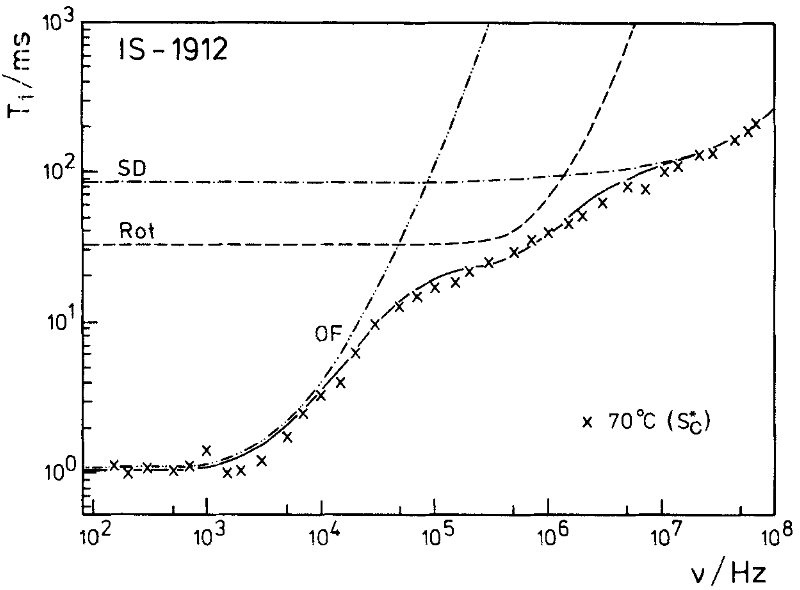

Figure 5. Curve fit of equation (1 *a*) and equations (1 *b*)–(1 *d*) to the experimental data for IS-1912 at 70°C (see figure 1) to illustrate the relaxation contributions in the S_C^* phase. The optimized model parameters are listed in the table.

[4, 10]. For details, we refer to the original literature [12, 13, 17–20]. Note that the concept of smectic order fluctuations employed is different from the concept of soft modes (Goldstone modes, amplitudons and phasons) [3, 4] related to the occurrence of ferroelectricity in liquid crystals.

By means of computer assisted curve fitting techniques [20, 21] it proved possible to describe all of our T_1 measurements in both materials quantitatively by equation (1 *a*) together with equations (1 *b*)–(1 *d*). As an example, the results are illustrated for the S_C^* phase of IS-1912 in figures 5 and 6. Evidently, the dominant contribution at low Larmor frequencies is T_{1OF} and at high frequencies T_{1SD}, whereas the third mechanism, T_{1ROT}, becomes important only in the transition range. The most striking feature is the extremely short value of T_{1OF} on the zero-field plateau ($\lesssim 1$ ms), because it differs from previous results for the S_C phase of TBBA [6, 7] by more than one order of magnitude ($\gtrsim 10$ ms), although the T_{1OF} dispersion regime is nearly identical in TBBA and IS-1912. The table lists the curve fitting parameters obtained by the relaxation analysis and reveals some systematic variations in the S_C^* temperature interval. As is expected, the translational and rotational jump times (τ_{SD} and τ_{Rot}) become shorter at higher temperatures (activation barriers $E \approx 20$ and $35\,\mathrm{kJ\,mol^{-1}}$, respectively), and the width of the collective mode spectrum ($\nu_{c_{low}}$ to $\nu_{c_{high}}$) narrows, in particular due to the decrease of $\nu_{c_{high}}$; we should note that a comparably low value of the upper mode cutoff has never been observed before! Similarly, it seems reasonable to find a related reduction of the plateau parameters B and C, because the geometrical molecular quantities involved (spin pair separations and orientations, as well as order parameter) [12, 18, 19] have temperature dependences suggesting such a shift. The only mysterious finding is the small *increase* of the T_{1OF} plateau parameter A (by a factor of 1·5 if tilt angles from the literature [10] are used), or the related T_{1OF} plateau *decrease* at higher temperatures, since all other dispersion

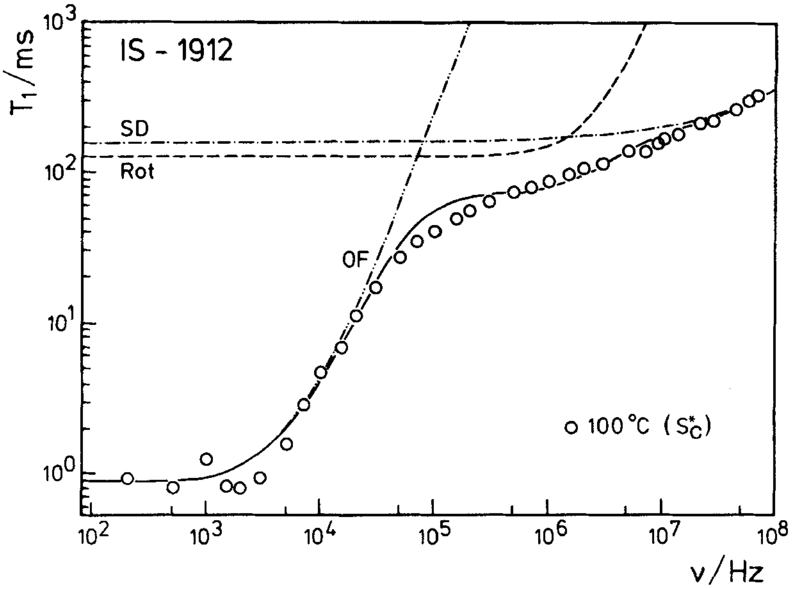

Figure 6. Curve fit of equation (1 *a*) and equations (1 *b*)–(1 *d*) to the experimental data for IS-1912 at 100°C (see figure 1) to illustrate variations of the relaxation contributions in the S_C^* phase. The optimized model parameters are listed in the table.

plots shown in figures 1 and 3 demonstrate just the opposite behaviour, as seen by the shifts at low frequencies. The normal lengthening [5–7] and the unusual shortening of T_{1OF} as a function of temperature have to be ascribed to the competing variations of the mesogenic properties which determine A and $\nu_{c_{low}}$ in the Blinc formalism [16].

A detailed discussion of all model fits in terms of the underlying molecular properties (elastic constants, viscosities, order parameters, tilt angles, self-diffusion constants, coherence lengths, spin pair separations and orientations, so far as available) is given elsewhere [21]. The table includes some data of the calculated self-diffusion constant, D, in IS-1912 and the related distance of closest spin approach, d, to demonstrate that our treatment is self-consistent. D turns out to be of the same order as for comparable high temperature smectogens [22], the value of d is approximately the molecular diameter. Another important finding is that the N.M.R. rotational correlation times, τ_{Rot}, are in qualitative accord with a dielectric relaxation process at MHz frequencies ($\nu = 1/(2\pi\tau_{Rot})$) which, as in our approach, is believed to be associated with molecular rotation about the short axis [3, 4, 23].

Somewhat surprisingly, the $T_1 \sim \nu^1$ dispersion law involved in equation (1 *b*) also led to satisfactory fits for DOBAMBC [21], where the experimental $T_1(\nu)$ profiles in range I are notably weaker and more like $T_1 \sim \nu^{(0\cdot5+\delta)}$ with $\delta < 0\cdot5$. This nematic-like behaviour of the collective relaxation contribution in smectic mesophases has been predicted for a long time [17] and was recently discussed theoretically in greater detail by Vilfan *et al.* [24], with the important result that, essentially depending on the dimensionality of the collective mode propagation, the T_{1OF} dispersion law changes from a linear to a square-root relation [25, 26], well known for nematic liquid crystals. Therefore, it is necessary to contrast the two concepts, and possibly combine them to achieve the best results. Such work is in progress [21], but we have no simple answer to the question about the meaning of the distinction. Since the linear dispersion has

Optimized model parameters obtained by the curve fits of equation (1 *a*) and equations (1 *b*)–(1 *d*) shown in figures 5 and 6. The fit of the amplitude factor A and the angle ϕ_{nH} are strongly correlated and allow various combinations within the experimental error limits for $T_1(\nu)$. Preference was given to the solution with ϕ_{nH} near the S_C^* tilt angle given in the literature [10] by making use of the finding that the smectic layer normal orients parallel to the magnetic field [2, 3].

	Order fluctuation term				Self-diffusion term		Rotation term	
	A/s^{-2}	$\nu_{\mathrm{c\,low}}/\mathrm{Hz}$	$\nu_{\mathrm{c\,high}}/\mathrm{Hz}$	$\phi_{nH}/°$	B/s^{-2}	$\tau_{\mathrm{SD}}/\mathrm{s}$	C/s^{-2}	$\tau_{\mathrm{Rot}}/\mathrm{s}$
70°C	$2{\cdot}5 \times 10^6$	$3{\cdot}5 \times 10^3$	$47{\cdot}7 \times 10^3$	27	$7{\cdot}5 \times 10^9$ $(D = 5{\cdot}1 \times 10^{-11}\,\mathrm{m^2\,s^{-1}}$, $d = 4{\cdot}6 \times 10^{-10}\,\mathrm{m})$	7×10^{-10}	$6{\cdot}5 \times 10^7$	$9{\cdot}5 \times 10^{-8}$
100°C	$3{\cdot}7 \times 10^6$	$4{\cdot}0 \times 10^3$	$13{\cdot}5 \times 10^3$	22	$6{\cdot}5 \times 10^9$ $(D = 9{\cdot}8 \times 10^{-11}\,\mathrm{m^2\,s^{-1}}$, $d = 4{\cdot}8 \times 10^{-10}\,\mathrm{m})$	4×10^{-10}	$4{\cdot}4 \times 10^7$	$3{\cdot}5 \times 10^{-8}$

recently also been found to be absent in a non-chiral smectic phase [27], it obviously has little to do with ferroelectricity.

So, regardless of this open question, the main result of our work at the present state is the finding that in ferroelectric mesogens, as in other nematic or smectic liquid crystals, collective molecular motions such as smectic undulation waves [17] or partly nematic-like director fluctuations [17, 24], are a very effective low frequency relaxation mechanism. This contribution can be stronger (IS-1912) or weaker (DOBAMBC) than noticed for example for TBBA [6, 7], but a peculiar motional spectrum could not be verified. Our N.M.R. measurements also do not show the ferroelectric soft modes seen by dielectric and optical mixing spectroscopy [3, 4, 23, 28], which is not surprising in view of the related, very low dielectric absorption frequencies ($\nu \lesssim 100\,\mathrm{Hz}$), where field cycling N.M.R. techniques have problems in eliminating the perturbing local field effects, and novel, poorly understood alternatives [29, 30] have to be used. However, it is surprising that the collective modes verified by T_1 studies between 10^3 and 10^5 Hz have never been reported or examined in dielectric or optical investigations, although in this case the necessary spectroscopic frequency range is accessible to all three methods.

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