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NMR field-cycling study of proton and deuteron spin relaxation in the nematic liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl

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NMR field-cycling measurements of the deuteron spin relaxation dispersion $T_1(\nu)$ for the fully deuteriated nematic liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl (5CB-d_{19}) over a broader Larmor frequency range ($\nu \approx 10$ kHz to 30 MHz) than reported so far in the literature basically confirm the magnetic relaxation mechanisms previously observed by frequency dependent proton spin studies of various nematogenic molecules, namely collective nematic modes of the director field in the kilohertz regime, and anisotropic reorientations of individual molecules (mainly self-diffusion for the protons and mainly rotations about the long axis for the deuterons) in the megahertz range. Within the experimental error limits such a model allows a self-consistent interpretation of the available deuteron and proton $T_1(\nu)$ results for deuteriated or protonated 5CB, respectively. In particular, the magnitudes of the measured order fluctuation contributions are in approximate accordance, i.e. within a factor of less than two, with theoretical estimates from NMR line splittings and the relevant material parameters. More exact and more extensive deuteron studies are needed to locate the origin of the observed minor inconsistency.

1. The problem

For more than 20 years, nuclear magnetic resonance (NMR) relaxation studies have been frequently used to analyse the complex anisotropic reorientations of molecules in the liquid-crystalline state [1, 2]. The basic idea of this NMR method is that the relaxation rates reflect the intra- and the intermolecular interactions of the nuclear spin magnetization with local magnetic and electric fields, and these fields are modulated by the underlying molecular motions [3]. Different kinds of reorientations like for example rotational or translational jumps can be, at least in principle, distinguished by analysing the Fourier spectra of the time dependent interactions [3], *if* the experiment provides sufficient data about the spectrum, i.e. over an adequately broad frequency range [4]. In practice, the problem with most known experimental results comes from the circumstance that standard (commercial) NMR spectrometers are restricted to a relatively small range of the magnetic resonance (Larmor) frequency in the megahertz regime, due to the strongly decreasing signal strength at lower frequencies or the related magnetic (Zeeman) fields. This narrow window is generally insufficient for a reliable evaluation of the motional spectrum, though some of the

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difficulties could be reduced by considering different alternative, highfield relaxation processes like longitudinal, transverse, rotating frame, dipolar or quadrupolar decays of the spin polarization [1–3].

Through the development of fast field-cycling NMR devices and procedures [4] it has become possible in recent years to extend the range of the motional spectrum seen by longitudinal spin relaxation experiments by many orders of magnitude, namely with the help of field-dependent measurements, which remove the classical frequency limits by cycling the external Zeeman field between different strengths, corresponding to selectable different Larmor frequencies. This field cycling method allows us to combine periods of high signal sensitivity with periods where the spin relaxation process experiences adjustable frequency components of the motional spectrum, selectable from standard high to almost arbitrarily low values, and it has been successfully applied to many kinds of solid and liquid materials [4]. Since the field-cycle transits should be short compared with the considered relaxation times or at least not significantly longer, and the relaxation times in liquid crystals become typically rather short at low magnetic fields (of the order of milliseconds), the application of the field-cycling technique to liquid-crystalline mesophases generally requires especially powerful instruments.

The still scarce field-cycling measurements of the longitudinal relaxation time T_1 as a function of the nuclear spin Larmor frequency ν (relaxation dispersion) performed up until now on liquid crystals (see, for example, [5–8]) have clearly demonstrated that most conclusions about the effective or dominating relaxation mechanism derived only on the basis of standard high field NMR data are generally not in acceptable agreement with the new findings obtained at lower magnetic fields. In particular, this concerns the significance of collective molecular reorientation such as nematic or smectic director field fluctuations [9], usually denoted order fluctuations of the director (OF or OFD). As first predicted independently by Pincus [10] and Blinc *et al.* [11], nematic type director fluctuations in the liquid-crystalline state should lead to a characteristic square-root dependence of the longitudinal nuclear spin relaxation rate $1/T_1$ on the Larmor frequency $\nu \equiv \omega/2\pi$ of the spin species, i.e.

$$\frac{1}{T_{1\mathrm{OF}}(\nu)} = \frac{A}{\nu^{1/2}} = \frac{(2\pi)^{1/2}A}{\omega^{1/2}}, \tag{1}$$

where the proportionality factor A depends on microscopic and macroscopic material parameters. These include the molecular geometry of the spin positions, the order parameter, the viscoelastic constants which determine the spectrum of the director modes, and the orientation of the director relative to the Zeeman field in the NMR experiment. Since almost any other spin relaxation model involves a small frequency range where T_1 can be approximated by a square-root expression $T_1 \approx \mathrm{const}_1 + \mathrm{const}_2 * \nu^{1/2}$[4, 9, 12], it is indeed extremely problematical to separate the Pincus–Blinc contribution from other potential molecular reorientations.

Making use of fast field-cycling T_1 techniques to determine the form of the longitudinal relaxation dispersion for proton spins in liquid crystals, the exact square-root law has been found more or less pronounced in all nematogens investigated for rather low values of ν, typically between 10 kHz and 500 kHz, and the data show intensity factors A in rather good agreement (≈ 500 to $10000\ \mathrm{s}^{-3/2}$) with estimates from the molecular parameters. Unfortunately, the proton relaxation as a rule only reveals a single relaxation rate averaged over all proton sites on the molecule, so that such results do not directly distinguish unlike kinds of motions of individual molecular segments, and consequently are hard to compare with for example deuteron or carbon NMR relaxation data, where different spin positions are in principle easily separable from the much better resolved spectrum [2], but where low frequency field-cycling techniques are more difficult to perform [4] and some preliminary measurements have been reported only very recently [2, 13, 14]. More extensive data for a systematic comparison of the T_1 dispersions of unlike nuclear spin species are clearly needed to understand and eventually to eliminate the inconsistencies in the literature about the underlying mechanisms, which essentially originate from the following experimental findings.

(i) As first observed by Orwoll *et al.* [15] for the deuteriated liquid crystal 4,4′-dimethoxyazoxybenzene (PAA), the frequency dependence of the longitudinal deuteron relaxation time in the standard megahertz range is generally negligibly small compared with proton results obtained at similar Larmor frequencies for the non-deuteriated molecule. Hence, the presence or absence of a characteristic $T_1 \sim \nu^n$ law with $n = 1/2$ is not necessarily equivalent with the presence or absence of the collective OFD process usually attributed to a special value of the exponent n.

(ii) At that time this behaviour was unexpected, however the surprisingly weak or even vanishing frequency dependence of the deuteron spin relaxation in the standard megahertz regime, was later confirmed for numerous deuteriated nematogens, in particular by extensive investigations of Dong *et al.* [16] and Vold *et al.* [17], and has also been observed by carbon NMR [18].

(iii) When recently more powerful field-cycling devices made it possible, for the first time, to measure the deuteron relaxation dispersion of some favourable, selectively deuteriated liquid crystals [2, 13, 14] at lower νs, it was found that the range of more or less frequency independent deuteron relaxation rates extends to surprisingly low values of ν, where for the protons the $T_1 \sim \nu^{1/2}$ profile is already fully developed.

The molecule 4-*n*-pentyl-4′-cyanobiphenyl (5CB) considered in this work is a nematogen with a relatively strong deuteron $T_1(\nu)$ variation at high Larmor frequencies for some deuteriated spin positions in the pentyl group, where Counsell *et al.* [19] observed $T_1(30\,\mathrm{MHz})/T_1(10\,\mathrm{MHz}) \approx 1{\cdot}5$. Though really the observed T_1 change is rather a small effect due to the restricted frequency range, it is not negligible compared with the experimental error limits of typically 5–10 per cent. More than that, the ratio 1·5 is close to what should be expected from a square-root law which gives $(30/10)^{1/2} = 1{\cdot}7$. This and similar findings have initiated extensive experimental and theoretical studies on the deuteron spin relaxation in various cyanobiphenyls (see for example, [18–25]) to understand the underlying reorientation processes. Deuteron relaxation measurements on 5CB are known for several selectively deuteriated species, namely for 5CB-d_1 and 5CB-d_2 (1 or 2 deuteron positions neighbouring one of the two phenyl rings), 5CB-d_6 (partially deuteriated alkyl chain), and also for 5CB-d_{15} (11 deuteron alkyl chain positions and 4 deuteron positions in the neighbouring phenyl ring), at frequencies between 12 MHz and 46 MHz. In this paper we present measurements of $T_1(\nu)$ on the fully deuteriated molecule 5CB-d_{19} over the considerably enlarged range from 10 kHz to 7 MHz, and contrast the new results with the proton T_1 dispersion obtained for the non-deuteriated 5CB system as well as with model calculations and high field measurements reported in the literature [19, 20, 23]. Within the present experimental error limits the deuteron and proton data can be interpreted essentially consistently by properly taking into account the Pincus–Blinc OFD mechanism, which in addition to reorientations of individual molecules, noticeably affects the relaxation rates of both protons and deuterons at Larmor frequencies below $\nu \approx 500\,\mathrm{kHz}$.

2. Experimental techniques and results

2.1. *NMR apparatus*

The application of fast field-cycling techniques to determine the frequency dependence of the longitudinal proton relaxation time T_1 by suitable Zeeman field-cycles and radio-frequency pulse sequences has been described previously [4, 5]. To extend such measurements to deuteron spins, it was necessary to improve the available instruments with regard to both signal sensitivity and spectral resolution. This was achieved by various new concepts [14], namely the construction of a more powerful field-cycling magnet (1·2 T) and current switching network (50 kW), refinements of the data aquisition and averaging techniques, and the combination of field-cycling with fast Fourier signal transformation to evaluate the spectra from the free induction decay of the signal. At present, the new spectrometer (deuteron detection frequency: $\nu_D = 6{\cdot}8\,\mathrm{MHz}$) does not yet allow to separate satisfactorily the relaxation dispersion of all deuteron sites in 5CB-d_{19} because of still insufficient spectral resolution and signal strength for larger field-cycles, but this does not change the basic results of the analysis. The proton measurements were performed on an older field-cycling apparatus [6, 7] (proton detection frequency: $\nu_P = 8{\cdot}9\,\mathrm{MHz}$). Some additional data for $\nu_P > 10\,\mathrm{MHz}$ and $\nu_D > 10\,\mathrm{MHz}$ were obtained by conventional fixed field instruments [5–8] or taken from the literature [19, 20, 23].

2.2. *Sample preparation*

Normal, non-deuteriated 5CB was purchased from Merck and filled in the sample tubes of our apparatus (diameter 1 cm, sample volume 1 cm^3) by the usual freeze-pump-thaw technique without further purification. The synthesis of the per-deuteriated material 5CB-d_{19} ($\approx 0{\cdot}7\,\mathrm{cm}^3$) essentially followed the procedure used by Gray *et al.* [26] to deuteriate 5CB-d_{15}. Details will be described elsewhere. We preferred the fully deuteriated compound because of the absence of dipolar deuteron–proton interactions.

2.3. *NMR measurements*

2.3.1. *Spectra*

In contrast to the proton NMR spectrum of non-deuteriated 5CB (see figure 1, top) which does not allow us to measure individual T_1s of distinct proton positions on the molecule separately because of the strong dipolar coupling and the related strong line overlaps, the deuteron spectrum of 5CB-d_{19} shows without any spin decoupling techniques (see figure 1, bottom) seven well-resolved line doublets, which can be assigned to five non-equivalent deuteron positions on the alkyl chain (C_1–C_5) and to two non-equivalent sites on the phenyl rings ($R_{1-6}, R_{7,8}$). The assignment of the different line splittings to the molecular sites was made on the basis of the analysis by Counsell for 5CB-d_{15}, where only the phenyl ring neighbouring the alkyl group was deuteriated. As easily seen by the comparison of the 5CB-d_{19} spectrum with the 5CB-d_{15} spectrum (see figure 1, middle), the fully deuteriated molecule (i) gives an additional line doublet ($R_{7,8}$) with a splitting $\Delta\nu$ of 7·6 kHz, and (ii) it shows a stronger intensity of the ring doublet (R_{1-6}) with $\Delta\nu$ of 10·6 kHz than the corresponding line pair of the 5CB-d_{15} spectrum. The intensity ratio of the two ring doublets for 5CB-d_{19} is approximately

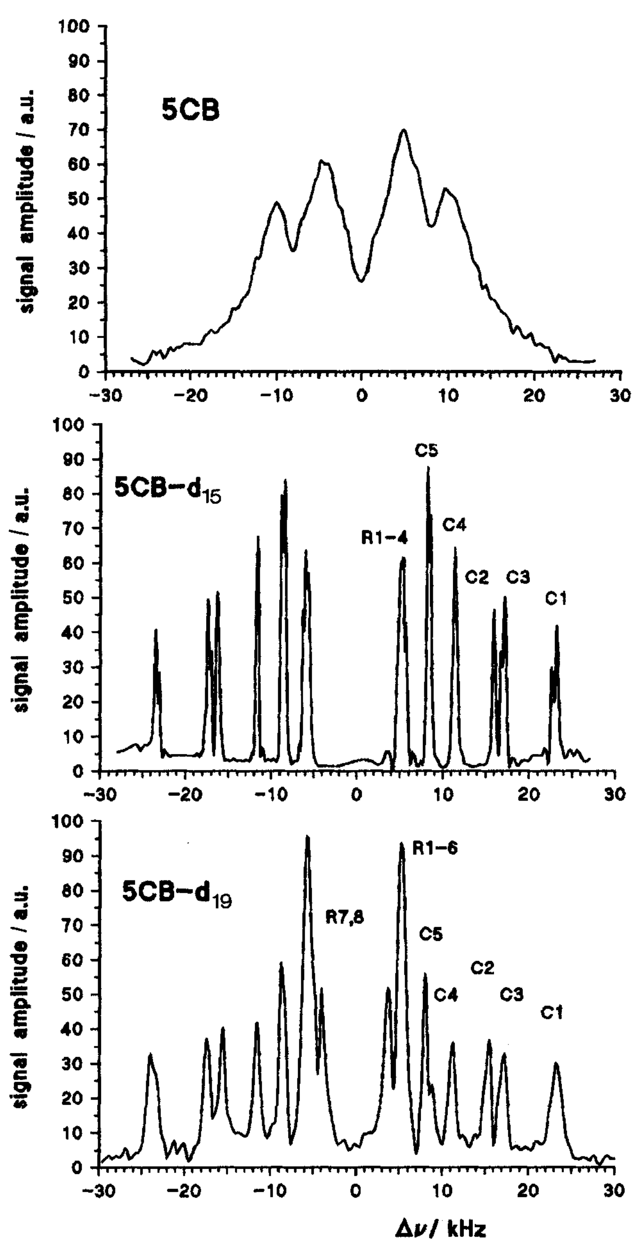

Figure 1. Comparison of several 5CB spectra considered in this field-cycling study. Top: Proton spectrum of non-deuteriated 5CB at 28 MHz and 25°C. Middle: Deuteron spectrum of selectively deuteriated 5CB-d_{15} at 30 MHz after Counsell *et al.* [19]. Bottom: Deuteron spectrum of per-deuteriated 5CB-d_{19} at 6·8 MHz and 25°C in the steady state fast field-cycling magnet. Ri denotes ring, Ci denotes chain deuteron positions.

Table 1. Dipolar proton and quadrupolar deuteron line splittings for 5CB-d_{19} (this work) and 5CB-d_{15} (after [19]).

5CB-d_{15} deuteron splittings		5CB-d_{19} deuteron splittings		5CB proton splittings	
position	$\Delta\nu$/kHz	position	$\Delta\nu$/kHz	position	$\Delta\nu$/kHz
—	—	R_{7-8}	7·6		
R_{1-4}	10·5	R_{1-6}	10·6	R_{1-8}(?)	9·5
C_5	16·2	C_5	17·1		
C_4	22·5	C_4	22·9	C_{1-5}(?)	21·5
C_3	33·5	C_3	35·0	—	
C_2	31·1	C_2	31·8	($\overline{\Delta\nu}$ = 15·5)	
C_1	46·6	C_1	47·9		

6 : 2. So the differences between the two spectra suggest that the cyano group in 5CB-d_{19} reduces the quadrupole coupling constant of the nearest ring deuterons ($R_{7,8}$) and thus causes a different line splitting, whereas all other ring positions (R_{1-6}) are not affected and exhibit within experimental error the same line splitting as the ring deuterons in 5CB-d_{15} (R_{1-4}). Table 1 lists the quadrupolar splittings obtained from the 5CB-d_{19} spectrum together with Counsell *et al.*'s data for 5CB-d_{15} [19]. The agreement is excellent, where comparable.

2.3.2. *Proton relaxation*

The proton T_1 relaxation dispersion of 5CB, illustrated in figure 2 at two temperatures, shows the characteristic frequency dependence observed in previous field-cycling measurements [4–8] of nematogens. In the nematic phase (at 30°C) there exists a broad square-root law regime, which starts from a low frequency plateau ($\nu < 10$ kHz) and ends by slowly approaching a high frequency plateau ($\nu > 1$ MHz). Such a $T_1 \sim \nu^{1/2}$ range disappears in the isotropic phase (at 38°C). As represented by the related temperature dependent measurements in figure 3, the nematic–isotropic transition at 36·5°C entails a discontinuous T_1 change with a positive sign at low ν values and a negative sign at high ν values, so that the $T_1(\nu)$ plots for the nematic and isotropic state, respectively, have a crossing point near 250 kHz. This feature, important to analyse $T_{1\mathrm{OF}}$, is generally overlooked in the literature, essentially due to the unavailability of low field data. Evaluation of T_1 for different parts of the proton spectrum did not reveal noticeable changes of the dispersion profiles.

Complementary measurements at still higher proton Larmor frequencies in the conventional megahertz range (above 30 MHz, not included in the diagrams because of the present restrictions to the accessible deuteron resonance range), demonstrate the existence of the high frequency $T_1(\nu)$ plateau more clearly [5, 7, 21] and furthermore the expected beginning of a second, new dispersion step with increasing slope, which becomes considerably steeper near 100 MHz than the low frequency square-root profile shown. This well-known, typical overall behaviour was first observed and systematically analysed for numerous familiar high and low temperature nematic liquid crystals like PAA and 4-*n*-methoxybenzylidene-4′-butyaniline (MBBA) [4, 5], but is also well established for several nematic *n*-alkyl- and *n*-alkyloxy-4′-cyanobiphenyls (*n*CBs, *n*OCBs) like, for example, 7CB or 7OCB [5, 7, 8]. So the new proton relaxation study of 5CB does not reveal anything unexpected or unusual, if we

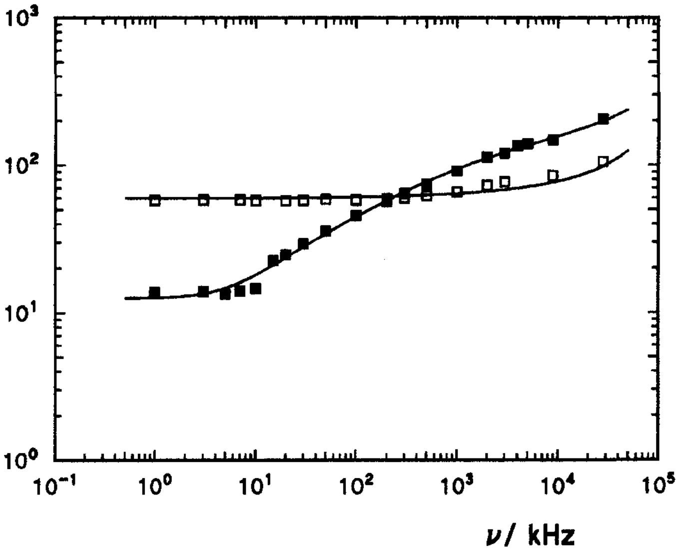

Figure 2. Longitudinal proton spin relaxation dispersion $T_1(\nu)$ for non-deuteriated 5CB in the nematic phase (■, 30°C) and in the isotropic phase (□, 38°C). The nematic–isotropic transition was measured at $T_{NI} = 36{\cdot}5$°C. The plots are model fits with equation (3).

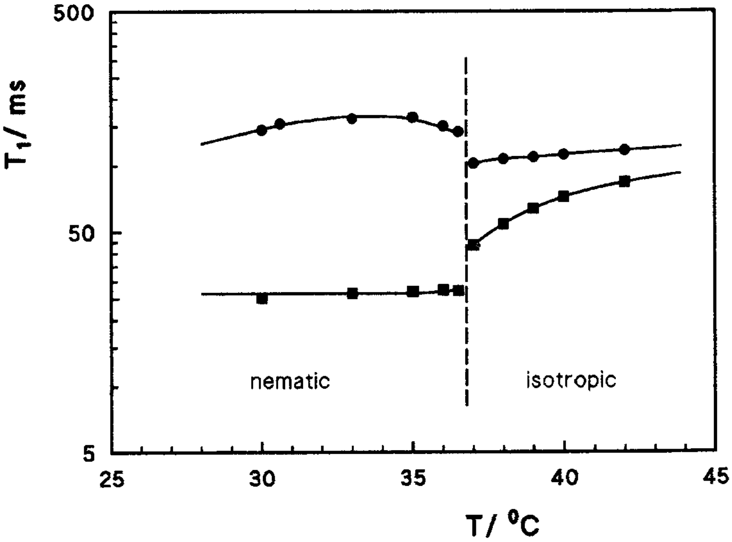

Figure 3. Temperature dependence of the longitudinal proton spin relaxation time $T_1(T)$ for non-deuteriated 5CB near the nematic–isotropic transition in both phases. The $T_1(T)$ discontinuity at T_{NI} is positive for low ν and negative for high ν. ●, 8·9 MHz; ■, 20 kHz.

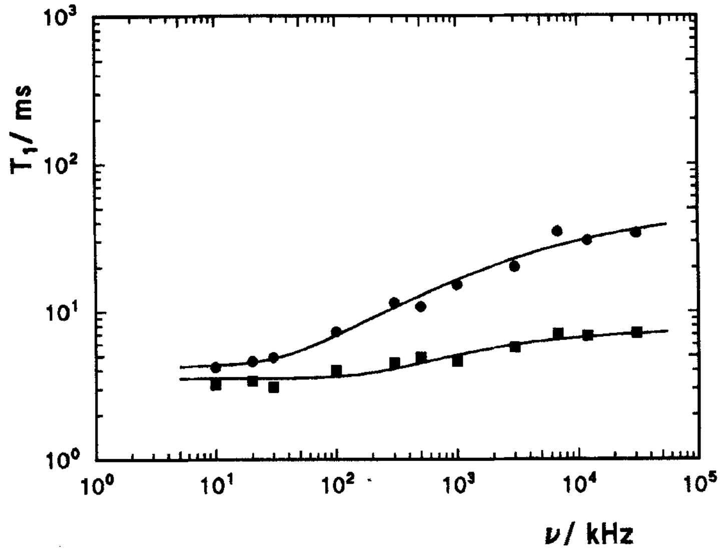

Figure 4. Longitudinal deuteron spin relaxation dispersion for per-deuteriated 5CB-d_{19} in the nematic phase at 30°C. The exact meaning of chain (C) and ring (R) as average deuteron sites is illustrated by figure 6. Chain deuterons (●) show a much stronger T_1 frequency dependence than ring deuterons (■). Data at 30·7 MHz are taken from Counsell *et al.* [19], and the plots are model fits to equations (5) and (6*b*).

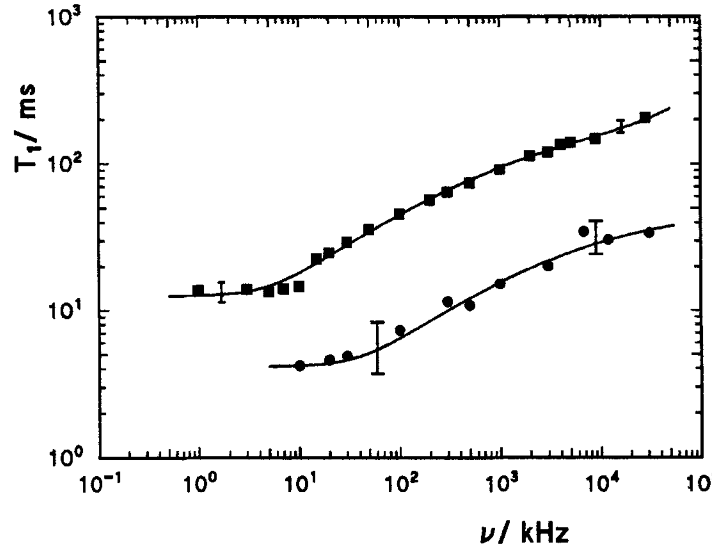

Figure 5. Comparison of the longitudinal proton and deuteron relaxation dispersion for 5CB (■) and 5CB-d_{19} (●), respectively. The plots are model fits to equations (3), (5) and (6).

take into account the different phase transition temperatures and molecular parameters compared with other low temperature nematogens.

2.3.3. *Deuteron relaxation*

Figure 4 presents our deuteron T_1 dispersion measurements on nematic 5CB-d_{19} at 30°C, and figure 5 contrasts these results with the proton data of figure 2 over the frequency ranges presently accessible to the fast field-cycling method, slightly extended by some standard high field studies for ν above 10 MHz. Since in the field-cycling mode not (yet) all seven doublets of the deuteron 5CB-d_{19} spectrum (see figure 1) allow a satisfactory separation of the pertinent T_1 relaxation rates because of the presently somewhat insufficient signal quality and resolution, the deuteron measurements were evaluated only for several average spin positions, namely for the chain window (bonds to carbons $C_1 \ldots C_5$), the ring window (bonds to carbons R_{1-6} and $R_{7,8}$), and the overall window (bonds to $C_1 \ldots C_5$, R_{1-6}, $R_{7,8}$). Neither the C_1 position, which gives the shortest relaxation time of the chain dueterons, nor the $R_{7,8}$ site, could be treated individually with acceptable error limits ($< \pm 50$ per cent) under field-cycling conditions. Two typical deuteron spectra, obtained in the course of field-cycling relaxation processes at 30 kHz and 300 kHz, respectively, and the considered spectral windows, are shown in figure 6.

Though the experimental error limits of the deuteron field-cycling results are still relatively large (± 50 per cent below $\approx 10^2$ kHz and ± 25 per cent above 10^2 kHz) due to the small maximum detection field stength of 1·2 T and some problems with the fast

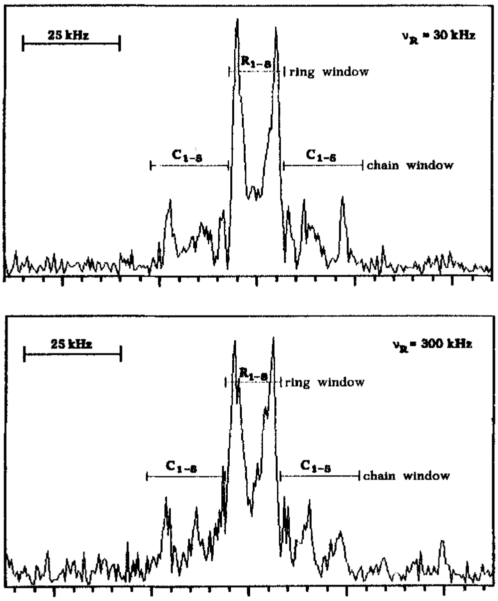

Figure 6. Illustration of the deuteron 5CB-d_{19} spectrum in a detection field of 1·04 T ($\nu_D = 6{\cdot}8$ MHz) and the spectral chain and ring windows considered for a typical field-cycling relaxation measurement. The spectra were obtained after field-cycles between 1·04 T to lower fields [4] corresponding to relaxation frequencies ν_R of 30 kHz and 300 kHz, respectively. Signal FIDs following a $\pi/2$ pulse ($\approx 10\,\mu$s) in the detection field were averaged 256 times before calculating and filtering the power Fourier transform. The length of the low field period, excluding the transit times, was 5 ms.

current switch regulation, the dispersion data obtained clearly demonstrate several details which were not recognized previously, but which are most important for a quantitative understanding of the underlying processes.

(i) Over the whole frequency range considered, the deuteron relaxation times are much shorter, up to more than one order of magnitude, than the related proton data. (At low νs, where the chain deuteron T_1s approach 1 ms, T_1 becomes comparable to the switching times of our apparatus, which is the main reason for the decreasing low field accuracy.)

(ii) As expected from the high field studies, the deuteron chain relaxation times are considerably longer than the ring T_1s at the same frequency. The new aspect is that the chain positions involve a strong frequency dependence, whereas the ring positions do not, and hence the two dispersion plots approach each other in the kilohertz range.

(iii) The dispersion profile of the chain deuterons reveals an approximate square-root law over a rather broad range, namely at medium frequencies, where such a behaviour is also visible by the proton measurements. Obviously, the slope of the $T_1(\nu)$ profile decreases at higher νs, in accord with results available in the literature for $\nu > 10$ MHz [19, 20, 23]. In the light of the minor variations reported in the literature, where the greatest change amounts to $T_1(30\,\mathrm{MHz})/T_1(10\,\mathrm{MHz}) \approx 1{\cdot}5$ for the C_1 position, the total effect seen by figure 4, where $T_1(6{\cdot}8\,\mathrm{MHz})/T_1(10\,\mathrm{kHz}) \approx 10$, is surprisingly large!

(iv) The relaxation dispersion of the ring deuterons is very weak compared with that of the chain deuterons, but not completely negligible within the error of the T_1 data. It becomes observable only at much lower frequencies than for the chain positions, and we should note that such behaviour is opposite to the findings by proton studies of selectively deuteriated molecules [4, 5], where the available results clearly show the stronger frequency dependence of the ring protons' T_1.

In comparison with our previous, preliminary deuteron field-cycling studies on easier to handle, selectively deuteriated PAA (PAA-d_6, PAA-d_8) and MBBA (MBBA-d_6, MBBA-d_{14}) molecules [2, 13, 14], the new measurements on 5CB-d_{19} exhibit qualitatively similar features and relaxation mechanisms in all these nematic systems. The form of the various deuteron $T_1(\nu)$ profiles is basically the same, and we always find T_1(protons) > T_1(chain deuterons) > T_1(ring deuterons). However, in detail there exist obvious distinctions. On the one hand, 5CB-d_{19} involves much faster deuteron relaxation rates than PAA or MBBA for the deuteron sites investigated by fast field-cycling up to now. On the other hand, the chain positions exhibit a stronger T_1 dispersion than observed for the chain deuterons of PAA or MBBA, in agreement with the reported high field NMR results. This behaviour, which essentially is a corollary of the 5CB anomaly pointed out earlier, will be analysed in the following section.

3. Discussion and conclusions

3.1. *General*

Whereas the original work of Counsell *et al.* [19] on the high field deuteron relaxation of nematic 5CB-d_{15} could not give a satisfactory explanation of the non-vanishing T_1 frequency dependence observed for the chain positions, Dong [23] recently suggested a model of molecular rotations (small step symmetric top, superimposed with correlated intramolecular reorientations), which allowed him to explain the available experimental data in the range betweeen 10 MHz and 30 MHz quantitatively, without the need to take into account order director fluctuations. However, the extrapolation of Dong's model to kilohertz frequencies deviated drastically from the new field-cycling low-frequency points of figure 4, namely by approximately a factor of 10 for the chain positions and by a factor of 2 for the ring sites. Dong's theoretical predictions give much too long relaxation times, and this discrepancy not only supports Counsell's early, qualitative speculations that a correct description of the relaxation mechanism should include some kind of slow collective motions like director fluctuations. More than that, the deviations are also very reasonable because a process which dominates the proton T_1 dispersion under special conditions (low νs) should not be completely absent or negligible in the related deuteron measurements.

Using for the proton spins the concept developed in previous studies from proton results with appropriate modifications, i.e. a superposition of collective order fluctuations with translational and rotational motions of individual molecules, and for the deuteron spins a superposition of order fluctuations with individual rotational reorientations, model fits give OFD intensities for both the protons and deuterons, which have the correct order of magnitude as estimated from the NMR line splittings and from the viscoelastic constants. However, since data on the viscosities and Frank elastic constants scatter broadly, and our approach is still restricted to two average deuteron positions on the molecule (see figure 6), further more accurate measurements could lead to minor inconsistencies than those indicated in the following discussion.

3.2. *Proton relaxation*

In the range between ≈ 1 kHz and ≈ 10 MHz, the proton data for the nematic phase can be approximated as in most nematogens by two simple relaxation contributions, namely a broad square-root term caused by slow director order fluctuations ($T_{1\mathrm{OF}}$) and a frequency independent term due to faster non-collective translational and rotational molecular reorientations ($T_{1\mathrm{TR}}$). However, such an oversimplified model with just two fitting parameters (A, B),

$$\frac{1}{T_1(\nu)}=\frac{1}{T_{1\mathrm{OF}}}+\frac{1}{T_{1\mathrm{TR}}}=\frac{A}{\nu^{1/2}}+B, \tag{2}$$

proves inadequate at both low and high νs, and improves considerably, if we include a low cut-off frequency near 10 kHz in the first term, and a shallow transition to another dispersion step near 5 MHz in the second. Reasons for this kind of refinement are numerous and well known. For simplicity, and on the basis of prior proton $T_1(\nu)$ studies, we have introduced on the one hand an empirical cut-off ν_c, which may be ascribed either to local Larmor frequency shifts in the sample [27] or to a finite maximum OF mode length [11]. On the other hand we have considered a Harmon–Muller type dispersion of the $T_{1\mathrm{TR}}$ contribution expected for dominant translational molecular reorientations ($T_{1\mathrm{T}}$), i.e. translational self-diffusion, at the beginning of the related relaxation dispersion step [12]. This roughly leads to another square-root dependence of T_1. The plots given by figure 2 illustrate the good quality of data-to-model fits by means of the refined, four parameter expression

$$\frac{1}{T_1(\nu)}=\frac{1}{T_{1\mathrm{OF}}}+\frac{1}{T_{1\mathrm{T}}}=\frac{A}{(\nu^2+\nu_c^2)^{1/4}}+B(1-\alpha\nu^{1/2}), \tag{3}$$

Table 2. Optimized model parameters (A, B, ν_c, α) of the 5CB proton and 5CB-d_{19} deuteron relaxation model, equations (3), (5) and (6), obtained by standard non-linear Levenberg–Marquard curve fitting methods.

	5CB-d_{19} deuterons			5CB protons	
	Nematic			Nematic	Isotropic
	Chain sites	Ring sites		Average site	
$A_{(i)}/\mathrm{s}^{-3/2}$	44300 ± 15%	18400 ± 30%	$A/\mathrm{s}^{-3/2}$	5290 ± 10%	≤ 50
	$A_{(C)}:A_{(R)}=2{\cdot}4$				
$B_{(i)}/\mathrm{s}^{-1}$	19·3 ± 10%	160 ± 10%	B/s^{-1}	5·7 ± 10%	16·8 ± 10%
	$B_{(C)}:B_{(R)}=0{\cdot}12$				
$\nu_{c(i)}/\mathrm{kHz}$	40·0 ± 15%	13·4 ± 25%	ν_c/kHz	5·09 ± 10%	≤ 0·5
			α/kHz^{-1}	$1{\cdot}90\times10^{-3}\pm15\%$	$2{\cdot}76\times10^{-3}\pm15\%$

where ν_c and α determine the beginning of the low and high frequency $T_1(\nu)$ plateaus, respectively. Table 2 summarizes the best fitting parameters (A, B, ν_c, α) obtained by a standard Levenberg–Marquard least-squares optimization procedure, which gives $A \approx 0$ for the isotropic phase, as expected. We should emphasize that the available measurements are not sufficient to distinguish the considered refinements in equation (3) from various alternatives suggested in the literature [1–4] (for example modifications of $T_{1\mathrm{OF}}$ due to long and short OF-mode cut-offs; extensions of $T_{1\mathrm{TR}}$ caused by correlated motions of coupled spin pairs; special order fluctuation effects near the nematic–isotropic transition), because of too similar model properties. For this reason, we restrict the present discussion to the two most disputed primary model parameters A and B.

The experimental result $A \approx 5290\,\mathrm{s}^{-3/2} \pm 10$ per cent compares well with values obtained for other low temperature nematogens, like MBBA (A at $30°\mathrm{C} \approx 7000\,\mathrm{s}^{-3/2}$) or 7CB ($A$ at $30°\mathrm{C} \approx 4500\,\mathrm{s}^{-3/2}$) [5], and hence is roughly consistent with estimates from the molecular geometry and material constants involved in the OF intensity factor [11]. However, since the individual, dynamically averaged spin pair orientations and separations on the 5CB molecule are not directly available to calculate A, in principle a more sensitive model test should be possible by analysing A in terms of the underlying line splittings $\Delta\nu_i$ [1–3], which for a proton spectrum with a single average relaxation rate gives

$$A = \frac{\sqrt{\pi}}{2} (\langle \Delta\nu \rangle)^2 k_B T \frac{\eta^{1/2}}{K^{3/2}}, \tag{4}$$

where $\langle \Delta\nu \rangle$, η, and K denote the average (effective) line splitting, viscosity and Frank elastic modulus, respectively. Unfortunately, the available K data for 5CB at room temperature scatter by more than a factor of 2·5 [21, 28, 29]! Taking $\langle \Delta\nu \rangle = 16\,\mathrm{kHz}$ from figure 1 together with $\eta = 6{\cdot}3 \times 10^{-2}\,\mathrm{Ns\,m}^{-2}$ [28] and $K = 1{\cdot}3 \times 10^{-11}\,\mathrm{N}$ [29], we find $A(\mathrm{theor.}) = 5150\,\mathrm{s}^{-3/2}$ in good agreement with the experimental finding. But using $K = 5 \times 10^{-12}\,\mathrm{N}$ reported by Lewis *et al.* [21] leads to $A(\mathrm{theor.}) = 21580\,\mathrm{s}^{-3/2}$ and thus to a significant discrepancy.

In addition the parameter B is of comparable magnitude ($\approx 1 \ldots 10\,\mathrm{s}^{-1}$) as found previously for other low temperature liquid crystals like MBBA or 7CB [5], and hence by means of the Harmon–Muller theory [12] or related translational relaxation models [3] reflects at 25°C rather similar self-diffusion constants D of approximately $2\times10^{-11}\,\mathrm{m^2\,s^{-1}}$ in these nematics. The problem with such T_1 results is that in the still rare case where more direct, i.e. model independent diffusion studies are known as for example for MBBA or PAA [30, 31], the relaxation dispersion analysis always leads to much too small a jump rate and diffusion constants. As a consequence, since $T_{1\mathrm{T}}\sim D$ [3], to eliminate this inconsistency we have to include additional, rotational processes in the high field dispersion [32, 33], which, however, are not easy to disentangle from the dispersion profiles without independent measurements of the diffusion tensor. Preliminary pulsed-field gradient measurements [34, 35] on 5CB indicate that at 35°C its component perpendicular to the director field ($D_\perp$) is about $7{\cdot}2\times10^{-10}\,\mathrm{m^2\,s^{-1}}$, i.e. much larger than that derived from the T_1 data, so that the proton high field relaxation must involve non-negligible rotational inter- and intramolecular reorientations.

3.3. *Deuteron relaxation*

The far-reaching parallels between the proton and deuteron spin relaxation dispersion profiles suggest as a first approach similar models with appropriate modifications, which take into account the site-dependence of T_1 and the weakness of the intermolecular spin couplings in deuteron systems. To satisfy the first requirement, equation (2) has to allow for different values of both A and B at non-equivalent deuteron positions, in accord with the resolved doublet splittings. The second aspect demands an interpretation of the $T_{1\mathrm{TR}}$ term primarily by molecular rotational ($T_{1\mathrm{R}}$) instead of dominant translational ($T_{1\mathrm{T}}$) self-diffusion. For simplicity, we replaced the Harmon–Muller expression [12] by the Woessner formalism [32, 33] for reorientation of ellipsoidal molecules in the fast rotation limit, which gives instead of equation (3) the model expressions

$$\frac{1}{T_{1(i)}(\nu)}=\frac{1}{T_{1\mathrm{OF}(i)}}+\frac{1}{T_{1\mathrm{R}(i)}}=\frac{A_{(i)}}{(\nu^2+\nu_{\mathrm{c}(i)}^2)^{1/4}}+B_{(i)}, \tag{5}$$

with (i) referring in this case to either ring (R) or chain (C) sites. The fits were performed together with the constraint imposed by the independently measured deuteron line splittings,

$$A_{(\mathrm{C})}:A_{(\mathrm{R})}=(\Delta\nu_{(\mathrm{C})}:\Delta\nu_{(\mathrm{R})})^2\cong(30:10)^2=9, \tag{6a}$$

or more generally

$$\begin{aligned}A_{(\mathrm{C})}:A_{(\mathrm{R})}&=(\Delta\nu_{(\mathrm{C})}:\Delta\nu_{(\mathrm{R})})^2\cong(17:11)^2\ldots(48:11)^2\\&=2{\cdot}4\ldots20,\end{aligned} \tag{6b}$$

allowing that the weight of the unlike chain deuterons on the average $T_{1(\mathrm{C})}$ is not equal. The result is illustrated by figure 4. In spite of the relatively large experimental scatter of the low frequency data, the model optimization of the fitting parameters $A_{(\mathrm{C})}$, $A_{(\mathrm{R})}$, $B_{(\mathrm{C})}$, $B_{(\mathrm{R})}$, $\nu_{\mathrm{c(C)}}$ and $\nu_{\mathrm{c(R)}}$ listed in table 2 produced a clear least-squares minimum. Note that the best fit of the ring deuteron relaxation dispersion, which is too weak to be determined alone by the $T_{1(\mathrm{R})}$ profile, is not obtained with the constraint in equation (6 *a*), but by means of equation (6 *b*) and the smallest admissible ratio $A_{(\mathrm{C})}:A_{(\mathrm{R})}$, in other words the ring contribution is surprisingly strong.

Evaluating the $A_{(i)}$s at 30°C by the deuteron equivalent of equation (4) [1–3]

$$A_{(i)}=\frac{\sqrt{\pi}}{2}(\Delta\nu_{(i)})^2 k_B T\frac{\eta^{1/2}}{K^{3/2}} \tag{7}$$

gives, at 30°C with $\Delta\nu_{(C)}=30\,\mathrm{kHz}$, $\Delta\nu_{(R)}=10\,\mathrm{kHz}$ and with the viscosity η and elastic constant K (28, 29] selected as in the case of the proton data, the OF intensities $A_{(C)}(\mathrm{theor.})=18000\,\mathrm{s}^{-3/2}$ and $A_{(R)}(\mathrm{theor.})=2000\,\mathrm{s}^{-3/2}$, i.e. values too low compared with the experimental results $A_{(C)}\cong 44\,300\,\mathrm{s}^{-3/2}$ and $A_{(R)}\cong 18\,400\,\mathrm{s}^{-3/2}$. However, making use of the smaller elastic constant reported in the literature [21], entails $A_{(C)}(\mathrm{theor.})=75400\,\mathrm{s}^{-3/2}$, which now is too large, whereas $A_{(R)}(\mathrm{theor.})=8400\,\mathrm{s}^{-3/2}$ is still too small. So the uncertainties and errors of both K and η can roughly eliminate most of the observed inconsistencies, but not all,. by distributing the deviations by factors of between 0·7 to 1·5 to both the proton and deuteron studies. Obviously, for the deuteron relaxation the model fits somewhat overestimate the OF contribution, in particular where the square-root regime is only weakly seen. The slightly too short experimental deuteron $T_{1(i)}$s probably indicate the presence of another low frequency relaxation process, not easily resolvable from the available 5CB data, or a minor frequency dependence of the B terms expected by Dong's model [23], or both. An additional T_1 process (deuteron–deuteron cross-relaxation) has been clearly observed in selectively deuteriated high temperature nematics like PAA-d_6 and PAA-d_8 [13, 14], where the slower relaxation rates allowed a more accurate low field analysis. If we extrapolate the square-root law to 30 MHz, the OF contribution to the total relaxation rate is about 30 per cent for the chain deuterons and about 3 per cent for the ring deuterons, respectively.

A similar quantitative discussion of the parameters B and $B_{(i)}$ is not yet feasible because of the missing or at least incomplete understanding of self-diffusion in 5CB and most nematic liquid crystals. Though the B terms can be determined with higher accuracy than the A terms, their different origins in equations (3) and (5), respectively, and the rather unspecific, broad proton T_1 dispersion profile at high νs together with the almost absent deuteron T_1 dispersion, prevent a convincing unambiguous assignment to a well-defined reorientation process; and this fact does not allow a reliable estimate of the high field relaxation time ratio T_1(proton)/T_1(deuteron) without numerous uncontrollable assumptions. To solve the problem, we are making systematic self-diffusion studies of low molar mass nematogens by means of a special combination of NMR field-cycling with pulsed field-gradient techniques [30, 31], which however for the 4-*n*-alkyl-4′-cyanobiphenyls like 5CB prove particularly difficult due to the extremely short transverse relaxation time [34, 35].

In spite of the existing open questions, the various B parameters reveal a notable behaviour not seen as clearly in previous studies. It was first pointed out by Rutar *et al.* [36] through T_1 measurements on normal and ring-deuteriated MBBA at standard megahertz frequencies that the two ratios T_1(proton)/T_1(deuteron) and T_1(deuteron, site 1)/T_1(deuteron, site 2) could not be understood with a model restricted to dominant molecular rotations about either the short or the long ellipsoidal axis. In other words, proton and deuteron spin relaxation reflect different types of molecular rotations! On the one hand, the experimental deuteron T_1s are much too short or the proton T_1 data are too long compared with theoretical estimates which consider only the faster reorientations about the short axis [3, 32, 36]. Furthermore, the site dependence of the individual deuteron $T_{1(i)}$s deviates strongly from the required relation with the quadrupolar doublet splittings $\Delta\nu_{(i)}$, namely [36]

$$\frac{1}{T_{1R(i)}} \sim S^2(3\cos^2\phi_{(i)}-1)^2 \sim (\Delta\nu_{(i)})^2, \tag{8}$$

where S is the second rank orientational order parameter and $\phi_{(i)}$ is the angle between the relevant C–D bond and the main molecular axis. On the other hand, considering only proton reorientations about the long axis by the expression [36]

$$\frac{1}{T_{1R}} \sim S^2(\sin^2 2\phi + \sin^4\phi), \tag{9}$$

where $\phi \equiv \langle\phi_i\rangle$ denotes the mean inclination of the i proton spin pairs relative to the main axis, gives too weak a rotational contribution to the total relaxation rate, in particular when the angle is small as for the ring groups, and hence does not solve the inconsistency with the self-diffusion constant discussed earlier. Such effects are more clearly pronounced for 5CB than for MBBA. For example, tables 1 and 2 show that $B_{(C)}:B_{(R)} \approx 0{\cdot}12$, whereas $(\Delta\nu_{(C)}:\Delta\nu_{(R)})^2 \approx 10$ (or in the range between 2 and 20, if we allow unlike weightings of different line doublets according to equation (6 *b*)). The obvious overestimate of the self-diffusion relaxation rate $1/T_{1T}$ by equation (3) is not easy to correct by a rotational term $1/T_{1R}$ as in equation (9).

So the new 5CB data qualitatively confirm Rutar *et al.*'s conclusions about the different importance of the two rotational processes (∥ or ⊥ to the long molecular axis) for the proton and deuteron T_1 relaxation, respectively. This is a reasonable finding due to the unlike orientations of the dipolar H–H and quadrupolar C–D coupling tensors at the same spin position. For instance, according to equation (9) and its deuteron analogue (ϕ replaced by $\phi_{(i)}$), rotations about the long axis are a rather negligible relaxation mechanism for the ring ortho-proton pairs, ($\phi \approx 0$), but not a negligible one for ortho-deuteron sites ($\phi_{(R)} \approx 65°$). Hence the chain positions produce a complex mixture of both rotational effects, and are hard to disentangle from the T_1 dispersion profile without additional information about the angles involved. As a consequence of the dissimilar rotational relaxation processes for protons and deuterons, respectively, the order fluctuation term is generally less clearly seen for the deuterons as for the protons, though this could have turned out otherwise because of the absence or negligible self-diffusion contribution for the quadrupolar coupled spins.

In view of these difficulties for a quantitative calculation the essential new comes from the comparison of the $B_{(i)}$ terms with the $A_{(i)}$ terms result in the model fits of equation (5). Though, as evident from the $T_{1(R)}$ profile in figure 4, the accuracy of the model parameter $A_{(R)}$ and hence also of the ratio $A_{(C)}:A_{(R)}$ is poor, the data fit clearly demonstrates that $A_{(C)}:A_{(R)} \gg 1$ as expected for reorientations about the short molecular axis, whereas $B_{(C)}:B_{(R)} \ll 1$ as expected for motions about the other, the long axis. This dramatic change of the relaxation intensities strongly supports the basic concept of our model in equations (3)–(7), namely that the high and low frequency regimes reflect quite different dynamic processes.

The analysis of the secondary model parameters (ν_c, α) will be given in a forthcoming paper [37, 38] about more suitable, selectively deuteriated nematic 4,4′-di-*n*-alkyloxyazoxybenzenes, where the low and high frequency plateaus reveal more details, and where the significantly longer relaxation times can be studied with better accuracy, and model independent measurements on the anisotropic self-diffusion tensor are already available.

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