

MEASUREMENT OF DEUTERON SPIN RELAXATION TIMES IN LIQUID CRYSTALS by a BROADBAND EXCITATION SEQUENCE

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I. Introduction

Liquid crystals are composed of flexible organic molecules and capable of forming different ordered structures in their mesophases. Nuclear spin relaxation [1], [2] is a powerful technique that provides useful information on the molecular dynamics of liquid crystals. There are collective director fluctuations, molecular reorientation and internal rotations in flexible end chains. Recently internal dynamics of mesogenic molecules has attracted much attention. Both theoretical [3], [4] and experimental [5], [6] studies have been carried out. Experimentally carbon-13 and deuterium may be used to probe internal dynamics of flexible mesogens. In aligned samples of deuterated liquid crystals, deuterium NMR spectroscopy yields well-resolved spectral lines having different quadrupolar splittings for various atomic sites. These quadrupolar splittings result from incomplete averaging by anisotropic reorientation of molecules in the mesophases. For a single deuterium spin ($I=1$), there are five independent spin relaxation times [7]. These are two spin-lattice relaxation times and three independent spin-spin relaxation times. Since the deuterium Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin-lattice relaxation times are given by [7], [8]

$$\begin{aligned} T_{1Z}^{-1} &= J_1(\omega_0) + 4J_2(2\omega_0) \\ T_{1Q}^{-1} &= 3J_1(\omega_0), \end{aligned}$$

they can be used to separate the two spectral densities of motion $J_1(\omega_0)$ and $J_2(2\omega_0)$. Accurate determination of these spectral parameters as a function of temperature and the Larmor frequency (ω_0) is necessary for testing various motional models.

Both T_{1Z} and T_{1Q} can be simultaneously measured by the Jeener-Broekaert (J-B) method [9] or the selective-inversion method [5]. However a separate experiment has to be performed for the deuterons on each labelled site in order to maximize their quadrupolar order for better signal-to-noise considerations. The J-B sequence has been used to determine T_{1Z} and T_{1Q} in several nematogens [10]. The pulse sequence was modified using an additional 45° pulse to produce the net effect of subtracting the equilibrium M_∞ signal from the J-B signal. Here we examine the modification of the J-B sequence (Table 1) to produce [11] a broadband excitation sequence (Table 2) in order to minimize the number of separate experiments required to give T_{1Z} and T_{1Q} for various deuterons on an alkyl chain. Recently this broadband J-B excitation sequence was used to create quadrupolar order with same efficiency on all the labelled sites in a liquid crystal [12].

TABLE 1

J-B Sequence with Phase-cycling						Receiver
ϕ_1	ϕ_2	ϕ_3	Aqu T	ϕ_4	Aqu T	Phase ^a
x	y	x	+			0
-y	x	y	-			90
x	y	-x	-			0
-y	x	-y	+			90
				y	+	90
				x	-	0
				-y	-	90
				-x	+	0
				-x	+	0
				-y	-	90
				x	-	0
				y	+	90
x	-y	-y	+			90
-y	-x	-x	-			0
x	-y	y	-			90
-y	-x	x	+			0

^a +/- during acquisition (Aqu) denotes addition to or subtraction of the signal from computer memory; cycling of the receiver phase minimized the quadrature images.

TABLE 2

Broadband J-B Sequence with Phase-cycling										Receiver
ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	Aqu T	ϕ_6	Aqu T			Phase
x	-y	y	y	x	+					0
-y	-x	x	x	y	-					90
x	-y	y	y	-x	-					0
-y	-x	x	x	-y	+					90
						y	+			90
						x	-			0
						-y	-			90
						-x	+			0
						-x	+			0
						-y	-			90
						x	-			0
						x	-			0
						y	+			90
x	y	-y	-y	-y	+					90
-y	x	-x	-x	-x	-					0
x	y	-y	-y	y	-					90
-y	-x	-x	-x	x	+					0

2. Experimental

The deuterium T_{1Z} and T_{1Q} were measured on a home-built superheterodyne coherent pulsed NMR spectrometer operating at 15.3 and 46.05 MHz for deuterium with a Varian 15 in electromagnet and a 7.1 Tesla Oxford superconducting magnet. The $\pi/2$ pulse width of ca. $4.5 \mu\text{s}$ was produced by an Amplifier Research Model 200L power amplifier. Pulse control, signal collection, Fourier transformation and data processing were performed using a General Electric

1280 computer [10]. Both the J-B sequence and the broadband J-B excitation sequence (Figure 1) were used with the appropriate phase-cycling [9] of RF and receiver phases to rid of the unwanted double quantum coherence (see Tables 1 and 2). Several nematogens (5CB, MBBA and 60CB) were employed to check the spin relaxation times obtained by the two different multipulse sequences.

3. Results and Discussion

In figure 2 we show a comparison of the J-B sequence (2(a)) and the broadband J-B excitation sequence (2(b)) for a set of partially relaxed spectra at 15.3 MHz in the nematic phase of 4-n-pentyl- d_{11} -4'-cyano-2,3,5,6- d_4 -biphenyl (5CB- d_{15}). Minimal phase correction was required and the baseline of each spectrum has been corrected. In figure 2(a) the J-B sequence was set to maximize the quadrupolar order of the C_4 methylene deuterons. In comparison with the J-B sequence, we found that maximum quadrupolar order was created for all the chain deuterons with $\tau = 5\mu\text{s}$ (or an excitation bandwidth of ca. 75 kHz). In table 3 we summarize the T_{1Z} and T_{1Q} measured at 33.2°C in 5CB- d_{15} by the two different J-B sequences. As seen in this table, their values agree with each other for all the labelled sites within experimental errors.

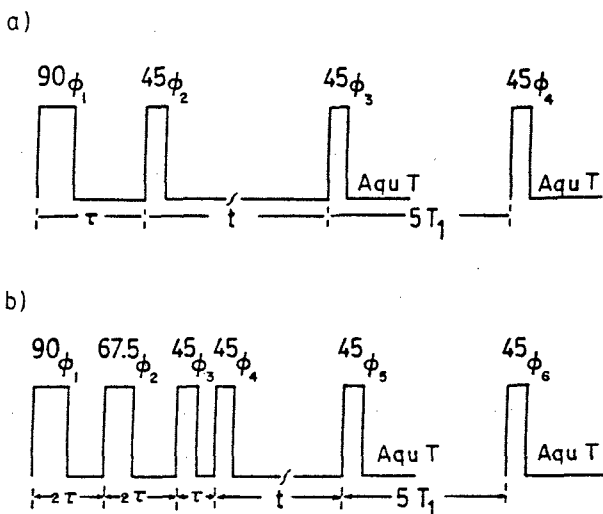


Figure 1 (a) J-B sequence, (b) broadband J-B excitation sequence.

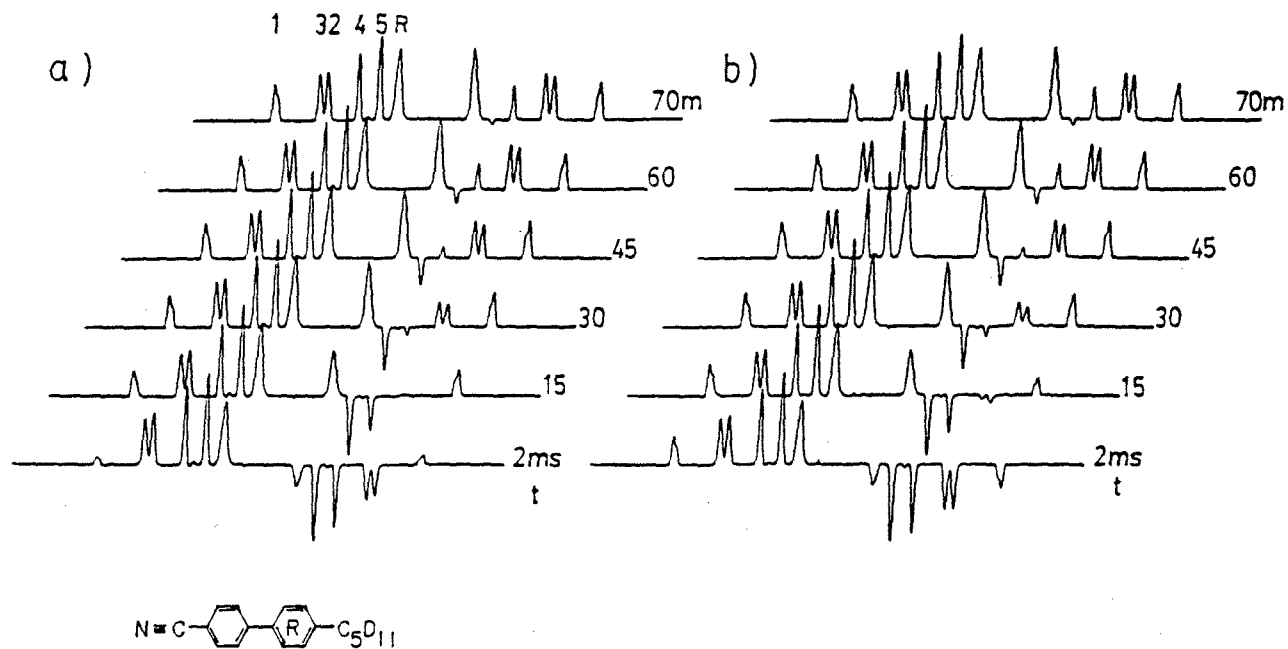


Figure 2 Plots of partially relaxed spectra at 33.2°C and 15.3 MHz. (a) Using the J-B sequence, (b) Using the broadband J-B excitation sequence.

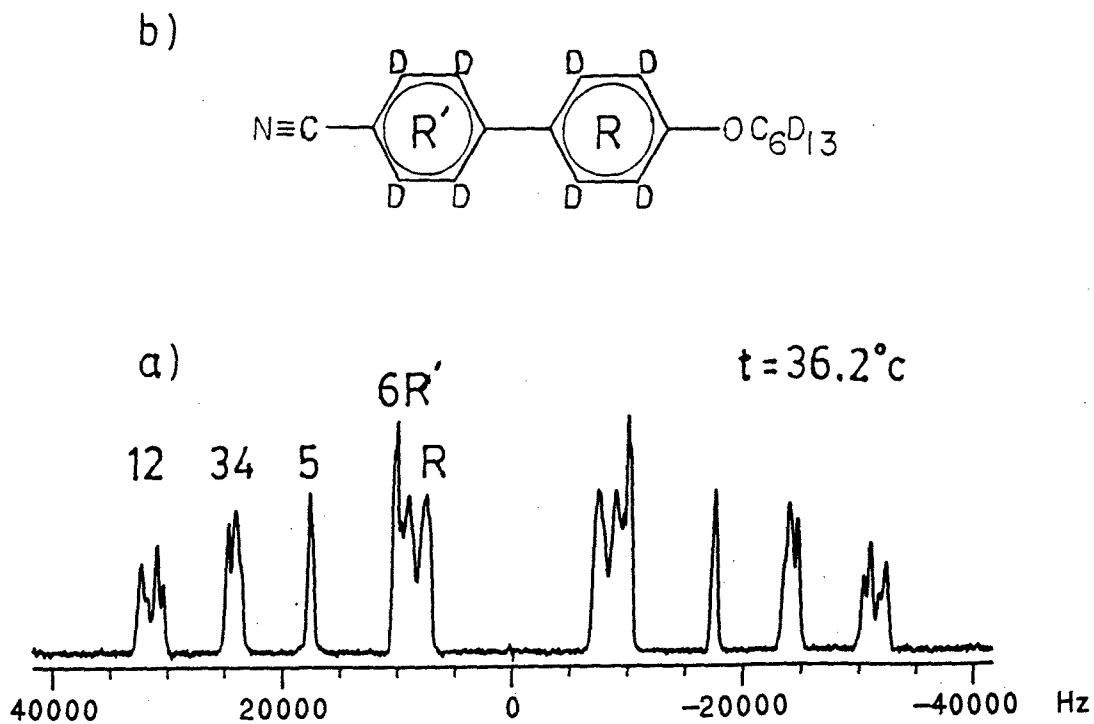


Figure 3 (a) A typical deuterium NMR spectrum of 60CB- d_{21} showing the peak assignments; (b) A schematic diagram of a 60CB- d_{21} molecule.

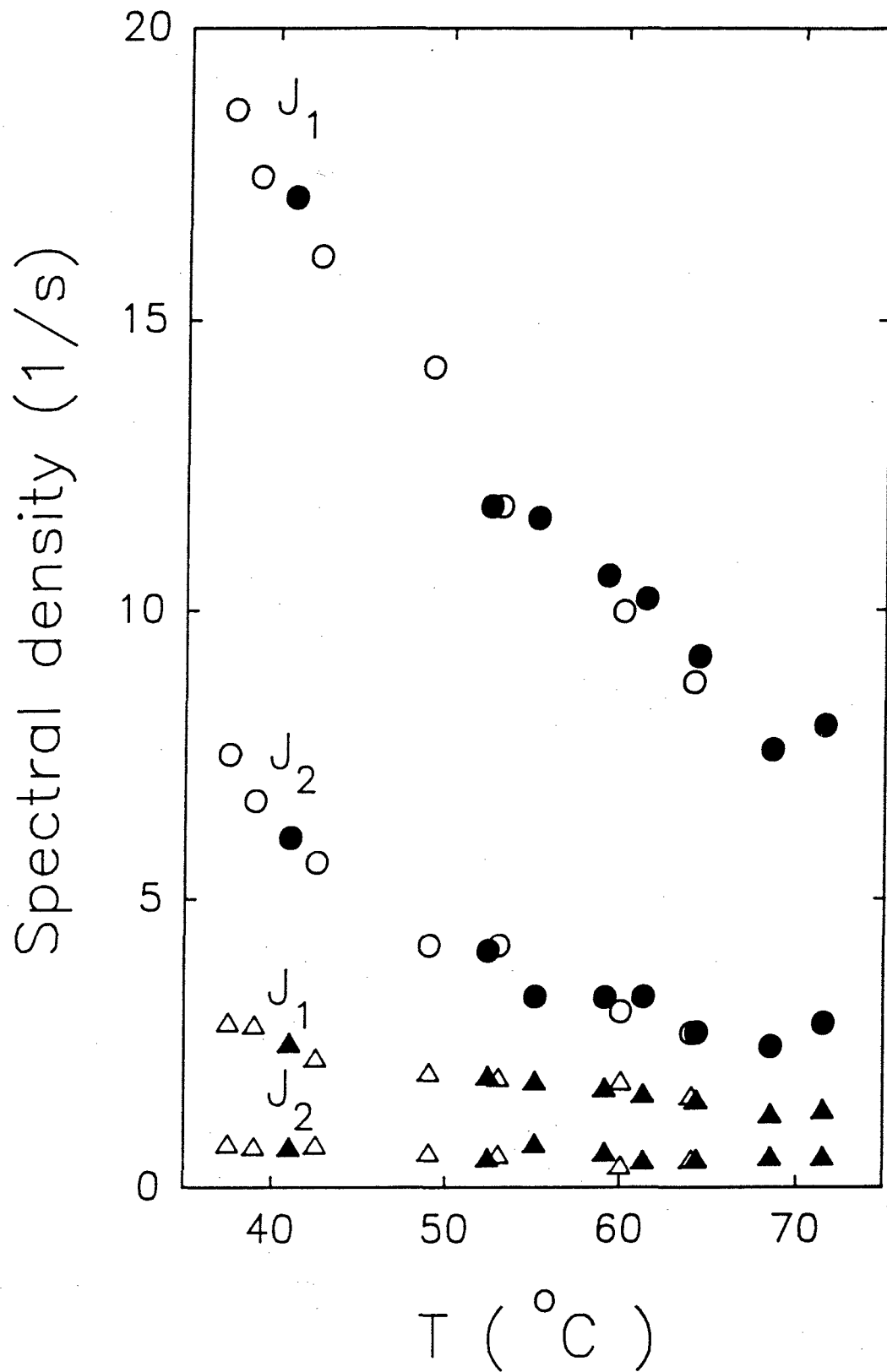


Figure 4 Plots of spectral densities versus temperature in the nematic phase of 60CB-d₂₁. Open symbols are obtained by the broadband J-B excitation sequence, while closed symbols by the J-B sequence. ○ and △ denote data for C₄ and C₆, respectively.

TABLE 3

Comparison of T_{1Z} and T_{1Q} in ms measured at 15.3 MHz and 33.2°C for 5CB-d ₁₅						
	C_1	C_2	C_3	C_4	C_5	Ring
T_{1Z}	12.6 (13.5)	26.9 (25.8)	30.0 (30.7)	55.4 (48.9)	159 (137)	8.5 (9.1)
T_{1Q}	10.4 (10.1)	21.5 (21.8)	22.8 (26.4)	51.9 (46.1)	107 (104)	10.9 (11.4)

* T_1 values in parentheses were obtained by the J-B sequence, while those without parentheses were obtained by the broadband J-B excitation sequence.

Figure 3 shows the molecular structure of 60CB-d₂₁ and a typical deuterium NMR spectrum for this mesogen at 15.3 MHz. We have used both pulse sequences to measure spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ for all the labelled sites except the ring R' , because of excessive overlapping of its signal with that from the methyl (C_6) at high temperatures. The agreement between the two methods are extremely good. As an example, we show in figure 4 plots of spectral densities versus temperature for C_4 and C_6 . Since the relaxation times of the methyl deuterons are much longer than those of the ring R' deuterons, the overlapped doublet signals can still be used to determine T_{1Z} and T_{1Q} for the methyl deuterons as long as t is chosen larger than 40 ms in the pulse sequence.

Finally MBBA-d₁₃ has been studied at 15.3 MHz using the J-B sequence [10]. For comparison we summarize in Table 4 the results obtained using the broadband J-B excitation sequence at 26°C and at 15.3 and 46 MHz. Thus both $J_1(\omega_0)$ and $J_2(2\omega_0)$ show frequency dependence. The frequency dependence of $J_2(2\omega_0)$ is weaker; it is negligible for the methine deuteron (C_0). Currently we are analyzing the temperature and frequency dependences of the measured spectral parameters in MBBA using models [3], [4] proposed for flexible mesogens.

In conclusion, the relaxation data can be effectively obtained in liquid crystals by using the broadband J-B excitation sequence.

TABLE 4

Measurements of $J_1(\omega_0)$ and $J_2(2\omega_0)$ in s ⁻¹ for MBBA-d ₁₃ at 26°C (ω_0 = Larmor frequency in MHz) using broadband excitation					
ω_0	$J_1(\omega_0)$		$J_2(2\omega_0)$		
	15.3	46	15.3	46	
C_0	49.8	36.2	24.9	27.7	
C_1	40.7	21.0	15.1	10.2	
C_2	14.6	9.0	6.7	5.4	
C_3	13.7	7.5	5.1	4.0	
C_4	1.73	1.58	1.05	0.98	

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