

NMR proton spin dynamics in thermotropic liquid crystals subject to multipulse excitation

R. H. Acosta,* R. C. Zamar,† and G. A. Monti

Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, Ciudad Universitaria, X5016LAE Córdoba, Argentina

(Received 27 June 2003; published 22 October 2003)

Previous experiments of NMR spin-lattice relaxation times as a function of the Larmor frequency, as measured with the field-cycling technique (FC), were shown to be very useful to disentangle the various molecular motions, both local and collective, that dominate the relaxation in different time scales in liquid crystals. However, there are many examples where the known theoretical models that represent the molecular relaxation mechanisms cannot be fitted to the experimental trend in the region of low fields, making it difficult to obtain reliable values for the spectral densities involved, especially for the cooperative motions which dominate at low frequencies. In some cases, these anomalies are loosely ascribed to “local-field” effects but, to our knowledge, there is not a detailed explanation about the origin of these problems nor the range of frequencies where they should be expected. With the aim of isolating the dipolar effects from the influence of molecular dynamics, and taking into account the previous results in solids, in this work we investigate the response of the proton spin system of thermotropic liquid crystals 4-pentyl-4'-cyanobiphenyl (5CB) and 4-octyl-4'-cyanobiphenyl (8CB) in nematic and smectic *A* phases, due to the NMR multipulse sequence $90_y^\circ-(\tau-\theta_x-\tau)_N$. The nuclear magnetization presents an early transient period characterized by strong oscillations, after which a quasistationary state is attained. Subsequently, this state relaxes towards internal equilibrium over a time much longer than the transverse relaxation time T_2 . As occurs in solids, the decay time of the quasistationary state T_{2e} presents a minimum when the pulse width θ_x and the offset of the radiofrequency are set to satisfy resonance conditions (spin-lock). When measured as a function of the pulse spacing τ in “on-resonance” experiments, T_{2e} shows the behavior expected for cross relaxation between the effective Zeeman and dipolar reservoirs, in accordance with the thermodynamic theory previously developed for solids. Particularly, for values of τ comparable with T_2 , the relaxation rate follows a power law $T_{2e} \propto \tau^{-2}$, in all the observed cases, for the resonance conditions $\theta_x = \pi/3$ and equivalent frequency $\omega_e = \pi/3\tau$. When τ is similar to or greater than typical dipolar periods, the relaxation rate becomes constant and for τ much shorter than T_2 , the thermodynamic reservoirs get decoupled. These experiments confirm that the thermodynamic picture is valid also in liquid crystals and the cross relaxation between the reservoirs can be detected without interference with spin-lattice relaxation effects. Accordingly, this technique can be used to estimate the frequency range, where cross-relaxation effects can be expected when Zeeman and dipolar reservoirs are put in thermal contact with each other and with the lattice, as in FC experiments. In particular, the present results allow us to associate the anomalies observed in low-field spin-lattice relaxation with nonadiabatic energy exchange between the reservoirs.

DOI: 10.1103/PhysRevE.68.041705

PACS number(s): 61.30.-v, 76.60.Es, 77.84.Nh

I. INTRODUCTION

Thermotropic liquid crystals are molecular mesophases with a high degree of molecular orientational order, but have no complete positional order. Consequently, the proton system in liquid crystals presents considerable residual dipolar interaction energies within the molecules, while their intermolecular dipolar interactions are averaged to zero due to the rapid individual molecular motions as rotations and self-diffusion [1].

Nuclear spin relaxation plays an important role in the study of molecular dynamics in these systems. Experiments of spin-lattice relaxation times as a function of the Larmor frequency $T_1(\omega)$ as measured with the fast field-cycling technique (FC) were shown to be very useful to disentangle the various molecular motions, both local and collective, that

dominate the relaxation in different time scales in liquid crystals.

It is well known that the collective mechanism called order fluctuations of the director (OFD) drives the spin relaxation in the low-frequency domain, while in the conventional megahertz range the individual molecular motions dominate [2]. However, in the region of low fields some problems still remain in the analysis of data. There are many examples in the literature where the known theoretical models that represent the molecular relaxation mechanisms cannot be fitted to the experimental trend, being difficult to obtain reliable values for the spectral densities involved, especially for the cooperative motions. In the nematic phase, the well known $T_1 \propto \nu^{1/2}$ Larmor frequency dependence is observed generally in the Larmor frequency range $10^3-5 \times 10^5$ Hz. However, it is frequently observed that as the Larmor frequency decreases from about 30 kHz, T_1 data decrease noticeably faster than expected due to the OFD and the individual motions [2–6]. The Larmor frequency range where the slow motions predominate in T_1 experiments is narrower in the smectic phases than in nematic phases, making it even more

*Present address: Max Planck Institut für Polymerforschung, Ackermannweg 10, 55128-Mainz, Germany.

†Electronic mail: zamar@famaf.unc.edu.ar

difficult to disentangle the relevant relaxation mechanisms in this frequency range [2,6].

In some cases, these “anomalies” are loosely ascribed to “local-field effects” [7] but, to our knowledge, there is neither a detailed explanation about the origin of these effects nor the range of frequencies where they should be expected. Since in the FC experiments the evolution of the magnetization is observed after a rapid lowering of the external magnetic field, for some range of final fields, near the local field, the spin system could be unable to maintain a state of internal semiequilibrium of the whole system during the cycling of the field. In such a case, effects of cross relaxation between Zeeman and dipolar reservoirs could be superimposed to spin-lattice relaxation during the free evolution of the system, appearing as an extra source of relaxation.

In order to avoid the local-field effects and to be able to detect only the dynamic aspect of the relaxation at low fields in thermotropic liquid crystal polymers, experiments of transverse deuteron spin relaxation time were performed using a quadrupole echo pulse train $90_y^\circ - \tau - (90_x^\circ - 2\tau)_N$, as a function of the pulse spacing [8]. Alternatively, an experiment on protons that yields a direct estimate of the Larmor frequency range where the local-field effects have noticeable influence, might be helpful in interpreting T_1 data in nematic and smectic phases.

In this work we investigate the response of the proton system of liquid crystals, under the application of the multi-pulse sequence $90_y^\circ - \tau - (\theta_x - 2\tau)_N$, also called generalized Ostroff-Waugh sequence (OW) [9,10]. This kind of experiment was performed in the past in simple crystalline solids, and then it was demonstrated that the experimental results can be properly described by means of a theoretical framework based on a thermodynamic approach. After a short transient period, the spin system attains a quasistationary state consisting of effective Zeeman and dipolar quasiinvariants. When the effective field is sufficiently low, but still higher than the local fields, the overlap of the dipolar levels corresponding to neighbor Zeeman levels permits that total energy-conserving transitions between the Zeeman levels cause transfer of energy between the Zeeman and secular dipolar reservoirs. Then, the long-time decay of the magnetization was explained in terms of the cross relaxation between effective Zeeman and dipolar quasiinvariants. The theory predicts, and it was experimentally observed, that the decay time T_{2e} as a function of the pulse spacing τ follows a power law $T_{2e} \propto \tau^{-k}$, where the exponent depends on special resonance conditions of the experiment [11–14]. By modifying the pulse spacing, it is possible to control the modulus of the effective Zeeman field sensed by the spins. Then, experiments of $T_{2e}(\tau)$ are useful to investigate the frequency range where cross relaxation takes place.

Due to the occurrence of strong residual dipolar couplings and the complexity of the frequency spectrum, proton NMR transverse relaxation behavior of thermotropic liquid crystals is very similar to that found in solids. Then, it is meaningful to inquire if in mesophases $T_{2e}(\tau)$ would respond in the same way. In case of a positive answer, this experiment would allow one to isolate cross-relaxation effects from spin-lattice relaxation.

We present the results of T_{2e} as a function of the pulse spacing, in liquid crystalline samples of 4-pentyl-4'-cyanobiphenyl (5CB) and 4-octyl-4'-cyanobiphenyl (8CB) in the nematic and smectic *A* phases. The experimental results show that the thermodynamic picture used for solids is also consistent with the behavior of T_{2e} in liquid crystals, and that the effects of the dipolar interactions dominate the response of the spin system in a wide range of pulse separation times. Accordingly, it is shown that these experiments can provide useful information about the many-spin processes, which are noticeable also in NMR experiments at low Larmor fields in liquid crystals.

In Sec. II we outline the theoretical framework that leads to the $T_{2e} \propto \tau^{-2}$ dependence developed for solids. Section III describes the experimental setup. In Sec. IV we present the acquisition of the echotrain and show that the stroboscopic resonance condition can be met for the nematic phase of 5CB. In this section we also analyze the dependence of T_{2e} on τ in different phases of 5CB and 8CB.

II. THEORETICAL BACKGROUND

In this section we summarize aspects of the theoretical background existing for solids which are necessary to interpret the experimental results. The presentation does not intend to be exhaustive; the full reasoning can be found in the literature.

The time behavior of the magnetization in the OW experiment depends strongly on the many-body nature of the dipolar spin interaction as well as on the parameters of the external fields. The observed long-time decay of the magnetization contradicts the standard average Hamiltonian theory (AHT) [15,16] according to which, after the transient period the magnetization would remain constant until the effects of the spin-lattice relaxation become observable.

By applying the Floquet theory, Maricq showed that it is possible to adapt the laws of statistical thermodynamics to describe systems with Hamiltonians that depend explicitly on time, and that the apparent paradox about the long-time decay can be solved by adopting a generalized version of the AHT [13,14]. Using these ideas, the problem of pulsed spin locking in solid CaF_2 was described in detail in terms of the effective Hamiltonian. It was shown that the effective Hamiltonian is the sum of two (or more) commuting observables (quasiinvariants) plus small off-diagonal terms, and accordingly that in the quasistationary state the situation can be described in terms of weakly coupled thermodynamic baths, which finally relax towards a common temperature with a characteristic decay time T_{2e} . The relaxation rate was calculated combining the Provotorov saturation theory [17] with the average Hamiltonian. In this perturbative approach, the rate of the thermal mixing of the reservoirs is controlled by nonsecular terms of the effective Hamiltonian, considered as perturbations to the quasi-invariants. The theory predicts a dependence of the signal decay time on the pulse spacing τ in the form of a simple power law $T_{2e} \propto \tau^{-k}$, with the exponent determined by particular resonance conditions satisfied by the time dependent fields, without connection with the specific relaxation mechanism. This “universal” macro-

scopic behavior is associated with the multispin character of the dipolar Hamiltonian, which determines the influence of the microscopic events occurring in the intervals between pulses.

The Hamiltonian for the system under the periodic excitation $90_y^\circ - \tau - (\theta_x - 2\tau)_N$ in the rotating frame is

$$\mathcal{H}(t) = -\omega(t)I_x + \Delta I_z + H_{20}^d, \quad (1)$$

where I_x and I_z are components of the angular momentum operator \mathbf{I} ; Δ is the frequency offset from the proton resonance, H_{20}^d is the secular part of the dipolar interaction and

$$\omega(t) = \theta \sum_{k=1}^{\infty} \delta(t - (2k-1)\tau) \quad (2)$$

represents the pulse sequence. The rf pulses have a nutation angle θ , phase x , and are separated by a time 2τ .

The Hamiltonian $\mathcal{H}(t)$ is periodic, with period τ , $\mathcal{H}(t + \tau) = \mathcal{H}(t)$. According to Floquet's theorem [18], the periodicity implies that the evolution operator takes the form

$$U(t) = P(t)e^{-i\bar{H}t}, \quad (3)$$

where $P(t)$ is a unitary periodic operator with period τ , satisfying $P(0) = U(0) = 1$, and \bar{H} is a time independent Hermitian operator ("effective" Hamiltonian).

Since $P(n\tau) = 1$, under stroboscopic observation the spin system appears to evolve under a time independent Hamiltonian, the effective Hamiltonian playing a role similar to the energy in time independent systems. This is the result of the AHT [19] used to interpret the spectra in high resolution experiments in solids. This formalism successfully describes the response of the spins under multipulse sequences for cycling times much shorter than T_2 . In the Floquet formalism, $P(t)$ and \bar{H} are obtained as series expansions and it can be demonstrated [13] that the lowest-order term in the series for \bar{H} is the average of $\mathcal{H}(t)$ over one period. The other contributions are equal to those obtained in the usual derivation of the AHT by means of the Magnus expansion. The evolution of the spin system between stroboscopic observations is taken into account via $P(t)$, which allows one to distinguish the real time dependent problem from an effective conservative one. In this way the AHT can be generalized to extend its validity for long times.

Under general conditions for the parameters θ , Δ , and τ , a rapid convergence of the Floquet series for $P(t)$ and \bar{H} cannot be assured. Then, another frame, the *toggling frame*, is introduced in such way that the terms $-\omega(t)I_x + \Delta I_z$ do not appear in the Hamiltonian of the spin system. The action of the offsets and pulse on the magnetization over a period τ are considered as an effective rotation by an angle $\omega_e 2\tau$ around the effective axis $\hat{\mathbf{n}}$, where ω_e and $\hat{\mathbf{n}}$ depend on θ , τ , and Δ [12,13]. Therefore, an "interaction frame" is introduced through the unitary operator

$$U_0(2\tau) = e^{-i\omega_e \hat{\mathbf{n}} \cdot \mathbf{I} 2\tau} = e^{-i\Delta I_z \tau} e^{i\theta I_x} e^{-i\Delta I_z \tau}. \quad (4)$$

The former equation imposes the following conditions to be satisfied by ω_e and $\hat{\mathbf{n}}$:

$$\cos(\omega_e \tau) = \cos(\Delta \tau) \cos(\theta/2), \quad (5)$$

and

$$n_1 = -\frac{\sin(\theta/2)}{\sin(\omega_e \tau)}, \quad n_2 = 0, \quad n_3 = -\frac{\cos(\theta/2)\sin(\Delta \tau)}{\sin(\omega_e \tau)}. \quad (6)$$

For a given value of τ the effective frequency must satisfy the additional *resonance* condition

$$\omega_e = n\pi/m\tau, \quad (7)$$

for n and m integers, in order to keep the periodicity of the Hamiltonian. This condition means that n complete rotations are made in m cycles of 2τ each. Under these conditions the interaction-frame Hamiltonian is periodic, and the evolution operator is that of Eq. (3). When the parameters θ and $\Delta \tau$ are set to satisfy the *resonance* conditions, observation of the system at times which are integer multiples of $m2\tau$ will show a component of the magnetization fixed along the effective axis, which implies a state of pulse spin locking [20]. After a time of the order of few T_2 the component of the magnetization lying in the plane perpendicular to the effective axis decays to zero, and a quasistationary state is attained, which can be represented with a diagonal "thermodynamic" density operator involving effective Zeeman and dipolar reservoirs. In this state a difference between the populations of the energy levels of spins along the direction of the effective field is established, which tends to disappear while the spin system absorbs the quanta of the dipole-dipole interaction modulated by the rf [11,12].

The quasistationary state established in the early time scale evolves towards a new equilibrium state with a decay time T_{2e} . The existence of nonsecular mixing terms in the effective Hamiltonian, which arise due to the discrete nature of the pulses, makes the two reservoirs to equalize their temperatures. Since the interaction between the two baths is weak, the τ (or ω_e) dependence of T_{2e} can be obtained by means of the Provotorov theory [17]. The reasoning, based on the perturbation theory, considers that the Zeeman and dipolar reservoirs are weakly coupled by the first correction term to the average Hamiltonian that does not commute with the unperturbed Hamiltonian in the tilted toggling frame [14]. The order involved depends on the resonance condition; for example, for $m=3$ and $n=1$ (three spin process), the relaxation is governed by second order terms, which are linear in τ . Since the main contribution to the τ dependence of the relaxation rate comes from the quadratic dependence on the strength of the mixing term, in this case it is predicted that $T_{2e} \propto \tau^{-2}$, when the experiment is performed "on resonance." This last condition can be met, for instance, by varying τ and Δ for a fixed value of θ in order to satisfy both Eqs. (5) and (7).

It should be realized that in thermotropic liquid crystals, the proton distribution within the molecule can be considered as a system of weakly coupled spin pairs. According to this

fact, there are two dipolar reservoirs, associated with the intrapair and interpair dipolar interactions [21,22]. Therefore, in experiments performed in liquid crystals it should be expected that the long-time evolution will not show an exponential decay.

III. EXPERIMENT

The measurements presented in this work were performed in a Bruker MSL300 spectrometer operating at 300 MHz using a standard proton probe, the $\pi/2$ pulse length was set between 4.5 and 4.75 μs . Samples were packed without previous purification in 4 mm outer diameter ZrO sample holders fitted with Kel-F end caps. The samples were heated until they reached their isotropic (*I*) phase and then cooled down in presence of the magnetic field to the desired temperature corresponding to the nematic (*N*) or smectic *A* (*Sm A*) phases. Due to the considerable amount of heat transfer by the rf pulses [23], the following procedure was implemented. The sample temperature was set just below the *N-I* transition temperature (T_{NI}) and a burst of 4096 π pulses with 10 μs spacing was applied with a repetition time of 10 sec, the signal was acquired after the last pulse. A transition from the *N* to the *I* phase could be observed in the NMR lineshape. The repetition time was varied until the transition was no longer induced; this situation corresponded to a delay of 20 sec. All the experiments shown were performed with a repetition time of 50 sec. As the sequence used to probe the sample heating by rf pulses was the most disadvantageous one (due to the long rf trains used and the short spacing between pulses), we can assure that the temperature of the samples was not appreciably affected by the irradiation during the actual multipulse experiment.

IV. RESULTS AND DISCUSSION

In this section we describe the results obtained by the application of the generalized Ostroff-Waugh sequence to different liquid crystals in the *N* and *Sm A* phases as well as the verification of the resonance condition.

A. Decay of the magnetization

The relaxation rates T_{2e} were determined by direct observation of the amplitude decay of successive echoes during a pulse train employing a four step phase cycling scheme. One acquisition was taken in the center of the interval defined by two subsequent pulses. Figure 1 shows the evolution of the magnetization for $\tau = 17 \mu\text{s}$ and $\theta = \pi/3$; the offset frequency was set to 8.94 kHz, according to the resonance condition corresponding to $m=3$. The transverse magnetization lasts for a time much longer than T_2 (40 μs estimated by the Hahn echo sequence). The inset shows the transient period, in which the quasistationary state is established after a time period of several T_2 . The occurrence of oscillations is another common feature with solids. Such behavior could also be ascribed to oscillations of the magnetic energy back and forth between the Zeeman and dipolar reservoirs [24].

Contrary to the experiments in solid CaF_2 , where the time dependence of the magnetization can be represented with a

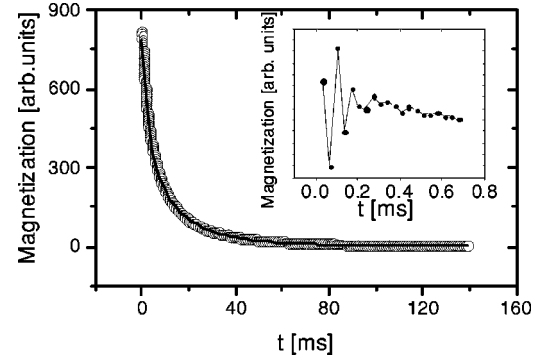


FIG. 1. Evolution of the magnetization for the resonance condition $m=3$ with $\tau=17 \mu\text{s}$, $\theta=\pi/3$, and $\Delta=8.94 \text{ kHz}$ for nematic 5CB at 303 K. The data correspond to 16 scans of the point in the center of the interval defined by the θ pulses. The inset shows the transient period in which the quasistationary state is established after 0.6 ms. The results can be described by a two exponential decay with characteristic times of 1.9 and 7.9 ms.

single decaying exponential function, in liquid crystals the long-time evolution of the signal can be fitted as a sum of two exponential functions with different decay constants. As mentioned in Sec. II, this feature could be associated with the presence of more than one dipolar quasiinvariant in liquid crystals. In fact, we verified that a combination of two exponential functions perfectly fits the long-time evolution of the magnetization, with decay constants differing nearly by a factor of 5. For $m=3$ and $\tau=10 \mu\text{s}$, we obtain values of 24 and 5 ms for the relaxation times. We could observe that the behavior of the two relaxation times as a function of τ is qualitatively the same, showing the two parameters the dependence τ^{-2} . The short relaxation time exhibits a noticeable experimental dispersion for high values of τ , being rather difficult to determine its value accurately in this range. Hereinafter we refer only to the longer relaxation time as T_{2e} .

B. Resonance condition

We now analyze the situation in which the resonance condition is met. We study the resonance for $m=3$, which defines an effective resonance frequency $\omega_e = \pi/3\tau$. If a pulse $\theta = \pi/3$ is used, we obtain from Eq. (5)

$$\cos \Delta \tau = \frac{\cos(\pi/3)}{\cos(\pi/6)}. \quad (8)$$

We denote Δ_R the radiofrequency that satisfies Eq. (8) for an arbitrary value of τ . Thus, a departure δ of the irradiation frequency from the resonance condition can be expressed as

$$\delta = \Delta - \Delta_R. \quad (9)$$

When the effective Larmor frequency ω_e is greater than a typical dipolar frequency ω_D , under resonance conditions the whole energy from the external fields is transferred to the Zeeman bath, and a minimum in the decay time of the quasistationary state is to be expected [11,12]. To verify the existence of the minimum of the decay time, we varied sys-

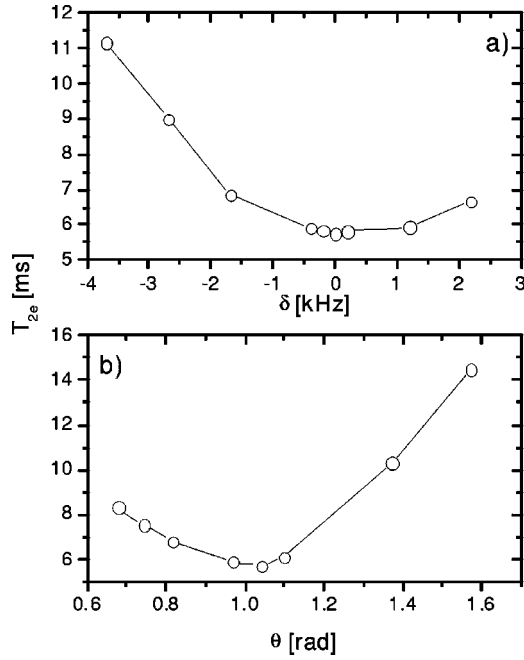


FIG. 2. Determination of the stroboscopic resonance condition for $m=3$ in nematic 5CB at 303 K. For $\omega_e = \pi/3\tau$ and $\tau = 20 \mu\text{s}$, a value $\Delta_R = 7.6$ kHz is obtained from Eq. (8). (a) $T_{2e}(\delta)$ shows a minimum when $\delta=0$ for fixed values of τ and θ . (b) $T_{2e}(\theta)$ also shows the expected minimum when $\theta = \pi/3$ for fixed values τ and Δ .

tematically the irradiation frequency around Δ_R in order to obtain a measure of $T_{2e}(\delta)$. For $\omega_e = \pi/3\tau$ and $\tau = 20 \mu\text{s}$ a value $\Delta_R = 7.6$ kHz is obtained from Eq. (8). The results of this experiment for 5CB in the nematic phase at 303 K are shown in Fig. 2(a). The presence of a minimum in $T_{2e}(\delta)$ is clearly observed for $\delta=0$. The resonance condition for the nutation angle can be verified in similar way. Figure 2(b) shows the result of different experiments in which the irradiation frequency is fixed at $\Delta = 7.6$ kHz and the pulse length is varied for the same sample at the same temperature. Again, a minimum of $T_{2e}(\theta)$ is obtained for $\theta = \pi/3$.

C. Evolution of the quasiequilibrium state

In Fig. 3 we show the dependence of T_{2e} on the pulse separation τ for 5CB in the N phase at 303 K when the resonance condition (8) is met for $m=3$ and $\theta = \pi/3$. For each value of τ , the offset in the irradiation frequency was adjusted in order to satisfy Eq. (8), namely, $\Delta\tau = 0.955$. The behavior $T_{2e} \propto \tau^{-2}$ is observed over the wide range 10–40 μs of values of τ , which corresponds to effective frequencies in the range 1.0×10^5 – 2.6×10^4 rad/s. For $\tau \sim 40 \mu\text{s}$ a departure from the square law in the relaxation rates occurs, T_{2e} becoming constant for $\tau \geq 70 \mu\text{s}$ ($\omega_e \leq 1.5 \times 10^4$ rad/s). A feature like this should be expected taking into account that when the effective frequency is similar to or smaller than a typical dipolar frequency, the rate of the cross relaxation should not depend on ω_e . Then, a plateau should be expected for $\omega_e \sim \omega_D$, i.e.,

$$\omega_e = \pi/3\tau_D \sim \omega_D. \quad (10)$$

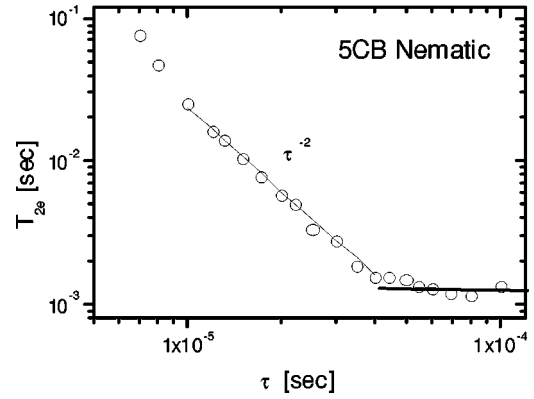


FIG. 3. T_{2e} vs τ for nematic 5CB at 303 K at the resonance condition with $m=3$ (effective frequency $\omega_e = \pi/3\tau$) and nutation angle $\theta = \pi/3$. The irradiation frequency Δ is varied in order to satisfy the stroboscopic resonance condition, $\delta=0$. The solid line shows the dependence $T_{2e} \propto \tau^{-2}$ for $10 \mu\text{s} \leq \tau \leq 40 \mu\text{s}$. T_{2e} is constant for about $\tau > 70 \mu\text{s}$ ($\omega_e < 1.5 \times 10^4$ rad/s). Taking into account the scaling factor of 0.5 of the effective dipolar Hamiltonian (see the text), the frequency cutoff is in agreement with typical dipolar couplings of the 5CB molecule.

Note that the dipolar part of the unperturbed effective Hamiltonian is the secular dipolar Hamiltonian relative to the laboratory frame scaled by the factor $\frac{1}{2}(3 \cos^2\alpha - 1)$, where α is the angle between the directions of the effective field and the external magnetic field, namely, $\tan \alpha = n_3/n_1$ according to Eq. (6) [12–14]. In our experiment this factor is 0.5. In 5CB the dipolar coupling between *ortho* protons in the core is 2.46×10^4 rad/s, and 3.09×10^4 rad/s for the proton pair corresponding to the α -carbon in the alkyl chain, at 300 K [25,26]. Taking into account the factor 0.5 of the effective dipolar Hamiltonian, the dipolar frequency associated with the cutoff effective frequency is about 3×10^4 rad/s, which is in agreement with the values of the reported dipolar couplings for different bonds in the molecule. In Fig. 4(a) we show the $T_{2e}(\tau)$ dependence for 8CB in the N phase at 310 K for the same resonance condition as in nematic 5CB. The same behavior is obtained as in the preceding case for the $T_{2e} \propto \tau^{-2}$ power law with a similar value of τ_D .

The results for 8CB in the Sm A phase at 299 K are shown in Fig. 4(b). While the presence of the square law can be clearly identified for a wide range of values of τ , two different aspects can be separately addressed with respect to the nematic phase. First, the departure from the square law for long times occurs at a smaller value of τ_D , which seems most reasonable taking into account that the most ordered phase has a bigger dipolar coupling. From Fig. 4(b), using a value of $\tau \approx 45 \mu\text{s}$ the frequency plateau can be estimated, giving 4.6×10^4 rad/s. The dipolar couplings for the Sm A phase can be estimated from the order parameters, S , via the relation

$$\omega_D(T_{SmA}/T_{NI}) = \omega_D(T_N/T_{NI}) \frac{S(T_{SmA}/T_{NI})}{S(T_N/T_{NI})}, \quad (11)$$

where the reduced temperature $T_{SmA}/T_{NI} = 0.952$ corresponds to 299 K and $T_N/T_{NI} = 0.975$ corresponds to 306 K;

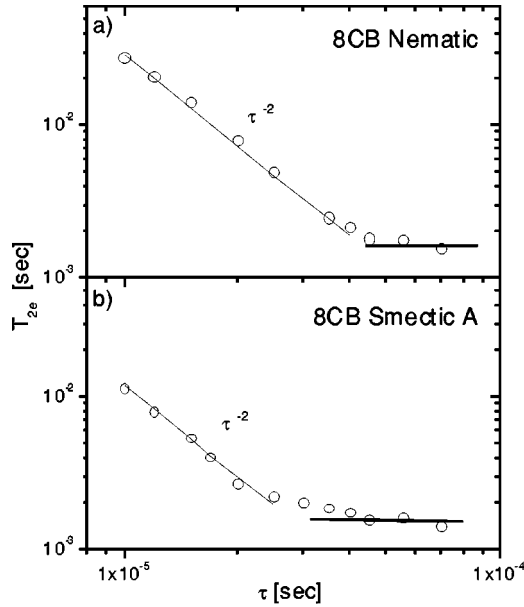


FIG. 4. (a) T_{2e} vs τ for nematic 8CB at 310 K at the resonance condition with $m=3$ and a nutation angle $\theta=\pi/3$. The irradiation frequency Δ is varied in order to satisfy the stroboscopic resonance condition, $\delta=0$. In concordance with the results of nematic 5CB, the dependence $T_{2e} \propto \tau^{-2}$ is verified for $10 \mu\text{s} \leq \tau \leq 40 \mu\text{s}$, and a similar behavior for values of $\tau > 40 \mu\text{s}$ is observed. (b) T_{2e} vs τ for smectic A 8CB at 299 K for the same resonance condition as in the nematic phase. The departure from the square law occurs for a value of $25 \mu\text{s}$, and the plateau corresponds to $\omega_e \sim 4.6 \times 10^4$ rad/s, which is consistent with the dipolar couplings in this phase.

at this temperature ω_D is nearly the same as for nematic 5CB at 300 K. The values for the order parameter were taken from the literature [27]. The dipolar couplings obtained are 2.9×10^4 rad/s for the *ortho* pair and 3.6×10^4 rad/s for the proton pair corresponding to the α -carbon in the alkyl chain. Second, it is observed to be a faster relaxation of the quasi-equilibrium state. Presumably this fact is related to the former feature.

The existence of three regimes of T_{2e} as a function of τ (or ω_e), clearly shown in Figs. 3 and 4, can be understood resorting to the thermodynamic picture. When the effective Zeeman frequency becomes similar to or lower than the dipolar frequency, $\omega_e \leq \omega_D$, the probability of transitions which conserve the total energy becomes independent of the effective field. In this range, the process is governed by the dipolar transitions. In the opposite limit, $\omega_e \gg \omega_D$, the process of thermal mixing between the reservoirs becomes ineffective because of increasing effective field, transitions in which a Zeeman quantum is compensated by a dipolar transition become less and less probable as they involve the rearrangement of a high number of spins. In this range of effective frequencies, the reservoirs get decoupled, and the processes involving energy exchange with the lattice could become appreciable in the behavior of T_{2e} . In the limit of $\tau \rightarrow 0$, it can be expected that $T_{2e} \rightarrow T_{1\rho}$ [28]. Finally, the process of cross relaxation is dominant in the intermediate range, where a clear dependence $T_{2e} \propto \tau^{-2}$ is observed.

Another way to interpret the limits in the behavior of the magnetization as a function of τ is by comparing the pulse spacing with the characteristic microscopic decay time, which is associated with the dipolar dynamics. When the pulse spacing is much shorter than the characteristic time of the “time correlation function” corresponding to the cross-relaxation process, which is of the order of T_2 , the evolution of the many-body spin interactions in the intermediate intervals between pulses has a small effect on the general behavior of the magnetization. In terms of the Floquet theory, in this limit the operator $P(t)$ does not play a role in the long-time evolution of the magnetization. For these values of τ , T_{2e} becomes sensitive to the spectral distribution of the dipole reservoir, especially in the wings [24,29]. For increasing values of τ , the many-spin dynamics begins to play a role in the intervals between pulses, as a consequence of which the behavior of the magnetization presents thermodynamic characteristics, such as the cross-relaxation between the reservoirs. For τ going to zero the dipolar interactions do not evolve in time between the pulses, and the thermal baths do not exchange energy. In this limit, the problem can be considered as a conservative one, except for the influence of spin-lattice relaxation. By a similar reasoning, when τ is longer than the correlation time, it can be expected that the cross-relaxation rate will not depend on the length of the interval between pulses.

Due to the possibility of detecting cross relaxation by means of the pulsed spin-lock experiments in liquid crystals, this technique can be used for determining the frequency range where cross relaxation is likely to occur when Zeeman and dipolar reservoirs are put in thermal contact (between them and with the lattice), as can happen within the low magnetic field range in fast field-cycling experiments. Considering the scaling of the dipolar Hamiltonian in the multi-pulse experiment, the power law $T_{2e} \propto \tau^{-2}$ is observed in the “equivalent” frequency ranges 8–30 kHz and 13–30 kHz in the nematic and smectic phases, respectively. As already mentioned, the literature shows many examples where the $T_1(\nu)$ data fall below the profiles predicted by any molecular motional driven relaxation mechanism for Larmor frequencies lower than about 25 kHz [2–6]. The coincidence of this range with the frequency interval where the cross-relaxation is observed in pulsed spin-lock experiments suggests that the anomalies of $T_1(\nu)$ are due to nonadiabatic energy exchange between the spin reservoirs. This effect could become noticeable in the Larmor frequency range, where the energy transfer between the Zeeman and dipolar reservoirs takes place at a lower rate than the cycling of the magnetic field [30]. Since the experimental technique involves the rapid lowering and raising of the external magnetic field applied to the sample, the possibility exists that at low Larmor frequencies (but still higher than the dipolar frequencies), the mechanism of internal equilibration of the whole spin system is not efficient enough to maintain a state of semiequilibrium during the cycling of the external field. In such a case, the effects of cross relaxation between Zeeman and dipolar reservoirs could be superimposed on spin-lattice relaxation during the free evolution of the system, appearing as an extra source of relaxation.

Summarizing, our experimental results clearly show that the response of the proton spin system to the OW pulse sequence in liquid crystals is consistent with a thermodynamic view. In particular, the characteristic dependence of $T_{2e} \propto \tau^{-2}$, clearly observed in “on-resonance” experiments, indicates that the long-time evolution of the spin system can be associated with cross relaxation between the effective Zeeman and dipolar reservoirs. The fact of $T_{2e}(\tau)$ being independent of the molecular dynamics, makes pulsed spin-lock a useful technique to investigate the frequency range where cross-relaxation should be observed in studies of spin-lattice relaxation in low magnetic fields.

Though we verified the existence of multispin processes that are responsible for the solid-like behavior of the spin

system due to the pulse spin locking experiment, the nature of these mechanisms still remains unknown. The long-lived molecular motions, which are characteristic of liquid crystals, could have important effects on the evolution of the spin coherences in these systems.

ACKNOWLEDGMENTS

This work was partially supported by SeCYT-UNC and Agencia Córdoba Ciencia. R.A. thanks SeCYT-UNC for financial support for the research. G.M. acknowledges support from CONICET, Argentina.

-
- [1] P. DeGennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon, Oxford, 1993).
- [2] F. Noack, M. Notter, and W. Weiss, *Liq. Cryst.* **3**, 907 (1988).
- [3] R. Kollner, K.H. Schweikert, and F. Noack, *Liq. Cryst.* **13**, 483 (1993).
- [4] F. Noack, in *Encyclopedia of NMR*, edited by D.M. Grant and R.K. Harris (Wiley, New York, 1995), p. 1980.
- [5] J. Struppe and F. Noack, *Liq. Cryst.* **20**, 595 (1996).
- [6] R.H. Acosta, Ph.D. thesis, Fa.M.A.F., Córdoba, Argentina, 2002.
- [7] J. Stohrer, G. Grobner, D. Reimer, K. Weisz, C. Mayer, and G. Kothe, *J. Chem. Phys.* **95**, 672 (1991).
- [8] N. Heaton, D. Reimer, and G. Kothe, *Chem. Phys. Lett.* **195**, 448 (1992).
- [9] E.D. Ostroff and J.S. Waugh, *Phys. Rev. Lett.* **16**, 1097 (1966).
- [10] P. Mansfield and D. Ware, *Phys. Lett.* **22**, 133 (1966).
- [11] L.N. Erofeev, B.A. Schumm, and G.B. Manelis, *Zh. Éksp. Teor. Fiz.* **75**, 1837 (1978) [*Sov. Phys. JETP* **48**, 925 (1979)].
- [12] Yu.N. Ivanov, B.N. Provotorov, and É.B. Fel'dman, *Zh. Éksp. Teor. Fiz. Pis'ma Red.* **27**, 164 (1978) [*Sov. Phys. JETP* **48**, 930 (1979)].
- [13] M. Matti Maricq, *Phys. Rev. B* **31**, 127 (1985).
- [14] M. Matti Maricq, *Phys. Rev. B* **36**, 516 (1987).
- [15] J.S. Waugh, L.M. Huber, and U. Haeberlen, *Phys. Rev. Lett.* **20**, 180 (1968).
- [16] U. Haeberlen and J.S. Waugh, *Phys. Rev.* **175**, 453 (1968).
- [17] B.N. Provotorov, *Zh. Éksp. Teor. Fiz.* **41**, 1582 (1961) [*Sov. Phys. JETP* **14**, 1126 (1962)].
- [18] M. Matti Maricq, *Phys. Rev. B* **25**, 6622 (1982).
- [19] U. Haeberlen, *High Resolution NMR in Solids* (Academic, New York, 1976).
- [20] M. Matti Maricq, *Phys. Rev. B* **33**, 4501 (1986).
- [21] O. Mensio, C.E. González, R.C. Zamar, D.J. Pusiol, and R.Y. Dong, *Physica B* **320/1-4**, 416 (2002).
- [22] O. Mensio, Ref. [6].
- [23] B.M. Fung, *J. Magn. Reson.* (1969-1992) **86**, 160 (1990).
- [24] P. Mansfield and D. Ware, *Phys. Rev.* **168**, 318 (1968).
- [25] B. Stevansson, A.V. Komolkin, D. Sandström, and A. Maliniak, *J. Chem. Phys.* **114**, 2332 (2000).
- [26] E. Ciampi, G. De Luca, and J.W. Emsley, *J. Magn. Reson.* **129**, 207 (1997).
- [27] W. Guo and B.M. Fung, *J. Chem. Phys.* **95**, 3917 (1991).
- [28] W.K. Rhim, D.P. Burum, and D.D. Elleman, *Phys. Rev. Lett.* **37**, 1764 (1976).
- [29] S. Clough, *Phys. Lett.* **24A**, 49 (1967).
- [30] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961).