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Dipolar quasi-invariants in ^{1}H NMR of nematic thermotropic liquid crystals

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We analyze the experimental conditions needed for creating two kinds of dipolar order, namely, intrapair and interpair order in thermotropic liquid crystals. By adapting to the case of liquid crystals the model of weakly coupled spin pairs first developed for oriented hydrated salts, we obtain that the dipolar signal at every preparation time can be regarded as a weighted sum of the pure intra- and pure interpair signals; the weights being determined by the amount of each kind of order resulting from the preparation sequence. The dipolar signal predicted by the model is symmetric in the preparation and observation times and the intrapair component is, in a good approximation, proportional to the time derivative of the FID, regardless of the number of different dipolar couplings (inequivalent pairs) present in the molecule. From this model we obtain a prescription for preparing the different dipolar orders both when the pairs are strictly equivalent or when they are not. The applicability of the spin thermodynamics approach in liquid crystals is tested in two typical thermotropic nematic samples: PAAd_6 (methyl deuterated *p*-azoxyanisole) and 5CB (4′-pentyl-4-biphenyl-carbonitrile).

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I. INTRODUCTION

Because of their high degree of orientational order, thermotropic liquid crystals (LC) exhibit a strong residual nuclear spin dipole-dipole energy associated with the interaction between protons belonging to the same molecule; this interaction is not averaged out by the individual diffusive molecular motions. Like in the NMR of solids, in liquid crystals the Zeeman energy of the proton spin system has an appreciable magnitude in thermal equilibrium provided that the external magnetic field is much larger than the local fields (a few kilogauss). On the contrary, the equilibrium dipolar energy at ordinary temperature is too small to be observed directly, being necessary to previously prepare the system in a state of higher dipolar order. Such a state can be achieved for example by the Jeener-Broekaert (JB) experiment [1], which consists of the rf pulse sequence: $(90^{\circ}_{x}-t_{12}-45^{\circ}_{y}-t_{23}-45^{\circ}_{y})$. The two first phase shifted pulses, separated a time interval t_{12}, prepare the dipolar order and a third, read pulse at a time t_{23} from the second makes the dipolar order detectable. Studying the attenuation of the dipolar signal as a function of t_{23} allows, in principle, to measure the dipolar spin-lattice relaxation time, T_{1D} [2–5].

Several similarities are found between the proton NMR of thermotropic LC in the nematic phase as PAAd_6 (methyl deuterated *p*-azoxyanisole) [2] and 5CBd_{11} (chain deuterated 4′-pentyl-4-biphenyl-carbonitrile) [5] and some crystalline hydrated salts like gypsum [6] or potassium oxalate monohydrate (POMH) [8]: The Zeeman free induction decay signals (FID) attenuate much faster than the irreversible spin-lattice processes and the dipolar signal shapes depend on the preparation times t_{12}. The latter behavior has been attributed to the occurrence of two dipolar quasi-invariants, namely intrapair and interpair.

In these hydrated salts the spin system consists of equivalent pairs of strongly dipolar coupled spin-$\frac{1}{2}$ nuclei belonging to the same water molecule, weakly coupled with protons of the other molecules. The dipolar part of the spin Hamiltonian is then a sum of the intrapair and the interpair interactions. Due to the noticeably different magnitude of the two kinds of dipolar couplings, four independent quasi-invariants are expected at high magnetic fields, namely the Zeeman, intrapair dipolar and interpair dipolar energies and the deviation of the singlet state population from its equilibrium value. The feasibility of measuring independently these quasi-invariants in gypsum was demonstrated by Eisendrath, Stone, and Jeener [7]. The NMR spectrum of these systems shows a resolved doublet due to spin-spin (intrapair) interaction. The width and structure of each peak of the doublet is attributed to the interpair interaction. The shape of the time domain dipolar signal prepared with the JB sequence in hydrated salts is strongly dependent on the preparation time because the Zeeman order can be alternatively transferred to different kinds of dipolar order. This behavior was successfully accounted for by the model of weakly interacting, equivalent pairs of strongly coupled protons [6,8].

Due to the important and yet unexploited potential of the dipolar order relaxation experiments in LC and other mesophases, in this work we aim to discuss the experimental conditions needed for creating and measuring the evolution of the two kinds of dipolar order in liquid crystals. The relaxation time of intrapair dipolar order is very sensitive to the slow cooperative motions, even within the MHz Larmor frequency range. This feature distinguishes the dipolar from the Zeeman relaxation rates since the latter reflects the individual motions as well as the collective fluctuations at high frequencies [5,9–12]. Accordingly, measurement of the intrapair and interpair proton dipolar quasi-invariants as a function of externally controlled parameters such as temperature, larmor frequency, sample confinement, sonication, etc., provide independent parameters which may contribute to disen-

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*Electronic address: gonzalce@famaf.unc.edu.ar tangling the underlying spectral densities of the superimposed molecular motions.

It is the purpose of this work to explore the applicability of the spin thermodynamics treatment previously developed for solids [7], to describe the dipolar signals in LC. Since in a wide class of liquid crystals the dipolar interactions can also be grouped into intra- and interpair, we adapt the model of weakly interacting spin pairs for liquid crystals.

The interactions relevant for proton NMR experiments in LC differ from those in hydrated solids: (i) The interpair contribution in hydrated salts originates in the interaction between the proton spin belonging to a water molecule and all the other pairs in the sample while in LC, the dipolar interaction between protons belonging to different molecules averages to zero due to the characteristic mobility of the mesophases, therefore only protons at the same molecule have a residual dipolar interaction. (ii) The number of spins within each LC molecule is usually small and might not be enough for the spin thermodynamics approach to be applicable. (iii) Each molecule bears several protons which have different dipolar couplings with their neighbors; in fact a relatively simple LC molecule may have several inquivalent spin pairs. Then it is meaningful to ask about the actual number of quasi-invariants that can be experimentally distinguished and how to prepare the ordered states.

An example of a simple LC that might be identified with the case of weakly coupled, equivalent proton pairs is PAAd_6. These molecules have eight protons in two benzene rings. Only the *ortho* protons in each ring are strongly coupled while the coupling with those at position *meta* and *para* is much weaker. In the nematic phase all the molecules attain a similar average orientation with respect to the high external field, so all the pairs can be considered as approximately equivalent. That is, each PAAd_6 molecule has four pairs of strongly coupled protons, the interaction of protons belonging to different pairs within the molecule being much weaker.

A different example is 5CB, whose molecules have 19 protons with very different dipolar couplings. However one realizes that the magnitude of the dipolar couplings could be grouped in two categories: The more strongly coupled pairs are the two *ortho* pairs in each benzene ring (4918 Hz [13]–4477 Hz [14]) the CH$_2$ pairs and the CH$_3$ in the alkyl chain (3900, 3560, 3200, 2200, and 2400 Hz [15]). The main interactions comprised in the second group are the coupling between the closest protons belonging to different rings (1742 Hz) and between *meta* and *para* protons within each ring (360 and 56 Hz, respectively).

Despite that the spin system of liquid crystals is different to that in solid hydrated salts, with the aim of describing the dipolar signals and finding the appropriate experimental settings for measuring the relaxation times, we adopt the picture of weakly coupled spin pairs for LC and analyze its applicability. The similarity between the experimental behavior and the fact that the dipolar interactions may be grouped into stronger and weaker supports our assumption.

II. WEAKLY INTERACTING SPIN PAIRS

In this section we adapt the model of equivalent, weakly interacting spin pairs [6,8] to the case of nonequivalent pairs with the aim of describing the dipolar signals in liquid crystals. From this analysis we deduce the conditions for preparing the different kinds of order in liquid crystals.

In LC, as well as in hydrated salts, the proton spin Hamiltonian at high magnetic fields can be written as

$$\mathcal{H}_S = \mathcal{H}_Z + \mathcal{H}_D = \mathcal{H}_Z + \mathcal{H}_P + \mathcal{H}_I, \tag{1}$$

where $\mathcal{H}_Z$ is the Zeeman Hamiltonian and the secular dipolar interaction energy $\mathcal{H}_D$ averaged over the motion, is separated into two terms: a strong intrapair contribution $\mathcal{H}_P$ and a term that accounts for the weaker interpair interaction $\mathcal{H}_I$. Assuming that in 5CB and PAAd_6 the relation $|\mathcal{H}_Z| \gg |\mathcal{H}_P| \gg |\mathcal{H}_I|$ holds (for high magnetic fields), in a perturbative approach we keep only the part of the interpair Hamiltonian that is secular with respect to the $\mathcal{H}_Z$ and $\mathcal{H}_P$ and therefore satisfies $[\mathcal{H}_P, \mathcal{H}_I] = 0$. This amounts to assuming that the dipolar intrapair and interpair energies are quasi-invariants of the motion [7] besides the Zeeman energy. In this picture $\mathcal{H}_Z + \mathcal{H}_P$ is regarded as the unperturbed Hamiltonian and the weaker dipolar interaction between spins belonging to different pairs has the perturbative effect of widening the unperturbed levels.

The secular part of the intrapair Hamiltonian *in LC* is

$$\begin{aligned}\mathcal{H}_P &= \frac{\mu_0}{2\pi}\hbar^2\gamma^2 \sum_A \left\langle \frac{1 - 3\cos^2(\theta_{12}^A)}{(r_{12}^A)^3} \right\rangle (3I_z^{A1}I_z^{A2} - \mathbf{I}^{A1}\cdot\mathbf{I}^{A2}) \\ &= \sqrt{\frac{2}{3}}\hbar \sum_A \omega_P^A T_{2,0}^A,\end{aligned} \tag{2}$$

where $A1$ and $A2$ label the two spins of each pair A within the molecule; the brackets mean average over the distribution of angles θ_{12}^A and distances r_{12}^A through the sample [16]; $T_{2,0}^A = (2/\sqrt{6})(3I_z^{A1}I_z^{A2} - \mathbf{I}^{A1}\cdot\mathbf{I}^{A2})$ is the second rank secular, irreducible, tensor operator associated to the spin pair A; and $\omega_P^A = (3\mu_0\hbar\gamma^2/8\pi)\langle[1-3\cos^2(\theta_{12}^A)]/(r_{12}^A)^3\rangle$ is the dipolar frequency corresponding to the half splitting of the doublet, that may be different for each kind of pair in the molecule.

The statistical operator of a spin system in thermal equilibrium in an external field $\mathbf{B}_0 = B_0\hat{z}$ in the high temperature approximation is $\rho_0 = [\mathcal{I} - \beta_0\omega_0 I_z]/\mathrm{Tr}\{\mathcal{I}\}$, with ω_0 the Larmor frequency and $\beta_0 = (k_B T)^{-1}$, T the sample temperature and $\mathcal{I}$ the identity operator. The FID at time t after a $(\pi/2)_x$ pulse on resonance and later evolution under the dipolar Hamiltonian is

$$S_Z = M_0\,\mathrm{Tr}\{I_y e^{-(i/\hbar)\mathcal{H}_D t} I_y e^{(i/\hbar)\mathcal{H}_D t}\} \equiv M_0\,\mathrm{Tr}\{I_y \tilde{I}_y(t)\}, \tag{3}$$

where $M_0 = \beta_0\omega_0\gamma\hbar^2/\mathrm{Tr}\{\mathcal{I}\} \equiv \gamma\hbar C$ is the equilibrium magnetization and the symbol $\tilde{I}_y(t)$ stands for the spin operator evolved in time with the truncated dipolar Hamiltonian, $\mathcal{H}_D = \mathcal{H}_P + \mathcal{H}_I$. By writing the evolution under $\mathcal{H}_P$ explicitly using Eq. (A1) from the Appendix, the FID can be rewritten as

$$S_Z = M_0 \sum_A \mathrm{Tr}\{I_y \widehat{I_y^A}\}\cos(\omega_P^A t) + \sqrt{\frac{2}{3}}\,\mathrm{Tr}\{I_y[T_{20}^A, \widehat{I_y^A}]\}\sin(\omega_P^A t), \tag{4}$$

where we defined $\widehat{I_y^A} \equiv e^{-(i/\hbar)\mathcal{H}_I t}(I_y^{A1} + I_y^{A2})e^{(i/\hbar)\mathcal{H}_I t}$ as the spin operator of the spins belonging to the A pair, evolved in time under the interpair Hamiltonian only.

In the particular case of equivalent pairs, the FID reduces to the known expression [8] of a damped oscillatory function of frequency ω_P

$$S_Z^{equiv} = M_0[G(t)\cos(\omega_P t) + U(t)\sin(\omega_P t)], \tag{5}$$

with

$$G(t) = \frac{1}{\mathrm{Tr}\{I_y^2\}}\,\mathrm{Tr}\{I_y \widehat{I_y}\},$$

$$U(t) = \frac{i}{\mathrm{Tr}\{I_y^2\}}\,\mathrm{Tr}\{I_y[T_{20}, \widehat{I_y}]\}.$$

The correlation functions G and U measure the adiabatic loss of coherence due to the evolution under the static interpair Hamiltonian. The autocorrelation function $G(t)$ is an even function of time, as evident from its definition, while $U(t)$ is an odd function whose time dependence is, to the lowest order, proportional to t^3.

In the general case of weakly interacting spin pairs (not necesarily equivalent), the density operator at a time τ after the two (on resonance) preparation pulses of the JB sequence is

$$\rho(t_{12}, \tau) = e^{-(i/\hbar)\mathcal{H}_D \tau} P_{4y}^- e^{-(i/\hbar)\mathcal{H}_D t_{12}} I_y e^{(i/\hbar)\mathcal{H}_D t_{12}} P_{4y}^+ e^{(i/\hbar)\mathcal{H}_D \tau},$$

where $P_{4y}^{\pm} \equiv \exp^{\pm i I_y \pi/4}$ and its action over $\mathcal{H}_P$ is written in Eq. (A2) of the Appendix. The mean dipolar energy calculated with this density operator is $\langle \mathcal{H}_D \rangle = \langle \mathcal{H}_P \rangle + \langle \mathcal{H}_I \rangle$, with

$$\langle \mathcal{H}_P \rangle = \mathrm{Tr}\{\mathcal{H}_P \rho(t_{12}, \tau)\} = \frac{1}{2} C\,\mathrm{Tr}\{[I_y, \mathcal{H}_P]\widetilde{I}_y(t_{12})\},$$

$$\langle \mathcal{H}_I \rangle = \mathrm{Tr}\{\mathcal{H}_I \rho(t_{12}, \tau)\} = C\,\mathrm{Tr}\{P_{4y}^+ \mathcal{H}_I P_{4y}^- \widetilde{I}_y(t_{12})\},$$

$$\langle \mathcal{H}_Z \rangle = 0. \tag{6}$$

These quantities depend on the preparation time but are independent of the time τ elapsed after the second pulse, as a consequence of having kept only the secular part of the intra- and interpair Hamiltonians. However they will change with the evolution time t_{23} due to spin lattice relaxation processes. The mean dipolar energy at any time after the preparation pulses is formally identical to that calculated with a spin temperature density matrix that represents a state of equilibrium with "dipolar inverse temperatures" [1,7,17,18]

$$\rho_e = [\mathcal{I} - \beta_Z \mathcal{H}_Z - \beta_P \mathcal{H}_P - \beta_I \mathcal{H}_I]/\mathrm{Tr}\{\mathcal{I}\}, \tag{7}$$

with

$$\beta_P \equiv \langle \mathcal{H}_P \rangle / \mathrm{Tr}\{\mathcal{H}_P^2\} \text{ and } \beta_I \equiv \langle \mathcal{H}_I \rangle / \mathrm{Tr}\{\mathcal{H}_I^2\}, \tag{8}$$

where the expectation values of the dipolar Hamiltoninan are those given in Eq. (6).

However, during an interval comparable with the needed for the coherences to decay the density matrix is obviously nondiagonal and the spin system cannot be represented by a quasiequilibrium spin operator like the one of Eq. (7). At this point we assume, because the experiments confirm this hypothesis, that if the observation pulse of the JB sequence is applied after a time t_{23} longer than the one needed for the coherence decay, the expectation value of any observable can be calculated by using the high temperature quasiequilibrium form of density matrix given by Eq. (7).

The dipolar signal at time t after the read pulse is the component of the magnetization which is in phase with the read pulse of the JB sequence. We find that it is a sum of the two terms involving the dipolar parts of the Hamiltonian:

$$S_D(t) = \gamma\hbar\,\mathrm{Tr}\{\rho_f(t) I_y\} \equiv S_{intra} + S_{inter}, \tag{9}$$

with $\rho_f(t) \equiv e^{-(i/\hbar)\mathcal{H}_D t} P_{4y}^- \rho_e P_{4y}^+ e^{(i/\hbar)\mathcal{H}_D t}$ and

$$S_{intra} = \tfrac{1}{2}\gamma\hbar\beta_P(t_{12})\mathrm{Tr}\{[I_y, \mathcal{H}_P]\widetilde{I_y(t)}\},$$

$$S_{inter} = \gamma\hbar\beta_I(t_{12})\mathrm{Tr}\{P_{4y}^- \mathcal{H}_I P_{4y}^+ \widetilde{I_y(t)}\}, \tag{10}$$

where we used Eqs. (A2)–(A4) of the Appendix. The amplitudes of these dipolar signals are proportional to the corresponding inverse temperature, which give a measure of the amount of order that can be transferred from the Zeeman to the dipolar thermal reservoirs through the JB sequence.

According to the definition of the inverse temperatures of Eqs. (8) and (6), the dipolar signal predicted by Eq. (10) is symmetric in the preparation and the observation times, t_{12} and t respectively. It is worth to point out that this symmetry is also a consequence of assuming the validity of spin thermodynamics in this spin system. The most important feature of Eq. (9) is that the dipolar signal obtained at every preparation time is the superposition of a pure intrapair signal and a pure interpair component. The weight of each of them is determined by the amount of each kind of order resulting from the preparation sequence. This description has previously been proposed by Dumont, Jeener, and Broekaert [6] for interpreting the dipolar signal at any preparation time in crystalline gypsum as a combination of the dipolar intramolecular and intermolecular components.

It is convenient for our subsequent analysis of the signals to make evident the relationship between the intrapair part of the dipolar signal and the FID. With this purpose we write the time derivative of Eq. (3) as

$$\frac{dS_Z}{dt} = \frac{M_0 i}{\hbar}\mathrm{Tr}\{\widetilde{I}_y(t)[I_y, (\mathcal{H}_P + \mathcal{H}_I)]\}, \tag{11}$$

where we used the invariance of traces under cyclic permutations. Then, by comparing Eqs. (11), (8), and (6) we can write the intrapair inverse temperature as

$$\beta_P = \frac{C}{2\mathrm{Tr}\{\mathcal{H}_P^2\}}\mathrm{Tr}\{[I_y,\mathcal{H}_P]\tilde{I}_y(t_{12})\}$$
$$= \frac{C}{2\mathrm{Tr}\{\mathcal{H}_P^2\}}\left(\frac{-i}{\gamma C}\frac{dS_z}{dt}\bigg|_{t_{12}} - A(t_{12})\right), \qquad (12)$$

where $A(t) = \mathrm{Tr}\{[I_y,\mathcal{H}_I]\tilde{I}_y(t)\}$.

The intrapair dipolar signal is then a function of the time derivative of the Zeeman signal:

$$S_{intra} = K\left[a_1 \left.\frac{dS_z}{dt}\right|_{t_{12}}\frac{dS_z}{dt} + a_2\left(\left.\frac{dS_z}{dt}\right|_{t_{12}} A(t) - A(t_{12})\frac{dS_z}{dt}\right) + a_3 A(t_{12})A(t)\right], \qquad (13)$$

where we defined $a_1=(-1/M_0)$; $a_2=i/\hbar$; $a_3=M_0/\hbar^2$, and $K=3/(8\Sigma_A\omega_P^{A2})$. The leading term of Eq. (13) is the first one; the others are much smaller, at most of order $|\mathcal{H}_I|/|\mathcal{H}_P+\mathcal{H}_I|$ compared with the first.

Summarizing, we find that in weakly coupled spin pairs the dipolar signal is symmetric in the preparation and observation times and the intrapair component is, in a good approximation, proportional to the time derivative of the FID. These two qualities are common with the case of ordinary solids with a regular distribution of spins [1] (like the ^{19}F in CaF_2) where there is only one dipolar quasi-invariant.

According to Eqs. (12) and (13), one should expect to prepare the *maximum amount of intrapair dipolar order for* t_{12} *at the maximum of the derivative of the FID* in general systems of weakly coupled spin pairs. Under this experimental condition the spin system is put in a state where the observable related to the intrapair Hamiltonian attains its maximum expectation value. As shown in Sec. III, in the studied examples S_D and dS_Z/dt are proportional and the maximum intrapair order that can be prepared is also *practically pure* intrapair order because the interpair contribution is negligible within that experimental conditions. It is worth mentioning that this method for preparing the intrapair order, as well as the symmetry in t_{12} and t hold, regardless of the number of different dipolar couplings (inequivalent pairs) present in the molecule.

With regard to the preparation of the interpair order, it can be seen from Eqs. (12) and (4) that β_P is a sum of trigonometric functions of a number of frequencies. It is an oscillatory function of t_{12} both in cases in which the spin system is composed by strictly equivalent pairs or when the intrapair dipolar couplings are not very disperse. Being $S_{intra}(t)$ proportional to the intrapair inverse temperature, choosing the preparation time so that $\beta_P(t_{12})$ crosses through zero assures the selection of *pure interpair order*. $S_D=S_{inter}$.

The case of equivalent pairs is contained within the former prescription. In that case, the maximum derivative of the FID coincides with the first zero of the FID occurring at $t=\pi/(2\omega_P)$, provided the function $G(t)$ attenuates slowly. Therefore β_P crosses through zero when $\omega_P t_{12}=\pi$ and then the pure interpair signal $S_D=S_{inter}$ can be prepared by choosing t_{12} to fit this condition.

In summary, the former are the conditions that should be used to prepare the maximum intrapair and the pure interpair signals in the general case of weakly interacting spin pairs. Under the mentioned conditions all the order present in the spin system after the initial Zeeman polarization may be transferred either into the mostly pure intra- or into the pure interpair states.

III. EXPERIMENT

In this section we show the experimental dipolar signals from PAAd_6 at 27 MHz and 5CB at 300 MHz in the nematic phase and compare them with the predictions of the model of weakly interacting spin pairs. Then we use the prescription for preparing mostly pure intra- or interpair signals for measuring the relaxation times of each dipolar quasi-invariant separately in PAAd_6 at 16 MHz.

Experiments at 27 MHz were carried out in a homemade NMR spectrometer; a Bruker MSL300 was used for measurements at 300 MHz. Every experiment begins observing the FID of the isotropic phase to find the on-resonance condition and to set the receiver phase so that all the signal (Zeeman) is in one channel. In the isotropic phase no dipolar signal appears after the observation pulse of the JB sequence. When the temperature is lowered to the nematic range, the channel which is in phase with the read pulse has the dipolar signal while the Zeeman signal is in the 90° out of phase channel. When increasing t_{23} the dipolar signal attenuates to zero while the Zeeman signal rises to a maximum. It is then crucial to keep them in separate channels to have a good quality measurement of the relaxation times, especially in the interpair case where the S/N ratio is lower. In the LC analyzed in this work we observed that the dipolar signals (at any fixed t_{12}) keep the same shape at every evolution time t_{23}, provided the observation pulse comes after the coherences have decayed.

A. PAAd_6

The FID of nematic PAAd_6 is a damped oscillatory function: the solid line of Fig. 1(a) is the signal at 402 K and 27 MHz. The dashed line shows that within the first two periods ($t < 380$ μs) the FID can be approximately described by an attenuated cosine function of one well defined frequency of 33.8 kHz. The term $G(t)\cos(\omega_P t)$ of Eq. (5) leads the behavior of the FID at short times, which is consistent with assuming that PAAd_6 is a case of equivalent pairs. However, Eq. (5) fails in describing the signal at longer times where, according to this model, the term $U(t)\sin(\omega_P t)$ should be appreciable [8]. This might indicate that PAAd_6 has an insufficient number of protons for the solidlike approach for the coherence decay to be valid. We see that the model of weakly interacting spin pairs describes accurately the early evolution of the FID, that is the time interval which is relevant for preparing the maximum amounts of dipolar order.

It has been reported that the shapes of the dipolar signals depend noticeably on the preparation time of the JB sequence [2]. We also observed this feature and found that the

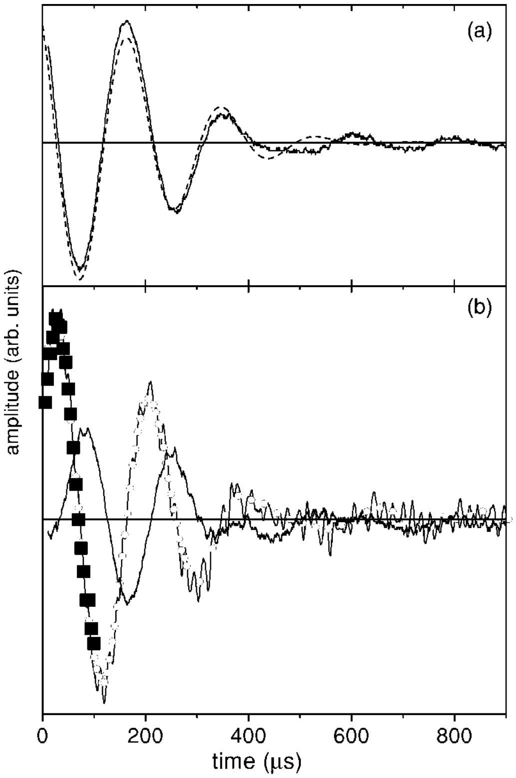

FIG. 1. (a) FID signal of PAAd_6 (solid) and a fitting (dotted line) with Eq. (5). (b) Dipolar intrapair signal (small circles) and dipolar interpair signal (solid). The intrapair signal coincides with the amplitude (squares) of the dipolar signals at different preparation times. There is also coincidence with the time derivative of the experimental FID (noisy solid line) at every time.

largest dipolar signal occurs at $t_{12}=t_a=(40\pm 3)$ μs. This is precisely the preparation time at which the numerical time derivative of the FID has its maximum and the FID crosses through zero because it coincides with the condition $\omega_P t_a = \pi/2$. According to the model described in the former section, the dipolar signal so prepared (zero FID and maximum derivative) contains the largest possible intrapair component that can be observed in this compound by the JB sequence. The curve in small circles in Fig. 1(b) is the dipolar intrapair signal corresponding to a preparation time $t_{12}=40$ μs and the (noisy) solid line over it is the numerical time derivative of the FID (multiplied by a scaling factor). These curves coincide at all acquisition times.

The squares in Fig. 1(b) that also coincide with the curve in circles for times shorter than 110 μs, represent the amplitude of the dipolar signal at a fixed time $t=40$ μs obtained with different preparation times. The coincidence shows that the dipolar signals are symmetric in the preparation and evolution times, in agreement with Eq. (9). Because of the symmetry, this is an alternative way of scanning the shape of the dipolar signal for times shorter than the dead time of the receiver [1], as shown by the squares that correspond to $t_{12} < 20$ μs in Fig 1(b).

Now we look for the time $t=t_b$ at which the intrapair signal crosses through zero, that is, when $\beta_P(t_{12})=0$. The signal obtained with a preparation time $t_{12}=t_b=80\pm 5$ μs has pure interpair character and is plotted as a solid line in Fig. 1(b). This pure interpair signal is 90° out of phase with respect to the intrapair signal. In PAAd_6 $t_b=2t_a$ in accordance with the description of the FID in terms of equivalent pairs of the preceeding paragraph. Also it is worth to notice that the amplitude of this interpair component at $t=t_a$ is negligible, then, the signal prepared with $t_{12}=t_a$ can be considered as a *pure* intrapair signal, besides being the largest.

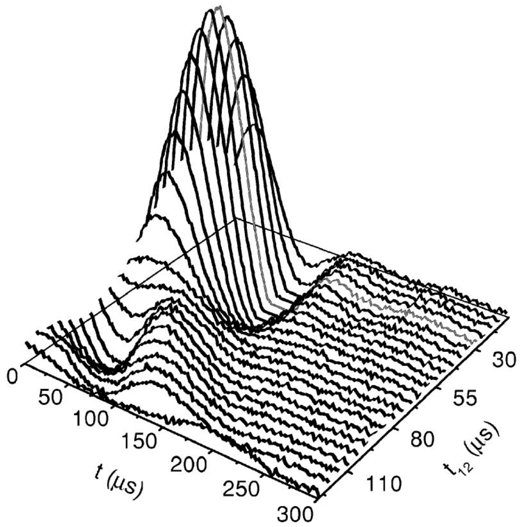

FIG. 2. Waterfall plot of the dipolar signals in nematic 5CB at 308 K, as a function of the preparation time of the JB pulse sequence. The signal shape changes with the preparation time.

B. 5CB

Figure 2 shows a collection of dipolar signals of nematic 5CB obtained at 300 MHz and 306 K at different preparation times t_{12}. In all these signals t_{23} is fixed at 4 ms. This interval is large enough to allow the coherences to decay but small compared with the spin lattice relaxation times (T_{1Z} $=634$ ms and $T_{1D}=247$ ms). The amplitude of the dipolar signals grows with increasing t_{12} and then decreases, keeping the same shape in the range 5 $\mu\text{s} < t_{12} < 55$ μs. The maximum amplitude is obtained with $t_{12}=31$ μs. For $t_{12} > 55$ μs the signals change their shape. This behavior is consistent with the occurrence of more than one dipolar quasi-invariant.

The FID of nematic 5CB at 308 K is the solid line of largest amplitude in Fig. 3. In the experiment, the condition for preparing maximum dipolar signal (dashed line of Fig. 3 and open circles in the inset of this figure) is met for a preparation time equal to that of the steepest FID ($t_{12}=31$ μs at $T=308$ K), as predicted by Eq. (13). Notice that this time differs from the first zero of the FID which occurs at t_0 $=46$ μs, because 5CB is not a case of equivalent pairs. The numerical derivative of the experimental FID multiplied by a scaling factor is the solid line (behind the circles) in the inset of Fig. 3. This figure shows the complete coincidence with the measured pure intrapair signal for every time. This indicates that the terms in $A(t)$ in Eq. (13) are in fact negligible in comparison with the one that involves the intrapair energy.

The intrapair dipolar signal is symmetric in the preparation and evolution times as shown in the inset of Fig. 3,

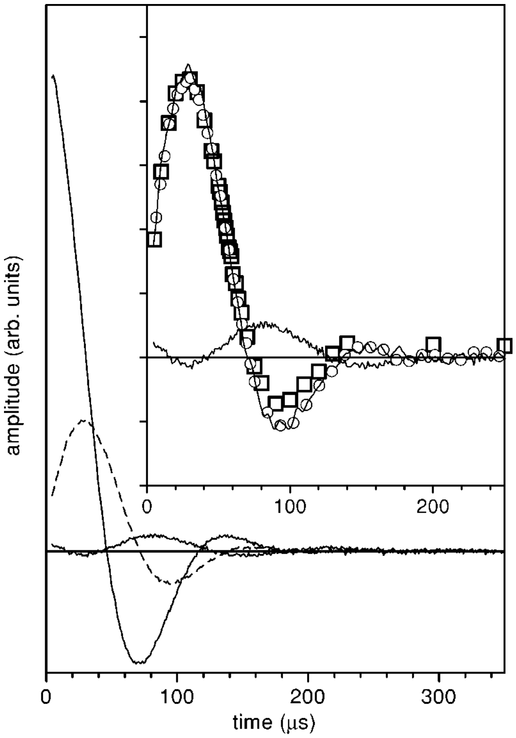

FIG. 3. Zeeman FID signal of nematic 5CB (largest solid line); the dipolar intrapair signal (dashed) and dipolar interpair signal (solid) have lower amplitude. Inset: the intrapair signal (circles) coincides with the time derivative of the FID (solid line superimposed to the circles). The interpair signal is the solid, lower amplitude line. Coincidence with the squares for times less than 80 μs shows the symmetry respect to the preparation and the observation times.

where the plot in squares represents the amplitude of the dipolar signal at a fixed time $t=31$ μs for different preparation times. This curve corresponds to a cut along the t_{12} axis of Fig. 2. It coincides with the intrapair signal for times shorter than 80 μs; at longer preparation times the circles follow a similar shape but have smaller amplitude. This fact may be due to other attenuation processes that are not taken into account by this closed-spin system approach. The symmetry at short times is verified for every t (that is, for different cuts in Fig. 2) as predicted by Eq. (9).

The first zero of the intrapair signal, that is also the condition for having pure interpair order, occurs at $t=72$ μs at 308 K. The dipolar signal obtained with this preparation time is the lowest amplitude curve in Fig. 3.

The change in shape of the dipolar signals for different t_{12} can be displayed by plotting the time t_0 at which the dipolar signal crosses through zero as a function of the preparation time. The open circles of Fig. 4 are the experimental values of t_0 for 5CB at 308 K. The curve slope changes sharply within a narrow time interval near the t_{12} values needed for preparing the interpair order. The time at which the change occurs depends on temperature according with the order parameter (or the dipolar frequency) of the nematic. This characteristic curve can be explained by recalling that the dipolar signal obtained for each preparation time t_{12} is the weighted sum of the intra- and interpair contributions. The weighting factors are the intra- or the interpair amounts of order that can be prepared in the sample, as predicted by Eq. (9). An estimation of these amplitudes should involve the calculation of β_P and β_I, which is a heavy task for 5CB because of the huge number of degrees of freedom involved. However, making use of the symmetry in the preparation and evolution times, one can assume that the amplitude of the pure intra- and the pure interpair signals at a given time is proportional to the intra- and to the interorder that can be prepared with t_{12} equal to that given time. If this is so, one might reproduce the plot of Fig. 4 using only the "mostly pure" signals S_{intra} and S_{inter}. The curve in squares in this figure was calculated in this way. Of course it does not coincide with the curve in circles for times larger than 80 μs because the symmetry also fails in this interval. In PAAd_6 we could also reproduce the phase of the dipolar signals as a function of the preparation time, with the same procedure used in 5CB.

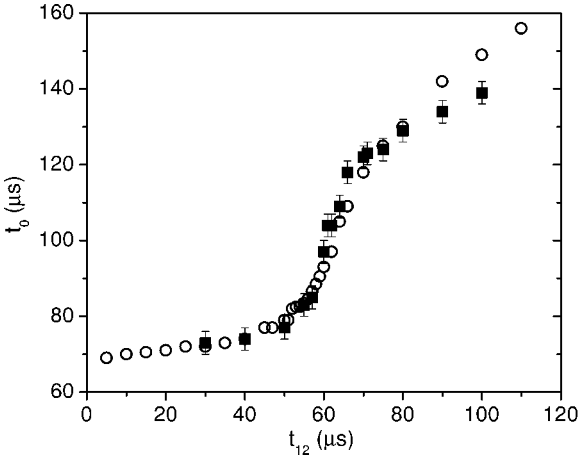

FIG. 4. Time at which the dipolar signals cross through zero as a function of the preparation time of the JB pulse sequence. Open circles: from the experiment, squares: reconstructed from the weighted sum of the experimental pure intra- and interpair signals. The signals undergo a $\pi/2$ phase change when going from intrapair through interpair.

In this way the larger component leads the resultant signal shape. The phase changes from the one of the intracomponent to that of the intercomponent within the short interval where both components have comparable weight. In 5CB this happens for 55 $\mu s < t < 70$ μs (as seen in Fig. 3). This is also consistent with the fact that the pure interpair signal is also the one with lowest amplitude. That is, the greater the ratio M=intra-amplitude/inter-amplitude, the steeper the phase plot.

C. Relaxation times

Once we have a prescription for finding the most pure intra- or interpair signals, we use it for measuring the separate relaxation times. The signal attenuation as a function of t_{23} is a single exponential when measured in the former conditions. This fact suggests that no appreciable cross relaxation occurs between the intra- and interquasi-invariants nor with the unobserved singlet state (contrarily to the case of hydrated salts [6]). The temperature dependence of the relax-

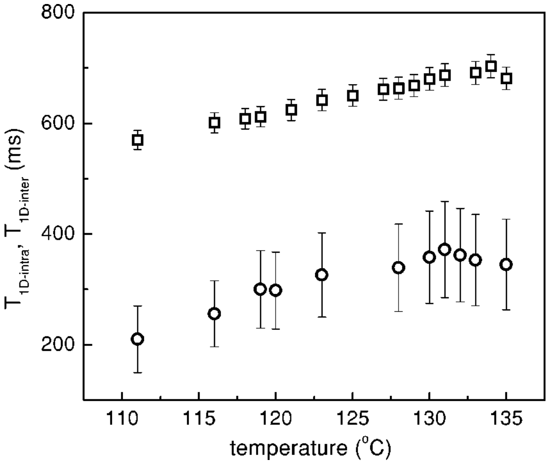

FIG. 5. Relaxation times of the intrapair (squares) and interpair order (circles) in PAAd_6 in the nematic phase at 27 MHz.

ation time of each dipolar quasi-invariant at 27 MHz in PAAd_6 is shown in Fig. 5. $T_{1Dinter}$ (circles) is noticeably lower than $T_{1Dintra}$ (squares) in the whole (nematic) temperature range and their temperature dependences are also different. In 5CB at 27 MHz the difference in the temperature behavior of the two relaxation times is more marked [5], possibly because the motion of the methyl groups in the alkyl chain might be a more efficient mechanism for relaxing the intrapair order. These characteristic features show that the measurement of each parameter can provide distinct information to study the different molecular motions that drive relaxation. At the present, to our knowledge, there are no theoretical models in the literature that describe the temperature or the Larmor frequency dependence of $T_{1Dinter}$. Besides, the theory for $T_{1Dintra}$ that is based on the high temperature (weak order) approximation, does not provide a satisfactory description of its frequency dependence [19,20].

IV. DISCUSSION

In this work we verified that it is possible to bring the proton spin system of a liquid crystal into states of intrapair and interpair states of dipolar order through the JB sequence and to measure their relaxation times separately. By assuming that in liquid crystals the proton spin system can be considered as a set of weakly coupled spin pairs, we deduce the experimental prescription needed to create these states of dipolar order. After successfully tried in PAAd_6 and 5CB, wecan anticipate the applicability of this thermodynamic approach for a wide class of similar liquid crystals.

In PAAd_6, the time t_a needed for preparing the maximum amount of intrapair order coincides with the first zero of the FID. This feature indicates that the model of *equivalent pairs* is well justified in this compound. In 5CB, t_a is the one predicted by Eq. (13), which shows the adequacy of considering the spin system of 5CB as formed by weakly interacting pairs.

In the case of nonequivalent pairs, the Hamiltonian has all the (commuting) terms with indices A of Eq. (2), therefore, the initial Zeeman polarization could in principle be transferred to more than one intrapair quasi-invariant. However, in the nematic compounds analyzed in this work only two dipolar quasi-invariants can be distinguished. This is consistent with the fact that the criteria for preparing the pure intra- and interpair orders yielded by this model basically rely only on the fact that $|\mathcal{H}_P| \gg |\mathcal{H}_I|$, which is also a common characteristic in ordinary thermotropic LC. In terms of the underlying spin thermodynamics that we adopted for describing the signals, the experiment suggests that protons attain a single spin temperature when they are brought into a state of intra- or interpair order.

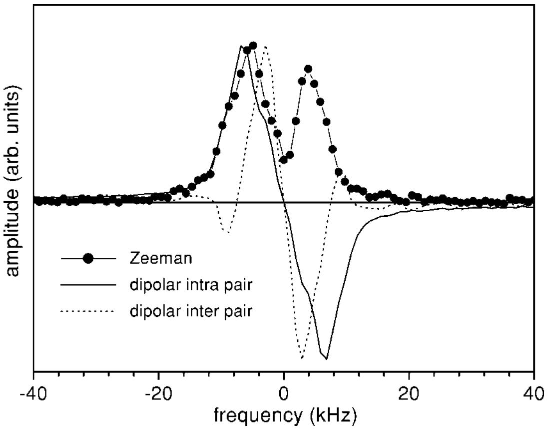

FIG. 6. Fourier transforms of the FID (circles), the intrapair dipolar signal (solid), and the interpair dipolar signal (dotted) of 5CB in the nematic phase.

If the different couplings are not widely spread one could still expect signal shapes as the one of 5CB; however, if the dipolar couplings are continuously spread over a wide range, the overall shape may be very different to the former case. The case of the smectic phase might be this limit.

An alternative way of recognizing the intra- or intercharacter of the dipolar signals is through their Fourier transforms. As clearly shown by Eisendrath, Stone, and Jeener [7] for the ideal case of an ensemble of weakly coupled equivalent spin pairs, the Fourier transform of S_{intra}, the intrapair order has one component of the doublet in absorption and the other in emission while the interpair order manifests as a spectrum that is emissive on one side of the line and absorptiveon the other side. When choosing the preparation times according to the criteria shown above, the spectra of the FID and the dipolar signals of 5CB show these characteristic features, as shown in Fig. 6. This fact reinforces the conclusion that it is correct to treat 5CB within the spin thermodynamics approach of weakly coupled spin pairs. In spite of the fact that the simple molecule of PAAd_6 looks as a good example of this weakly-interacting-pairs model, the spectra of its Zeeman, intrapair and interpair signals do not have the expected characteristics: all of them have an unavoidable phase change and no phase shift causes them to be neither in absorption nor in emission. This failure is consistent with the fact that the time domain signals could not be described by this model either for $t > 350\ \mu$s. Conceivably, this simple spin system cannot be considered as closed during the whole decoherence time.

In Fig. 5 the relaxation time of each quasi-invariant has a different value and different temperature dependence, indicating that each one reflects differently the various relaxation mechanisms. This feature was also observed in nematic 5CB at 16 MHz [5] where the difference in the temperature dependences of dipolar relaxation times is more marked than in PAAd_6. One could take advantage of this fact because it implies that another experimental parameter is available for studying the relaxation mechanisms associated with molecular motion.

The ratio of dipolar intra- to interpair signal amplitudes is $M \simeq 3$ in 5CB while in 5CBd_{11} it is smaller: $M \simeq 1.6$ [5]. The only difference between these two compounds is that 5CB intrapair signal originates in the core *and* in the chain protons while in 5CBd_{11} both the intrapair and the interpair signal come only from the core protons. This suggests that the interpair signal is mainly originated in the cores, with almost no contribution from the chains. This idea is consistent with having different sensitivity to the various relaxation mechanisms.

A further experimental detail is worth mentioning: In Eq. (9) we assumed that the irradiation pulses are on-resonance with the Larmor frequency, ω_0. For sufficiently low fields H_0, all the nuclei have the same resonance frequency, however, at higher fields the chemical shifts are observable. For example, the resonance line of 5CB in the isotropic (liquid) phase is of 1 kHz width when observed at $\omega_0 \sim 30$ MHz but it is a structured spectrum of 4 kHz width at $\omega_0 = 300$ MHz. This fact makes it very difficult (and in some compounds impossible) to measure the dipolar relaxation time in the interpair condition at higher fields. The dipolar signal is detected in the same direction of the first preparation pulse. Under ideal conditions the Zeeman signal is 90° out of phase respect to the dipolar signal at every evolution time t_{23}, however, due to the chemical shifts, the optimal preparation times are not the same for every dipolar pair and part of the Zeeman signal contaminates the dipolar signal especially at longer t_{23}. Although this fact is not a problem when just recording the dipolar signals (because this is done at short t_{23}, when $\beta_Z \simeq 0$) it is a major difficulty when measuring the relaxation times. Due to the fact that the dipolar and Zeeman signals have opposite time evolution (the first decreases and the second grows with t_{23}), depending on the relative values of T_{1D} and T_{1Z} there is a "window of opportunity" [21] where the detection of the dipolar can be restricted to. A simpler and more accurate solution is to perform the measurements at a lower external field, where the chemical shift is negligible.

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APPENDIX

Here we summarize some relations useful for the calculations in the body of the paper. Evolution of a spin operator under the truncated dipolar Hamiltonian (intra- and interpair)

$$\begin{aligned}\widetilde{I_y}(t) &= e^{-(i/\hbar)\mathcal{H}_I t}\left(e^{-(i/\hbar)\mathcal{H}_P t} I_y e^{(i/\hbar)\mathcal{H}_P t}\right) e^{(i/\hbar)\mathcal{H}_I t} \\ &= e^{-(i/\hbar)\mathcal{H}_I t}\Sigma_A\Big(I_y^A \cos(\omega_P^A t) - i\sqrt{\tfrac{2}{3}}[T_{20}^A, I_y^A]\sin(\omega_P t)\Big)e^{(i/\hbar)\mathcal{H}_I t}. \end{aligned} \tag{A1}$$

Effect of a 45_y^o pulse on the intrapair Hamiltonian

$$\begin{aligned}P_{4y}^- \mathcal{H}_P P_{4y}^+ &= \hbar\sqrt{\tfrac{2}{3}}\Sigma_A \omega_P^A P_{4y}^- T_{20}^A P_{4y}^+ \hbar\sqrt{\tfrac{2}{3}}\Sigma_A \omega_P^A \\ &\quad \times\left[-\sqrt{\tfrac{3}{32}}(T_{22}^A - T_{2-2}^A) + \frac{1}{4}T_{20}^A + i\sqrt{\tfrac{3}{8}}(T_{21}^A - T_{2-1}^A)\right],\end{aligned} \tag{A2}$$

where T_{2j} are the spherical tensors of rank 2.

Because of the commutation relations of I and T_{2j}, it is

$$(T_{21} - T_{2-1}) = -2i[I_y, T_{20}]. \tag{A3}$$

In the calculation of the intrapair dipolar signal we used

$$\begin{gathered}\mathrm{Tr}\{e^{-(i/\hbar)\mathcal{H}_D t} T_{20} e^{(i/\hbar)\mathcal{H}_D t} I_y\} = \mathrm{Tr}\{T_{20} I_y\} = 0, \\ \mathrm{Tr}\{e^{-(i/\hbar)\mathcal{H}_D t}(T_{22} - T_{2-2}) e^{(i/\hbar)\mathcal{H}_D t} I_y\} = 0, \\ \mathrm{Tr}\{[I_y, T_{20}]\widetilde{I_y}\} = \mathrm{Tr}\{[\widetilde{I_y}, T_{20}] I_y\}.\end{gathered} \tag{A4}$$

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