PHYSICAL REVIEW E **74**, 051702 (2006)

Proton NMR relaxation of the dipolar quasi-invariants of nematic methyl deuterated para-azoxyanisole within the high-temperature Redfield relaxation theory

H. H. Segnorile, L. Barberis, C. E. González, and R. C. Zamar*

Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba M. Allende y H. de la Torre–Ciudad Universitaria, X5016LAE Córdoba, Argentina

(Received 24 September 2005; revised manuscript received 28 August 2006; published 3 November 2006)

The high-temperature Redfield spin-lattice relaxation theory is used for calculating the relaxation times of the different dipolar quasi-invariants in an eight-spin system which represents methyl deuterated para-azoxyanisole (PAAd_6) in the nematic phase. According to previous experiments, this system can be considered as composed of weakly coupled pairs of strongly interacting spins, the ortho protons of the aromatic rings, thus, it possesses four quasi-invariants of the motion: Zeeman, dipolar intrapair and interpair, and singlet orders. We write the set of coupled differential equations which describe the relaxation of the generalized inverse spin temperatures of the four quasi-invariants. The relaxation constants are then calculated in terms of experimental two-spin spectral densities of the lattice motions. The relation between the multispin and the two-spin spectral densities is also deduced. Calculation shows that the Zeeman and singlet quasi-invariants are uncoupled from the dipolar ones, and that the relaxation time of the singlet order is much longer than those of the Zeeman and dipolar orders. The calculated cross relaxation rate between the dipolar orders through the lattice is small enough to be observable in the experiment. We also show that the nonsecular term associated with the collective motions dominates relaxation of the intrapair and interpair energies in PAAd_6, while the local motions do not play a significant role, in qualitative agreement with the reported experimental behavior. The dipolar relaxation times predicted by the theory are significantly larger than the experimental ones, the difference being even more pronounced for the interpair quasi-invariant. We show that the discrepancy cannot be overcome neither by resorting to a realistic model for the spin system nor considering the various possible cross-relaxation pathways among the quasi-invariants. This feature points out the high- temperature approximation as a source of the discrepancy. We discuss the effect that slow and ultraslow molecular modes could have on the relaxation of the dipolar order.

DOI: 10.1103/PhysRevE.74.051702 PACS number(s): 61.30.−v, 76.60.−k, 76.60.Es, 82.56.Na

I. INTRODUCTION

Nuclear magnetic resonance (NMR) spin-lattice relaxation methods have been used for many years for studying the complex anisotropic reorientation of molecules in the liquid crystal mesophases. The measured quantities are the relaxation times which depend on the fluctuations of the interactions of the nuclear spins with the molecular environment or lattice.

In addition to the fast, liquidlike diffusive molecular motions (translation and rotations) and directly related with the typical ordering of the liquid crystal (LC) mesophases, LC molecules undergo slow, collective motions called order director fluctuations (ODFs) [1]. This kind of motion causes the relaxation time of the Zeeman order T_{1Z} (commonly called spin-lattice relaxation time) to be strongly dependent on the Larmor frequency. The frequency dispersion of T_{1Z} was measured in nematic liquid crystals and other complex mesophases by means of field-cycling experiments, which clearly showed that the cooperative motions dominate the Zeeman relaxation within the low frequency range (few hundreds of kHz) [2].

Because of the molecular orientational ordering, LC exhibit a high average intramolecular dipolar energy. This allows preparing the proton spin system in initial quasiequilibrium states of strong dipolar order which relax towards thermal equilibrium with the lattice with characteristic relaxation times T_{1D}. In fact, similarly to the case of hydrated salts [3,4], by means of the Jeener-Broekaert (JB) pulse sequence [5] it is possible to prepare two kinds of dipolar ordered states in LC, namely, intrapair and interpair dipolar order, and to measure their relaxation times independently [6–8]. These quasi-invariants relax exponentially, each with a different relaxation rate and temperature behavior. For example, in 5CB (4′-pentyl-4-biphenyl-carbonitrile) at 14 MHz, $T_{1\mathrm{Dinter}}$ is almost insensible to temperature changes, which is a typical behavior of the ODF mechanism, while $T_{1\mathrm{Dintra}}$ presents a considerable dispersion with temperature, reflecting the influence of reorientations of the alkyl chain protons [7,9]. In PAAd_6 (methyl deuterated para-azoxyanisole) at 27 MHz the temperature behavior of both parameters is consistent with the ODF mechanism, but the interpair relaxation is much more efficient than the intrapair one through the whole nematic temperature range [7,8]. These features suggest that measuring both dipolar relaxation times can provide independent information relevant for estimating the contribution of the several superimposed molecular motions.

Larmor frequency and temperature dependent T_{1D} experiments in several thermotropic liquid crystals showed that the cooperative molecular fluctuations have a strong relative weight in the relaxation of the intrapair dipolar ordered state, even within the MHz frequency range [9–11]. This is the remarkable characteristic of T_{1D} that makes it especially con-

---

*Electronic address: zamar@famaf.unc.edu.ar venient for studying collective molecular dynamics in mesophases. However, the magnitude of the ODF contribution to $T_{1\mathrm{Dintra}}$ could not be explained within the standard, high-temperature Redfield spin-lattice relaxation theory (HTR) [12,13] while using simplified models for the spin system. The relaxation time predicted by a two-spin model [14], within this theory, is much greater than the experimental intrapair dipolar one. The difference depends on the Larmor frequency as $\nu^{1/2}$ [9,10], which is the dependence of the ODF spectral density [15]. Further refinements of the model which consider only the intrapair dipolar quasi-invariant in a four-proton system did not provide the correction to the discrepancy either [11,16].

The potential of dipolar order relaxation as a technique for studying correlated motions in complex fluids, on the one hand, and the need for a test of the essential hypotheses underlying the spin-lattice relaxation theory on the other hand, motivated us to perform a calculation based on a realistic model of the spin system which also allows cross relaxation among the quasi-invariants through the lattice. We inquire if the mentioned facts: the marked difference between the dipolar relaxation times and the discrepancy between theoretical and experimental intrapair relaxation time, can be assigned to mechanisms described by the usual HTR theory or if, on the contrary, more general theories are necessary to take into account the occurrence of slow or ultraslow motions. The purpose of this work is to obtain secure estimates of the spin-lattice relaxation rates and of the cross relaxation among the quasi-invariants through the lattice in PAAd_6, within the HTR theory under the hypothesis of spin temperature [17]. Then, by comparing the estimates with the experiment, we explore the limits imposed by the basic hypotheses of the high-temperature Markovian relaxation theory.

It is known that in PAAd_6 the magnitudes of some of the dipolar couplings of protons belonging to different rings are comparable to, or even larger than, the dipolar couplings between protons in meta and para position within the benzene rings [18]. Therefore we consider the eight interacting protons of the molecule as the spin system, as explained in Sec. II A. This theoretically tractable model has enough complexity to display the characteristic features of a multispin system. As experimentally demonstrated [8], the proton system in PAAd_6, as well as in other simple nematic thermotropic liquid crystals (such as the cyanobiphenyls), can be treated as an ensemble of molecules composed of weakly coupled pairs of strongly interacting spins. Therefore, one expects four quasi-invariants of the motion in such a system: Zeeman (Z), dipolar intrapair (intra), dipolar interpair (inter), and singlet (sing) orders [4].

In Sec. III we write the set of coupled differential equations for the generalized inverse spin-temperatures and obtain the characteristic relaxation rates of the four quasi-invariants in terms of spectral densities of the lattice motions. Based on previous experiments on the Zeeman relaxation time in PAAd_6, we estimate the spectral densities of the relevant molecular mechanisms in Sec. IV A. Also we calculate the contributions of the different molecular motions to the relaxation parameters. The calculated relaxation times of the intrapair and interpair dipolar quasi-invariants are then compared in Sec. V with the reported experimental behavior.

In Appendix D we generalize to the multispin case the formalism developed in the literature for the calculation of two-spin spectral densities [19]. We write the multispin spectral densities in terms of that related with the autocorrelation of the strongest spin pair; this spectral density is the one that can be extracted from the Zeeman relaxation data. A description of the reference frames used in the calculations is presented in Appendix A, and the main assumptions used are listed in Appendix B. In Appendix C we outline the calculation of the dipolar couplings and the time correlation functions of the different motions.

II. THE HAMILTONIAN

Molecular dynamics in LC is highly correlated, which in principle, would make necessary to treat the statistical properties in terms of ensembles of molecules pertaining to correlated regions or domains, instead of individual molecules. However, within the high-temperature approximation, a simplified treatment of NMR relaxation in terms of representative molecules is realistic.

The Hamiltonian of the system includes the Zeeman interaction (each spin with the external magnetic field $\mathbf{B}_0$ which defines the z axis), the dipolar interaction between spins, and the lattice energy (thermal bath):

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_D + \mathcal{H}_L. \tag{1}$$

In units of $\hbar$ the Zeeman Hamiltonian is $\mathcal{H}_Z = -\gamma B_0 \Sigma_i \mathbf{I}_i^z$, with γ the proton gyromagnetic ratio and $\mathbf{I}_i^z$ the z component of the spin operator of each resonant nucleus. $\mathcal{H}_D$ represents the dipolar interaction between every pair of spins within the sample, and $\mathcal{H}_L$ is the lattice Hamiltonian.

It is now convenient to add and subtract the average over the motion of the dipolar Hamiltonian $\overline{\mathcal{H}_D}$ which is independent of time and of the lattice variables, with the purpose of rewriting the Hamiltonian as

$$\mathcal{H} = \mathcal{H}_S + \mathcal{H}_{\mathrm{SL}} + \mathcal{H}_L. \tag{2}$$

In this way, the spin Hamiltonian $\mathcal{H}_S = \mathcal{H}_Z + \overline{\mathcal{H}_D}$ involves only spin variables, and the second term stands for the fluctuations of the spin-lattice interaction from their average value $\mathcal{H}_{\mathrm{SL}} = \mathcal{H}_D - \overline{\mathcal{H}_D}$ [20]. Due to the fast molecular motions the average value of the intermolecular dipolar interactions are negligibly small; therefore, $\mathcal{H}_S$ contains only the (average) dipolar interactions within the molecule.

Spin lattice relaxation is in principle driven by lattice fluctuations that may both involve mechanisms referring to the representative molecule, like the rotational diffusion (ROT) and the order fluctuations of the director (ODF) or mechanisms that relate different molecules, such as translational self-diffusion (DIF). Experiment showed that the relative contribution of intermolecular mechanisms to relaxation of the dipolar order in PAAd_6 is small [11]. Then, for the sake of simplicity, in calculating the relaxation rates of dipolar quasi-invariants (i) we assume that intermolecular mechanisms are statistically independent of intramolecular ones and (ii) we consider only the intramolecular interactions in the spin-lattice Hamiltonian. Consequently, in terms of the

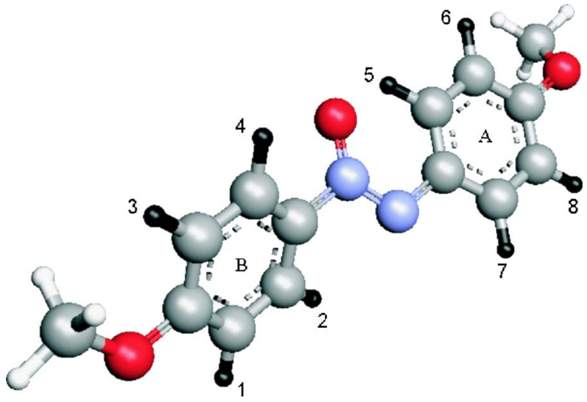

FIG. 1. (Color online) Sketch of the PAAd_6 molecule. Protons in the benzene rings are numbered as used in the calculations.

second rank tensor operators of spin $\mathbf{A}_{ij}^{q}$ and lattice $\mathbf{F}_{ij}^{q}$, we write

$$\mathcal{H}_{\mathrm{SL}} = \sum_{q} \sum_{i<j} \Delta \mathbf{F}_{ij}^{q} \mathbf{A}_{ij}^{q}, \tag{3}$$

where the indices $i,j=1,\ldots,8$ number all the interacting spins as in Fig. 1, $q=0$, ± 1, ± 2 and

$$\mathbf{A}_{ij}^{0} = \mathbf{I}_i^z \mathbf{I}_j^z - \frac{1}{4}(\mathbf{I}_i^+ \mathbf{I}_j^- + \mathbf{I}_i^- \mathbf{I}_j^+)$$

$$\mathbf{A}_{ij}^{\pm 1} = -\frac{3}{2}(\mathbf{I}_i^z \mathbf{I}_j^\pm + \mathbf{I}_i^\pm \mathbf{I}_j^z)$$

$$\mathbf{A}_{ij}^{\pm 2} = -\frac{3}{4}\mathbf{I}_i^\pm \mathbf{I}_j^\pm . \tag{4}$$

We defined $\Delta \mathbf{F}_{ij} \equiv \mathbf{F}_{ij} - \overline{\mathbf{F}_{ij}}$ as the difference between the time dependent lattice operators and their ensemble average. In consistence with the high-temperature approximation, the lattice operators can be replaced by functions [13,21]

$$F_{ij}^{0} = \frac{\mu_0 \hbar \gamma^2}{4\pi r_{ij}^3}(1 - 3\cos^2\theta_{ij}),$$

$$F_{ij}^{\pm 1} = \frac{\mu_0 \hbar \gamma^2}{4\pi r_{ij}^3}\sin\theta_{ij}\cos\theta_{ij} e^{\mp i\phi_{ij}},$$

$$F_{ij}^{\pm 2} = \frac{\mu_0 \hbar \gamma^2}{4\pi r_{ij}^3}\sin^2\theta_{ij} e^{\mp 2i\phi_{ij}}, \tag{5}$$

where θ_{ij} and ϕ_{ij} are the polar and azimuthal angles of the internuclear vector relative to a frame with the z'' axis parallel to the external magnetic field. It is worth mentioning the consequences that this high temperature approximation has. The master equation which we use later to describe the spin dynamics [Eq. (10)] is obtained after two steps [13], first the general Markovian master equation in operator form is expanded up to linear terms in $\beta_R \mathcal{H}_S$, where β_R is the "inverse temperature" of the reservoir, and $[1-\mathcal{H}_S/(k_B T)]$ is identified with the thermal equilibrium density operator, second, the density operator appearing in the linear term of the approximate master equation is replaced by its form of infinite temperature. The master equation so obtained has the correct detailed balance for finite temperatures, but with a relaxation superoperator which coincides with that of the semiclassical master equation. Physically, this approximation implies the neglecting of correlation between spin and lattice degrees of freedom in the microscopic time scale [21].

TABLE I. Proton-proton dipolar interactions.

i	j	$\overline{F_{ij}^0}$ (Hz)	k	i	j	$\overline{F_{ij}^0}$ (Hz)	k
5	6	−3813.5	1	4	5	−152.1	15
7	8	−3800.8	2	2	3	134.3	16
1	2	−3529.5	3	6	7	118.0	17
3	4	−3515.2	4	4	6	−113.7	18
2	5	−689.1	5	3	5	−103.0	19
4	7	−617.4	6	3	8	−83.6	20
5	7	359.2	7	1	6	−80.2	21
6	8	358.7	8	1	7	−63.0	22
2	4	357.4	9	2	8	−59.0	23
1	3	346.1	10	3	6	−55.6	24
3	7	−211.5	11	1	8	−43.2	25
2	6	−205.0	12	2	7	−36.9	26
4	8	−200.1	13	1	4	−31.5	27
1	5	−198.6	14	5	8	−1.5	28

A. Model for the spin system of the PAAd_6 molecule

The numerical calculations carried out in this work are based on a PAAd_6 molecule having the following characteristics. The molecule is considered as rigid, with average values of angles and distances obtained from the literature [18]. The effect of internal motion involving the angles between axes and planes of the benzene rings is only considered through the averaging it introduces. We assume that these internal motions provide a negligible contribution to the correlation functions (defined in Appendix C), as their correlation time is much smaller than those of the external motion such as rotation and ODF [22,23].

The average secular components of the lattice tensor (dipolar couplings) involved in the spin Hamiltonian defined in Eq. (6) are listed in Table I. The dipolar couplings $\overline{F_{ij}^0}$ are sorted by their magnitude, indices i, j label protons as in Fig. 1 and index k labels the different pairs of interacting spins. The details of the calculation of these dipolar couplings for a nematic LC with cylindrical rod shaped molecules are given in Appendix C. In order to test the suitability of the model adopted for the spin system, we calculated the NMR free induction decay (FID) yielded by the model and compared its spectrum with the experimental one. Fig. 2 shows the high-frequency part of the NMR doublet of PAAd_6. The dashed line is the experimental spectrum [24]. The infinitely-sharp-line spectrum below is calculated from the Liouvillian time evolution of a closed, eight-spin system. The dipolar Hamiltonian used is that of Eq. (6) with the dipolar couplings

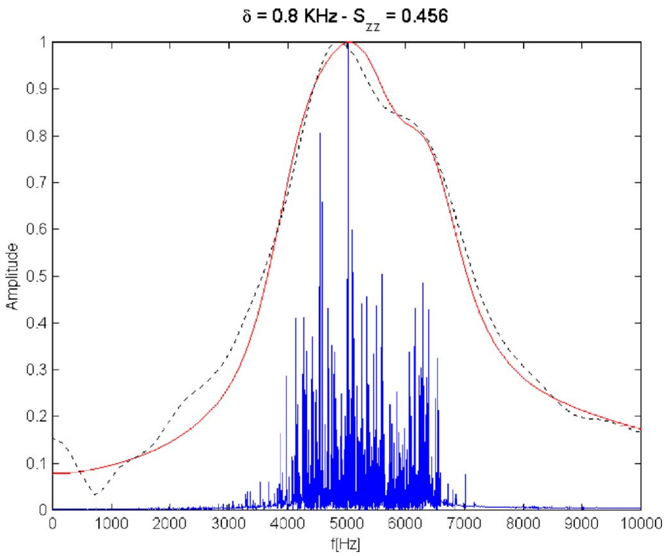

FIG. 2. (Color online) Comparison between the high frequency part of the experimental doublet of PAAd_6 at 402 K and 27 MHz (dashed line) [24] and the one calculated with the model molecule (solid).

of Table I. We adopted the order parameter $S_{zz}=0.456$. Line broadening effects due to the interaction with other nuclei (e.g., deuterium, nitrogen), local magnetic field inhomogeneities, chemical shifts, etc., are taken into account by assigning a Gaussian of 0.8 kHz (at half height) to each narrow peak, finally obtaining the calculated amplitude spectrum (solid line). We consider that the qualitative agreement between the calculated and the measured spectra indicates that the actual spin system can be adequately represented by the one described here.

B. The spin Hamiltonian

The high field approximation consists in truncating the average dipolar Hamiltonian keeping only the secular ($q=0$) term, that is $\bar{\mathcal{H}}_D \rightarrow \overline{\mathcal{H}_D^0}$. The use of such a truncated Hamiltonian in the evolution operator in the interaction picture is consistent with a semiclassical form of the relaxation theory. In fact, truncation has the consequence of ruling out terms of pure quantum character [21].

In order to simplify notation we replace the two indices that number the interacting spins in Eqs. (4) and (5) by only one index, k that designates the pair. Then, the spin Hamiltonian can be written as

$$\mathcal{H}_S = \mathcal{H}_Z + \sum_k \overline{F_k^0}\mathbf{A}_k^0, \tag{6}$$

where $\overline{F_k^0} = \frac{\mu_0 \hbar \gamma^2}{4\pi r_{k0}^3}\mathcal{S}_{zz}(1-3\cos^2\beta_{MQ}^{k0})$, $\mathcal{S}_{zz}$ is the order parameter and β_{MQ}^{k0} the angle between the kth internuclear vector and the molecular z axis [see Eq. (C7)].

It is evident from Table I that the dipolar couplings with $k=1$, 2, 3, and 4 are at least five times greater than the others. This fact allows us to recognize four pairs of strongly coupled spins which interact weakly with the other spins. In consistence with this picture, the dipolar part of the spin Hamiltonian can be written as a sum of a strong "intrapair" contribution due to the *ortho* pairs and a much weaker "interpair" one due to the other pairs. Additionally, we keep only the secular part of the interpair Hamiltonian with respect to the Zeeman and the intrapair terms [4,25]. The validity of this truncation is supported by the experimental evidence that $\overline{\mathcal{H}_{\text{intra}}^0}$ and $\overline{\mathcal{H}_{\text{inter}}^{0'}}$ behave as quasi-invariants in PAAd_6 (the prime denotes truncation) [6,8]. Then the spin Hamiltonian is

$$\mathcal{H}_S = \mathcal{H}_Z + \overline{\mathcal{H}_D^0}, \tag{7}$$

where

$$\overline{\mathcal{H}_D^0} = \overline{\mathcal{H}_{\text{intra}}^0} + \overline{\mathcal{H}_{\text{inter}}^{0'}}. \tag{8}$$

III. SPIN-LATTICE RELAXATION

The time dependence of the expectation value of any quasi-invariant $\mathcal{H}_{\mathcal{O}}$ (with $\mathcal{O}=Z$, intra, inter, or sing) of the spin system is given by

$$\frac{d\langle \mathcal{H}_{\mathcal{O}}\rangle}{dt} = \frac{d}{dt}\,\mathrm{Tr}_s\{\mathcal{H}_{\mathcal{O}}\sigma\}, \tag{9}$$

where Tr_s stands for the trace over the spin variables and $\sigma \equiv \mathrm{Tr}_R\{\rho\}$ is the reduced density matrix, obtained after tracing the density operator ρ of the whole system over the lattice variables [26]. In the high-temperature limit, the spin operator in the interaction picture satisfies the master equation [13]

$$\frac{d\sigma^*(t)}{dt} = -\frac{1}{2}\int_{-\infty}^{\infty} dt' \overline{[\mathcal{H}_{\text{SL}}^*(t),[\mathcal{H}_{\text{SL}}^*(t'),\Delta\sigma^*(t)]]}, \tag{10}$$

where $\Delta\sigma^*(t) \equiv \sigma^*(t) - \sigma_{\text{eq}}$, σ_{eq} is the equilibrium density matrix, and the overbar means average over the lattice ensemble at equilibrium. Equation (10) is the high-temperature form of the general Markovian master equation, which represents the spin dynamics in the "coarse-grained" time scale [21,27]. The validity of the Markovian approach relies on the possibility of finding a time scale larger than the lattice correlation times but smaller than the relaxation times. Formally, in the interaction picture the time dependence of the spin-lattice Hamiltonian

$$\mathcal{H}_{\text{SL}}^*(t) = \mathcal{U}^{-1}(\mathcal{H}_D - \overline{\mathcal{H}_D})\mathcal{U}, \tag{11}$$

is given by the time evolution operator

$$\mathcal{U} = e^{-i(\mathcal{H}_S+\mathcal{H}_L)t} = e^{-i\mathcal{H}_S t}e^{-i\mathcal{H}_L t} \equiv \mathcal{U}_S\mathcal{U}_L.$$

Then

$$\mathcal{H}_{\text{SL}}^*(t) \rightarrow \sum_k \sum_{q=-2}^{2} \Delta F_k^q(t)\mathcal{U}_S^{-1}\mathbf{A}_k^q\mathcal{U}_S. \tag{12}$$

The time dependence of the functions $\Delta F_k^q(t)$ is assumed as a stochastic process representing the molecular motion (see Appendix C).

Through application of the Jeener-Broekaert pulse sequence, the proton spin system can be brought into states of semiequilibrium which can be represented by a high-temperature density matrix of the form [8]

$$\sigma^{*}(t) = [\mathcal{I} - \sum_{\mathcal{O}} \beta_{\mathcal{O}}(t)\mathcal{H}_{\mathcal{O}}]/\mathrm{Tr}\{\mathcal{I}\}, \tag{13}$$

where $\beta_{\mathcal{O}}$ stands for β_Z, β_{intra}, or β_{inter}, the inverse "spin temperatures" of the Zeeman and dipolar reservoirs, and $\mathcal{I}$ is the identity operator. By adequately adjusting the time interval between the preparation pulses of the JB sequence, it is possible to prepare initial states where only $\beta_{\text{intra}} \neq 0$ or $\beta_{\text{inter}} \neq 0$. The relaxation time of the dipolar order so obtained is measured by recording the dipolar FID signal as a function of the interval between the preparation and the reading pulses. The singlet order (s order) cannot be directly prepared through the JB sequence, however, the singlet population could change through the cross relaxation with other quasi-invariants via the lattice. Then we include this quasi-invariant in the calculation of the relaxation times. This is achieved by adding a term $\beta_{\text{sing}}(t)\mathcal{H}_{\text{sing}}$ in Eq. (13), where $\beta_{\text{sing}}(t)$ is related with the chemical potential and $\mathcal{H}_{\text{sing}} \propto \Sigma_{k=1}^{4} \vec{\mathbf{I}}^{(2k-1)} \cdot \vec{\mathbf{I}}^{(2k)}$[4,25]. Each term of operator $\mathcal{H}_{\text{sing}}$ represents the difference between the population of the singlet state and the average population of the triplet states of the corresponding spin pair.

Starting from Eq. (10) a set of coupled differential equations for the spin observables can be obtained. After replacing Eq. (13) in Eq. (10), multiplying both members by $\mathcal{H}_{\mathcal{O}}$, taking the trace over the spin variables and using Eq. (9), we find

$$\frac{dx_{\mathcal{O}}(t)}{dt} = -\sum_{\mathcal{P}} T^{-1}_{\mathcal{O}\mathcal{P}}[x_{\mathcal{P}}(t) - x^{0}_{\mathcal{P}}], \tag{14}$$

where $x_{\mathcal{O}}(t) = \beta_{\mathcal{O}}(t)\sqrt{\mathrm{tr}_s\{\mathcal{H}^2_{\mathcal{O}}\}}$ [25], and the indices $\mathcal{O}$ and $\mathcal{P}$ run over Z, intra, inter, and sing. The symbol $T^{-1}_{\mathcal{O}\mathcal{P}}$ stands for the spin-lattice relaxation rate of each quasi-invariant directly with the lattice (when $\mathcal{O} = \mathcal{P}$) or the spin-lattice cross-relaxation rate between the different reservoirs (when $\mathcal{O} \neq \mathcal{P}$). These parameters can be written in terms of the spectral densities of the molecular motions J^{q}_{kl} and the spin coefficients $c^{q}_{kl(\mathcal{O}\mathcal{P})}$

$$T^{-1}_{\mathcal{O}\mathcal{P}} = \sum_{q=-2}^{2} \sum_{kl} c^{q}_{kl(\mathcal{O}\mathcal{P})} J^{q}_{kl}(q\omega_0). \tag{15}$$

The spin coefficients involving the spin operators of pairs k and l are

$$c^{q}_{kl(\mathcal{O}\mathcal{P})} = \frac{\mathrm{tr}_s\{[\mathcal{H}_{\mathcal{O}}, \mathbf{A}^{q}_{k}][\mathbf{A}^{-q}_{l}, \mathcal{H}_{\mathcal{P}}]\}}{2\sqrt{\mathrm{tr}_s\{\mathcal{H}^2_{\mathcal{O}}\}}\sqrt{\mathrm{tr}_s\{\mathcal{H}^2_{\mathcal{P}}\}}} = c^{-q}_{lk(\mathcal{P}\mathcal{O})}. \tag{16}$$

The spectral densities, defined as

$$J^{q}_{kl}(\omega) = (-1)^{q}\int_{-\infty}^{\infty} G^{q}_{kl}(\tau) e^{-i\omega\tau} d\tau, \tag{17}$$

have the property $J^{q}_{kl}(q\omega_0) = J^{-q}_{lk}(-q\omega_0)$, within the high-temperature approximation. The correlation function $G^{q}_{kl}(\tau) = \overline{\Delta F^{q*}_{k}\Delta F^{q}_{l}(\tau)}$ only depends on the time interval τ since it is calculated at thermal equilibrium, where the probability density functions are stationary. Then

$$T^{-1}_{\mathcal{O}\mathcal{P}} = T^{-1}_{\mathcal{P}\mathcal{O}}. \tag{18}$$

The set of relaxation rates of Eq. (15) can then be arranged in a symmetric matrix $\mathbf{R}$. In Sec. IV B we show that such matrix is clearly simplified in the particular case of PAAd_6. Within this molecular geometry there is no coupling between the Zeeman and the singlet quasi-invariants nor between each of these and the dipolar ones. By using repeated indices in Eq. (15) ($\mathcal{O} = \mathcal{P}$) only once and replacing $T^{-1}_{\text{intra,inter}}$ by T^{-1}_{mix}, the $\mathbf{R}$ matrix is

$$\mathbf{R} = \begin{bmatrix} T^{-1}_{Z} & 0 & 0 & 0 \\ 0 & T^{-1}_{\text{intra}} & T^{-1}_{\text{mix}} & 0 \\ 0 & T^{-1}_{\text{mix}} & T^{-1}_{\text{inter}} & 0 \\ 0 & 0 & 0 & T^{-1}_{\text{sing}} \end{bmatrix}. \tag{19}$$

In order to solve this simplified problem we find the eigenvalues of Eq. (19):

$$T^{-1}_{a} = T^{-1}_{Z}, \tag{20}$$

$$T^{-1}_{b} = \frac{(T^{-1}_{\text{intra}} + T^{-1}_{\text{inter}})}{2} + k\frac{(T^{-1}_{\text{intra}} - T^{-1}_{\text{inter}})}{2}$$

$$= T^{-1}_{\text{intra}}\frac{1}{1-\mu} - T^{-1}_{\text{inter}}\frac{\mu}{1-\mu}, \tag{21}$$

$$T^{-1}_{c} = \frac{(T^{-1}_{\text{intra}} + T^{-1}_{\text{inter}})}{2} - k\frac{(T^{-1}_{\text{intra}} - T^{-1}_{\text{inter}})}{2}$$

$$= -T^{-1}_{\text{intra}}\frac{\mu}{1-\mu} + T^{-1}_{\text{inter}}\frac{1}{1-\mu}, \tag{22}$$

$$T^{-1}_{d} = T^{-1}_{\text{sing}}, \tag{23}$$

where we defined

$$k = \sqrt{1 + 4\frac{(T^{-1}_{\text{mix}})^2}{(T^{-1}_{\text{intra}} - T^{-1}_{\text{inter}})^2}}, \quad \text{with } 1 \leq k \leq \infty$$

and

$$\mu = \frac{k-1}{k+1}, \quad \text{with } 0 \leq \mu \leq 1.$$

Using these definitions, the solutions of the coupled first order differential equations of Eq. (14) can be written explicitly as

$$\begin{bmatrix}\beta_Z(t)\\ \beta_{\text{intra}}(t)\\ \beta_{\text{inter}}(t)\\ \beta_{\text{sing}}(t)\end{bmatrix}=\begin{bmatrix}e^{-T_a^{-1}t} & 0 & 0 & 0\\ 0 & C_{11}(e^{-T_b^{-1}t}+\mu e^{-T_c^{-1}t}) & C_{12}(e^{-T_b^{-1}t}-e^{-T_c^{-1}t}) & 0\\ 0 & C_{21}(e^{-T_b^{-1}t}-e^{-T_c^{-1}t}) & C_{11}(\mu e^{-T_b^{-1}t}+e^{-T_c^{-1}t}) & 0\\ 0 & 0 & 0 & e^{-T_d^{-1}t}\end{bmatrix}\begin{bmatrix}\beta_Z(0)\\ \beta_{\text{intra}}(0)\\ \beta_{\text{inter}}(0)\\ \beta_{\text{sing}}(0)\end{bmatrix}+\begin{bmatrix}(1-e^{-T_a^{-1}t})\\ \frac{T_{11}^{-1}}{T_b^{-1}}(1-e^{-T_b^{-1}t})+\frac{T_{12}^{-1}}{T_c^{-1}}(1-e^{-T_c^{-1}t})\\ \frac{T_{21}^{-1}}{T_b^{-1}}(1-e^{-T_b^{-1}t})+\frac{T_{22}^{-1}}{T_c^{-1}}(1-e^{-T_c^{-1}t})\\ (1-e^{-T_d^{-1}t})\end{bmatrix}\beta_{\text{eq}} \tag{24}$$

where $\beta_{eq}=\frac{1}{K_BT}$, K_B is the Boltzmann constant, and T is the temperature. The other constants used in Eq. (24) are defined as

$$C_{11}=\frac{k+1}{2k}=(\mu+1)^{-1},$$

$$C_{12}=\sqrt{\mu}C_{11}\frac{\sqrt{\text{tr}_s\{H_{\text{inter}}^2\}}}{\sqrt{\text{tr}_s\{H_{\text{intra}}^2\}}}=\sqrt{\mu}C_{11}C,$$

$$C_{21}=\sqrt{\mu}C_{11}C^{-1},$$

$$T_{11}^{-1}=C_{11}(T_{\text{intra}}^{-1}+CT_{\text{mix}}^{-1})+C_{12}(T_{\text{inter}}^{-1}+C^{-1}T_{\text{mix}}^{-1}),$$

$$T_{12}^{-1}=\mu C_{11}(T_{\text{intra}}^{-1}+CT_{\text{mix}}^{-1})-C_{12}(T_{\text{inter}}^{-1}+C^{-1}T_{\text{mix}}^{-1}),$$

$$T_{21}^{-1}=C_{21}(T_{\text{intra}}^{-1}+CT_{\text{mix}}^{-1})+\mu C_{11}(T_{\text{inter}}^{-1}+C^{-1}T_{\text{mix}}^{-1}),$$

$$T_{22}^{-1}=-C_{21}(T_{\text{intra}}^{-1}+CT_{\text{mix}}^{-1})+C_{11}(T_{\text{inter}}^{-1}+C^{-1}T_{\text{mix}}^{-1}). \tag{25}$$

It is worth noticing that $\frac{T_{11}^{-1}}{T_b^{-1}}+\frac{T_{12}^{-1}}{T_c^{-1}}=1$ and $\frac{T_{21}^{-1}}{T_b^{-1}}+\frac{T_{22}^{-1}}{T_c^{-1}}=1$, according to the previous definitions.

The amplitude of the dipolar signal in the JB experiment is proportional to $\beta_{\text{intra}}(t)+\beta_{\text{inter}}(t)$. According to Eq. (24), by preparing the dipolar order for example in the intrapair condition [that is, $\beta_{\text{intra}}(0)\neq 0$ and $\beta_{\text{inter}}(0)=0$], the subsequent signal evolves towards the equilibrium with the lattice (in principle) with a two-exponential trend with constants T_b and T_c. However, by expanding the two exponentials, and using Eqs. (21) and (22) one gets

$$\begin{aligned}\beta_{\text{intra}}(t)&=\frac{\beta_{\text{intra}}(0)}{\mu+1}(e^{-T_b^{-1}t}+\mu e^{-T_c^{-1}t})\\ &\quad+\left[\frac{T_{11}^{-1}}{T_b^{-1}}(1-e^{-T_b^{-1}t})+\frac{T_{12}^{-1}}{T_c^{-1}}(1-e^{-T_c^{-1}t})\right]\beta_{\text{eq}}\\ &\simeq\beta_{\text{intra}}(0)\left[1-\frac{T_b^{-1}+\mu T_c^{-1}}{\mu+1}t\right.\\ &\quad\left.+\frac{1}{2}\left(\frac{T_b^{-1}+\mu T_c^{-1}}{\mu+1}\right)^2t^2+\ldots\right]\\ &\quad+\beta_{\text{intra}}(0)\Delta_{\text{intra}}(t)\\ &\simeq\beta_{\text{intra}}(0)[e^{-T_{\text{intra}}^{-1}t}+\Delta_{\text{intra}}(t)]\end{aligned} \tag{26}$$

$$\beta_{\text{inter}}(t)\simeq\beta_{\text{inter}}(0)[e^{-T_{\text{inter}}^{-1}t}+\Delta_{\text{inter}}(t)], \tag{27}$$

where we used that $T_{\text{intra}}^{-1}=\frac{T_b^{-1}+\mu T_c^{-1}}{\mu+1}$, and $T_{\text{inter}}^{-1}=\frac{\mu T_b^{-1}+T_c^{-1}}{\mu+1}$, according to Eqs. (21) and (22). The quantities $\Delta_{\text{intra}}(t)$ and $\Delta_{\text{inter}}(t)$ represent the difference between the monoexponential approximation and the biexponential exact evolution for the intrapair and interpair dipolar quasi-invariants. In both cases the first term of the correction is the quadratic one, namely,

$$t^2(T_b^{-1}-T_c^{-1})^2\frac{\mu}{2(\mu+1)^2}.$$

In the former equations we neglected the term proportional to β_{eq} because $\frac{\beta_{\text{eq}}}{\beta_{\text{intra}}(0)}\ll 1$ and $\frac{\beta_{\text{eq}}}{\beta_{\text{inter}}(0)}\ll 1$.

IV. CALCULATION OF THE RELAXATION CONSTANTS *R*

Now we estimate the contributions to the dipolar relaxation rates from the different molecular motions, in order to compare with the experimental data of $T_{1\text{Dintra}}(T)$ and $T_{1\text{Dinter}}(T)$ [8]. We use Eqs. (15) with the coefficients c_{kj}^q calculated for the eight-spin model of PAAd_6, and the spectral densities estimated from independent T_{1Z} experimental data.

A. Spectral densities

Because of the very different time scales of the director modes and the local reorientations, these fluctuations can be normally averaged separately, and the spectral densities can be expressed as a sum of contributions from the ODF and ROT (see Appendix D and Ref. [19])

$$J_{kl}^q=J_{kl}^{q\text{ODF}}+J_{kl}^{q\text{ROT}}. \tag{28}$$

We also show in Appendix D that the spectral densities can be scaled with respect to the autocorrelation of the *o*-spin pair, that is,

$$J_{kl}^q=\epsilon_k\epsilon_l J_{oo}^q, \tag{29}$$

where each ϵ_k is the ratio of the dipolar coupling of the *k*th pair to the one of the *o* pair.

An estimation of the spectral densities of the relevant relaxation processes, can be made by comparing the Larmor frequency dependent T_{1Z}^{-1} data with the theoretical expression

$$T_{1Z}^{-1}=\frac{9}{32}\sum_{ll}J_{ll}^{q}(q\omega_0)+R_{\mathrm{DIF}}, \tag{30}$$

where the first term comes from the intramolecular mechanisms represented in Eq. (15) (the spin coefficients $c_{kl(\mathcal{ZZ})}^{q}=0$ for $k\neq l$ and $c_{kl(\mathcal{ZZ})}^{q}=\frac{9}{32}$ for $k=l$ in an eight-spin system) and R_{DIF} stands for translational diffusion [28] since, in contrast with $T_{1\mathrm{D}}$, intermolecular mechanisms play a role in Zeeman relaxation. Besides, we keep only the spectral densities associated with the ortho pairs since they are much larger than those involving more distant protons due to the particular geometry of the PAAd_6 molecule. Also, we assume that the four pairs are equivalent since their dipolar couplings do not differ more than 5%. So, Eq. (30) can be written as

$$T_{1Z}^{-1}\simeq\frac{9}{8}[J_{oo}^{1\mathrm{ODF}}(\omega)+J_{oo}^{1\mathrm{ROT}}(\omega)+J_{oo}^{2\mathrm{ROT}}(2\omega)]+R_{\mathrm{DIF}}, \tag{31}$$

where we replaced the spectral densities J_{ll}^{q} by that corresponding to the strong o pair. Also we used the fact that in the limit of small-amplitude ODF the term $J_{oo}^{2\mathrm{ODF}}$ can be neglected [15,29].

Equation (31) is a simple expression that is used to estimate the spectral densities from the experiment. Within the low frequency regime, where the contribution from the local motions is small, $T_{1Z}^{-1}\simeq\frac{9}{8}J_{oo}^{1\mathrm{ODF}}$, and comparison with the experimental data at 403 K [11] gives in PAAd_6 the estimate $J_{oo}^{1\mathrm{ODF}}=0.267\ \mathrm{s}^{-1}$, within 10% [30,40].

The ROT spectral densities can be estimated from field-cycling data by following the procedure described in reference [31]. We obtained $J_{oo}^{1\mathrm{ROT}}=0.034\ \mathrm{s}^{-1}$ within 20% error and $J_{oo}^{2\mathrm{ROT}}\leq 0.015\ \mathrm{s}^{-1}$. Finally, by assuming the extreme motional narrowing condition, the secular (q=0) spectral density can be estimated by the simple relation $J_{oo}^{0\mathrm{ROT}}=6J_{oo}^{1\mathrm{ROT}}$ [13]. In this way, we obtain the value $J_{oo}^{0\mathrm{ROT}}=0.204\ \mathrm{s}^{-1}$. By using the former estimates in Eq. (29), we generate all the spectral densities needed for calculating the relaxation rates of Eq. (15).

B. Relaxation matrix

The calculated values of the relaxation rates of Eq. (15) (in s^{-1}) are

$$\mathbf{R}=\begin{bmatrix}0.3496 & 0 & 0 & 0\\ 0 & 0.9995 & 0.2133 & -0.0023\\ 0 & 0.2133 & 0.7178 & 0\\ 0 & -0.0023 & 0 & 0.0128\end{bmatrix}. \tag{32}$$

The elements of this matrix are given within an error of 10% and show the following features. (i) The zeros of this matrix show that the Zeeman order is disconnected from the other reservoirs. (ii) All the elements relating the s order with the dipolar orders are about three orders of magnitude smaller than the dipolar relaxation rates, hence, it can be expected no observable effect associated with the s order. This fact is the basis for neglecting the corresponding matrix elements in Eq. (19). (iii) The relative size of T_{mix}^{-1} indicates a weak mutual interaction of the dipolar reservoirs through the lattice. (iv)

TABLE II. Contribution to the relaxation rates (in s^{-1}) from the different motions for $q=0$, 1, and 2.

q	Process	T_{intra}^{-1}	T_{inter}^{-1}	T_{mix}^{-1}
0	ODF	0	0	0
0	ROT	0.00101	0.00060	−0.00015
1	ODF	0.88528	0.60728	0.18921
1	ROT	0.11273	0.07733	0.02410
2	ODF	0	0	0
2	ROT	0.00052	0.03261	0.00001

The predicted direct spin-lattice relaxation time for the singlet reservoir is much longer than the relaxation times of the Zeeman and dipolar reservoirs (about 78 s), similar to the experimental value reported for 2,3-dibromothiophene [32]. Table II shows the detail of the contributions to the elements of **R** from the ODF and ROT for the different values of q.

V. DISCUSSION AND CONCLUSIONS

Numbers in Table II show that the dominant contributions to the relaxation rates come from $q=1$, while the contributions from the $q=0$ and $q=2$ processes are much smaller. It is worth to notice the secular terms, namely spin processes which affect the dipolar energy without concomitant change of the Zeeman energy, do not contribute significantly to the dipolar order relaxation in the problem analyzed in this work, even when $J_{oo}^{0\mathrm{ROT}}$ and $J_{oo}^{1\mathrm{ODF}}$ have similar size. The calculated dipolar relaxation rates of the eight-spin system are clearly governed by the ODF, while the ROT contribute the 16%. This prediction agrees with the experiment because the temperature dependences of both $T_{1\mathrm{Dintra}}$ and $T_{1\mathrm{Dinter}}$ in PAAd_6 are approximately linear [8], indicating that ODF dominate relaxation. Also, this result is compatible with the statement that $T_{1\mathrm{D}}$ is selectively sensitive to the collective motions. The ROT term with $q=2$ is greater in T_{inter} than in T_{intra}, the total ROT contribution being slightly larger in T_{inter}.

From Eqs. (26) and (27) we define

$$\delta_{\mathrm{intra}}(t)=\frac{|\Delta_{\mathrm{intra}}(t)|}{e^{-T_{\mathrm{intra}}^{-1}t}},\qquad \delta_{\mathrm{inter}}(t)=\frac{|\Delta_{\mathrm{inter}}(t)|}{e^{-T_{\mathrm{inter}}^{-1}t}}, \tag{33}$$

as a measure of the relative difference between the single-exponential approximation and the biexponential exact evolution for the intrapair and interpair dipolar quasi-invariants. By replacing the values of Eq. (32) into Eqs. (21) and (22), we obtain that for $t\simeq 2T_{\mathrm{intra}}$ or $t\simeq 2T_{\mathrm{inter}}$, the relative differences δ_{intra} and δ_{inter} are, respectively, less than 0.12 and 0.15. That is to say, according to the theory, the expected time evolutions of the dipolar spin temperatures should not differ appreciably from a single exponential behavior in such a time scale. The experimental decay reported for measurements of the dipolar relaxation times [8] using the JB sequence in PAAd_6 and other liquid crystals [7] indeed show this behavior. Inasmuch as the experiment behaves as a single exponential, one can identify the measured decay constants with the calculated ones, that is, $T_{1\mathrm{Dintra}}\equiv T_{\mathrm{intra}}$ and

$T_{1\text{Dinter}} \equiv T_{\text{inter}}$. However, the reported experimental values of the dipolar relaxation times at 402 K and 27 MHz are $T_{1\text{Dintra}}=680$ ms and $T_{1\text{Dinter}}=345$ ms [6,8], which are markedly lower than the theoretically predicted: $T_{\text{intra}}=1000.5$ ms and $T_{\text{inter}}=1393.1$ ms. In addition, the calculation predicts similar values for T_{intra} and T_{inter}, which disagrees with the experimental relationship.

Calculation of the quantities δ from Eq. (33) using the experimental values $T_{1\text{Dintra}}$ and $T_{1\text{Dinter}}$ for different values of T_{mix}^{-1}, yields $\delta_{\text{intra}} < 0.05$ for $t < 3T_{\text{intra}}$ and $\delta_{\text{inter}} < 0.05$ for $t < 3T_{\text{inter}}$ with $T_{\text{mix}}^{-1} < 0.2133\ \text{s}^{-1}$. This suggests that the actual coupling between the dipolar quasi-invariants through the lattice is weak.

Our calculation shows that the s order of the eight-spin system in the nematic phase is motionally isolated. This is also consistent with the reported single exponential evolution of the spin temperatures. Thus, in this system it is not possible to detect the s order in experiments of dipolar order relaxation. This situation contrasts with the case of oriented hydrated salts, where the spin-lattice relaxation is driven by a different kind of mechanism. In these solids, the fluctuations of the secular interpair interaction, caused by the exchange of the protons of the water molecules, represent a very efficient mechanism for the relaxation of the dipolar quasi-invariants, as well as for the spin-lattice cross coupling of the intrapair and singlet reservoirs [4,25].

Thus, in this work we show that the remarkable difference between predicted and measured values cannot be assigned to (i) erroneous interpretation of the decay rates due to a possible coupling between the quasi-invariants, (ii) neglecting of the multispin character of the problem, (iii) errors introduced by the model. This means that the occurrence of other efficient relaxation pathways should be considered. Such mechanisms, driven by the ODF, are not contemplated by the usual HTR theory.

Dipolar order relaxation theories that start from the Markovian master equation are valid, in principle, for lattice fluctuations with correlation times $\tau_C \ll T_{1\text{D}}$. However, the high-temperature approximation amounts to considering that each spin behaves independently of the other nuclei within the microscopic time scale, thus, screening the microscopic correlation between the spin and lattice variables. In fact, under this approximation, the dipolar term of the spin Hamiltonian does not play a role in the time evolution of $\mathcal{H}_{\text{SL}}$, as can be seen in the steps yielding Eqs. (15) and (16), and also in Ref. [16]. This feature has the effect of restricting the applicability of this approach to short correlation times, that is $\omega_D \tau_C \ll 1$, disregarding the occurrence of fluctuation lifetimes comparable to or even longer than the inverse of the dipolar frequency ω_D.

The fact that in LC the lifetime of the slow ODF modes is comparable to ω_D^{-1} thus points out the high-temperature approximation as a source of the noticeable disagreement between calculated and measured relaxation times. In a recent work, by using a generalized spin-temperature relaxation theory in the Markovian regime, which does not assume high temperature (or weak order), a theoretical expression for an additional contribution to the dipolar intrapair relaxation rate of pure quantum character was derived. Starting from the quantum Markovian master equation it was shown that a contribution exists with a Larmor frequency dependence which is consistent with the experiments, and the magnitude of which may attain a macroscopic size in highly correlated systems [21]. The existence of a contribution of this type indicates that effects of correlated interaction between spins and lattice can be of importance in dipolar order relaxation.

The occurrence of motions having long correlation times, even comparable to $T_{1\text{D}}$, was suggested in the literature. Through an experiment based on the stimulated-echo pulse sequence, ODF modes with correlation times in the range of milliseconds to hundreds of milliseconds was reported in nematic 5CB [33]. The fact that this relaxation mechanism does not manifest in the "usual" relaxation times as the Zeeman and intrapair ones, could be understood looking at the experiment of dipolar order relaxation on a gypsum crystal subjected to low-amplitude, low-frequency rotational vibration as a whole. It was predicted and verified in gypsum, that externally driven quasiadiabatic variations of the Hamiltonian do not perturb quasi-invariants that depend on the populations of the intrapair energy levels (namely, the Zeeman and intrapair energies and the s order) [3]. This kind of motion introduces an additional relaxation mechanism of the interpair order, with a rate proportional to the square of the angular velocity [34] and temperature independent.

According to this, if ultraslow modes in LC could be considered as quasiadiabatic transformations, they would only affect the interpair quasi-invariant and might explain at least a part of the discrepancy. By the same analysis, the intrapair relaxation in LC would not be perturbed by such kind of motion. This reasoning is reinforced by the fact that the strong Larmor frequency dependence of $T_{1\text{Dintra}}$ observed in PAAd_6 and other LC is consistent with the "Markovian" square-root law of the ODF, over a wide range of external magnetic fields. A detailed investigation of the effects of ultraslow modes on the dipolar energy relaxation demands exploring spin-lattice relaxation theories valid for the non-Markovian regime, as the formalisms developed for studying quasiadiabatic evolution of thermodynamic observables [35,36].

Summarizing, in this work we use the high-temperature Redfield relaxation theory to calculate the dipolar quasi-invariant relaxation times in an eight-spin system that represents the proton system of PAAd_6. We study the relaxation of the several quasi-invariants within the spin thermodynamics framework, and consider the cross relaxation between the reservoirs through the lattice. We analyze the contributions to the dipolar relaxation rates from the different kinds of molecular motions and find that the local motions do not play a significant role in PAAd_6. Instead, the calculation predicts that the ODF dominate the relaxation of both dipolar quasi-invariants, in qualitative agreement with the reported experimental temperature behavior. However, we find that the predicted dipolar relaxation times are significantly larger than the experimental ones, the difference being more pronounced for the interpair quasi-invariant. We show that the discrepancy cannot be overcome by resorting to a more realistic model for the spin system or considering the various possible cross-relaxation pathways among the quasi-invariants. Therefore, we conclude that the usual HTR theory underestimates the role of the collective fluctuations in the relaxation

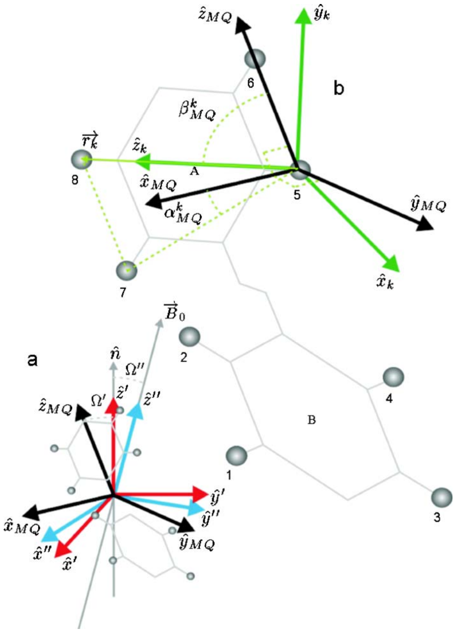

FIG. 3. (Color online) (a) Reference frames through which $\widetilde{F}^0_k(t)$ is transformed. (b) PAAd_6 molecule showing the angles α^k_{MQ} and β^k_{MQ} corresponding to the interproton vector with k=28 (according to Table I).

of the dipolar quasi-invariants in PAAd_6. The difference might be related with the effect of slow or ultraslow correlated motions that are not taken into account in the high-temperature relaxation theory.

ACKNOWLEDGMENTS

We would like to thank J. Jeener for suggesting the very low frequency part of the spectrum of ODF's as a possible source of relaxation, to be treated as quasiadiabatic changes of the coupling Hamiltonian. We also acknowledge helpful discussions with O. Mensio. This work was supported by SECYT from Universidad Nacional de Córdoba, ANPCyT, and Fundación Antorchas (Argentina). H.H.S. acknowledges CONICET (Argentina) for financial support.

APPENDIX A: REFERENCE FRAMES

In the following sections we write the multispin spectral densities of the liquid crystal uniaxial molecule in terms of $J^q_{oo}(\omega)$. The procedure generalizes the formalism developed for two-spin spectral densities of the literature [19].

In order to describe the different molecular motions in the LC mesophase, we define the reference systems depicted in Fig. 3. The external field $\vec{B}_0$ determines the $\hat{z}''$ axis of the laboratory system $(xyz)''$. A second frame, $(xyz)'$, is chosen in such a way that the $\hat{z}'$ axis coincides with the local director $\hat{n}$. $\Omega''(t)$ designates the Euler angles (α'' and β'') between these two coordinate systems and $\Omega'(t)$ names the angles [α'(azimuthal), β'(polar), and γ'(axial)] between the director frame and a frame $(xyz)_{MQ}$ fixed to the molecule. The orientation of each interproton vector $\vec{r}_k$ in this frame is $\Omega^k_{MQ}(t)$, defined by α^k_{MQ} and β^k_{MQ}. Finally we introduce a set of frames $(xyz)_k$ with the z_k axes in the direction of the interproton vector of the kth pair. In such coordinate systems, the lattice tensor operator adopts the simple expression $\widetilde{F}^0_k(t)=\frac{-\mu_0\hbar\gamma^2}{2\pi r^3_k(t)}$. With these definitions we can write the time dependent lattice operators in the laboratory frame $F^q_k(t)$ as the result of three successive transformations of $\widetilde{F}^0_k(t)$, through the systems of Fig. 3:

$$F^q_k(t)=\sum\nolimits_{q'q''}D^{2*}_{qq''}[\Omega''(t)]D^{2*}_{q''q'}[\Omega'(t)]D^{2*}_{q'0}[\Omega^k_{MQ}(t)]\widetilde{F}^0_k(t), \tag{A1}$$

where D^2 is the Wigner matrix of second rank [37].

APPENDIX B: ASSUMPTIONS CONCERNING THE DESCRIPTION OF LC

The basic assumptions underlying our reasoning are the following:

(1) The angular variables of the different reference frames are statistically independent. Then, the local director motion, represented by $D^2_{qq''}[\Omega''(t)]$, is uncoupled from the individual molecular motion given by $D^2_{q''q'}[\Omega'(t)]$ (originated in intermolecular mechanical interaction). In addition, both motions are uncoupled from the internal molecular modes, $D^{2*}_{q'0}[\Omega^k_{MQ}(t)]\widetilde{F}^0_k(t)$.

(2) The probability distribution of the molecular orientation in the local director frame $\Omega'(t)$, is independent from γ'. That is, we assume that molecules behave as cylindrical rods. This is valid if the order parameter $S_{xx}-S_{yy}$ is small in comparison with S_{zz}, which is the case for PAAd_6 [38]. Also the angles α' and β', are statistically uncoupled from γ'.

(3) The different kinds of molecular motion in LC have different time scales [18,22]. Modes involving the different parts of the molecule, such as torsions and vibrations, and the rotation around the molecular principal axis (described by γ') have the shortest correlation times. Slower than these are motions involving α' and β', namely, those motions labeled as ROT. Finally, the cooperative motions described by α'' and β'' (such as the ODF) have the largest correlation times.

APPENDIX C: DIPOLAR COUPLINGS AND CORRELATION FUNCTIONS

In this section we calculate the dipolar couplings shown in Table I, that are mean values of the lattice operators. Also we deduce expressions for the time correlation functions of the different motions. Within the semi-classical approximation, the lattice operators $\mathbf{F}^q_k(t)$ are replaced by the time functions $F^q_k(t)$; in thermal equilibrium, their expectation values are

$$\overline{\mathbf{F}^q_k}\equiv\langle\mathbf{F}^q_k\rangle\equiv\mathrm{tr}\{\rho\mathbf{F}^q_k\}\Rightarrow\overline{F^q_k}\equiv\langle F^q_k\rangle\equiv\int F^q_k p(F^q_k)dF^q_k, \tag{C1}$$

where ρ is the density matrix, $p(F^q_k)$ is the probability of F^q_k, and both the overline and the brackets stand for ensemble averages.

Using approximation (B1) the average of Eq. (A1) is the product of averages:

$$\overline{F_k^q} = \sum\nolimits_{q'q''} \overline{D^{2*}_{qq''}[\Omega'']}\,\overline{D^{2*}_{q''q'}[\Omega']}\,\overline{D^{2*}_{q'0}[\Omega^k_{MQ}]\widetilde{F}^0_k}, \tag{C2}$$

where

$$\overline{D^{2*}_{qq''}[\Omega'']} = \langle e^{iq\alpha''} d^2_{qq''}(\beta'')\rangle = \overline{D^2_{qq''}[\Omega'']}^{*}, \tag{C3}$$

$$\begin{aligned}\overline{D^{2*}_{q''q'}[\Omega']} &= \langle e^{iq''\alpha'} d^2_{q''q'}(\beta') e^{iq'\gamma'}\rangle = \overline{D^2_{q''q'}[\Omega']}^{*}\\ &= \langle e^{iq''\alpha'} d^2_{q''q'}(\beta')\rangle\langle e^{iq'\gamma'}\rangle = \langle e^{iq''\alpha'} d^2_{q''0}(\beta')\rangle\delta_{q',0},\end{aligned} \tag{C4}$$

$$\begin{aligned}\overline{D^{2*}_{q'0}[\Omega^k_{MQ}]\widetilde{F}^0_k} &= -\frac{\mu_0\hbar\gamma^2}{2\pi}\left\langle e^{iq'\alpha^k_{MQ}} d^2_{q'0}(\beta^k_{MQ})\frac{1}{r_k^3}\right\rangle\\ &= -\frac{\mu_0\hbar\gamma^2}{2\pi r_{k0}^3} e^{iq'\alpha^{k0}_{MQ}} d^2_{q'0}(\beta^{k0}_{MQ})\\ &= \overline{D^2_{q'0}[\Omega^k_{MQ}]\widetilde{F}^{0*}_k}.\end{aligned} \tag{C5}$$

In Eq. (C4) we used also approximation (B2) and $\delta_{m,n}$ is the Krönecker delta. In Eq. (C5), the angles α^{k0}_{MQ}, β^{k0}_{MQ} and the internuclear distance r_{k0} of the kth proton pair interaction, correspond to the average rigid molecule as given in Ref. [18].

In the high field approximation, one only keeps the term of the Hamiltonian with $\overline{F^0_k}$ ($q=0$). This leaves the intensity of the dipolar coupling as

$$\overline{F^0_k} = \frac{\mu_0\hbar\gamma^2}{4\pi r_{k0}^3}(1-3\cos^2\beta^{k0}_{MQ})\sum\nolimits_{q''}\langle d^2_{0q''}(\beta'')\rangle\langle e^{iq''\alpha'} d^2_{q''0}(\beta')\rangle. \tag{C6}$$

In the case of a LC in a uniaxial phase, like nematic PAAd_6: $\langle d^2_{0q''}(\beta'')\rangle = \delta_{q'',0}$. Using this in Eq. (C6), the dipolar coupling becomes

$$\overline{F^0_k} = \frac{\mu_0\hbar\gamma^2}{4\pi r_{k0}^3}\mathcal{S}_{zz}(1-3\cos^2\beta^{k0}_{MQ}), \tag{C7}$$

where $\mathcal{S}_{zz} = \langle d^2_{00}(\beta')\rangle = \langle(3\cos^2\beta'-1)/2\rangle$ is the order parameter.

The correlation functions are defined as

$$\begin{aligned}\overline{\mathbf{F}^{q\dagger}_k\mathbf{F}^q_l(\tau)} &\equiv \langle\mathbf{F}^{q\dagger}_k\mathbf{F}^q_l(\tau)\rangle \equiv \mathrm{tr}\{\rho\mathbf{F}^{q\dagger}_k\mathbf{F}^q_l(\tau)\}\\ &\Rightarrow \overline{F^{q*}_k F^q_l(\tau)} \equiv \langle F^{q*}_k F^q_l(\tau)\rangle\\ &\equiv \int F^{q*}_k F^q_l(\tau) p(F^{q*}_k; F^q_l(\tau),\tau)\, dF^{q*}_k\, dF^q_l(\tau),\end{aligned} \tag{C8}$$

where $p(F^{q*}_k; F^q_l(\tau),\tau) = p(F^{q*}_k)p(F^q_l(\tau),\tau | F^{q*}_k)$ is the probability of having F^{q*}_k as the initial value and $F^q_l(\tau)$ after a time τ; $p(F^q_l(\tau),\tau|F^{q*}_k)$ is the conditional probability. The calculation of the correlation function is made at thermodynamic equilibrium, then the result can only depend on the time difference τ, due to the stationary character of the probability distribution functions.

For collective motions, the correlation functions of the elements of the Wigner matrices are

$$\begin{aligned}\langle D^2_{qq''}[\Omega'']D^{2*}_{qp''}[\Omega''(\tau)]\rangle &= \langle e^{iq[\alpha''(\tau)-\alpha'']} d^2_{qq''}(\beta'') d^2_{qp''}[\beta''(\tau)]\rangle\\ &= \hat{g}^{\mathrm{ODF}}_{qq'',qp''}(\tau).\end{aligned} \tag{C9}$$

For local molecular motions

$$\langle D^2_{q''q'}[\Omega']D^{2*}_{p''p'}[\Omega'(\tau)]\rangle = \hat{g}^{rot}_{q''q',p''p'}(\tau)\hat{g}^{rot'}_{q',p'}(\tau), \tag{C10}$$

where we used approximation (B2) to factorize the correlation function and defined

$$\hat{g}^{\mathrm{ROT}}_{q''q',p''p'}(\tau) = \langle e^{-iq''\alpha'} e^{ip''\alpha'(\tau)} d^2_{q''q'}(\beta') d^2_{p''p'}[\beta'(\tau)]\rangle \tag{C11}$$

and

$$\hat{g}^{\mathrm{ROT}'}_{q',p'}(\tau) = \langle e^{-iq'\gamma'} e^{ip'\gamma'(\tau)}\rangle. \tag{C12}$$

Finally, the correlation function associated with the internal molecular motion (int) is

$$\begin{aligned}&\langle D^2_{q'0}[\Omega^k_{MQ}]\widetilde{F}^0_k D^{2*}_{p'0}[\Omega^l_{MQ}(\tau)]\widetilde{F}^0_l(\tau)\rangle\\ &\quad= \langle e^{-iq'\alpha^k_{MQ}} e^{ip'\alpha^l_{MQ}(\tau)} d^2_{q'0}(\beta^k_{MQ}) d^2_{p'0}(\beta^l_{MQ}(\tau))\widetilde{F}^0_k\widetilde{F}^0_l(\tau)\rangle\\ &\quad= \hat{g}^{\mathrm{int}(kl)}_{q'0,p'0}(\tau).\end{aligned} \tag{C13}$$

Time correlation functions such as Eqs. (C9), (C10), and (C13), can be represented in a general form as

$$\begin{aligned}\hat{g}^C_{m,n}(\tau) &= \langle f_m f^*_n(\tau)\rangle = [\langle f_m f^*_n\rangle - \langle f_m\rangle\langle f^*_n\rangle]\zeta^C_{m,n}(\tau) + \langle f_m\rangle\langle f^*_n\rangle\\ &= \Delta\hat{g}^C_{m,n}\zeta^C_{m,n}(\tau) + \hat{g}^C_{m,n}(\infty),\end{aligned} \tag{C14}$$

where $\Delta\hat{g}^C_{m,n} \equiv \hat{g}^C_{m,n}(0) - \hat{g}^C_{m,n}(\infty)$ and $\zeta^C_{m,n}(\tau)$ is a decreasing function of τ, so that $\zeta^C_{m,n}(0)=1$ and $\lim_{\tau\to\infty}\zeta^C_{m,n}(\tau)=0$. This function decreases with a characteristic time $\tau^C_{m,n}$ that represents the lifetime of the correlation. An example could be an exponential function $\zeta^C_{m,n}(\tau) = e^{-|\tau|/\tau^C_{m,n}}$ [39]. By applying Eq. (C14) in Eq. (C12), we finally obtain

$$\hat{g}^{\mathrm{ROT}'}_{q',p'}(\tau) = \hat{g}^{\mathrm{ROT}'}_{q',q'}(\tau)\delta_{p',q'}, \tag{C15}$$

with

$$\hat{g}^{\mathrm{ROT}'}_{q',q'}(\tau) = [(1-\delta_{q',0})\zeta^{\mathrm{ROT}'}_{q',q'}(\tau) + \delta_{q',0}]. \tag{C16}$$

APPENDIX D: PROPERTIES OF THE SPECTRAL DENSITIES OF A LIQUID CRYSTAL

In this appendix we write the multispin spectral densities of the liquid crystal molecule in terms of $J^q_{oo}(\omega)$. The procedure generalizes the formalism developed for two-spin spectral densities of the literature [19].

The spectral densities are defined as

$$J^q_{kl}(\omega)=(-1)^q\int_{-\infty}^{\infty}G^q_{kl}(\tau)e^{-i\omega\tau}d\tau, \tag{D1}$$

with $G^q_{kl}(\tau)$, the correlation function

$$G^q_{kl}(\tau)=\langle\Delta F^{q*}_k\Delta F^q_l(\tau)\rangle=(-1)^q\langle\Delta F^q_l\Delta F^{-q}_k(\tau)\rangle, \tag{D2}$$

where $\Delta F^q_k(t)=F^q_k(t)-\overline{F^q_k(t)}$. We also used $F^{q*}_k=(-1)^qF^{-q}_k$ in Eq. (D2).

Using Eq. (A1) to write Eq. (D2) explicitly, we have

$$\begin{aligned}G^q_{kl}(\tau)=\sum\nolimits_{q'q''}\sum\nolimits_{p'p''}&\langle(D^2_{qq''}[\Omega'']D^2_{q''q'}[\Omega']D^2_{q'0}[\Omega^k_{MQ}]\tilde{F}^0_k\\&-\overline{D^2_{qq''}[\Omega'']D^2_{q''q'}[\Omega']D^2_{q'0}[\Omega^k_{MQ}]\tilde{F}^0_k})\\&\times\{D^{2*}_{qp''}[\Omega''(\tau)]D^{2*}_{p''p'}[\Omega'(\tau)]D^2_{p'0}[\Omega^l_{MQ}(\tau)]\tilde{F}^0_l(\tau)\\&-\overline{D^{2*}_{qp''}[\Omega''(\tau)]D^{2*}_{p''p'}[\Omega'(\tau)]D^2_{p'0}[\Omega^l_{MQ}(\tau)]\tilde{F}^0_l(\tau)}\}\rangle.\end{aligned} \tag{D3}$$

Making use of assumptions (B1) and (B2) and Eqs. (C9), (C10), and (C13), Eq. (D3) takes the form

$$\begin{aligned}G^q_{kl}(\tau)=\sum\nolimits_{q'q''p''}&\hat{g}^{\mathrm{ODF}}_{qq'',qp''}(\tau)\hat{g}^{\mathrm{ROT}}_{q''q',p''q'}(\tau)\hat{g}^{\mathrm{ROT}'}_{q',q'}(\tau)\hat{g}^{\mathrm{int}(kl)}_{q'0,q'0}(\tau)\\&-\hat{g}^{\mathrm{ODF}}_{qq'',qp''}(\infty)\hat{g}^{\mathrm{ROT}}_{q''q',p''q'}(\infty)\hat{g}^{\mathrm{ROT}'}_{q',q'}(\infty)\hat{g}^{\mathrm{int}(kl)}_{q'0,q'0}(\infty).\end{aligned} \tag{D4}$$

In writing Eq. (D4) we also used Eqs. (C15) and (C16).

Due to the structure of Eq. (C14), it can be seen that Eq. (D4) is a sum of products of different $\zeta^C_{m,n}(\tau)$ functions. In the case that these functions possess very different decay times, the time dependence of such term is governed by the function with the shortest correlation time. According with assumption (B3), the correlation time of the internal motions and rotations around the principal molecular axis are both smaller than those of the other motions. In view of these time scales, the contribution to the spectral densities $J^q_{kj}(\omega)$ from terms that involve functions $\zeta^{\mathrm{int}(kl)}_{q'0,q'0}(\tau)$ and $\zeta^{\mathrm{ROT}'}_{q',q'}(\tau)$ in Eq. (D4) will be smaller than the other contributions, and can be neglected. This can be seen from the Fourier transform for $\zeta^C_{m,n}(\tau)=e^{-|\tau|/\tau^C_{m,n}}$:

$$\Upsilon^C_{m,n}(\omega)=\int_{-\infty}^{\infty}e^{-|\tau|/\tau^C_{m,n}}e^{-i\omega\tau}d\tau=\frac{2\tau^C_{m,n}}{1+(\omega\tau^C_{m,n})^2}. \tag{D5}$$

When $\omega\tau^C_{m,n}\lesssim 1$ the quantity $\Upsilon^C_{m,n}(\omega)$ is of the order of $\tau^C_{m,n}$. Then we can neglect in Eq. (D4) the contributions from fluctuations of terms with $\zeta^{\mathrm{int}(kl)}_{q'0,q'0}(\tau)$ and $\zeta^{\mathrm{ROT}'}_{q',q'}(\tau)$.

Under this assumption, Eq. (D4) results in

$$\begin{aligned}G^q_{kl}(\tau)&=\sum\nolimits_{q'q''p''}[\hat{g}^{\mathrm{ODF}}_{qq'',qp''}(\tau)\hat{g}^{\mathrm{ROT}}_{q''q',p''q'}(\tau)\\&\qquad-\hat{g}^{\mathrm{ODF}}_{qq'',qp''}(\infty)\hat{g}^{\mathrm{ROT}}_{q''q',p''q'}(\infty)]\hat{g}^{\mathrm{ROT}'}_{q',q'}(\infty)\hat{g}^{\mathrm{int}(kl)}_{q'0,q'0}(\infty)\\&=\sum_{q''p''}[\hat{g}^{\mathrm{ODF}}_{qq'',qp''}(\tau)\hat{g}^{\mathrm{ROT}}_{q''0,p''0}(\tau)-\hat{g}^{\mathrm{ODF}}_{qq'',qp''}(\infty)\hat{g}^{\mathrm{ROT}}_{q''0,p''0}(\infty)]\\&\qquad\times d^2_{00}(\beta^{k0}_{MQ})d^2_{00}(\beta^{l0}_{MQ})\tilde{F}^0_{k0}\tilde{F}^0_{l0},\end{aligned} \tag{D6}$$

where we used

$$\hat{g}^{\mathrm{ROT}'}_{q',q'}(\infty)=\delta_{q',0}, \tag{D7}$$

$$\hat{g}^{\mathrm{int}(kl)}_{00,00}(\infty)=\overline{d^2_{00}(\beta^k_{MQ})\tilde{F}^0_k d^2_{00}(\beta^l_{MQ})\tilde{F}^0_l}, \tag{D8}$$

with

$$\overline{d^2_{00}(\beta^k_{MQ})\tilde{F}^0_k}=d^2_{00}(\beta^{k0}_{MQ})\tilde{F}^0_{k0}, \tag{D9}$$

and $d^2_{00}(\beta^{k0}_{MQ})=[3\cos^2(\beta^{k0}_{MQ})-1]/2$, $\tilde{F}^0_{k0}=-\frac{\mu_0\hbar\gamma^2}{2\pi r^3_{k0}}$.

It is worth noting that in Eq. (D6) the sum does not contain elements depending of the interproton vectors, namely of indices k and l. Thus, the expression for the multispin correlation function can be expressed in a simple form as

$$G^q_{kl}(\tau)=\epsilon_k\epsilon_l G^q_{oo}(\tau), \tag{D10}$$

where

$$\epsilon_k=\frac{d^2_{00}(\beta^{k0}_{MQ})}{d^2_{00}(\beta^{o0}_{MQ})}\frac{\tilde{F}^0_{k0}}{\tilde{F}^0_{o0}}=\left(\frac{r_{o0}}{r_{k0}}\right)^3\left[\frac{3\cos^2(\beta^{k0}_{MQ})-1}{3\cos^2(\beta^{o0}_{MQ})-1}\right],$$

the index o stands for the pair having the stronger interaction energy, namely the ortho pair. For uniaxial LC $\epsilon_k=\overline{F^0_k}/\overline{F^0_o}$, where $\overline{F^0_k}$ is the dipolar coupling of the kth pair. Finally, by replacing Eq. (D10) in Eq. (D1), we get

$$J^q_{kl}(\omega)=\epsilon_k\epsilon_l J^q_{oo}(\omega). \tag{D11}$$

Now we use the fact that the time scales of the local and collective molecular motions are well separated [approximation (B3)], to write Eq. (D6) in a form that yields the spectral density as a sum of different contributions. According with the picture presented in Ref. [22], the correlation times can be ordered as $(\tau^{\mathrm{int}(kl)}_{q'0,q'0},\tau^{\mathrm{ROT}'}_{q',q'})\ll\tau^{\mathrm{ROT}}_{q''q',p''q'}\ll\tau^{\mathrm{ODF}}_{qq'',qp''}$, and using Eq. (C14) we write

$$\begin{aligned}\hat{g}^{\mathrm{ODF}}_{qq'',qp''}(\tau)\hat{g}^{\mathrm{ROT}}_{q''0,p''0}(\tau)&=[\Delta\hat{g}^{\mathrm{ODF}}_{qq'',qp''}\zeta^{\mathrm{ODF}}_{qq'',qp''}(\tau)+\hat{g}^{\mathrm{ODF}}_{qq'',qp''}(\infty)]\\&\qquad\times[\Delta\hat{g}^{\mathrm{ROT}}_{q''0,p''0}\zeta^{\mathrm{ROT}}_{q''0,p''0}(\tau)+\hat{g}^{\mathrm{ROT}}_{q''0,p''0}(\infty)]\\&\approx\Delta\hat{g}^{\mathrm{ODF}}_{qq'',qp''}\hat{g}^{\mathrm{ROT}}_{q''0,p''0}(\infty)\zeta^{\mathrm{ODF}}_{qq'',qp''}(\tau)\\&\quad+\hat{g}^{\mathrm{ODF}}_{qq'',qp''}(0)\Delta\hat{g}^{\mathrm{ROT}}_{q''0,p''0}\zeta^{\mathrm{ROT}}_{q''0,p''0}(\tau)\\&\quad+\hat{g}^{\mathrm{ODF}}_{qq'',qp''}(\infty)\hat{g}^{\mathrm{ROT}}_{q''0,p''0}(\infty).\end{aligned} \tag{D12}$$

Substituting Eq. (D12) in Eq. (D6),

$$G^q_{kl}(\tau)=[g^{\mathrm{ODF}}_q(\tau)+g^{\mathrm{ROT}}_q(\tau)]d^2_{00}(\beta^k_{MQ})d^2_{00}(\beta^l_{MQ})\tilde{F}^0_k\tilde{F}^0_l, \tag{D13}$$

where

$$g^{\mathrm{ODF}}_q(\tau)=\sum\nolimits_{q'',p''}\Delta\hat{g}^{\mathrm{ODF}}_{qq'',qp''}\hat{g}^{\mathrm{ROT}}_{q''0,p''0}(\infty)\zeta^{\mathrm{ODF}}_{qq'',qp''}(\tau),$$

$$g^{\mathrm{rot}}_q(\tau)=\sum\nolimits_{q'',p''}\hat{g}^{\mathrm{ODF}}_{qq'',qp''}(0)\Delta\hat{g}^{\mathrm{ROT}}_{q''0,p''0}\zeta^{\mathrm{ROT}}_{q''0,p''0}(\tau). \tag{D14}$$

Using Eq. (D13) in Eq. (D1), one finally gets

$$J^q_{kl}(\omega)=J^{q\mathrm{ODF}}_{kl}(\omega)+J^{q\mathrm{ROT}}_{kl}(\omega), \tag{D15}$$

where:

$$
\begin{aligned}
J_{kl}^{q\mathrm{ODF}}(\omega) &= d_{00}^{2}(\beta_{MQ}^{k0})d_{00}^{2}(\beta_{MQ}^{l0})\widetilde{F}_{k0}^{0}\widetilde{F}_{l0}^{0}(-1)^{q} \\
&\quad \times \int_{-\infty}^{\infty} g_{q}^{\mathrm{ODF}}(\tau)e^{-i\omega\tau}d\tau, \\
J_{kl}^{q\mathrm{ROT}}(\omega) &= d_{00}^{2}(\beta_{MQ}^{k0})d_{00}^{2}(\beta_{MQ}^{l0})\widetilde{F}_{k0}^{0}\widetilde{F}_{l0}^{0}(-1)^{q}\int_{-\infty}^{\infty} g_{q}^{\mathrm{rot}}(\tau)e^{-i\omega\tau}d\tau.
\end{aligned}
\tag{D16}
$$

In summary, the outline of the reasoning we followed is as follows. We obtained Eq. (D4) under the assumptions (B1) and (B2). Equations (D6), (D10), and (D11)are obtained by considering that the correlation time of the internal motions and the rotation about the molecular principal axis are much smaller than the other [hypothesis (B3)]. Finally, we get Eqs. (D13) and (D15) by assuming that the time scale of the local molecular motions is well differentiated from the collective ones (B3).

[1] P. DeGennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon, Oxford, 1993).

[2] F. Noack, M. Notter, and W. Wiess, Liq. Cryst. **3**, 907 (1988); R. Kimmich and E. Anoardo, Prog. Nucl. Magn. Reson. Spectrosc. **44**, 257 (2004).

[3] E. Dumont, J. Jeener, and P. Broekaert, Phys. Rev. B **49**, 6763 (1994).

[4] H. Eisendrath, W. Stone, and J. Jeener, Phys. Rev. B **17**, 47 (1978).

[5] J. Jeener and P. Broekaert, Phys. Rev. **157**, 232 (1967).

[6] H. Schmiedel, S. Grande, and B. Hillner, Phys. Lett. **91A**, 365 (1982).

[7] O. Mensio, C. E. González, R. C. Zamar, D. J. Pusiol, and R. Y. Dong, Physica B **320**, 416 (2002).

[8] O. Mensio, C. E. González, and R. C. Zamar, Phys. Rev. E **71**, 011704 (2005).

[9] O. Mensio, R. C. Zamar, E. Anoardo, R. Acosta, and R. Dong, J. Chem. Phys. **123**, 204911 (2005).

[10] R. C. Zamar, E. Anoardo, O. Mensio, D. J. Pusiol, S. Becker, and F. Noack, J. Chem. Phys. **109**, 1120 (1998).

[11] O. Mensio, R. C. Zamar, D. J. Pusiol, and S. Becker, J. Chem. Phys. **110**, 8155 (1999).

[12] A. G. Redfield, Adv. Magn. Reson. **1**, 1 (1965).

[13] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).

[14] R. G. C. Mc. Elroy, R. T. Thompson, and M. M. Pintar, Phys. Rev. A **10**, 403 (1974).

[15] P. Pincus, Solid State Commun. **7**, 415 (1969).

[16] O. Mensio, C. E. González, and R. C. Zamar, J. Chem. Phys. **116**, 1530 (2002).

[17] M. Goldman, *Spin-Temperature and Nuclear Magnetic Resonance in Solids* (Oxford University Press, New York, 1970); J. Jeener, *Advances in Magnetic Resonance* (Academic, New York, 1968), Vol. III.

[18] J. B. Ferreira, A. F. Martins, D. Galland, and F. Volino, Mol. Cryst. Liq. Cryst. **151**, 283 (1987).

[19] R. Y. Dong, *Nuclear Magnetic Resonance of Liquid Crystals*, 2nd ed. (Springer Verlag, New York, 1997).

[20] P. S. Hubbard, Phys. Rev. **109**, 1153 (1958).

[21] R. C. Zamar and O. Mensio, J. Chem. Phys. **121**, 11927 (2004).

[22] A. J. Dianoux, J. B. Ferreira, A. F. Martins, A. M. Giroud, and F. Volino, Mol. Cryst. Liq. Cryst. **116**, 319 (1985).

[23] A. V. Komolkin, A. Laaksonen, and A. Maliniak, J. Chem. Phys. **101**, 4103 (1994).

[24] O. L. Mensio, Ph.D. thesis, Universidad Nacional de Córdoba, Córdoba, 2002.

[25] A. Keller, Adv. Magn. Reson. **12**, 183 (1988).

[26] K. Blum, *Density Matrix Theory and Applications* (Plenum, New York, 1981).

[27] M. Goldman, J. Magn. Reson. **149**, 160 (2001).

[28] B. M. Fung, R. D. Orwoll, and C. G. Wade, J. Chem. Phys. **64**, 148 (1976).

[29] R. Blinc, D. L. Hogenboom, D. E. O'Reilly, and E. M. Peterson, Phys. Rev. Lett. **23**, 969 (1969).

[30] Beyond the small amplitude limit, higher order terms in the fluctuating angle are needed and nonzero contributions to $J_{oo}^{2\mathrm{ODF}}$ and $J_{oo}^{0\mathrm{ODF}}$ are deduced in the literature [19,40]. However, we find that these two contributions in PAAd_6 (with $q=0$ and $q=2$) are negligible compared with $J_{oo}^{1\mathrm{ODF}}$.

[31] O. Mensio, R. C. Zamar, F. Casanova, D. J. Pusiol, and R. Y. Dong, Chem. Phys. Lett. **356**, 457 (2002).

[32] M. Carravetta and M. H. Levitt, J. Chem. Phys. **122**, 214505 (2005).

[33] R. Kimmich, *NMR: Tomography, Diffusometry, Relaxometry* (Springer-Verlag, Berlin, 1997); F. Grinberg and R. KImmich, J. Chem. Phys. **103**, 365 (1995).

[34] J. F. J. M. Pourquié and R. A. Wind, Phys. Lett. **55A**, 347 (1976).

[35] T. Charpentier, F. Dzheparov, J. F. Jacquinot, and J. Virlet, C. R. Phys. **5**, 387 (2004).

[36] J. Jeener, J. D. Bell, P. Broekaert, E. Dumont, and Marianne Koenig, Adv. Magn. Reson. **14**, 95 (1990).

[37] M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).

[38] St. Limmer, H. Schmiedel, B. Hillner, A. Lösche, and S. Grande, J. Phys. (France) **41**, 869 (1980).

[39] P. Ukleja, J. Pirs, and J. W. Doane, Phys. Rev. A **14**, 414 (1976).

[40] R. L. Vold, W. H. Dickerson, and R. R. Vold, J. Magn. Reson. (1969–1992) **43**, 213 (1981).