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## Slow dynamics in a liquid crystal: $^1\text{H}$ and $^{19}\text{F}$ NMR relaxometry

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Spin-lattice relaxation rates ( $R_{1\text{H}}$  and  $R_{1\text{F}}$ ) of two nuclear species ( $^1\text{H}$  and  $^{19}\text{F}$ ) are measured at different temperatures in the isotropic phase of a liquid crystal (4'-butoxy-3'-fluoro-4-isothiocyanatotolane-4OFTOL), over a wide range of Larmor frequency (10 kHz–50 MHz). Their dispersion profiles are found to be qualitatively very different, and the  $R_{1\text{F}}$  in particular shows significant dispersion (varying over two orders of magnitude) in the entire isotropic range, unlike  $R_{1\text{H}}$ . The proton spin-lattice relaxation, as has been established, is mediated by time modulation of magnetic dipolar interactions with other protons (case of *like* spins), and the discernable dispersion in the mid-frequency range, observed as the isotropic to nematic transition is approached on cooling, is indicative of the critical slowing of the time fluctuations of the nematic order. Significant dispersion seen in the  $R_{1\text{F}}$  extending to very low frequencies suggests a distinctly different relaxation path which is exclusively sensitive to the ultra slow modes apparently present in the system. We find that under the conditions of our experiment at low Zeeman fields, spin-rotation coupling of the fluorine with the molecular angular momentum is the dominant mechanism, and the observed dispersion is thus attributed to the presence of slow torques experienced by the molecules, arising clearly from collective modes. Following the arguments advanced to explain similar slow processes inferred from earlier detailed ESR measurements in liquid crystals, we propose that slowly relaxing local structures representing such dynamic processes could be the likely underlying mechanism providing the necessary slow molecular angular momentum correlations to manifest as the observed low frequency dispersion. We also find that the effects of the onset of cross-relaxation between the two nuclear species when their resonance lines start overlapping at very low Larmor frequencies (below  $\sim 400$  kHz), provide an additional relaxation contribution. © 2011 American Institute of Physics. [doi:10.1063/1.3672180]

### I. INTRODUCTION

The laterally fluorinated liquid crystal compounds have attracted recent attention because of their potential applications in display technology and telecommunications.<sup>1–9</sup> The replacement of hydrogen with the fluorine on the aromatic core reduces the melting point and smectogenity leading to a wide nematic range. Mixtures of these singly or doubly fluorinated compounds on the aromatic cores have high figure-of-merit, low viscosity, and high birefringence, which are the favorable physical parameters for liquid crystal display devices. Detailed dielectric studies were carried out on singly fluorinated compounds to examine the correlation times of reorientations.<sup>6</sup> Our present interest is to examine possible differences in the relaxation mechanisms of  $^1\text{H}$  and  $^{19}\text{F}$  residing on the molecule of a singly fluorinated liquid crystal (both nuclei being spin- $\frac{1}{2}$ , with comparable gyromagnetic ratios differing by about 6%) using NMR relaxometry. This has the potential to yield perhaps different perspectives of dynamic processes of the same molecule as reported by the two distinct probing nuclei. With this objective we chose a member of the

tolane family, 4'-butoxy-3'-fluoro-4-isothiocyanatotolane-4OFTOL, with the molecular structure and phase sequence as indicated in Fig. 1. This family of liquid crystals was earlier investigated with detailed dielectric studies to infer on the molecular reorientational dynamics and its possible correlation to the structure.<sup>6</sup> We present the frequency dispersion of spin-lattice relaxation rates of the nuclei ( $R_{1\text{H}}$  and  $R_{1\text{F}}$ , of proton and fluorine, respectively) at different temperatures in the isotropic phase of this system, and attempt to interpret them in terms of the underlying molecular processes. Analysis of  $R_{1\text{H}}$  data indicates that slowest processes aiding its dispersion are the pretransitional effects arising from the nematic order fluctuations, affecting the time correlations of the reorientational dynamics of the molecules. The dramatic enhancement of  $R_{1\text{F}}$  at lower frequencies, and its presence even at the highest of the temperatures in the isotropic phase where the critical effects are not so evident in  $R_{1\text{H}}$  dispersion, suggests the presence of another type of slow molecular processes in the system (not accessed by protons) and sensed by fluorine apparently by a qualitatively different relaxation path. Among the possible interactions relevant to this nucleus, we argue that the fluorine spin-rotation interaction (its coupling constant being significant relative to proton) is primarily

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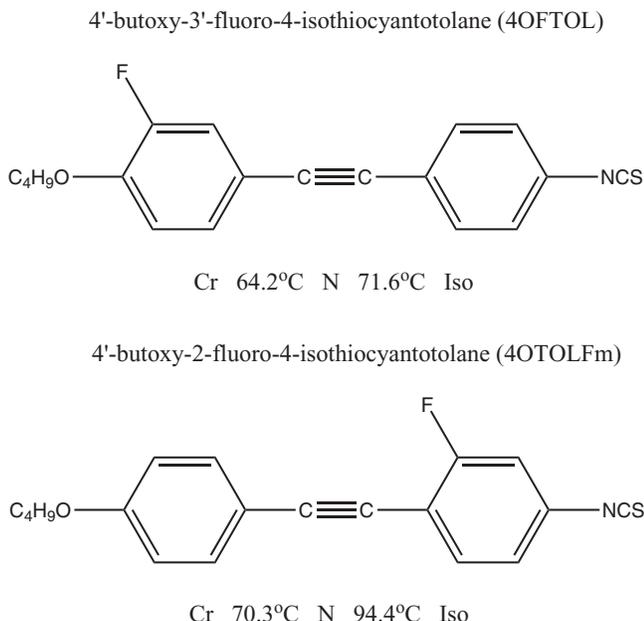


FIG. 1. Molecular structure and phase sequence of liquid crystal 4OFTOL (molecular structure of 4OTOLFm is also given for comparison).

mediating this relaxation and thus helping fluorine to report on time correlations of molecular angular momentum components. This then suggests that there are very slow components in such time correlations, pointing to correspondingly slow local torques experienced by the reorienting molecules. We attempt to connect this finding to the earlier observations of slowly relaxing local structures (SRLS), also referred to as cages, based on detailed ESR measurements, and suggest its applicability to possibly account for the present experimental observations.

A subtle change takes place as far as the dipolar interaction between the lone fluorine and the neighbouring protons is concerned, at the very low frequency end of this field-cycling experiment. In NMR terms<sup>10</sup> the H-F dipolar interaction, which is of hetero-nuclear nature (case of unlike spins) at high fields (weak-coupling limit), acquires a homo-nuclear character (case of like spins) at low enough fields (strong-coupling limit). Here, the resonance lines of the two species (despite the differences in gyromagnetic ratios) start overlapping, promoting additional mechanism (called cross-relaxation  $T_{21}$  process<sup>11</sup>). In the present sample, we find that this facilitates additional effective coupling of fluorine to the lattice via the proton spin reservoir, below about 400 kHz, and its efficacy increases as the lines progressively overlap.

The paper is organized as follows. In Sec. II we describe the experimental details and present data on the proton and fluorine spin-lattice relaxation rates in this system. In Sec. III, we discuss the relaxation mechanisms appropriate to interpret the observations. In Sec. IV,  $R_{1H}$  and  $R_{1F}$  dispersions at different temperatures are analyzed based on these models, leading to an estimation of the relevant molecular dynamic parameters. The last section summarizes the conclusions of this study.

## II. EXPERIMENTAL DETAILS

The sample used in this study was synthesized in the laboratories of the Warsaw group, and the method of synthesis and characterization of some of the properties are discussed earlier.<sup>12,13</sup> In our work we sealed the compound in a standard NMR tube after removing the dissolved oxygen through freeze-pump-thaw cycles. Frequency dispersions of proton and fluorine spin-lattice relaxation rates,  $R_{1H}$  and  $R_{1F}$ , are measured at four different temperatures in the isotropic phase, over a wide frequency range, with a commercial fast field-cycling NMR relaxometer (Stelar, Italy) to cover 10 kHz–10 MHz, supplemented by home-built variable-field pulsed NMR spectrometer for higher end frequencies (10–50 MHz). In all the cases, we find that the magnetization recoveries could be fitted to a simple exponential over at least three decades of time, permitting the determination of a unique spin relaxation rate associated with the specific spin magnetization. This corresponds to decoupled evolution of proton and fluorine Zeeman reservoirs.<sup>10</sup> The frequency dependence of the relaxation rates of both the nuclei are shown in Figs. 2 and 3. These rates are also measured as a function of temperature at chosen Larmor frequencies  $\nu_L$  ( $\omega = 2\pi\nu_L$ ) for both the nuclei and the results are shown in Figs. 4 and 5. Temperature of the sample was maintained by passing dry air over the sample to an accuracy of  $\pm 0.1$  °C. Relative errors in the relaxation rate measurements of proton are within 2% and are within 5% for fluorine. The frequency dispersion data of proton clearly show the onset of critical fluctuations even at 11 °C away from the isotropic to nematic transition temperature ( $T_{NI}$ ). The temperature variation of proton data (Fig. 4) further confirms the contribution of critical fluctuations near, and as well as far away, from the transition. In comparison, the relaxation rate dispersions of fluorine are however qualitatively very different. The  $R_{1F}$  values show a steady and very significant enhancement at low frequency regions, and this persists at all the temperatures in the isotropic phase (Fig. 3). The temperature variation of  $R_{1F}$  (Fig. 5) is also qualitatively different from the

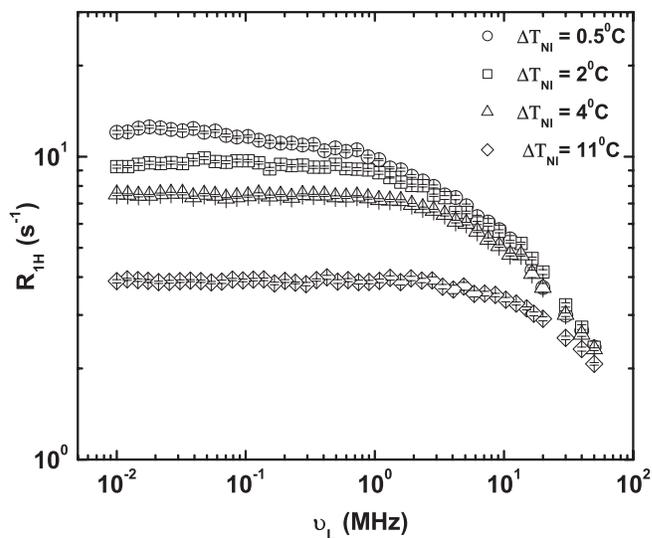


FIG. 2. Proton spin-lattice relaxation rate at different temperatures as a function of Larmor frequency.

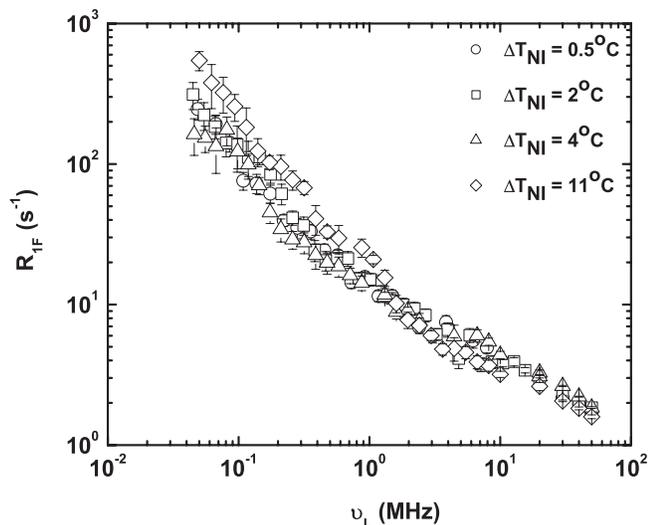


FIG. 3. Fluorine spin-lattice relaxation rate at different temperatures as a function of Larmor frequency.

behavior of proton relaxation rates. These observations point to possible differences in the relaxation pathways of the two nuclear species, even though they reside on the same liquid crystal molecule.

### III. RELAXATION MECHANISMS

Spin-lattice relaxation of protons in these systems occurs typically via the time modulation of dipolar interactions<sup>10,14,15</sup> and the relevant dynamic mechanisms that are of interest to the NMR experiment are: individual molecular reorientations modulating intra-molecular dipolar couplings; translational diffusion effecting the inter-molecular dipolar interactions; collective dynamics arising from critical fluctuations of the nematic order; and possibly a constant background contribution from such other processes which are

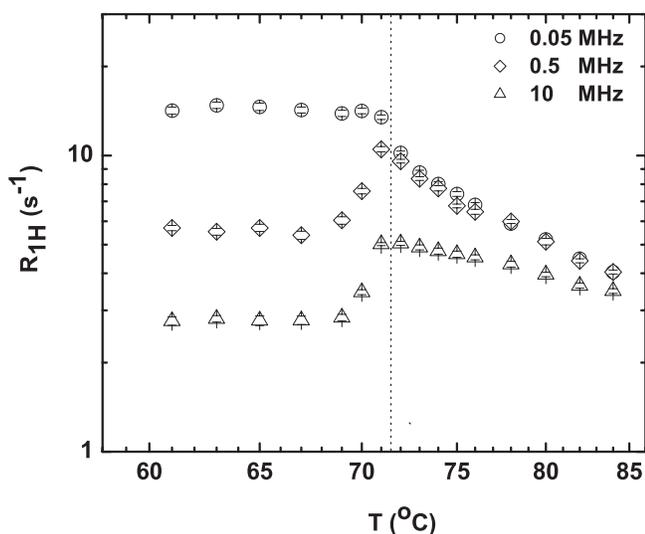


FIG. 4. Proton spin-lattice relaxation rates plotted against temperature at different Larmor frequencies. The dotted line in the figure indicates the isotropic-nematic transition temperature.

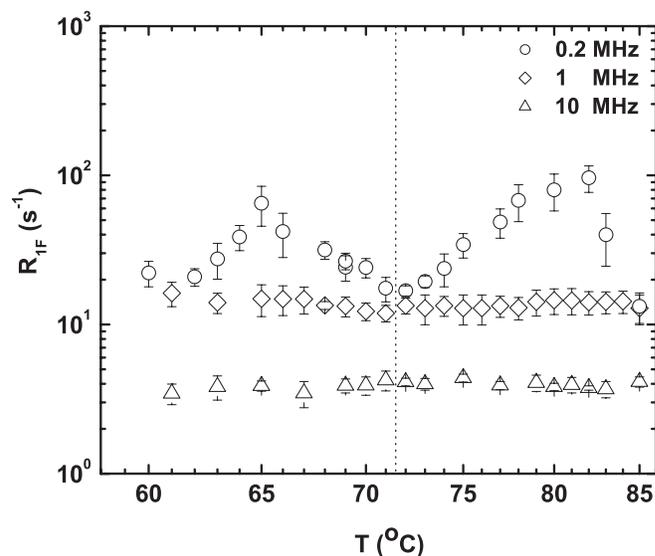


FIG. 5. Fluorine spin-lattice relaxation rates plotted against temperature at different Larmor frequencies. The dotted line in the figure indicates the isotropic-nematic transition temperature.

too fast for the experiment. We find from the analysis of the proton data that the translational diffusion contribution is practically constant over the frequency range, and hence cannot be distinguished from the background. The dispersion contribution to the data thus is primarily attributed as due to molecular reorientations ( $R$ ) about the molecular short axes and to critical fluctuations (CF). The experimental value of the relaxation rate is assumed to be a sum of all such contributions, neglecting the possible statistical correlations among them.

Analysis of the proton dispersion data is carried out by separating the contribution from different mechanisms as

$$R_{1H} = R_{1H0} + R_{1HR} + R_{1HCF}. \quad (1)$$

Here  $R_{1H0}$  represents a frequency independent contribution from all processes too fast on the time scale of the experiment. Dynamic models accounting for  $R_{1HR}$  from reorientational process<sup>10,16</sup> and for  $R_{1HCF}$  from order parameter critical fluctuations are well documented earlier,<sup>14,17</sup> and lead to the determination of corresponding correlation times ( $\tau_R$  and  $\tau_{CF}$ ) and their couplings to the spin system ( $A_R$  and  $A_{CF}$ ).

Analysis of the fluorine data ( $R_{1F}$ ), qualitatively different from proton, requires additional considerations. Apart from the dipolar coupling with protons (hetero-nuclear) and with fluorine nuclei on other molecules (homo-nuclear), chemical shift anisotropy (CSA), and spin-rotation interaction (SR) of fluorine with the molecular angular momentum need to be considered. While CSA, being field-dependent, is significant in relaxing fluorine in normally applicable fields, the present experiments focusing on very low fields make this interaction ineffective. Thus, in the case of fluorine we find that intra-molecular dipolar interaction via hetero-nuclear coupling with proton, and spin-rotation interaction involving molecular angular momentum time modulations, are more appropriate.<sup>18-21</sup> The contributions to  $R_{1F}$  from the modulation of the dipolar interaction are represented by  $R_{1FR}$  (from

R mechanism) and  $R_{1FCF}$  (from CF mechanism), while the constant background is included in  $R_{1F0}$ . It may be noted that, considering the very similar nature of proton and fluorine (both spin- $\frac{1}{2}$  and very nearly the same gyromagnetic ratio), the order of magnitude of the contributions from this mechanism to the  $R_{1F}$  data as well as the analytical dependence on frequency are expected to be comparable to the case of proton (but for a caveat mentioned below), and hence are not expected to be able to account for the steep increase (by about 150 times) in the fluorine relaxation rate in the low frequency region. Thus the problem of interpretation of rather simple looking, monotonically increasing relaxation rate of fluorine, all the way to kHz region, is one of finding suitable low frequency phenomena whose combined effect is to sustain this steady increase. We find that a single mechanism cannot reproduce this data, and our analysis indicates the need to include several qualitatively different processes to account for this steadily increasing strong coupling of fluorine to the lattice.

The caveat referred to earlier is concerned with the consequences of hetero-nuclear dipolar coupling on the spin-lattice relaxation of individual spin reservoirs.<sup>10</sup> In principle there should be a coupling between the two Zeeman systems and the observed magnetization recovery could be multi-exponential due to the coupling.<sup>10</sup> However the experimental observation of a single exponential decay of the magnetization rules out this coupling. But, in the presence of hetero-nuclear dipolar interactions the spectral density  $J^{(0)}$  at the difference-frequency can also in principle contribute to the individual spin-lattice relaxation rate according to the following equation,<sup>10</sup> thus leading to a low frequency ( $\omega_F - \omega_H$ ) component

$$R_{1F}^{\text{FH}} = A^{\text{FH}} \left[ \frac{1}{12} J^{(0)}(\omega_F - \omega_H) + \frac{3}{2} J^{(1)}(\omega_F) + \frac{3}{4} J^{(2)}(\omega_F + \omega_H) \right].$$

From an analysis based on this modified equation for the dipolar relaxation rate including a  $J^{(0)}$  contribution at low frequencies, we find that it is not adequate to account for the steep increase of the relaxation rate at low frequencies.

The second mechanism which is specifically effective for fluorine in relation to proton, is the coupling of this nuclear spin to the (transient) fields generated by molecular rotations (spin-rotation interaction–SR), and is expressed as<sup>18</sup>

$$H_{\text{SR}} = -\hbar S.C.J.$$

Here  $J$  is the angular momentum of the molecule,  $C$  is the spin-rotation interaction tensor, and  $S$  is the nuclear spin under consideration. Considering the case of a quantized spin in the NMR experiment, and fast molecular reorientations in the isotropic phase, the tensorial character of the spin-rotation constant can be approximated for simplicity to a constant, as is the case for example for a spherically symmetric molecule. The spin-lattice relaxation rate of fluorine is then expressible as<sup>19</sup>

$$R_{1\text{FSR}} = A_{\text{SR}} T \frac{\tau_{\text{SR}}}{1 + \omega^2 \tau_{\text{SR}}^2}, \quad (2)$$

$$A_{\text{SR}} = k_B \hbar^2 I_M (2C_{\perp}^2 + C_{\parallel}^2).$$

Here,  $I_M$  is the moment of inertia of the molecule,  $C_{\parallel}$  and  $C_{\perp}$  are the elements of the spin-rotation interaction tensor of the fluorine nucleus in the principal axes system.  $A_{\text{FSR}}$  represents the effective coupling of the nucleus under consideration to the SR process, and is dependent on the strength of the coupling tensor. Proton dispersion data are not sensitive to this mechanism because of its relatively weak coupling to the molecular angular momentum.<sup>20</sup> For typical molecules constituting simple liquids,  $\tau_{\text{SR}}$ , the correlation time associated with the angular momentum fluctuations of the molecule, is in the range of  $10^{-12}$  to  $10^{-13}$  s (too fast on NMR experimental time scale), and hence for such processes no dispersion is to be expected (Eq. (2)). The temperature dependence of the present data at low frequencies (Fig. 5) indicates the signature of SR (increase of relaxation rate with increase of temperature). Observed sensitivity of this data to temperature at low enough Larmor frequencies and the dramatic enhancement of the rate at such low frequencies even at elevated temperatures (Fig. 3), together with the strong pointer to SR as perhaps the only effective mechanism in this case, motivate further discussion on possible sources of slow modulations affecting the SR mechanism.

Earlier investigations on the line shapes of ESR spectra<sup>22</sup> showed that the simple rotational dynamic models were not adequate in explaining the observed line width variations with different spin probes.<sup>23</sup> The time domain 2D ESR methods also confirm this observation.<sup>24</sup> These ESR observations were explained in terms of slowly relaxing local structures within the liquid crystal medium, modulating the rotational diffusion of the ESR probes. Thus the dynamics corresponds to a rotational diffusion in the presence of an orienting potential of mean torque, which itself is undergoing a simple rotational diffusion on much slower time scale. This is viewed as a cage inducing local ordering, tumbling isotropically on a well separated time scale (relative to ESR time scales).<sup>23–25</sup> It was also seen from the ESR work that the coupling of the ESR probe to such slow processes is dependent on the size and anisotropy of the probing molecule—bigger the size of the ESR probe, the dramatic were the slow motional effects on the spectral features. In the present case the fluorine bearing liquid crystal molecule itself is a (nuclear) probe, thus the coupling to such SRLS mechanism is expected to be at its maximum. We thus are led to explore this dynamic process as a possible source of the observed strong coupling of the fluorines to the lattice via the SR interaction.

There is a quantitative difference, however, in adapting this model to the present case. The relaxation of the ESR probe (typically a free radical of a chosen molecular geometry) is sensitive to the reorientational dynamics of the spin bearing molecule, and thus reports on its time correlations. Within the SRLS model, interpretation of the ESR observations then relates to evaluating the effects of the corresponding stochastic processes, accounted for at the level of Smoluchowski equation, coarse graining the angular momentum variables. And, the assumed isotropic diffusion of the local structures represents a simplified representation of these modes under Brownian approximation. In the present case, involving a nuclear spin sensitive to the (random) time variations of local magnetic fields generated due to the

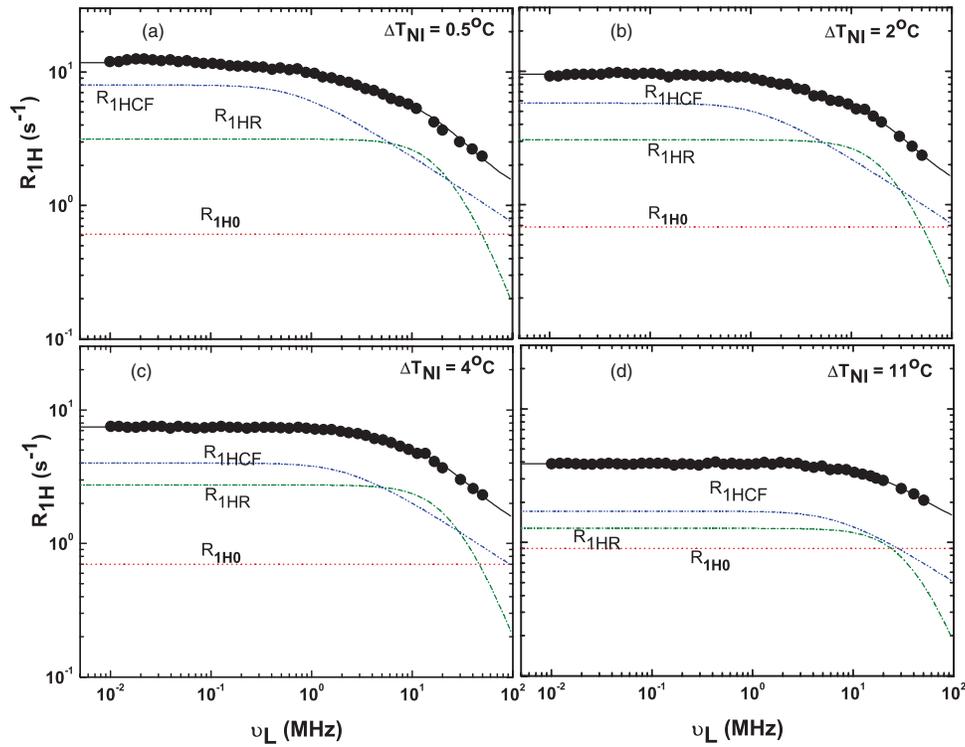


FIG. 6. Proton spin-lattice relaxation rate dispersions fitted to Eq. (1) at different temperatures: (a)  $\Delta T_{\text{NI}} = 0.5^\circ\text{C}$ , (b)  $\Delta T_{\text{NI}} = 2^\circ\text{C}$ , (c)  $\Delta T_{\text{NI}} = 4^\circ\text{C}$ , and (d)  $\Delta T_{\text{NI}} = 11^\circ\text{C}$ . The solid line represents the fit of Eq. (1) to the experimental data. The color dotted lines indicate the contributions of different relaxation mechanisms. The values of the fitted parameters are given in Table I.

corresponding reorientational dynamics of the spin-bearing probe molecule, it is the time correlations of these fields that influence the nuclear spin-lattice relaxation. Consequently the angular momentum correlation times that appear in the expression for the nuclear spin relaxation rate<sup>18</sup> are in effect connected, in the present system, in a more subtle manner to these underlying collective motions. While a quantitative analysis of such effects requiring Fokker-Planck-Kramer level description does not seem feasible at this time, it is still useful to consider the applicability of that model in qualitative terms to interpret the present work. We consider thus the correlation time (say,  $\tau_C$ ) derivable from the low frequency dispersion of fluorine relaxation rates with a Lorentzian fit, as indicative of the time scale of slow modulations of the spin-rotation interaction, and propose that the underlying dynamics is associated with the SRLS mechanism. We thus analyze the corresponding data based on this simplified model, by representing its contribution as

$$R_{\text{IFC}} = A_{\text{FC}} \frac{\tau_C}{1 + \omega^2 \tau_C^2}. \quad (3)$$

Here  $A_{\text{FC}}$  is a (temperature dependent) measure of the coupling of the fluorine to these slow modes.

We interpret the experimental data on fluorine by expressing the observed relaxation rate  $R_{\text{IF}}$  as

$$R_{\text{IF}} = R_{\text{IF0}} + R_{\text{IFR}} + R_{\text{IFCF}} + R_{\text{IFC}}. \quad (4)$$

The first term comprises of contributions from all fast processes, including contribution from the SR mechanism un-

der fast angular momentum relaxations (Eq. (2), with  $\omega\tau_{\text{SR}} \ll 1$ ).

#### IV. ANALYSIS AND DISCUSSION

The proton dispersion data are fitted to Eq. (1) at the four temperatures, as shown in Fig. 6. Each dispersion is decomposed into a frequency-independent contribution (from fast processes, like molecular reorientations around the long-axes and alkyl chains). We also find from our analysis that the inter-molecular dipolar interaction modulated by the translational diffusion is also relatively fast on the experimental time scale, and hence leads to a constant contribution along with the other such processes. This leaves the possible dispersion mechanisms as: reorientations around the short-axes and critical fluctuations of the order parameter of the transition. The model parameters are determined based on a nonlinear least squares procedure<sup>26</sup> and are summarized in Table I. The experimental data as well as the analysis (Table I) clearly show that correlation times of critical fluctuations of the nematic order ( $\tau_{\text{CF}}$ ) are significantly high near the transition (Fig. 6(a),  $\Delta T_{\text{NI}} = 0.5^\circ\text{C}$ ,  $\tau_{\text{CF}} \approx 363$  ns), and persist even at elevated temperatures in the isotropic phase (Fig. 6(d),  $\Delta T_{\text{NI}} = 11^\circ\text{C}$ ,  $\tau_{\text{CF}} \approx 35$  ns)—somewhat unusual in typical liquid crystals. For comparison, the correlation times obtained from this technique for other liquid crystals near their corresponding transition temperatures are much lower: e.g., in 4'-butoxy-2-fluoro-4-isothiocyanatotolane (4OTOLFm, Fig. 1) and 4'-octyloxy-4-cyanobiphenyl (8OCB) these are 68 ns and 180 ns, respectively. Further, their dispersion

TABLE I. Optimized values of the parameters extracted by fitting the  $^1\text{H}$  NMR spin-lattice relaxation rate dispersions in the isotropic phase at different temperatures to Eq. (1).

$\Delta T_{\text{NI}}$ ( $^{\circ}\text{C}$ )	$R_{\text{IHO}}$ ( $\text{s}^{-1}$ )	$A_{\text{IHR}}$ ( $10^9 \text{ s}^{-2}$ )	$\tau_{\text{R}}$ (ns)	$A_{\text{HCF}}$ ( $10^3 \text{ s}^{-3}$ )	$\tau_{\text{CF}}$ (ns)
0.5	$0.61 \pm 0.01$	$0.79 \pm 0.024$	$3.96 \pm 0.07$	$18.8 \pm 4.4$	$362.9 \pm 10.7$
2	$0.68 \pm 0.01$	$0.87 \pm 0.03$	$3.51 \pm 0.07$	$18.1 \pm 6.1$	$203.0 \pm 7.4$
4	$0.7 \pm 0.008$	$0.79 \pm 0.01$	$3.49 \pm 0.07$	$17 \pm 2.5$	$110.7 \pm 1.8$
11	$0.9 \pm 0.006$	$0.54 \pm 0.16$	$2.38 \pm 0.25$	$12.9 \pm 3.0$	$35.1 \pm 6.3$

effects on the relaxation rate are not seen to persist beyond 5–6  $^{\circ}\text{C}$  above the transition.<sup>27,28</sup> Dielectric studies on 4OFTOL (Ref. 6) suggest that the transverse dipole moment of this molecule is not completely averaged out due to hindering of the wing rotation about the para axes of the molecules, arising from the location of fluorine atom on the core (Fig. 1). In 4OTOLFm on the other hand fluorine is located in the meta position on the aromatic core and the averaging was found to be more effective. We note that this observed partial averaging of the molecular transverse dipole moment in 4OFTOL reported from the dielectric studies, and its relatively longer life times of the nematic clusters inferred from the present work are perhaps correlated. The remnant transverse dipoles on the molecules of 4OFTOL could be providing additional mechanism in promoting the formation of the nematic clusters during the pretransitional behavior, reflected in their enhanced life times. It may further be noted that this difference between the structures of 4OFTOL and 4OTOLFm also leads to a difference in their order parameter values.<sup>6</sup> The value of  $\tau_{\text{R}}$  is found to vary from about 4.0 ns to 2.4 ns as the sample is heated above the transition temperature (Table. I). In comparison its variation over a corresponding range of temperature in a related system, 4OTOLFm, is from about 1.7–1.4 ns,<sup>27</sup> suggesting a higher activation energy for the rotational dynamics in the present system. The temperature dependence of the relaxation rate at low frequencies (Fig. 4) is consistent with the above observations.

While analyzing the more pronounced fluorine dispersion based on Eq. (4), we use the correlation times ( $\tau_{\text{R}}$  and  $\tau_{\text{CF}}$ ) as inputs obtained from the proton results. An attempt to fit the data based on the processes included in Eq. (4), with relevant correlation times consistent with the proton dispersions, immediately suggested that a distinction need to be made between the contribution from mechanisms that operate via the dynamic processes included in Eq. (4) and an extra path to the lattice created at very low frequencies (below  $\sim 400$  kHz) by the onset of overlap of the resonance lines of the two nuclear species. In terms of the nuclear spin Hamiltonian, this corresponds to gradual change from weak coupling (WC) regime (i.e., when the dipolar interaction strength between the fluorine and proton spins is much smaller than the difference in their resonance frequencies) to strong coupling (SC) regime.<sup>10</sup> In the latter limit, the energy-conserving mutual spin flip-flop terms of the two nuclear spins in the dipolar Hamiltonian become significant, providing an additional path for the equilibration of the fluorine system. We therefore proceed with the analysis of this data in two steps. We first attempt to fit the fluorine data in the WC regime (with Eq. (4)) utilizing of course the dynamic

information from the proton results. The relaxation rates computed based on these best fit parameters, extrapolated to the SC regime (very low frequency region) then correspond to predicted values based on these proposed dynamic processes. The observed differences between these values and the experimental data (below  $\sim 400$  kHz) are due to the additional mechanism of the cross-relaxation arising from the overlap of the two resonance lines.<sup>11</sup> The second step of analysis thus involves interpretation of these deviations based on considerations of overlap of the resonance lines.

Analyzing the fluorine data in the WC regime, we find that R and CF mechanisms are not adequate, particularly evident considering the strong dispersion even at  $\Delta T_{\text{NI}} = 11$   $^{\circ}\text{C}$  where the CF mechanism is at its weakest in effecting a dispersion as per the proton data. Observed strong dispersion extending monotonically into the low frequency regime thus requires invoking a slow enough process modulating a qualitatively different spin-lattice coupling, different from that of the protons. It is known that the spin-rotation coupling constant of fluorine is much stronger (typically 5 times) than that of proton,<sup>20</sup> and the relaxation rate varies proportional to its square. This mechanism is qualitatively different in its coupling to the dynamic processes, in that it connected to correlations of molecular angular momentum components, rather than of the reorientations. The experimental evidence, in conjunction with the analysis of the proton data, thus indicates that the observed strong fluorine-lattice coupling is perhaps due to a very effective spin-rotation interaction (relative to protons), and the observed dispersion extending to the low frequencies should thus be due to the presence of very slow time correlations of the angular momentum correlations. It is in this context that the ESR results seem to provide a clue to the origin of slow torques needed to effect such slow angular momentum dynamics. We interpret the results now in terms of Eq. (4), which incorporates additional slow mechanism which is expected to reflect the effect of the SRLS dynamics (isotropic Brownian rotational diffusion of local structures). We present the best fit strengths of the fluorine spin system with the lattice from different mechanisms, i.e.,  $A_{\text{FR}}$  (short-axes reorientations),  $A_{\text{FCF}}$  (order parameter critical fluctuations),  $A_{\text{FC}}$  (effect of slowly relaxing local structures), along with  $\tau_{\text{C}}$  (time scales of slow torques arising from the underlying slow modes) in Table II. We observe that  $\tau_{\text{C}}$  is in the range of 260–300 ns, and is practically unaffected by temperature within the errors of estimation. We also find that the corresponding coupling strength ( $A_{\text{FC}}$  in the Table II) increases as the system is heated into the isotropic phase. The contributions  $A_{\text{FR}}$  and  $A_{\text{FCF}}$  represent the coupling of the fluorine system to the lattice via the hetero-nuclear intra-molecular

TABLE II. Optimized values of the parameters extracted by fitting the  $^{19}\text{F}$  NMR spin-lattice relaxation rate dispersions in the isotropic phase at different temperatures to Eq. (4).

$\Delta T_{\text{NI}}$ ( $^{\circ}\text{C}$ )	$A_{1\text{FR}}$ ( $10^9 \text{ s}^{-2}$ )	$\tau_{\text{R}}$ (ns)	$A_{\text{FCF}}$ ( $10^3 \text{ s}^{-3}$ )	$\tau_{\text{CF}}$ (ns)	$A_{\text{FC}}$ ( $10^8 \text{ s}^{-2}$ )	$\tau_{\text{C}}$ (ns)
0.5	$0.41 \pm 0.11$	3.96	$14.2 \pm 1.9$	362.8	$0.086 \pm 0.009$	$292.2 \pm 61.9$
2	$0.45 \pm 0.01$	3.51	$14.4 \pm 0.13$	203.0	$0.113 \pm 0.006$	$261.8 \pm 29.1$
4	$0.62 \pm 0.01$	3.49	$15.0 \pm 0.14$	110.7	$0.091 \pm 0.006$	$260.1 \pm 33.5$
11	$0.41 \pm 0.20$	2.38	$16.4 \pm 0.36$	35.1	$0.22 \pm 0.01$	$273.0 \pm 26.5$

dipolar interaction with protons, arising due to the different time modulations. We assume that the inter-molecular homo- or hetero-nuclear interactions involving fluorine (modulated by translational diffusion) are negligible, and if any would be essentially frequency independent in keeping with the observations based on the proton data. As may be seen from Figs. 6 and 7, the relaxation rates of proton and fluorine differ by more than an order of magnitude at low frequencies. The constant background term ( $R_{1\text{F0}}$ ) was found to be relatively very small, with comparable errors, and hence their values are set to zero (not quoted in Table II). The case of protons is different, since they have significant homo-nuclear inter-molecular interactions and hence could lead to discernible (though) constant contribution to their relaxation rate.

The analysis of the data in the SC limit (typically below 400 kHz in the present sample) qualitatively differs from above. We find that the extrapolated relaxation rates based on the fit parameters of the dynamic model used in the high frequency regime (WC) deviate substantially, and systematically, from the experimental observations (Fig. 3).

The additional contribution in the SC regime arises from a qualitatively different relaxation path available to the fluorine system, once the fluorine and proton resonance lines start significantly overlapping. In terms of nuclear spin Hamiltonian comprising of the Zeeman term and a perturbing nuclear dipole-dipole interaction, and with the valid assumption of conservation of the total energy of the Hamiltonian, the question is connected with finding out the probability of resonant absorption at a given frequency. This in turn inquires into the rate at which the Zeeman and dipolar energies could come into mutual equilibrium.<sup>11</sup> A higher order perturbation calculation is in principle necessary, with repeated operation of the interaction Hamiltonian on the system. This involves operator products of alternating terms comprising of either of  $A$  and  $B$  (secular and pseudo-secular terms in the dipolar interaction<sup>10</sup>) on one hand, and one of the transition inducing terms ( $C$ ,  $D$ ,  $E$ , and  $F$ ) on the other. This could be simplified,<sup>11</sup> with a combination of perturbation calculation for the transition inducing terms, and method of moments for  $A$  and  $B$  terms. The resulting transition probability for the Zeeman energy of

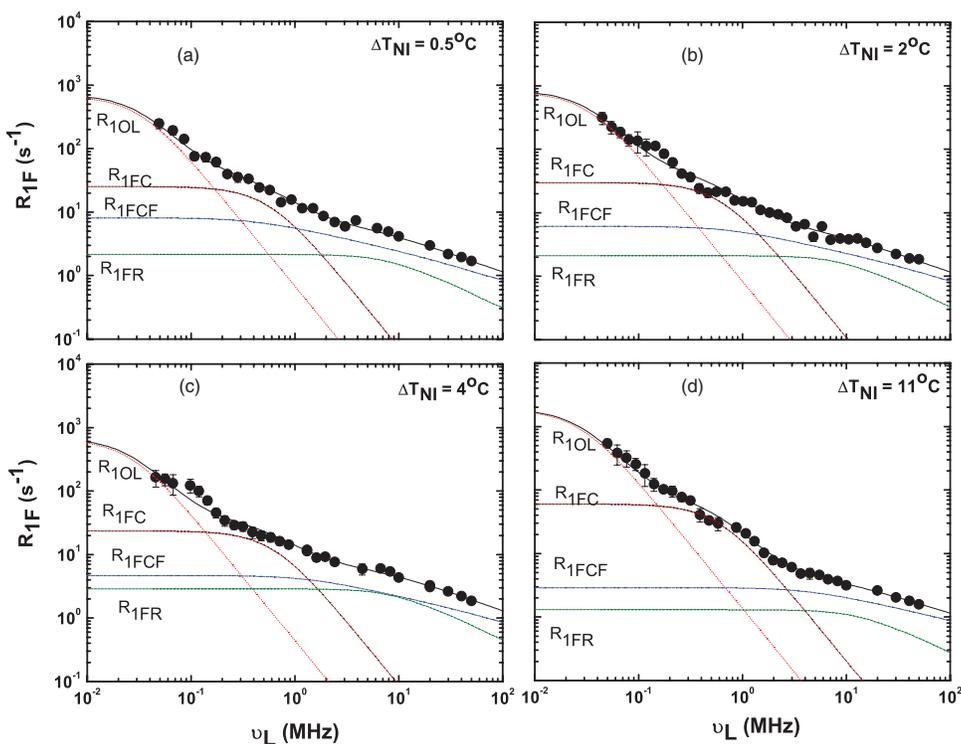


FIG. 7. Fluorine spin-lattice relaxation rate dispersions fitted to Eq. (4) at different temperatures: (a)  $\Delta T_{\text{NI}} = 0.5^{\circ}\text{C}$ , (b)  $\Delta T_{\text{NI}} = 1^{\circ}\text{C}$ , (c)  $\Delta T_{\text{NI}} = 4^{\circ}\text{C}$ , and (d)  $\Delta T_{\text{NI}} = 11^{\circ}\text{C}$ . The solid line represents the fit of Eq. (4) and cross-relaxation contribution to the experimental data. The color dotted lines indicate the contributions of different relaxation mechanisms. The values of the fitted parameters are given in Table II.

a spin to be converted into dipolar energy leads to a characteristic time ( $T_{21}$ ), which is intermediate in nature between the spin-spin relaxation time and the spin-lattice relaxation time. This process will become rapidly ineffective if the Zeeman splitting of the spins becomes larger than the spin-spin (dipolar) coupling among them. This interesting manifestation is effective in the SC regime, wherein the differences in the Zeeman energy splittings of the two distinct spin species become comparable to the line width. In other words if the applied Zeeman field is low enough for the two spins systems to have overlapping resonance lines, then a fresh mechanism comes into play in relaxing the Zeeman energy to equilibrium. The simplified expression for  $T_{21}^{-1}$ , assuming specific line shapes for the two NMR lines (of proton and fluorine) is given by<sup>11</sup>

$$T_{21}^{-1} = A_{OL} \int \int g_H(v') g_F(v'') \delta(v' - v'') dv' dv'' \quad (5)$$

with

$$A_{OL} = |\langle E_H, E_F | H_{HF}^d | E_H \pm h\nu, E_F \pm h\nu \rangle|^2.$$

Here  $A_{OL}$  is related to the square of the matrix element of Hamiltonian involving simultaneous energy-compensating flip-flops of the two spin species mediated by the  $B$  term in the dipolar interaction. To proceed further, we assume Lorentzian shapes for both the resonance lines with widths  $\Delta_H$  and  $\Delta_F$ , for proton and fluorine respectively. The resultant contribution to the fluorine relaxation rate, effective only at low enough frequencies, is denoted by  $R_{1OL} = T_{21}^{-1}$ , and is directly dependent on the extent of overlap of the two lines. With this additional mechanism, we express the total computed contribution as

$$R_{1F}^T = R_{1F} + R_{1OL}.$$

We interpret the differential contribution in the SC regime, ( $R_{1EXPT} - R_{1F}$ ), as due to  $R_{1OL}$ , and fit the corresponding data to Eq. (5) to obtain the three variable parameters ( $A_{OL}$ ,  $\Delta_H$ , and  $\Delta_F$ ). In Fig. 7, we include  $R_{1OL}$ , along with contributions from dynamic models ( $R_{1F}$  from

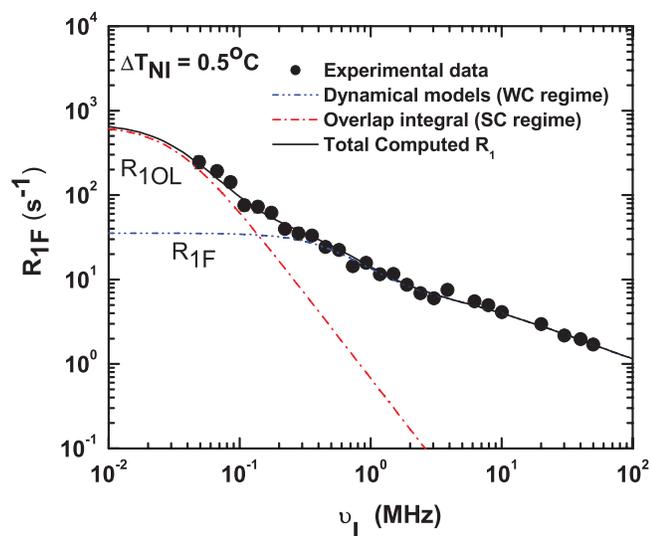


FIG. 8. Fluorine spin-lattice relaxation rate from dynamical models and cross-relaxation (overlap integral) at  $\Delta T_{NI} = 0.5$  °C.

Eq. (4)) to compare with the experimental data. Figure 8 depicts exclusively the effect of the contribution from this mechanism very near the transition. In view of the limited number of data points pertaining to this region of overlap (due to instrument limitations) the data fit to  $R_{1OL}$  in terms of Eq. (5) can at best be viewed as a demonstration of this interesting mechanism that could be detected in the FCNMR experiment, and the values of the fit parameters are thus providing reasonable order-of-magnitude estimates. We observe that the width of the Lorentzian line of the protons remains essentially constant with temperature (about 4 kHz) while that of the fluorine increases from about 20 kHz at the highest temperature to nearly 24 kHz very near the transition point. For comparison let the deviations of the experimental data at a given temperature from the prediction of dynamic models ( $R_{1F}$  in Eq. (4)) take place at some threshold value of the frequency ( $\nu_T$ , say) at the onset of discernible overlap of the lines. We find that  $\nu_T$  increases progressively with decrease of temperature and is maximum near the transition temperature. This is indicative of expected line broadening due to pretransitional effects, and the observed temperature variation of  $\Delta_F$  seems to support this. It may be further pointed out that the line widths obtained here are intrinsic and are free from the instrument artifacts (i.e., different from apparent line width values due to field inhomogeneities), since the observations pertain to dipolar interactions between nuclei residing on the same molecule. The experimentally measured values of these widths obtained from the respective free induction decays, which include contributions from field and sample inhomogeneities as well, are found to be about 45 kHz (for  $^{19}\text{F}$ ) and 16 kHz (for  $^1\text{H}$ ). These values are consistent with the observed (intrinsic) line width data, if we introduce identical correction factors to make up for the artifacts of the experiment. Finally, while the fluorine relaxation is seen to be profoundly influenced in the SC regime, such is not the case with protons—this mechanism does not lead to discernible additional contribution in this limit. This reflects the fact that there are several protons residing on the molecule having homo-nuclear dipolar interaction all through the dispersion regime (and thus having appreciable overlap integrals always), and hence addition of one more such coupling with fluorine is not making an observable difference.

## V. CONCLUSIONS

The present study attempts to interpret qualitatively different spin-lattice relaxation dispersions of two very similar nuclei with close gyromagnetic ratios ( $\gamma_H \approx \gamma_F$ , within 6%) in the isotropic phase of a liquid crystal. While there are a large number protons ( $^1\text{H}$ ) residing on the liquid crystal molecule, a lone fluorine ( $^{19}\text{F}$ ) is attached to the aromatic core of the molecule. Despite the limited access of the fluorine to couple to the lattice via the less ineffective hetero-nuclear dipolar interaction with protons, its relaxation rate shows strong dispersion and much stronger coupling to the lattice (by over an order of magnitude). This is interpreted as due to the effective coupling of fluorine to the lattice through spin-rotation interaction, and to the presence of slow enough modes in the system to produce appropriate correlations in the

angular momentum components of the molecules. Thus the chosen system is in a fortuitous circumstance of sampling two types of correlations of the dynamic processes of the system: molecular reorientational correlations through proton data and its angular momentum correlations through fluorine data. Interpretation of the experimental data is carried out recognizing this distinction. The FCNMR experiment also allows an effective contact of the fluorine system with protons (despite their differing  $\gamma$ 's) at low enough frequencies. In this regime, called the strong-coupling limit, the hetero-nuclear coupling acquires an effective homo-nuclear component due to the overlap of the resonance lines. This leads to cross-relaxation between the two spin systems, and its effect is especially dramatic on the spin-lattice relaxation of the lone fluorine in the molecule. The differing temperature dependences of the relaxation rates of the two nuclear species clearly indicate the presence of two distinct underlying molecular processes, but reported differently by the two participating probes. In that sense it seems profitable to probe the molecular dynamics through field-cycling NMR relaxometry with different nuclear spins with differing relaxation pathways. The interpretation of fluorine relaxation data based on SR interaction necessitated a scenario to include slow torques. Based on the conclusions of the earlier ESR experiments,<sup>23–25</sup> it is proposed that SRLS mechanism could be applicable to the present case leading to observed slow modes, even though quantitative analysis of the composite stochastic process at this stage is not feasible. Finally, the present FCNMR experiments<sup>27</sup> provide perhaps the first evidence of such slow modes with a direct mapping of their representative spectral density.

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