Quasi-equilibrium states in thermotropic liquid crystals studied by multiple quantum NMR

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Previous work showed that by means of the Jeener-Broekaert (JB) experiment, two quasi-equilibrium states can be selectively prepared in the proton spin system of thermotropic nematic liquid crystals (LC) in a strong magnetic field. The similarity of the experimental results obtained in a variety of LCs in a broad Larmor frequency range, with crystal hydrates, supports the assumption that also in LC the two spin reservoirs into which the Zeeman order is transferred, originate in the dipolar energy and that they are associated with a separation in energy scales: a constant of motion related to the stronger dipolar interactions ($\mathcal{S}$), and a second one corresponding to the weaker dipolar interactions ($\mathcal{W}$), truncated with respect to the Zeeman and the strong dipolar part. We study the nature of these quasiinvariants in nematic 5CB (4'-pentyl-4-biphenyl-carbonitrile) and measure their relaxation times by encoding the multiple quantum coherences of the states following the JB pulse pair on two orthogonal bases, Z and X. The experiments were also performed in powder adamantane at 301 K which is used as a reference compound having only one dipolar quasiinvariant. We show that the evolution of the quantum states during the build up of the quasi-equilibrium state in 5CB prepared under the $\mathcal{S}$-condition is similar to the case of powder adamantane. Also, we find that their quasi-equilibrium density operators have the same tensor structure. In contrast, the second constant of motion, whose explicit operator form is not known, involves a richer composition of multiple quantum coherences of even order greater than two, on the X basis, in consistency with the truncation inherent in the definition of this dipolar quasiinvariant. We exploited the exclusive presence of coherences of high order (± 4, ± 6, ± 8), besides 0 and ± 2 to measure the spin-lattice relaxation time $T_{\mathcal{W}}$ accurately, so avoiding experimental difficulties that usually impair dipolar order relaxation measurement such as Zeeman contamination at high fields, and also superposition of the different quasiinvariants. This procedure opens the possibility of measuring the spin-lattice relaxation of a quasiinvariant independent of the Zeeman and $\mathcal{S}$ reservoirs, so incorporating a new relaxation parameter useful for studying the complex molecular dynamics in mesophases. In fact, we report the first measurement of $T_{\mathcal{W}}$ in a liquid crystal at high magnetic fields. The comparison of the obtained value with the one corresponding to a lower field (16 MHz) points out that the relaxation of the $\mathcal{W}$-order strongly depends on the intensity of the external magnetic field, similarly to the case of the $\mathcal{S}$ reservoir, indicating that the relaxation of the $\mathcal{W}$-quasiinvariant is also governed by the cooperative molecular motions.

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