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UNIAXIAL RESTRICTED MOLECULAR REORIENTATION IN LIQUID CRYSTALS

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The model of the restricted, uniaxial, on the segment of the circle confined rotational diffusion of the proton within the molecule has been utilized for the interpretation of the published spin-lattice relaxation rates for the ring deuterons in 5CB - d_{15} liquid crystal in the nematic phase.

1. Introduction

The ordering of the transverse molecular oxes, which occurs in certain low temperature smectic liquid crystalline phases, is conveniently measured by ^{13}C NMR and ^{14}N NQR methods[1]. These measurements offer a firm evidence that the uniaxial reorientation of the molecular cores around their long axis are strongly biased in the sense that the uniform circular reorientations are no longer allowed.

Although it is generally assumed that in the nematic and also smectic A liquid crystalline phases the molecular uniaxial rotation is not biased, an evidence has been presented, based upon the cold neutron scattering techniques, that the MBBA rigid molecular core is in the nematic phase subjected to the localized reorientation. It has been modelled as uniaxial, on the segment of the circle of an apex angle ϕ_o, restricted rotational diffusion[2], restricted due to the steric hindrance of the adjacent molecules. It is expected that the proposed model would likely be of an interest in the low temperature biaxial smectics, and for this reason an additional and an independent test of its validity would be most helpful. In this respect, it is our purpose to show that the deuteron[3] spin-lattice relaxation rates, R, of the ring deuterons of 5CB-d_{15} nematic liquid crystal (which is locally slightly biaxial[4] can be understood in terms of the proposed restricted uniaxial rotational diffusion model

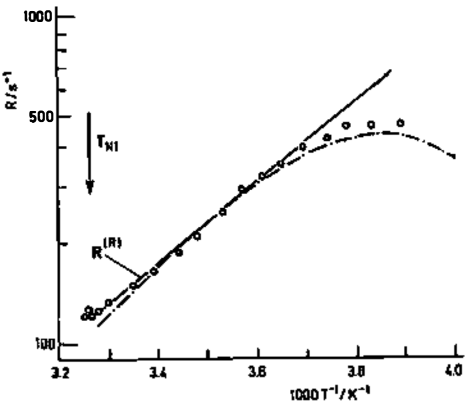

Fig.1. The values R as a function of reciprocal temperature for 5CB-d_{15} ring deuterons in the nematic liquid crystalline phase.

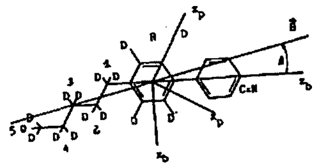

Fig.2. The molecule 5CB-d_{15} and the z coordinate axes defining the laboratory ($\vec{B}$), molecular (z_b) and deuteron principal axis (z_p).

As presented in Fig.1, the measured values[3] of R, for the ring deuterons only, see Fig.2, at the lowest temperature depart from the linear dependence on the T^{-1}.

2. Theoretical Background

The deuteron spin-lattice relaxation rate, R, is calculated by standard approach[3]. The calculation is essentially reduced to the evaluation of the expression

$$R = J_1(\omega_0) + 4J_2(2\omega_0) \quad (1)$$

$$J_h(h\omega_o) = \int < F^{(2,h)}(0) \cdot F^{(2,h)}(t)^* > \cos(h\omega_o)\, dt \qquad (2)$$

where $F^{(2,h)}(t)$ is h-th component of the irreducible spherical tensor representing the quadrupolar interaction expressed in the laboratory frame with the z axis parallel to the external magnetic field[3]. The angular bracket denotes an ensemble average.

As known, the principal frame for the quadrupolar interaction tensor for the deuteron at the site under consideration has its z-axis (denoted by z_p in Fig.2) along the C-D bond direction. In the principal axes system only $F_{pr}^{(2,0)}$ is to be considered nonzero[3], and equal to $\sqrt{3/2}\, q_{cd}$, where q_{cd} is the quadrupole coupling constant equal to q_{cd} = 185 kHz.

In order to incorporate into the calculation of R, for the ring deuteron, the model of the uniaxial restricted reorientation around the body z_b axis, Fig.2, one seeks the relationship between the time independent quantity $F_{pr}^{(2,h)}$ expressed in the principal axes of the quadrupolar interaction tensor and the time dependent component $F^{(2,h)}$ expressed in the laboratory system. This is accomplished by the two consecutive transformations of the reference frames depicted in Fig.2, namely the rotation of the principal axis system into the body frame and next the rotation from the body laboratory frame, defined by $\vec{B}$.

Then, the following is valid (in our case j" = 0),

$$F^{(2,h)}(t) = \sum_{i',j''} D^{(2)}_{i',h}\left(\Omega(t)\right) \cdot D^{(2)}_{j'',i'}\left(\Omega_{CD}\right) \cdot F_{pr}^{(2,j'')} \qquad (3)$$

where $D^{(2)}$ denotes the rotational matrix of the order 2, and $\Omega(t)$ is the set of Euler angles describing the appropriate axis transformation. Note that the set of Euler angles transforming the principal frame into the ring fixed frame is time independent. One proceeds by assuming a) that the restricted molecular reorientation occurs around the molecular para axis-z_b - and the angles $\alpha(t)$ and $\alpha(0)$ are uncorrelated and b) since the extent to which the molecular long axes fluctuations[5] around its average orientation in space is unknown, in the first approximation one puts $\beta(t) \approx \beta(0)$. The last assumption is certainly invalid close to the nematic-isotropic transition point, however this is the region which does not interest us at all in this work.

The correlation function to be calculated now reads

$$G_h(t) = \langle F^{(2,h)}(0) \, . \, F^{(2,h)}(t)^* \rangle = \langle e^{-ih\gamma(0)} . \, e^{ih\gamma(t)} \rangle \, . \tag{4}$$
$$\sum_{i'} \langle \, | D^{(2)}_{i',h} (\alpha, \beta, 0)|^2 \rangle | D_{0,i'} (\Omega_{CD})|^2 . |F^{(2,0)}_{pr}|^2$$

where h=1,2. The ensemble average $\langle e^{-ih\,\gamma(0)} . e^{ih\,\gamma(t)} \rangle$ to be calculated is just a particular term of the general expression appearing in the calculation of the incoherent scattering function $S(Q,\omega)$ for this model of reorientation[2)], and reads:

$$\langle e^{-ih\gamma(0)} \, . \, e^{ih\gamma(t)} \rangle = \frac{2}{\phi_o^2} \cdot \Bigg\{ \frac{1-\cos(h\,\phi_o)}{h^2} + 2 \sum_{r=1}^{\infty} \Bigg[\frac{h^2 |1-(-1)^r \cos(h\,\phi_o)|}{\left[\left(\frac{\pi r}{\phi_o}\right)^2 - h^2\right]^2} \, . \, e^{-\frac{r^2 \pi^2 D}{\phi_o^2} \cdot t} \, . \left(1-\delta_{h,\left(\frac{\pi r}{\phi_o}\right)}\right) + \frac{\phi_o^2}{8} \, \delta_{h,\left(\frac{\pi r}{\phi_o}\right)} . \, e^{-h^2 D t} \Bigg] \Bigg\} \tag{5}$$

where D is the unknown "angular" rate constant for the described process. The second rotational matrix in eq. (4) is just equal to $P_2(\cos \beta_{CD})$, where β_{CD} = 60 degrees, and the first one can be expressed in terms of the usual order parameters of the order two and four, i.e. S_2 and S_2 and S_4. The expression is to be evaluated at the resonance frequency for deuterons in question, where ω_o = 30.7 MHz. Defining the temperature dependent coefficients, from eq. (4), as A(T) and B(T), one finds (uncorreladed α's)

$$A(T) = \frac{3}{2} \langle \sin^2\beta \, . \cos^2\beta \rangle . |P_2(\cos \beta_{CD})|^2 \; ;$$
$$B(T) = \frac{3}{8} \langle \sin^4\beta \rangle |P_2(\cos \beta_{CD})|^2 \tag{6}$$

It is to be noted that both coefficients above exhibit relatively weak temperature dependence, as it is evident from the expressions $A=0.003125 + 0.002232S_2 - 0.00536S_4$, and $B=0.012500 - 0.017857S_2 + 0.00536S_4$. Inserting eq. (5) into eq. (4) and using the defining expression eq. (1), the relaxation rate is for the case of the restricted (i.e. biased rotation) reorientational model written as:

$$R = \frac{6\, q_{CD}^2}{\pi^2 D} \cdot \sum_{j=1}^{\infty}\sum_{h=1}^{2} \frac{|1-(-1)^j \cos(h\,\phi_o)|}{[(\frac{\pi j}{\phi_o})^2 - h^2]^2} \times \frac{(hj)^2 \cdot a_h}{j^4 + \left[\frac{h\,\omega_o \phi_o^2}{\pi^2 D}\right]^2} \qquad (7)$$

where, a_1 = A(T) and a_2 = B(T), eq. (6) (uncorreladed α' s).

3. Results and Discussion

If, on the other hand, one assumes that the Euler angles, $\alpha(0)$, and $\alpha(t)$ change slowly in time, meaning that the long molecular axis does not process, then in eq. (4) all i' terms have to be taken into account. In this case the coefficients A(T), and B(T) read: A(T) = 0.15313 - 0.037948S + 0.123213S_4, and B(T) = 1.02500 - 0.05804S - 0.13393S_4. The curves are sensitive to the value of the apex angle ϕ_o, but much more so to the value of the rate constant, D, as a function of temperature.

Now, assuming the Arrehenius relationship, D=D'$\times$ exp(-E'/T), to describe validity the temperature dependence of the angular rate constant, D, for the process described, the nematic phase ring deuteron spin-lattice relaxation rates can under certain condition indeed describe the experiment as presented in Fig.1. The computation is a sensitive probe of the apex angle value ϕ_o, which seems to be (almost) temperature independent quantity. On Fig.1 is presented a case of computation for the value of the apex angle ϕ_o=5.5 rad (D'=1.4x10(+15)s^{-1} and E'=-4.78x10(+3)) K. Here, D' is the rate constant taken at the infinite temperature. If the apex angle is close to 2π or just π, the uniaxial reorientation of the ring deuterons along the body para axis is in this symmetrical case clearly identical. It is to be emphasized that the reorientation in question is not the flipping motion (180 degrees jumps between the two potential minima) but can be described in terms of the diffusion on the segment of the circle of an apex angle π.

The apparent controversy regarding the local biaxiallity even in the nematic liquid crystals and the 360 degrees uniaxial rotational molecular motion in these phases can be now very simply resolved. It can be shown that for $\phi_o=2\pi$, eq. (5) reduces to exponential terms and consequently the relaxation rate R is in this case (apart from the numerical constant) in its form the same as for the simple rotational diffusion model. Thus, it is possible to interpret the experiments in terms of expressions which in reality correspond to different physical situations and as far as liquid crystals are concerned a very important and indcative information is offered by the measurement of the local biaxial parameter. It would seem that this being nonzero, the uniaxial reorientation is not likely to be different from the just described.

The proposed model of uniaxial reorientation seems to be the only one able to relate the notion of the local biaxiallity and the molecular reorientational motion (biased rotation), particularly in low temperature liquid crystalline phases.

In conclusion, the temperature dependence of the published deuteron spin-lattice relaxation time measurements for the phenyl ring in the nematic phase of 5CB-d_{15} liquid crystal is interpreted in terms of the uniaxial biased rotation model, according to which the phenyl ring is subjected to the continuous, along its para axis rotational diffusion on the segment of the circle of an apex angles ϕ_0 = 5.5 rad. This conclusion is in agreement with the previously established fact that the ordering of the phenyl ring exhibits a slight biaxiallity. These deuteron spin-lattice relaxation time measurements seem to constitute an independent evidence that even in the high temperature nematic phases the molecular uniaxial rotation might be biased.

References

1. R. Blinc, J. Dolinsek, M. Luzar and J. Selinger, Liquid Cryst., 3, (1988) 663.

2. B. Cvikl and u. Dahlborg, M. Copic, J. Peternelj, T. Kinell and V. Dimic, J.A. Janik, submitted for publication.

3. P.A. Beckmann, J.W. Emsley, G.R. Luckhurst and D.L. Turner, Molec. Phys., 59 (1986) 97.

4. J.W. Emsley, G.R. Lockhurst and C.P. Stockley, Molec. Phys., 44 (1981) 565.

5. B. Cvikl, Liquid Cryst., 2, (1987) 149.