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COMMENT ON "MOLECULAR ORDER VERSUS CONFORMATIONAL CHANGES IN THE LIQUID-CRYSTAL PHASES"

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ABSTRACT : We show that the theoretical arguments of Bos and Doane[3] to explain the relative temperature dependence of the deuteron NMR splittings in liquid crystals, in terms of more than one order parameter, can be seriously questioned, and that for TBBA, the explanation should necessarily introduce the temperature dependence of the averages over the internal motions.

In deuterium magnetic resonance (DMR) studies of liquid crystals, it is generally observed that, even in the uniaxial phases, the splittings corresponding to deuterons at different sites of the molecules are not proportional to one another when the temperature is varied. This result is often interpreted by authors[1] by the fact that, the actual molecules being not rigid objects, the preferred conformation changes with temperature. In recent papers[2,3] Doane et al have proposed a different explanation, namely that these temperature dependences can be fully explained in terms of more than one order parameter each having a different temperature dependence. In particular, it is claimed[3] that the uniaxial phases are characterized by the two order parameter S_{zz}^{ZZ} and $S_{xx}^{ZZ} - S_{yy}^{ZZ}$, and for the tilted smectic C phase, the third order parameter S_{yz}^{ZZ} is also required. In these expressions, xyz refer to a molecular frame with Oz along the long molecular axis and XYZ refers to a laboratory frame with OZ along the static magnetic field $\underline{H}_0$.

In this letter, we question the theoretical arguments put forward to explain these results and we show on one example that this explanation is probably not the correct one. On the other hand, the experimental analysis of ref. 3 and thus its conclusions has been criticized by other authors[4].

We first repeat the calculation of the DMR splitting $\Delta\nu_i$ of a deuteron D_i. If we assume that the e.f.g. tensor is axially symmetric around the C-D_i bond, we have

$$\Delta\nu_i = \frac{3}{2}\frac{e^2q_iQ}{h} S^{ZZ}_{uu} \tag{1}$$

with

$$S^{ZZ}_{uu} = \langle P_2[\cos(\underline{u}^i,\underline{H}_o)]\rangle \tag{2}$$

where $\underline{u}^i$ is the unit vector along the C-D_i bond. The other symbols have their usual signification[3]. To calculate explicitly $\Delta\nu_i$, we can use the ordering tensor formalism[5] $S^{\alpha\beta}_{\mu\nu}$ with α,β = X,Y,Z and μ,ν = x,y,z or equivalently the Euler angle formalism. In this case, we define Ψ,θ,ϕ as the three Euler angles which bring the molecular Oxyz frame onto the laboratory OXYZ frame. Physically, Ψ is the angle which defines the molecular rotation around the Oz axis, and θ and ϕ are spherical coordinates which define the molecular Oz axis in the laboratory frame.

With these definitions, it can be easily shown that we have either[5]

$$\Delta\nu_i = \frac{3}{2}\frac{e^2q_iQ}{h} \sum_{\mu,\nu=x,y,z} S^{ZZ}_{\mu\nu}\langle u^i_\mu u^i_\nu\rangle \tag{3}$$

or equivalently,

$$\Delta\nu_i = \frac{3}{2}\frac{e^2q_iQ}{h}[A+B+C+D+E] \tag{4}$$

with

$$A = \langle P_2(\cos\beta_i)\rangle\langle P_2(\cos\theta)\rangle = \langle P_2(\cos\beta_i)\rangle S^{ZZ}_{zz} \tag{5a}$$

$$B = \frac{3}{4}\langle\sin^2\beta_i\cos2\alpha_i\rangle\langle\sin^2\theta\cos2\Psi\rangle = \frac{1}{2}\langle\sin^2\beta_i\cos2\alpha_i\rangle(S^{ZZ}_{xx}-S^{ZZ}_{yy})$$

$$C = \frac{3}{4}\langle\sin2\beta_i\cos\alpha_i\rangle\langle\sin2\theta\cos\Psi\rangle = \langle\sin2\beta_i\cos\alpha_i\rangle S^{ZZ}_{xz} \tag{5c}$$

$$D = \frac{3}{4}\langle\sin^2\beta_i\sin2\alpha_i\rangle\langle\sin^2\theta\sin2\Psi\rangle = \langle\sin^2\beta_i\sin2\alpha_i\rangle S^{ZZ}_{xy} \tag{5d}$$

$$E = \frac{3}{4}\langle\sin2\beta_i\sin\alpha_i\rangle\langle\sin2\theta\sin\Psi\rangle = \langle\sin2\beta_i\sin\alpha_i\rangle S^{ZZ}_{yz} \tag{5e}$$

In these expressions, the u^i_μs are the components, and β_i, α_i the spherical co-ordinates, in the molecular frame, of the unit vector $\underline{u}^i$. Note also that the angle ϕ do not appear in the formulae. The brackets around the $u^i_\mu u^i_\nu$ in Eq. (3) or around the functions of α_i and β_i in Eqs. (5) stand for an average over the internal motions. These motions are assumed not to be coupled with the overall molecular motions.

We now come to the theoretical argument of ref. 3 to justify that for the uniaxial phases, only the terms A and B are non-zero. This argument is that three order parameters S^{ZZ}_{xz}, S^{ZZ}_{xy} and S^{ZZ}_{yz} are zero by symmetry, because the medium is apolar! This cannot be the reason because the apolar condition, namely the fact that the XY plane is a plane of symmetry for the medium, implies that only off-diagonal terms $S^{\alpha\beta}_{\mu\nu}$ with $\alpha \neq \beta$ are zero[5]. Since such terms do not appear in the expression of the splitting, this symmetry argument is irrelevant in the present problem. In fact, it seems that there has been confusion in ref. 3 between the microscopic properties associated with the indexes $\alpha\beta$ and the molecular properties associated with the indexes μ ν. This confusion is equivalent in interchanging the laboratory and the molecular frames, or in terms of the Euler angles, in interchanging Ψ and ϕ. It seems that the same confusion has been made in another paper of the same group[6] where the authors present extensive nuclear quadrupole resonance calculations in liquid crystals.

It is important to note that Eqs. (3) and (4) are very general since no hypothesis is made on the nature of the phase (uniaxial or biaxial, polar or apolar), and on the properties of the molecules (shape, intermolecular forces). The only assumption made concerns the decomposition of the motion at the spin sites into an internal motion and an overall molecular motion. The fact that only the five order parameters $S^{ZZ}_{\mu\nu}$ among the 25 $S^{\alpha\beta}_{\mu\nu}$ are requested in the expression of the splitting is a property of NMR in high magnetic field. It should be stressed however that this is true because the ordering tensor is defined from a laboratory frame with $\underline{OZ} = \underline{H}_o$. If the director $\underline{n}$ is along $\underline{H}_o$, as it is usually the case for the uniaxial phases which have been aligned by simply cooling the sample in the field, the meaning of the $S^{ZZ}_{\mu\nu}$ appearing in Eqs. (5) are the usual ones[5]. If on the contrary, we are dealing with "aligned" tilted smectic phases or with a situation where $\underline{H}_o$ has been rotated with respect to the direction of alignment of the molecules, it may be convenient to express the $S^{ZZ}_{\mu\nu}$ in terms of the more physical quantities $S^{\alpha'\beta'}_{\mu\nu}$ where $\alpha',\beta' = X',Y',Z'$ with OX',OY',OZ' along characteristic directions of the medium.(e.g. for a smectic C phase, OZ' is naturally chosen along the normal to the planes and OX' along the C director). Clearly, in this case, all the 25 $S^{\alpha'\beta'}_{\mu\nu}$ will a priori be involved in the most general expression of the splitting.

Now, if one wants to reduce the number of terms in Eq. (4), it is necessary not to make assumptions on the symmetry of the phase[3], but on the symmetry and the time scale of the molecular motions which affect the angles Ψ and θ, namely the rotation around the long axis and the polar fluctuations of this axis about $\underline{H}_o$. If these motions are sufficiently rapid compared to the time scale of NMR ($\sim 10^{-6}$ s for DMR) and occur in a mean-field orientational potential $V(\Psi,\theta,\phi)$ such that $V(-\Psi,\theta,\phi) = V(\Psi,\theta,\phi)$, then S^{ZZ}_{yz} and S^{ZZ}_{xy} are zero and Eq. (4) reduces to three terms A, B and C only. If in addition $V(\pi-\Psi,\theta,\phi) = V(\Psi,\theta,\phi)$, then $S^{ZZ}_{xz} = 0$ and Eq. (4) reduces to the terms A and B only. This is just what the authors of ref. 3 claim to be the situation for the uniaxial phases. We show here that this situation is associated to the above mentioned properties of the motions, independently of the fact that the medium is apolar. Concerning a more general case, it seems difficult to imagine which properties should have the potential to be such that S^{ZZ}_{xz} and S^{ZZ}_{xy} are zero, but S^{ZZ}_{yz} different of zero, as it is claimed to be the case for the smectic C phase.

We now return to the situation described by the terms A and B only and try to see if it applies to the mesophases of TBBA. We have, dropping the index ZZ for simplicity :

$$\Delta\nu_i = \Delta\nu_i(A)+\Delta\nu_i(B) = \frac{3}{2}\,\frac{e^2 qiQ}{h}[<P_2(\cos\beta_i)>S_{zz}+\frac{1}{2} <\sin^2\beta_i\cos 2\alpha_i>(S_{xx}-S_{yy})] \qquad (6)$$

Let us estimate an upper value for the contribution $\Delta\nu_i(B)$. We clearly have

$$|\Delta\nu_i(B)| \leq \frac{3}{4}\left|\frac{e^2 qiQ}{h}(S_{xx}-S_{yy})\right| \qquad (7)$$

For this calculation, we use the results of refs. 7 and 8. In these papers, assuming that the rotation around the Oz axis and the fluctuations of this axis are not coupled, it has been shown that in the lowest temperature range of the smectic C phase, we have $<\cos 2\Psi> < 0.005$. It is likely that the value of this parameter is (much) smaller in the uniaxial smectic A and nematic phases. On the other hand, S_{zz} is found to vary from ~ 0.8 near the smectic C-smectic H transition to ~ 0.32 near the nematic-isotropic transition[8]. Since the motions are assumed independent, we have $S_{xx}-S_{yy} \approx <\frac{3}{2}\sin^2\theta><\cos 2\Psi> = (1-S_{zz})<\cos 2\Psi>$. With $<\cos 2\Psi> = 0.005$ and the above values of S_{zz}, we find that $S_{xx}-S_{yy}$ varies between ~ 0.001 and 0.0035. With $e^2q_iQ/h \approx 177$ kHz[8], Eq. (7) finally shows that the contribution of $\Delta\nu_i(B)$ to Eq. (6) is (much) smaller than 0.13 - 0.46 kHz in the smectic C, smectic A and nematic phases of

TBBA. This result means that in these phases, the second term of Eq. (6) is negligible in practice since it is always within the uncertainty with which the deuteron splittings are measured from the spectra[9,10]. It may be argued that this result has been obtained within the assumption of uncoupled motions, which may be rather rough. We have thus repeated the calculation of $S_{xx}-S_{yy}$ in the presence of some coupling. For this purpose, we have assumed the simplest potential of the required symmetry, namely $V(\Psi,\theta,\phi) = aP_2(\cos\theta)+\frac{3}{2}b\sin^2\theta\cos 2\Psi$ and calculated numerically the values of the parameters a and b which explain the above values of S_{zz} and $<\cos 2\Psi>$. Then using these values of a and b, we have calculated $S_{xx}-S_{yy} = \frac{3}{2}<\sin^2\theta\cos 2\Psi>$. The extreme values found for $S_{xx}-S_{yy}$ are now $\sim$ 0.002 and 0.005 corresponding to $\Delta\nu_i(B)$ (much) smaller than 0.26 - 0.66 kHz. It is seen that also in this case $\Delta\nu_i(B)$ is negligible. These results show that if the theory of ref. 3 applied to TBBA, all the deuteron splittings of the TBBA should remain proportional as the temperature is varied. However, from the data of refs. 9 and 10, it is observed that they are not. The only way to explain this result is to assume that the $<P_2(\cos\beta_i)>$ are functions of temperature[1] or, more precisely, that the internal averages at the different deuteron sites do not have the same temperature dependence. This will be detailed in a forthcoming paper.

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