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A special method of deformational correction in N.M.R. of molecules dissolved in liquid crystals

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A simple method of deformational correction for the N.M.R. spectral parameters of molecules dissolved in liquid crystals is described. The method is applicable to the different isotopically substituted derivatives of the molecules belonging to the cubic point groups. Its validity is verified for the dipolar and quadrupolar couplings observed in the molecules CH_4, CD_4 and CH_3D dissolved in the liquid crystals Merck Phase IV, Merck ZLI 1167 and their mixtures.

1. Introduction

In analysing the N.M.R. spectral parameters of molecules in liquid crystals the correlation between the reorientational and vibrational motions should be allowed for. It arises from the anisotropic intermolecular forces and gives rise to the so-called deformational contributions to the spectral parameters (as well as small higher order terms) [1–3]. When the expressions of the deformational contributions are introduced into the equations of the spectral parameters, detailed information on the undistorted molecular properties (geometry etc.) and on the anisotropic forces acting on the segments of the molecules may be obtained.

It is shown here that in some cases the experimental values of the spectral parameters of different isotopic species of the molecule can be used to correct them for deformations. The resulting parameters can be subjected to the simple analysis which neglects entirely the deformational contributions. It allows the determination of the undistorted molecular properties, but information on the details of the anisotropic forces is lost. The method is tested for the dipolar and quadrupolar couplings of the isotopic species $^{13}CH_4$, $^{12}CD_4$ and $^{13}CH_3D$ of methane.

2. Theory

The weak-orientation limit of the deformational contribution to the N.M.R. observable T_{aniso} can be written as [3, 4]

$$T^{d}_{\text{aniso}} = \frac{1}{5}\sum_{r,s} F^{-1}_{rs} \sum_{\alpha,\beta} T_{\alpha\beta,r} A_{\alpha\beta,s}. \qquad (1)$$

Here F^{-1}_{rs} is the inverse of the harmonic force constant matrix in the symmetry coordinate representation and $T_{\alpha\beta,r}$ and $A_{\alpha\beta,s}$ are the derivatives of the tensors $T_{\alpha\beta}$ and $A_{\alpha\beta}$ with respect to the symmetry coordinates, S_r and S_s, taken at the equilibrium geometry. The tensor $T_{\alpha\beta}$ describes molecular properties such as dipolar or quadrupolar coupling and the observable T_{aniso} is $\langle T_{\parallel}\rangle - T_{\text{iso}}$ where $\langle T_{\parallel}\rangle$ is the average value of the element of $\mathbf{T}$ in the direction of the axis of the uniaxial environment (i.e. the director) and T_{iso} is one-third of the average value of the trace of $\mathbf{T}$ [3]. The symmetric and traceless *interaction tensor* $A_{\alpha\beta}$ is defined by the truncated series expansion of the anisotropic potential energy U_{ext} of the molecule in terms of the direction cosines of the director in the molecular frame, $\cos\theta_\alpha$ [1, 3]

$$U_{\text{ext}} = -\frac{3}{2}\sum_{\alpha,\beta} A_{\alpha\beta}\cos\theta_\alpha\cos\theta_\beta. \tag{2}$$

The tensor elements $T_{\alpha\beta}$ and $A_{\alpha\beta}$ in equation (1) are referred to the Eckart axis system of the molecule. The definition of this system involves the nuclear masses; generally a change in the masses gives rise to translation and rotation of the Eckart axis system with respect to the molecule. Consider now the axes μ, ν which do *not* depend on the masses and coincide with the Eckart axes α, β only if the molecule is the most symmetric member of a group of different isotopic species. The relations between the tensor elements in this special axis system, $T_{\mu\nu}$, and in the Eckart axis system, $T_{\alpha\beta}$, are

$$T_{\alpha\beta} = \sum_{\mu,\nu} l_{\mu\alpha} l_{\nu\beta} T_{\mu\nu}, \tag{3}$$

where $l_{\mu\alpha}$ are the cosines of the angles between the μ and α axes. Hence

$$T_{\alpha\beta,r} = \sum_{\mu,\nu} (l_{\mu\alpha} l_{\nu\beta})_r T^{\text{e}}_{\mu\nu} + \sum_{\mu,\nu} l^{\text{e}}_{\mu\alpha} l^{\text{e}}_{\nu\beta} T_{\mu\nu,r}, \tag{4}$$

where the subscript r signifies differentiating (in equilibrium) with respect to the symmetry coordinate S_r (defined identically for all the isotopically related molecules) and e denotes the value at the equilibrium geometry. If the Eckart axes are chosen to coincide in equilibrium for all the different isotopic species, then the cosines $l^{\text{e}}_{\mu\alpha}$ ($= 1$ or 0) are isotope independent. Thus, the latter term in equation (4) is isotope independent, if the trivial effect of the nuclear mass dependence of the tensor $T_{\mu\nu}$ (arising from the magnetogyric ratios etc.) is ignored.

Hence, the deformational contribution in equation (1) can be written as

$$T^{d}_{\text{aniso}} = \frac{2}{3}\sum_{\mu,\nu} T^{\text{e}}_{\mu\nu} S^{*}_{\mu\nu} + T^{*}_{\text{aniso}}, \tag{5}$$

where

$$S^{*}_{\mu\nu} = \frac{3}{10}\sum_{r,s} F^{-1}_{rs} \sum_{\alpha,\beta} (l_{\mu\alpha} l_{\nu\beta})_r A_{\alpha\beta,s}, \tag{6}$$

$$T^{*}_{\text{aniso}} = \frac{1}{5}\sum_{r,s} F^{-1}_{rs} \sum_{\alpha,\beta}\sum_{\mu,\nu} l^{\text{e}}_{\mu\alpha} l^{\text{e}}_{\nu\beta} T_{\mu\nu,r} A_{\alpha\beta,s}. \tag{7}$$

The first term in equation (5) has exactly the same form as the equilibrium contribution to T_{aniso},

$$T^{\text{e}}_{\text{aniso}} = \frac{2}{3}\sum_{\mu,\nu} T^{\text{e}}_{\mu\nu} S^{D}_{\mu\nu}, \tag{8}$$

where $S^{D}_{\mu\nu}$ is the orientational tensor (referenced to the director) [3]. Thus, to a good approximation (neglecting the vibrational corrections, which are very small in the weak-orientation limit)

$$T_{\text{aniso}} - T^{*}_{\text{aniso}} = \frac{2}{3}\sum_{\mu,\nu} T^{\text{e}}_{\mu\nu}(S^{D}_{\mu\nu} + S^{*}_{\mu\nu}). \tag{9}$$

The parameters $T_{\text{aniso}} - T^*_{\text{aniso}}$ behave as if they originated from an ideal, strictly rigid molecule suffering no deformations. The tensor $S^D_{\mu\nu} + S^*_{\mu\nu}$ is physically different from the true orientational tensor $S^D_{\mu\nu}$. Formally, however, they have same characteristics; both are symmetric and traceless second rank tensors which are specified by the same number of independent parameters (this number is determined by the symmetry of the molecule).

The term T^*_{aniso} in equation (7) is isotope independent, if the parent molecule of the isotopic species belongs to one of the cubic point groups (ignoring the isotope dependence of the magnetogyric ratios and the nuclear quadrupole moments). Then $A^e_{\mu\nu} = 0$ and therefore the derivatives $A_{\alpha\beta,s}$ are isotope independent (*cf.* equation (4) which is valid for the tensor $A_{\alpha\beta}$ also), provided that the interactions do not depend on the nuclear masses. This term can be determined experimentally, because it is simply the observable T_{aniso} of the parent molecule ($S^D_{\mu\nu} + S^*_{\mu\nu}$ is zero as a result of the cubic symmetry, and thus $T_{\text{aniso}} = T^*_{\text{aniso}}$). Hence, the observables T_{aniso} of the other isotopic species can be corrected by the experimental parameters T^*_{aniso}. The resulting parameters $T_{\text{aniso}} - T^*_{\text{aniso}}$ can be analysed as if the deformations were absent, to obtain unperturbed molecular properties (tensor elements $T^e_{\mu\nu}$) but an incorrect orientational tensor ($S^D_{\mu\nu} + S^*_{\mu\nu}$).

3. Application to methane

Burnell and de Lange [5] have observed that their N.M.R. results on methane and its deuteriated analogues behave as if the deformational contributions were isotope independent. This result can now be reinterpreted as a verification of the validity of these theoretical predictions for the molecules and liquid crystals studied.

To obtain more experimental data, the isotopic species $^{13}CH_4$, $^{12}CD_4$ and $^{13}CH_3D$ (from Merck, Sharp and Dohme) were studied in the liquid crystals Merck Phase IV (eutectic mixture of *p*-methoxy-*p*′-*n*-butyl-azoxybenzenes), Merck ZLI 1167 (a mixture of three cyclohexyl-cyclohexanes) and their mixtures. The ^1H, ^2H and ^{13}C N.M.R. spectra were recorded on a JNM-GX400 spectrometer at 308 K. Coaxial 5 mm o.d. double tube systems with $CDCl_3$ as a locking substance in the annulus were used in measuring the ^1H and ^{13}C spectra, whereas the ^2H spectra were obtained from 10 mm o.d. tubes without locking. The dipolar couplings of $^{13}CH_3D$ were resolved with the aid of the program LEQUOR [6] (in the present paper the dipolar and quadrupolar couplings, D_{ij} and B_i, are defined as in [5]). These couplings are given in the table together with the values of the dipolar couplings of $^{13}CH_4$ corresponding, as accurately as possible, to the compositions and temperatures of the samples containing $^{13}CH_3D$.

To obtain the dipolar couplings of $^{13}CH_4$ at all the relevant compositions of the solvent, linear least-squares fits to the experimental values were performed. The results are shown in figure 1. For example, it was not possible to resolve the very small HH splittings of $^{13}CH_4$ in ZLI 1167, but it may be concluded from figure 1 that the corresponding D_{HH} (referenced to the director) is about $-0{\cdot}09$ Hz. Incidentally, this result seems to confirm the suggestion of Burnell and de Lange [5] that the D_{HH} of $^{13}CH_4$ is negative in the closely related liquid crystal ZLI 1132.

The species $^{13}CH_3D$ belongs to the point group C_{3v} and therefore its tensor $S^D_{\mu\nu} + S^*_{\mu\nu}$ is specified by one independent parameter. Hence, the ratios of the corrected couplings $D_{ij} - D^*_{ij}$ and $B_i - B^*_i$ should be solvent-independent constants (D^*_{ij} and B^*_i are the corresponding couplings in the T_d species $^{13}CH_4$ and $^{12}CD_4$ which have been appropriately scaled by the magnetogyric ratios, when necessary). The theoretical

Dipolar couplings (referenced to the director) of $^{13}CH_3D$ and $^{13}CH_4$ in the liquid crystals Phase IV, ZLI 1167 and their mixtures.

wt % ZLI 1167 (*a*)	$D_{HH}(CH_3D)$/Hz	$D_{HD}(CH_3D)$/Hz	$D_{CH}(CH_3D)$/Hz	$D_{CD}(CH_3D)$/Hz	$D_{HH}(CH_4)$/Hz	$D_{CH}(CH_4)$/Hz
0	−4·603(22) (*c*)	0·960(29)	5·89 (5)	3·260(14)	0·462 (*d*)	9·763
20	−4·259(23)	0·647(30)	2·18 (5)	2·415 (5)	0·382	6·260
40	−4·170 (4)	0·723 (5)	−0·629 (8)	1·911 (5)	0·248 (*e*)	3·234 (*e*)
58	−4·316 (8)	0·957(10)	−3·003(18)	1·533 (6)	0·140	0·586
84 (*b*)	−4·252(10)	0·692(12)	−6·176(20)	–	−0·001 (*e*)	−3·837 (*e*)
100 (*b*)	−4·446(26)	0·718(34)	−9·36 (6)	0·422(18)	−0·091 (*e*)	−6·500

(*a*) The samples contained $^{13}CH_3D$ or $^{13}CH_4$ at approximately 1 atm.

(*b*) The director was perpendicular to the magnetic field.

(*c*) Uncertainties in parentheses are one standard deviation in the last figure quoted.

(*d*) Uncertainties of the couplings of CH_4 are estimated to be within 0·05 Hz for D_{HH} and 0·5 Hz for D_{CH} (a source of uncertainty is that the spectra of CH_4 and CH_3D were obtained from different sample tubes and thus the two molecules were not in exactly identical surroundings).

(*e*) Values estimated by the linear least squares fits to the experimental couplings (see figure 1).

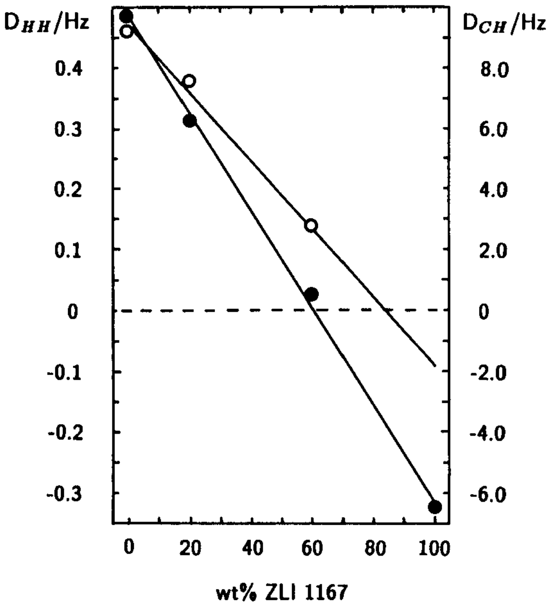

Figure 1. The dipolar couplings (referenced to the director) of $^{13}CH_4$, D_{CH} (full circles) and D_{HH} (open circles), as a function of the composition of the liquid crystal solvent. The straight lines are the linear least-squares fits to the experimental results.

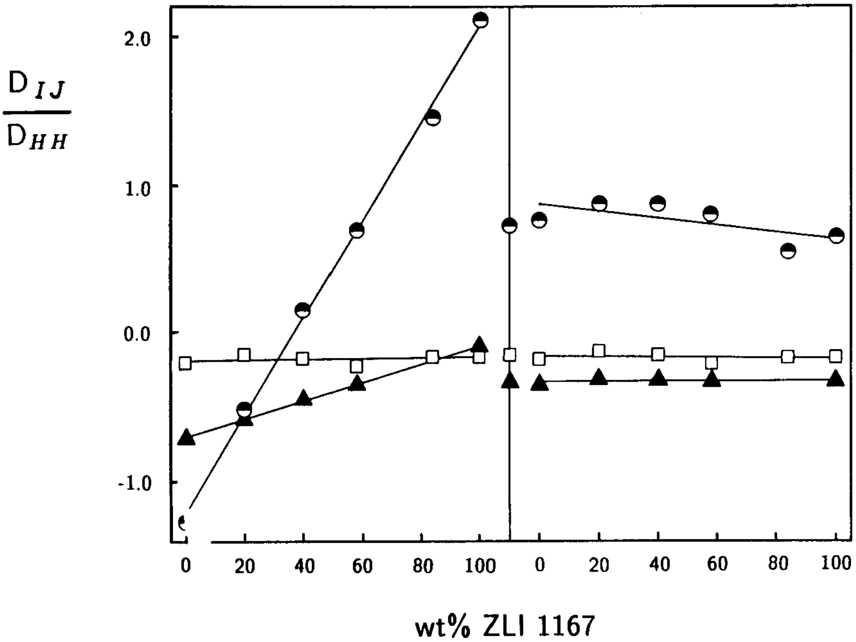

Figure 2. The ratios of the dipolar couplings of $^{13}CH_3D$, D_{HD}/D_{HH} (squares), D_{CH}/D_{HH} (circles) and D_{CD}/D_{HH} (triangles), as a function of the composition of the liquid crystal solvent. The ratios of the uncorrected couplings are on the left, those of the corrected couplings are on the right, and the theoretical equilibrium values of the ratios are shown in the middle of the figure. The straight lines are the linear least-squares fits to the experimental results.

values of these ratios can be calculated from the known equilibrium properties of the methane molecule (tetrahedral bond angles, bond lengths of 1·0858 Å [7], and (*ab initio*) deuterium quadrupole coupling constants of 200·4 kHz [8]). The theoretical ratios of the dipolar couplings ($D^e_{HH} : D^e_{HD} : D^e_{CH} : D^e_{CD} = 1 : -0{\cdot}1535 : 0{\cdot}7300 : -0{\cdot}3361$) are shown in figure 2 together with the corresponding uncorrected and corrected experimental values.

The validity of the theoretical framework is confirmed: the ratios of the corrected couplings are nearly constants and, moreover, are in good agreement with the predicted values. The linear least-squares fits to the corrected ratios result in the lines whose slopes (≈ 0) and intercepts ($\approx D^e_{ij}/D^e_{HH}$) agree with the theory within their statistical errors.

Finally, the quadrupolar couplings B_D determined in the liquid crystal mixture 58 wt % ZLI 1167/42 wt % Phase IV are also consistent with the theory. The values of B_D for CH_3D and CD_4 are $-87{\cdot}5 \pm 1{\cdot}0$ Hz and $-21{\cdot}4 \pm 1{\cdot}0$ Hz, respectively. Hence, the ratio B_D/D_{HH} is 20·3 for the uncorrected couplings of CH_3D and 14·8 for the corrected couplings, the latter value being in agreement (within its estimated uncertainty) with the theoretical ratio of $B^e_D/D^e_{HH} = 14{\cdot}0$.

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