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Tritium nuclear magnetic resonance study of T_2, HT, and DT dissolved in nematic solvents

E. E. Burnell,[1] C. A. de Lange,[2] A. L. Segre,[3] D. Capitani,[3] G. Angelini,[4] G. Lilla,[4] and J. B. S. Barnhoorn[2]
[1]*Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada V6T 1Z1*
[2]*Laboratory for Physical Chemistry, University of Amsterdam, Nieuwe Achtergracht 127, 1018 WS Amsterdam, The Netherlands*
[3]*Istituto di Strutturistica Chimica, Consiglio Nazionale delle Ricerche, Area della Ricerca di Roma, Via Salaria km 29, 300 Montelibretti, Casa Postale 10 00016 Monterotondo Stazione, Roma, Italy*
[4]*Istituto di Chimica Nucleare, Consiglio Nazionale delle Ricerche, Area della Ricerca di Roma, Casa Postale 10 00016 Monterotondo Stazione, Roma, Italy*

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A tritium nuclear magnetic resonance study is carried out on the T_2, HT, and DT isotopomers of dihydrogen dissolved in various nematic phases, including a zero-electric-field-gradient mixture. *Ab initio* calculations are performed to reproduce the observed dipolar couplings. Within the framework of the ‘‘mean-field’’ approximation, the results provide support for a picture in which two independent contributions to the solute orientation can be distinguished. One contribution involves a liquid-crystal-dependent interaction between the mean solvent electric-field gradient and the solute molecular quadrupole moment. The other contribution is of unknown origin; however, it is essentially identical in all liquid crystals and it can be modeled adequately with a phenomenological mean-field interaction. A remarkable feature of this second interaction is that it causes the average orientation of the asymmetrical isotopomers, and especially of HT, to behave differently from the symmetrical species. [S1063-651X(97)03501-0]

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I. INTRODUCTION

Nuclear magnetic resonance (NMR) studies of molecular dihydrogen (H_2) and its deuteriated analogs (HD and D_2) as solutes in nematic liquid crystals have yielded a plethora of fascinating and useful information both about the behavior of these quantum solutes in ordered fluid media and about the intermolecular forces acting on these systems [1–6]. The present insights that have resulted from this research can be summarized as follows.

First, the isotopomers of dihydrogen show a sizable isotope effect on the second-rank orientation parameter $S_{pq} = \langle \frac{3}{2}\cos^2\theta_{pq} - \frac{1}{2} \rangle$, where θ_{pq} signifies the angle between the pq internuclear direction and the liquid-crystal director and the angular brackets denote averaging over the rotational degrees of freedom of the solute molecule. These S_{pq} can be obtained from the dipolar splittings observed in the NMR of partially oriented dihydrogens. The differences in the rotational ladders for the H_2, HD, and D_2 molecules are the main reason for the differences in their orientation parameters, which amount to about 14%. This has been explained by considering the perturbation of the ‘‘mean field’’ provided by the liquid-crystal environment on the freely rotating and vibrating solute molecules [1,2]. In fact, these results are a simple and instructive demonstration of quantum-mechanical effects that can be observed in the condensed phase at room temperature.

Second, for each isotopomer of dihydrogen both the sign and the magnitude of the degree of orientation S_{pq} are highly liquid-crystal dependent. This makes the dihydrogens excellent and physically very-well-characterized solute molecules whose degree of orientation can be exploited in order to probe the mechanisms that underlie the interaction between a solvent mean field and some solute electronic property [1,2,5].

Third, for the deuterium containing isotopomers the ratio of observed dipolar and quadrupolar couplings in the NMR spectra is not constant for each isotopomer, but is strongly liquid-crystal dependent. This has been taken to be an indication for an extra anisotropic contribution to the quadrupolar couplings, which arises from the presence of a nonzero average electric-field gradient (EFG) in the liquid-crystal solvent [2,3,7,8].

Fourth, the interaction between this nonzero EFG and the solute molecular quadrupole moment accounts for most of the degree of orientation of the isotopomers of dihydrogen. Because the average EFG can be either positive or negative, depending on the liquid crystal used [2–4,6], this interaction can explain both the sign and the magnitude of the orientation parameter.

Fifth, in view of the above considerations it should come as no surprise that, by mixing nematic liquid crystals with opposite average EFG's in appropriate proportions, nematic mixtures with zero EFG could be composed [4,6,9]. The use of such ‘‘magic mixtures’’ has constituted a veritable breakthrough because it allows the experimentalist to distinguish between various physical mechanisms contributing to the orientation of the solute molecules and to obtain information about the internal liquid-crystal field [10–13]. When the isotopomers of dihydrogen were dissolved at low concentration in such zero-EFG mixtures it was found that their degree of orientation was removed to a large extent. This can be taken as a strong indication that the main factor contributing to the orientation in typical nonzero-EFG nematic phases arises from the interaction between the solvent EFG and solute molecular quadrupole moment [4,6]. In all cases there is a small remnant orientation parameter with a negative sign for the dihydrogens [4,6]. The physical basis underlying this small negative orientation is still not well characterized. This issue will be addressed below.

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TABLE I. Experimental dipolar couplings (accurate to ~0.3 Hz) and tritium chemical shift differences (in Hz, accurate to ~1 Hz) for T_2, HT, DT, and H_2 dissolved in various nematic solvents. The gyromagnetic ratios (in $G^{-1}\ sec^{-1}$) and indirect couplings (in Hz) employed in this work are also given.

		Observed dipolar couplings				Tritium chemical shift differences	
Solvent	Temperature (K)	D_{HH}	D_{TT}	D_{HT}	D_{DT}	TT-HT	TT-DT
EBBA[a]	300	3019.2	4152.1	3576.9	584.0	−41.0	−11.9
5CB[b]	300	−738.7	−1015.7	−840.6	−142.8	−41.0	−11.9
Magic mixture[c]	317	120.0	170.5	164.5	24.2	−41.1	−9.9
1132[d]	300		−3113.0				

	J_{HH}	J_{DD}	J_{TT}	J_{HT}	J_{HD}	J_{DT}
	278.2	6.6	316.5	296.7	42.7[e]	45.5
γ_H	26751.27					
γ_D	4106.48					
γ_T	28533.81					

[a] Sample contains 200 torr T_2 and 550 torr D_2.
[b] Sample contains 200 torr T_2 and 550 torr D_2.
[c] Sample contains 200 torr T_2, 300 torr D_2, and 200 torr H_2.
[d] Sample contains 200 torr T_2.
[e] From [1]. The other J_{ij} are calculated from J_{HD}=42.7 Hz and the γ's.

Sixth, although the overall isotope effects on the solute orientation of the dihydrogens are relatively well understood, the HD order parameter is consistently somewhat more negative than predicted from the solvent mean field. By assuming that the situation can be modeled by a diatomic moving inside an infinite cylinder of a certain diameter, the HD molecule, contrary to H_2 and D_2, rotates about a center of mass that does not coincide with its geometrical center. Hence, in this model HD can approach the walls of the cylinder somewhat more closely, which could explain the deviation from the behavior predicted on the basis of the simple mean field alone [6].

Finally, the simplicity of the dihydrogens as solute molecules allows detailed quantum chemical *ab initio* calculations that have explored the importance of the interaction between nonzero solvent EFG's and solute molecular quadrupole moments. These calculations have provided appreciable support for and contributed to our current understanding as summarized above [14].

The present paper is concerned with a NMR study of the tritium containing isotopomers of dihydrogen, viz., T_2, HT, and DT. Tritium is an ideal nucleus from the NMR point of view, with the highest gyromagnetic ratio of all known nuclei, thus allowing for unusually sensitive detection by means of NMR. Since tritium possesses nuclear spin $I=\frac{1}{2}$, dipolar splittings will dominate the NMR spectra of these molecules partially oriented in nematic phases. Also, the HT molecule is an excellent candidate for exploring the possibly deviant character of the asymmetrical isotopomers in more detail. Moreover, a study of these isotopomers dissolved in a number of nematic phases including a magic mixture complements and completes previous research on H_2, HD, and D_2 and allows for a critical examination of the predictions of the theories and models that have been developed to explain the previous results for H_2, HD, and D_2.

II. EXPERIMENT

NMR Pyrex glass sample tubes of 5 mm external and 3 mm internal diameter were used. Liquid-crystal solvents were placed into the tubes and the tubes were then connected to a vacuum line. The liquid crystals were thoroughly degassed using various freeze-pump-thaw cycles. Next, varying amounts of T_2, H_2, and D_2 (see the footnotes to Table I) were allowed into the glass rack and the NMR tubes, and the tubes were then sealed. Great care was taken to ensure that the pressure in the NMR tubes never exceeded 700 torr and that the total amount of radioactivity was kept below 220 mCi. In some cases the region of the tubes above the liquid-crystal solvent was irradiated for a period of 10 h employing a ^{60}Co γ cell with a dose rate of 10 500 Gy/h at 28 °C in order to achieve isotopic scrambling and to produce the asymmetrical isotopomers of dihydrogen. Before allowing the sample tubes into the NMR spectrometer they were tested in an oven at approximately 70 °C and shaken up carefully to ensure optimum diffusion of the dihydrogens throughout the solvent.

The liquid crystals used were *N*-(4-ethoxybenzylidene)-4-n-butylaniline (EBBA), a eutectic mixture of trans-4-*n*-alkyl-(4-cyanophenyl)-cyclohexane (alkyl denotes propyl, pentyl, and heptyl) and trans-4-*n*-pentyl-(4′-cyanobiphenyl-4)-cyclohexane (1132), 4-(*n*-pentyl)-4′-cyanobiphenyl (5CB), and a magic mixture consisting of 30.75 wt. % EBBA and 69.25 wt. % 5CB for which the deuterium nuclei of the solute D_2 experience a zero external EFG at 317 K.

Proton and tritium NMR spectra were obtained on a Bruker AMX 600 NMR spectrometer operating at 600.13 MHz for proton and 640.12 MHz for tritium. The proton and tritium spectra were recorded at the same temperature, which was controlled by means of a variable-temperature gas flow

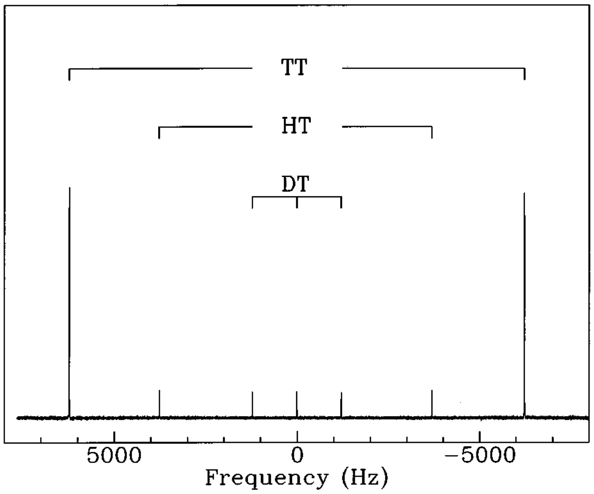

FIG. 1. Tritium NMR spectrum of a mixture of T_2, H_2, and D_2 in EBBA at 300 K after irradiation of the sample tube in order to achieve isotope scrambling.

unit. The nitrogen gas was preheated using a Haake thermostat K20 and thermally regulated by a Bruker Eurotherm Variable Temperature unit. The sample temperature was kept constant to ± 0.1 K. About 30 min were allowed for equilibration to the temperature at which the experiments were carried out. The spectra obtained in the nematic phases of the various solvents were taken with nonspinning sample tubes and without the use of a lock signal. A relaxation delay of order 3 sec and a 90° pulse width of 9 μsec were used.

III. RESULTS AND DISCUSSION

Figure 1 presents the tritium NMR spectrum of the three tritium containing isotopomers, obtained by isotope scrambling after irradiation of a mixture of T_2, H_2, and D_2, in EBBA at 300 K. The isotopomers are indicated by combs above the spectrum. In Fig. 2 a tritium spectrum of the same isotopomers obtained in similar fashion in 5CB at 300 K is shown.

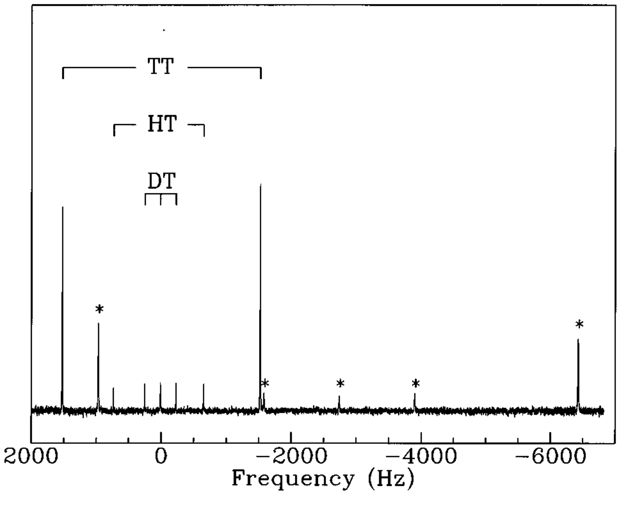

FIG. 2. Tritium NMR spectrum of a mixture of T_2, H_2, and D_2 in 5CB at 300 K after irradiation of the sample tube in order to achieve isotope scrambling. Note the presence of an oriented impurity, indicated by asterisks.

Tritium spectra of T_2 oriented in nematic phases consist of a doublet with spacing $3|D_{TT}|$; spectra of HT show a doublet with splitting $|2D_{HT}+J_{HT}|$; spectra of DT show a 1:1:1 triplet with a spacing of $|2D_{DT}+J_{DT}|$. Proton spectra of H_2 consist of a doublet with spacing $3|D_{HH}|$ [1,15]. In these expressions for the splittings J_{pq} is the scalar indirect spin-spin coupling. The direct dipolar coupling is defined as

$$D_{pq} = -\frac{h}{4\pi^2}\frac{\gamma_p\gamma_q}{r_{pq}^3}S_{pq}, \tag{1}$$

where the quantities γ_p and γ_q are the gyromagnetic ratios of nuclei p and q, r_{pq} is their internuclear distance, and S_{pq} is the orientation parameter associated with the internuclear axis of the solute [16].

A highly oriented impurity of unknown origin can be observed in the proton NMR spectra of the pure nematic phases of both 1132 and 5CB . This impurity gives rise to a two-line spectrum. The impurity must therefore contain two protons at small internuclear distance. As the NMR spectrum of Fig. 2 clearly shows, when deuterium or tritium containing isotopomers of dihydrogen are dissolved in these liquid crystals the protons of the impurity slowly exchange with the added species.

The dipolar couplings and chemical shift differences for T_2, HT, and DT obtained from tritium NMR, and those for H_2 obtained from proton NMR, dissolved in a number of liquid-crystal solvents are summarized in Table I. It is assumed that the proton and tritium spectra, which were obtained sequentially, represent identical experimental conditions. In view of the linewidths of approximately 6 Hz that were typically obtained, line positions could be determined with an accuracy of about 0.5 Hz. In the same table the gyromagnetic ratios and the J couplings employed in this work are also given. The J couplings are calculated from the known value for J_{HD}, which amounts to +42.7 Hz as measured from the deuterium NMR spectrum of HD in the isotropic phase of 1132 at 385 K [1]. Since the indirect coupling in the dihydrogens is almost completely determined by the Fermi contact interaction, J is essentially isotropic and scales as the gyromagnetic ratios.

The dependence of the chemical shift differences in Table I on the solute orientation, i.e., on the liquid-crystal solvent, is small. In principle, because one isotopomer could be viewed as an internal reference for the other, the solvent dependence of the chemical shift differences allows a determination of the chemical shift anisotropy. In such a situation differences in solvent effects on the molecule considered and on the reference compound, which normally plague measurements of proton chemical shift anisotropies, would be expected to be quite small [15,17–20]. However, any attempt to extract reliable chemical shift anisotropies from the observed small 1–2 Hz differences reported in Table I is doomed to failure in view of the experimental inaccuracies in the line positions.

It is clear from Table I that the tritium chemical shift differences for a given liquid crystal show an isotope effect that depends on which nucleus is bonded to the tritium. As pointed out above, the numbers essentially do not vary with a change in sign of the dihydrogen order parameter. Thus the observed chemical shift differences reported in Table I are effectively differences in the isotropic chemical shifts of the tritium nuclei in the various isotopomers. The observed isotope dependence of these isotropic chemical shifts is interesting in its own right and probably reflects a slight breakdown of the Born-Oppenheimer approximation. A detailed quantum chemical calculation would be required to investigate this phenomenon further.

It is important to amalgamate the previous results on H_2, HD, and D_2 and the present results on H_2, T_2, HT, and DT into a single consistent set of data for all the six isotopomers of dihydrogen. In view of the fact that the experimental results were collected at different times, under different experimental conditions, at different temperatures, and on different spectrometers careful attention should be given to the normalization procedures required to bring all the couplings into line. Consequently, comparisons below that involve D_2 and HD are less reliable than those that involve the dipolar couplings measured in this work, and reported in Table I, for H_2, T_2, HT, and DT. It is worth noting that safety considerations imposed completely different conditions on radioactive samples and ''cold'' ones. NMR experiments with the relatively insensitive deuteron nucleus can be performed only at a rather higher concentration, i.e., pressure, than is compatible with tritiated samples.

For EBBA the dipolar couplings involving H_2, HD, and D_2 are taken from previous work [1]. To account for slight differences in experimental conditions between the previous proton and deuteron spectra, the value of D_{DD} from the deuteron spectrum is first multiplied by the ratio of D_{HD} couplings observed in both spectra. Since D_{HH} was measured both in the previous and in the present experiments, this dipolar coupling was used in a similar manner to scale the previous to the present experimental results.

Since there are no data for H_2 and HD from previous experiments that involve the present EBBA-5CB mixture, it is somewhat complicated to obtain a consistent set of couplings for all isotopomers. However, there have been experiments involving H_2, HD, and D_2 dissolved in a different zero-EFG mixture made up from EBBA and 1132. By employing a similar scaling procedure as discussed above for EBBA, these dipolar couplings were related to those of the present experiment. It should be realized that the values of D_{DD} and D_{HD} for the magic mixture are fraught with some uncertainty. However, the most dramatic effects below are based on the proton and tritium spectra reported in Table I. The dipolar couplings for a given liquid crystal reported in Table I were obtained from proton and tritium spectra that were acquired under identical experimental conditions, without removing the sample from the spectrometer. Thus comparisons between couplings within the same liquid crystal are good to the accuracy of the couplings reported in Table I.

The full set of experimental results for all six isotopomers of dihydrogen dissolved in the various liquid-crystal solvents, including the magic mixture, is given in Table II. In order to remove the simple scaling effects of the gyromagnetic ratios on the dipolar couplings, all the couplings have been multiplied by the appropriate gyromagnetic ratios to allow a direct comparison with D_{HH}.

TABLE II. Complete set of dipolar couplings (in Hz) obtained for the six isotopomers of dihydrogen dissolved in different nematic phases. The effects of the gyromagnetic ratios have been removed by scaling to the HH coupling. Experimental values of dipolar couplings are accurate to about three units in the last decimal place.

Solvent	D_{HH}	D_{DD}	D_{TT}	D_{HD}	D_{HT}	D_{DT}
EBBA	3019.2	3482	3649.6	3258	3353.5	3567
5CB	-738.7		-892.8		-788.1	-872
magic mixture	120.0	142[a]	149.9	140[a]	154.2	148
1132			-2736.2			

[a] From [6] for 55 wt. % 1132 in EBBA at 300.7 K in combination with numbers from Table I for the mixture used in the present study.

A. Experimental distinction of orientation mechanisms

When several orientation mechanisms are present, each mechanism contributes to the dipolar couplings observed in the dihydrogens. The degree of orientation associated with each mechanism is invariably small, of order $|10^{-2}|$ or less. This implies that, in the expansion of the Boltzmann factor that contains the sum of the potential energies corresponding to each orientation mechanism, to an excellent approximation only the first-order terms are important. Hence the contributions from different orientation mechanisms to the overall dipolar couplings are simply additive.

The experimental dipolar couplings of all the isotopomers of dihydrogen in the various nematic phases, including the magic mixture, are summarized in Table II. It is now tempting to investigate whether previous ideas about orientation mechanisms are reflected in these results. In the component liquid crystals EBBA and 5CB it is thought that the dominant orientation mechanism constitutes the interaction between the solvent average nonzero EFG and the solute molecular quadrupole moment. In addition, there is another mechanism at play whose origin is still uncertain. In the zero-EFG magic mixture the main contribution to the solute orientation has been removed as evidenced by the dipolar couplings, which are much smaller than those observed in the component liquid crystals. If it is now assumed that the orientation mechanism that is remnant in the magic mixture is virtually identical in all solvents and is therefore also present in the component liquid crystals, one can in principle subtract the dipolar couplings measured in the mixture from those in the component liquid crystals. If the above assumption were upheld, one would expect that the dipolar couplings in the component liquid crystals that remain after subtraction of the mixture dipolar couplings would show an internal consistency indicative of the presence of a *single* orientation mechanism. This would mean that the ratios between dipolar couplings would be essentially the same in each component liquid crystal. This idea can be subjected to a purely experimental check without having to take recourse to any theoretical calculation. In order to execute this test one has to give proper attention to the factors that are relevant in comparing dipolar couplings obtained in different nematic phases. Specifically, the mean degrees of orientation of the different nematic solvents have to be taken into account.

TABLE III. Dipolar couplings (in Hz) of the six isotopomers of dihydrogen dissolved in EBBA and 5CB obtained by subtraction of a scaling factor times the dipolar couplings measured in the magic mixture. Details of the procedure are discussed in the text. When possible, ratios of dipolar couplings in EBBA and 5CB are given. The results of *ab initio* calculations for the dipolar couplings as well as the best-fit F_{ZZ} values (in 10^{11} statvolt cm^{-2}) are also presented.

				Experiment			
Scaling factor		D_{HH}	D_{DD}	D_{TT}	D_{HD}	D_{HT}	D_{DT}
(EBBA) (mixture × 1.560)		2832.0	3260	3415.8	3040	3113.0	3337
(5CB) (mixture × 1.073)		−867.5		−1053.5		−953.5	−1031
Ratio		−3.265		−3.242		−3.265	−3.238
				Ab initio calculations			
	F_{ZZ}	D_{HH}	D_{DD}	D_{TT}	D_{HD}	D_{HT}	D_{DT}
EBBA	−8.500	2866.2	3253.0	3392.6	3051.8	3117.5	3322.3
5CB	2.586	−881.5	−1001.1	−1044.3	−938.9	−959.2	−1022.6
Ratio		−3.251	−3.249	−3.249	−3.250	−3.250	−3.249

The degrees of orientation of the liquid crystals are taken to be proportional to either the α deuteron splitting of deuteriated 5CB or the ring deuteron splitting of deuteriated EBBA. In order to determine the ratio of the degrees of orientation of 5CB and the magic mixture we use the experimental values of 51.09 kHz obtained at 300 K for pure 5CB-α,β-d_4 [21] and of 47.63 kHz obtained at 317 K for 5CB-α,β-d_4 in the same mixture as used in the present study [9]. In order to determine the orientation ratio of EBBA and the magic mixture we use 21.18 kHz obtained at 300 K for pure EBBA-d_2 [22] and 13.58 kHz obtained at 317 K for EBBA-d_2 in the same mixture as used in the present study [9].

Using the degrees of orientation of the liquid-crystal solvents as discussed above we can now subtract the dipolar couplings obtained in the magic mixture, multiplied by the appropriate scaling factor, from those measured in EBBA and 5CB. The results of this procedure are given in Table III. Also, the ratios of the dipolar couplings for the isotopomers of dihydrogen in EBBA and 5CB after the mixture couplings have been subtracted off are presented. These ratios show a variation of less than 1%. This should be contrasted with the ratios that can be calculated from the dipolar couplings of the dihydrogens dissolved in EBBA and 5CB in Table II, before subtracting off the mixture couplings. In the latter case the ratios vary by up to 4%. Already on purely experimental grounds it can be argued that the results in EBBA and 5CB, after subtraction of the mixture couplings, can be rationalized in terms of a single orientation mechanism. Finally, it should be emphasized that the results discussed in this paragraph do not depend strongly on the precise estimates of the liquid-crystal degrees of orientation used in the scaling procedure. In addition, because of the various uncertainties involved in the scaling procedure, no great precision can be attached to the numbers in Table III. They represent semiquantitative estimates of dipolar couplings for the single orientation mechanism that remains after subtraction of a best estimate of the mixture dipolar couplings.

B. Comparison with *ab initio* calculations

Ab initio calculations that model the interaction between a solvent average EFG and a solute molecular quadrupole moment have been carried out previously for the isotopomers H_2, HD, and D_2. In these calculations thermal expectation values for NMR observables of dihydrogen and its isotopomers partially oriented in nematic phases are calculated from first principles. The starting point is the use of high-quality nuclear wave functions and highly correlated electronic wave functions calculated for many different internuclear distances [23,24]. In the calculations on dihydrogen vibrational anharmonicity, centrifugal distortion, the changes of the molecular quadrupole moment with internuclear distance, and the dependence of the molecular quadrupole moment on the rotational quantum number have been included [14]. These calculations are now extended to the isotopomers T_2, HT, and DT which are the subject of the present paper.

The results of these *ab initio* calculations for the dihydrogen isotopomers dissolved in EBBA and 5CB are summarized in Table III. Since the EFG is the only adjustable parameter, its value has been determined by performing a least-squares fit to the experimental dipolar couplings after subtraction of the mixture couplings. The quality of the fit is reasonable, although far from perfect. Of course, the same fitting procedure can also be carried out on the observed dipolar couplings in EBBA and 5CB *before* subtracting off the couplings measured in the magic mixture. The results of this procedure (not shown) give a root-mean-square deviation that is significantly worse than the one presented here. This provides additional support for a picture in which the solute orientation is predominantly determined by a virtually liquid-crystal-independent contribution in addition to the interaction between the solvent average EFG and solute molecular quadrupole moment. Finally, it should be noted that the calculations for different values of the ZZ component of the average EFG, F_{ZZ} predict ratios of the various dipolar couplings that are virtually the same for all the couplings and are, moreover, in good agreement with the experimental ratios obtained after subtraction of the mixture couplings.

C. Orientation of the dihydrogen isotopomers in a ''magic mixture''

We shall now focus on the small degree of orientation observed for the dihydrogen isotopomers dissolved in the magic mixture. In this mixture the contribution to the orientation arising from an interaction between the average electric-field gradient present in the anisotropic solvent and the molecular quadrupole moment of the solute dihydrogens, which usually dominates the average orientation in liquid crystals, does not play a role. As discussed above, the main features of our experimental results of the dihydrogen isotopomers dissolved in magic mixture can be summarized as follows. First, each isotopomer is characterized by a small negative orientation parameter. Second, the asymmetrical isotopomers have a more negative orientation parameter than expected on the basis of mean-field calculations alone. These points will be discussed in the present section.

If an identical mean-field orientational mechanism is operative in all liquid crystals, then it is expected that the relative values of solute dipolar couplings from a given liquid-crystal solvent should essentially be independent of the liquid crystal. This is the result obtained in Table III above after the mixture couplings have been subtracted from the experimentally observed couplings. However, the couplings from the magic mixture do not follow this trend. Thus there appears to be a liquid-crystal-independent contribution to the orientational ordering. The origin of this contribution, taken here to be the ordering measured in the magic mixture, is mysterious. Previous calculations of the orientational order of the isotopomers of dihydrogen employed a simple mean-field interaction between some solute molecular property $\beta_{\|}-\beta_{\perp}$ and a liquid-crystal mean field G [2]. First-order perturbation theory for a rigid rotor yields the following equation for the order parameter:

$$
\begin{aligned}
S={}&\frac{G(\beta_{\|}-\beta_{\perp})}{\sum_{J,m_J} e^{-BJ(J+1)/kT}}\sum_{J,m_J} e^{-BJ(J+1)/kT}\\
&\times\Bigg[-\frac{1}{kT}\left\{\frac{3}{2}\left(\frac{(J+1)^2-m_J^2}{(2J+1)(2J+3)}\right.\right.\\
&\left.\left.+\frac{J^2-m_J^2}{(2J+1)(2J-1)}\right)-\frac{1}{2}\right\}^2\\
&+\frac{9}{2B}\left\{\frac{[(J+2)^2-m_J^2][(J+1)^2-m_J^2]}{(2J+1)(2J+3)^2(2J+5)(-4J-6)}\right.\\
&\left.+\frac{(J^2-m_J^2)[(J-1)^2-m_J^2]}{(2J-3)(2J-1)^2(2J+1)(4J-2)}\right\}\Bigg],
\end{aligned}
\tag{2}
$$

where B is taken as the vibrationally averaged molecular rotational constant. The summations are over those J's and m_J's that are consistent with the Pauli principle given the nuclear spin states. We now fit this equation by least squares, adjusting $G(\beta_{\|}-\beta_{\perp})$, which is assumed to be isotopomer independent, to the complete set of mixture dipolar couplings. The results of this mean-field calculation are presented in Table IV. For comparison we include the experimental dipolar couplings for the magic mixture. We also present dipolar couplings relative to D_{HH}. The agreement of the ratios between experiment and calculation is far from satisfactory for the more asymmetrical isotopomers HD and HT.

Inconsistent numbers for HD and HT are also observed in other experiments. Note especially in Tables II and III that the absolute value of the dipolar coupling D_{HT} for the most asymmetric of the isotopomers is much smaller than D_{TT} in all cases except the mixture, where it is larger. In a similar vein, it has been noted before that values for D_{HD} in a number of liquid-crystal solvents are consistently more negative than expected on the basis of the solvent mean field [6]. Ratios between any two dipolar couplings can be calculated from the entries in Table II. The variation of these ratios with liquid crystal is minor for the symmetrical isotopomers, not very significant for DT, appreciable for HD, and large for HT. In this context we note that the asymmetrical solutes all possess a center of mass that differs from the center of geometry. It is a striking observation that the extent to which the center of mass differs from the centre of geometry correlates with the above experimental observations. Therefore, it seems feasible that the observed differences with these asymmetrical isotopomers could arise from the loss of symmetry. General mean-field theories such as discussed above and the *ab initio* calculations in Sec. III B are not sensitive to the center of mass and thus cannot explain these observations.

TABLE IV. Comparison of experimental dipolar couplings (in Hz) in the magic mixture with results of mean-field calculations and results of a model that accounts for the shift of the center of mass in the asymmetrical isotopomers. Experimental values of dipolar couplings are accurate to about three units in the last decimal place.

	D_{HH}	D_{DD}	D_{TT}	D_{HD}	D_{HT}	D_{DT}
Experiment	120.0	142	149.9	140	154.2	148
Mean-field calculation	127.3	146.4	153.6	136.5	139.7	149.9
Center of mass model	134.6	152.0	158.0	159.7	184.2	161.4
$\frac{D_{ij}}{D_{\mathrm{HH}}}$ experimental	1	1.18	1.25	1.16	1.29	1.23
$\frac{D_{ij}}{D_{\mathrm{HH}}}$ mean field	1	1.15	1.21	1.07	1.10	1.18
$\frac{D_{ij}}{D_{\mathrm{HH}}}$ center of mass	1	1.13	1.18	1.19	1.37	1.20

Next, the observation that the asymmetrical isotopomers of dihydrogen have a more negative orientation parameter than suggested by mean-field calculations will be discussed on the basis of a phenomenological treatment. A calculation that takes into account the shift of the center of mass away from the center of geometry has been proposed previously to account for the deviant behavior of HD [6]. In this picture the liquid crystal is modeled as a continuum with the solute sitting in a hollow cylinder of infinite length and of radius R_0. The solute rotates around its center of mass, which is located on the cylinder axis. The interaction between solute and solvent cylinder is taken to be a Lennard-Jones (6-12) potential function with empirical constants $\epsilon = 2\times10^{-22}$ J and $\sigma=3$ Å. The asymmetrical isotopomers sweep out a relatively large volume such that the lighter atom comes in close proximity to the cylinder wall. Hence the asymmetrical isotopomers experience more of an attractive force than do the symmetrical ones. The interaction energy of each atom in the solute is written

$$
u_{\mathrm{ext}}^{(2)}(\theta,r)=-\Delta A(r)P_2(\cos\theta),
\tag{3}
$$

where r is the distance of the atom from the center of gravity of the molecule and θ is the angle between the molecular symmetry and cavity axes. The interaction parameter $\Delta A(r)$ is [25]

$$\Delta A(r)=\frac{\pi^2}{96R_0^9}\rho\epsilon\sigma^{12}\sum_{k=0}^{\infty}\frac{k(2k+5)(2k+7)(2k+9)!!}{9!!(2k)!!}\times\left(\frac{r}{R_0}\right)^{2k}-\frac{5\pi^2}{3R_0^3}\rho\epsilon\sigma^6\sum_{k=0}^{\infty}\frac{k(2k+1)!!}{(2k)!!}\left(\frac{r}{R_0}\right)^{2k}, \tag{4}$$

where ρ (taken as 0.10 Å^{-3}) is the number density of the solute atoms. The value used for R_0 is 6 Å, which means, considering the van der Waals radii of the atoms, that the radius of the hollow part of the cavity is ~4.5 Å. The order parameters for each isotopomer are calculated from Eq. (2), setting $G(\beta_{\parallel}-\beta_{\perp})=\Sigma_{\text{atoms}}\Delta A(r)$.

We now apply this approach to the complete set of dihydrogen isotopomers using the same parameters as in Ref. [6], the only difference being that we use the average rather than the equilibrium internuclear distance for the isotopomers. The results of this calculation are presented in Table IV. We also present dipolar couplings relative to D_{HH}. In comparison with the experimental and mean-field values, these ratios reveal that inclusion of the center-of-mass effect has little influence on D_{DT}, a significant influence on D_{HD}, and a very large influence on D_{HT}. It appears that the above calculations, which are admittedly crude, overcompensate for the center-of-mass effect in HD and HT. However, this center-of-mass model explains both the negative order parameters and the more negative orientation found for the asymmetrical isotopomers. Thus this model appears to encompass the basic physics at the root of the orientation of the dihydrogen isotopomers in the magic mixture.

IV. CONCLUSION

The present research on T_2, HT, and DT, in combination with previous work on the isotopomers H_2, HD, and D_2 of dihydrogen dissolved in various nematic phases including a zero-EFG magic mixture, provides a wealth of information about the ordering of these species in nematic phases. The results underline once more that in the component liquid crystals the dominant contribution to the solute orientation arises from an interaction between a nonzero EFG with the solute molecular quadrupole moment.

In addition to this liquid-crystal-dependent orientation mechanism there is a relatively small contribution that appears to be virtually independent of the liquid-crystal solvent. The magnitude of this interaction is reflected in the strongly decreased degree of orientation and the corresponding dipolar couplings that remain for all the isotopomers in the zero-EFG magic mixture.

When the liquid-crystal-independent couplings as obtained from the magic mixture are subtracted from the dipolar couplings observed in the component liquid crystals, the remaining liquid-crystal-dependent dipolar couplings should solely result from the interaction between a nonzero EFG and the solute molecular quadrupole moment. This particular interaction can be reasonably well modeled by *ab initio* calculations.

The liquid-crystal-independent contribution to the solute orientation, which leads to the observed dipolar couplings for the isotopomers of dihydrogen observed in the magic mixture, can be modeled in a phenomenological fashion, based on a simple mean-field approach [Eq. (2)]. Previous work indicated that the asymmetrical isotopomer HD did not completely fit the trend predicted by these calculations. When considering the liquid-crystal-independent contribution in somewhat more detail it is apparent that the even more asymmetrical isotopomer HT shows the same behavior in an even more outspoken fashion. In the magic mixture the orientation parameter of HT is clearly more negative than that of T_2, contrary to what our calculations predict. A model based on a Lennard-Jones interaction between the solute and surrounding liquid-crystal solvent [Eq. (4)] provides evidence that the unusual behavior of the asymmetrical isotopomers could be due to the fact that the center of mass around which the molecule rotates and the geometrical center do not coincide for the asymmetrical species.

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