Molecules with Large-Amplitude Torsional Motion Partially Oriented in a Nematic Liquid Crystal: Ethane and Isotopomers

E. E. Burnell*

Chemistry Department, University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada, V6T 1Z1

C. A. de Lange,[‖] J. B. S. Barnhoorn, I. Aben,[‡] and P. F. Levelt[§]

Laser Centre, Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands

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An NMR study on ethane and five isotopomers dissolved in the nematic liquid crystal Merck ZLI 1132 is performed. A consistent set of dipolar and quadrupolar couplings is obtained. The dipolar couplings are corrected for harmonic vibrational effects, while the contribution from the torsional motion is incorporated classically. The corrected dipolar couplings cannot be understood in terms of a reasonable molecular structure unless effects of the reorientation−vibration interaction are taken into account. Assuming that the reorientation−vibration contributions that are known for the methyl group in methyl fluoride are transferable to ethane, excellent agreement between observed and calculated dipolar couplings is obtained on the basis of the ethane gas-phase structure. The observed and calculated deuterium quadrupolar couplings show discrepancies supporting the notion that average electric field gradients are important in liquid-crystal solvents. An important consequence of the transferability of the reorientation−vibration correlation is that in other molecules with a methyl group the same procedure as for ethane can be followed. Inclusion of this effect generally removes the need to interpret changes in observed dipolar couplings in terms of elusive chemical effects.

1. Introduction

Nuclear magnetic resonance (NMR) of small well-characterized molecules dissolved in liquid-crystal solvents is of interest for a number of reasons. First, relative geometries that can be compared to gas-phase structures can be obtained in the liquid phase from the dipolar couplings observed for orientationally ordered molecules. Despite the multitude of studies that have been carried out, the extent to which the liquid-crystal environment affects solute structure is still a matter of debate.[1] Because zero-point vibrations typically have amplitudes of 0.1 Å, bond lengths accurate to better than 0.01 Å can be obtained only if averaging over the vibrational motion is dealt with appropriately. Second, small probe molecules have proved to be extremely valuable in elucidating details about the intermolecular anisotropic potential in orientionally ordered liquids and about the mechanisms that contribute to the orientational order of such solute species.[2,3] Seminal papers in this field have employed molecular hydrogen[4−6] and its deuterated[7−9] and tritiated[10] isotopomers, as well as methane and its isotopomers.[11−13] From such studies, it has become apparent that in liquid-crystal solvents both short- and long-range interactions generally contribute to the orientational order. Under favorable conditions, these contributions can be obtained separately when different liquid crystals and so-called "magic mixtures" are employed.[2,3]

In this paper, another relatively well characterized molecule, ethane, CH_3CH_3, and five of its isotopomers, viz. $^{13}CH_3CH_3$,

CH_3CD_3, CH_3CH_2D, $^{13}CH_3CH_2D$, and $CH_3{}^{13}CH_2D$, are studied as solutes in nematic liquid crystals. When a series of molecules is studied, a comparison of observed NMR coupling parameters, such as dipolar and quadrupolar couplings, can be made only if the various species are studied under exactly the same experimental conditions. This is particularly true for isotopomers of the same molecule because isotope dependences are generally small. It would therefore be preferable to study all of the species under consideration in the same NMR sample tube. Unfortunately, with gases dissolved in liquid crystals there is an upper limit to the pressure one can allow in a sealed NMR tube. In addition, too much spectral overlap of signals resulting from different species may pose an assignment problem. Hence, it is usually necessary in practice to dissolve the isotopomers in more than one sample tube. Under such conditions, careful attention must be given to scaling the results obtained in the different tubes. In our study, we have obtained a consistent set of carefully scaled experimental NMR dipolar and quadrupolar couplings for ethane and its isotopomers.

When considering molecular vibrational motions, a case of special interest is the large-amplitude torsional motion associated with the rotation of methyl groups. Clearly, ethane is a benchmark example of a solute undergoing this type of internal rotation. A study of ethane and its isotopomers is therefore expected to be instructive. The torsional motion in ethane is a one-dimensional vibrational mode belonging to the A_{1u} irreducible representation of the D_{3d} symmetry group that does not interact with any of the other vibrational modes. For an accurate determination of solute relative geometries, the application of detailed vibrational corrections is crucial, and methods have been developed to achieve this. The usual approach is valid for small-amplitude vibrational motions and utilizes truncated Taylor

* Corresponding author. E-mail: elliott.burnell@ubc.ca.
‖ E-mail: cdelange@few.vu.nl.
‡ Present address: SRON, National Institute for Space Research, Sorbonnelaan 2, 3584 CA Utrecht, The Netherlands.
§ Present address: KNMI, P.O. Box 201, 3730 AE De Bilt, The Netherlands.

expansions (see Section 3). The large-amplitude torsional mode cannot be treated in the same manner and should be dealt with separately (see Section 4). Moreover, the torsional motion can couple with the overall rotational motion,[14−16] and the possible importance of this interaction should be considered. Because ethane in the gas phase has been studied widely with an abundance of physical methods, much is known about the molecule. Key papers report the r_z structure,[17] the height of the torsional barrier,[17] and the harmonic force field.[18,19] A detailed discussion of the type of information required from molecular force fields to obtain accurate structural parameters will be given in Section 4.

The experimental dipolar couplings are analyzed by employing a model in which the gas-phase r_z structure and the torsional barrier from the literature are used. Harmonic vibrational corrections are calculated from the available second-order force field. The importance of harmonic vibrational corrections was realized and implemented long ago.[20−22] The torsional motion is taken into account by classical averaging over the internal rotational motion and by using appropriate Boltzmann weighting factors. A model based on these molecular parameters is not capable of satisfactorily reproducing the observed dipolar couplings by solely adjusting the orientation parameters associated with each isotopomer. Attempts to adjust structural parameters as well led to better quality fits but to unrealistic structures and barriers. Clearly something is missing in this approach.

An effect that is often neglected in NMR studies of orientationally ordered species is the interaction between reorientational and vibrational motions. For highly symmetric solute molecules such as CH_4 and CD_4, the orientational order in a nematic liquid crystal is expected to be zero. Nevertheless, small dipolar and quadrupolar splittings that arise from the reorientation−vibration coupling mechanism are observed. The detailed quantum-mechanical basis for this effect has been derived in a number of publications.[11−13] Because the calculation of this so-called "nonrigid" contribution to the dipolar coupling is somewhat complicated, applications to only a few relatively simple solutes have been carried out to date. In addition to the work on the methanes, extensive studies of acetylene,[23] benzene,[24] methyl fluoride,[25] and their isotopomers should be mentioned.

The implementation from first principles of the reorientation−vibration coupling mechanism to ethane was considered. In this case, the calculation involves a large number of unknown interaction parameters and was therefore abandoned. Instead, a novel approach was chosen, based on the fact that the force field associated with a methyl group is essentially transferable from one molecule to the next. This appears to be particularly true for the methyl halides,[26] hence the transfer of the reorientation−vibration couplings obtained in a previous extensive study on methyl fluoride and its isotopomers[25] was incorporated into the ethane results. The ethane dipolar couplings corrected in this manner were subjected to a fitting procedure that allowed only orientation parameters and a scaling factor (vide infra) to vary. The fit obtained was of excellent quality, indicating that incorporation of reorientation−vibration coupling is crucial. Moreover, the transferability of the methyl fluoride results to methyl groups in other molecules appears to be a very attractive possibility.

When molecular structures are deduced from liquid-crystal NMR, discrepancies are often observed and ascribed to all sorts of effects, such as specific chemical interactions, exchange between several sites in the liquid-crystal environment, and the

like. It will be shown that in representative cases (e.g., $^{13}CH_3I$) inclusion of the reorientation−vibration coupling leads to a situation where all the observations can be explained on the basis of a single gas-phase structure, thus removing the need for more elusive explanations.

Finally, an analysis of the quadrupolar couplings measured for the deuterated ethanes leads to discrepancies very similar to those obtained when deuterated hydrogens and methanes were studied in nematic phases.[7,12,13] Our current results lend strong support to the notion that average external electric field gradients present in liquid-crystal solvents should not be ignored in the interpretation of measured quadrupolar couplings.

2. Experimental Section

Ethane isotopomers CH_3CH_3, CH_3CD_3, and CH_3CH_2D were used without further purification. Couplings to ^{13}C were obtained in the proton NMR spectra from satellite lines of ^{13}C in natural abundance. The liquid-crystal mixture Merck ZLI 1132 was used without further purification; *N*-(4-ethoxybenzylidene)-4′-*n*-butylaniline (EBBA) was synthesized following the procedure outlined in ref 27.

The gaseous solutes were condensed into 5-mm od NMR tubes containing degassed liquid-crystal ZLI 1132 or EBBA and flame sealed. NMR spectra were run on a Bruker MSL 400 spectrometer. The sample temperature was controlled at 298 K for the ZLI 1132 samples (300 K for the EBBA sample) using the Bruker air-flow system.

Spectral simulation software (Bruker PANIC for single-solute samples and LEQUOR[28] for a sample containing the three isotopomers, CH_3CH_3, CH_3CD_3, and CH_3CH_2D) was used to obtain the dipolar and quadrupolar couplings reported in Table 1. The indirect couplings utilized in the analysis are listed in Table 1 and were taken from refs 29−33. The labeling of the nuclei and the definition of the molecule-fixed x, y, and z axes is given in Figure 1.

To obtain a self-consistent set of dipolar couplings, we scaled values from samples containing a single solute using the value of D_{HH} for the same compound in the sample containing three solutes. Spectra of ^{13}C isotopomers, obtained simultaneously with the ^{12}C spectrum from the ^{13}C satellites in the proton spectrum, were scaled using the same factor as for the ^{12}C isotopomer. To ensure identical conditions, a deuteron spectrum was obtained immediately following the proton spectrum without removing the sample from the NMR probe. Because of signal-to-noise considerations, ^{13}C satellites were not observed in the deuteron spectra and hence ^{13}CD couplings were not obtained.

3. Theoretical Background

In this section, the theory underlying the analysis of our experimental results for ethane and its isotopomers will be discussed. We shall emphasize the role of a contribution to the dipolar and quadrupolar couplings that is often not considered, viz. the so-called vibration−rotation interaction. It is in a sense unfortunate that in the original development of the theory of solutes dissolved in nematic phases fictitious rigid solutes were taken as a starting point.[34,35] Later it was realized, almost as an afterthought, that for a more realistic description vibrational corrections should also be incorporated.[20−22] In the present analysis we shall take *nonrigid* solute molecules as our starting point, and we shall see how, in addition to the well-known vibrational corrections, the vibration−rotation contribution then arises quite naturally.

TABLE 1: Experimental and Scaled Dipolar and Quadrupolar Couplings (in Hz) from Solutes in ZLI 1132 at 298 K[a]

	CH_3-CH_3'	$^{13}CH_3-CH_3'$	CH_3-CD_3	$CH_3-CH_2'D$	$^{13}CH_3-CH_2'D$	$CH_3-^{13}CH_2'D$
			experimental couplings from separate tubes			
D_{HH}	647.593 (15)	647.263 (23)	654.296 (7)	632.335 (13)	632.491 (31)	632.545 (32)
$D_{HH'}$	−257.407 (12)	−257.259 (31)		−251.92 (18)	−252.023 (42)	−252.004 (44)
D_{HD}			−40.019 (20)	−38.527 (25)	−38.466 (56)	−38.507 (52)
D_{DD}			15.636 (16)			
$D_{H'D}$				97.873 (34)	97.886 (59)	97.904 (60)
$D_{H'H'}$				628.946 (24)	629.112 (56)	629.156 (50)
D_{CH}		395.011 (80)			385.977 (86)	381.578 (107)
$D_{CH'}$		−118.054 (73)			−115.815 (98)	−115.38 (85)
B_D			−2512.178 (20)	−2478.769 (23)		
			experimental couplings from solutes in the same tube			
D_{HH}	609.328 (8)		607.742 (4)	608.815 (4)		
$D_{HH'}$	−242.216 (7)			−242.569 (3)		
D_{HD}			−37.191 (3)	−37.088 (4)		
D_{DD}						
$D_{H'D}$				94.227 (5)		
$D_{H'H'}$				605.503 (7)		
D_{CH}						
$D_{CH'}$						
			couplings from separate tubes scaled to D_{HH} values from same tube			
D_{HH}	609.33	609.02	607.74	608.82	608.97	609.02
$D_{HH'}$	−242.20	−242.06		−242.55	−242.65	−242.63
D_{HD}			−37.17	−37.09	−37.04	−37.07
D_{DD}			14.52			
$D_{H'D}$				94.23	94.25	94.26
$D_{H'H'}$				605.55	605.71	605.75
D_{CH}		371.67			371.62	367.39
$D_{CH'}$		−111.08			−111.51	−111.09
B_D			−2333.43	−2386.57		

[a] Experimental couplings (in Hz) for CH_3-CD_3 in EBBA at 300 K are: $D_{HH} = 565.531$ (17); $D_{HD} = -34.726$ (20); $D_{DD} = 13.521$ (16); and $B_D = -2118.029$ (20). J couplings in Hz from[29−33] used in the analysis are: CH_3CH_3': $J_{HH'} = 8.0$; $^{13}CH_3CH_3'$: $J_{HH'} = 8.0$, $J_{CH} = 125.0$, $J_{CH'} = -4.5$; CH_3CD_3: $J_{HD} = 1.23$, $J_{DD} = -0.29$; $CH_3CH_2'D$: $J_{HH'} = 8.0$, $J_{HD} = 1.23$, $J_{H'D} = -1.92$; $^{13}CH_3CH_2'D$: $J_{HH'} = 8.0$, $J_{HD} = 1.23$, $J_{H'D} = -1.92$, $J_{CH} = 125.0$, $J_{CH'} = -4.5$, $J_{CD} = -0.7$; $CH_3^{13}CH_2'D$: $J_{HH'} = 8.0$, $J_{HD} = 1.23$, $J_{H'D} = -1.92$, $J_{CH'} = 125.0$, $J_{CH} = -4.5$, $J_{CD} = 19.0$
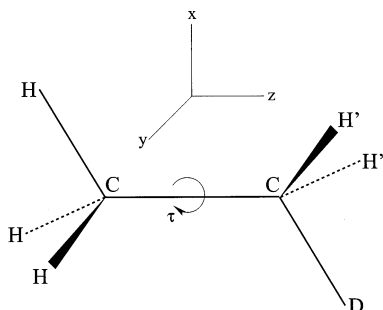
Figure 1. Ethane, the x, y, and z axes are fixed in the CH_2D group.

The orientational order of a solute dissolved in a nematic liquid crystal arises from the anisotropy $\Delta F = F_{||} - F_{\perp}$ in the mean liquid-crystal field, which often has cylindrical symmetry around the direction of the space-fixed magnetic field direction, Z. The potential, U, that describes the interaction leading to solute orientational order in this anisotropic mean field is given by[13,25]

$$U = -\frac{1}{3}\Delta F \beta_{kl}(Q_m) \, \mathbf{S}_{kl}(\Omega) \qquad (1)$$

with the orientation operator

$$\mathbf{S}_{kl}(\Omega) = \frac{3}{2}\cos\theta_{kZ}\cos\theta_{lZ} - \frac{1}{2}\delta_{kl} \qquad (2)$$

where k and l are molecule-fixed axes x, y, and z for the solute (see Figure 1) and $\cos\theta_{kZ}$ is the direction cosine between the molecule-fixed k axis and the space-fixed Z axis. The Einstein convention that implies summation over repeated indices that

indicate Cartesian coordinates is used throughout this paper. The quantity $\Delta F = F_{||} - F_{\perp}$ is the anisotropy of the liquid-crystal mean field interacting with the solute. The potential is a function of both the vibrational normal modes, Q_m, of the solute and of the Euler angles, Ω, that describe its orientation. In principle, this potential couples vibrational and reorientational motions.

In the potential defined in eq 1 it is assumed that the interaction between solvent and solute can be written in a simple bilinear form, in which solvent and solute properties are introduced in a factorized manner. The simple model that we employ here gives a picture of the liquid-crystal environment as providing an average second-rank mean field tensor, F_{ij}, that interacts with some second-rank tensorial property, β_{ij}, of the solute molecule. Tensor β_{ij} is supposed to be determined by the electronic structure and hence the geometry of the solute molecule, and therefore depends on its vibrational (normal) coordinates. Because this potential will be used to predict second-rank tensorial properties such as dipolar and quadrupolar couplings, there is no need to consider possible higher-order terms. It should be stressed that the form of the potential defined in eq 1 does not require specific knowledge of the orientation mechanism. The interaction is written as $\Delta F \beta_{kl}(Q_m)$, but the values of these quantities are unknown without specific assumptions about the actual nature of the orienting interaction. Moreover, there is no a priori reason that a single mechanism should dominate the orienting process. Hence, the $\Delta F \beta_{kl}(Q_m)$ quantities should in general be viewed as a sum of contributions $\Delta F^i \beta^i_{kl}(Q_m)$ for every interaction, i.

We shall now treat the potential, U, of eq 1 as a perturbation on the zeroth-order problem, for which we take the harmonic

approximation for the vibrational problem and the rigid rotor for the rotational degree of freedom. The zero-order wave function will then be a simple product of harmonic oscillator wave functions for each normal mode and a rigid rotor wave function.

The observables that we wish to calculate are the dipolar and quadrupolar couplings that are measured by means of NMR. These observables have the following general form

$$A(Q_m, \Omega) = a_{kl}(Q_m)\mathbf{S}_{kl}(\Omega) \qquad (3)$$

that is, they depend on both the rotational and vibrational coordinates and have a multiplicative structure. In particular, we shall be interested in thermodynamic expectation values of operator A

$$A(T) = \sum_n P_n(T) \langle n|A(Q_m, \Omega)|n\rangle \qquad (4)$$

$$P_n(T) = e^{-E_n/kT} / \sum_j e^{-E_j/kT}$$

where n labels the rotational−vibrational quantum states and P_n is the familiar Boltzmann factor. If we neglect vibrational excitation at temperature T, then without the perturbation of eq 1 we find

$$A^{(0)}(T) = \langle 0|\, a_{kl}(Q_m)|\,0\rangle \sum_J P_J^{(0)}(T)\, \langle J|\mathbf{S}_{kl}(\Omega)|\,J\rangle \qquad (5)$$

where $|0\rangle$ is the vibrational ground state and J is a shorthand notation for all rotational quantum numbers that label the unperturbed rotational states. It can be shown easily that the sum in eq 5 vanishes for a rigid rotor so that for a freely rotating and vibrating molecule (or for one interacting with its environment in an isotropic way) observables of the form given in eq 3 will have a vanishing expectation value. To get a finite contribution, one has to take into account the change in the rotational−vibrational wave function induced by the anisotropic interaction of eq 1. By standard perturbation theory we have to first order

$$|0J\rangle^{(0+1)} = |0J\rangle^{(0)} + \sum_{nJ' \neq 0J} \frac{|nJ'\rangle\langle nJ'|U|0J\rangle}{E_{0J}^{(0)} - E_{nJ'}^{(0)}} \qquad (6)$$

where the sum is over all vibrational and rotational excitations.

The β tensor describes some electronic property of the solute and can be expanded in a truncated Taylor series in terms of the normal coordinates, Q_m, of the solute

$$\beta_{kl}(Q_m) = \beta_{kl}^e + \sum_m (\partial\beta_{kl}/\partial Q_m)^e Q_m + \dots \qquad (7)$$

The normal coordinates, Q_m, stand for small displacements away from the equilibrium structure. The derivatives are evaluated at the equilibrium structure, e, of the solute. The choice of normal coordinates is not essential; the Taylor expansion of eq 7 could also be formulated in terms of other coordinates such as Cartesian displacement coordinates, symmetry displacement coordinates, or internal displacement coordinates. It is important to note at this point that the use of truncated Taylor expansions can be expected to be realistic only for small-amplitude vibrational modes. The large-amplitude torsional internal motion cannot be dealt with in the same spirit. The incorporation of the torsional mode will therefore be deferred to Section 4.

Inserting eq 7 into eqs 1 and 6 and using the properties of the harmonic oscillator wave functions, we obtain[13]

$$|0J\rangle^{(0+1)} = |0J\rangle^{(0)} - \frac{1}{3}\Delta F\beta_{kl}^e \sum_{J' \neq J} \frac{|0J'\rangle\,\langle J'|\mathbf{S}_{kl}|J\rangle}{E_J^{(0)} - E_{J'}^{(0)}} -$$

$$\frac{1}{3}\Delta F \sum_{m,\text{all } J'} \sqrt{\frac{\hbar}{2\omega_m}} \left(\frac{\partial\beta_{kl}}{\partial Q_m}\right)^e |mJ'\rangle \frac{\langle J'|\mathbf{S}_{kl}|J\rangle}{E_J^{(0)} - E_{J'}^{(0)} - \hbar\omega_m} \qquad (8)$$

where the second term contains only rotational excitations and the third term excitations where only one normal mode is excited once. Hence, the sum over m is a sum over all normal modes. Using this perturbed wave function in eq 4 to calculate the perturbed expectation value of the operator A, we obtain to first order in ΔF

$$A(T) = \sum_J P_J^{(1)}(T)\, ^{(0)}\langle 0J|a_{ij}(Q_m)\mathbf{S}_{ij}(\Omega)|0J\rangle^{(0)} +$$

$$2\sum_J P_J^{(0)}(T)\, ^{(0)}\langle 0J|a_{ij}(Q_m)\mathbf{S}_{ij}(\Omega)|0J\rangle^{(1)} \qquad (9)$$

For $P^{(1)}(T)$ we find

$$P_J^{(1)}(T) = -P_J^{(0)}(T)\,E_J^{(1)}(T)/kT + P_J^{(0)}(T)\sum_{J'} P_{J'}^{(0)}(T)\,E_{J'}^{(1)}(T)/kT$$

$$= -P_J^{(0)}(T)\,E_J^{(1)}(T)/kT \qquad (10)$$

$$E_J^{(1)}(T) = -\frac{1}{3}\Delta F\beta_{kl}^e\,\langle J|\mathbf{S}_{kl}|J\rangle$$

The second contribution to $P^{(1)}(T)$ contains the same summation as eq 5 and therefore vanishes. Equations 8−10 completely determine $A(T)$ in terms of matrix elements of $\mathbf{S}_{ij}$ with respect to rigid-rotor wave functions. These matrix elements can be worked out easily in the spherical and symmetric top cases.

We now expand $a_{ij}(Q_m)$ in a Taylor series up to and including the second-order term

$$a_{ij}(Q_m) = a_{ij}^e + \sum_m \left(\frac{\partial a_{ij}}{\partial Q_m}\right)^e Q_m + \frac{1}{2}\sum_{m,n} \left(\frac{\partial^2 a_{ij}}{\partial Q_m \partial Q_n}\right)^e Q_m Q_n + \dots \qquad (11)$$

Inserting this expression into eq 9 we obtain

$$A(T) = A^{\text{rig}}(T) + A^a(T) + A^h(T) + A^{\text{nonrigid}}(T) \qquad (12)$$

with

$$A^{\text{rig}}(T) = \sum_J P_J^{(1)}(T)\, a_{ij}^e\, \langle J|\mathbf{S}_{ij}|J\rangle -$$

$$\frac{2}{3}\Delta F a_{ij}^e \beta_{kl}^e \sum_{J,J'(J'\neq J)} P_J^{(0)}(T) \frac{\langle J|\mathbf{S}_{ij}|J'\rangle\langle J'|\mathbf{S}_{kl}|J\rangle}{E_J^{(0)} - E_{J'}^{(0)}} \qquad (13)$$

and

$$A^{\text{nonrigid}}(T) =$$

$$-\frac{2}{3}\Delta F \sum_{m,J,J'} P_J^{(0)}(T) \frac{\hbar}{2\omega_m}\left(\frac{\partial a_{ij}}{\partial Q_m}\right)^e\left(\frac{\partial\beta_{kl}}{\partial Q_m}\right)^e \frac{\langle J|\mathbf{S}_{ij}|J'\rangle\langle J'|\mathbf{S}_{kl}|J\rangle}{E_J^{(0)} - E_{J'}^{(0)} - \hbar\omega_m} \qquad (14)$$

We obtain expressions for $A^a(T)$ and $A^h(T)$ that are similar to

Ethane and Isotopomers

J. Phys. Chem. A, Vol. 109, No. 48, 2005 **11031**

that for $A^{\text{rig}}(T)$ by replacing a_{ij}^{e} in eq 13 by

$$\sum_m \left(\frac{\partial a_{ij}}{\partial Q_m}\right)^{\text{e}} \langle Q_m \rangle_T \text{ and } \sum_{m,n} \left(\frac{\partial^2 a_{ij}}{\partial Q_m \partial Q_n}\right)^{\text{e}} \langle Q_m Q_n \rangle_T$$

The first three terms in eq 12 involve an averaging over vibrational and rotational motions in which these degrees of freedom are strictly decoupled. The last term is the lowest-order contribution that arises from a correlation that exists between the vibrational and rotational motions. Higher-order terms that result from this correlation have been neglected.

The first three terms of eq 12 result in the usual equilibrium, anharmonic, and harmonic contributions to the dipolar couplings after the appropriate thermal averages over the vibrational motions have been taken into account. Given the rigid equilibrium structure, the first contribution to eq 12 can be calculated. To calculate the anharmonic and harmonic contributions to the dipolar couplings, detailed knowledge about experimental or theoretical force fields is required. For most simple molecules the harmonic force field is relatively well-known, but information on the anharmonic force field is often lacking.

For a harmonic vibrational potential, the relevant results can be summarized as follows

$$\langle Q_m Q_n \rangle = \delta_{mn} \langle v_m | Q_m^2 | v_m \rangle \qquad (15)$$

$$\langle v_m | Q_m^2 | v_m \rangle = \frac{h}{2\pi\omega_m} \left(v_m + \frac{1}{2}\right) \qquad (16)$$

where v_m is the vibrational quantum number and ω_m is the vibrational frequency of normal mode m. By taking a quantum average over all vibrational states[36,37] we obtain

$$\left\langle v_m + \frac{1}{2} \right\rangle_T = \frac{1}{2} \coth\left(\left(\frac{h}{2\pi}\right)\frac{\omega_m}{2kT}\right) \qquad (17)$$

from which the required thermal average of $\langle Q_m Q_n \rangle$ is evaluated readily.

For a harmonic potential, the vibrational quantum average of each normal coordinate $\langle Q_m \rangle$ is zero. Moreover, $\langle Q_m^p Q_n^q \rangle = 0$ whenever one of the exponents, p or q, is odd. However, for an anharmonic potential the quantum averages over totally symmetric normal modes need not vanish. These quantum averages depend on the higher-order anharmonic cubic and possibly quartic force fields. When the semidiagonal cubic anharmonic force constants Φ_{mll} of the potential expressed in normal coordinates are known, we have[36−38]

$$\langle Q_m \rangle = -\frac{1}{2\omega_m^2} \sum_l \Phi_{mll} \langle v_l | Q_l^2 | v_l \rangle \qquad (18)$$

Boltzmann thermal averages are then obtained as in the case of the harmonic contributions (see eqs 16 and 17).

At this point two simplifying assumptions can be made. First, for the ethanes the rotational level spacings are small compared to kT. Hence, the full quantum-mechanical treatment of the rotational degree of freedom can be replaced by classical averaging over all orientations. Second, the rotational energy differences in eq 14 are small compared to the vibrational level spacings, with J and J' differing by two at most. Therefore, the familiar closure relationship can be employed, and we obtain

$$A^{\text{nonrigid}} = \frac{1}{3} \Delta F \sum_m \left(\frac{\partial a_{ij}}{\partial Q_m}\right)^{\text{e}} \left(\frac{\partial \beta_{kl}}{\partial Q_m}\right)^{\text{e}} \frac{1}{\omega_m^2} \langle \mathbf{S}_{ij} \mathbf{S}_{kl} \rangle_{\text{rotations}} \quad (19)$$

The relevant classical thermal averages can be calculated using Boltzmann statistics

$$S_{kl} = \langle \mathbf{S}_{kl} \rangle_{\text{rotations}} = \frac{\int \mathbf{S}_{kl} \exp(-U(\Omega)/kT)\, d\Omega}{\int \exp(-U(\Omega)/kT)\, d\Omega} \quad (20)$$

$$\langle \mathbf{S}_{ij} \mathbf{S}_{kl} \rangle_{\text{rotations}} = \frac{\int \mathbf{S}_{ij} \mathbf{S}_{kl} \exp(-U(\Omega)/kT)\, d\Omega}{\int \exp(-U(\Omega)/kT)\, d\Omega} \quad (21)$$

The $\langle \mathbf{S}_{kl} \rangle_{\text{rotations}}$ are the familiar S_{kl} Saupe order parameters that describe the orientational order of the solute in the liquid-crystal solvent. In this context, we note that for molecules such as H_2 and its isotopomers, where rotational splittings are significant in comparison to $kT \approx 200$ cm^{-1}, quantum-mechanical averaging over the overall rotation is required to explain the observed isotope effects on the orientational order.[5]

We now focus on the dipolar couplings. Because the rotational degree of freedom can be treated classically, considerable simplification is obtained for the equilibrium, anharmonic, and harmonic contributions

$$D_{\mu\nu} = \langle d_{kl,\mu\nu} \rangle_{\text{vibrations}} \langle \mathbf{S}_{kl} \rangle_{\text{rotations}} + \langle d_{kl,\mu\nu} \mathbf{S}_{kl} \rangle_{\text{vibrations,rotations}} =$$
$$D_{\mu\nu}^{\text{e}} + D_{\mu\nu}^{\text{a}} + D_{\mu\nu}^{\text{h}} + D_{\mu\nu}^{\text{nonrigid}} \quad (22)$$

with

$$d_{kl,\mu\nu} = -\frac{h\gamma_\mu\gamma_\nu}{4\pi^2} \left(\cos\theta_{\mu\nu,k} \cos\theta_{\mu\nu,l}/r_{\mu\nu}^3\right) \quad (23)$$

Here $\cos\theta_{\mu\nu,k}$ signifies the direction cosine between the internuclear $\mu\nu$-direction and the molecule-fixed k-direction, and $r_{\mu\nu}$ is the instantaneous internuclear distance.

The terms in eq 22 are

$$D_{\mu\nu}^{\text{e}} = d_{kl,\mu\nu}^{\text{e}} S_{kl} \quad (24)$$

$$D_{\mu\nu}^a = \sum_m \left(\frac{\partial d_{kl,\mu\nu}}{\partial Q_m}\right)^{\text{e}} \langle Q_m \rangle_T S_{kl} \quad (25)$$

$$D_{\mu\nu}^h = \frac{1}{2} \sum_{m,n} \left(\frac{\partial^2 d_{kl,\mu\nu}}{\partial Q_m \partial Q_n}\right)^{\text{e}} \langle Q_m Q_n \rangle_T S_{kl} \quad (26)$$

$$D_{\mu\nu}^{\text{nonrigid}} = \frac{1}{3} \Delta F \sum_m \left(\frac{\partial d_{kl,\mu\nu}}{\partial Q_m}\right)^{\text{e}} \left(\frac{\partial \beta_{ij}}{\partial Q_m}\right)^{\text{e}} \frac{1}{\omega_m^2} \langle \mathbf{S}_{kl} \mathbf{S}_{ij} \rangle_{\text{rotations}} \quad (27)$$

Expressions for the derivatives $(\partial d_{kl,\mu\nu}/\partial Q_m)^{\text{e}}$ and $(\partial^2 d_{kl,\mu\nu}/\partial Q_m \partial Q_n)^{\text{e}}$ have been given in various places.[11,20,23,39] It should be noted that for small orientational order (when only terms proportial to ΔF are carried in the expansion of the exponential that contains the orienting potential in eqs 20 and 21) the equilibrium, anharmonic, and harmonic contributions to the dipolar couplings are proportional to the solute orientation parameters, S_{kl}, whereas the nonrigid contribution shows a different dependence. All four contributions scale with ΔF (the anisotropy in the liquid-crystal field) if terms of order $(\Delta F)^2$ are neglected. For the quadrupolar couplings, expressions very

similar to those of the dipolar ones can be obtained. Anisotropies in indirect couplings are neglected throughout this paper.

The truncation of the Taylor expansion of the β tensor after the linear term leads to a number of a priori unknown parameters in the description, viz. $\Delta F \beta_{kl}^e$ and $\Delta F(\partial \beta_{kl}/\partial Q_m)^e$. Within the Born–Oppenheimer approximation, the β tensor is transferable from one isotopomer to the next. The isotopic dependence of the derivatives of the β tensor with respect to the normal coordinates is not trivial; there are subtle effects that have to do with the Eckart conditions that are usually invoked to obtain an optimal separation of vibrational and rotational motions.[11,13] The above parameters are not all independent; they depend on the point group symmetry of the solute in its equilibrium geometry. The dependencies between the parameters can therefore best be derived by formulating the problem in terms of symmetry coordinates, rather than normal coordinates. For more details, the reader is referred to the literature.[11,13]

4. Results and Discussion

4.1. Ethane Dipolar Couplings. A consistent set of experimental NMR dipolar couplings for ethane and its isotopomers studied in the present work is given in Table 1. These couplings are the starting point for our analysis. Ideally one would want to calculate all of the contributions to the dipolar couplings given in eq 22 from information available in the literature to see to what extent the experimental couplings can be reproduced.

The theory in Section 3 was developed in terms of Taylor expansions around the equilibrium geometry of the ethane molecule. This choice has been made for a very good reason. The equilibrium structure represents the location of the minima of the potential energy surface, is not affected by molecular vibrations, and is isotope-independent. Hence, all of the isotopomers of ethane possess the same equilibrium structure. The use of the equilibrium geometry is important for another reason. In principle, the vibrational and rotational degrees of freedom cannot be decoupled completely. To deal with this problem, the Eckart conditions of zero angular momentum[40] that lead to the definition of body-fixed axes are imposed. To treat the different ethane isotopomers on the same footing as much as possible, the use of the equilibrium geometry appears to be a judicious choice.[11]

If structural data are derived from spectroscopic experiments of any sort, then molecular zero-point vibrations are always present and have to be accounted for. Ideally, one would wish to obtain accurate data for the equilibrium structure of the molecule, but this requires very detailed information about the harmonic and anharmonic molecular force field. Usually the harmonic force field is available to a sufficient degree of accuracy. In contrast, the anharmonic force field is known for only a limited number of small molecules, and ethane is not among them. Hence, the equilibrium structure for ethane is not available, and consequently the "rigid" contribution $D_{\mu\nu}^e$ of eq 24 cannot be calculated. This clearly presents a problem.

In general, for two nuclei, 1 and 2, at a fixed distance r_e, both located on the z axis, with x and y perpendicular to z, the presence of vibrations leads to small displacements (Δx_1, Δy_1, Δz_1, Δx_2, Δy_2, and Δz_2). The so-called r_g structure is defined as

$$r_g = r_e + \langle \Delta z \rangle + \frac{1}{2r_e}(\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle) + ... \quad (28)$$

with $\Delta z = \Delta z_1 - \Delta z_2$ and so forth, and with the angular brackets

signifying averaging over all vibrational motions. The expansion has been truncated after terms of order 2. The second-order terms can be evaluated if the harmonic force field is known. The first-order term $\langle \Delta z \rangle$ requires knowledge of the anharmonic force field. Unfortunately, the only experimental structure available for ethane is the so-called r_z structure,[17] which has both methyl groups in the preferred staggered configuration (r_{CH} = 1.0940 Å, r_{CC} = 1.5351 Å, $\angle_{HCC}$ = 111.17°). This r_z structure is related to r_e in the following way[41,42]

$$r_z = r_e + \langle \Delta z \rangle \quad (29)$$

To proceed we assume that, instead of starting from the preferred r_e structure, the slightly different experimental r_z structure[17] can be employed to calculate

$$D_{\mu\nu}^z = d_{kl,\mu\nu}^z S_{kl} \quad (30)$$

with eq 22 becoming

$$D_{\mu\nu} = D_{\mu\nu}^z + D_{\mu\nu}^h + D_{\mu\nu}^{nonrigid} \quad (31)$$

The ensuing isotope dependencies that are inherent in this choice are ignored. The contributions $D_{\mu\nu}^z = D_{\mu\nu}^e + D_{\mu\nu}^a$, which include averaging of classical internal rotation about the CC bond (vide infra), are presented in Table 2 and are seen to dominate over the various vibrational effects.

The harmonic contribution can be obtained from the experimental harmonic force field, F_{ij}, defined in terms of symmetry displacement coordinates and based on the r_z structure.[19] Because the NMR suite of least-squares fitting programs employed to obtain optimal correspondence between experimental and calculated couplings computes harmonic corrections in terms of internal displacement coordinates, a transformation of the force field in terms of symmetry coordinates to one in terms of internal coordinates is required. How to perform this transformation is described in detail in ref 43. The so-called valence force constants, k_{ij}, expressed in terms of the symmetry force constants, F_{ij}, are tabulated in ref 18. The redundancies in this procedure are dealt with by setting a number of k_{ij} values deemed to be small equal to zero. The harmonic corrections to the dipolar couplings are calculated and listed in Table 2. The torsional mode that belongs to the A_{1u} irreducible representation of the D_{3d} group (and cannot couple with any other vibrational mode) is not included in this treatment and will be considered separately.

As indicated before, the torsional motion must be treated separately for two reasons. First, the truncated Taylor expansions employed in the treatment of small-amplitude normal modes are inadequate for large-amplitude internal rotation. Second, the coupling between torsional motion and overall rotation must be considered.[14–16]

The torsional potential energy, $V(\tau)$, possesses 3-fold periodicity as a function of the torsional angle, τ, and can be expanded in a Fourier series truncated after the second term as

$$V(\tau) = \frac{V_3}{2}(1 - \cos 3\tau) + \frac{V_6}{2}(1 - \cos 6\tau) + ... \quad (32)$$

Experimental values for the quantities that determine the height and shape of the barrier are known and are V_3 = 2.882 kcal/mol and V_6 = 0.020 kcal/mol.[17] Because the torsional motion does not couple to any other vibrational mode, a separation of variables can be performed leading to a one-dimensional

TABLE 2: Scaled Experimental and Calculated Dipolar Couplings Plus Contributions $D_{\mu\nu}^{z}$, $D_{\mu\nu}^{h}$, and $D_{\mu\nu}^{\text{nonrigid}}$ to the Calculated Dipolar Couplings (in Hz) from Solutes in ZLI 1132 at 298 K

		$D_{\mu\nu}^{\text{exptl}}$ (scaled)	$D_{\mu\nu}^{\text{calcd}}$ eq 31	$D_{\mu\nu}^{\text{exptl}} - D_{\mu\nu}^{\text{calcd}}$	$D_{\mu\nu}^{z}$ eq 30	$D_{\mu\nu}^{h}$ eq 26	$D_{\mu\nu}^{\text{nonrigid}}$ from ref 25 see text
CH_3-CH_3'	D_{HH}	609.328	609.396	−0.068	616.784	−3.617	−3.771
	$D_{HH'}$	−242.197	−242.083	−0.114	−239.704	−2.378	0
$^{13}CH_3-CH_3'$	D_{HH}	609.017	609.1	−0.083	616.536	−3.687	−3.749
	$D_{HH'}$	−242.058	−241.965	−0.093	−239.608	−2.357	0
	D_{CH}	371.671	371.606	0.065	397.628	−12.484	−13.538
	$^{a}D_{H'H'}$	609.017	609.13	−0.113	616.536	−3.634	−3.771
	$D_{CH'}$	−111.078	−110.829	−0.249	−110.54	−0.402	0.113
CH_3-CD_3	D_{HH}	607.742	607.762	−0.02	615.882	−4.348	−3.771
	D_{HD}	−37.172	−37.079	−0.093	−36.742	−0.337	0
	D_{DD}	14.523	14.377	0.147	14.513	−0.044	−0.092
	B_{D}	−2333.433	−2298.654	−34.78			
$CH_3-CH_2'D$	D_{HH}	608.815	608.885	−0.07	616.724	−4.067	−3.771
	D_{HD}	−37.094	−36.98	−0.114	−36.626	−0.353	0
	$D_{HH'}$	−242.549	−242.532	−0.017	−240.222	−2.31	0
	$D_{H'D}$	94.233	93.911	0.322	94.816	−0.378	−0.527
	$D_{H'H'}$	605.552	605.502	0.05	614.829	−4.547	−4.78
	B_{D}	−2386.57	−2342.795	−43.78			
$^{13}CH_3-CH_2'D$	D_{HH}	608.965	609.058	−0.093	616.943	−4.136	−3.749
	D_{HD}	−37.035	−36.973	−0.062	−36.623	−0.35	0
	$D_{HH'}$	−242.648	−242.652	0.004	−240.36	−2.292	0
	D_{CH}	371.62	371.561	0.059	397.891	−12.791	−13.538
	$D_{H'D}$	94.245	93.943	0.302	94.852	−0.382	−0.527
	$D_{H'H'}$	605.712	605.667	0.045	615.018	−4.571	−4.78
	$D_{CH'}$	−111.507	−111.456	−0.051	−111.094	−0.386	0.025
$CH_3-{}^{13}CH_2'D$	D_{HH}	609.017	609.13	−0.113	616.98	−4.079	−3.771
	D_{HD}	−37.075	−36.994	−0.081	−36.643	−0.351	0
	$D_{HH'}$	−242.63	−242.611	−0.019	−240.317	−2.293	0
	D_{CH}	−111.088	−110.854	−0.234	−110.62	−0.347	0.113
	$D_{H'D}$	94.262	93.938	0.324	94.855	−0.389	−0.527
	$D_{H'H'}$	605.754	605.708	0.046	615.095	−4.618	−4.769
	$D_{CH'}$	367.385	367.381	0.004	394.395	−12.972	−14.043
EBBA CH_3-CD_3	D_{HH}	565.531	565.534	−0.003	576.806	−4.072	−7.199
	D_{HD}	−34.726	−34.726	0	−34.411	−0.315	0
	D_{DD}	13.521	13.384	0.137	13.592	−0.041	−0.167
	B_{D}	−2118.029	−2152.81	34.78			

^{a} The experimental value of $D_{H'H'}$ in $^{13}CH_3-CH_3'$ is set equal to D_{HH} in the spectral fitting program.

Schrödinger equation for the torsional motion where $V(\tau)$ represents the potential energy. Truncating $V(\tau)$ after the V_3 term, this differential equation reduces to the so-called Mathieu equation whose eigenvalues and eigenfunctions have been tabulated.[16,44,45] In principle, the V_6 term can be taken into account with perturbation theory. At a given temperature, the dipolar couplings can then be calculated as an expectation value of the dipole operator, while obtaining the thermal average over all of the torsional levels populated according to the appropriate Boltzmann factors. Hence, the full quantum-mechanical treatment of the torsional problem can be performed, albeit with a considerable amount of effort.

Now we turn to the problem of coupling between torsional and overall rotational motions. In the absence of this coupling, the torsional-rotational problem can be described in terms of wave functions that are products of torsional wave functions, obtained following the above prescriptions, and rigid rotor wave functions appropriate for the overall rotation of the molecule. In principle, the torsional−rotational coupling can now be incorporated via perturbation theory. Clearly, this procedure is expected to converge much better for high than for low torsional barriers. In the case of ethane, the separations between rotational levels are much smaller than those between torsional levels. This situation defines the so-called high-barrier limit. In this limit, there are three equivalent and almost independent potential wells. Tunneling splittings arising from the torsional−rotational

coupling are small for low torsional levels and increase for levels closer to the top of the barrier. Under our experimental conditions, the influence of the lower torsional levels dominates completely because the higher torsional levels are hardly populated. A detailed quantum-mechanical analysis shows that in our experimental NMR study on ethane and its isotopomers the torsional−rotational interaction can be neglected safely. This is not necessarily the case for high-resolution spectroscopic studies, for example, those employing microwave spectroscopy, where evidence for tunneling splittings can often be observed.

Alternatively, the effect of the torsional motion on the dipolar couplings can be computed by using classical averaging while employing the untruncated $V(\tau)$ potential of eq 32 and appropriate Boltzmann weighting of the torsional potential. In such a classical picture, tunneling effects do not exist. When we compare our classical results with those of the full quantum-mechanical treatment, the differences appear to be slight. This is another indication that the neglect of tunneling effects arising from the torsional−rotational interaction is warranted. In view of all of the approximations that are involved in the full analysis of our NMR results, only results from the classical averaging procedure will be employed in the following. This classical averaging over the torsional motion is incorporated in the dipolar couplings calculated from the r_z structure presented in Table 2.

So far the contribution to the dipolar couplings arising from

11034 *J. Phys. Chem. A, Vol. 109, No. 48, 2005*

Burnell et al.

TABLE 3: Orientational Order Parameters, Nonrigid Scale Factors, and rms Values from Fits to Dipolar Couplings for Solutes in ZLI 1132 at 298 K

order parameter	no nonrigid	nonrigid from CH_3F	CH_3F nonrigid scaled
CH_3-CH_3			
S_{zz}	0.056398 (63)	0.056645 (9)	0.056681 (3)
$^{13}CH_3-CH_3$			
S_{zz}	0.056146 (58)	0.056593 (8)	0.056658 (3)
CH_3-CD_3			
S_{zz}	0.056253 (98)	0.056554 (13)	0.056598 (5)
CH_3-CH_2D			
S_{xx}	−0.028307 (126)	−0.028410 (17)	−0.028425 (6)
S_{zz}	0.056337 (95)	0.056632 (13)	0.056676 (5)
S_{xz}	0.001184 (519)	0.000451 (71)	0.000344 (25)
$^{13}CH_3-CH_2D$			
S_{xx}	−0.027883 (117)	−0.028366 (16)	−0.028436 (6)
S_{zz}	0.055914 (82)	0.056596 (11)	0.056696 (5)
S_{xz}	0.002231 (471)	0.000615 (64)	0.000378 (24)
$CH_3-^{13}CH_2D$			
S_{xx}	−0.028296 (122)	−0.028418 (17)	−0.028436 (6)
S_{zz}	0.056322 (83)	0.056651 (11)	0.056699 (4)
S_{xz}	0.001678 (180)	0.000512 (25)	0.000341 (10)
nonrigid factor	0	1	1.146 (4)
rms/Hz	2.52	0.34	0.12
EBBA at 300 K			
CH_3-CD_3			
S_{zz}	0.052348 (5)	0.052743 (2)	0.053007 (8)
nonrigid factor	0	1	1.670 (21)
rms/Hz	0.34	0.15	0.06

the reorientation−vibration interaction has not been taken into account. A least-squares fit on the complete set of dipolar couplings (calculated for the r_z structure, corrected for harmonic vibrations, and including the effect of the barrier classically) was carried out neglecting this contribution. In the fit only the independent Saupe orientation parameters of the isotopomers (1 for each molecule with axial symmetry, 3 for each molecule with a plane of symmetry, hence 12 in total) were varied while all of the structural parameters and those defining the barrier were kept fixed. Although convergence was reached, the rms value of the fit was not satisfactory, with differences between experimental and calculated dipolar couplings well outside their error ranges. The Saupe order parameters obtained for all of the molecules and the resulting rms are given in Table 3. A series of fits was also performed in which structural parameters and/or the barrier parameter, V_3, were varied. This led in all cases to much better quality fits with acceptable rms values, but the changes required in structural and/or barrier parameters were unreasonably large.

Next, the problem of calculating the contributions to the dipolar couplings arising from the reorientation−vibration interaction was considered. In such a calculation, one has to contend with a large number of unknown parameters: (i) $\Delta F \langle \beta_{zz} - 1/2(\beta_{xx} + \beta_{yy}) \rangle$, which signifies the product of ΔF and the anisotropy of the β tensor averaged over all vibrations; and (ii) parameters of form $\Delta F (\partial \beta_{kl}/\partial Q_m)^e$, one for each one-dimensional normal mode, and two for each doubly degenerate normal mode of the ethane molecule. Of course, one can try to obtain these unknowns by fitting the calculated to the observed dipolar couplings. However, together with the unknown Saupe order parameters that also have to be obtained from the fit, the problem becomes underdetermined quickly.

At this point, an alternative strategy was developed. Contributions to all of the dipolar couplings arising from the reorientation−vibration coupling, $D_{\mu\nu}^{\text{nonrigid}}$, were calculated from the

theoretical expressions in a previous extensive study on methyl fluoride and a series of its isotopomers. The relevant unknown parameters were obtained from a least-squares fitting procedure to all observed dipolar couplings[25] (see eq 27). In the CH_3F study, excellent agreement was generally obtained between calculated and observed dipolar couplings. Because there are ample indications that the harmonic and anharmonic force fields for a methyl group do not depend strongly on the molecule that the methyl group is part of,[26] there is justification for the transferability of the quantities $D_{\mu\nu}^{\text{nonrigid}}$ from methyl fluoride to ethane. Some nonrigid contributions can be transferred immediately, whereas for others some degree of improvisation is required. The contribution to the ethane dipolar coupling between a proton or a deuteron in one methyl group and the ^{13}C in the other methyl group is obtained from the nonrigid contribution to the HF or DF coupling in methyl fluoride by scaling with the appropriate ratio between F and ^{13}C gyromagnetic ratios. The nonrigid contribution to the coupling between protons or deuterons in different methyl groups in the ethanes was set equal to zero.

After transfer of the $D_{\mu\nu}^{\text{nonrigid}}$ contributions from the methyl fluoride to the ethane case, a least-squares fitting procedure was performed in which structure and barrier parameters were kept fixed, and where only the Saupe orientation parameters for the isotopomers were varied (see Table 3). Clearly, the introduction of the nonrigid contributions in the manner discussed above led to a very large improvement in the rms obtained in the fit. A last improvement that was introduced has to do with the fact that there is no way of knowing whether the experimental conditions in the methyl fluoride and ethane experiments are truly identical. However, because the $D_{\mu\nu}^{\text{nonrigid}}$ quantities scale with the anisotropy, ΔF, of the liquid-crystal field, a final least-squares analysis was performed in which, in addition to the Saupe order parameters, only a single multiplication factor that scales all of the nonrigid contributions was varied. This procedure led to an even better rms than before. The dipolar couplings calculated from this fit are presented in Table 2; the Saupe order parameters, the scaling factor, and the rms are presented in Table 3. The calculation shows that the nonrigid couplings have to be scaled up by only 15% compared to what they are in the independent CH_3F experiments. The agreement between calculated and experimental dipolar couplings is excellent and lends strong support to the present approach where nonrigid contributions based solely on methyl group transferability are employed.

As shown in Table 3, the order matrices for the CH_3-CH_2D isotopomers in ZLI 1132 are close to those expected for cylindrical symmetry. This indicates that the role of the CD bond does not deviate much from that of the CH bond. Also from Table 3, we note that the degrees of orientational order in ZLI 1132 and EBBA are very similar; this is consistent with a picture in which ethane behaves as a "magic solute"[2] where the interaction between a small solute quadrupole moment and an average solvent electric field gradient is expected to be minor compared to dominant size and shape effects. This situation differs from that of solutes with an appreciable quadrupole moment (such as methyl iodide, to be discussed in section 4.3), resulting in very different orientational order in the same liquid crystals, ZLI 1132 and EBBA.

4.2. Ethane Quadrupolar Couplings. Deuterium quadrupolar couplings B_D^{observed} for isotopomers CH_3CD_3 and CH_3-CH_2D in ZLI 1132 and CH_3CH_2D in EBBA have been measured. The intramolecular electric field gradient tensor that interacts with the deuterium quadrupole moment is assumed

Ethane and Isotopomers

J. Phys. Chem. A, Vol. 109, No. 48, 2005 **11035**

to be axially symmetric about the CD bond. For a rigid r_e or r_z structure, the deuterium coupling constant is then defined as[12,13]

$$B_{\mathrm{D}}^{\mathrm{rig}} = \frac{3}{4h} eV_{\parallel}^{\mathrm{rig}} Q_{\mathrm{D}} S_{cc} \tag{33}$$

where $V_{\parallel}^{\mathrm{rig}} = V_{cc}^{\mathrm{D}}$ is the negative of the electric field gradient at the site of the deuterium nucleus, defined along the direction c of the CD bond, eQ_{D} is the nuclear quadrupole moment of the deuterium nucleus, and S_{cc} is the Saupe orientation parameter of the CD bond. S_{cc} can be expressed in terms of the Saupe order parameters, S_{kl}, defined in terms of the molecule-fixed axes, x, y, and z, as

$$S_{cc} = S_{kl} \cos \theta_{kc} \cos \theta_{lc} \tag{34}$$

where $\cos \theta_{kc}$ is the direction cosine of angle θ between the k axis and the CD bond direction. Hence, S_{cc} can be calculated from the S_{kl} values obtained from the fit to the dipolar couplings. The application of vibrational corrections to the experimental quadrupolar couplings is notoriously complicated and is therefore neglected.[46] $B_{\mathrm{D}}^{\mathrm{rig}}$ can be calculated only if a value for the intramolecular field gradient, $V_{\parallel}^{\mathrm{rig}}$, is known. However, the quadrupolar couplings measured in ZLI 1132 and EBBA cannot be reproduced with the same value of $V_{\parallel}^{\mathrm{rig}}$. If any fixed value for this quantity is taken, then discrepancies arise. This is an indication that the observed couplings, $B_{\mathrm{D}}^{\mathrm{observed}}$, include an extra liquid-crystal dependent term, $B_{\mathrm{D}}^{\mathrm{external}}$, in addition to $B_{\mathrm{D}}^{\mathrm{rig}}$.

As in previous studies on molecular hydrogen, methane, and their isotopomers,[7,12,13] the discrepancies between experimental and calculated quadrupolar couplings, $B_{\mathrm{D}}^{\mathrm{external}}$, are ascribed to the presence of an average external electric field gradient (at the site of the deuteron nucleus) provided by the liquid-crystal environment

$$B_{\mathrm{D}}^{\mathrm{observed}} = B_{\mathrm{D}}^{\mathrm{rig}} + B_{\mathrm{D}}^{\mathrm{external}} \tag{35}$$

Extensive previous studies have shown that for ZLI 1132 and EBBA the average external field gradients are of similar magnitude but of opposite sign. Because a reliable experimental value for $eV_{\parallel}^{\mathrm{rig}} Q_{\mathrm{D}}/h$ does not exist, we adjust its value to 177.9 kHz to obtain an equal but opposite discrepancy in the quadrupolar couplings measured in ZLI 1132 and EBBA. The experimental and calculated quadrupolar couplings obtained in this way are given in Table 2. The value obtained for $eV_{\parallel}^{\mathrm{rig}} Q_{\mathrm{D}}/h$ is not unreasonable for a deuterium nucleus in a CD bond. Moreover, apart from their magnitudes that are a factor of ~2 smaller than what was observed before with molecular hydrogen and methane, the signs of $B_{\mathrm{D}}^{\mathrm{external}}$ (= experimental − calculated in Table 2) are consistent with what was found previously for ZLI 1132 and EBBA. Similar findings were obtained for a collection of aromatic solutes dissolved in ZLI 1132, EBBA and a magic mixture of these component liquid crystals.[47] Therefore, the present experiments on ethane and its isotopomers lend additional support to the notion that average external electric field gradients are important in these liquid crystals.

4.3. Implications for Other Solutes. Because the incorporation of the dipolar couplings arising from the reorientation−vibration mechanism was found to be essential in the analysis of our ethane results, using the same approach as discussed above should be considered for other solutes as well. Because the corrections to the dipolar couplings due to reorientation−vibration correlation are known for $^{13}\mathrm{CH}_3\mathrm{F}$, they can be transferred to other $^{13}\mathrm{CH}_3$-containing molecules. In a recent

TABLE 4: Nonrigid Corrections to Published Data for Methyl Iodide in EBBA and ZLI 1132[a]

	$D_{\mathrm{HH}}^{\mathrm{exptl}}$	$D_{\mathrm{CH}}^{\mathrm{exptl}}$	$D_{\mathrm{HH}}^{\mathrm{exptl}} - D_{\mathrm{HH}}^{\mathrm{nonrigid}}$	$D_{\mathrm{CH}}^{\mathrm{exptl}} - D_{\mathrm{CH}}^{\mathrm{nonrigid}}$	ξ'	ξ''
EBBA	168.71	150.7	173.87	136.31	0.901	1.056
	213.07	194.5	218.23	180.11	0.882	1.003
	243.2	214.8	248.36	200.41	0.911	1.026
	262.87	239.51	268.03	225.12	0.883	0.985
	271.67	239.95	276.83	225.56	0.911	1.016
ZLI 1132	990.4	794.29	993.67	806.1	1.003	1.020
	1123.86	901.15	1127.13	912.96	1.004	1.022

[a] The ξ parameters, which are unity for exact agreement between the NMR dipolar couplings and the microwave structure of the methyl group, are calculated from the following equations:

$$\xi' = \left(\frac{D_{\mathrm{CH}}}{D_{\mathrm{HH}}}\right)_{\mathrm{exptl}} \left(\frac{1 + p_{\mathrm{HH}}^{\mathrm{h}}}{1 + p_{\mathrm{CH}}^{\mathrm{h}}}\right) \left(\frac{g_{\mathrm{HH}}}{g_{\mathrm{CH}}}\right)$$

$$\xi'' = \left(\frac{D_{\mathrm{CH}}}{D_{\mathrm{HH}}}\right)_{\mathrm{exptl}} \left(\frac{1 + p_{\mathrm{HH}}^{\mathrm{h}} + p_{\mathrm{HH}}^{\mathrm{nonrigid}}}{1 + p_{\mathrm{CH}}^{\mathrm{h}} + p_{\mathrm{CH}}^{\mathrm{nonrigid}}}\right) \left(\frac{g_{\mathrm{HH}}}{g_{\mathrm{CH}}}\right)$$

We note that these definitions differ slightly from the ones given in ref 1; however, ξ' is in fact the parameter plotted in Figures 1 and 2 of that paper. In these equations, p_{ij}^{h} is the harmonic vibrational correction to the dipolar couplings (taken from ref 1) and $p_{ij}^{\mathrm{nonrigid}} = D_{ij}^{\mathrm{nonrigid}}/D_{ij}^{\mathrm{microwave}}$ where $D_{ij}^{\mathrm{microwave}}$ is calculated from $D_{ij}^{\mathrm{exptl}} = D_{ij}^{\mathrm{microwave}}(1 + p_{ij}^{\mathrm{h}}) + D_{ij}^{\mathrm{nonrigid}}$. The g_{ij} are geometrical parameters calculated from the microwave structure.[48]

study, new results and literature data for $^{13}\mathrm{CH}_3\mathrm{I}$ dissolved in a large variety of thermotropic and lyotropic liquid-crystal solvents were analyzed.[1] In this analysis, harmonic vibrational corrections were taken into account, but the reorientation−vibration interaction was neglected entirely. It was found that for given CH and HH internuclear distances, obtained from gas-phase microwave spectroscopy, the HCH angle derived from the dipolar couplings varied appreciably from one experiment to the next. Such "solvent-dependent structures" are often rationalized in terms of specific chemical interactions between solute and solvent or as resulting from the exchange of the solute between several "sites" in the liquid-crystal environment with different orientational order. It is of interest to see what the effect of incorporating reorientation−vibration corrections will be on the $^{13}\mathrm{CH}_3\mathrm{I}$ structure.

There are two problems in transferring the reorientation−vibration corrections from $^{13}\mathrm{CH}_3\mathrm{F}$ to $^{13}\mathrm{CH}_3\mathrm{I}$ because there is no guarantee that the $^{13}\mathrm{CH}_3\mathrm{F}$ and $^{13}\mathrm{CH}_3\mathrm{I}$ results are obtained under the same experimental conditions and with the same ΔF factor. In the ethane case, the latter complication invoked the need to do some ΔF scaling. Lacking this information, we transfer the $^{13}\mathrm{CH}_3\mathrm{F}$ nonrigid corrections to $^{13}\mathrm{CH}_3\mathrm{I}$ assuming a temperature of 302 K and otherwise identical experimental circumstances. Moreover, $^{13}\mathrm{CH}_3\mathrm{F}$ corrections are available only for liquid crystals ZLI 1132 and EBBA. In Table 4, the ratios of $D_{\mathrm{CH}}/D_{\mathrm{HH}}$ are compared without (ξ' in column 5 of Table 4[1]) and with (ξ'' in column 6 of Table 4) the incorporation of reorientation−vibration corrections. It is apparent that, despite the above inadequacies in the procedure, these reorientation−vibration corrections can explain the deviations of the factor ξ' from 1.0 quite adequately. Hence, when reorientation−vibration effects are accounted for, there is no need to invoke the concept of solvent-dependent structures. In addition, it should be pointed out that the reorientation−vibration corrections are not proportional to the Saupe orientation parameters. Hence, their neglect is especially detrimental in cases where the solute orientational order is relatively small. This agrees with previous observations in the literature.[1]

5. Conclusions

Simple, well-characterized molecules dissolved in nematic phases have proved to be extremely useful probes of the intermolecular potential. After work on hydrogen and methane and their isotopomers, an NMR study on ethane, a benchmark example of a molecule possessing large-amplitude torsional motion, dissolved in ZLI 1132 is undertaken. In addition, five isotopomers have been studied and a consistent set of dipolar and quadrupolar couplings is obtained for this series of solutes. The averaging over the harmonic vibrational motions required to correct the dipolar couplings for vibrational effects is performed in the usual manner. The effect of the internal rotation on the dipolar couplings is accounted for by classical averaging over the torsional mode. The corrected dipolar couplings should not be interpreted in terms of a reasonable molecular structure unless effects of the reorientation−vibration interaction are taken into account. Assuming that the reorientation−vibration contributions that are known for the methyl group in methyl fluoride are transferable to ethane, excellent agreement between observed and calculated dipolar couplings on the basis of the ethane gas-phase structure is obtained. These results convincingly show that the interaction between liquid crystal and solute does not lead to deformation of the gas-phase structure of the solute, provided that the reorientation−vibration interaction is included. Neglect of this effect is therefore generally not warranted.

Previously, the interpretation of the observed quadrupolar couplings caused difficulty in experiments on deuterated isotopomers of molecular hydrogen and methane dissolved as solutes in nematic liquid crystals.[7,12,13] The discrepancies between experimental and calculated quadrupolar couplings were resolved by assuming that an average external electric field gradient present in the liquid-crystal solvent interacts with the deuterium nuclei in the solutes. The quadrupolar couplings obtained for the deuterated ethanes in this work show very similar discrepancies. The current results lend strong support to the notion that average external electric field gradients present in liquid-crystal solvents cannot be ignored in the interpretation of measured quadrupolar couplings.

The transferability of the reorientation−vibration contributions to the dipolar couplings from a methyl group in one solute (CH_3F) to that in another (ethane) has important consequences. Often changes in observed dipolar couplings that arise if different liquid-crystal solvents are employed are interpreted in terms of ad hoc effects, such as specific chemical interactions, or in terms of solutes that exchange between various different sites in the anisotropic environment. Inclusion of the reorientation−vibration effects for methyl groups following the same procedure as outlined in this paper for ethane generally removes the need to interpret changes in observed dipolar couplings by invoking elusive chemical effects.

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