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An *ab initio* study of molecular hydrogen and its deuterated analogues partially oriented in nematic liquid crystals

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Thermal expectation values for nuclear magnetic resonance (NMR) observables for molecular hydrogen and its isotopically substituted analogues partially oriented in nematic liquid crystal solvents are calculated from first principles. High-quality nuclear wavefunctions and available data for highly correlated electronic wavefunctions at many different geometries are used from the literature. In the present description vibrational anharmonicity, centrifugal distortion, the changes of the nuclear quadrupole coupling with internuclear distance, and the dependence of the molecular quadrupole moment on the rotational quantum number have been included. The results strongly support previous conclusions that hydrogens in nematic phases are predominantly oriented through the interaction between their molecular quadrupole moment and the non-zero average external electric field gradient present in these solvents. In addition, the present theoretical results provide the basis for obtaining reliable estimates of such average external electric field gradients from a single NMR observable.

1. Introduction

In order to understand the mechanisms responsible for the partial orientation of molecules dissolved in liquid crystal solvents the use of small probe molecules such as hydrogen and its deuterated analogues has been extremely helpful. Such studies have brought to light that in nematic liquid crystals the presence of a non-zero average electric field gradient (efg) is important [1–5]. The interaction between these efg's and the solute molecular quadrupole moments provides the predominant contribution to the degree of orientation of hydrogens and its isotopomers and is far from negligible in the case of other solutes. These average efg's are temperature and concentration dependent properties of the solvent, and, depending on the solvent chosen, can have either a positive or a negative sign. This situation can be nicely exploited by forming mixtures of nematic liquid crystals possessing efg's with opposite signs in order to arrive at a novel type of solvent with an average efg of virtually zero. These so-called 'magic mixtures' have led to a real breakthrough in the general separation and elucidation of various orienting mechanisms which are now known to play a role.

In a description of the orientation of probe molecules in liquid crystal solvents a mean field approximation is the obvious starting point. Small probe molecules such as the hydrogens are eminently suitable to test the mean field approximation, since information on its electronic structure and molecular properties is available, either from experiment or from theory, in as much detail as desired. In the present paper the probe molecule in the anisotropic environment is considered as essentially freely

vibrating and rotating, with the anisotropic mean field potential only providing a small perturbation which, for one thing, does not significantly affect the electronic structure of the molecule. An important consequence of this perturbation which couples some electronic property of the solute with some average 'field' of the solvent is that it generates a correlation between the vibrational and reorientational motions of the probe molecule. In order to explore the details of this correlated motion a sufficiently detailed description of the free molecule is necessary. In this context the inclusion of vibrational anharmonicity and of centrifugal distortion should be considered.

An excellent experimental method for studying molecules partially oriented in an anisotropic solvent is by means of nuclear magnetic resonance (NMR). The relevant NMR observables are the intramolecular dipolar coupling which is determined by the distance between magnetic nuclei, and the quadrupolar coupling which arises from the magnitude of the electric field gradient present at the site of the nuclei with $I \geq 1$. In a full description which can predict NMR observables it is therefore important to include variations of the intramolecular electric field gradients as a function of internuclear distance. Moreover, when the predominant orienting mechanism is provided by the interaction between the overall molecular quadrupole moment and the non-zero average efg in the solvent, it will also be necessary to include the changes of the molecular quadrupole moment with vibrational and rotational state. Since the NMR observables are expectation values obtained at the temperature of the experiment, the Boltzmann population of all the relevant levels will obviously play a key role.

In order to put previous ideas on orientation mechanisms on as firm a basis as possible, inclusion of all the above effects in a full calculation on hydrogen and its deuterated analogues is a desirable goal. This goal is achieved in the present *ab initio* study, in which the importance of all the contributions mentioned above can be judged separately. The results from this calculation will be seen to strongly support conclusions arrived at previously and, in addition, will provide a simple means of obtaining a reliable estimate of average liquid crystal efg's from a single NMR coupling measured for one of the hydrogens.

2. Theory

2.1. Vibrational and rotational equations of motion

For the diatomic hydrogen molecule in its $^1\Sigma_g^+$ electronic ground state the spin-free vibrating rotator model is adopted [6]. By referring all coordinates to the centre of mass of the system the translational kinetic energy can be separated off and will not be considered here.

In the absence of external fields and in the Born–Oppenheimer approximation the (time-independent) Schrödinger equation describing the nuclear motion is given by [6, 7]

$$\begin{aligned} H\psi(r, \vartheta, \varphi) &= \left[-\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] \psi(r, \vartheta, \varphi) \\ &= \left[-\frac{\hbar^2}{2\mu r^2} \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - J^2 \right) + V(r) \right] \psi(r, \vartheta, \varphi) = E\psi(r, \vartheta, \varphi), \end{aligned} \quad (1)$$

with

$$J^2 = -\frac{1}{\sin^2 \vartheta} \left[\sin \vartheta \frac{\partial}{\partial \vartheta} \sin \vartheta \frac{\partial}{\partial \vartheta} + \frac{\partial^2}{\partial \varphi^2} \right]; \quad J_z = \frac{1}{i} \frac{\partial}{\partial \varphi},$$

where spherical polar coordinates are used, i.e. r is the internuclear distance, and ϑ and φ are the usual polar angles that specify the orientation of the internuclear vector with respect to a space-fixed axis system X, Y, Z . In equation (1) μ is the (nuclear) reduced mass of the system and $V(r)$ is the potential energy function for the nuclei which varies as a function of internuclear distance. The latter represents the electronic energy including the nuclear repulsion for fixed relative positions of the nuclei. Although corrections to this electronic energy due to coupling of the electronic and nuclear motion can be included in $V(r)$ [8], these corrections are not expected to change the results obtained significantly and have been neglected in this study.

By a partial separation of variables

$$\psi(r, \vartheta, \varphi) = \frac{1}{r} T(r) Y(\vartheta, \varphi),$$

the well-known radial equation is obtained

$$\left[\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + E - V(r) - \frac{\hbar^2}{2\mu r^2} J(J+1) \right] T(r) = 0. \quad (2)$$

The angular function can be identified as a spherical harmonic $Y_{JM}(\vartheta, \varphi)$ with J and M the rotational quantum numbers. The term containing J in equation (2) reflects the vibrational effect on the instantaneous moment of inertia (centrifugal distortion). The solution of the radial equation requires knowledge of the electronic potential energy function $V(r)$. The crudest approximation of the internal (vibrational) motion is to assume that $V(r)$ can be adequately described by a Hooke's law potential function, expressing the potential energy as a quadratic function of the nuclear coordinates. This can be considered as a fair approximation to the true $V(r)$ for small displacements away from the equilibrium internuclear separation r_e only, and corresponds to expanding the true $V(r)$ in a Taylor series in powers of $r - r_e$ and neglecting all powers beyond the second. More realistically, vibrational anharmonicity is allowed for by retaining higher powers in this series. In the case of molecular hydrogen $V(r)$ has been calculated numerically by solving the wave equation for the motion of the electrons for the molecular energy in the fixed-nuclei approximation [9, 10]. Using this accurate internuclear potential the radial equation can be solved for the vibrational and rotational energy levels $E_{v,J}$ and the corresponding nuclear wavefunctions. Usually the Numerov-Cooley numerical integration method is chosen for solving equation (2). In the present paper the radial equation is solved by the variational method, expanding $\psi(r, \vartheta, \varphi)$ in terms of linear combinations of products of simple harmonic oscillator wavefunctions and spherical harmonics.

The orientational effects of small solutes in nematic liquid crystals result in observable dipolar and quadrupole NMR line splittings and can be adequately modelled assuming that the anisotropic environment provides a (relatively small) mean-field orienting potential. Snijders *et al.* [2] have developed a general theory for these orientational effects built upon the assumption that the orienting mean-field

potential explains the orientation of a solute via its interaction with an electronic property $\Delta(r)$ of that solute. For molecular hydrogen, possessing cylindrical symmetry around the internuclear vector taken as the molecule-fixed z -axis, this potential has the general form [1, 2]

$$H^{\text{liquid crystal}} = \Delta(r)S_{zz}, \quad (3)$$

where S_{zz} is the orientation operator, describing the orientation of the solute

$$S_{zz} = \frac{3}{2} \cos^2 \vartheta - \frac{1}{2} = \left(\frac{4\pi}{5}\right)^{1/2} Y_{20}(\vartheta, \varphi). \quad (4)$$

Note the dependence of the orienting potential on both the internuclear distance r and the polar angles ϑ and φ , thus introducing a correlation between the associated vibrational and rotational (orientational) motions of the hydrogen molecule. This interaction potential can be considered as a single-molecule potential that generally can be written as a series expansion in terms of an appropriate complete basis. In equation (3) this expansion is restricted to the first term (of rank two) of this expansion, in accordance with the uniaxial symmetry of the nematic phase.

If the mean-field orienting perturbation $H^{\text{liquid crystal}}$ is added to equation (1), and after substitution of

$$\psi(r, \vartheta, \varphi) = \frac{1}{r} \chi(r, \vartheta, \varphi)$$

we obtain the following equation of motion for a single molecule in an orienting field

$$\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2\mu r^2} J^2 + V(r) + \Delta(r)S_{zz} \right] \chi(r, \vartheta, \varphi) = E\chi(r, \vartheta, \varphi). \quad (5)$$

In equation (5) the potential energy function $V(r)$ is formally divided into a harmonic and an anharmonic part

$$V(r) \equiv V^{\text{harmonic}}(r) + V^{\text{anharmonic}}(r) = \frac{1}{2}\mu\omega^2(r - r_e)^2 + V^{\text{anharmonic}}(r),$$

with ω the angular frequency of the corresponding harmonic oscillator. This partition facilitates the evaluation of matrix elements as will be discussed later.

By introducing the dimensionless normal coordinate x

$$x = \alpha(r - r_e), \quad \alpha^2 = \frac{\mu\omega}{\hbar},$$

and writing

$$\chi(r, \vartheta, \varphi) = \Phi(x, \vartheta, \varphi),$$

to simplify notation, equation (5) can be rearranged to

$$\begin{aligned} H\Phi(x, \vartheta, \varphi) &= (H^{\text{harmonic}} + H^{\text{anharmonic}} + H^{\text{centrifugal distortion}} \\ &\quad + H^{\text{liquid crystal}})\Phi(x, \vartheta, \varphi) \\ &= E\Phi(x, \vartheta, \varphi), \end{aligned}$$

with

$$\left. \begin{aligned} H^{\text{harmonic}} &= -\frac{1}{2}\hbar\omega\left(\frac{\partial^2}{\partial x^2} - x^2\right), \\ H^{\text{anharmonic}} &= V^{\text{anharmonic}}\left(r_e + \frac{x}{\alpha}\right) = V\left(r_e + \frac{x}{\alpha}\right) - \frac{1}{2}\hbar\omega x^2, \\ H^{\text{centrifugal distortion}} &= \frac{\hbar^2}{2\mu\left(r_e + \frac{x}{\alpha}\right)^2} J^2, \\ H^{\text{liquid crystal}} &= \Delta\left(r_e + \frac{x}{\alpha}\right) S_{zz}. \end{aligned} \right\} \quad (6)$$

The solutions of equation (6) yield both the wavefunctions and energies for the diatomic molecule in the presence of an orienting mean-field interaction from which expectation values for operators associated with NMR observables can then be calculated. In particular, it is assumed here that the external perturbation in equation (3) does not modify the molecular electronic structure, and therefore allows us to utilize the accurately calculated electronic properties of molecular hydrogen for this purpose.

Due to the presence of $H^{\text{liquid crystal}}$ in equation (6) a separation into vibrational and rotational variables is no longer feasible. It should be noticed that the rotational quantum number J is no longer a constant of the motion in equation (6), in contrast with M which still serves to characterize the solution.

To solve equation (6), $\Phi(x, \vartheta, \varphi)$ is expected in terms of a set of basis functions taken as a set of simple products of normalized harmonic oscillator wavefunctions $\varphi_v(x)$ and spherical harmonics $Y_{JM}(\vartheta, \varphi)$

$$\left. \begin{aligned} \Phi(x, \vartheta, \varphi) &= \sum_{v,J,M} c_{vJM} \varphi_v(x) Y_{JM}(\vartheta, \varphi) \equiv \sum_{v,J,M} c_{vJM} |vJM\rangle, \\ \varphi_v(x) &= N_v H_v(x) \exp\left(-\frac{1}{2}x^2\right), \quad N_v = \left[\left(\frac{1}{\pi}\right)^{1/2} \frac{1}{2^v v!}\right]^{1/2}, \end{aligned} \right\} \quad (7)$$

with $H_v(x)$ a Hermite polynomial of degree v .

The linear expansion coefficients c_{vJM} in equation (7) are determined by the variation method via a diagonalization of the Hamiltonian matrix representation in this (truncated) basis set. These simple product basis functions are an appropriate choice for an approximate solution of equation (6) for the lowest vibrational-rotational states which are of particular interest here. The success of the above approach obviously depends upon a judicious choice of a particular basis set, the number of basis functions retained and the particular functions chosen. These matters are discussed in more detail in section 2.4.

2.2. Hamiltonian matrix

For the evaluation of the matrix elements of the Hamiltonian the operator H in equation (6) has been divided into several parts as indicated. Using the well-known properties of the harmonic oscillator eigenfunctions and the spherical harmonics H^{harmonic} is readily seen to give only non-zero diagonal matrix element contributions

$$\begin{aligned} \langle \Phi(x, \vartheta, \varphi) | H^{\text{harmonic}} | \Phi(x, \vartheta, \varphi) \rangle \\ = \sum_{v', J', M'} \sum_{v, J, M} c_{v' J' M'}^* c_{v J M} \hbar \omega (v + \frac{1}{2}) \delta_{v' v} \delta_{J' J} \delta_{M' M}. \end{aligned} \quad (8a)$$

To determine the matrix element contributions of $H^{\text{anharmonic}}$ the numerical internuclear potential data calculated by Kolos and Wolniewicz for molecular hydrogen [9] have been employed. Formally these are

$$\begin{aligned} \langle \Phi(x, \vartheta, \varphi) | H^{\text{anharmonic}} | \Phi(x, \vartheta, \varphi) \rangle \\ = \sum_{v', J', M'} \sum_{v, J, M} c_{v' J' M'}^* c_{v J M} \langle v' | V^{\text{anharmonic}} \left(r_e + \frac{x}{\alpha} \right) | v \rangle \delta_{J' J} \delta_{M' M}. \end{aligned} \quad (8b)$$

The radial integrals in equation (8b) have a suitable form to be evaluated using the Gaussian quadrature numerical integration technique based on an (interpolating) Hermite polynomial [11, 12]. When this method is used for the actual calculation of the integrals involving the harmonic oscillator eigenfunctions $|v\rangle$ and some function g of the internuclear distance r (or the reduced normal coordinate x), the function values must be known at the appropriate Gauss points, i.e. the zeros x_i of the interpolating Hermite polynomial H_n of degree n

$$\left. \begin{aligned} \langle v' | g(x) | v \rangle &= N_v N_{v'} \int_{-\infty}^{\infty} \exp(-x^2) f(x) dx, \quad \text{with } f(x) = H_v(x) H_{v'}(x) g(x), \\ \text{and} \\ \int_{-\infty}^{\infty} \exp(-x^2) f(x) dx &= \sum_{i=1}^n w_i f(x_i) + R_n, \quad w_i = \frac{2^{n-1} n! \sqrt{\pi}}{n^2 [H_{n-1}(x_i)]^2}. \end{aligned} \right\} \quad (9)$$

The remainder R_n vanishes for polynomials f of a degree less than or equal to $2n - 1$ (provided that the integrated function possesses no singularity). The zeros x_i of the interpolating Hermite polynomial H_n used and the associated weights w_i were calculated with a small Pascal program using an algorithm taken from the literature [13].

The calculation of the radial integrals in equation (8b) using equation (9) requires the values of the internuclear potential function $V^{\text{anharmonic}}$ at the zeros x_i which are normally not located at the internuclear distances for which numerical data are available. The appropriate x_i values have been obtained through interpolation by a natural cubic spline [14–16].

Similar to equation (8a) and (8b), the matrix contributions of $H^{\text{centrifugal distortion}}$ are given by

$$\begin{aligned} \langle \Phi(x, \vartheta, \varphi) | H^{\text{centrifugal distortion}} | \Phi(x, \vartheta, \varphi) \rangle \\ = \sum_{v', J', M'} \sum_{v, J, M} c_{v' J' M'}^* c_{v J M} \langle v' | \frac{\hbar^2}{2\mu \left(r_e + \frac{x}{\alpha} \right)^2} | v \rangle \langle J' M' | J^2 | J M \rangle, \end{aligned} \quad (8c)$$

where

$$\langle J'M' | J^2 | JM \rangle = J(J+1) \delta_{J'J} \delta_{M'M}.$$

The calculation of the radial integrals in equation (8c) is straightforward as the radial part of the centrifugal distortion Hamiltonian is an analytical function, and the required values at the Gauss points can be evaluated directly.

Finally, the contributions of $H^{\text{liquid crystal}}$ are given by

$$\begin{aligned} & \langle \Phi(x, \vartheta, \varphi) | H^{\text{liquid crystal}} | \Phi(x, \vartheta, \varphi) \rangle \\ &= \sum_{v', J', M'} \sum_{v, J, M} c_{v' J' M'}^* c_{v J M} \langle v' | \Delta \left(r_e + \frac{x}{\alpha} \right) | v \rangle \langle J'M' | S_{zz} | JM \rangle. \quad (8d) \end{aligned}$$

The orientational integrals in equation (8d) are obtained, using equation (4) and the Gaunt formula for integrals of the product of three spherical harmonics [11, 17]

$$\begin{aligned} & \langle J'M' | S_{zz} | JM \rangle \\ &= \delta_{M'M} \left\{ \begin{aligned} & \delta_{J'J+2} \frac{3}{2} \frac{1}{(2J+3)} \left(\frac{[(J+2)^2 - M^2][(J+1)^2 - M^2]}{(2J+1)(2J+5)} \right)^{1/2} \\ & + \delta_{J'J} \frac{J(J+1) - 3M^2}{(2J-1)(2J+3)} \\ & + \delta_{J'J-2} \frac{3}{2} \frac{1}{(2J-1)} \left(\frac{(J^2 - M^2)[(J-1)^2 - M^2]}{(2J-3)(2J+1)} \right)^{1/2} \end{aligned} \right\}. \quad (10) \end{aligned}$$

For the calculation of the radial integrals in equation (8d) the orienting interaction Δ must be specified. It has been established from experimental studies of molecular deuterium dissolved in various liquid crystal solvents that the interaction between the molecular quadrupole moment and a mean efg accounts for most (but not all) of the orientational ordering [4]. If this particular interaction is assumed to be solely responsible for the orientation of molecular hydrogen and its deuterated analogues, then [3]

$$\Delta(r) = -\frac{1}{2} F_{zz} Q_{zz}. \quad (11)$$

Recently, Emerson *et al.* [18] studied some of the fundamental approximations usually made in the Maier-Saupe theory of nematics for a model nematogen which includes both anisotropic repulsive and attractive forces. Their molecular dynamics calculations show that the intermolecular vectors for near-neighbour intermolecular separations are anisotropically distributed. Such a non-spherical distribution is required in a molecular field description for electrostatic interactions (such as between the electric quadrupole tensor of the solute and the efg provided by the environment) to give non-vanishing contributions to the orientational order in a nematic. However, a quantitative treatment of an anisotropic distribution of intermolecular vectors remains difficult, as separate averaging over the magnitude and orientation of interparticle distances may not be warranted. In the present approach we therefore truncate the mean field potential at the second rank term as in equation (3), and furthermore assume that the orienting potential can be factored into a product of terms which solely depend on the solvent and solute, respectively, as in equation (11). F_{zz} is the component of the traceless mean efg tensor in space-fixed axes, with the

symmetry axis Z oriented along the external magnetic field for nematic liquid crystals which orient along and possess cylindrical symmetry around this direction. Q_{zz} is the zz component of the molecular quadrupole moment tensor of hydrogen in molecular-fixed axes x, y, z . The radial integrals in equation (8d) can now be evaluated, similarly to those in equation (8b). Starting from the accurate numerical data for the H_2 molecular quadrupole moment as a function of internuclear distance from calculations of Poll and Wolniewicz [19], cubic spline interpolation and Gauss–Hermite quadrature integration have again been employed.

Now, for specific values of F_{zz} , the matrix representation $\mathbf{H}$ can be obtained. A look at equations (8) shows immediately that this matrix is relatively sparse. In fact, due to the properties of both the spherical harmonics to describe the orientational behaviour of the wavefunctions Φ and the orientational operator S_{zz} , $\mathbf{H}$ possesses a block-diagonal form. It can be written as a direct sum of $(2J + 1)$ submatrices that can be labelled according to the rotational quantum number M , the constant of the motion,

$$\mathbf{H} = \mathbf{H}^{M=-J} \oplus \mathbf{H}^{M=-J+1} \oplus \dots \oplus \mathbf{H}^{M=J-1} \oplus \mathbf{H}^{M=J}. \quad (12)$$

Furthermore, every sub-matrix $\mathbf{H}^M$ can again be written as a direct sum of two sub-matrices by collecting product basis functions $|vJM\rangle$ with even and odd values of J in two distinct groups:

$$\mathbf{H}^M = \mathbf{H}^{M;\text{even } J} \oplus \mathbf{H}^{M;\text{odd } J}, \quad (13)$$

and

$$\mathbf{H}^M = \mathbf{H}^{-M}.$$

In solving for the c_{vJM} for a particular state Φ and its associated energy attention can be focused upon a single block, due to the independent behaviour of the submatrices. Without the external perturbation $H^{\text{liquid crystal}}$ there are $2J + 1$ different degenerate levels for each value of J corresponding to the different values of M . $H^{\text{liquid crystal}}$, when present, removes this degeneracy: the levels are separated into pairs of degenerate levels (that can be labelled by $\pm M$), except for $M = 0$, which is non-degenerate. Even the (symmetric) submatrices are relatively sparse, as is visualized in figure 1, but with the development of computing techniques it is not too hard to diagonalize large symmetric matrices, even when a desktop personal computer is used for this purpose. In the present paper the well-known Jacobi method for real symmetric matrices [20] has been used to obtain the states Φ and their energy to calculate NMR observables of molecular hydrogen in nematic liquid crystals.

2.3. Calculation of NMR observables

For the hydrogen molecule and its deuterated analogues the operator $\mathbf{A}$ associated with an observable such as the dipolar or the quadrupolar couplings, that can be measured by NMR, can be written [2] as the product of a radial part $a_{zz}(r)$ and the orientation operator defined in equation (4)

$$\mathbf{A}(r, \vartheta, \varphi) = a_{zz}(r)S_{zz}(\vartheta, \varphi). \quad (14)$$

For the dipolar coupling the radial part is equal to

$$a_{zz}(r) = -\frac{\hbar}{2\pi} \frac{\gamma_i \gamma_j}{r^3}, \quad (14a)$$

with γ_i and γ_j the gyromagnetic ratios of the interacting nuclei i and j .

Figure 1. Structure of the partitioned submatrix $\mathbf{H}^M$; even or odd J when the basis functions $|vJM\rangle$ with a particular value for M are grouped according to the value of J (either even or odd). See discussion in section 2.4.

When $\mathbf{A}$ is taken to be the operator associated with the quadrupolar coupling observed for hydrogen molecules containing a deuteron the radial part $a_{zz}(r)$ is given by

$$a_{zz}(r) = -\frac{3}{4} \frac{eQ_D}{h} V_{zz}(r), \quad (14b)$$

where Q_D is the nuclear quadrupole moment of the deuteron and $V_{zz}(r)$ is the intramolecular electric field gradient along the internuclear direction. $V_{zz}(r)$ has been determined for molecular hydrogen using highly correlated wavefunctions [21–23]. Note that in equation (14b) possible contributions to the electric field gradient due to external charges have not been included. Reid and Vaida [21, 22] have obtained an accurate value for Q_D by combining the results of their virtually exact calculations of $V_{zz}(r)$ with values for the electric quadrupole interaction constant from molecular beam magnetic resonance experiments: $Q_D = 0.2860 \text{ fm}^2$.

The quantity that is actually observed in an NMR experiment is the thermodynamic expectation value of the operator $\mathbf{A}$

$$\langle \mathbf{A}(r, \vartheta, \varphi) \rangle_T = \sum_m P_m \langle m | \mathbf{A}(r, \vartheta, \varphi) | m \rangle, \quad \text{with } P_m = \frac{\exp(-E_m/kT)}{\sum_i \exp(-E_i/kT)}. \quad (15)$$

Temperature effects are included in this average at temperature T via the Boltzmann

weight factors P_m that account for the thermal occupation of the states Φ_m with energy E_m . In principle, all populated vibrational-rotational states do contribute but the hydrogen molecules are somewhat unusual in the sense that their rotational as well as their vibrational levels are widely spaced. At normal temperatures the contribution of the insignificantly populated vibrationally excited states can be safely neglected and only a relatively limited number of rotational states associated with the vibrational ground state need to be considered in an actual calculation of the temperature weighted average in equation (15).

In the following the calculated thermodynamic expectation values for the dipolar and quadrupolar couplings will be referred to by their usual symbols, D and B respectively.

After inserting the basis set expansion in equation (7) for the states Φ_m the temperature and quantum average in equation (15) can be evaluated using

$$\langle m | \mathbf{A}(r, \vartheta, \varphi) | m \rangle = \sum_{v', J', M'} \sum_{v, J, M} c_{v' J' M'; m}^* c_{v J M; m} \langle v' | a_{zz}(r) | v \rangle \langle J' M' | S_{zz} | J M \rangle. \quad (16)$$

The calculation of numerical values for the NMR observables from this equation requires, besides evaluation of the linear expansion coefficients $c_{v J M; m}$ for the states Φ_m as discussed in the previous paragraph, the calculated values for the radial integrals $\langle v' | a_{zz}(r) | v \rangle$. The Gauss-Hermite quadrature numerical integration technique in equation (9) has again been used for this purpose. For the dipolar coupling D the required values at the Gauss points x_i can be directly calculated. For the quadrupolar coupling B the numerical data for the intramolecular electric field gradient function $V_{zz}(r)$ calculated by Reid and Vaida [21] have again been interpolated by a cubic spline to obtain values for the efg at the zeros of the interpolating Hermite polynomial used in the Gauss quadrature integration.

Furthermore, the symmetry restrictions imposed by the Pauli principle on the full molecular wavefunction under interchange of the two identical nuclei for homonuclear diatomics must be obeyed when equation (16) is used to calculate temperature weighted expectation values for NMR observables. Under ordinary circumstances both molecular hydrogen and molecular deuterium can be considered as consisting of two distinct molecular species, one with symmetric (ortho) and one with antisymmetric (para) nuclear spin wavefunctions. This restricts the linear expansion coefficients $c_{v J M; m}$ in equation (16) to non-zero values for

$$\begin{array}{ll} \text{even } J: & \text{para-H}_2, \quad \text{ortho-D}_2, \\ \text{odd } J: & \text{ortho-H}_2, \quad \text{para-D}_2, \\ \text{all } J: & \text{HD.} \end{array}$$

Hence, separate values for D and B are obtained for each of these molecular hydrogen species. When the external perturbation Δ due to the liquid crystal environment is taken to be the interaction between the molecular quadrupole moment and an external mean efg F_{zz} as in equation (11), there is an additional contribution to the value of the quadrupolar coupling B [3]

$$B^{\text{external efg}} = -\frac{3}{4} \frac{eQ_D}{h} F_{zz}. \quad (17)$$

As a consequence of the presence of an external efg F_{zz} the thermal expectation value

for the quadrupolar coupling B comprises two contributions:

$$B = B^{\text{intramolecular efg}} + B^{\text{external efg}}, \quad (18)$$

with $B^{\text{intramolecular efg}}$ stemming from the intramolecular efg that can be evaluated from equations (14), (14*b*), (15) and (16), and $B^{\text{external efg}}$ given by equation (17).

2.4. Computational details

The set of basis functions in equation (7) used in this study to describe the vibrational and rotational states of molecular hydrogen contains a number of adjustable parameters. One can vary the number of harmonic oscillator basis functions and spherical harmonics. Also, for the harmonic oscillator functions used the angular frequency ω and the location of the minimum of potential energy of the corresponding oscillator can be adjusted. No elaborate optimization of these parameters has taken place. They were fixed to sufficiently realistic values. The angular frequency of the harmonic oscillator basis functions was fixed to 4400, 3800 and 3100 cm^{-1} for H_2 , HD and D_2 respectively and centred at a common internuclear distance $r_e = 0.741404 \text{ \AA} = 1.40105 \text{ a.u.}$ All physical constants were taken from [24] except for the gyromagnetic ratio of the deuteron γ_D which was taken from [25]. For the nuclear reduced masses we used $\mu = 918.055, 1223.87$ and 1835.198 a.u. for H_2 , HD and D_2 , respectively. Primarily, we used 40 harmonic oscillator basis functions to describe the radial part of $\Phi(x, \vartheta, \varphi)$ in equation (7) and an interpolating Hermite polynomial of degree 76 to obtain the radial matrix elements by Gauss–Hermite quadrature integration. The accuracy of this integration scheme for the evaluation of molecular properties has been tested for a hydrogen molecule with its potential energy function described by the well-known Morse potential [26, 27]. Neglecting centrifugal distortion by setting J equal to zero we obtained an accuracy of at least 16 significant figures. When an internuclear distance potential grid of Morse potential energies analogous to the data of Kolos and Wolniewicz for the hydrogen molecule [9] was used in combination with cubic spline interpolation to evaluate the required values at the Gauss points, the accuracy in the molecular energies was at least six significant figures.

Another point in the calculation of NMR observables is the number of rotational states associated with the vibrational ground state taken into account. If too large J values for the spherical harmonics included in the basis set are taken, the dimension of the sub-matrices $\mathbf{H}^M$ to be diagonalized and hence the overall calculation time increases greatly. Since the rotational levels associated with these high J values are hardly populated, inclusion of such contributions is not needed. We have found that using spherical harmonics in equation (7) with J values of 0–10 (thereby with $J_{\text{max}} = 10$ including $(J_{\text{max}} + 1)^2$ rotational levels) was sufficient.

All calculations were performed in extended precision (19–20 decimal digits) on an Apple Macintosh IICI personal computer, featuring a 25 MHz Motorola MC68030 CPU and MC68882 floating-point coprocessor. The IICI was equipped with 8 Mb DRAM and a 64 Kb 25 ns static RAM direct memory mapped cache board. A typical calculation of NMR observables from first principles for a hydrogen molecule took approximately five hours on the Apple Macintosh IICI.

The structure of the partitioned submatrix $\mathbf{H}^{M; \text{even or odd } J}$ when the basis functions $|vJM\rangle$ with a particular value for M are grouped according to the value of J (either

even or odd) is shown in figure 1. The dimension of each submatrix is equal to the number of harmonic oscillator basis functions.

The matrix elements occurring in the white space of figure 1 are equal to zero. Non-zero matrix elements are found in the off-diagonal (light grey) submatrices when the liquid crystal perturbation $H^{\text{liquid crystal}}$ is present. $H^{\text{liquid crystal}}$ also contributes to the (dark grey) submatrices on the diagonal. The latter would be the only non-zero blocks if the external perturbation is absent and attention is focused on an isolated vibrating and rotating gas-phase hydrogen molecule.

The values of J associated with the submatrices of $\mathbf{H}^{M;\text{even or odd } J}$ in figure 1 are found in the following way. The value for $J_{\text{low-end}}$ can be determined from the value of M associated with the submatrix under consideration from:

	odd M	even M
$J_{\text{low-end, even } J}$	$M + 1$	M
$J_{\text{low-end, odd } J}$	M	$M + 1$

The value of $J_{\text{high-end}}$ can be derived from the maximum value of J used in the full (truncated) set of basis functions $|vJM\rangle$, J_{max}

	odd J_{max}	even J_{max}
$J_{\text{high-end, even } J}$	$J_{\text{max}} - 1$	J_{max}
$J_{\text{high-end, odd } J}$	J_{max}	$J_{\text{max}} - 1$

We introduce the notation

$$[n/2] = \begin{cases} n/2, & \text{for even } n, \\ (n-1)/2, & \text{for odd } n, \end{cases}$$

i.e., $[n/2]$ equals the integral part of $n/2$.

The number of blocks that occur along the diagonal of $\mathbf{H}^{M;\text{even or odd } J}$ are given by

even J_{max} and even J	even J_{max} and odd J
or	or
odd J_{max} and odd J	odd J_{max} and even J
$[(J_{\text{max}} + 2 - M)/2]$	$[(J_{\text{max}} + 1 - M)/2]$

The block labels K , L for the submatrices in $\mathbf{H}^{M;\text{even or odd } J}$ are equal to

$$[(J - J_{\text{low-end}} + 2)/2].$$

If, e.g., $J_{\text{max}} = 10$, $M = 1$ then for $\mathbf{H}^{M;\text{even } J}$, $J_{\text{low-end}} = 2$, $J_{\text{high-end}} = 10$, number of blocks = 5; $J_{\text{max}} = 10$, $M = 1$ then for $\mathbf{H}^{M;\text{odd } J}$, $J_{\text{low-end}} = 1$, $J_{\text{high-end}} = 9$, number of blocks = 5.

3. Results and discussion

In table 1 results of calculations using the *ab initio* quantum mechanical model described in the previous sections are presented for molecular hydrogen and its deuterated analogues. It is assumed that the interaction of an external efg F_{ZZ} with the molecular quadrupole moment of the hydrogen molecule is solely responsible for the orientation of the solute. The range of sample values for the efg F_{ZZ} includes the available estimates of the external efg present in various nematic liquid crystal solvents from NMR experiments employing molecular deuterium as a probe molecule [1–5, 28]. A number of observations that have been made before in these studies—using a gas-phase molecule model with additional simplifying assumptions about the internal and rotational motions—are confirmed by the much more advanced calculations presented here.

The (temperature dependent) mean efg F_{ZZ} present in a nematic liquid crystal can have a positive or negative sign depending on the particular solvent chosen and accounts for the sign and magnitude of the observed orientation and NMR spectral parameters. When the calculated values for the dipolar couplings of HD and D₂ are scaled by a factor γ_H/γ_D and $(\gamma_H/\gamma_D)^2$ respectively to eliminate the trivial effect of the different magnetogyric ratios upon these couplings, the major effect of replacing a hydrogen by a deuterium in molecular hydrogen is to increase the dipolar coupling scaled to H₂-values by almost 7%. This effect is essentially of quantum mechanical origin and cannot be explained classically [1]. The experimental observation that the hydrogen species with a larger average internuclear distance has a smaller orientation is confirmed in a natural way by the quantum mechanical model.

The summations over the separate even and odd J -ladders for the *ortho*-D₂ and *para*-D₂ species respectively give virtually identical calculated NMR observables. This is quite remarkable, especially in view of the different values of the molecular quadrupole moment for each rotational state contributing to the thermal expectation values. Calculations for lower temperatures down to 220 K give similar results in agreement with experimental observations made for undercooled liquid crystal samples that the two molecular deuterium modifications show NMR spectra that can be described by the same spectral parameters within experimental error [1].

Also included in table 1 are ratios of both the total calculated quadrupolar coupling and the quadrupolar coupling due to the intramolecular efg at a deuteron to the dipolar coupling, B^{tot}/D and B^{int}/D , respectively. The latter ratio is essentially a molecular property and of importance in the design of zero-efg mixtures of liquid crystals. By adjusting the amounts mixed of the component liquid crystals that possess average efgs of opposite sign in a controlled way the resulting average efg of the mixture can be adjusted to zero. In this way the orienting interaction with the molecular quadrupole moment—that accounts for most of the orientation of molecular hydrogen—can be removed selectively for these mixtures, resulting in a small remaining orientation [3–5]. It is worthwhile to note in table 1 that not only the ratio B^{int}/D is remarkably constant for the various strengths and signs of F_{ZZ} but so is B^{tot}/D . The experimentally observed ratios are somewhat larger and show more distinct variations throughout the series of nematic solvents studied than the calculated values presented for B^{tot}/D in table 1. Previously, the discrepancy between the experimentally observed quadrupolar coupling B for molecular deuterium and the quadrupolar coupling for this molecule in the gas phase, stemming from the intramolecular efg only, was used to monitor the mean efg F_{ZZ} present and this is

Table 1. Thermal expectation values for the dipolar coupling D and quadrupolar coupling B (species containing deuteron(s) only) for various hydrogen molecules at 298 K (table 1(a)) and 320 K (table 1(b)) calculated from first principles for some values of an external electric field gradient F_{zz} interacting with the molecular quadrupole moment. Values calculated for *para*-H₂ are included for comparison with the other isotopically substituted hydrogen molecules only, as *para*-H₂ has no NMR spectrum. See section 2 for details of the model used (the results in table 1 were obtained using 40 harmonic oscillator basis functions and an interpolating Hermite polynomial of degree 76 in numerical integration).

Table 1 (a)

External efg $F_{zz}/10^{-4}$ a.u.	Molecule	Order parameter $S_{zz}/10^{-3}$	Quadrupolar				B^{int}/D	B^{ext}/D	B^{int}/D
			Quadrupolar coupling B^{int}/Hz	Quadrupolar coupling B^{ext}/Hz	Quadrupolar coupling $B^{tot} = B^{int} + B^{ext}/\text{Hz}$	Dipolar coupling D/Hz	Dipolar coupling D^{scaled}/Hz		
-4.0	<i>ortho</i> -H ₂	-15.382				4373.409	4373.409		
	<i>para</i> -H ₂	-15.340				4361.680	4361.680		
	HD	-16.322		-2671.905	-2470.306	714.993	4657.740	-22.507*	-24.344*
	<i>ortho</i> -D ₂	-17.334		-2847.369	-2645.769	117.029	4966.379	-22.608	-24.330
	<i>para</i> -D ₂	-17.334		-2847.365	-2645.765	117.029	4966.372	-22.608	-24.330
-3.0	<i>ortho</i> -H ₂	-11.575				3290.911	3290.911		
	<i>para</i> -H ₂	-11.543				3282.066	3282.066		
	HD	-12.283		-2010.737	-1859.538	538.073	3505.215	-22.513*	-24.344*
	<i>ortho</i> -D ₂	-13.046		-2142.996	-1991.796	88.080	3737.856	-22.614	-24.330
	<i>para</i> -D ₂	-13.046		-2142.993	-1991.793	88.080	3737.851	-22.614	-24.330
-2.0	<i>ortho</i> -H ₂	-7.742				2201.120	2201.120		
	<i>para</i> -H ₂	-7.721				2195.191	2195.191		
	HD	-8.217		-1344.993	-1244.193	359.924	2344.686	-22.519*	-24.343*
	<i>ortho</i> -D ₂	-8.728		-1433.601	-1332.801	58.923	2500.546	-22.619	-24.330
	<i>para</i> -D ₂	-8.728		-1433.599	-1332.799	58.923	2500.543	-22.619	-24.330
-1.0	<i>ortho</i> -H ₂	-3.884				1104.121	1104.121		
	<i>para</i> -H ₂	-3.873				1101.141	1101.141		
	HD	-4.122		-674.728	-624.328	180.562	1176.247	-22.525*	-24.343*
	<i>ortho</i> -D ₂	-4.379		-719.247	-668.847	29.563	1254.556	-22.625	-24.330
	<i>para</i> -D ₂	-4.379		-719.246	-668.846	29.563	1254.555	-22.625	-24.330

1-0	<i>ortho</i> -H ₂	3-909					-1111-150	-1111-150	
	<i>para</i> -H ₂	3-898					-1108-140	-1108-140	
	HD	4-149	679-129	-50-400		628-729	-181-744	-1183-953	-22-536*
	<i>ortho</i> -D ₂	4-409	724-070	-50-400		673-670	-29-762	-1263-004	-22-635
1-882	<i>para</i> -D ₂	4-409	724-069	-50-400		673-669	-29-762	-1263-003	-24-329
	<i>ortho</i> -H ₂	7-376					-2096-944	-2096-944	
	<i>para</i> -H ₂	7-356					-2091-254	-2091-254	
	HD	7-831	1281-723	-94-853		1186-870	-343-011	-2234-508	-22-541*
2-0	<i>ortho</i> -D ₂	8-321	1366-646	-94-853		1271-793	-56-174	-2383-888	-22-640
	<i>para</i> -D ₂	8-321	1366-644	-94-853		1271-791	-56-174	-2383-884	-24-329
	<i>ortho</i> -H ₂	7-842					-2229-235	-2229-235	
	<i>para</i> -H ₂	7-820					-2223-185	-2223-185	
3-0	HD	8-325	1362-596	-100-800		1261-796	-364-655	-2375-502	-22-541*
	<i>ortho</i> -D ₂	8-847	1452-891	-100-800		1352-091	-59-720	-2534-333	-22-641
	<i>para</i> -D ₂	8-847	1452-890	-100-800		1352-090	-59-720	-2534-330	-24-329
	<i>ortho</i> -H ₂	11-799					-3354-156	-3354-156	
4-0	<i>para</i> -H ₂	11-767					-3345-037	-3345-037	
	HD	12-528	2050-334	-151-200		1899-134	-548-714	-3574-535	-22-547*
	<i>ortho</i> -D ₂	13-313	2186-389	-151-200		2035-189	-89-871	-3813-858	-22-646
	<i>para</i> -D ₂	13-313	2186-386	-151-200		2035-186	-89-871	-3813-853	-22-646
4-0	<i>ortho</i> -H ₂	15-780					-4485-809	-4485-809	
	<i>para</i> -H ₂	15-737					-4473-595	-4473-595	
	HD	16-758	2742-275	-201-600		2540-676	-733-905	-4780-935	-22-552*
	<i>ortho</i> -D ₂	17-808	2924-484	-201-600		2722-884	-120-212	-5101-446	-22-651
	<i>para</i> -D ₂	17-808	2924-480	-201-600		2722-881	-120-212	-5101-439	-22-651

* For comparison with D₂ the ratio of the quadrupolar and dipolar coupling for HD is multiplied by a factor γ_H/γ_D .
 D^{scaled} , for HD dipolar coupling D is multiplied by factor γ_H/γ_D ; for D₂ the dipolar coupling is multiplied by factor $(\gamma_H/\gamma_D)^2$.
 $\gamma_D = 26751.965 \times 10^4 \text{ rad T}^{-1} \text{ s}^{-1}$ ($10^4 \text{ rad T}^{-1} \text{ s}^{-1} = 1 \text{ rad G}^{-1} \text{ s}^{-1}$),
 $\gamma_H = 4106.6 \times 10^4 \text{ rad T}^{-1} \text{ s}^{-1}$,
1 statvolt cm⁻² = $2.997925 \times 10^6 \text{ V m}^{-2}$,
1 a.u. of efg = hartree/ $ea_0^2 \text{ V m}^{-2}$; hartree = $e^2/(4\pi\epsilon_0 a_0)$.

(continued)

Table 1 (continued)
Table 1 (b)

External efg $F_{zz}/10^{-4}$ a.u. of efg	Molecule	Order parameter $S_z/10^{-3}$	Quadrupolar coupling B^{int}/Hz	Quadrupolar coupling B^{ext}/Hz	Quadrupolar coupling $B^{\text{tot}} = B^{\text{int}} + B^{\text{ext}}/\text{Hz}$	Dipolar coupling D/Hz	Dipolar coupling $D^{\text{scaled}}/\text{Hz}$	B^{tot}/D	B^{int}/D
-4.0	<i>ortho</i> -H ₂	-14.610				4149.852	4149.852		
	<i>para</i> -H ₂	-14.587				4143.511	4143.511		
	HD	-15.440	-2523.621	201.600	-2322.021	675.705	4401.803	-22.386*	-24.330*
	<i>ortho</i> -D ₂	-16.321	-2676.639	201.600	-2475.039	110.078	4671.414	-22.484	-24.316
-3.0	<i>para</i> -D ₂	-16.321	-2676.625	201.600	-2475.025	110.078	4671.388	-22.484	-24.316
	<i>ortho</i> -H ₂	-10.992				3122.056	3122.056		
	<i>para</i> -H ₂	-10.974				3117.276	3117.276		
	HD	-11.617	-1898.735	151.200	-1747.535	508.397	3311.890	-22.392*	-24.330*
-2.0	<i>ortho</i> -D ₂	-12.281	-2014.032	151.200	-1862.832	82.829	3515.040	-22.490	-24.315
	<i>para</i> -D ₂	-12.281	-2014.022	151.200	-1862.822	82.829	3515.020	-22.490	-24.315
	<i>ortho</i> H ₂	-7.350				2087.767	2087.767		
	<i>para</i> -H ₂	-7.339				2084.564	2084.564		
-1.0	HD	-7.770	-1269.804	100.800	-1169.004	340.001	2214.898	-22.398*	-24.329*
	<i>ortho</i> -D ₂	-8.214	-1347.022	100.800	-1246.222	55.398	2350.939	-22.496	-24.315
	<i>para</i> -D ₂	-8.214	-1347.015	100.800	-1246.215	55.398	2350.952	-22.496	-24.315
	<i>ortho</i> -H ₂	-3.681				1047.057	1047.057		
-1.0	<i>para</i> -H ₂	-3.681				1045.448	1045.448		
	HD	-3.897	-636.876	50.400	-586.476	170.531	1110.907	-22.404*	-24.329*
	<i>ortho</i> -D ₂	-4.120	-675.659	50.400	-625.259	27.788	1179.241	-22.501	-24.315
	<i>para</i> -D ₂	-4.120	-675.656	50.400	-625.256	27.788	1179.234	-22.501	-24.315

reflected in the observed B/D ratio. An estimate of F_{ZZ} was obtained in these studies [1, 3–5] using

$$B^{\text{external efg}} = -\frac{3}{4} \frac{eQ_D}{h} F_{ZZ} = B^{\text{experimental}} - D^{\text{experimental}} \left(\frac{B^{\text{int}}}{D} \right)_{\text{no external efg}}. \quad (19)$$

For molecular deuterium a value of -24.59 for B/D at 298 K has been used previously as an indication for the absence of an external efg in a nematic solvent [3–5]. If in a similar vein it is assumed that the averaging over intramolecular and reorientational motions can be carried out separately in equation (14), for a particular quantum state expectation values of the quadrupolar and dipolar coupling become products of a radial term and an orientational part. In our calculations an indication for B^{int}/D in the absence of a perturbing efg can then be obtained as the ratio of 0.75 times the thermally averaged expectation value for the deuteron quadrupole coupling and the thermally averaged expectation value of $-h/(4\pi^2)\gamma_D^2\langle r^{-3} \rangle$. For the hydrogens the population of the vibrationally excited states can be safely neglected. If we use values for the quadrupole coupling constant and $\langle r^{-3} \rangle$ computed with the method described in section 2 in the absence of an external efg, we obtain a B^{int}/D value of -24.46 at 298 K for D_2 . This value is about 0.5% lower than the previous value of -24.59 [3–5]. This difference is essentially due to the fact that we obtain consistently lower *ab initio* values than those of Reid and Vaida [21, 22] and Bishop and Cheung [23] for the electric field gradients $\langle V_{zz}(r) \rangle$ calculated in various rotational states over which thermal averaging takes place. In the presence of an external efg F_{ZZ} , with typical magnitudes as given in table 1, virtually identical results of -24.46 for B^{int}/D , calculated in the same spirit as above, are obtained, indicative of the fact that the interaction between the external efg and the molecular quadrupole moment indeed presents a small perturbation for the hydrogens. If in the presence of an external efg B^{int}/D is calculated correctly as the ratio of the thermodynamic expectation value for the quadrupolar coupling and the thermodynamic expectation value for the dipolar coupling, computed separately from equation (15) and (16) with the appropriate expression (14) for the associated operator (and therefore *without* invoking the assumption that averaging over intramolecular and reorientational motions can be performed separately) a value for B^{int}/D of typically -24.33 is obtained, as can be seen in table 1.

For a free molecule in field-free space the electric field gradients at the nuclear sites are due to the intramolecular charge distribution only. The presence of an external potential source, either in the gas phase or in a condensed phase stemming from nearby molecules, provides not only an efg at the nucleus directly but also distorts the intramolecular electronic charge distribution, thus modifying the intramolecular efg. In the present paper these Sternheimer (anti)shielding effects, including their anisotropic orientation dependence, are neglected by assuming that the external perturbation does not modify the electronic structure. This circumvents the laborious calculation of accurate electronic properties of molecular hydrogen in the presence of an external potential, in particular of the efg at a nuclear site and the molecular quadrupole moment. The reported values of the efg F_{ZZ} should therefore be taken as an estimate, as the present calculation does not include these anisotropic polarization effects of the external efg F_{ZZ} as yet.

Barker *et al.* [4] noted that the experimental dipolar and quadrupolar couplings for molecular hydrogens do not pass through zero at the same temperature. This

should be true if a single orienting interaction like that between the efg and the molecular quadrupole moment accounts for all the observed ordering. In a careful examination of the experimental data for hydrogens in both pure liquid crystals and mixtures with low values for the efg by van der Est *et al.* [5] a roughly constant, positive value was noted for the difference $D_{\text{HD}} - (D_{\text{HH}} + D_{\text{DD}})/2$ (with D_{HD} and D_{DD} scaled by the appropriate gyromagnetic ratios to bring them in line with D_{HH}). This could be accounted for by including an additional orienting interaction that phenomenologically modelled the van der Waals forces between the atoms in the solute and the solvent molecules and included both attractive and repulsive terms. If from the results in table 1 values for $D_{\text{HD}} - (D_{\text{HH}} + D_{\text{DD}})/2$ are calculated, the obtained values reflect both the sign and the magnitude of the external efg F_{ZZ} . This is in contrast with the experimentally observed constant, positive value for this quantity and supports the notion that at least one relatively minor additional orienting interaction is required to explain the couplings for hydrogens in nematics in greater detail.

For the range of values F_{ZZ} employed in the present study the calculated NMR observables show an almost linear behaviour. This can be seen in figure 2 where the expectation values B , D and S_{zz} calculated at 298 K in table 1 (a) are visualized. The

Figure 2. Dipolar couplings D (figure 2(a)), quadrupolar couplings B (figure 2(b)) and order parameters S_{zz} (figure 2(c)) for molecular hydrogen dissolved in a nematic liquid crystal for some values of an external electric field gradient F_{ZZ} as calculated from first principles for a single orienting interaction between this efg F_{ZZ} and the molecular quadrupole moment of the solute at 298 K. The dipolar couplings for HD and D_2 have been scaled by $(\gamma_{\text{H}}/\gamma_{\text{D}})$ and $(\gamma_{\text{H}}/\gamma_{\text{D}})^2$, respectively. *Ortho*- H_2 : open squares, HD: open triangles, *ortho*- D_2 : open circles.

(continued)

(b)

(c)

Figure 2. (continued).

results in table 1 provide a quick and easy way to obtain an estimate of the external efg F_{ZZ} present in a nematic liquid crystal solvent, once the NMR spectral parameters of molecular hydrogen or any of its deuterated analogues used as a probe molecule for the efg present in that particular solvent have been obtained. However,

this approach hinges on the assumption that the interaction between F_{zz} and the molecular quadrupole moment is solely responsible for the orientation of the solute. It differs from the physically more appealing way, used before, of evaluating the external efg F_{zz} in such a way that it accounts for the difference between the gas phase B/D ratio and the corresponding ratio as observed in the nematic solvent.

In table 2 the experimental couplings for the various modifications of molecular hydrogen in the liquid crystal 1132 at 298 K as measured by Burnell *et al.* [1] are listed. A natural cubic spline defined by the results of table 1 has been used to interpolate for the external efg F_{zz} from both the experimental dipolar and quadrupolar coupling measured for a single species. From the value of F_{zz} obtained in this way the dipolar and quadrupolar couplings for all the different isotopomers are then calculated and compared with the experimentally observed values. As can be seen in table 2 the agreement is quite good. We have obtained similar results for the available data of molecular hydrogen in other nematic solvents and at other temperatures. The actual values of F_{zz} obtained in this way are more than 10% larger than previously reported estimates for various nematic solvents [3], possibly because the value of F_{zz} is now allowed to be responsible for all of the observed ordering.

As discussed in the theoretical section, the total Hamiltonian in equation (5) comprises a number of terms including the centrifugal distortion and the vibrational anharmonicity. The computational scheme used here allows for an easy means to estimate their relative importance on the calculated values for the NMR observables by omitting the corresponding terms from the Hamiltonian. The results for some of these alternative calculations for *ortho*-D₂ are summarized in table 3 (*para*-D₂ gave identical results which are therefore not shown). In table 3 results obtained for a much simpler description of the hydrogen molecule taken as a rigid rod as developed by Snijders *et al.* [2] are also included. In this model the orienting interaction between the external efg and the molecular quadrupole moment is taken into account by standard first-order perturbation theory to calculate the thermal expectation values, treating the rotational degree of freedom as a quantum mechanical rigid rotor. Remarkably, this straightforward approach gives results that compare well with the results obtained when the complete Hamiltonian in equation (6) is used, although the B^{int}/D ratio obtained for the value of the external efg F_{zz} used in table 3 is significantly lower than for the full description from first principles, partly due to the lower, fixed internuclear distance. Apparently, in the simple 'rigid rod' model there is a significant degree of fortuitous cancellation.

The results obtained for the analysis of the experimental couplings of D₂ in the nematic liquid crystal 1132 at 298 K [1, 3] are also included in table 3 for comparison. The value of the external efg F_{zz} was calculated from the difference between the experimentally observed and theoretical B/D ratio treating the anharmonicity and centrifugal distortion as perturbations of a harmonically oscillating, quantum mechanical rotor [1, 3–5].

If the vibrational effect on the instantaneous moment of inertia is neglected in equation (8c) and the familiar expression for a rigid rotor with rotational constant B_e is used instead, the molecular quadrupole moment interacting with the orienting external efg becomes essentially independent of the rotational degree of freedom as well. However, this results in only minor changes in the obtained thermal expectation values.

Table 2. Determination of the value of the external efg F_{zz} present in the nematic liquid crystal 1132 at 298 K from a single experimental NMR coupling of a molecular hydrogen species (data taken from [1]) by interpolation of the calculated dipolar and quadrupolar couplings listed in table 1 (a) using a natural cubic spline. From the obtained estimate of F_{zz} both dipolar and quadrupolar couplings are calculated and compared with the available experimental data for the various isotopically substituted hydrogen species.

Hydrogen species	Experimental couplings ^a			Interpolated external efg $F_{zz}/10^{-4}$ a.u. of efg	D^{scaled} calculated from F_{zz}	B calculated from F_{zz}	$D^{\text{exp}} - D^{\text{calc}} / \text{Hz}^d$	$B^{\text{exp}} - B^{\text{calc}} / \text{Hz}$	$S_{zz}/10^{-3}$ calculated from interpolated F_{zz}
	Dipolar coupling D/Hz	Dipolar coupling $D^{\text{scaled}}/\text{Hz}$	Quadrupolar coupling B/Hz						
H_2	-2340.9 ± 0.3	-2340.9 ± 0.3		2.100	H_2 HD	-2340.90 -2494.51	0 5.56 2.76	26.79	8.234 8.743
HD^b	-382.07 ± 0.15	-2488.95 ± 0.98		2.095	D_2 H_2 HD D_2	-2661.33 -2335.68 -2488.95 -2655.39	-23.68 -5.22 0 -29.61	41.62	9.290 8.216 8.723 9.269
HD^c	-382.5 ± 0.6	-2491.75 ± 3.91	1351.8 ± 0.6	2.097	H_2 HD D_2	-2338.31 -2491.75 -2658.38	-2.59 0 -26.63	28.23 43.49	8.225 8.733 9.280
D_2	-63.27	-2685.00	1461.49	2.118	H_2 HD D_2	-2361.72 -2516.70 -2685.00	20.82 27.75 24.95	14.97	8.308 8.820 9.373
HD^c	-382.5 ± 0.6	-2491.75 ± 3.91	1351.8 ± 0.6	2.142	From B H_2 HD D_2 H_2 HD	-2388.14 -2544.86 -2715.05 -2409.45 -2567.58	47.24 55.91 53.11 30.05 68.55	0 12.94	8.401 8.919 9.477 8.476 9.000
D_2	-63.27	-2685.00	1461.49	2.161	D_2	-2739.29	78.63 75.83 54.29	-12.07 0	9.562

^a Taken from [1].

^b From ^1H NMR.

^c From ^2H NMR.

^d In case two values (HD) are listed: upper for difference with experimental ^1H NMR value, lower for difference with ^2H NMR value.

$\gamma_{\text{H}} = 26.751 \cdot 965 \times 10^4 \text{ rad T}^{-1} \text{ s}^{-1}$ ($10^4 \text{ rad T}^{-1} \text{ s}^{-1} = 1 \text{ rad G}^{-1} \text{ s}^{-1}$); $\gamma_{\text{D}} = 4106.6 \times 10^4 \text{ rad T}^{-1} \text{ s}^{-1}$; 1 a.u. of efg = hartree/ $ea_0^2 \text{ V m}^{-2}$; hartree = $e^2/(4\pi\epsilon_0 a_0)$.

Table 3. Calculated thermal expectation values for dipolar coupling D and quadrupolar coupling B for molecular deuterium (identical results for both *ortho*- D_2 and *para*- D_2) at 298 K for several descriptions of the hydrogen molecule in the presence of an external electric field gradient $F_{zz} = 1.882 \times 10^{-4}$ a.u. of electric field gradient. This value for F_{zz} gives a contribution $B^{\text{ext}} = -94.853$ Hz to the quadrupolar coupling (see equation (18)). The latter two columns list the ratios of the calculated (total) quadrupolar coupling, B^{tot} , and the quadrupolar coupling due to the intramolecular efg, B^{int} , to the calculated dipolar coupling D respectively.

Model details	Order parameter $S_{zz}/10^{-3}$	Quadrupolar coupling B^{int}/Hz	Quadrupolar coupling B^{ext}/Hz	Quadrupolar coupling $B^{\text{tot}} = B^{\text{int}} + B^{\text{ext}}/\text{Hz}$	Dipolar coupling D/Hz	B^{tot}/D	B^{int}/D
1	8.313	1409.02	-94.853	1314.17	-57.738	-22.761	-24.404
2	8.224	1377.84	-94.535	1283.31	-56.025	-22.906	-24.593
3	8.398	1394.58	-94.853	1299.73	-57.087	-22.767	-24.429
4	8.248	1375.41	-94.853	1280.56	-56.212	-22.781	-24.469
5	8.321	1366.65	-94.853	1271.79	-56.174	-22.640	-24.329

- 1 Equilibrium internuclear distance $r_e = 0.741\,404 \times 10^{-10}$ m, rotational constant $B_e = 30.462\text{ cm}^{-1}$ (taken from [30]), molecular quadrupole moment $Q_{zz} = 0.649 \times 10^{-26}$ esu cm^{-2} (taken from [31]), quadrupole coupling constant = 225.99 kHz (based on value calculated for q' at $r = 1.4\,a_0$ from [20], see [29]), rotational degree of freedom treated as quantum mechanical rigid rotor (see [2]).
 - 2 Analysis of experimental couplings of D_2 in 1132 at 298 K as explained in [3-5], using a value for the external efg $F_{zz} = 6.080 \times 10^{11}$ statvolt $\text{cm}^{-2} = 1.876 \times 10^{-4}$ a.u. of efg taken from [3].
 - 3 Complete Hamiltonian in equation (6), but artificially fixed molecular quadrupole moment $Q_{zz} = 0.649 \times 10^{-26}$ esu cm^2 [31].
 - 4 Hamiltonian term $H^{\text{centrifugal distortion}}$ in equation (6) replaced by the standard rigid rotor expression with the rotational constant B_e .
 - 5 Complete Hamiltonian in equation (6), model as described in section 2.
- Descriptions 3-5 employed: 40 harmonic oscillator basis functions centred at $r_e = 0.741\,404 \times 10^{-10}$ m, with frequency $\omega = 3100\text{ cm}^{-1}$, interpolating Hermite polynomial for numerical integration of degree 76.
- All descriptions listed above used the range for J of 0-10 for the calculated thermal expectation values.
- D^{scaled} , the dipolar coupling D for D_2 multiplied by factor $(\gamma_H/\gamma_D)^2$.
- $\gamma_H = 26\,751.965 \times 10^4\text{ rad T}^{-1}\text{ s}^{-1}$ ($10^4\text{ rad T}^{-1}\text{ s}^{-1} = 1\text{ rad G}^{-1}\text{ s}^{-1}$); $\gamma_D = 4106.6 \times 10^4\text{ rad T}^{-1}\text{ s}^{-1}$; 1 a.u. of efg = hartree/ $ea_0^2\text{ V m}^{-2}$, hartree = $e^2/(4\pi\epsilon_0 a_0)$; 1 a.u. of electric quadrupole moment = $ea_0^2\text{ cm}^2$.

4. Conclusions

We have calculated from first principles thermal expectation values for NMR observables for molecular hydrogen and its isotopically substituted analogues dissolved in nematic liquid crystal solvents. In our calculations we have employed high-quality nuclear wavefunctions and available data for highly correlated electronic wavefunctions at many different geometries from the literature. In our description of hydrogens partially oriented in nematic phases vibrational anharmonicity, centrifugal distortion, the changes of the nuclear quadrupole coupling with internuclear distance, and the dependence of the molecular quadrupole moment on the rotational quantum number have been included. The results strongly support previous conclusions drawn from experimental studies and simplified theoretical considerations of molecular hydrogen and deuterated analogues that, when dissolved in nematic liquid crystals, appear to be predominantly oriented through the interaction between their molecular quadrupole moment and the average external electric field gradient present in these solvents. In addition, the present theoretical results provide the basis for obtaining reliable estimates of such average external electric field gradients from a single NMR observable.

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