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Effects of repulsion and dispersion forces in liquid crystals: Alignment and deformation of H_2 solute

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The roles of steric repulsions and dispersional attractions in determining the behavior of solute molecules in liquid crystals are investigated by computer simulations of simple model systems. These systems involve a hydrogen molecule (H_2) dissolved in a rigid lattice consisting of parallel, infinitely long cylinders, which interact pairwise additively with the H atoms of the solute. The thermal motion of the H_2 molecule (at 300 K) is simulated by Monte Carlo and molecular-dynamics methods, which are shown to lead to identical results for all the studied properties, including the centrifugal distortion. The resulting orientational order parameters S are invariably positive at all densities and structures of the lattice, irrespective of the details of the functional form of the interaction potential. The main role of the attractive forces is to pull the solute against the hard cores of the solvent molecules, thus enhancing the effects of the repulsions (increasing S). The implication is that the negative experimental S values observed in several liquid crystals cannot be attributed to the effects of repulsion and dispersion forces; the presence of other interactions, such as electrostatic forces, appears to be essential. The repulsive forces lead to slight orientation-dependent compression of H_2, with the result that the nuclear dipolar and quadrupolar couplings D_{HH} and B_D are changed by -0.7% and -1.1%, respectively (regardless of the lattice structure and the detailed form of the interaction potential). This points to the inference that the stretching-mode contributions to the orientation-dependent molecular deformations in liquid crystals are generally small, and gives support to the frequently made assumption that NMR spectral parameters of partially oriented molecules can normally be analyzed in terms of a model that includes only the bending-mode deformations.

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I. INTRODUCTION

The anisotropic intermolecular forces responsible for the orientational ordering in liquid crystals have been the subject of much interest in recent years. An important area of research in this field is the study of small probe molecules dissolved in mesophases. It circumvents the difficulties resulting from the structural complexity (low symmetry and flexibility) of the constituent molecules of typical liquid crystals. The primary experimental technique in this approach is nuclear-magnetic-resonance (NMR) spectroscopy, which has proved to yield quite detailed information on the anisotropic solute-solvent interactions [1]. Conventionally, this information has been obtained in the form of the orientational order parameters of the solute molecules [2]. Lately it has become possible to subject the NMR data to a more elaborate analysis that describes the intermolecular forces in terms of the torques acting on the individual bonds of the solutes [3–5].

There have been many efforts to model the mechanism of orientational ordering in liquid crystals. These models attribute the ordering to the effects of various intermolecular forces, and there is no consensus on what interaction has the most important effect. As a general rule, the models are based on interactions such as hard-core repulsions [6] or anisotropic dispersion forces [7], which tend to favor parallel alignment of the molecules. It is interesting that in many cases such interactions are not capable of explaining the forces acting on the solute molecules in liquid crystals. In particular, the torques acting on the CH bonds of the solutes have displayed unexpected but very consistent behavior: the analyses of the NMR data of a substantial number of molecules have revealed that in a certain (very general) class of liquid crystals the CH bonds tend invariably to orient perpendicular to the alignment axis (director) of the solvent molecules [5]. The relevance of this finding is reinforced by the observation that the behavior of molecular hydrogen (H_2) is similar to that of the CH bonds: both tend to orient perpendicular to the director in exactly the same liquid crystals [8,9]. This strengthens the confidence in the credibility of the obtained values for the torques, as they have been determined by two entirely different methods: the orienting forces experienced by the hydrogen molecule have been deduced directly from the orientational order parameters, while the forces experienced by the CH bonds have been derived from the small orientation-dependent molecular deformations, making use of a theoretical model [3–5]. The implication from the results is that there is a common interaction mechanism behind the dominant parts of the torques acting on the HH and CH bonds. In view of the consistency of the results, this mechanism does not appear to be due to any specific chemical interaction, particularly as the studied probes include such relatively inert molecules as hydrogen and methane.

Two models have been advanced to account for the unexpected behavior of the solute molecules in mesophases. The first model is based on the hypothesis that the solutes experience a significant average electric-field gradient produced by the surrounding liquid-crystal molecules [10]. The interaction of this field gradient with the molecular quadrupole moment tensor results in a torque that tends to orient the molecule either parallel or perpendicular to the director. In particular, the HH and CH bonds should experience similar torques, as their quadrupole moments (along the bonds) appear to be positive (their preferred orientation should be perpendicular to the director in the liquid crystals where the field gradient along the director is negative) [11]. The second model is based on the assumption that the solutes experience the average interspace between the liquid-crystal molecules as a cylindrically symmetric cavity whose diameter is comparable to the lateral dimensions of the solvent molecules [4]. At the center of such a cavity the normal van der Waals interaction of the atoms of the solute molecule with the surroundings leads directly to torques that favor either the parallel or perpendicular orientation (in these cases the net interaction is repulsive or attractive, respectively). It has been shown that this model can provide qualitatively correct predictions about the forces experienced by the molecular hydrogen and methane in different liquid crystals [4].

The role of dispersional van der Waals attraction together with short-range repulsion in determining the behavior of the solutes in liquid crystals is the subject of the present study. The fundamental question is as follows: do the solute molecules sample such regions of the solvent that the dispersion-plus-repulsion interaction alone can account for the observed torques (as assumed in the second model), or is the presence of other interactions, such as electrostatic forces, essential (as assumed in the first model)? A related question is as follows: do the intermolecular forces induce significant orientation-dependent perturbations on the bond lengths? This is an important issue, because in most cases such perturbations are essentially ignored in determining the torques acting on the bonds, i.e., the solvent-induced molecular distortions are assumed to be dominated by bond-bending deformations. This assumption is necessary, because the information content of the NMR spectral data is usually insufficient to allow the determination of the forces that tend to change the lengths of the bonds. The result of the analyses of a large body of NMR data lend considerable support to the soundness of this approximation [5,12]. However, it is essential to obtain direct and independent information on this matter, as it has an important influence on the credibility of the method of analysis.

In order to answer these two questions, we have carried out computer simulations on simple solute-solvent systems modeling a hydrogen molecule at infinite dilution in various liquid-crystal environments. In these simulations, the liquid-crystal molecules are taken to be parallel, infinitely long cylinders, which exert repulsive and attractive forces on the atoms of the solute molecule. These model systems should exhibit the essential features of the behavior resulting from the repulsion and dispersion interaction. In particular, hydrogen serves as an ideal probe molecule, as its response to the intermolecular forces is very straightforward. Its orientational order parameter allows a direct interpretation in terms of the torque acting on the HH bond, and a large body of detailed experimental information on these torques is available [8,9]. These data have shown that the behavior of hydrogen reflects the torques acting on the CH bonds of a general solute molecule in liquid crystals. In addition, the orientation-dependent deformation of the hydrogen molecule is a convenient object of investigation, as it reveals directly the force tending to change the length of the HH bond.

II. THEORY

A. Molecular orientation and deformation

In a uniaxial environment the probability density of finding an axially symmetric molecule at the orientation θ (equal to the angle between the molecular symmetry axis and the director) can be expanded as [13]

$$P(\theta)=\frac{1}{4\pi}[1+5SP_2(\cos\theta)+\cdots] . \tag{1}$$

Here, $P_2(\cos\theta)=\frac{1}{2}(3\cos^2\theta-1)$ is the second-order Legendre polynomial and its average value $S=\langle P_2(\cos\theta)\rangle$ is the second rank orientational order parameter of the molecule. In the case of the hydrogen molecule the orientational distribution $P(\theta)$ is expected to be rather close to isotropic, and thus the two terms shown in Eq. (1) should describe it adequately.

The deformation of a diatomic molecule by the interaction with the solvent can be described by the function $\Delta\bar{r}(\theta)=\bar{r}(\theta)-r_e$, where $\bar{r}(\theta)$ is the average value of the bond length at the orientation θ and r_e is its equilibrium value (in a free molecule). Here and below the overbar denotes averaging over the internal motion of the molecule at a particular orientation, while the angular brackets denote the remaining averaging over the reorientational motion. The function $\Delta\bar{r}(\theta)$ may be expressed as a series expansion in terms of Legendre polynomials:

$$\Delta\bar{r}(\theta)=\Delta r_0+\Delta r_2P_2(\cos\theta)+\cdots . \tag{2}$$

The orientation-independent term Δr_0 contains the normal anharmonic rovibrational contribution Δr_0^{α}, which is present in a free molecule, and an additional solvent-induced contribution Δr_0^{d}. The coefficient Δr_2 is the amplitude of the orientation-dependent modulation of the bond length: if Δr_2 is positive, then the bond is elongated from $r_e+\Delta r_0$ by an amount $+\Delta r_2$ at the parallel orientation with respect to the director ($\theta=0$), and compressed by $-\Delta r_2/2$ at the perpendicular orientation.

The coefficients Δr_0 and Δr_2 can be determined from the average values of $\Delta\bar{r}(\theta)$ and $\Delta\bar{r}(\theta)P_2(\cos\theta)$ over the reorientational motion of the molecule: if the series (1) and (2) are truncated after the $P_2(\cos\theta)$ terms, then

$$\langle\Delta\bar{r}(\theta)\rangle=\Delta r_0+\Delta r_2S \tag{3}$$

and

$$\langle \Delta\bar{r}(\theta)P_2(\cos\theta)\rangle = \Delta r_0 S + \Delta r_2(\tfrac{1}{5}+\tfrac{2}{7}S) \ . \tag{4}$$

Alternatively, these coefficients can be resolved from the average values of $\Delta\bar{r}(\theta)$ determined in different domains of the orientation θ. For example, if $\langle\ \rangle_+$ and $\langle\ \rangle_-$ denote the reorientational averaging in the domains where $P_2(\cos\theta)>0$ and <0, respectively, then the values of Δr_0 and Δr_2 can be extracted from the averages $\langle \Delta\bar{r}(\theta)\rangle_+$ and $\langle \Delta\bar{r}(\theta)\rangle_-$ by the equations

$$\langle \Delta\bar{r}(\theta)\rangle_+ = \Delta r_0 + \Delta r_2 \langle P_2(\cos\theta)\rangle_+ \tag{5}$$

and

$$\langle \Delta\bar{r}(\theta)\rangle_- = \Delta r_0 + \Delta r_2 \langle P_2(\cos\theta)\rangle_- \ , \tag{6}$$

which are obtained from Eq. (2). Here the values of $\langle P_2\rangle_+$ and $\langle P_2\rangle_-$ can be calculated by the truncated series (1), resulting in the expressions

$$\langle P_2(\cos\theta)\rangle_+ = \frac{1+(3\sqrt{3}-2)S}{3(\sqrt{3}-1)+5S} \tag{7}$$

and

$$\langle P_2(\cos\theta)\rangle_- = \frac{-1+2S}{3-5S} \ . \tag{8}$$

The values of Δr_0 and Δr_2 solved from Eqs. (3) and (4) should be close to those solved from Eqs. (5) and (6), provided that the fourth- and higher-order terms in the series (1) and (2) are small and the average values obtained from the computer simulation are close to the true expectation values.

B. Deformational contributions to NMR observables

NMR observables of a diatomic molecule corresponding to axially symmetric and traceless second rank tensors T (such as dipolar and quadrupolar coupling tensor) can be written as

$$\langle \bar{T}_{\parallel}(\theta)\rangle = \langle \bar{T}(\theta)P_2(\cos\theta)\rangle \ , \tag{9}$$

where $\bar{T}_{\parallel}(\theta)$ and $\bar{T}(\theta)$ are the average values (over the intramolecular motion) of the elements of T in the directions of the director and of the bond axis, respectively [1]. The contribution to $\langle \bar{T}_{\parallel}(\theta)\rangle$ due to solvent-induced molecular deformation can be evaluated by approximating the bond-length dependence of $\bar{T}(\theta)$ by the leading term of the Taylor series around the equilibrium geometry:

$$\bar{T}(\theta) = T_e + T_1\Delta\bar{r}(\theta) + \cdots \ . \tag{10}$$

Here, T_1 is the derivative of the principal value $T(\Delta r)$ with respect to $\Delta r \equiv r - r_e$, taken in equilibrium. Thus, using Eq. (4), the observable can be written as

$$\begin{aligned}\langle \bar{T}_{\parallel}(\theta)\rangle &= T_e S + T_1\langle \Delta\bar{r}(\theta)P_2(\cos\theta)\rangle + \cdots \\ &= T_e S + T_1\Delta r_0 S + T_1\Delta r_2(\tfrac{1}{5}+\tfrac{2}{7}S) + \cdots \ . \end{aligned}\tag{11}$$

The term linear in Δr_0 contains the contribution $T_1\Delta r_0^d S$, which is due to the orientation-independent part of the solvent-induced molecular deformation (Δr_0^d). The term linear in Δr_2 is the principal contribution due to the anisotropy of the deformation.

The magnitudes of these deformational contributions relative to the equilibrium contribution, $T_e S$, are determined by the ratio T_1/T_e. In the case of the dipolar coupling D_{HH}, the principal value is of the functional form $T(\Delta r)=C/r^3$, where C is a constant, and thus $T_1/T_e = -3/r_e = -4.0469$ Å^{-1}. In the case of the quadrupolar coupling B_D in the hydrogen molecule, a quadratic interpolation of the three values of the electric-field gradient calculated by Bishop and Cheung [14] results in $T_1/T_e = -6.604$ Å^{-1} at $r_e = 0.7413$ Å.

C. Model systems

In the present simulations, the hydrogen molecule was modeled by a classical system of two mass points of 1.67×10^{-27} kg bound by the Morse potential

$$V_M(r) = D_e(1-e^{-\alpha(r-r_e)})^2 \ , \tag{12}$$

where $D_e = 0.761$ aJ ($=4.75$ eV), $r_e = 0.7413$ Å, and $\alpha = 1.945$ Å^{-1} ($=\sqrt{k/2D_e}$, where $k = 575.6$ N m^{-1} is the molecular harmonic force constant) [15].

With the special object of calculating the behavior of small solute molecules in liquid crystals, a simple model system for a nematic solvent is a rigid lattice consisting of parallel, axially symmetric molecules of infinite length. The interaction energy between an atom in the solute molecule and a segment in the solvent molecule may be described by the Lennard-Jones (LJ) 6-12 potential function

$$V_{\mathrm{LJ}}(R') = 4\epsilon\left[\left[\frac{\sigma}{R'}\right]^{12} - \left[\frac{\sigma}{R'}\right]^{6}\right] , \tag{13}$$

where R' is the distance between the centers of the atom and the segment, and ϵ and σ are empirical parameters (so-called Lennard-Jones force constants) [16]. If the centers of the segments in the liquid-crystal (LC) molecule are evenly distributed on the molecular symmetry axis with the linear number density ρ (segments per unit length), then the total potential energy between the atom in the solute molecule and a whole liquid-crystal molecule is

$$\begin{aligned} V_{\mathrm{LC}}(R) &= \rho\int_{-\infty}^{\infty} V_{\mathrm{LJ}}(\sqrt{R^2+z^2})dz \\ &= 4\epsilon'\left[\eta\left[\frac{\sigma}{R}\right]^{11} - \left[\frac{\sigma}{R}\right]^{5}\right] . \end{aligned}\tag{14}$$

Here, $\epsilon' = \frac{3}{8}\pi\epsilon\sigma\rho$, $\eta = \frac{21}{32}$, and R is the distance of the atom from the symmetry axis of the solvent molecule.

To obtain values for the parameters ϵ, σ, and ρ, the constituent segments in the liquid-crystal molecules may be taken to be benzene rings, with $\rho = 1$ ring per 5 Å. The force constants for the interaction between a hydrogen atom and a benzene ring, estimated from the available data for molecular force constants by making use of the empirical "combining laws" [16], are of the order of $\epsilon = 9\times10^{-22}$ J and $\sigma = 4$ Å, respectively. Thus the preferred value for the factor ϵ' in Eq. (14) is 8.5×10^{-22} J

($=0.005$ eV). Most of the simulations were carried out by using this value, together with $\sigma=4$ Å. In order to study the sensitivity of the results to the choice of the parameters, some simulations were performed with different values for these parameters.

Two different crystal structures were used. First, to attain a homogeneous matrix, the liquid-crystal molecules were arranged on a simple two-dimensional square lattice (the molecular long axes perpendicular to the lattice plane, with the nearest-neighbor intermolecular distance a). Second, to model a microscopically inhomogeneous structure, the molecules were arrayed on an imperfect hexagonal lattice having vacancies at the centers of the hexagons (this corresponds to a perfect hexagonal structure where a basis containing *two* molecules is attached to every lattice point; if the intermolecular distance is b, then these lattice points are separated by $b\sqrt{3}$). The simulations were carried out using equal densities for the two crystal structures. Thus, the nearest-neighbor intermolecular distances in the square and hexagonal lattices, a and b, were coupled by equation

$$4a^2=3\sqrt{3}b^2\ . \tag{15}$$

The present model for the liquid-crystal molecules (taken to be chains of benzene rings, with $\rho=1$ ring per 5 Å) leads to the value of $a=5.4$ Å (or $b=4.8$ Å), if the number density of the benzene rings in the lattice is equated with that in liquid benzene, $\rho=6.76\times10^{27}$ molecules per m^3. This value of a is consistent with the equilibrium separation of a benzene molecule from a liquid-crystal molecule, $R_e=5.6$ Å, which minimizes the corresponding intermolecular potential-energy function $V_{\rm LC}(R)$ (14). Thus it may be concluded that the density of a real liquid-crystal matrix is reproduced by the value of the order of $a=5.5$ Å. The simulations were performed with the values of $a=5$, 5.5, 6, 7, 8, 9, and 10 Å at a temperature of $T=300$ K.

D. Simulation methods

Both types of simulations, described in the following sections, were carried out for a system of two separate atoms, constituting the H_2 molecule with the Morse potential (12). The molecule was free to move in three dimensions and free even to dissociate, which, however, never occurred at 300 K with the potentials above. The internal and external potentials experienced by the atoms were identical in both types of simulations. In the computations the external potential experienced by an atom was a sum of contributions from nine (three by three) periodically adjacent unit cells, one cell containing the molecule and eight other cells next to the first one in the xy plane. Due to the short range of the 11-5 potential (14), no cutoff was applied. Computationally the simulations were three-dimensional, although there were no external forces acting on the hydrogen molecule in the z direction.

1. Molecular dynamics

The molecular-dynamics simulation was accomplished by a numerical solution of the classical Newtonian equations for the motion of the hydrogen atoms. Here we have adopted the predictor-corrector method of Beeman combined from the procedures of Rahman and Verlet [17]. Thus, starting from the initial values of the position $\mathbf{r}_i(0)$, velocity $\mathbf{v}_i(0)$, and acceleration $\mathbf{a}_i(0)=0$ for the ith atom, the position after the time interval Δt is evaluated from the formula

$$\mathbf{r}_i(t+\Delta t)=\mathbf{r}_i(t)+\Delta t\mathbf{v}_i(t)+\frac{\Delta t^2}{6}[4\mathbf{a}_i(t)-\mathbf{a}_i(t-\Delta t)]\ . \tag{16}$$

From Newton's second law

$$\mathbf{a}_i(t)=\frac{-\nabla_i V_i(\mathbf{r}_i(t))}{m_i}\ , \tag{17}$$

where the potential energy of the ith atom, $V_i(\mathbf{r}_i)$, is the sum of contributions from the Morse potential, $V_M(r)$ (12), and from the potentials of the liquid-crystal molecules, $V_{\rm LC}(R_{ik})$ (14). With the notations $r=|\mathbf{r}_i-\mathbf{r}_j|$ for the bond length of the hydrogen molecule and $R_{ik}=[(x_i-X_k)^2+(y_i-Y_k)^2]^{1/2}$ for the distance of the ith atom from the symmetry axis of the kth solvent molecule, we can write

$$V_i(\mathbf{r}_i)=V_M(r)+\sum_{k=1}^{M}V_{\rm LC}(R_{ik})\ , \tag{18}$$

where $\mathbf{r}_i=(x_i,y_i,z_i)$, and M is the number of considered liquid-crystal molecules at positions (X_k,Y_k). The velocity of the ith atom is evaluated from [17]

$$\mathbf{v}_i(t+\Delta t)=\mathbf{v}_i(t)+\frac{\Delta t}{6}[2\mathbf{a}_i(t+\Delta t)+5\mathbf{a}_i(t)-\mathbf{a}_i(t-\Delta t)]\ . \tag{19}$$

The initial values of atomic positions were random (in a limited range) and initial accelerations were set to zero, but the initial velocities were taken from the Maxwell-Boltzmann distribution, as described below.

In order to obtain the molecular properties from the Maxwell-Boltzmann distribution, the molecule was allowed to exchange kinetic energy with its environment through a simulated heat bath. This was accomplished by simulated random inelastic collisions of the atoms in H_2. With the given average collision time interval τ_0, the actual time intervals between collisions were computed from

$$\tau=-\tau_0\ln[\xi(0,1)]\ , \tag{20}$$

where $\xi(0,1)$ is a uniformly distributed random number in the interval (0,1). In the simulated collision, to each of the velocity components v_q ($q=x,y$, and z) of both atoms i a new random value was assigned from the Maxwell-Boltzmann velocity distribution function

$$\frac{dN_{v_q}}{dv_q}=\frac{N}{\sqrt{\pi}v_{m_i}}\exp\left[-\frac{v_q^2}{v_{m_i}^2}\right]\ . \tag{21}$$

Here, $v_{m_i}=\sqrt{2k_BT/m_i}$ is the most probable speed of the atom i of mass m_i at the temperature T. For the hydrogen atom $v_{m_i}=2230\ \mathrm{m\,s^{-1}}$ at $T=300$ K.

2. *Metropolis algorithm*

A Monte Carlo integration over the configuration space of a system can be done conveniently using the Metropolis algorithm [18]. For a closed system (canonical ensemble) it gives the statistical average over the Maxwell-Boltzmann distribution at a given temperature. If the interaction potentials of the system are velocity independent, the equilibrium value of a specified quantity F is obtained as an average from a large number of configurations C as

$$\langle F\rangle=\frac{1}{C}\sum_{i=1}^{C}F_i\ , \tag{22}$$

where instead of a random selection, the configurations are selected to sample the Maxwell-Boltzmann distribution of one-particle energies. This is accomplished by moving randomly one particle after another in a limited range in the position space of the system and accepting the new configuration $i+1$ with energy E_{i+1}, if the energy change $\Delta E=E_{i+1}-E_i$ satisfies

$$\Delta E=\begin{cases}\leq 0 & \text{or}\\ >0 & \text{and } \xi(0,1)<e^{-\Delta E/k_BT}\ ,\end{cases} \tag{23}$$

where $\xi(0,1)$ is uniformly distributed random number in the range (0,1). If the new configuration is not accepted, the old one is counted again with $F_{i+1}=F_i$. The random replacement of one configuration by another is limited to a motion of an atom in a range $(-\Delta q,\Delta q)$ in each coordinate $q=x$, y, and z using a uniform distribution $\xi(-\Delta q,\Delta q)$. The same random procedure as in the molecular-dynamics simulation was used for the initial atomic positions.

III. RESULTS AND DISCUSSION

A. Simulations

The two simulation methods, molecular dynamics and Monte Carlo with the Metropolis algorithm, resulted in essentially the same data for the molecular properties, thus confirming the reliability of used numerical methods and computer codes. A natural control for the molecular-dynamics simulation is to monitor the energies of the various degrees of freedom of the molecular motion in order to verify the correct equipartition. Therefore, we kept track of the kinetic energies of the molecular translation and rotation, as well as of the kinetic and potential energies of the vibrational motion. As expected, the average energies of all seven degrees of freedom were close to $\frac{1}{2}k_BT$.

The time step Δt in the molecular-dynamics simulations were chosen to be 0.1 fs, although even the value 1 fs seemed to give fairly accurate energies for the various degrees of freedom. Runs of 0.5 ns of simulation time already gave relatively final values for the monitored averages compared to the runs of 3 ns with 30×10^6 steps, which were carried out for all considered structures. The collision time period (in the heat bath) was chosen to be $\tau_0=500$ fs, which is of the same order of magnitude as the period between the collisions of the hydrogen molecule and the liquid-crystal molecules. The value of τ_0 was checked down to 50 fs with no detectable effects in the results. With these parameters the average temperature of the molecule usually deviated less than 5 K from the preferred 300 K and the deviations never exceeded 10 K.

The Metropolis Monte Carlo algorithm is more efficient in the evaluation of equilibrium averages than the molecular-dynamics method, because it does not solve the full dynamics. Also, only one numerical parameter needs to be given, namely the limit for the random relocations of atoms in space, Δq. The range from 0.01 to 1.0 Å was examined and values less than 0.2 Å were found acceptable with the increasing accuracy and decreasing convergence. The value of 0.05 Å was then chosen as a good compromise. Running 15×10^6 steps of the Metropolis simulation with this parameter gave about as good convergence as running 30×10^6 steps of the molecular-dynamics simulation.

The average internal potential energy of the molecule, $\langle \bar{V}_M\rangle$, was used as a direct control in both simulation methods. As a matter of fact, owing to the effects of anharmonicity and centrifugal distortion, $\langle \bar{V}_M\rangle$ of a Morse oscillator should not be exactly equal to $\frac{1}{2}k_BT$. A theoretical calculation of the rovibrational average (cf. the Appendix) of the potential energy of H_2 in a free space at 300 K leads to a correction of +2.0% to $\frac{1}{2}k_BT$ (i.e., apparently $T=306$ K). In a solvent the repulsive forces from the neighboring molecules tend to compress the H_2 molecule, making the correction smaller. The results of the simulations were in excellent agreement with these predictions. The average value of the temperatures T evaluated by the equation $\langle \bar{V}_M\rangle=\frac{1}{2}k_BT$ was in both methods 304 K, and the maximum deviations from this value were 8 and 3 K in the molecular-dynamics and Metropolis simulations, respectively.

B. Orientational order

Figure 1 shows the computed orientational order parameters S of the hydrogen molecule as functions of the density parameter a of the liquid-crystal environment. The repulsion and dispersion forces as described by the Lennard-Jones potential function (13) are observed to provide very efficient orientation mechanism. At the density of a real liquid crystal ($a=5.5$ Å), the computed S is 0.249 and 0.039 in the square and hexagonal lattice, respectively. These values are much larger than any of the available experimental order parameters of molecular hydrogen: the S values of H_2 measured in 11 different nematic liquid crystals at a temperature of about 300 K vary from -0.011 to $+0.008$ [8,9]. In fact, to obtain a comparison with experiment, the computed S values should be scaled by the order parameter of the real liquid-crystal molecules (typically about 0.6). Furthermore, the present method of simulation tends to overestimate the S values also because it is based on classical mechanics. For example, a quantum-mechanical averag-

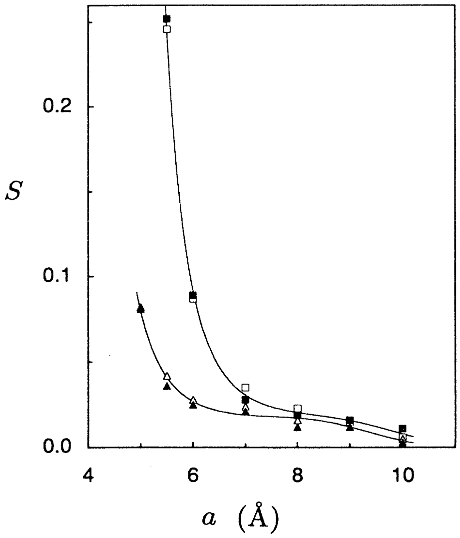

FIG. 1. The relationships between the order parameter S of the hydrogen molecule and the density parameter a of the crystal lattice. The points are computed by Monte Carlo and molecular-dynamics simulations (open and solid symbols, respectively) in the square (□,■) and hexagonal (△,▲) lattices. The solid curves are least-squares fits to the points using functions of the form $S=\exp(c_0+c_1a+c_2a^2+c_3a^3)$. The values of the coefficients c_0, c_1, c_2, and c_3 are 49.618, -19.029 Å^{-1}, 2.2792 Å^{-2}, and -0.09207 Å^{-3} (square lattice) and 31.389, -14.022 Å^{-1}, 1.8620 Å^{-2}, and -0.08289 Å^{-3} (hexagonal lattice).

ing over the rotational levels of H_2 in a simple mean field of the functional form of $P_2(\cos\theta)$ results in S, which is about 75% of the value resulting from a classical calculation (at 300 K) [8]. Thus the computed S values should be multiplied by a correction factor of the order of 0.5, but this is not sufficient for lowering them to the experimental range.

An obvious reason for the less efficient orientational ordering in true liquid crystals is the fact that the molecules in a real liquid are not arranged on a perfect lattice. There is a distribution of cavities in the liquid, and the solute molecules tend to occupy these cavities, rather than more dense regions. Thus the intermolecular forces acting on the solute molecules are less efficient, and the order parameter is reduced. This is evidenced by the striking drop in the computed S value when the liquid-crystal molecules are rearranged, at a constant density, from the perfect square lattice to an imperfect hexagonal lattice. This indicates that the computed S values would reach the experimental range, if still more imperfect lattice structures were used in the simulation.

The tendency of the solute molecules to reside in cavities is also demonstrated by the computed average values of the distance of the center of mass of H_2 from the nearest liquid-crystal molecule, $\langle R_{\mathrm{CM}}\rangle$. Indeed, at a given density $\langle R_{\mathrm{CM}}\rangle$ is always manifestly larger in the hexagonal lattice than in the square lattice. In fact, the order parameter S seems to be determined by the value of $\langle R_{\mathrm{CM}}\rangle$ alone, regardless of the details of the crystal structure. This is displayed in Fig. 2, where the S values are plotted as a function of $\langle R_{\mathrm{CM}}\rangle$. All the points fall on a single curve, irrespective of whether they are computed using the square or hexagonal lattice. This relation suggests that the experimental range of S could be reached at the density of a real liquid crystal by using a lattice structure where the average nearest-neighbor solute-solvent separation $\langle R_{\mathrm{CM}}\rangle$ is of the order of 4.6 Å (considering the correction factor 0.5).

It is noteworthy that the computed order parameters are invariably positive at all densities of the two crystal structures. This result does not seem to be sensitive to the values of the Lennard-Jones force constants ϵ and σ, nor to the details of the functional form of the site-site potential $V(R')$. The sensitivity of the results to the choice of the potential was investigated by performing a number of special Monte Carlo simulations at $a=7$ Å in the hexagonal lattice. In this system the standard Monte Carlo run (with $\epsilon=9\times10^{-22}$ J and $\sigma=4$ Å) resulted in $S=0.024\pm0.003$ (the statistical uncertainty is the standard deviation of the mean, estimated from the set of 15 independent S values computed in subchains of 10^6 steps each). Essentially the same result ($S=0.025\pm0.004$) was obtained when the depth of the potential well was doubled ($\epsilon=18\times10^{-22}$ J), but when the range of the potential was halved ($\sigma=2$ Å), S decreased to the value of 0.013 ± 0.003. Similar changes resulted when the steep-

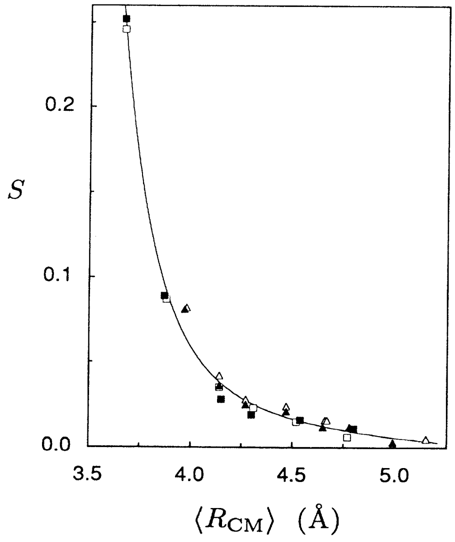

FIG. 2. The order parameter S as a function of the average nearest-neighbor solute-solvent separation $\langle R_{\mathrm{CM}}\rangle$. The computed data have the same symbols as in Fig. 1. The solid curve is a least-squares fit to the points using the function $S=\exp(c_0+c_1x+c_2x^2+c_3x^3)$, where $x=\langle R_{\mathrm{CM}}\rangle$. The values of the coefficients c_0, c_1, c_2, and c_3 are 141.16, -91.317 Å^{-1}, 19.509 Å^{-2}, and -1.4198 Å^{-3}, respectively.

ness of the repulsive part of the potential was altered: the S values corresponding to the Lennard-Jones 6-24 and 6-8 (rather than 6-12) potential were 0.029 ± 0.003 and 0.014 ± 0.002, respectively. (Generally, for an index of repulsion of $2n$, the coefficient η in Eq. (14) is $\eta=8(2n-2)!/3[2^{n-1}(n-1)!]^2$.) Comparable results were obtained with an exponential-type repulsion of the form $U_0\exp(-\alpha R/R_e)$, where R_e is the equilibrium separation of the hydrogen atom from the liquid-crystal molecule [then $U_0=20\epsilon'(\sigma/R_e)^5e^{\alpha}/\alpha$]: the S values corresponding to the steepness parameters $\alpha=20$ and 10 were 0.030 ± 0.003 and 0.012 ± 0.004, respectively [with $R_e=(231/160)^{1/6}\sigma=4.2525$ Å= the equilibrium separation in the standard potential $V_{\mathrm{LC}}(R)$ (14)]. Finally, when the attractive part of the potential was switched off by omitting the second term on the right-hand side of Eq. (14), the resulting S was 0.015 ± 0.002.

These results may be summarized by saying that in the considered system the hydrogen molecule receives its alignment primarily in collisions with the hard cores of the solvent molecules. The harder the cores are (i.e., the steeper the repulsive part of the intermolecular potential is), the larger the order parameter S is. The main role of the attractive forces is to pull the solute against the cores of the solvent molecules, thus enhancing the effects of the repulsions (increasing S). Away from the cores the attractive forces tend to decrease the S value. Actually, it has been shown [4] that in the central regions of the cavities in liquid crystals the attractions may result in *negative* S, i.e., H_2 tends to orient perpendicular to the axis of the cavities. In the present study this behavior was investigated in the hexagonal lattice at $a=6$ Å by determining the value of the order parameter of H_2 close to the centers of the hexagons. Specifically, in computing the average value of $P_2(\cos\theta)$ only those configurations were counted where the nearest-neighbor solute-solvent separation R_{CM} was larger than $b-r_e/2$, where b is the "radius" of the hexagon (equal to the length of its side) and r_e is the bond length of H_2. As expected, negative S values were obtained: Monte Carlo and molecular-dynamics simulations resulted in $S=-0.013\pm0.009$ and -0.015 ± 0.009, respectively. It has been suggested [4] that the negative signs of some of the *experimental* order parameters of H_2 might also be manifestations of this behavior. However, the present results indicate that the central regions of the cavities make only a minor contribution to S, as H_2 spends most of its time very close to the liquid-crystal molecules. Thus, the suggested explanation does not appear to be feasible: in all probability the dispersional van der Waals forces acting on the atoms of the hydrogen molecule are not capable of accounting for the negative experimental S values.

The cases of negative S seem to involve different kinds of intermolecular forces. An obvious candidate is the electrostatic interaction between the electric multipole moments of the solute and solvent molecules. Indeed, it has been shown [12] that the interaction between the molecular quadrupole moments may make a considerable contribution to S, provided that the cylindrical cavity occupied by the solute is rather short. This is compatible with the suggestion of Patey *et al.* [10] that molecules dissolved in liquid crystals experience an appreciable external electric-field gradient, which affects both their quadrupolar couplings B and order parameters S. The present results may be interpreted to lend support to the existence of such a field gradient.

C. Molecular deformation

Unlike the order parameter S, the solvent-induced molecular deformation can be described accurately by classical mechanics. This is due to the fact that the average force exerted by the solvent along the bond is a slowly varying function of the bond-stretching coordinate $\Delta r=r-r_e$ and can be expressed as a rapidly converging series $F_e(\theta)+F_1(\theta)\Delta r+\cdots$. Thus the total force along the bond can be written as $F(\Delta r,\theta)=-k\Delta r+F_e(\theta)+F_1(\theta)\Delta r+\cdots$, where $-k\Delta r$ is the leading (harmonic) term in the expansion of the intramolecular force. This series can be rewritten as $F=-(k-F_1)(\Delta r-\Delta r_d)+\cdots$, where $\Delta r_d=F_e/(k-F_1)$. This means that the sole effect of the external force on F is to shift the equilibrium position of the harmonic vibration from r_e to $r_e+\Delta r_d(\theta)$ and to change the harmonic force constant from k to $k-F_1(\theta)$. As the molecular reorientational motion is slow in comparison with the vibrational motion, the latter motion can be calculated separately in different orientations as if $\Delta r_d(\theta)$ and $F_1(\theta)$ were constants (adiabatic approximation). Hence the classical and quantum-mechanical calculations lead to identical results, as far as the expectation value of the bond length of the harmonic oscillator is concerned. Furthermore, the anharmonic contributions to this expectation value (due to the higher-order terms in the intramolecular potential) are, to a good approximation, independent of the external forces and do not influence the solvent-induced part of the molecular deformation [4]. Thus the present classical method of simulation should be quite adequate for a detailed analysis of the orientation-dependent changes in the bond length.

The dependence of the bond length on the molecular orientation is straightforwardly measured by the differences $\langle\Delta\bar{r}(\theta)P_2(\cos\theta)\rangle-\langle\Delta\bar{r}(\theta)\rangle S$ and $\langle\Delta\bar{r}(\theta)\rangle_+-\langle\Delta\bar{r}(\theta)\rangle_-$. According to Eqs. (3)–(6), they are directly proportional to the deformation amplitude Δr_2, which can therefore by readily determined from them. It is remarkable that these differences appear to be dependent exclusively on the order parameter S, regardless of the crystal structure. This is demonstrated in Fig. 3, which shows their values as functions of S. Indeed, in both cases the overall behavior of all the points, whether computed in the square or hexagonal lattice, displays a universal one-to-one relationship to S. The implication is that these and the other similarly invariant relationships (Figs. 2–5) may be valid for a wide class of different lattice structures, including that of a real liquid crystal.

Figure 4 shows the different averages of the bond-stretching coordinate, $\langle\Delta\bar{r}\rangle$, $\langle\Delta\bar{r}\rangle_+$, and $\langle\Delta\bar{r}\rangle_-$, as functions of S. As in Fig. 3, the points fall on crystal-structure-independent (nearly linear) lines. According to Eqs. (3), (5), and (6), in a *free* space (i.e., $S=0$) all three of these averages should be equal to Δr_0^{α} (as the solvent-

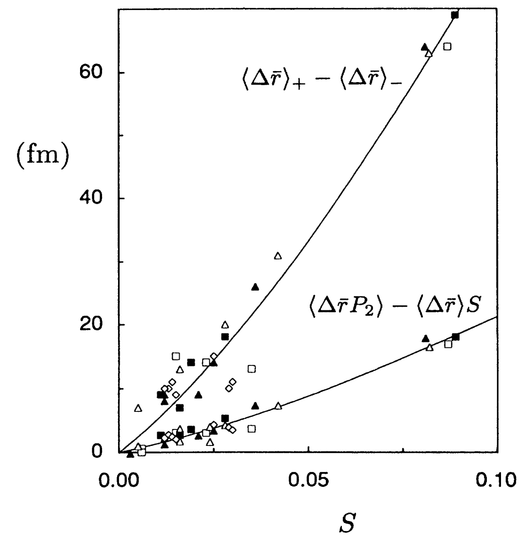

FIG. 3. The differences $\langle \Delta\bar{r}(\theta)P_2(\cos\theta)\rangle - \langle \Delta\bar{r}(\theta)\rangle S$ and $\langle \Delta\bar{r}(\theta)\rangle_+ - \langle \Delta\bar{r}(\theta)\rangle_-$ as functions of the order parameter S. The computed data have the same symbols as in Fig. 1, except that the results of the special simulations with the modified potentials (◇) have also been incorporated in the figure. The solid lines are least-squares fits to the data (including the points at $S = 0.25$, which are not shown in the figure) using the polynomials $c_1S + c_2S^2 + c_3S^3$. The values of the coefficients c_1, c_2, and c_3 are 121.3, 1277, and −3671 fm (for $\langle \Delta\bar{r}P_2\rangle - \langle \Delta\bar{r}\rangle S$) and 467.1, 4614, and −13 143 fm (for $\langle \Delta\bar{r}\rangle_+ - \langle \Delta\bar{r}\rangle_-$).

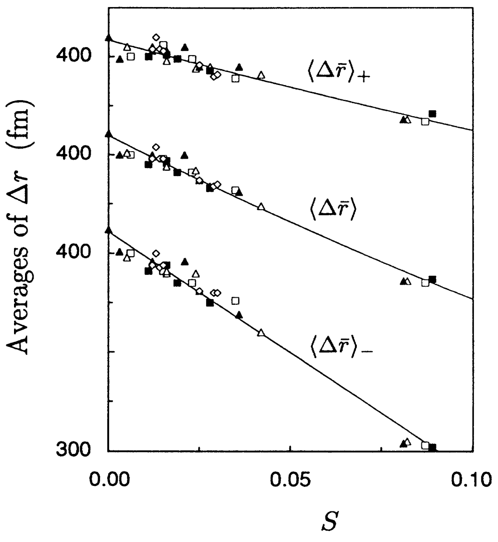

FIG. 4. The different averages of the bond-stretching coordinate, $\langle \Delta\bar{r}\rangle$, $\langle \Delta\bar{r}\rangle_+$, and $\langle \Delta\bar{r}\rangle_-$, as functions of the order parameter S. The computed data have the same symbols as in Fig. 3. The solid lines are least-squares fits to the data (including the points at $S = 0.25$, which are not shown in the figure) using the polynomials $c_0 + c_1S + c_2S^2$. The values of the coefficients c_0, c_1, and c_2 are 409.8, −923, and 930 fm (for $\langle \Delta\bar{r}\rangle$), 408.5, −496, and 370 fm (for $\langle \Delta\bar{r}\rangle_+$), and 410.9, −1226, and 39 fm (for $\langle \Delta\bar{r}\rangle_-$).

induced contributions Δr_0^d and Δr_2 vanish). The theoretical value of the unperturbed rovibrational average Δr_0^α is 408.5 fm (see the Appendix). The results of the simulations are in excellent agreement with these predictions: the plots of the three averages do converge to a single point, which coincides with the theoretical Δr_0^α.

Figure 4 indicates that the intermolecular forces from the crystal lattice tend to *compress* the hydrogen molecule. The special Monte Carlo simulations described in the preceding section (at $a = 7$ Å in the hexagonal lattice) show that this result is quite insensitive to the choice of the site-site potential-energy function. The computed values of $\langle \Delta\bar{r}\rangle$ were 392 fm (standard Lennard-Jones 6-12 potential), 387 fm ($\epsilon = 18 \times 10^{-22}$ J), 404 fm ($\sigma = 2$ Å), 384 fm (Lennard-Jones 6-24 potential), 398 fm (Lennard-Jones 6-8 potential), 385 fm (repulsion of the form $U_0 \exp(-\alpha R/R_e)$ with $\alpha = 20$), 398 fm (the exponential repulsion with $\alpha = 10$), and 398 fm (the repulsive part of the standard Lennard-Jones 6-12 potential alone). In all these cases the standard deviation of the mean is about 2 fm. Actually all these values, together with the corresponding S values reported in the preceding section, fit remarkably well with the points shown in Fig. 4. Thus the relationship between $\langle \Delta\bar{r}\rangle$ and S appears to be very generally valid, as far as the lattice structures and site-site potential functions are concerned. As a matter of fact, the results of the special Monte Carlo simulations indicate that similar generality applies to *all* the invariant relationships shown in Figs. 2–5, with one natural exception. The anomalous case is the $S - \langle R_{\mathrm{CM}}\rangle$ relationship in the run where the range of the potential was halved ($\sigma = 2$ Å): not surprisingly, the resulting average nearest-neighbor solute-solvent separation $\langle R_{\mathrm{CM}}\rangle$ was exceptionally small, 3.21 Å, while the order parameter ($S = 0.013$) fell in its normal range.

It is known that normally the bonds of small molecules dissolved in condensed phases are slightly *stretched* with respect to their gas phase lengths [19]. The stretching becomes observable in downward (red) solvent shifts of their vibrational frequencies [19]. The fact that the present simulations result in a compression of the H_2 molecule is a direct consequence of the simple site-site formulation of the intermolecular force model. In this "zero-order" model the interaction sites (the hydrogen atoms in H_2) are considered as isolated entities, and thus the parameters ϵ and σ are taken to be constants. In reality the electronic structure associated with the sites depends on the bond length r. In particular, the electric polarizability is generally an increasing function of r, and therefore also the parameter ϵ is expected to increase with r. Hence, the attractive (dispersion) part of the interaction tends to elongate the bond by favoring larger ϵ values. Indeed, Pratt and Chandler [20] and Herman and Berne [21] have shown that a reasonable r dependence of ϵ is quite sufficient for producing a bond stretching that surpasses the compression. It is important to note that the elongation due to this mechanism is only weakly dependent on the molecular orientation, because in liquid crystals the anisotropic part of the dispersion interaction is small in comparison with the isotropic contribution [22]. Thus, the orientation dependence of the molecular deformation, which is the main subject of the present study, should not be significantly influenced by the disregard of the r dependence of ϵ.

Finally, Fig. 5 displays the isotropic and anisotropic deformation amplitudes, Δr_0^d and Δr_2, as functions of S. They were determined from two separate sets of data [$\langle \Delta\bar{r} \rangle$ and $\langle \Delta\bar{r} P_2(\cos\theta) \rangle$, as well as $\langle \Delta\bar{r} \rangle_+$ and $\langle \Delta\bar{r} \rangle_-$] using Eqs. (3) and (4) as well as (5) and (6), together with the equation $\Delta r_0 = \Delta r_0^\alpha + \Delta r_0^d$, where $\Delta r_0^\alpha = 408.5$ fm. Figure 5 shows that these two procedures lead to virtually identical results; this confirms the conjecture that the higher-order terms in the series (1) and (2) are negligible. In addition, as in Figs. 2–4, the resulting relationships are invariant with respect to the lattice structure and interaction potential. There is a simple interrelation between the two deformation amplitudes: within the statistical uncertainty $\Delta r_0^d = -\Delta r_2$. According to Eq. (2), this means that the solvent-induced change in the bond length is zero when the molecule is parallel with the director (and negative at all the other orientations). This behavior is a straightforward consequence of the present models for the nematic solvent and intermolecular interaction: as the parameters of the site-site potential are taken to be constants, there are no external forces left along the bond when it is parallel with the (infinitely long) liquid-crystal molecules.

Figure 5 shows that the deformation amplitudes Δr_0^d and Δr_2 are, to a good approximation, directly proportional to the order parameter S. There are small systematic deviations from the direct proportionality, and third-order polynomials $\Delta r = c_1 S + c_2 S^2 + c_3 S^3$ have to be used in order to obtain good fits to all the computed points up to $S = 0.25$. However, in the experimentally relevant range of S (up to $S = 0.01$) the second- and third-order terms are negligible. Thus, according to Eq. (11), the leading term of the deformational contribution to the NMR observable $\langle \bar{T}_\parallel \rangle$ can be written as $T_1 \Delta r_2 / 5 = T_1 c_1 S / 5$, where $c_1 = 604$ fm (see the caption of Fig. 5). This term is -0.49% of the equilibrium contribution $T_e S$ if the observable is the dipolar coupling D_{HH}, and -0.80% of $T_e S$ if $\langle \bar{T}_\parallel \rangle$ is the quadrupolar coupling B_D. As discussed above, quantum-mechanical effects may be assumed to reduce the order parameter S by about 25% while leaving the deformation amplitudes Δr_0^d and Δr_2 unchanged (it should be noted that the force acting on the bond at a particular orientation does not depend on S). Thus the slope c_1 should be multiplied by a correction factor of about $\frac{4}{3}$, which means that the deformational contributions $T_1 c_1 S / 5$ are -0.65% of D_{HH}^e and -1.06% of B_D^e.

These numbers are quite small in comparison with the magnitudes of the deformational corrections usually involved in the analyses of experimental NMR data of various molecules dissolved in liquid crystals. In particular, in the one-bond dipolar couplings involving protons (such as D_{CH}), the deformational corrections are typically several percent [5]. This points to the inference that the orientation-dependent molecular deformations are normally dominated by the bending modes. Hydrogen is an exceptional molecule in the sense that its deformation is due to the stretching mode alone. Thus, as the deformation of H_2 is small, it is tempting to infer that the stretching contribution to the molecular deformation is generally small. In fact, in analyzing NMR data it is common to disregard altogether the forces tending to change the lengths of the bonds, on the grounds that the bonds are relatively stiff. The present results give definite evidence for the soundness of this approximation.

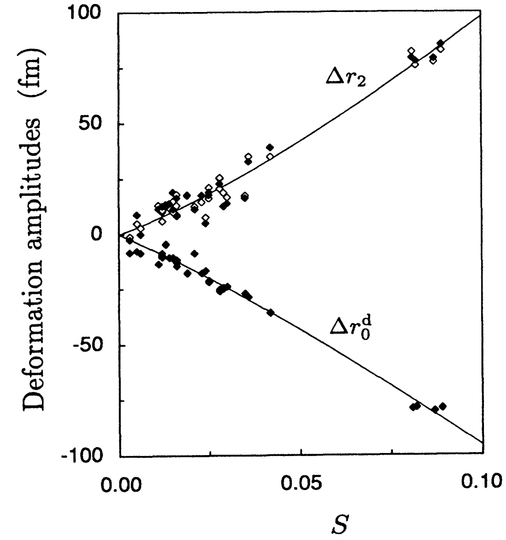

FIG. 5. The dependencies of the deformation amplitudes Δr_0^d and Δr_2 on the order parameter S. The points are calculated by Eqs. (3) and (4) (◇) as well as (5) and (6) (◆) from the results of all the simulations (Monte Carlo and molecular-dynamics runs in the square and hexagonal lattice, including the special simulations with the modified potentials). The solid lines are least-squares fits to the data (including the points at $S = 0.25$, which are not shown in the figure) using the polynomials $c_1 S + c_2 S^2 + c_3 S^3$. The values of the coefficients c_1, c_2, and c_3 are -732, -3207, and 9716 fm (for Δr_0^d) and 604, 5198, and $-14\,464$ fm (for Δr_2).

The small deformational corrections to D and B of the hydrogen molecule result in even smaller correction of -0.4% to the ratio B/D. Burnell, de Lange, and Snijders [8] have observed that in several liquid crystals the absolute values of B/D are about 6% smaller than in the gas phase. In view of the present results, it is evident that such large solvent effects cannot be attributed to the molecular deformation. This conclusion applies also to the orientation-independent stretching due to the bond-length dependence of the molecular polarizability. In order that this latter mechanism could account for the deviation of -6% in the ratio B/D, the resulting isotropic deformation amplitude should be $\Delta r_0^d = 0.02$ Å, i.e., 3% of r_e. The real bond-length change is expected to be one order of magnitude less, considering that the vibrational frequency shifts of H_2 dissolved in simple liquids are typically of the order of -0.5% (which corresponds to the bond stretching of 0.2%) [23]. This gives further support to the suggestion of Patey *et al.* [10] that solutes in liquid crystals experience a significant extramolecular electric-field gradient. The interaction of the nuclear quadrupole moment with such a field gradient gives rise to an additional contribution to B, which may be responsible for the solvent effect on B/D. Indeed, the same field gradient that accounts for the value of B/D is also capable of explaining the main features of the unusual orientational ordering of H_2: it has been shown [9,10] that the calculated order parameters S resulting from the interaction of this gradient with the molecular quadrupole moment are in good overall agreement with the experimental S values.

IV. CONCLUSIONS

The two questions propounded in the introduction may be answered as follows.

(1) Solute molecules in liquid crystals sample such regions of the solvent that the net effect of the repulsion and dispersion forces is to produce torques that tend to orient the bonds *parallel* with the director. Thus, the repulsion and dispersion forces alone cannot account for the experimentally observed torques acting on the CH and HH bonds of solutes. Other interactions, such as electrostatic forces, must also play an essential role in determining the behavior of solute molecules in liquid crystals.

(2) The repulsive forces lead to slight orientation-dependent compression of the bonds, resulting in relatively small changes in NMR spectral parameters (in H_2 the dipolar and quadrupolar couplings D_{HH} and B_D are changed by -0.7% and -1.1%, respectively). The molecular deformations arising from the bond-bending modes lead usually to markedly larger corrections to NMR parameters. The implication is that NMR spectral parameters of molecules dissolved in liquid crystals can normally be analyzed in terms of a model that includes only the bending-mode deformations.

ACKNOWLEDGMENT

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APPENDIX

Since the motions of the hydrogen molecule are treated by classical mechanics, the average value of its bond length in a free space can be calculated by the classical Boltzmann statistics. The motion of the two hydrogen atoms about their center of mass is reduced to an equivalent one-particle problem by using the spherical polar coordinates of one hydrogen atom relative to the other, which is taken as the origin. Thus the average value of the bond-stretching coordinate $\Delta r = r - r_e$ can be computed by the equation

$$\langle \Delta \bar{r} \rangle = \Delta r_0^{\alpha} = \frac{4\pi}{Z} \int_0^{\infty} dr\, r^2 (r - r_e) e^{-V_M(r)/k_B T} , \qquad \text{(A1)}$$

where Z is the partition function

$$Z = 4\pi \int_0^{\infty} dr\, r^2 e^{-V_M(r)/k_B T} . \qquad \text{(A2)}$$

At the temperature $T = 300$ K the result is $\Delta r_0^{\alpha} = 408.5$ fm, when the Morse potential $V_M(r)$ with the parameters D_e, α, and r_e specified with Eq. (12) is used.

It should be noted that Eq. (A1) leads to a true rovibrational average, which incorporates the effects of vibrational anharmonicity as well as the centrifugal distortion. The latter originates from the Jacobian of the transformation from Cartesian to spherical coordinates, i.e., from the weighting factor r^2, which is present in the integrals in (A1) and (A2). This factor can be rewritten as $r^2 = \exp[-V_C(r)/k_B T]$, where $V_C(r) = -2k_B T \ln r$. Thus r^2 can be formally interpreted as a Boltzmann factor corresponding to a spherically symmetric potential $V_C(r)$. This means that Eq. (A1) can be taken to signify averaging over the one-dimensional vibrational motion of the molecule in a potential $V_M(r) + V_C(r)$, rather than averaging over the three-dimensional rovibrational motion in the Morse potential $V_M(r)$. The force corresponding to the potential $V_C(r)$ is $F_C(r) = -dV_C(r)/dr = 2k_B T/r$, which can be identified with the average value of the centrifugal force acting on the bond of instantaneous length r: $k_B T$ is the average rotational energy of the diatomic molecule, $\frac{1}{2}\mu r^2 \langle \omega^2 \rangle$, and therefore $F_C(r) = \mu r \langle \omega^2 \rangle$, where $\mu = m/2$ is the reduced mass and ω is the angular velocity.

The truly one-dimensional averaging of Δr over the vibrational motion [omitting the weighting factor r^2 in Eqs. (A1) and (A2)] leads to the result $\Delta \bar{r} = 211.7$ fm. This is the vibrational contribution to Δr_0^{α}, which is due to the anharmonicity of the Morse potential. The rest of Δr_0^{α}, 196.8 fm, is due to the centrifugal force. Indeed, it is in good agreement with the value of 194 fm obtained by the well-known approximate formula for the centrifugal distortion, $\langle \Delta r \rangle = 2k_B T / r_e k$, which ignores the anharmonic terms in the vibrational potential (k is the harmonic force constant) [24].

In the Monte Carlo method, the averaging is carried out over the three-dimensional motion of the hydrogen molecule, and therefore the effects of the centrifugal distortion are automatically included. Thus, notwithstanding the profoundly dynamic nature of the centrifugal effects, the Monte Carlo method is capable of resulting in exactly the same rotational-vibrational properties as the full molecular-dynamics calculation.

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