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VIBRATIONAL PROPERTIES OF LIQUID CRYSTAL MOLECULES FROM *AB INITIO* COMPUTER SIMULATION

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Abstract We determine the molecular vibrational frequencies and displacement patterns for the 4-4' pentyl-cyanobiphenyl (5CB) molecule by first principles density functional theory. All dynamic properties of the isolated molecule are obtained directly by diagonalisation of the dynamical matrix, the elements of which are determined from Hellmann-Feynman Forces. Periodic boundary conditions are used which allow for the expansion of the molecular electronic wavefunction in terms of a delocalised plane wave basis set. These calculations are in excellent agreement with the results of vibrational spectroscopy and they provide a reliable means of predictive modelling of molecular properties and can be applied to as yet unsynthesised molecules.

INTRODUCTION

It is now very well established that certain properties of anisotropic molecular fluids are well described by simple excluded volume models such as hard ellipsoids[1,2,3]. However, there is an emerging body of evidence which suggests that atomistic-level detail is not negligible (such as the oscillation of the nematic-isotropic transition temperature with tail length)[4]. and that the most accurate LC simulations should incorporate molecular shape and at least a certain degree of molecular flexibility[5].

A principal goal of quantum chemical simulations is the parameter-free determination of the energy and electronic charge distribution in a molecule. From this, it is possible to determine bond character, equilibrium geometry, energy differences between various molecular conformations and vibrational properties (harmonic and anharmonic force fields). Vibrational properties are particularly important as they provide a direct measure of bond strength and molecular flexibility. The majority of existing methods of computer simulation make use of localised basis sets in which the molecular electronic wavefunction is expanded. For these calculations, results have been found to depend on the type of basis set used[6]. Coupled cluster calculations afford the most accurate treatment of electron correlation but are limited to molecules containing fewer than about 10 atoms and are inapplicable to liquid crystals[7].

As a result of the importance of understanding dynamical properties of molecules, vibrational spectroscopy has become an important probe of molecular structure and intermolecular interactions. One of the most common analytical applications of molecular spectroscopy is in the assignment of various infrared or Raman signals to frequencies of molecular constituents such as CN stretch modes. For large, complex molecules such as liquid crystals, these assignments are only approximate and it is therefore important to develop an understanding of how the frequencies of mesogenic fragments are altered by chemical environment. Vibrational spectroscopy is also sensitive to low-frequency intermolecular modes however, there has been some question as to whether low-frequency intra-molecular modes may complicate the interpretation of the low-frequency vibrational spectroscopic data.

The objectives of this paper are to (i)introduce an efficient computational means of determining equilibrium molecular geometry and vibrational frequencies of liquid crystal molecules; (ii)to compare the accuracy of the method with other quantum chemistry techniques and to experiment and (iii)to explore the nature of low-frequency molecular vibrations in the prototypical nematogen 5CB.

COMPUTATIONAL METHODS

The calculation method is based on techniques which have traditionally been applied to the electronic structure of infinitely extended solids. Specifically, we use density functional theory of Kohn and Sham (DFT)[8] which states that the electronic ground state of a system is a unique functional of the electron density and that the ground state corresponds to an energy minimum.

The total energy depends both on the electronic degrees of freedom as well as the atom positions. The full expression is of the form

$$E(\psi_i) = T[\rho(r)] + \int V_{ion}(r)\rho(r)dr + \frac{e^2}{2}\int \frac{\rho(r)\rho(r')}{r-r'}drdr' + E_{xc}[\rho(r)] + E(\{R_I\}) \quad (1)$$

Term one corresponds to the electronic kinetic energy, term two involves the electron-ion interaction, term 3 is the Hartree electrostatic interaction and term 4 includes the many-body effects of exchange and correlation and the last term represents the electrostatic interaction between ions. The main approximations which enter our implementation of density functional theory involve term 2 and term 4. In the former case we describe the electron-ion interaction through a pseudopotential[9]. We use the generalised gradient approximation (GGA)[10] for the exchange and correlation energy. We also impose periodic boundary conditions. This allows for the expansion of the molecular electronic in terms of a delocalised plane wave basis set rather than a localised set. The advantage of a plane wave basis set is that is that its convergence toward completeness is easily tested. The coefficients of the plane waves are then treated as variational parameters in a search for the electronic configuration which minimises the total energy. Many minimisation algorithms exist but we have chosen to use the conjugate gradients scheme in this implementation. Details of this algorithm can be found elsewhere[11]. The resulting ground state charge density can then be reconstructed directly from the electronic wavefunctions from $\rho(r) = 2\sum_i |\psi_i(r)|^2$.

So far we have only discussed the determination of the ground state electronic configuration. We now turn to the case of the equilibrium molecular geometry. Firstly it is necessary to optimise the bond lengths and bond angles and then to determine the energy differences between various competing conformations. The determination of the optimum atomic positions follows from the Hellmann-Feynman theorem[12] which states that the force on an atom at position R_l is

$$F = \frac{\partial E}{\partial R_l} \tag{2}$$

The atoms are then moved under the influence of these forces until the forces are below some pre-determined tolerance which is typically of order 0.1eV/Å. We determine the vibrational properties from a direct calculation of the full dynamical matrix of force constants[13,14]. The procedure is as follows: the force constants of a crystal relate the displacements of the ions from their equilibrium positions to the resulting forces. If the k^{th}ion in the l^{th} unit cell has displacement u_{lk} from an equilibrium position x_{lk}, then the forces on the ions are given by

$$F_{lk} = \Phi_{lkl'k'} u_{l'k'} \tag{3}$$

where Φ are the harmonic force constants. In order to find the phonon frequencies and eigenvectors at some wavevector, the Fourier transformed dynamical matrix must be formed, consisting of the force constants scaled by ionic masses:

$$D_{\alpha\beta}(kk') = \frac{1}{\sqrt{m_k m_{k'}}} \frac{F_{\alpha k}}{\xi} \tag{4}$$

When complete, this matrix is then diagonalised to find the molecular vibration frequencies and eigenvectors.

For the case where molecules have high symmetry it is necessary to calculate only a subset of the possible $3N$ distortions. The remaining elements can be determined from the transformation matrices of the point group.

RESULTS

Test calculations on small molecules

In order to test the reliability of our method we have applied our method to a variety of relatively small molecules to which previous quantum chemical simulations have been applied. The results are shown for ethene in Tables 1.

TABLE 1 Vibrational frequencies for ethane calculated by various *ab initio* methods.

Symmetry	Description of mode	This Work	Observed Ref. 15	HF[6] 6-31G	MP2[6] 6-31G*	CCSD[7] cc-pVTZ	DFT[16] TZVP+
$\omega_1(a_g)$	CH_2 *s*-stretch	3132	3153	3344	3231	3157	3056
$\omega_2(a_g)$	CC stretch	1670	1655	1856	1724	1672	1637
$\omega_3(a_g)$	CH_2 scis	1360	1397	1499	1425	1369	1330
$\omega_4(a_u)$	CH_2 twist	1049	1044	1155	1083	1047	1011
$\omega_5(b_{1g})$	CH_2 *a*-stretch	3149	3232	3394	3297	3219	3117
$\omega_6(b_{1g})$	CH_2 rock	1225	1245	1353	1265	1242	1195
$\omega_7(b_{1u})$	CH_2 wag	969	969	1095	980	967	912
$\omega_8(b_{2g})$	CH_2 wag	932	959	1099	931	942	918
$\omega_9(b_{2u})$	CH_2 *a*-stretch	3191	3235	3420	3323	3246	3144
$\omega_{10}(b_{2u})$	CH_2 rock	835	842	897	873	823	797
$\omega_{11}(b_{3u})$	CH_2 *s*-stretch	3126	3147	3321	3222	3139	3045
$\omega_{12}(b_{3u})$	CH_2 scis	1444	1473	1610	1523	1479	1411

HF refers to Hartree Fock Level, MP2 to Moller Plessent electron correlation, and CCSD means coupled cluster with all single and double substitutions. The basis set cc-pVTZ is a correlation consistent polarised valence triple zeta., TZVP+ is a polarised triple-zeta valence basis set.
Abbreviations- scis: scissors, a: asymmetric, s: symmetric

It is clear that our plane wave density functional method gives vibrational frequencies for these molecules at a level of accuracy comparable to those obtained at the CCSD level of theory. We now proceed to apply this technique to the vibrational properties of the 5CB molecule.

Molecular Vibrations in 5CB

In the nematogen 5CB there are 38 atoms in a molecule which give 108 vibrational modes. The relaxed geometry for the plane conformer is described elsewhere[17]. In Fig. 1 we compare the calculated molecular vibrational frequencies with Raman spectroscopic data obtained at room temperature (in the nematic phase) and at low temperatures. Two immediate conclusions can be drawn from these results. Firstly, the first principles calculation of the mode frequencies appears to be very accurate over the very wide frequency range of 0 to 3500 cm^{-1}. In particular the CN stretch frequency at 2255cm^{-1} is in excellent agreement with experiment. At the higher frequencies, modes corresponding to CH stretching are calculated at frequencies slightly higher than those at which they are observed, which can be attributed to temperature factors..

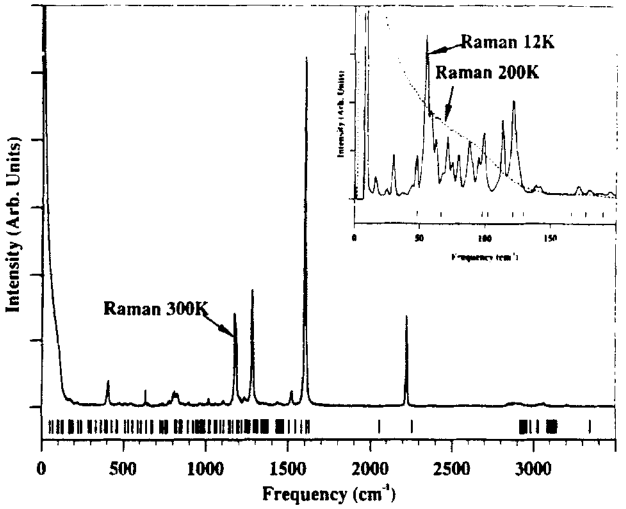

Figure 1. Raman spectrum of 5CB at room temperature over the range 0 to over 3500cm^{-1}. The tick marks show the frequencies of the 108 calculated mode frequencies. The inset shows the low-frequency region (0 to 150cm^{-1}) both at room temperature, 200K and 13K upon cooling. The results of our calculations suggest that the low temperature Raman spectra involve a complex combination of both intramolecular (internal) vibrations as well as long range intermolecular modes.

Secondly, it is also evident that there exist several modes having very low frequency (modes below ~100 cm^{-1}). These modes are molecular torsional motions which involve no bond length variation. In our Raman spectroscopy measurements, these modes are not discernible clearly on the pronounced Rayleigh wing of the nematic phase. Upon cooling into the solid phase, a very complex Raman spectrum is obtained at low frequency. Based on our theoretical calculations, it appears that this low frequency spectrum cannot be interpreted as arising purely from lattice modes characteristic of long range order in the solid. Instead the low frequency dynamical properties involve both lattice and intramolecular modes. A more detailed Raman study on 5CB will be presented elsewhere. In Fig. 2 we show a low frequency mode

CONCLUSIONS

We have demonstrated that a computational method adapted from large-scale electronic structure calculations on condensed matter can provide reliable, predictive information on complex molecules such as liquid crystals entirely from first principles. In this paper we have demonstrated the accuracy of the method for a small molecule to which standard quantum chemical techniques have been applied. For these systems the accuracy of our method is comparable or better. We then applied the method to the prototypical nematogen 5CB to determine the equilibrium structure, vibrational frequencies and compared them to experimental data.

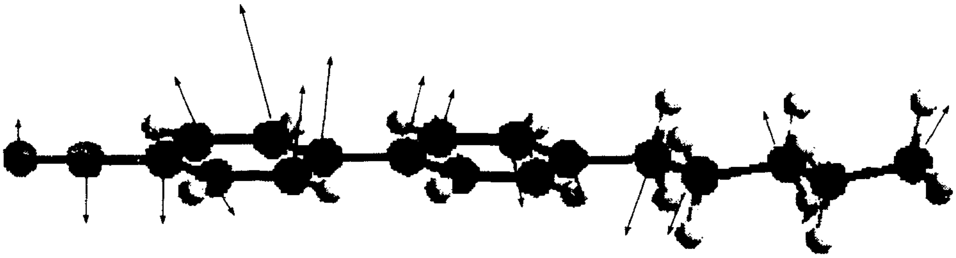

Figure 2. When determining the vibrational modes of 5CB, we also calculate the displacement undergone by each atom under excitation of that mode. We illustrate this here by showing a low frequency (286cm^{-1}) mode which resembles a standing wave along the length of the molecule.

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