

Conformational distribution of a ferroelectric liquid crystal revealed using fingerprint vibrational spectroscopy and the density functional theory

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(Received 16 February 2007; accepted 26 April 2007; published online 14 June 2007)

The authors have investigated the conformational structure of the ferroelectric liquid crystal compound 4-3-methyl-2-chloropentanoyloxy-4''-hexyloxy-biphenyl also known under the abbreviations 3M2CPHOB and C6 using vibrational (IR and Raman) spectroscopy. The measured spectra exhibit two bands corresponding to the C=O stretching vibration that are separated by 20 cm⁻¹. In contrast, the molecular structure comprises only one such group. They assigned the two bands to different conformers that coexist in a temperature range between 25 and 65 °C covering the entire mesophase of this material. This assignment is strongly confirmed by calculated vibrational spectra based on the density functional theory. © 2007 American Institute of Physics. [DOI: 10.1063/1.2741557]

I. INTRODUCTION

Vibrational IR and Raman spectroscopies have been proven to be ideal experimental methods for the investigation of molecular conformations and they were successfully applied to isolated molecules, either in the gas phase,¹ in matrices of noble gases,² or adsorbed on metallic nanoparticles.³ In spectra measured on molecular ensembles, unfortunately, the broadened spectral bands efficiently cover the subtle spectral fine structure caused by conformational changes occurring in the sample. The information, however, of the conformational distribution in bulk samples, especially as a function of environmental parameters, is of fundamental importance in the case of many molecules.

For organic compounds having a close neighborhood of atoms with high electronegativity, a rotational degree of freedom around a σ -bond results in a high variation of the distance of the involved atoms (or atomic groups). In this case, the force constants of the respective vibrations are strongly affected. Hence, if the corresponding vibrational frequencies are shifted by a value of the order of the width of the respective vibrational bands, we expect that the conformational effects can be observed using common spectroscopic (IR and Raman) techniques, even for bulk liquid samples.

In case of ferroelectric liquid crystals (FLCs) a detailed

orientational information is of particular interest. Certain effort has already been spent to provide a direct spectroscopic evidence of the preferred orientation of certain functional groups, which is a critical parameter for the creation of their ferroelectricity.^{4,5} For several kinds of liquid crystals the conformational distribution could play an essential role for such phenomena such as the spontaneous polarization sign reversal,⁶⁻¹¹ the twist inversion in cholesteric and ferroelectric phases,^{12,13} and the spontaneous chiral segregation of bent-core liquid crystals.¹⁴⁻¹⁶ Moreover, variations of the shape of the C=O stretching vibration band under variation of the temperature has been attributed to varying angles between the C=O bond and the benzene ring for two cases: a ferroelectric liquid crystal¹⁷ and a discotic liquid crystal.¹⁸ Up to now, however, it has not been clearly demonstrated that particular spectroscopic features can be assigned to different molecular conformations.

In this paper, we report an experimental evidence for two conformers of the ferroelectric liquid-crystalline compound 4-3-methyl-2-chloropentanoyloxy-4''-hexyloxy-biphenyl. We observed a separation of up to 20 cm⁻¹ between the frequencies for the C=O stretch vibration for the two conformers in both infrared and Raman spectra. The experimental results are confirmed by spectra calculated using the density functional theory, showing excellent agreement.

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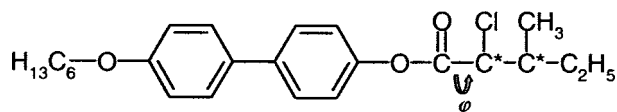


FIG. 1. Structural formula of the investigated ferroelectric liquid crystal compound 4-3-methyl-2-chloropentanoyloxy-4''-hexyloxy-biphenyl, abbreviated as 3M2CPHOB. φ is the torsional angle as discussed in the text. The material has the following phase diagram: CrG* 50 °C SmC* 54 °C and SmA* 64 °C Is.

II. EXPERIMENTS AND CALCULATIONS

A. Sample

The liquid crystal used in this study is 4-3-methyl-2-chloropentanoyloxy-4''-hexyloxy-biphenyl (see Fig. 1), also known under the abbreviations 3M2CPHOB and C6. Its synthesis and basic properties were reported in mid 1980s independently by two groups.^{19–21} With two chiral centers in the molecular structure, one of them substituted with an atom of chlorine; the compound and its homologues were known to exhibit relatively high values of the spontaneous polarization approaching 250 nC cm⁻².²¹ Our attention will be focused on the interaction between the chlorine and an oxygen from a neighboring carbonyl group (C=O).

B. Sample preparation and measurements

The sample for IR spectroscopy was sandwiched between two ZnSe windows. A mylar film having a thickness of approximately 5 μ m was used as a spacer. The filling temperature of the cell was a few degrees above the transition temperature to the isotropic phase. The measurements were performed using a commercial Bio-Rad FTS-6000 Fourier transform infrared spectrometer. The spectra having a resolution limit of 1 cm⁻¹ were obtained after accumulating 32 scans.

The Raman spectra were recorded using a commercial LabRam multichannel spectrometer. The setup comprised a Olympus BX41 confocal microscope with a charge coupled device detection system having 1024 pixels along the dispersion axis. A laser operating at 532.14 nm was used for excitation. The spectra were acquired in the range between 200–1850 cm⁻¹ with a spectral resolution of 6.21 cm⁻¹ using a grating with a groove density of 600 /mm. The spectra were collected once with an integration time of 1 s. The high resolution spectrum of the band at 1760 cm⁻¹ was measured using a grating with a groove density of 1800 /mm, an acquisition time 30 s, and a total accumulation of over 30 spectra.

Vibrational bands in the measured IR spectra were fitted with a convoluted Gaussian-Lorentzian line shape function; the measured Raman bands were fitted with a linearly combined Gaussian-Lorentzian line shape function.

C. Calculations

The density functional theory was used for (1) computing a potential barrier ΔE on rotation around C–C bond between C=O and C–Cl groups and for (2) simulating vibrational spectra for stable conformers. The computations were done using the commercial package GAUSSIAN03 Ref. 22 in-

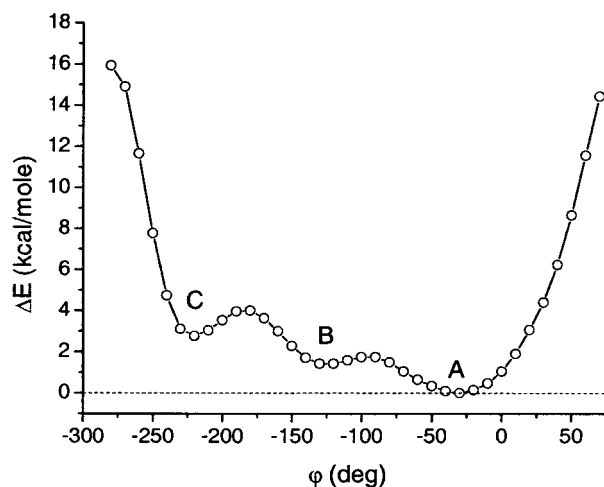


FIG. 2. Potential barrier ΔE for the rotation around the C–C bond between C=O and C–Cl groups.

cluding the functional B3LYP and the diffusive basis set 6-31+G* (the diffusive basis set was chosen because of the high electronegativity of atoms of oxygen and chlorine). The potential barrier was computed by varying the torsional angle O=C–C–Cl with a step width of 10°, calculating a single point energy for each step. A “tight” convergence criterion was used for the self-consistent-field procedure [and, additionally, a “quadratic convergence” parameter in order to improve stability of calculations using the diffusive basis set]. The geometries corresponding to the local minima on the potential barrier were used as starting points for full geometry optimizations, which practically kept the values of the investigated torsional angle. The resulting geometries were used for calculations of the vibrational (IR and Raman) spectra. The frequency calculations did not produce negative frequencies confirming that the minimizations were indeed complete. The computed force field for the vibrational spectra was scaled using the scaled quantum-mechanical (SQM) procedure^{23,24} including a transferrable set of scaling factors given by Baker *et al.*²⁴ (An application for SQM provided by Parallel Quantum Solutions.²⁵)

The theoretical spectra were prepared by putting Gaussian functions having a width of 8 cm⁻¹ on each calculated vibrational frequency. The calculated Raman intensities were additionally scaled to the differential Raman scattering cross section using the following equation:

$$\frac{d\sigma_j}{d\Omega} \approx \frac{(\bar{\nu}_0 - \bar{\nu}_j)^4}{\bar{\nu}_j} \frac{S_j}{1 - \exp(-hc\bar{\nu}_j/kT)}, \quad (1)$$

where $\bar{\nu}_0$ and $\bar{\nu}_j$ are the wave numbers of the excitation line and the normal mode, respectively, and h , c , and k are universal constants. The temperature T was chosen to be 340 K accounting for the experimental conditions.

III. RESULTS

As can be seen in Fig. 2, the potential barrier ΔE for rotation around the C–C bond between C=O and C–Cl groups consists of three minima. The barrier is a result of a nonrelaxed potential scan, which can only be a rough estimate of the energy values. However, we note that the energy

TABLE I. Torsional angles O=C–C–Cl (φ in Fig. 1) for optimized geometries (conformers A, B, and C), as well as the corresponding frequencies of the C=O stretching band (in parentheses: experimental values taken from a room temperature IR spectrum).

Conformer	Torsion (deg)	Frequency calculated (observed) (cm^{-1})
A	-30.3	1763 (1765)
B	-114.7	1744 (1746)
C	-199.8	1724 (···)

differences and the potential barriers between these three minima are below 4 kcal/mol. This value is insignificant comparing to kT , thus allowing easy interconversion between the different conformers. It is clear that the repulsive interaction between two negatively charged atoms of oxygen and chlorine is substantially different for the three conformers. As a result, we expect frequency shifts of certain vibrational bands between the conformers as well as differences in peak intensities. Such a difference is clearly visible in case of a well-defined stretching vibration of the carbonyl group (C=O), for which frequency shifts between the conformers are as large as 20 cm^{-1} (Table I).

There are, however, only two such bands visible in the experimental spectra, with frequencies in perfect agreement with the theoretical ones of conformers A and B. In addition, the band of C–O–C stretching mode at 1230 cm^{-1} has exceptionally high intensity in the theoretical spectrum of conformer C: The intensity is roughly ten times higher than the C–C stretching band about 1600 cm^{-1} , which is always a good reference for aromatic molecules. In contrast, the intensity of this band in the experimental spectrum does not exceed a typical value predicted for conformers A and B. Therefore, we conclude that the conformer C has a much lower, or none, occupation comparing with A and B, and cannot be observed in our experiments. In the following we limit our further discussion to the conformers A and B.

Figure 3 shows experimental and theoretical vibrational (IR and Raman) spectra for the bulk samples as well as the theoretical ones for conformers A and B separately. In the following we will discuss differences between spectra of both conformers. Characteristic features of the spectrum of conformer A are bands at 675 (IR) , 664 (Raman) , and $853 \text{ (IR and Raman)} \text{ cm}^{-1}$. A clear signature of conformer B is an IR band at 1350 cm^{-1} . IR bands at 1080 , 1121 , and 1158 cm^{-1} exhibit strong variations of intensity between spectra of conformers A and B, but cannot be considered exclusive indicators of either of them. All the bands listed above are strongly delocalized, i.e., the energy is dispersed over the primitives. Indeed, the total energy distribution analysis²⁶ shows many contributions (rarely exceeding 10% of the total energy), and all of these bands contain stretching and bending modes of atoms close to the torsional angle φ .

The most pronounced spectral feature remains at the band 1760 cm^{-1} , corresponding to the C=O stretching vibration. The carbonyl groups, in case of FLCs, are also the most important because of their contribution to the transversal component of the permanent dipole moment (and thus the

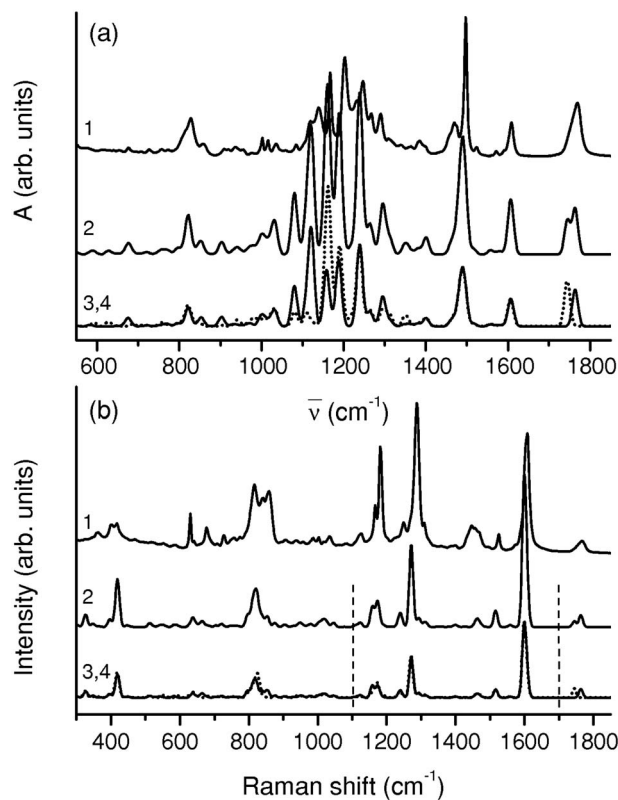


FIG. 3. Experimental and theoretical (a) infrared and (b) Raman spectra: (1) experimental spectrum (isotropic phase, 65°C) [(3) and (4)] theoretical spectra of conformer A (black) and B (gray), respectively, (2) weighted sum of spectra (3) and (4) calculated for conformers A and B. The weights maintain spectral contributions to the carbonyl stretching band. An offset between spectra introduced for improving clarity. Intensities of theoretical Raman spectra for frequencies below 1100 cm^{-1} have been increased by the factor of 3.

spontaneous polarization⁴). Moreover, stretching vibrations are reproduced by theoretical calculations with highest accuracy.

Figure 4 shows infrared and high resolution Raman spectra in the region around 1760 cm^{-1} . The spectral distribution was modeled assuming two contributions, showing high accuracy. We found that the central frequencies of the two peaks are strongly dependent on temperature and phase. In the IR spectra shown in Fig. 4(a), the higher frequency component was observed to shift from $1771 \text{ (} 65^\circ\text{C, isotropic phase)}$ to 1765 cm^{-1} (25°C, CrG^* phase) upon cooling of the sample. The lower frequency component ranged between 1757 and 1746 cm^{-1} . At room temperature the Raman spectrum shown in Fig. 4(b), taken from a crystal, the frequencies of both peaks are 1760 and 1756 cm^{-1} , respectively. As we can clearly see from Fig. 4, the relative spectral intensity of the two contributions are also strongly temperature dependent.

IV. CONCLUSIONS

We have shown a strong spectroscopic evidence of the conformational distribution of a ferroelectric liquid crystal. Our interpretation is supported by theoretical calculations based on the density functional theory. Importantly, we were able to probe the conformational distribution from a bulk

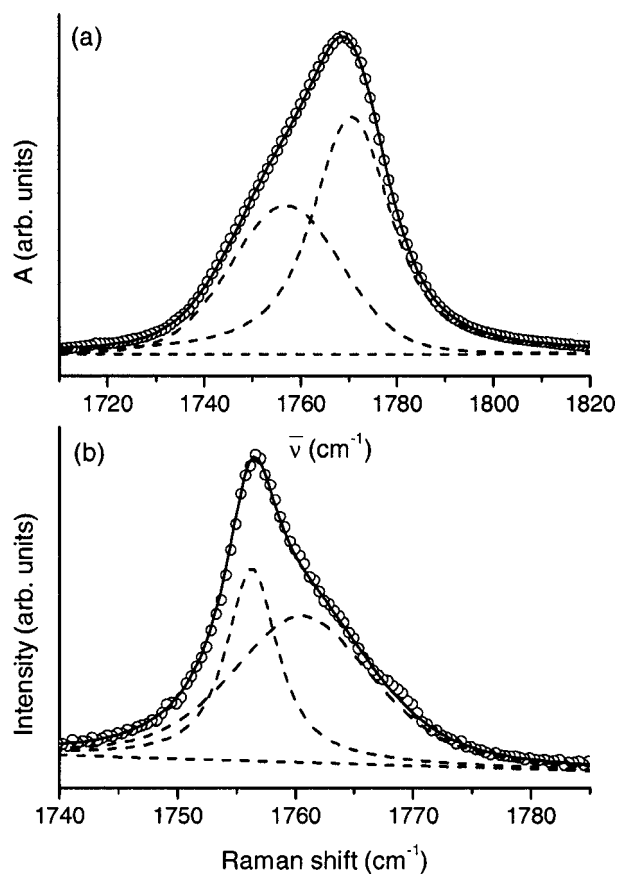


FIG. 4. Experimental (a) infrared and (b) Raman spectra of the band corresponding to the carbonyl stretching vibration. The infrared spectrum was acquired at 65 °C (isotropic phase); the Raman spectrum was acquired at room temperature (solid phase). The solid line is a fit to experimental points (circles); the dashed lines are components of the solid curve.

sample. It shows the possibility of performing such investigations on similar compounds, whenever the conformational distribution may be important from the point of view of their macroscopic properties, probing the molecular conformers in their *native* environment.

The necessary condition of such a study, we believe, lies in the molecular structure: strongly interacting atoms, or functional groups, close to each other, and as well close to the “active” part of the molecule. This condition seems quite difficult to meet, but anyway there are areas where possessing detailed information on molecular conformers is essential, such as, for example, for many biologically active molecules, including drugs. In case of Raman spectroscopy

probing the conformational distribution should also be possible in water solution. The results presented here should therefore encourage to perform careful studies on molecular conformers by applying standard IR and Raman spectroscopy techniques in combination with advanced methods of molecular modeling.

ACKNOWLEDGMENTS

The authors would like to thank Britt Schuster for help. Part of this work was funded by the EU network SAMPA.

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