PHYSICAL REVIEW E VOLUME 61, NUMBER 6 JUNE 2000

Coupling between molecular vibrations and liquid crystalline order parameters

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(Received 10 November 1999)

Specific Raman active modes in two prototype cyanobiphenyl liquid crystals are shown to display a temperature dependent softening proportional to either the nematic or smectic order parameters, while other vibrations (like the C≡N stretch mode) remain unaltered. This selective coupling between intramolecular vibrations and the liquid crystalline order is related to the intrinsic symmetry of the modes. The method provides a simple, microscopic, noninvasive optical technique with which the liquid crystalline order parameters can be qualitatively mapped out.

PACS number(s): 61.30.Eb, 64.70.Md, 33.20.Fb

Inelastic light scattering provides a myriad of information on different sorts of phase transitions [1]. This is achieved by either the direct observation of scattering from excitations related to the phase transition itself, or by indirectly monitoring the coupling of the order parameters to other excitations with a finite Raman cross section like phonons. Extensive examples of this sort exist in the literature about magnetic materials [2,3].

Liquid crystals (LC's) are characterized by complex phase transitions which may involve one or several order parameters in different temperature ranges [4]. One may argue that the internal vibrations of an individual LC molecule should not be the same when the molecule is placed in the average molecular fields (MF's) which are responsible for the different LC phases. Small changes in the electronic structure of the molecule coming from its interaction with the average MF within the LC should produce, accordingly, variations in the intramolecular modes. These changes are expected to be small, for the interactions characterizing the LC state are weak. A typical interaction energy is of the order of $\sim k_B T_c \sim 10$–30 meV, which should be compared with a typical electronic excitation energy ~ 3–5 eV. Thus one could *a priori* expect changes which should be no larger than $\Delta\omega/\omega \sim 10^{-2}$–$10^{-3}$. Moreover, the fact that the LC state is characterized by one or several macroscopic order parameters should impose well defined symmetry restrictions to the coupling between the macroscopic order and the phonons, as we shall show later.

In this Brief Report, we show that small but measurable frequency changes ($\Delta\omega/\omega \sim 10^{-3}$) in specific Raman active modes are seen in different phases of two prototype cyanoalkylbiphenyl LC's. Moreover, we show that while some modes are sensitive to the presence of a nematic order parameter, others respond only to the smectic order, or remain unchanged. This selective coupling of intramolecular vibrations to the different order parameters of the LC's not only adds another example to the field of inelastic light scattering of indirect monitoring of a phase transition, but also provides a powerful tool to qualitatively measure the LC order parameters themselves with a noninvasive microscopic technique like Raman scattering. In this sense, it may provide a useful method to monitor phase transitions in LC's in situations where other experimental techniques may turn out to be difficult.

Raman scattering has been used in the past both to characterize the intramolecular vibrations of different LC compounds and to study the orientational statistics of the nematic state [5]. These experiments use the fact that anisotropic Raman tensors can be associated with well defined vibrations (like the C≡N stretch), and that the average orientation of the bonds can be probed by an appropriate choice of the incident and scattered polarizations. No changes in the frequencies of Raman active vibrations have been reported so far in the nematic phase. More recently [6], ample changes (~ 15 cm^{-1}) in Raman active modes have been reported for a discotic LC at the transition between the isotropic and columnar nematic (D_h) phases. These large frequency changes in discotics have a different origin in the considerable electronic overlap among the π electrons of the central core of the molecules, which is a key feature of the D_h phase [7]. Frequency [8] and intensity [9] changes have been observed in spectroscopic studies of LC's in the transition from an isotropic liquid to a smectic phase and, in fact, we believe these to be the equivalent examples in LC's of the sort of phenomena observed in magnetic materials. We shall show below that specific modes can couple selectively to either the nematic or smectic phase, and we shall argue that this property is related to the intrinsic symmetry of the vibrations.

Raman experiments were performed in the polarized backscattering configuration with the 514.5-nm line of an Ar$^+$ laser (5 mW), and the data were taken by a T64000 triple subtractive Jobin-Yvon spectrometer coupled to a CCD. The spectra were recorded with ~ 0.2-cm^{-1} resolution in the ~ 20–$50\,^\circ$C temperature (T) range. Samples were placed inside a quartz-capillary tube in a hot stage. No preferential direction exists inside the sample for the ordered mesophases. The experiments were performed in two related 4-cyano-4′-n-alkylbiphenyl LC compounds, K_{15} and K_{24}

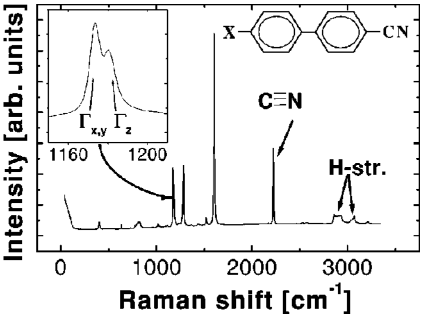

FIG. 1. Schematic molecular structure of K_{15} and K_{24} (upper-right corner), where $X = C_5H_{11}$ or C_8H_{17} for K_{15} and K_{24}, respectively, together with the Raman spectrum of K_{24}. A blowup of the doublet at ~1175 cm^{-1} is shown in the inset. The temperature dependencies of the C≡N, $\Gamma_{x,y}$, and Γ_z modes for both K_{24} and K_{15} are displayed in Figs. 2 and 3.

[11], for reasons that shall be made clear below. K_{15} and K_{24} have the schematic molecular structure shown in the upper-right corner of Fig. 1. The Raman spectra of these two LC compounds are essentially identical, for the added atoms in K_{24} do not change the most intense Raman active modes in the range ~1000–1800 cm^{-1}, which arise from the biphenyl backbone of the molecule [12]. The Raman spectrum of K_{24} in the isotropic phase is displayed in Fig. 1. Besides the high frequency H-stretch vibrations at ~3000 cm^{-1}, the spectrum comprises several peaks below ~1800 cm^{-1} from the biphenyl backbone of the molecule, and a C≡N stretch vibration at ~2220 cm^{-1}. We pay particular attention to the C≡N mode and a doublet ($\Gamma_{x,y}$,Γ_z) around ~1175 cm^{-1} which we explicitly show in the inset of Fig. 1. According to typical spectroscopic data of LC's, this doublet can be assigned to an aromatic in-plane deformation mode [12] which would transform like $(x^2+y^2+z^2)$ in the group theory jargon, except for the fact that it is split by the uniaxial character of the backbone, and renders two peaks that transform like z^2 and (x^2+y^2), respectively. The temperature induced frequency shifts of these peaks are discussed in Figs. 2 and 3. From the thermodynamic point of view, the main difference between K_{15} and K_{24} is the absence of a smectic A (S_A) phase in the former. K_{15} transforms from solid (K) to nematic (N) at 21–22 °C and from N to isotropic (I) at ~35°C. On the other hand, K_{24} goes from K to S_A at 21 °C, S_A to N at ~33 °C, and from N to I at 41–42 °C. Having essentially the same structure and the same Raman spectra, K_{24} helps one to understand the difference introduced by the S_A ordering.

Figures 2 and 3 display the frequency shifts of the C≡N, $\Gamma_{x,y}$, and Γ_z modes as a function of T in K_{24} and K_{15}, respectively. A positive frequency shift $\Delta\omega > 0$ in Figs. 2 and 3 implies a softening. Note that Γ_z displays a small but measurable softening below the N-I phase transition which is further enhanced in the S_A phase. Likewise, $\Gamma_{x,y}$ shows a softening of ~1.5 cm^{-1}, but only below the S_A-N transition temperature. Conversely, the C≡N vibration remains constant within the experimental error. If the same modes are monitored as a function of T in K_{15}, we observe that Γ_z softens below the N-I transition temperature, but neither $\Gamma_{x,y}$ nor the C≡N vibration display a change. Note that the softenings in Figs. 2 and 3 are well beyond the resolution which is ~0.2 cm^{-1}.

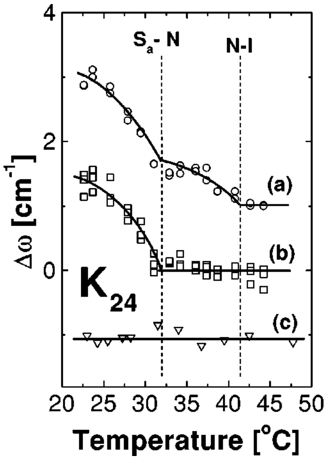

FIG. 2. Temperature induced frequency shifts of (a) Γ_z, (b) $\Gamma_{x,y}$, and (c) C≡N in K_{24}. The S_a-N and N-I phase transition temperatures are clearly indicated. The curves have been vertically shifted for display purposes. A positive $\Delta\omega$ implies a softening of the modes. Note that Γ_z and $\Gamma_{x,y}$ soften while the C≡N stretch vibration remains unaltered. $\Gamma_{x,y}$, however, softens below the S_a-N phase transition, while Γ_z is sensitive to the nematic order parameter. All the lines are guides to the eye.

On phenomenological grounds, the results of Figs. 2 and 3 are easy to interpret. There are, at least, three types of modes: one is coupled to the nematic order parameter [$\eta(T)$], the other couples to the smectic order parameter [$\sigma(T)$], and the third remains unchanged. In other words, the data in Figs. 2 and 3 clearly demonstrate the existence of an effective coupling between the different liquid crystalline phases and the intramolecular vibrations. This coupling affects the self-energies of the modes and it results in a frequency shift. The data in Figs. 2 and 3 suggest that the cou-

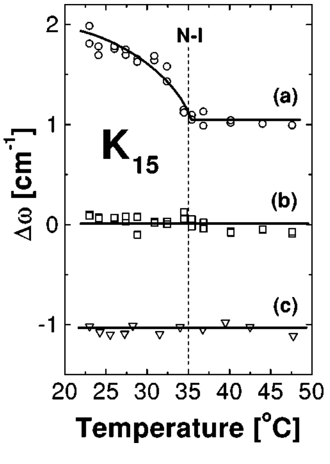

FIG. 3. Same peaks of Fig. 2 but in K_{15}. Note that, in this case, both $\Gamma_{x,y}$ and C≡N do not show a temperature dependence. This demonstrates that $\Gamma_{x,y}$ is, in fact, only sensitive to the smectic order parameter. Γ_z softens below the N-I phase transition as in Fig. 2. All the lines are guides to the eye. Further details are given in the text.

pling to $\eta(T)$ and $\sigma(T)$ must be selective according to the intrinsic symmetry. Note that the expected qualitative shape of $\eta(T)$ and $\sigma(T)$ can be seen in the data of Figs. 2 and 3. The data in Fig. 2 display the qualitative results expected form a mean-field treatment of the nematic-smectic-isotropic phase transitions [13], except for the fact that the *N-I* transition is weakly first order and, accordingly, the small jump in the order parameter at the *N-I* phase transition cannot be appreciated within the scatter of the data. Moreover, Fig. 2(a) resembles the data for $\eta(T)$ obtained from typical high-resolution birefringence (HRB) experiments [14]. HRB does not provide information on the smectic order parameter, something which is naturally obtained in this case by the different coupling of the modes to either $\eta(T)$ or $\sigma(T)$.

From the standpoint of the information on $\eta(T)$ and $\sigma(T)$ which can be gained with this method, there are several drawbacks to take into account. The frequency shifts are small, implying an unavoidable scatter in the data, and hampering a detailed analysis of the order parameters near the critical points. This limitation is, however, not intrinsic to the method, but is rather dependent on the particular experimental setup and data analysis. The most serious limitation is, perhaps, the fact that the relative coupling constants of the different order parameters are not known. This makes it difficult, for example, to quantitatively compare the softening of the $\Gamma_{x,y}$ mode $\propto\sigma(T)$ with respect to that of $\Gamma_z\propto\eta(T)$. Nevertheless, it is obvious that very important qualitative information on the order parameters can be obtained from the data, and this is particularly important if we take into account the fact that Raman scattering is a noninvasive and microscopic optical technique. One could, for example, measure the order parameters inside individual microscopic drops in a polymer dispersed LC as a function of *T*, external fields, or position. Much work was recently dedicated to the field of LC's in complex geometries [15] due to potential novel applications. A micro-Raman probe could provide important information on the local liquid crystalline order of these systems. In addition, the observation of a selective coupling between the intramolecular vibrations and the macroscopic order characterized by $\sigma(T)$ and $\eta(T)$ is interesting by itself. On the basis of our experimental results, we postulate a coupling Hamiltonian of the form

$$\hat{H}_{int.}\propto[A\,\eta(T)\hat{P}_{\Gamma_{1g}^{G_n}}+B\sigma(T)\hat{P}_{\Gamma_{1g}^{G_s}}], \tag{1}$$

where $\eta(T)$ and $\sigma(T)$ are, as before, the temperature dependent nematic and smectic order parameters, $\hat{P}_{\Gamma_{1g}^{G_n}}$-$\hat{P}_{\Gamma_{1g}^{G_s}}$ are projection operators which extract those modes that transform either like the Γ_{1g} representation of the $G_n=\mathbb{R}^3\times D_{\infty h}$ or $G_s=z\times\mathbb{R}^3\times D_{\infty h}$ point groups of the *N* and S_A phases, respectively [10], and A,B are arbitrary constants. There are several reasons to postulate this specific Hamiltonian: (i) it is linear in the order parameters $\eta(T)$ and $\sigma(T)$, and (ii) it rules out a direct coupling to modes that transform like *z*. Both the nematic and smectic orders are uniaxial, and do not distinguish z from $-z$. We believe this to be the fundamental reason why C≡N does not couple to either $\eta(T)$ or $\sigma(T)$ in this case. The chosen projection operators in Eq. (1) assure that the interaction is the same in terms of all the symmetry operations that leave the macroscopic order parameters invariant. The two independent basis functions that may represent the required symmetry properties are, precisely, z^2 and (x^2+y^2), and this is the reason why we used this notation before. $\hat{P}_{\Gamma_{1g}^{G_n}}$ extracts those modes that transform like z^2, and, in this manner, a coupling with an even uniaxial field representing the *N* phase is possible. Conversely, the average of interactions in directions perpendicular to the director (x,y) are different in the *N* and S_A phases, and should also be even with respect to both *x* and *y*. Accordingly, (x^2+y^2) is assigned to $\hat{P}_{\Gamma_{1g}^{G_s}}$. Within this interpretation, Γ_z and $\Gamma_{x,y}$ are aromatic in-plane deformation modes from the biphenyl backbone which transform like $\Gamma_{1g}^{G_n}$ (or z^2) or $\Gamma_{1g}^{G_s}$ [or (x^2+y^2)], and couple to $\eta(T)$ or $\sigma(T)$, respectively. The C≡N stretch vibration, on the other hand, transforms like *z* and, accordingly, does not belong to the Γ_{1g} representations of either G_n or G_s. Note that the interaction Hamiltonian (1) does not take into account the direct coupling between $\eta(T)$ and $\sigma(T)$, which is given by an additional term in the expansion of the Landau-free energy, and it is responsible for the shape in $\eta(T)$ below the S_A-*N* transition temperature [13,14] [seen in Fig. 2(a)]. Finally, the softening may be interpreted as a manifestation of the fact that the intramolecular vibrations help in the stabilization of the mesophases. However, we found other LC's (like 5.O4O.5) where specific modes *harden* as the temperature is lowered. A detailed understanding of the sign of this effect will require a proper microscopic treatment of the coupling Hamiltonian.

In closing, the main result of this paper is the observation of a selective coupling between the macroscopic order present in LC's with smectic and/or nematic phases, and intramolecular vibrations which are Raman active. We believe that changes in phonon self-energies in these sorts of phase transitions have a lot to reveal, in view of the fact that several order parameters can be qualitatively observed and measured with a single technique. This is possible because we are using the intramolecular vibrations as microscopic local probes, with their own intrinsic symmetry, for the liquid crystalline order. This situation is quite unique for a single noninvasive microscopic technique, and should certainly deserve further work, in particular in relation to other liquid crystalline phases, smectics or otherwise, that have not been studied here. Last, but not least, in our opinion it would be very interesting to understand the microscopic origin of the interaction Hamiltonian in terms of the intermolecular potentials and the electron-phonon interaction. This may provide a clue to the relation between the coefficients *A* and *B* in Eq. (1), and pave the road to quantitative comparisons between the different order parameters obtained by this method. Finally, in analogy with magnetic systems, a microscopic theory should explain not only the presence of frequency shifts in the different phases but also the existence of intensity changes in Raman active modes like the ones reported in Ref. [9].

M.N. acknowledges financial support from the Comisión Nacional de Energía Atómica (CNEA) at the Instituto Balseiro.

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