

Phonon self-energies and phase transitions in a prototype discotic liquid crystal

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Specific Raman active vibrations in the discotic liquid crystal nematogen hexakis(6-hexyloxy)triphenylene are shown to be sensitive to either the isotropic \leftrightarrow columnar or the columnar \leftrightarrow solid phase transitions. Changes in frequency and/or intensity of vibrations with specific symmetries demonstrate that the method can be used not only to monitor the phase transitions themselves with a microscopic and noninvasive optical technique, but also to gain physical information on the origin of the molecular interactions that produce them.

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Since the pioneering work of Chandrasekhar [1] on hexa-substituted esters of benzene, disk-shaped mesogens have been added to the conventional list of textbooklike substances that may display liquid crystalline phases [2]. The study of disklike nematogens has been very active in the last few years not only because of their intrinsic interest in the formation of new liquid crystalline phases, but also due to potential novel applications as fast photoconductors [3]. Although more than 20 years have elapsed since the original reports [1], our knowledge of discotic liquid crystalline phases is still somewhat limited as compared with the painstaking collection of experimental evidence available for other liquid crystals (LC's). Experiments well established in other LC's (like the angular dependence of the sound velocities in smectics or the order parameter measurements in nematics determined by Brillouin [4] and Raman [5] scattering, respectively) have not been performed so far for the discotic mesophases, and basic aspects of the application of the continuum and mean-field theories to them remain to be tested.

Optical spectroscopy has always played a central role in the understanding of LC's in view of the stunning variety of effects they display [6]. In particular, Raman spectroscopy has been used in the past to study the orientational statistics of nematic LC's through depolarization ratios of specific vibrations [7], and it is the only technique known so far that can give information on higher order parameters [7] (averages of the second and fourth Legendre polynomials over the orientational distribution). Still, it provided the first experimental evidence of serious discrepancies between the orientational statistics in nematics and the predictions of the mean-field Maier-Saupe theory [1]. Experiments of this sort exploit the fact that specific modes, like the C \equiv N stretch vibration in cyano-biphenyls, have anisotropic Raman tensors (\hat{R}) which can be probed by an appropriate choice of the incident (\vec{e}_L) and scattered (\vec{e}_S) polarizations. Large frequency changes are not normally seen in Raman active

modes of nematics at the phase transitions [5,7], and the measured intensities are modified not by an intrinsic change of \hat{R} but rather by a purely orientational effect. This implies that the molecular mean field responsible for the nematic ordering produces a negligible effect on the intramolecular vibrations being probed by Raman scattering. In other words, the *self-energies* of the modes are not modified, in a first approximation, by the nematic ordering. Small changes of the order of $\sim 10^{-3}$ in frequency are sometimes seen in the transitions to the nematic and smectic phases, and have recently been shown [8] to be related to the order parameters of the different phases. A very different situation occurs for discotics, however, in which the face-to-face interactions of molecules with good π -orbit overlap along the columns [3] may result in strong electronic and vibrational changes, as we shall show later.

In this paper we present nonresonant Raman data of the discotic liquid crystal hexakis(6-hexyloxy)triphenylene (HAT6) and show that, unlike the case of nematics, clear changes in the frequencies and/or intrinsic Raman intensities of the vibrations are monitored at the different phase transitions of this system. Furthermore, different modes are sensitive to different phase transitions according to their intrinsic symmetry. This provides a simple method not only to monitor the transitions themselves via frequency changes of Raman active modes, but also to learn more about the microscopic intermolecular electronic interactions that are responsible for the different phases.

HAT6 has the schematic molecular structure depicted in Fig. 1 and the sample [9] displayed two phase transitions in the temperature range of our experiments, to wit: (i) a solid (K) to columnar nematic (D_h) transition at $T_C^1 \sim 52^\circ\text{C}$ and (ii) a D_h to isotropic (I) transition at $T_C^2 \sim 95^\circ\text{C}$. The critical temperatures are a few degrees lower with respect to purified samples [10] due to the presence of a small fraction of impurities ($\ll 0.5\%$) from the fabrication process, which also produced a broad luminescence background in the visible range. Thus, Raman spectra were obtained with the 632.8-nm line of a He-Ne laser (15 mW), to partly suppress the luminescence, in both depolarized ($\vec{e}_L \perp \vec{e}_S$) and polarized ($\vec{e}_L \parallel \vec{e}_S$) backscattering configurations. The data were taken

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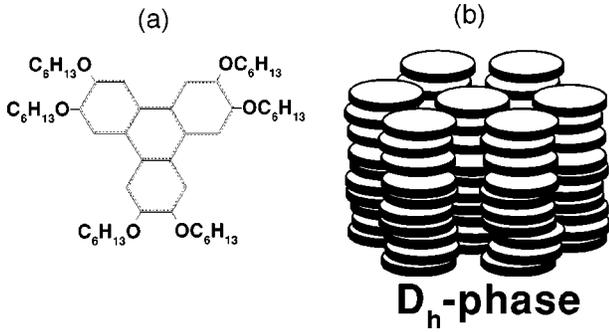


FIG. 1. Schematic molecular structure of hexakis(6-hydroxy)triphenylene (HAT6) and its columnar mesophase (D_h).

with 2-cm^{-1} resolution by a T64000 triple subtractive Jobin-Yvon spectrometer coupled to a charge-coupled device (CCD) detector. The sample was placed inside a quartz tube in a hot stage and the temperature (T) was monitored by a Pt resistor. No preferential direction exists in our cells for the columnar ordering and, therefore, the D_h and K phases are multidomain.

Figure 2 shows the depolarized Raman spectra of HAT6 centered at $\sim 1400\text{ cm}^{-1}$ in the region around the $I \leftrightarrow D_h$ phase transition. Three Raman active modes are present in this spectral range, which we label as Γ_1^a , Γ_1^b , and Γ_2 , for reasons that will be clear later. We concentrate on these peaks because they display the most interesting changes as a function of T . The Raman spectrum of HAT6 comprises, besides, another active mode at $\sim 720\text{ cm}^{-1}$ and a H-stretching band around 2900 cm^{-1} arising from the C₆H₁₃ sidebranches, which show little or no change as a function of T . Note in Fig. 2 that a considerable softening ($\sim 10\text{ cm}^{-1}$) occurs for the Γ_2 mode across the $I \leftrightarrow D_h$ phase transition. Moreover, the Γ_2 mode reduces its relative intensity with respect to both Γ_1^a and Γ_1^b across T_C^2 . This relative intensity reduction is, on the contrary, not observed at T_C^1 . The frequencies of the peaks can be continuously followed through both the $I \leftrightarrow D_h$ and $D_h \leftrightarrow K$ phase transitions, and this is shown in Fig. 3 for the full temperature range of our experiments. Note that the Γ_2 mode softens at T_C^2 and re-

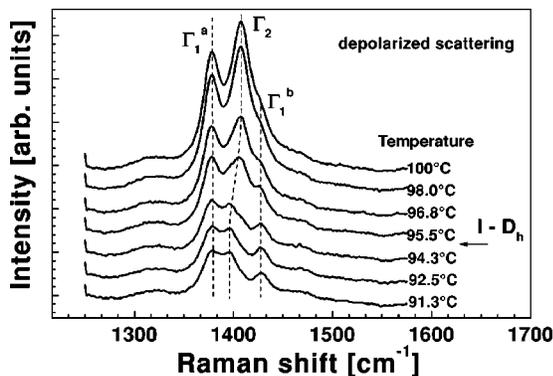


FIG. 2. Raman spectra centered at $\sim 1400\text{ cm}^{-1}$ taken with the 632.8-nm line of a He-Ne laser in the depolarized backscattering configuration as a function of T . The temperature range is around the $I \leftrightarrow D_h$ phase transition temperature (T_C^2), which is $\sim 95^\circ\text{C}$. Note the softening of the Γ_2 mode through the transition as well as its reduction in intensity.

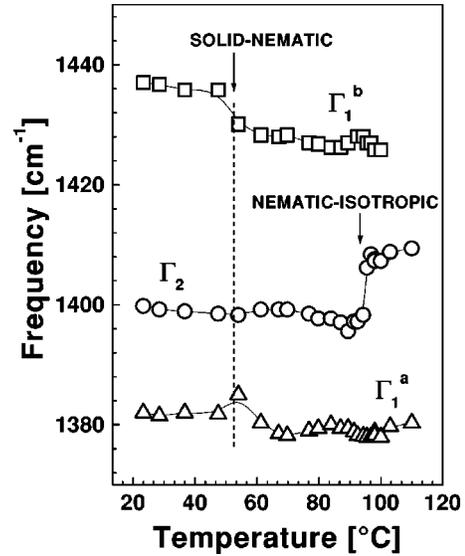


FIG. 3. Frequencies of the Γ_2 , Γ_1^a , and Γ_1^b modes vs T . The $I \leftrightarrow D_h$ (T_C^2) and $D_h \leftrightarrow K$ (T_C^1) phase transitions are clearly indicated. Note that Γ_2 softens at T_C^2 while Γ_1^a and Γ_1^b harden at T_C^1 . Roughly speaking, Γ_2 is insensitive to the $D_h \leftrightarrow K$ phase transition while the opposite holds for Γ_1^a and Γ_1^b at T_C^2 .

mains unaltered for lower temperatures even through the $D_h \leftrightarrow K$ phase transition. The opposite seems to hold for Γ_1^a and Γ_1^b , which display little or no variation at the $I \leftrightarrow D_h$ phase transition, but a measurable hardening at T_C^1 . As we shall show later, this sensitivity of the modes to the different phase transitions is directly related to their intrinsic symmetry. Further insight can be obtained from depolarization measurements in the I phase as shown in Fig. 4. To this end, the depolarization ratio ($\rho = I_\perp / I_\parallel$) is obtained from the depolarized $I_\perp(\vec{e}_L \perp \vec{e}_S)$ and polarized $I_\parallel(\vec{e}_L \parallel \vec{e}_S)$ scattering efficiencies, respectively. Figure 4 shows that $\Gamma_1^{a,b}$ display a larger

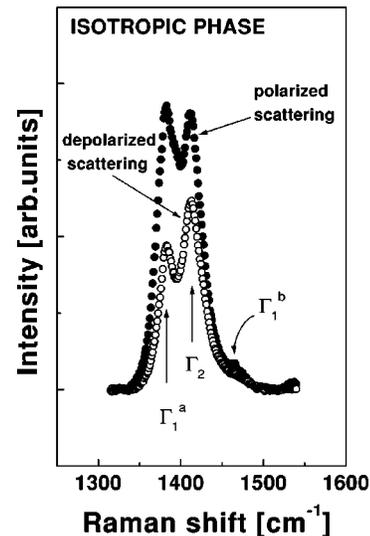


FIG. 4. Polarized and depolarized Raman backscattering spectra of the Γ_2 , Γ_1^a , and Γ_1^b modes in the I phase. $\Gamma_1^{a,b}$ show a larger depolarization ratio than Γ_2 , helping with the symmetry assignment of the modes in terms of the irreducible representations of D_{3h} . See the text for further details.

percentage change from I_{\parallel} to I_{\perp} than does the Γ_2 mode. This change is better appreciated for Γ_1^a than for Γ_1^b , simply because the latter is of smaller intensity and partly superimposed on the tail of the Γ_2 mode.

Summarizing, the basic experimental observations are (i) the softening (hardening) of the Γ_2 ($\Gamma_1^{a,b}$) mode at the $I \leftrightarrow D_h$ ($D_h \leftrightarrow K$) phase transition (Fig. 3); (ii) the intensity decrease of Γ_2 at T_C^2 relative to the $\Gamma_1^{a,b}$ modes (Fig. 2), and (iii) the different ρ 's of the modes (Fig. 4) revealing distinct intrinsic symmetries. Note that ρ is measured in the I phase where the intermolecular interactions are smaller and, accordingly, it is supposed to be intrinsic to the molecules. We shall dwell in what follows on the interpretation of these experimental facts.

Preliminary calculations of the vibrational modes of HAT6 with the Austin Model 1 (AM1) Hamiltonian [11] show that vibrations in the energy range between 1100 and 1600 cm^{-1} can be essentially attributed to the triphenylene core of the molecule (Fig. 1). However, an exact classification is not possible at this stage, for vibrational frequencies obtained by semiempirical methods are typically within 20% of the experimental ones and, moreover, some modes may appear inverted. The C_6H_{13} sidebranches of HAT6 are somewhat flexible but, inasmuch as the vibrations are confined within the inner core of the molecule, a classification in terms of the point group of the central triphenylene core (D_{3h}) is possible and useful in this case. Figure 4 shows that the $\Gamma_1^{a,b}$ modes display a depolarization ratio much less than 3/4, which automatically classifies them as totally symmetric vibrations [12]. We believe these peaks to be breathing modes of the central triphenylene core polarized in the ($\hat{x} - \hat{y}$) plane containing the σ_h mirror of D_{3h} . In contrast, the Γ_2 peak displays a ρ of ~ 0.7 , which is close to the theoretical $\rho = 3/4$ for vibrations of lower symmetry than Γ_1 . We assign this mode to a \hat{z} -polarized mode belonging to the Γ_2 representation of D_{3h} . There are several reasons for this assignment, which are based upon a physical picture of the molecular interactions at the $I \leftrightarrow D_h$ phase transition. The overwhelming experimental evidence from photoconductivity [3] and semiempirical electronic calculations [13] shows that interactions among the π electrons of the central triphenylene core are a key feature of the D_h phase. In the parent compound hexa(hexylthio)triphenylene (HHTT) [3], in which the oxygens of the sidebranches are replaced by sulfur, an order of magnitude change in the mobility of photo-generated carriers is seen across the $I \leftrightarrow D_h$ phase transition. The same mechanism produces a further increase of intracolumnar mobilities [3] when an additional degree of order appears in the helical columnar phase (H); a phase which is not present in HAT6 but is also a consequence of the considerable π -orbit overlap along the columns. Likewise, doping with Lewis acids [10] transforms HAT6 and parent compounds in quasi-one-dimensional (1D) semiconductors with bandlike conductivity along \hat{z} . The D_h phase can be seen, within this picture, as formed by individual molecules that weakly interact (allowing for bandlike conductivity) and can freely rotate in the plane perpendicular to the columns (contributing to the main source of disorder affecting the quasi-1D transport). We observe that a LC phase transition of this sort is somewhat different from what is found in con-

ventional nematics. Broadly speaking, the phase transition here is accompanied by a considerable electronic change in the individual molecules, and this is unlike conventional nematics where the independence of the molecules is preserved to a great degree in both the isotropic and nematic phases. Moreover, it is reasonable to assume within this framework that \hat{z} -polarized vibrations will be more directly linked to the $I \leftrightarrow D_h$ phase transition, owing to the fact that they directly modulate the intermolecular coupling. In addition, this interaction can lead to the formation of weakly coupled vibrations arising from \hat{z} -polarized modes. This should introduce both a weak dispersion and the presence of a *quasimomentum* (\vec{q}) for these modes. This might explain the intensity decrease of the Γ_2 mode across the $I \leftrightarrow D_h$ phase transition, whereas only collective modes with $\vec{q} \sim \vec{0}$ contribute. This is exactly what would happen in a scattering process within a solid where quasimomentum conservation must be fulfilled. The formation of a quasi-1D structure in the D_h phase could strongly affect the scattering efficiency of collective modes which were dispersionless in the I phase. On the other hand, a \hat{z} -polarized vibration is not expected to be very sensitive to the $D_h \leftrightarrow K$ phase transition, since the columns are already formed in the D_h phase and the important interaction in this case is among them. The assumption of a \hat{z} -polarized mode for Γ_2 , in this manner, can explain (i) the sensitivity of the mode frequency to the $I \leftrightarrow D_h$ transition, (ii) the relative intensity reduction across T_C^2 through the presence of a weak dispersion, (iii) the depolarization ratio in Fig. 4 (expected for the Γ_2 representation), and, finally, (iv) the insensitivity of the mode to the $D_h \leftrightarrow K$ transition. An important question remains, of course, as to whether a *softening* of a \hat{z} -polarized mode can be expected as coming from the incipient interaction among the molecules. AM1 calculations on simpler derivatives of benzene with nonsaturated π electrons, like benzoquinoline, show that it is possible to soften intramolecular modes by direct interaction with a neighbor molecule. These are molecules that, owing to their small size, do not show a liquid crystalline phase by themselves, but can be forced to interact on a computer. The redistribution of electronic charge arising from the direct interaction of π electrons results in the softening of intramolecular vibrations by creating a collective mode between the two molecules. This is, however, a demonstration of possibility rather than a proof, and a normal mode calculation with several stacked HAT6 molecules (which is outside our present computational capabilities) would be necessary to fully clarify this point. Finally, the breathing $\Gamma_1^{a,b}$ modes should not be very sensitive to the intermolecular coupling along \hat{z} . In fact, the molecules can rotate along \hat{z} in the D_h phase with relative ease. One would expect, in general, that vibrations with eigenvectors that are essentially polarized in the σ_h mirror plane would have less influence on the intermolecular coupling which is dominated by π orbitals along \hat{z} . These vibrations should be sensitive, nevertheless, to the $D_h \leftrightarrow K$ phase transition in which the intercolumnar interaction leads to a frozen solid phase below T_C^1 . In this manner, the hardening of $\Gamma_1^{a,b}$ at T_C^1 , their insensitivity to the $I \leftrightarrow D_h$ phase transition, and the intrinsic ρ in the I phase (Fig. 4) can be naturally explained.

In conclusion, we have shown that HAT6 displays important changes in some of its Raman active modes at both the $I \leftrightarrow D_h$ and $D_h \leftrightarrow K$ phase transitions. Nonresonant Raman scattering can be used in this case as an additional technique to monitor the phase transitions and could, eventually, complement and expand the data obtained by more conventional methods like NMR spectroscopy [14]. To the very best of our knowledge, this is the first LC where ample changes in the vibrational Raman spectrum have been monitored at the different phase transitions, for conventional nematics show changes mainly in the depolarization ratios (ρ 's) of specific modes. Moreover, the study of the symmetry of the Raman active modes can shed some light onto the origin of the molecular electronic interactions, which are, ultimately, responsible for the liquid crystalline phases themselves. We hope that our data stimulate the search for similar or related phenomena in the Raman spectra of other discotics. Finally, it is worth noting that the large frequency change ($\sim 15 \text{ cm}^{-1}$) observed in this particular discotic at the $I \rightarrow D_h$ phase transition implies a considerable electronic

change which, in turn, implies a strong frequency shift of the modes. This situation is very different from the one observed in nematics and smectics, as mentioned previously, where small changes in frequency are seen, at best. This fact is certainly in agreement with the considerable electronic changes seen in photoconductivity [3] and, in a sense, implies that the $I \rightarrow D_h$ phase transition is of a somewhat different nature from a typical LC phase transition. The overlap of the electronic wave functions is negligible in both the isotropic and nematic phases in typical LC's, while in HAT6 and its parent compounds the hybridization of π orbitals with considerable electronic and vibrational changes seems to be the hallmark of the transition. Our results show that this overlap can be indirectly studied through the interaction with specific vibrational modes according to their different symmetries. In that sense, Raman scattering provides direct information on the molecular interaction that produces the different LC phases in discotics.

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