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Invited article
Differing applications of Raman scattering to liquid crystals

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An overview of the differing possibilities offered by Raman scattering in the study of liquid crystals is given, together with a few experimental examples of the least studied phenomena. Among them, changes in the intrinsic Raman polarizabilities and phonon self-energies as a function of temperature which provide, in principle, an experimental method for the study of coexisting and/or inhomogeneous phases through Raman imaging. We show that the C–H in-plane deformation mode of the phenyl rings is particularly suited to monitor both intrinsic scattering efficiencies and frequency changes. This mode is present in a large family of liquid crystal compounds and we present evidence indicating that the origin of these changes is its electron–phonon coupling to the lowest allowed electronic transition in the ultraviolet.

1. Introduction

Inelastic light scattering techniques (quasi-elastic, Rayleigh wing, Brillouin, and Raman) [1, 2] have provided a wealth of information since the early days of liquid crystal (LC) research on important physical properties of both the mesogenic molecules themselves, and the liquid crystalline mesophases. The milestone experiments of Chatelain [3] and the Orsay LC-Group [4] on quasi-elastic scattering in nematics, and the angular dependence of the sound velocities in smectics determined by Brillouin scattering [5], are two of the very many examples in which inelastic light scattering has given a direct view into some of the fundamental aspects of the physics of LCs. From the standpoint of Raman scattering, the technique has been used not only to study and characterize the intramolecular vibrations of different LC mesogens but also to gain information on the orientational ordering of the molecules through depolarization ratios of specific vibrations [6, 7]. More recently, it has been shown that *intrinsic changes* in the Raman polarizabilities can be observed in the different mesophases [8, 9] and, moreover, changes in the *self-energies* of specific vibrations are also easily monitored [10]. In our opinion, Raman scattering of molecular vibrations in LCs has not yet been fully exploited as a source of important microscopic information, and this is particularly true in situations where other techniques cannot easily be used. The pioneering works of Pershan *et al.* [5] and Averyanov and co-workers [11] in the 1970s have been little continued [6–9, 12]. Exceptions have been the work of Coles *et al.* [13], who developed a Raman spectrometer for transient electro-optic studies based on the same orientational effects used in [5], and, more recently, a few results on Raman depolarization ratios in ferro-, antiferro-, and ferri-electric phases of smectics [14].

It is worth mentioning at this stage that Raman scattering is a non-invasive spectroscopic technique which can be easily carried out in a set-up attached to a microscope, thus providing spatial resolution which is only restricted by a diffraction limit of the order of the laser wavelength (λ_L). In addition, it can be used with a *confocal microscope* where the depth of focus is limited by the presence of two conjugate pinholes and, therefore, in which high spatial resolution along the focusing direction can also be achieved. Confocal optical spectroscopy of this sort for Raman and fluorescence measurements is becoming a very important tool in biological studies of complex cellular structures [15]. Modern Raman spectrometers with high efficiency cooled CCD

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detectors can easily measure spectra from organic molecules with very low input laser powers (even $\ll 1$ mW), hence avoiding indirect spurious side effects like local heating through impurities; it also provides the possibility of changing the laser wavelength to the ultraviolet (UV) to achieve resonance with specific electronic transitions of the molecules. The spectra provide considerable information on local molecular orientations [5], mainly (but not exclusively) on aligned samples. In situations where no specific orientations are fixed by either boundary conditions or external fields, intrinsic changes in the polarizabilities [8, 9] or changes in frequency [10] (self-energies) can alternatively be used to detect phase transitions. The method is ideal for inhomogeneous samples where microscopic spatial resolution may be required; as well as in cases, such as in free-standing films, where other experimental techniques may be impossible or inappropriate. Furthermore, the data can be time-resolved [13] to provide information on the molecular dynamics upon application of low frequency or d.c. external electric fields [16]. Last, but not least, Raman signals can be stimulated at sufficiently high input laser powers [17]. This latter effect is caused by the huge intrinsic third order non-linear optical susceptibility of LCs (10^8 to 10^{11} with respect to the largest optical non-linearities found in semiconductors), which produces self-focusing and considerably reduces the stimulation threshold.

Notwithstanding the enormous potential of the Raman technique in understanding LCs, the field remains largely unexplored. Measurements on free-standing films have not yet been reported and time-resolved studies are few in number. The existence of frequency shifts (changes in phonon self-energies) in the different mesophases has not been widely used [9–11], and intrinsic changes in the Raman polarizabilities have been reported only in a few papers [8, 9]. Finally, clear-cut *microscopic* theoretical explanations for most of the observations are still missing, even though Averyanov and co-workers have considerably developed a phenomenological theory including the effect of local fields [11].

In this paper, we present an overview of the experimental possibilities offered by Raman scattering in LCs. To this end, we briefly review specific aspects and show examples of the least studied phenomena, namely: (i) frequency changes in a Raman active mode as a function of temperature (T), (ii) intensity changes due to a modification in the *intrinsic* polarizability of a mode, and (iii) dispersion measurements (laser energy dependence) of the intensity changes. One of the aims of the paper is to demonstrate that the C–H in-plane deformation mode of the phenyl rings (which is present in a vast family of LC compounds) is particularly suited for monitoring LC phase transitions through Raman scattering in unoriented samples. Furthermore, we shall show that there is experimental evidence for a microscopic understanding of these effects via the coupling of this specific mode with the lowest allowed electronic transition in the UV (which comes from orbitals that are localized around the phenyl rings). The paper is organized as follows: § 2 gives an overview of the different possibilities offered by Raman scattering, § 3 presents the experimental set-up and results and, finally, in § 4 a few conclusions are given.

2. Overview

2.1. *Orientational effects on Raman efficiencies*

The textbook example of Raman scattering in LCs [18] comes from orientational effects. The orientational order of nematics has been studied through depolarization ratios of specific vibrations. In fact, Raman is one of the few techniques which can provide information on higher rank order parameters (averages of the 2nd and 4th Legendre polynomials over the orientational distribution of the molecules). The measurements [5] offered some of the first experimental evidence in conflict with the predictions of the well established Maier–Saupe mean-field theory of nematics. Unfortunately, the Raman results are not in full agreement in this respect with other experimental techniques such as electron paramagnetic resonance (EPR) and neutron scattering, for reasons which have not yet been fully clarified in the literature [18]. Experiments of this sort exploit the fact that specific well characterized Raman active modes (like the C ≡ N stretch vibration) have anisotropic Raman tensors ($\hat{\alpha}_{i,j}$) which can be probed by a suitable choice of the incident ($\mathbf{e}_L$) and scattered ($\mathbf{e}_S$) polarizations. The theory of Raman depolarization ratios in nematic LCs has been thoroughly introduced in [6]. We reiterate here only the fundamental aspects.

Let us assume the existence of a Raman tensor for a specific vibration with a high uniaxial anisotropy of the form

$$\hat{\alpha} = \alpha_0 \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad (1)$$

where $a, b \ll 1$. The most useful cases are those in which the high uniaxial character of $\hat{\alpha}_{i,j}$ coincides with the main geometrical axis of the molecule (the long axis), thus providing a direct measurement of the orientational order of the phase. The scattering efficiency for a given pair of incident ($\mathbf{e}_L \equiv \mathbf{e}_i$) and scattered ($\mathbf{e}_S \equiv \mathbf{e}_j$) polarizations is given by $I_{i,j} \sim |\mathbf{e}_i \ \hat{\alpha} \ \mathbf{e}_j|^2$ [2]. By measuring three depolarization ratios with respect to $\mathbf{n}(\equiv \hat{z})$, and the depolarization ratio in the isotropic phase, a system of four equations is obtained. The four unknowns are:

the a and b coefficients in expression (1), and the thermal averages $\langle \cos^2 \beta \rangle$, $\langle \cos^4 \beta \rangle$ (where β is the angle of the long axis of the molecules with respect to **n**). In this manner, information on the averages of the first two Legendre polynomials, $\langle P_2(\cos \beta) \rangle$ and $\langle P_4(\cos \beta) \rangle$, can be gained.

There are, however, a few drawbacks to the technique. Among them are: (i) successful data processing requires previous knowledge of the ordinary and extraordinary indices of refraction, which are temperature dependent; (ii) the full set of depolarization ratios require measurements in both homeotropic and planar aligned LC cells; (iii) special care must be taken with unwanted depolarization coming from fluctuations in **n**; and (iv) the effects of local fields are normally ignored in nematics, but may play a significant role in certain circumstances. There are a few empirical rules to treat local fields in non-linear optical susceptibilities [19], but their influence remains an open question in many cases. Pershan and co-workers explicitly ignored the presence of local fields in their experiments [5, 6]. On the other hand, Averyanov and co-workers have extensively discussed the influence of local fields and claim that their intrinsic anisotropies strongly influences the experimental results [11].

2.2. *Time resolved Raman data*

Equation (1) shows that in a planar aligned LC cell the $I_{z,z}$ scattering efficiency is proportional to α_0^2 and can be measured by choosing both $\mathbf{e}_\mathrm{L}$ and $\mathbf{e}_\mathrm{S}$ to be parallel to $\mathbf{n} \equiv \hat{z}$. If we applied an electric field perpendicular to the surface of the cell and produce a Fréedericksz transition to a sample with homeotropic alignment (for a positive dielectric anisotropy), we would monitor a much lower scattering efficiency, for $a, b \ll 1$. The reorientation dynamics is in the msec range for typical LCs and, accordingly, it can be directly monitored by the Raman signal. This is the underlying principle of the measurements by Coles and co-workers [13]. Note that this is not conventional time-resolved Raman scattering in the sense that it is not a *pump and probe* experiment. This technique showed differences in the reorientation dynamics of localized modes in the biphenyl cores and the chains in alkyl cyanobiphenyls. A site-dependent reorientation dynamics was proposed and associated with the flexibility of the molecules. However, these results appear to be in contradiction with nuclear magnetic resonance (NMR) data [20]. These experiments give very important qualitative information without a full detailed account of local fields, order parameters, etc. In this paper, we are precisely interested in this sort of qualitative information available through Raman scattering, which does not heavily rely on data analysis through specific models.

2.3. *Third order non-linearities and Raman scattering*

Nematic LCs behave basically like non-linear optical materials with a Kerr-like non-linearity, i.e. a third order non-linear optical term (χ^3) in the expansion of the electric polarization. The χ^3 susceptibilities of liquid crystals are among the largest known for condensed matter and they are a prerequisite for the observation of self-focusing (SF) and self-phase modulation (SPM) of laser beams [21]. It has also been well established that SF can make power densities high enough at the focal point to allow for stimulated Raman (SRS) or Brillouin (SBS) scattering to occur well below the threshold expected from the natural scattering losses of these effects [22]. This, in fact, explained the apparent contradictions in the low thresholds that some organic liquids exhibit for SRS and SBS. The onset of SRS in a LC cell with planar alignment under constant wave (CW) illumination has recently been observed [17]. Most interestingly, the free surface of a nematic LC drop does not show a non-linear power dependence of the Raman signals (evidencing stimulation) unless the sample is supercooled [23]. Most of these results are awaiting a proper theoretical explanation.

Another possibility is that the electric field of the Raman probe beam itself induces a molecular reorientation and, accordingly, changes the measured intensity as a function of time. This is produced by the optical torque of the laser field which is, on the other hand, the microscopic origin of the large χ^3. This is a seemingly unique feature of Raman scattering in LCs taking into account that other equivalent Raman techniques such as coherent anti-Stokes Raman scattering (CARS) need two laser beams, one of which must be tuneable. Measurements of self-induced changes of this sort in Raman scattering exploit the high χ^3 of the LCs within time-resolved studies.

2.4. *Intrinsic changes in Raman polarizabilities*

For a given Raman tensor $\hat{\alpha}_{i,j}$ representing a specific vibration, the polarized backscattering intensity (crossed polarizers) for randomly oriented molecules (a nematic phase with multiple domains or an isotropic phase) is given by [2]

$$I_\perp \propto \frac{1}{2}[(\alpha_{x,x}-\alpha_{y,y})^2+(\alpha_{y,y}-\alpha_{z,z})^2+(\alpha_{z,z}-\alpha_{x,x})^2] + 3[\alpha_{x,y}^2+\alpha_{z,x}^2+\alpha_{y,z}^2] \qquad (2)$$

which reduces to $I_\perp \propto \alpha_{z,z}^2 \sim \alpha_0^2$ for a tensor with a high uniaxial anisotropy like (1). Orientational effects (i.e. intensity variations of the modes due to a change in the molecular principal axes of the Raman tensor with respect to a fixed laboratory frame) are eliminated in this case. Any observed changes in the Raman intensities of specific modes should arise, accordingly, from intrinsic changes of the Raman molecular polarizabilities. After Averyanov [11], we may argue that the changes in the Raman efficiencies are not intrinsic of the polarizabilities, but rather the result of local fields in the different LC phases. From an experimental point of view, however, we cannot measure the isolated polarizabilities and the local fields simultaneously. The distinction between both becomes important for the understanding of the underlying physics, but it is not crucial for qualitative determinations of phase changes in LCs. Changes of this sort have been reported in smectic phases [8] and, more recently, in a discotic LC [9]. The principal problem in these experiments is the change of the scattering volume produced by the turbidity of the different mesophases. However, this problem is eliminated if relative (normalized) intensities are measured among different modes, and it is also greatly minimized with confocal collecting optics in any case.

Raman polarizabilities depend on the electronic structure which, in turn, is weakly affected by the anisotropic dispersion forces producing the LC mesophases (which ultimately represent the local fields). The electronic structure provides the intermediate states in a typical Raman process like the Stokes scattering process depicted in figure 1, thus affecting the scattering efficiency. The lowest allowed electronic transition, coupled to a specific Raman active mode, will have the most important influence in the Raman scattering efficiency in the transparency region. Accordingly, one would expect to see appreciable changes only in those modes that are strongly coupled to these specific electronic states. We shall show in the experimental section that this is in fact the case for the C–H in-plane deformation mode of the phenyl rings.

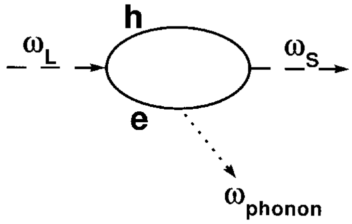

Figure 1. Feynman diagram representing the principal contribution to the Stokes Raman scattering process. The electronic excitations *e* and *h* are the intermediate virtual states producing the indirect coupling between the incident photon ω_L and the scattered vibration ω_{phonon}. The Stokes scattered photon is such that $\omega_S = (\omega_L - \omega_{\mathrm{phonon}})$. If the electronic states are modified by the presence of an external field, or by intermolecular forces, the *dressed* propagators must be used in this diagram. Hence, Raman intensities will indirectly depend upon these changes.

2.5. *Frequency changes in Raman active modes*

The coupling of specific vibrational modes with electronic orbitals of the molecule ensures that frequency and/or linewidth changes can be seen if the electronic states undergo modification due to external fields or intermolecular interactions. The microscopic origin of this effect is directly related to the changes in the Raman polarizabilities treated before, i.e. they can be considered an indirect consequence of the presence of local fields. Both effects are directly linked to the localized coupling between specific electronic orbitals and Raman active intramolecular vibrations. Simultaneous changes in frequency and linewidths of Raman active modes are called *self-energy* changes as treated by perturbation theory. These changes have been proposed to provide a method for a quantitative measurement of the order parameter in oriented nematics [11], and as a qualitative measurement of both nematic and smectic phases in unoriented samples [10].

It is quite interesting to realize that a very similar situation in terms of intensity and self-energy changes of Raman active modes exists in magnetic solids [24]. The presence of a macroscopic order parameter, which in this case is the magnetization, produces changes in phonon frequencies and/or intensities through the magnon–phonon interaction. The interaction Hamiltonian, however, is very well defined for magnetic systems while it is more difficult to treat in LCs. In addition, local fields are negligible in magnetic phases. In the case of LCs the *mean-field* molecular potential felt by a single molecule in nematics could be obtained from the Maier–Saupe theory, and could be extended to the smectic A phase with McMillan's model [25]. Microscopic mean-field molecular potentials for other phases are normally not known, although changes are observed in other smectic phases, as we shall show later.

2.6. *Resonant Raman scattering*

Most LCs absorb light in the UV (~350 nm and below). UV-Raman spectroscopy has been extensively used in biological molecules, principally in proteins [26], where the absorption bands of the polypeptide chains are located. The application to LCs is, on the other hand, almost non-existent. According to the well established theory of resonant Raman scattering in molecules, different resonant mechanisms through two or three intermediate electronic states are possible [27]. In the first case, totally symmetric modes (Γ_1) are enhanced, while for the second mechanism only modes contained in the product representation of the two intermediate electronic states can be made resonant. UV-resonant Raman scattering should provide very interesting information on localized molecular vibrations in LCs which could be enhanced by a proper choice of the incident wavelength. Moreover, it should offer the possibility of studying localized thermal effects by the direct absorption of the probe laser and could, eventually, be combined with time-resolved studies with the use of pulsed lasers. Indirect observations through resonant Raman scattering of dyes in dye-doped LCs in the visible are also possible. This very interesting area of research remains largely unexplored, although a few pre-resonance Raman results have been very recently published in [28].

2.7. *Surface molecular alignment*

Confocal Raman microscopy has been very recently used to demonstrate molecular orientation on the free surface of LC droplets [29]. The fact that the imaging is done through a confocal microscope ensures that the signals are surface sensitive. It was found that most experimental results can be understood by ignoring the effect on the polarization of the surface birefringence, thus simplifying the data analysis. We believe that the use of Raman spectroscopy in this particular case will open up exciting new opportunities for surface LC physics.

3. Experimental

In this section, we show a few experimental examples of the aforementioned topics. For reasons of space, we shall concentrate only on the least studied phenomena of frequency and/or intensity changes as a function of temperatute (T). To this end, we present Raman experiments which were performed in the polarized backscattering configuration with different lines of an Ar$^+$-laser (20 mW) or a HeNe-laser (10 mW), with the data being collected by a Renishaw Raman spectrometer coupled to a microscope with × 50 magnification, or a triple T64000 Jobin–Yvon Raman spectrometer. Peak positions could be obtained with a resolution of 0.5 cm^{-1} or better. The detection was performed by a CCD-array at a fixed wavelength position, thus avoiding possible problems with the backlash of the spectrometers in the determination of small frequency shifts. The spectra were recorded in the ~20–250°C range with typical integration times of 30 s. Small amounts of samples were placed onto a glass substrate inside a Linkam hot-stage adapted to the working distance of the microscope objective. The temperature was monitored by a Pt-resistor and was stable within ±0.1°C. No preferential alignment direction exists inside the samples for the ordered mesophases which, accordingly, display multidomains. Any changes in the intensity of the Raman modes come, accordingly, from intrinsic changes in the Raman polarizabilities, as stated in §2.4.

We used three different samples: (i) a dimeric LC (5.O4O.5) of the family of the α,ω-bis(4-n-alkylanilinebenzylidene-4′-oxy)alkanes [30] with a crystal (Cr) to smectic B (SmB) phase transition at $T_{\text{Cr–SmB}} \sim 133$°C, a SmB to smectic A (SmA) transition at $T_{\text{SmB–SmA}} \sim 162$°C, and a SmA to isotropic (I) transition at $T_{\text{SmA–I}} \sim 218$°C; (ii) a standard 4-cyano-4′-n-octylbiphenyl LC-compound (8CB) (Merck Ltd, UK) which goes from Cr to SmA at 21°C, SmA to nematic (N) at ~33°C, and from N to I at ~42°C; (iii) a 4-cyano-4′-n-octyloxybiphenyl sample (8OCB) (Merck Ltd, UK) with transitions from Cr to SmA at ~59°C, SmA to N at ~68°C, and N to I at ~80°C.

From the vibrational point of view, all these LCs have in common the presence of a C–H in-plane deformation mode of the phenyl rings at ~1177 cm^{-1} [31]. The mode is slightly shifted from one compound to another being at 1188 cm^{-1} in 8OCB, and at ~1175 cm^{-1} in 5.O4O.5 and 8CB. This vibration has both a relatively high Raman cross-section and a considerable interaction with the lowest $\pi \rightarrow \pi^*$ electronic transition in the UV of the phenyl rings [19]. Therefore, any change produced in the electronic states by the average mean-field of the liquid crystalline state will be felt in the Raman process depicted in figure 1, either through a change in the vertex representing the electron–phonon interaction, or through a modification in the electron–hole propagators.

Figure 2(a) shows the Raman spectrum of 8OCB at room temperature (RT); the normalized Raman intensity of the C–H in-plane deformation mode is shown as a function of T in figure 2(b). Note the presence of clear

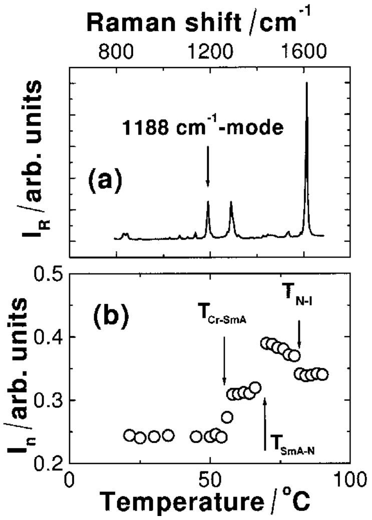

Figure 2. (a) Raman spectrum at room temperature and (b) normalized intensity I_n (with respect to the intensity of the C–C breathing mode at ~1600 cm^{-1}) of the C–H in-plane deformation mode at ~1188 cm^{-1} in 8OCB as a function of T. The intensity in (b) changes by roughly a factor of two between the Cr and the N phases, besides the presence of clear steps at the phase transition temperatures. These data were obtained with the 514.5 nm line of an Ar$^+$-laser.

steps at the transitions from Cr to SmA, SmA to N, and N to I which are all first order. Figures 3(*a*) and 3(*b*) show the Raman spectrum and the frequency change of the equivalent mode in 5.O4O.5 as a function of T, respectively. Again, clear changes can be observed at the phase transitions from Cr to SmB and SmA to I, and to a lesser extent form SmB to SmA. Note that a total frequency change of $\sim 5\,\mathrm{cm}^{-1}$ can be monitored, which implies $\Delta\omega/\omega \sim 4\times10^{-3}$. This is in accordance with a change in the energy of the first allowed electronic transition ($\sim 6\,\mathrm{eV}$) produced by a typical interaction energy of a liquid crystalline state ($\sim k_B T_c \sim 420\,\mathrm{K} \sim 35\,\mathrm{meV}$), $\Delta E/E \sim 5\times10^{-3}$.

An elementary explanation of the intensity changes of Raman active modes *without considering local fields* is as follows. The electronic susceptibility in the transparency region, at the laser frequency ω_L, is dominated by the dispersion of the first allowed transition ω_0 in the UV and can be written (in a one band model [19]) as:

$$\varepsilon(\omega) \sim A + \frac{B}{(\omega_0^2 - \omega_L^2)} \qquad (3)$$

where A and B are constants. According to Placzek [32], the Raman cross section will depend on the modulation of the electric susceptibility produced by the presence of a specific vibration $\mathbf{u} = \mathbf{u}_0 \exp(i\omega_{ph} t)$, i.e.

$$\frac{d\sigma}{d\Omega} \propto \frac{B\omega_0}{(\omega_0^2 - \omega_L^2)^2} (\vec{\nabla}_{\mathbf{u}}\omega_0 \ \mathbf{u}_0) \exp(i\omega_{ph} t). \qquad (4)$$

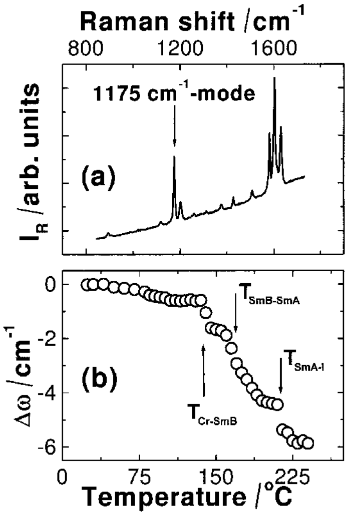

Figure 3. (*a*) Raman spectrum at room temperature and (*b*) frequency shift (with respect to the frequency in the Cr phase) of the C–H in-plane deformation mode at $\sim 1175\,\mathrm{cm}^{-1}$ in 5.O4O.5 as a function of T. There is a continuous hardening of the mode upon cooling with distinctive jumps at the phase transition temperatures (shown with vertical arrows). See the text for further details.

Let us consider, for example, the case of a LC changing from I to N. If ω_0 is modified by the interaction energy U_{int} producing the N phase, we have $\omega_0' = \omega_0 + \Delta\omega_0 \sim \omega_0 + U_{int}$, where $U_{int} \propto S^2$ in the Maier–Saupe theory. To lowest order in $\Delta\omega_0$, we expect an intensity change $\Delta I \propto S^2/(\omega_0^2 - \omega_L^2)^2$ from I to N. If we monitor the differences in intensities of the C–H in-plane deformation mode ΔI_R at two fixed temperatures in the N and I phases as a function of the incoming laser frequency ω_L, we should observe a resonant enhancement according to this elementary treatment. This is precisely what is observed in figure 4 where $\Delta I_R/I_R$ is measured for 8CB between two temperatures in the N (35°C) and I (50°C) phases for the nine lines of an Ar$^+$-laser at ~ 514, 502, 496, 488, 476, 472, 465, 457 and 454 nm, plus an additional measurement at 633 nm with a He-Ne laser. We believe that this is clear experimental evidence showing that changes in the electronic states produced by the intermolecular potential can be indirectly monitored through their effect on intramolecular vibrations using Raman scattering. The intensity and/or frequency changes observed in figures 2 and 3 are nothing but a manifestation of this coupling. As stated above, the main problem for a detailed quantitative understanding of these changes is the nature of the interaction Hamiltonian and the effect of local fields. Nevertheless, from an experimental point of view, changes in frequency and/or intensity of

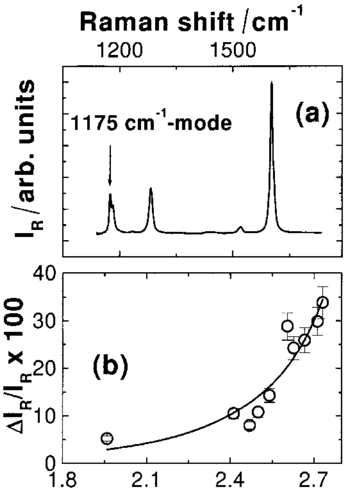

Figure 4. (*a*) Raman spectrum at room temperature and (*b*) relative change (in %) of the C–H in-plane deformation mode between the N and I phases as a function of the incident laser wavelength in 8CB. There is an increase from 5% to $\sim 30\%$ from $\sim 1.9\,\mathrm{eV}$ (He-Ne laser) to $\sim 2.7\,\mathrm{eV}$ (454 nm line of an Ar$^+$-laser) indicating that the most probable origin of this effect is the resonant coupling and the subsequent change (produced by the presence of the nematic order) in the lowest electronic transition. See the text for further details.

the sort displayed in figures 2 and 3 can be easily used to monitor inhomogeneous samples through Raman images. In fact, a change $\Delta\omega \sim 5\,\mathrm{cm}^{-1}$ in frequency is similar to those found in semiconductor wafers where Raman maps of stress distribution have been measured. Experiments on Raman mapping in inhomogeneous LC phases are in progress and will be reported elsewhere.

4. Conclusions

A brief overview and a few examples of the possibilities offered by Raman scattering in the study of LCs have been presented. Changes in phonon self-energies and/or scattering efficiencies of specific molecular modes are easily monitored and can be used as a microscopic *in situ* probe in situations where spatial inhomogeneities are present. We have presented particular examples of frequency and intensity changes in compounds 5.O4O.5 and 8OCB, respectively. We have also shown that the relative intensity change between the N and I phases of the C–H in-plane deformation mode in 8CB displays a resonant enhancement. A qualitative explanation of these phenomena is that the Raman signal depends on the modulation of the polarizability produced by a vibration, and this is affected if the intermediate electronic states are changed by the presence of a specific mesophase. We hope that our work encourages some effort towards a microscopic theoretical understanding of these phenomena, beyond the phenomenological level, as well as expanding the interest of Raman scattering as a versatile microscopic tool for the study and characterization of LCs.

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References

[1] Khoo, I. C., 1995, *Liquid Crystals, Physical Properties and Nonlinear Optical Phenomena* (New York: Wiley Interscience), p. 95.

[2] Hayes, W., and Loudon, R., 1978, *Scattering of Light by Crystals* (Toronto: Wiley).

[3] Chatelain, P., 1951, *Acta Cryst.*, **4,** 453.

[4] Orsay Liquid Crystal Group, 1969, *Phys. Rev. Lett.*, **22,** 1361.

[5] Liao, Y., Clark, N. A., and Pershan, P. S., 1973, *Phys. Rev. Lett.*, **30,** 639.

[6] Jen, S., Clark, N. A., Pershan, P. S., and Priestley, E. B., 1977, *J. chem. Phys.*, **66,** 4635; Jen, S., Clark, N. A., Pershan, P. S., and Priestley, E. B., 1973, *Phys. Rev. Lett.*, **31,** 1552.

[7] Miyano, K., 1978, *J. chem. Phys.*, **69,** 4807; Prasad, S. N., and Venugopalan, S., 1981, *J. chem. Phys.*, **75,** 3033.

[8] Kim, K. H., Takanishi, Y., Ishikawa, K., Takezoe, H., and Fukuda, A., 1994, *Liq. Cryst.*, **16,** 185.

[9] Nöllmann, M., and Etchegoin, P., 2000, *Phys. Rev. E*, **61,** 5345.

[10] Nöllmann, M., and Etchegoin, P., 2000, *Phys. Rev. E*, **61,** 7235.

[11] Averyanov, E. M., 1988, *Opt. Spectrosc. (USSR)*, **65,** 513; Averyanov, E. M., Zhuikov, V. A., Zyryanov, V. Ya., and Shabanov, V. F., 1984, *Sov. Phys. JETP*, **59,** 1227; Averyanov, E. M., Vaitkyavichyus, A., Korets, A. Ya., Sirutkaitis, R., Sorokin, A. V., and Shabanov, V. F., 1979, *Sov. Phys. JETP*, **49,** 910; Shabanov, V. F., Averyanov, E. M., Adomenas, P. V., and Spiridonov, V. P., 1978, *Sov. Phys. JETP*, **48,** 970.

[12] Nakajima, Y., Yoshida, H., Kobinata, S., and Maeda, S., 1980, *J. phys. Soc. Jpn.*, **49,** 1140.

[13] Booth, K. M., and Coles, H. J., 1993, *Liq. Cryst.*, **13,** 677; Coles, H. J., and Tipping, J., 1985, *Nature*, **316,** 136; Jones, W. J., Allott, R., Baran, J., Grofcsik, A., Kubinyi, M., and Stanley, M., 1996, *Mol. Phys.*, **88,** 1025.

[14] Yuzyuk, Yu. I., Sarmento, S., Simeão Carvalho, P., Almeida, A., Pinto, F., Chaves, M. R., and Nguyen, H. T., 1999, *Liq. Cryst.*, **26,** 1805.

[15] Xu, X. H., and Yeung, E. S., 1997, *Science*, **275,** 1106; Cole, N. B., Smith, C. L., Sciaky, N., Terasaki, M., Edidin, M., and Lippincott-Schwartz, J., 1996, *Science*, **273,** 797; Manni, J., 1996, *Biophotonics*, **3,** 44.

[16] Takezoe, H., Usui, H., Furuhata, K., Nakagiri, T., Fukuda, A., and Kuze, E., 1979, *J. Physique Coll. C3*, **40,** 217.

[17] Etchegoin, P., and Phillips, R. T., 1996, *Phys. Rev. E*, **54,** 2637.

[18] De Gennes, P. G., and Prost, J., 1995, *The Physics of Liquid Crystals*, 2nd Edn (Oxford: Clarendon Press), p. 53.

[19] Khoo, I. C., and Wu, S. T., 1993, *Optics and Nonlinear Optics of Liquid Crystals* (London: World Scientific), p. 342.

[20] Ciampi, E., Emsley, J. W., Luckhurst, G. R., Timimi, B. A., Kothe, G., and Tittelbach, M., 1997, *J. chem. Phys.*, **107,** 5907.

[21] Shen, Y. R., 1984, *The Principles of Nonlinear Optics* (New York: Wiley).

[22] Yariv, A., 1989, *Quantum Electronics*, 3rd Edn (New York: Wiley).

[23] Etchegoin, P., Fainstein, A., and Pregliasco, R. G., 1999, *Physica D*, **134,** 144.

[24] Baltensperger, W., 1970, *J. appl. Phys.*, **41,** 1052; Wakamura, K., and Arai, T., 1988, *J. appl. Phys.*, **63,** 5824; Chen, X. K., Irwin, J. C., and Franck, J. P., 1995, *Phys. Rev. B*, **52,** R13130; Suzuki, N., and Kamimura, H., 1972, *Solid State Commun.*, **11,** 1603; Hadjiev, V., Fainstein, A., Etchegoin, P., Trodahl, H. J., Bernhard, C., Cardona, M., and Tallon, J. L., 1999, *Phys. Stat. Solidi B*, **211,** R5.

[25] McMillan, W. L., 1971, *Phys. Rev. A*, **4,** 1238.

[26] Spiro, T. G. (editor), 1988, *Biological Applications of Raman Spectroscopy* (New York: J. Wiley).

[27] Albrecht, A. C., 1961, *J. chem. Phys.*, **34,** 1476.

[28] Dash, S. K., Singh, R. K., Alapati, P. R., and Verma, A. L., 2000, *Liq. Cryst.*, **27,** 269.

[29] Burhanudin, Z., and Etchegoin, P., 2000, *Chem. Phys. Lett.* (accepted for publication).

[30] Date, R. W., Imrie, C. T., Luckhurst, G. R., and Seddon, J. M., 1992, *Liq. Cryst.*, **12,** 203.

[31] Simova, P., Kirov, N., Fontana, M. P., and Ratajczak, H., 1988, *Atlas of Vibrational Spectra of Liquid Crystals* (Singapore: World Scientific).

[32] Cardona, M., 1982, in *Light Scattering in Solids II* (Berlin: Springer), p. 19.