PHYSICAL REVIEW A VOLUME 14, NUMBER 4 OCTOBER 1976

Temperature dependence of Raman scattering from monocrystalline terephtal-*bis*-butyl-aniline (TBBA): Low-frequency spectra*

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(Received 20 October 1975; revised manuscript received 26 January 1976)

Raman spectroscopy gives us a very useful tool for studying the vibrational dynamics of liquid crystals and, in particular, their structural phase changes. In order to investigate lattice mode nature of the structure sensitive low- and very low-frequency intermolecular modes of TBBA (terephtal-*bis*-butyl-aniline), we have studied the polarized Raman spectra from oriented monocrystals, and have followed the temperature dependence of such spectra from 90 to 300°K. The reported results are interpreted on the basis of a proposed dynamical model involving rotational Brownian motions in the crystalline phases.

INTRODUCTION

In recent years Raman spectroscopy has been a very useful tool in the investigation of the vibrational dynamics of mesomorphic substances (liquid crystals).[1,2] Of particular interest has been the connection between structural phase changes and the corresponding changes in the Raman spectrum.[3-6] In this respect the analysis of the structure sensitive low- and very low-frequency intermolecular modes is of special importance. In previous works[7,8] the Raman spectra (and particularly the low-frequency region) of terephtal-*bis*-butyl-aniline (TBBA) in its various phases and mesophases have been reported. TBBA in fact presents a total of nine phases, of which three are smectic and one nematic (see Fig. 1).

Apart from the wealth of phases, there are other points of interest in TBBA; in fact, the smectic C to smectic A transition may be continuous[9,14]; also, upon cooling from the smectic B phase, one encounters two extra phases[10] (see Fig. 1), which are subtle modifications of the smectic B structure. The smectic B phase itself shows considerable interest in that x-ray data imply a quasicrystalline structure for the smectic planes.[11] This last result was partially confirmed by Fontana and Schnur,[7] who reported that the low-frequency Raman spectrum ($w_s < 300$ cm^{-1}) of TBBA in the smectic B phase was very similar to the crystalline spectrum and that furthermore all the spectral features were essentially washed out at the smectic-B–smectic-C transition. Thus the low-frequency modes were assigned to be heavily coupled intermolecular vibrations, perhaps with lattice phonon characteristics.

In order to check lattice mode nature of the low- and very low-frequency spectra of TBBA and, more generally, to gain more detailed knowledge about intermolecular vibrational modes in mesomorphic substances, we have studied the polarized Raman spectra from oriented monocrystals of TBBA, and have followed the temperature dependence of such spectra from 90 to 300 °K (we have also studied the temperature range 300 °K up to the crystal–smectic-B transition, and the results will be reported separately). We believe that these measurements are the first of their kind; i.e., to our knowledge there are no reported polarized Raman spectra from monocrystalline mesomorphic substances, and certainly not as a function of temperature at low temperatures.

EXPERIMENTAL TECHNIQUES

Samples

Samples of TBBA were kindly given to us by Mme. Lambert of the Laboratoire de Physique des Solides, Orsay, France (the crystals were grown in the Laboratoire de Physique Crystalline of the University Paris-Sud). They were in powder, recrystallized powder, and crystalline form. Although we studied all three types, in this paper we shall be concerned only with TBBA monocrystals. These were of two types: thin long needles ($0.5 \times 0.2 \times 10$ mm^3) or large rectangular plates (typically $0.2 \times 5 \times 10$ mm^3). All samples were clear and yellow. In some cases the plates seemed to be composed of several needles stacked side by side.

Some samples were x-ray oriented[12]; however the needle geometry is so simply related to the monoclinic a, b, c axes of the TBBA unit cell (Fig. 2) that with a bit of care samples could be oriented by inspection.

Raman spectrometry

Spectra were taken with a conventional Raman system, consisting of a cw Ar laser, double monochromator followed by a third monochromator, photon counting, and either multiscaler storage or strip-chart recording. The third monchroma-

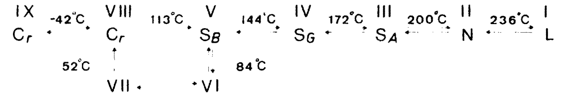

FIG. 1. Schematic diagram of TBBA structural transition (Ref. 10).

tor was mainly used to identify and discriminate against grating ghosts below 100 cm^{-1} (of which we only found one at 39 cm^{-1}) and of course to study the spectra close (within 4 cm^{-1}) to the laser line. Such spectra were taken with a bandpass of either 1 or 0.5 cm^{-1}. All other spectra were taken with a 3 cm^{-1} bandpass, unless otherwise stated.

All mesomorphic substances on which we had a chance to inflict our laser light are strongly affected by the light intensity; TBBA being yellow, it is even more strongly affected by the blue-green Ar laser lines. Thus in all our measurements, care was taken never to subject the sample to more than 20 mW of 4880- or 5154-Å laser light, with slightly defocussed entrance optics. It is important to take spectra at low power, not only to avoid heavy damage (i.e., volatilization) of the sample, but also because the spectra in the low-frequency region tend to be smeared out and lose detail at higher powers.

Another vexing problem in the Raman spectroscopy of TBBA is the sometimes strong background luminescence. Our samples were remarkably free of such luminescence. This, coupled to their good optical quality allowed us to take precise spectra at fast scanning speeds and low integration (or counting) times. For instance in Fig. 3 we show the polarized spectrum taken at 90 °K with a resolution of 1 cm^{-1}. Incident power at sample site was 20 mW of 4880-Å light, scan speed was 100 cm^{-1}/min and integration time was 0.1 sec. Noise was a few percent of signal.

The spectra were taken in both 90° and forward scattering geometries, and for various incident and scattered light polarizations. The results were however largely inconclusive, due mainly to depolarization effects (the samples are biaxial) and to a certain sample dependence of what small polarization effects were found. Therefore we shall not dwell on these measurements in this paper.

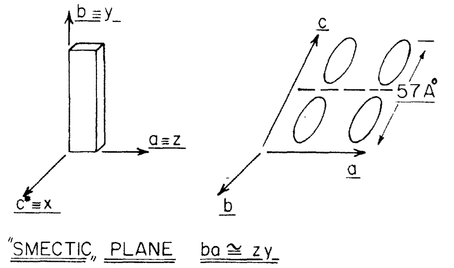

FIG. 2. Definition of scattering geometry relative to crystallographic axes of TBBA (c^+ is rotated by 25° relative to c).

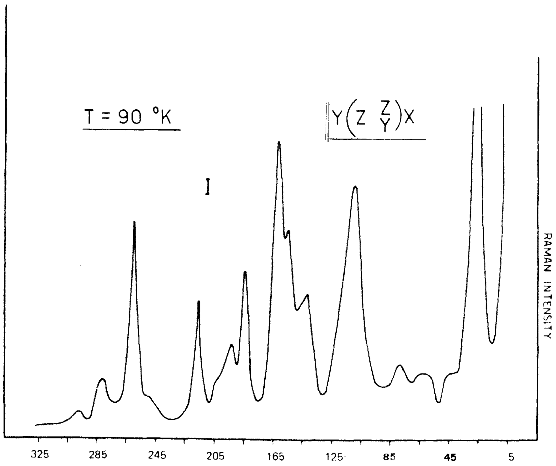

FIG. 3. Phase IX spectrum of TBBA at 90 °K; the lowest frequency peak has approximately twice the intensity of the other peaks.

Temperature variation and control

The samples were placed in good thermal contact with the cold finger of an optical cryostat, which was cooled by cold N_2 flux. Temperature could be varied by varying the pumping speed of the cold gas and/or by varying current in a resistance heater embedded in the cold finger. Stabilization of the temperature to ± 0.1 °K was achieved with an electronic temperature controller built in our laboratory. Temperature was monitored with a Cu-constantan thermocouple and read with a digital microvoltmeter. Since even at the powers used the laser is expected to have heated the sample somewhat, a temperature differential of some degrees may have existed between thermocouple and sample, even though the thermocouple itself was actually touching the sample. Thus the temperature reported may be accurate only within a few degrees.

TEMPERATURE DEPENDENCE OF THE SPECTRA

A typical low-temperature spectrum has been shown already in Fig. 3. The only features of such spectrum which were polarization dependent are shown in greater detail in Fig. 4, where we show also the detailed polarized spectra of the very strong peak at "20 cm^{-1}" (room-temperature value). Note that the peak actually shows a triplet structure at low temperatures. We shall not com-

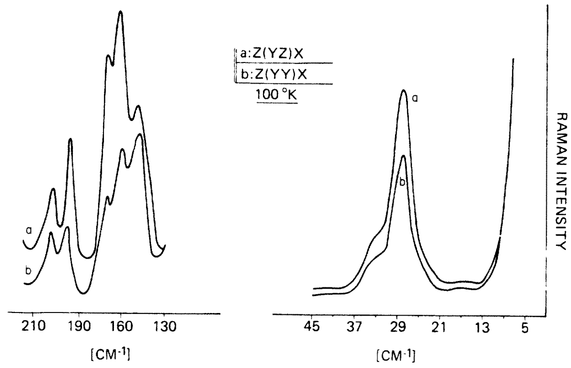

FIG. 4. Phase IX polarized spectra at 100 °K, in the region about 150 and 20 cm^{-1}.

ment on polarization effects further, since better sample control will have to be achieved before quantitative information can be obtained from such measurements.

As could be expected, temperature has a strong effect on the low-frequency spectra. In Figs. 3, 5, 6 we show some representative spectra taken in the $Y(Z--)X$ geometry. The most important feature of these data is to show that what appears as little bumps over a broad background at room temperature (or higher temperatures, of course) are actual well defined peaks broadened by the higher temperature. In fact each spectral feature can be followed continuously as temperature is raised from 90 °K to room temperature.

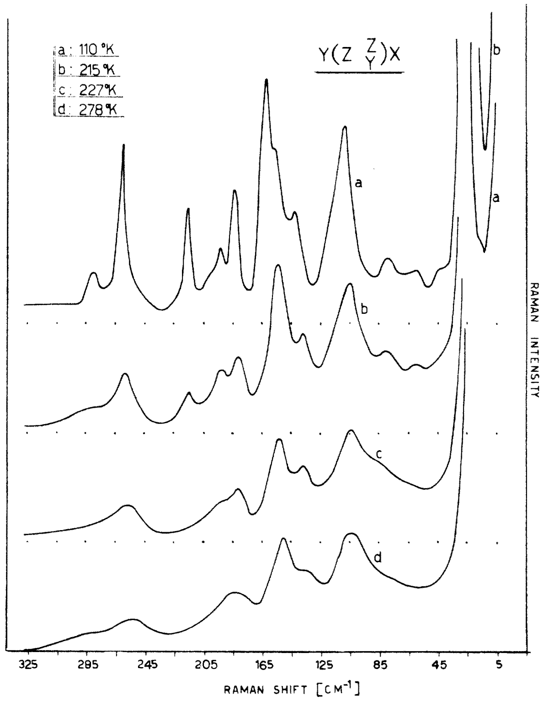

FIG. 5. Temperature dependence of overall spectra.

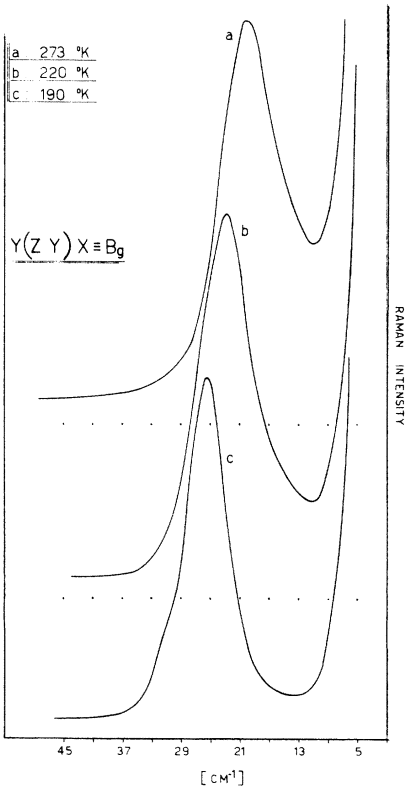

FIG. 6. “20-cm^{-1}” peak at some representative temperatures.

Another important effect is the sensitivity of the spectra to the structural transition first reported at − 42 °C (231 °K) on the basis of x-ray evidence.[10] Actually we could not observe any drastic or spectacular effects due to the phase transformation; the change had to be detected by subtler analysis of the data. For instance, in Fig. 7 we plot the measured peak frequency and half-width of the 20 cm^{-1} peak as a function of temperature. There is no discontinuity, but rather a behavior similar to what is observed in second-order phase transitions. However, the transformation shows a pronounced hysteresis; in Fig. 7(a) the peak frequency was obtained upon heating, whereas the results of Fig. 7(b) were obtained upon cooling. The transition temperatures we obtain are 235 and 220 °K, respectively. The presence of hysteresis then excludes that the transition we observe be a real second-order transition.

In order to obtain the half-width of the 20 cm^{-1} peak in the high-temperature region it was necessary to consider the rapid increase of quasielastic scattering as T was increased in phase VIII. At least part of this scattering is dynamical in nature, as could be determined by using the third

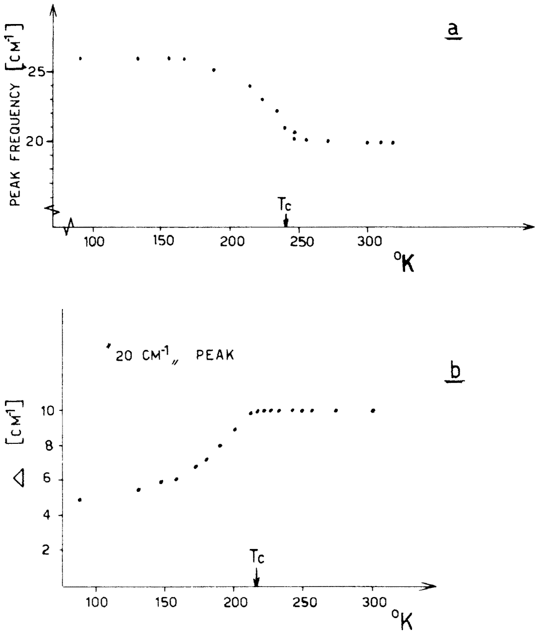

FIG. 7. Temperature dependence of peak frequency and half-width of "20-cm^{-1}" peak. (a) Obtained upon heating; (b) upon cooling.

monochromator to discriminate against the purely elastic background. In any case, if such an effect is not taken into account, the apparent half-width of the 20 cm^{-1} peak would be found to increase with temperature, and its shape would become more and more asymmetric. Once the quasielastic contribution is estimated and subtracted, the width is found to behave as shown in Fig. 7(b). It is interesting to note that the peak position and width vary together. Thus the peak frequency variation is predominantly due to an increase in the damping of the mode, rather than to a change in the intermolecular force constants. All in all, the 20 cm^{-1} peak seems to be rather insensitive to temperature changes.

A much more dramatic variation is shown by several higher-frequency peaks, of which the peak at 260 cm^{-1} [at 90 °K in $Z(Y--)X$ geometry] is the best example. In Fig. 8 we show the behavior of the half-width of such peak versus temperature. The break in the plot at the structural transition temperature is evident. Such break divides the observed behavior into a low-temperature region typical of anharmonic broadening,[13] and a high-temperature region, in which after an initial sharp increase right after the transition, the variation seems to saturate as room temperature is approached. A precise determination of the half-width for higher temperatures is very difficult due to the practical disappearance of the peak into a broad background, and thus it was not attempted.

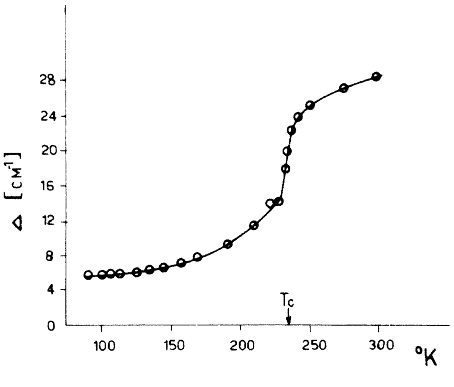

FIG. 8. Temperature dependence of the width of peak at 260 cm^{-1}.

It is important to note that some peaks are broadened much more by increasing temperature than others. In particular, besides the 260 cm^{-1} peak, similar behavior is shown by the peak at 215 cm^{-1}, which practically disappears above T_c, the peaks at 184, 195, and 143 cm^{-1}. On the other side, among the peaks which are less sensitive to temperature we may include the peaks at 110-, 162-, and of course the 20-cm^{-1} peak; thus it is actually these peaks that dominate the spectrum at higher temperatures, and remain as peaks even in the smectic B phase.

Finally, we wish to mention what appears to be another sample dependent effect we have observed. It is well known to those that study structural transitions by means of light scattering that at the phase transition the static pattern of light diffracted or reflected by the sample fluctuates in an amoeba-like fashion, producing sometimes very beautiful dynamic patterns on walls, etc. We have observed such behavior at the low-temperature VIII–IX transition only in those samples in which some polarization effects could be observed; in the other samples we could detect no visual evidence of the phase transition.

DISCUSSION OF THE RESULTS

The most interesting results of this work concern the temperature dependence of the spectra. We have already remarked that the continuous variation of spectral features between 90 °K and room temperature identifies as real vibrational modes the rather undistinct features present in the low-frequency spectra in the phases VIII and smectic B. Furthermore the persistence of some peaks in the smectic B phase observed by Fontana and Schnur is corroborated by the behavior of such peaks at lower temperatures, i.e., their relative insensitivity to temperature increase.

The most important effect of temperature is the large broadening it induces on some peaks, of which the 260-cm^{-1} peak is a good example. A quantitative analysis of such behavior is complicated by the presence of the structural transition at 235 °K (on heating). Qualitatively, however, data such as those reported in Fig. 8 may shed some light on the dynamics of the phase transition itself. In fact in any molecular crystal, there are basically two broadening mechanisms: anharmonic interactions and rotational Brownian motion. Whereas the first mechanism leads to a linear increase of the half-width with increasing temperature, the second one, related as it is to some jump activation energy, leads to an exponential increase.[13] The results of Fig. 8 can then be interpreted in the following manner: in the low-temperature phase IX, the TBBA molecules are fixed and intermolecular vibrations are increasingly damped by anharmonic coupling. As the transition temperature T_c is approached, the rotational jump mechanism becomes active, and it is indeed this incipient Brownian rotation that triggers the transition itself: the half-width then increases rapidly for T just above T_c. In the new phase VIII the structure is, however, changed and the rotational relaxation time stops decreasing exponentially: the peaks, with their new larger width due predominantly to hindered rotational motion, will still broaden with increasing temperature, but at a slower rate. Thus the rather featureless and broad spectra characteristic of phases VIII and S_B are due to this hindered rotation of the TBBA molecules.

This interpretation is in agreement with recent ideas and data about the dynamics of the crystal-smectic *B* transition.[10,14] In particular, since such a transition is supposed to be associated with the rotational motion of the TBBA molecule as a whole, the rotational relaxation we have discussed for the crystal VIII phase must be due to the two end tails of the molecule. Thus the low-temperature IX–VIII transition is due to a rotational relaxation involving the end tails of the molecule.

In this framework we may also understand the complete depolarization—in all samples—of the most temperature sensitive peaks. Furthermore such model explains naturally the persistence of some spectral features of the crystal phase into the smectic *B* phase; these features are due to those vibrational modes which, not being affected by the Brownian rotation of the crystal phase, are also not influenced by the freer rotation of the molecules in the smectic *B* phase.

The presence of a relaxational rotation mode in the crystal VIII phase is also confirmed by the appearance and strong increase of the quasielastic scattering (see for instance Figs. 4 and 6). We have verified the dynamic nature of this increase by using the third monochromator to discriminate against purely elastic scattering. Furthermore, in our measurements we had a "built-in" indicator of spurious light intensity in the form of a grating ghost at 39 cm^{-1}; we have monitored the intensity of such ghost when taking the spectra in the 20-cm^{-1} region as a function of temperature, and found such intensity to be essentially constant; thus the increase in scattering intensity below about 10 cm^{-1} is predominantly due to dynamic effects, such as the rotational relaxation present in the VIII phase. In fact, we observe, on top of a continuous increase of quasielastic intensity for $T < 180$ °K, a 50% jump in the intensity (at the fiduciary point of 9 cm^{-1} shift) at the structural transition at 235 °K (heating). This result, besides confirming our previous observation, implies that the behavior of quasielastic scattering is an important tool to study the structural transitions of TBBA, and particularly the crystal–smectic-*B* one.

CONCLUSION

The results reported in this paper confirm the earlier finding that the low-frequency spectrum of TBBA in both crystal VIII and S_B phases corresponds to well-defined peaks due to intermolecular modes.

The polarized spectra gave inconclusive results, partly because of sample birefringence and partly because of sample dependence of the polarization behavior. Thus in this area much remains to be done.

On the basis of the observed temperature behavior of the spectra, we have proposed a dynamical model for the crystal-IX–crystal-VIII transition based on the onset of rotational relaxation of the tails of TBBA molecules in phase VIII: within this model find a natural explanation the behavior of the half-width of the low-frequency Raman peaks, the persistence of some of these peaks in the S_B phase, the increase in quasielastic scattering in the VIII phase, and possibly the total and reproducible depolarization of the temperature sensitive peaks.

ACKNOWLEDGMENTS

The authors wish to thank Mme. Lambert and Mme. Levelut for useful and illuminating discussions.

*Work supported by the Consiglio Nazionale delle Ricerche under Research Contract No. 74.00854.63.115.7473.

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