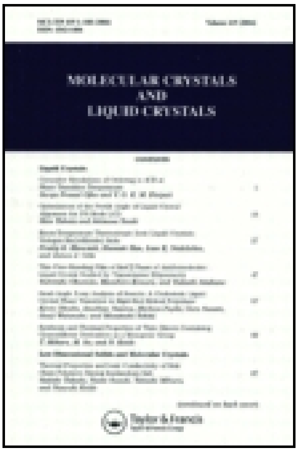

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Spectroscopic Investigations of Structural Transformations in Liquid Crystals

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Paper is devoted to Raman scattering study of structural transformations in frozen liquid crystal ABT in the process of its heating. Temperature region was from T=173 K up to T=343 K. A specific mechanism of inhomogeneous broadening in mesogenic systems is proposed. The mechanism consists in parametric action of valence angles deformations of molecules on high frequency vibrations. In its turn the molecular deformations depend on media structure. As a result the shape of parametrically dependent high frequency vibrational bands indirectly reacts to structural transformations in media.

Keywords: liquid crystals; molecular spectroscopy; band shape; phase transitions

INTRODUCTION

Comprehensive study of structure and structural transformations in mesogenic materials is of practical and academic value. The latter is accounted for the complex structure of liquid crystal (LC) molecules that can form rather rich set of phases including glass. General methods that are used for structural analysis are diffraction of electrons, neutrons and X-rays. They give quantitative structural characteristics of media. But qualitative information such as identification of states and observation of their evolution may much simply be determined by optical spectroscopy, in particular by vibrational Raman spectra [1].

Usually for this purpose low-frequency phonon Raman spectra (up to 300 cm^{-1}) are used. But in the case of such complex molecules as LC a problem connected with overlapping of phonon and intramolecular low-frequency spectra arises. The situation is worse in amorphous state. In this case low-frequency phonon spectrum represents a continuous distribution of intensity depending on frequency in contrast to typical narrow-band Raman spectra of molecular crystals.

In this context the possibility to investigate structural transformations in molecular systems by Raman spectroscopy of high-frequency intramolecular vibrations seems actual. Molecular Raman scattering is incoherent process, and hence it gives additive data on individual molecular states. But shape of individual molecular spectrum depends on a state of environment, more exactly on its structure and on statistical character of molecular motion. This idea was used in previous paper of the authors [2-4], where the form of vibrational Raman bands serves as an indicator of temperature induced structural transformations in MBBA. It was shown that some characteristic transformations of spectra really correspond to structural transformations indicated by calorimetric methods.

In the present paper we discuss a specific mechanism of shape formation of some vibration bands of LC molecules named by us as indirect parametric inhomogeneous broadening. In our opinion namely this mechanism is significant for broadening of studied bands.

Discussion is based on the results of Raman spectra investigations of temperature induced structural transformations in LC (p-amyloxy) benzyliden-N-toluidine (ABT) in the range from LC glass to isotropic liquid.

EXPERIMENT

Vibrational Raman spectra of ABT at different temperatures were investigated. Spectral-digital complex for the Raman spectra recording was used. This complex includes double monochromator, the photon counting system and PC-controller. Spectral width of device function did not exceed 1 cm^{-1}. The radiation source was Ar-laser. Wavelength of the exciting light was 488 nm, power was less then 0.1 Wt. So, radiation did not change appreciably the temperature of the sample. Measurements were made in spectral region 1550-1650 cm^{-1}.

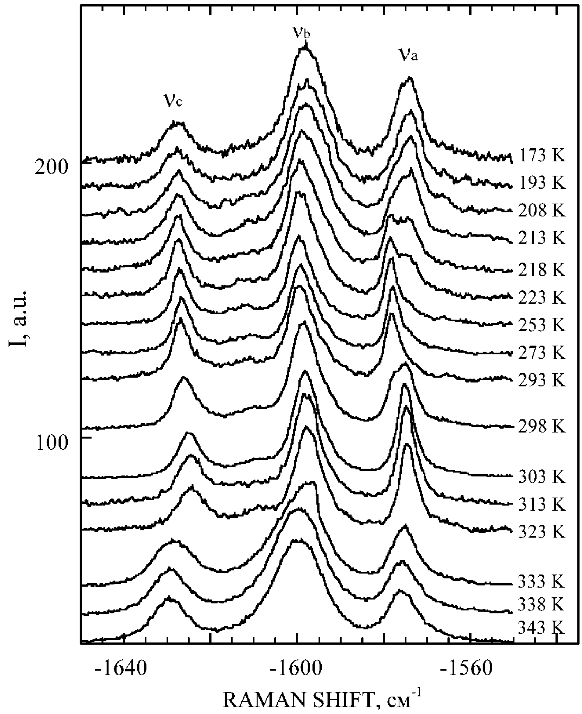

FIGURE 1 Band shape changing under heating after “shock” cooling of ABT

PC controlled system for the stabilization and control of sample temperature was employed. This system holds the sample temperature with the accuracy 0.3 K in the range 170-430 K. Unaligned ABT was placed in a sealed ampoule with diameter of 0.5 cm. The ampoule with LC in the state of isotropic liquid ($T \approx 390$ K) was quickly frozen by immersion in liquid nitrogen. The final temperature was 173 K.

The spectral measurements were performed during slow heating of the sample. Spectra were registered at fixed temperatures after annealing of sample during 15 minutes. Results of measurements are shown on Fig. 1.

BACKGROUND

For analysis of spectral bands form it is usually used an integral relation between distribution of intensity in spectrum and correlation functions of electrooptical characteristics of molecules. In the case of Raman scattering the known formula can be written [5]

$$I(\omega) \sim \int_{-\infty}^{\infty} dt e^{i(\omega-\omega_0)t} \sum_k G_k(t) \tag{1}$$

where $I(\omega)$ is a spectral distribution of intensity (band shape), ω_0 is the unperturbed frequency of the investigated molecular vibration,

$$G_k(t) = \left\langle \vec{\xi}_i \alpha_k \vec{\xi}_s \, \vec{\xi}_i \alpha_k(t) \xi_s \right\rangle \tag{2}$$

is a correlation function. Here k - is a number of molecule, α_k is a tensor of polarizability, $\vec{\xi}_i$ and $\vec{\xi}_s$ are polarization vectors of incident and scattered light correspondingly (usually perpendicular geometry $\vec{\xi}_i \perp \vec{\xi}_s$ is used). Summation in (1) is taken over all irradiative molecules.

Spectra of molecules depend on intermolecular interaction in media and on temperature. And these two factors determine a structure of material and characteristics of heat movement. It is simpler to analyse the influence of them on a band shape in the terms of moments of spectral distribution. Using the known formula of connection between central moments and correlation function [5]

$$m^{(k)} = (-i)^k \frac{d^k}{dt^k} G(t)\Big|_{t=0} , \tag{3}$$

relations for first and second moments can be obtained [6,7]

$$m_i^{(1)} \sim \sum_k \left\langle V_{ik} \right\rangle_{ex} , \qquad (4)$$

$$m_i^{(2)} \sim \sum_k \left\langle V_{ik}^2 \right\rangle_{ex} , \qquad (5)$$

where V_{ik} is a part of intermolecular potential dependent on vibrational coordinate of i-th molecule. Summation in (4), (5) is taken over molecules of environment. The average in (4) and (5) is carried out over translational and rotational variables of molecules. The values of averaged potentials are dependent on radial and orientational distribution functions, i.e. parameters of bands depend on space structure of media. It is known that the first central moment of distribution describes an asymmetry and shift of band and the second moment corresponds to band width.

If media is homogeneous and isotropic then

$$\left\langle V_{ik} \right\rangle = 0$$

and all

$$\sum_k \left\langle V_{ik}^2 \right\rangle$$

are equal. That is shapes and positions of partial bands of individual molecules are identical, and summation in (1) is replaced by multiplier n - particle number density:

$$\sum_k G_k(t) = nG(t) .$$

This case is named homogeneous broadening. It is realized in simple liquids.

In complex systems to which LC are attributed, band broadening is inhomogeneous in nature. Molecules are in structurally different environments and are subjected to different external perturbations. In consequence of that, $m_k^{(1)} \neq m_l^{(1)}$ and spectra of individual molecules are shifted relatively one another. Generally speaking they have different shape ($m_k^{(2)} \neq m_l^{(2)}$) too. Inhomogeneous broadening is considerably more complex problem for analytic calculation (with the exception of Doppler broadening).

It is the phonon spectra that are usually used when phase transitions in solids are investigated by vibrational spectroscopy. In the case of LC because of large mass of molecules these spectra are low-frequency. It is shown in [1] for MBBA that these frequencies are arranged in the region from 0 up to ~150 cm^{-1}. But low-frequency intramolecular vibrations fall within the same internal. Due to interaction of close as to frequency internal and external vibrations their interference occurs. Conformation movements of molecules are connected with their translational movements. It is the reason of high sensitivity of low-frequency spectra to phase transitions [1].

However the use of phonon spectra becomes difficult in the case of LC glass, where owing to high dispersion of vibrations the spectrum is a continuous distribution. In addition the overlapping of phonon and intramolecular low-frequency spectra introduces an essential complication.

More clear experimental information may be obtained in the investigation of high-frequency bands because they are well-defined and as it is shown on Fig. 1 this bands are varied considerably with temperature.

We propose a hypothesis of special broadening mechanism that explains discovered behavior of the bands. Considered LC molecules are flexible and their valence angles may be forced to deformations relatively easy. In its turn molecular deformations can influence on force constants of high-frequency vibrations shifting their frequencies. As frequencies of torsional vibrations are by a factor of 10^2 smaller than frequencies of the investigated bands so stated influence may be regarded as parametric. Thus shape of the observable bands depends on distribution of deformation angles of LC molecules. And this distribution in its turn depends on space structure of media. Such mechanism of band shape formation may be called indirect parametric inhomogeneous broadening.

Note that indirect broadening has been discussed in literature on band shape [8,9]. It was considered the mechanism of broadening of a high-frequency band due to changing of anharmonic intramolecular interaction between high- and low-frequency vibrations in the process of stochastic transitions between ground and first levels of low-frequency vibration.

For justification of dynamical possibility of the stated broadening mechanism computer simulation for single molecule of ABT were carried out. The results of calculations are presented in next paragraphs.

VIBRATIONAL FREQUENCY SPECTRA AND VALENCE ANGLES DEFORMATIONS

For a substantiation of the above offered mechanism of broadening it is expedient to receive estimations of influence of low-energy deformations of LC molecules on own vibrational frequencies. With this purpose vibrational spectra of a molecule in equilibrium and deformed states were calculated. Quantum mechanical estimations of frequencies of molecular vibrations were performed by semiempirical approximation AM1 of HFR SCF method.

As deformations the deviations of valence angle CNC (see Fig. 2) from equilibrium value on size up to 6 degrees was chosen.

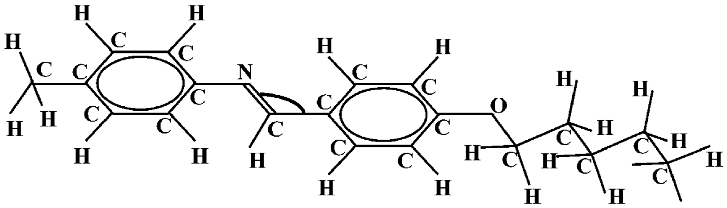

FIGURE 2 Formula of ABT. The deforming angle marked by arc.

Results of calculations for band ν_a (see Fig. 1) are given in Table1. One can see from the Table 1 that supposed dependence of own vibrational frequency on valence angle value really exists.

TABLE 1 Calculated influence of -C-N-C- valence angle deformations on the frequency of vibration ν_a.

Valence angle, degree	Frequency, cm^{-1}
116	1579
119	1578
121.9[(a)]	1576
125	1574
128	1573

*[(a)] denote equilibrium valence angle.

DISCUSSION

Now we analyze validity of proposed mechanism from the point of view of presented experimental results (see Fig.1). One can see the qualitative phenomenon of almost complete identity of band shapes in isotropic liquid and in quickly frozen sample. Inasmuch as temperatures of these states differ cardinally so it unambiguously points that the major mechanism of band formation is inhomogeneous broadening.

Considerable band narrowing under heating of the sample up to T≈220 K points on relaxation process that weakens original inhomogeneity. It is known that in many-atom molecular glasses namely relaxation of intramolecular states is a primary process. We suggest that reduction of distribution of bending and torsional deformations to conformity with sample temperature is the mentioned process. During further heating up to T≈300 K band widths are practically constant, but shifts of band positions are observed. Above this temperature the increase of band widths takes place. It corresponds to transition to mesophase and further to isotropic liquid.

Behavior of band ν_a in region from T=208 K up to T=223 K turns attention (see Fig. 1). It is clear that band is consisted of two subbands, and as temperature increase the "transfer" of intensity from low- to high-frequency component is occurred. And then above T≈295 K the band moves to low-frequency side. The same but less pronounced phenomenon is observed in band ν_b.

It may be suggested that the behaviour of the band ν_a is representation of relaxation process of fine-adjusting of molecular form to temperature induced media structure. Variation of valence angles acts on high-frequency vibrations by above considered intramolecular mechanism and results in observable band shifts. Non-coincided positions of the band at $T < 293$ K and at $T > 300$ K points on different equilibrium valence angle positions that in its turn says about the different media structure at lower and higher temperatures. At $T \approx 295$ K phase transition has to be.

CONCLUSION

Temperature induced structural transformations in mesogenic ABT were investigated by vibrational Raman spectroscopy. Nature of sensitivity of band shapes and positions to structure of media is discussed. The specific mechanism of inhomogeneous broadening that connects characteristics of high-frequency bands with distribution of valence angle values is proposed. Numerical calculations of frequency shift under valence angle deformation showed that effect really exist. Analysis of experimental data allows to state that equilibrium value of molecular valence angles changes under phase transitions in LC.

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