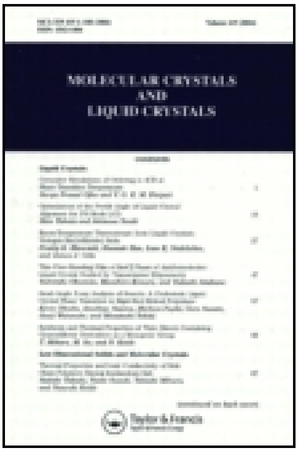

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Optical Study of the Phase Transitions in Liquid Crystals

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OPTICAL STUDY OF THE PHASE TRANSITIONS IN LIQUID CRYSTALS

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Abstract The temperature dependencies of vibrational bands parameters corresponding to intramolecular vibrations have been investigated for supercooled MBBA (N-p-methoxybenzylidene p-n-butylaniline) (from 163 K to 315 K) by Raman spectroscopy. The formation mechanisms of vibrational bands for various phases of MBBA have been established. Besides the nature of heterogeneous broadening for amorphous and nematic phases have been studied [1–6]

INTRODUCTION

Molecular spectroscopy gives exclusive possibilities for analysis of structural transformations in mesogeneous systems. Corresponding information is had as in frequency and integrated intensity of vibrational bands as in their width. The frequency and intensity are traditional source. And width isn't used for finding peculiarities of structural transformations usually. The correlations between frequencies and widths of vibrational bands in liquid crystals (LC) and their structures have been dicussed in last time.

Liquid-crystalline molecules have large size and are characterized considerable mobility of itself fragments. The frequencies of intramolecular vibrations are felt to molecular conformations. It is possibility to trace the connection between the changes of structure under phase transitions and molecular conformations using the analysis of temperature frequencies and widths dependencies . On other side, the analysis relative integrated intensities of vibrational bands have allowed to determine the dynamics of phase transitions and to obtaine the quantitative phase composition and conformational composition of certain phases.

It is well known that the widths of vibrational bands are determined by processes of energetic and phase relaxations [7] As rule, the rate of energetic relaxation is very small. These processes give small contribution in the widths of vibrational bands usually.

In liquid crystals the translational disordering gives the main contribution in bands broadening. Therefore we deal with typical heterogeneous broadening. The cooling of LC lead to different results in dependence on cooling rate. Under slow cooling the sample is crystallized in solid crystal. Vibrational bands are narrowed[3]. Peculiarities of temperature dependencies of vibrational bands parameters are connected with LC solid phase polymorphism. And under fast cooling LC transforms in amorphous (A) state which is the mixture of supercooled nematic (s/c N) and glass. It has been obtained in work [4] that A-phase is s/c N-phase under "shock" cooling. And glass don't form. The heating of the sample lead to series of phase transformations. They are revealed in temperature dependencies of the shape parameters of vibrational band width. It is worth to point the traditional methods of structural investigations of phase transitions (X-ray, neutron scattering and differential scanning calorymetry) don't allow to obtain information about intramolecular changes under structural transformations.

The aim of work is to create of the theory of formation vibrational bands contours in various phases of mesogenic medium and to use one for analysis of formation mechanisms of vibrational bands which are felt to conformations.

EXPERIMENT

The temperature transformations of Raman spectra was obtained with the use of automated spectrometer and automated thermostabilization system. Radiation source was Ar-laser. Spectral width of apparatus function did not exceed 1 cm^{-1} . The accuracy of temperature stabilization was 0.01 K.

In experiment it has been investigated the temperature dependence of widths (Figure 1)

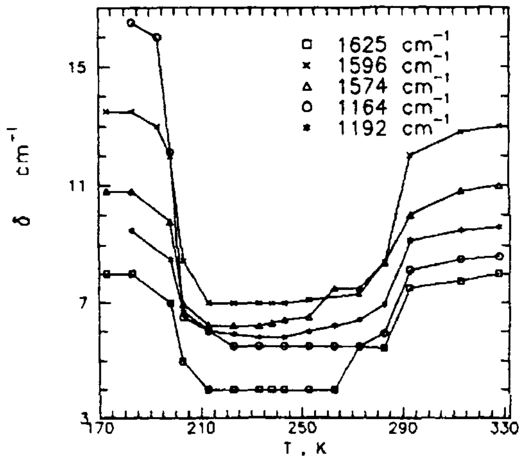

FIGURE 1 The tempereture dependencies of Raman bands width of supercooled MBBA.

and frequencies of vibrational bands of "shock" cooled MBBA in heating cycle from 163 K to 315 K. An ampoule with MBBA was placed in a vessel containing liquid nitrogen preliminary ("shock" cooling). The investigated frequencies are one corresponding intramolecular vibrations.

It has been found the vibrational spectra in temperature region from 175 K to 203 K (region of existing of amorphous phase) practically with spectra coincide measured in region of existing of the mesophase on widths (Figure 1), frequencies and relative intensities. It can be understood theoretically in following way.

MECHANISMS OF VIBRATIONAL BANDS FORMATION

Theory of Heterogeneous Broadening

In our experiment we deal with two essentially different states of matter: nematic liquid crystal (N) and amorphous (A) phase. It is interesting to analyze the mechanism of formation Raman bands contours in these two states by theoretical method.

The vibrational band contour is determined by character of motion of the molecules which scatter light and by structural relaxation processes in their environment. All these factors are reflected in formalism of formation mechanisms description of the vibrational bands contours in Raman spectra.

The distribution of intensities in Raman shape bands is determined by equation [8]

$$I(\omega)=\frac{\omega_0^4}{2\pi c^3}\sum_{\alpha,\beta,\gamma,\delta} n_\alpha n_\beta E_\gamma^- E_\delta^+ \, i_{\beta\delta\alpha\gamma}(\omega),$$

$$i_{\beta\delta\alpha\gamma}(\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty} dt \exp\left[-i\left(\omega-\omega_0\right)t\right]\left\langle P_{\beta\delta}(t)P_{\alpha\gamma}^*(0)\right\rangle \tag{1}$$

where E^+ is amplitude by exponents with negative and positive frequency describing incident radiation, ω_0 is frequency of incident light, n- vector of scattered light, $P_{\beta\delta}$ (t) is the electronic polarizability of molecules in Heizenberg's idea. The averaging was made on states of molecule.

For reception the angle dependence we have expanded tensor $P_{\beta\delta}$ on non-reducible spherical tensors P_{lm} and have changed laboratory coordinate system on molecular one. It have been obtained:

$$P_{\beta\delta}=\sum A_{\beta\delta}^{lm} \, D_{mm'}^{l} \, (\Omega) P_{lm'} \tag{2}$$

Here $A^{lm}_{\beta\delta}$ are coefficient of expansions on P_{lm} .$D^{l}_{mm'}$ is Vigner D- function, Ω are Eulers angles determining the orientation of molecular coordinate system relative to laboratory one.

Then we have made set expansion of $P_{lm'}$ on creation and annihilation operators (a^{+}_{s}, a_{s}) of quantums of the intramolecular vibration with number s:

$$P_{lm'} = P_{olm'} + \sum_{s}(P^{s}_{1lm'}\ a_{s} + P^{s\,*}_{1lm'}\ a^{+}_{s}\ ) + \ldots \tag{3}$$

After the substitution of the equations (2) and (3) in (1) we have obtained the expression for Raman intensity of the first order for the intramolecular vibration with number *s* through correlation function:

$$K^{l_1 m_1 m'_1}_{lmm'} = \left\langle \{D^{l}_{mm'}[\Omega(t)]\}\{(D^{l_1}_{m_1 m_1'})\ [\Omega(0)]\}^{*} P^{s}_{1lm'}(t) P_{1l_1 m'_1}(0) a_{s}(t) a^{+}_{s}(0) \right\rangle \tag{4}$$

This correlation function give most contribution in the intensity of Raman scattering in range of frequencies $\omega \approx \omega + \omega_{s}s$, where ω_{s} is the frequency of the intramolecular vibration with number s.

For calculation $K^{l_1 m_1 m'_1}_{lmm'}$ it has been made averaging on vibrational states of the molecule. It demands calculation of the correlation functions $U(t) = \langle a_{s}(t) a_{s}(0) \rangle$. Here averaging is made on vibrational states of molecule.

The molecule Hamiltonian taking into account its vibrational, rotational and translational movements may be presented in the following:

$$H = H_{0} + H' + F,$$

$$H_{0} = \sum_{s} \omega_{s}\left(a^{+}_{s} a_{s} + \frac{1}{2}\right), \hbar = 1 \tag{5}$$

$$H' = \sum_{s} \Delta\omega_{s}\left(a^{+}_{s} a_{s} + \frac{1}{2}\right),$$

where ω_{s} are average frequencies of intramolecular vibrations, $\Delta\omega_{s}$ is frequency change connected with fluctuation of harmonic potential function under rotational and translational movements of molecule, F is Hamiltonian of the rotational and translational movements of molecule. Inharmonicity of intramolecular vibrations may neglect for simplification.

For averaging in $U(t)$ it has been taken characteristic functions of Hamiltonian H_{0} as a full system of functions. Then, after set expansion of operator $\exp[-(H_{0} + H') \big/ (k_{B}T)]$ on H' and neglecting of small terms $\Delta\omega n(\omega_{s}) \big/ (k_{B}T)$ where $n(\omega_{s})$ are Plank occupation numbers, it has been obtained following expression:

$$U(t) = Z^{-1} \sum_{nn'} \exp\left(-\beta E^{0}_{n} - i\omega_{s}t\right) \left\langle n \middle| a^{*}_{s}(t) \middle| n' \right\rangle \left\langle n' \middle| a^{+}_{s}(0) \middle| n \right\rangle$$

$$Z = Sp\exp\left(-\beta H_{0}\right), a^{*}_{s}(t) = \exp\left[-i(H_{0} + F)t\right] a_{s}(t) \exp\left[i(H_{0} + F)t\right] \tag{6}$$

where $|n\rangle, E_n^O$ are characteristic functions and values of operator H_0. For obtaining of expression (6) it has been took into account that the F commutes with operators $a_s^+(0)$ and H_0.

For calculation of the matrix element $\langle n|a_s|n'\rangle$ it is necessary to write its equation of motion:

$$-i\frac{d}{dt}\left\langle n\middle|a_s^*\middle|n'\right\rangle = \sum_m [\langle n|H(t)|m\ \rangle\left\langle n\middle|a_s^*\middle|n'\ \right\rangle \exp\left(iE_{mn}^0 t\right) - \\ -\left\langle n\middle|a_s^*\middle|m\ \right\rangle\left\langle m|H(t)|n'\right\rangle \exp\left(iE_{n'm}^0 t\right), \tag{7}$$

where $E_{mn}^0 = E_m^0 - E_n^0$ and $H(t) = [\exp(-iet)]H'[\exp(iFt)]$

Taking into account that the non-diagonal matrix elements of operator H' are equal zero, after integration of the equation (7) it has been obtained:

$$\left\langle n\middle|a_s^*\middle|n'\right\rangle = \left\langle n|a_s(0)|n'\right\rangle \exp\left[-i\int_0^t \Delta\omega_s(t')dt'\right] \tag{8}$$

Here $\Delta\omega_s = [\exp(-iFt)]\omega_s[\exp(iFt)]$ (9)

Substituting equations (8) and (9) in (6) we have obtained:

$$U(t) = (1 + n\omega)\exp\left(-i\omega_s t\right)\exp\left[-i\int_0^t \Delta\omega_s(t')dt'\right] \tag{10}$$

In nematic phase rotational-translational movements is random, because $\Delta\omega(t)$have casual values. Their distribution may consider as Gausian. Usually characteristic times of rotational and translational movements are many greater than time of interactions of intramolecular vibrations. Therefore in expression (4), (10) may neglect the dependence rotational and translational coordinates of molecules on time. Thus it is possible to average on these coordinates with static Gausian distribution function. Science the $\Delta\omega(t)$ isn't depended on time , it has been made the average in equation (4) using method cumulantly averages and limiting by cumulants not over of the second order:

$$i_{\alpha\beta\delta\gamma}(\omega) = \sum_{lmm'} A_{\beta\delta}^{lm}(A_{\beta\delta}^{l_1m'_1})\left\langle D_{mm'}^l(\Omega) D_{m_1m'_1}^{l'_1}(\Omega) P_{1lm'}^s(\Omega)\left[P_{1l_1m'_1}^l(\Omega)\right]^*\right\rangle * \\ *\varphi\left(\omega - \omega_0 - \omega_s\right) \tag{11}$$

where $\varphi = \dfrac{1 + n\left(\omega_s\right)}{\sqrt{2\pi\left\langle\Delta\omega^2\right\rangle}} \exp\dfrac{-\omega^2}{2\left\langle\left(\Delta\omega_s\right)^2\right\rangle}$

Thus it have been received equation for width of band for nematik:

$$\delta_N = \left(2\ln 2\left\langle\left(\Delta\omega_s\right)^2\right\rangle\right)^{\frac{1}{2}}, \tag{12}$$

where $\left\langle (\Delta\omega_S)^2 \right\rangle$ is averaged with static distribution function of values $\Delta\omega_S$ in nematic. The shape of band is Gausian. Really Gausian shape of band are observed also in experiment.

For s/c N, glass phase the translational-rotational movements of the molecules are small. More considerable role is playing spatial heterogeneity of distribution of intermolecular fields connected with freezing translationaly-rotational states of molecules. Then under calculation of width may also neglect the dependence rotational and translational coordinates of molecules on time as in case N-phase. Therefore it is possible to average with static distribution function of values $\Delta\omega_s(t)$ on frizzed nematic.

Thus it have been received equation of width for A-phase:

$$\delta_A = \left[2\ln 2\overline{(\Delta\omega_S)^2} \right]^{\frac{1}{2}} \tag{13}$$

where $\left\langle (\Delta\omega_S)^2 \right\rangle$ was substituted on $\overline{(\Delta\omega_S)^2}$. The line designate the average on frizzed nematic.

Since A-phase was obtained by sharp freezing of nematic then the random various value $\Delta\omega_S$ on all volume of A-phase will be defined by practically such function as and distribution in nematic conditioned by translational-reorientational movements of molecules. Therefore one may wait that $\left\langle (\Delta\omega_S)^2 \right\rangle \approx \overline{(\Delta\omega_S)^2}$. The equality is just with accuracy determined by difference of parameters of the corresponding distribution functions for nematic and solid phases. Then it is correct following equality:

$$\delta_N \approx \delta_A \tag{14}$$

As indicated from Figure 1 this equality is confirmed by experiment. This tells about the nearness of parameters of the distributions mentioned over.

It has been obtained Gausian shape of bands as experimentally as theoretically. Therefore, in these two phases we deal with heterogeneous broadening of spectral bands. It is removing under transition in crystalline state in w hich band width have minimum value (5 cm^{-1})

So contribution of heterogeneous broadening in A and N phases is around 50% and phase transition from A-phase in crystalline state occur at T=203 K (Figure 1). Such sensibility of intramolecular vibrations to transitions "disorder-order" is confirmed in work[1] .

Complex Conformational Composition of Phases

Detailed investigations of the phase transitions dynamics[3] have allowed to obtain additional information about mechanisms of vibrational bands formation in various phases of MBBA (s/c N, N and crystal modifications). These investigations have given possibility to make the correct division of the complicated bands contours in different phases. So, for example, under phase transition from crystal to nematic it had been traced the broadening of the bands components and their insignificance displacements. These factors led to the overlapping of bands and to formation of complicated contours in nematic phase. Investigated band 1164 cm^{-1} is interpreted as bending CCH- vibration[9]. Therefore it is sensible to twisting of aniline ring relative to C=N-C plane. Using the connecting of frequency of bending vibration with twist-angle proposed by Mizuno[10] it may calculate the conformational angles for all investigated phases of MBBA. The analysis shows that the nematic phase presents thermodynamic equilibrium mixture of three conformers fractions with angles 44.4, 50.2 and 59.0. Therefore, the broadening of the bands is connected not only with transition to more disordered medium (nematic), but also with complex conformational structure of MBBA (overlapping of bands connected with the presence of three conformers in nematic phase). Overlapping of bands may lead as to asymmetric (band 1164 cm^{-1}) as to symmetric (band 1594 cm^{-1} bands. The mechanism of broadening connected with complicated conformational composition had been revealed also for phase of s/c N and some crystalline modifications of MBBA.

CONCLUSIONS

It has been obtained by experiment and has been conditioned by theory that the heterogeneous broadening is the dominating mechanism for vibrational bands formation in A and N phases. Although the nature of heterogeneous broadening is different for these phases, the shapes and widths of vibrational bands coincide approximately. The other mechanism of broadening is one conditioned by complex conformational composition of phase states. It is connected with overlapping of vibrational bands corresponding to different conformers.

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