

SPECTRAL AND THERMODYNAMIC PROPERTIES OF CHOLESTERYL MYRISTATE IN THE REGION OF PHASE TRANSITION*

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In this article we report on temperature dependence of Davydov splitting value FTIR spectra study for the in-phase CH₂ rocking vibrations of methylene chains in liquid crystalline cholesteryl myristate (CholC₁₄) for the temperature region from 100 K to the crystal melting point.

A statistic-dynamic model in terms of stochastic equations is used to explain the obtained results. We take into account the damping of vibrational excitons on orientational defects due to excitation of conformational, librational and position disorder degrees of freedom. The explicit expression for the theoretical dependence of Davydov splitting value of vibrational excitons on temperature was considered. Good agreement between the experimental data and the results of such dependence computer simulation is observed.

Key words: Liquid crystals; IR spectra; Davydov splitting; damping of vibrational excitons; conformational transitions; librations; orientation disordering.

1. INTRODUCTION

It is known [1–3] that in long-chain aliphatic crystals in the temperature range below the melting point the molecules can perform the orientational disordered motions of different types. It is clear that any distortions in the periodic location of atoms in the plane perpendicular to the long axis of the molecules should result in some peculiarities of intermolecular interactions. In particular, one could expect changes in the resonance dynamic intralayer interaction (Davydov splitting of vibrational excitons) in the orientational disordered phases.

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Earlier, when studying the effects of the intermolecular interaction and the problems of molecular dynamics in crystals of homologous series of odd-numbered long-chain normal paraffins, α -olefins, *n*-carboxylic acids, cholesteryl *n*-alkanoates and alkyl substituted aromatic compounds by the method of infrared spectroscopy, in particular, the temperature dependence of spectral peak positions for Davydov components of the intramolecular vibrations was observed [1–7]. These spectral components approach each other in the region of the order – orientational disorder phase transition. For nowadays, there is no commonly accepted explanation of the observed temperature dependence.

In this work we report on temperature dependence of Davydov splitting value FTIR spectra study for the in-phase CH₂ rocking vibrations of methylene chains in crystal cholesteryl myristate (CholC₁₄) for the temperature region from 100 K to the crystal melting point.

Also we use mechanisms, which adequately describe the observed effects for cholesteryl myristate as example. These mechanisms are related with the damping of vibrational excitons in crystals due to their interaction with orientational lattice defects, which appear due to the excitation of conformational, librational and position disorder degrees of freedom of organic molecules for the region of transitions in the different liquid crystal phases.

2. RESONANCE DYNAMICAL INTERMOLECULAR INTERACTION IN MOLECULAR CRYSTALS (THEORY)

Here we describe the contribution of the intermolecular interaction effects and molecular dynamics in the orientational disordered phase to the formation of the spectral bands of intramolecular vibrations in the framework of stochastic equations [8–10].

To determine the matrix of frequency oscillations $\hat{\Omega}$ we write the stochastic Hamiltonian of the system in the form:

$$\hat{H}(t) = \hat{H}^{(0)}(t) + V^{(1)}(t). \quad (1)$$

Here $\hat{H}^{(0)}(t) = \hat{P}(t) + V^{(0)}(t)$ is the Hamiltonian of the system, which describes weak influence of the thermostat, $V^{(0)}(t)$ is the stochastic potential energy of interaction between the molecules of the actual system and the bath, $V^{(1)}(t)$ is the stochastic potential energy of interaction between the *N* molecules of the actual system, which cause the Davydov splitting of vibrations. For convenience we assume that it is precisely the resonance dynamic intermolecular interaction that gives the main contribution to the perturbation of frequencies which are the elements of the matrix of oscillations $\hat{\Omega}$ and determines the magnitudes and the structure (symmetry) of the actual system.

Then, taking into account the processes of discrete frequency modulation, adapted Arrhenius law and binomial distribution of the actual system states and having performed averaging over the ensemble, we obtain the average value of the vibration frequency Davydov multiplet i -th component of the j -th normal vibration $\langle \Omega_i^{(j)} \rangle$ in the form [11]:

$$\langle \Omega_i^{(j)} \rangle = \omega_0^{(j)} + \frac{N \cdot \Delta\omega_i^{(j)}}{1 + \sum_{m=1}^p \exp\left(\frac{\Delta S_m T - \Delta E_{Am}}{k_B T}\right)}. \quad (2)$$

Here $\omega_0^{(j)}$ is the frequency of j -th intramolecular vibration, not perturbed by the resonance dynamic intermolecular interaction; $\Delta\omega_i^{(j)}$ is Davydov splitting in account of interaction of selected molecule with i -th molecule of actual system; E_{Am} is the activation energy; k_B is the Boltzmann constant; T is absolute temperature; ΔS_m is variation of entropy at m -transition in the excited state; ΔE_{Am} is variations of activation energy at m -transition in the excited state; m is number of the excited (conformational, librational, positional) state; $N \cdot \Delta\omega_i^{(j)}$ is Davydov splitting value of j -th intramolecular vibration in the low temperature ordered crystalline phase.

3. RESULTS AND DISCUSSION

Davydov splitting $\Delta\nu_{1,2}$ of deformation vibrations of methylene chains in the IR spectra of the long-chain aliphatic molecule crystals is observed in the case of translation non-equivalent packing of chains in the crystal. These packing is described by Vand orthorhombic subcell ($Z = 2$) [12]. The largest value of $\Delta\nu_{1,2}$ is observed for the in-phase rocking vibrations of methylene chains, for the crystals of the long-chain aliphatic compounds it usually equals to 10–12 cm^{-1} [1, 3]. The case of cholesteryl myristate is interesting for us, since in its crystal state (Fig. 1) a dense packing of fully extended trans-isomer methylene chains was observed [13].

It's known [4] that CholC₁₄ ($\text{CH}_3(\text{CH}_2)_{n-2}\text{COOC}_{27}\text{H}_{45}$) temperatures of phase transitions are 308 K (SC-Sm), 345 K (Sm-Chol) and 351 K (Chol-IL), measured in the cooling regime. The value of Davydov splitting: $\Delta\nu_{1,2} = \nu_1 - \nu_2 = 731\text{--}719 \text{ cm}^{-1}$ at $T = 100 \text{ K}$ (Fig. 2), which is characteristic for the odd-number long-chain n -paraffins [1]. In the Sm phase the Davydov splitting value decreases abruptly and is equal to zero in Chol liquid crystal phase (Fig. 3).

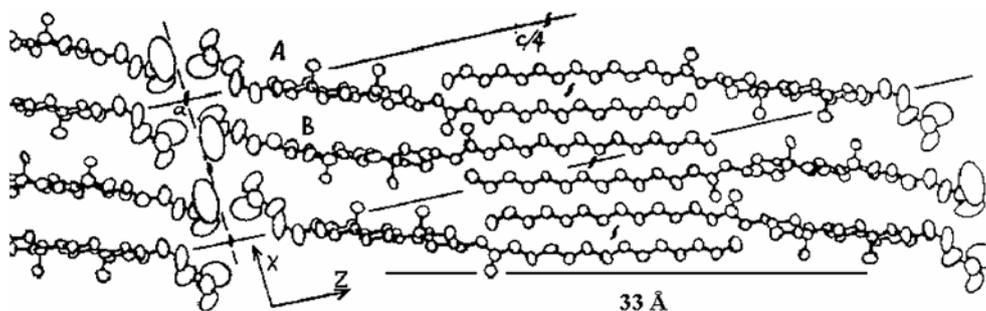
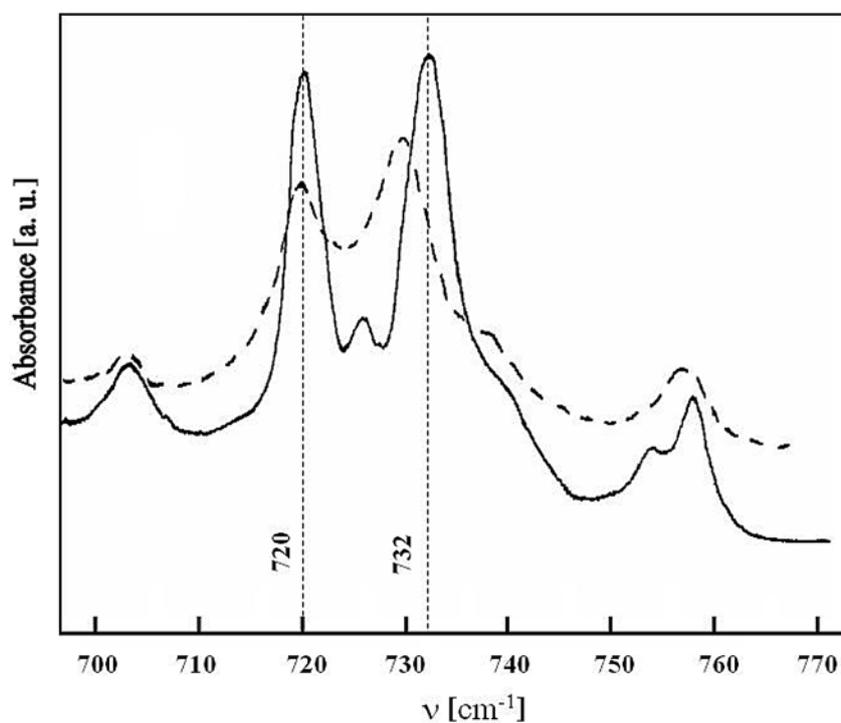


Fig. 1 – Crystal structure of cholesteryl myristate [13].

Fig. 2 – IR-spectra of cholesteryl myristate CHolC14 at $T = 300$ K (dashed line) and $T = 100$ K (solid line).

The theoretical dependence of the Davydov splitting value on temperature from equation (2) has the form ($m = 2$ in Eq. (2)):

$$\Delta\nu_{1,2}^{(j)}(T) = \frac{\Delta\omega_{1,2}^{(j)}}{1 + e^{\frac{\Delta S_1 T - \Delta E_{A1}}{k_B T}} + e^{\frac{\Delta S_2 T - \Delta E_{A2}}{k_B T}}}, \quad (3)$$

where $\Delta\omega_{1,2}^{(j)}$ is the value of Davydov splitting of intramolecular vibrations for

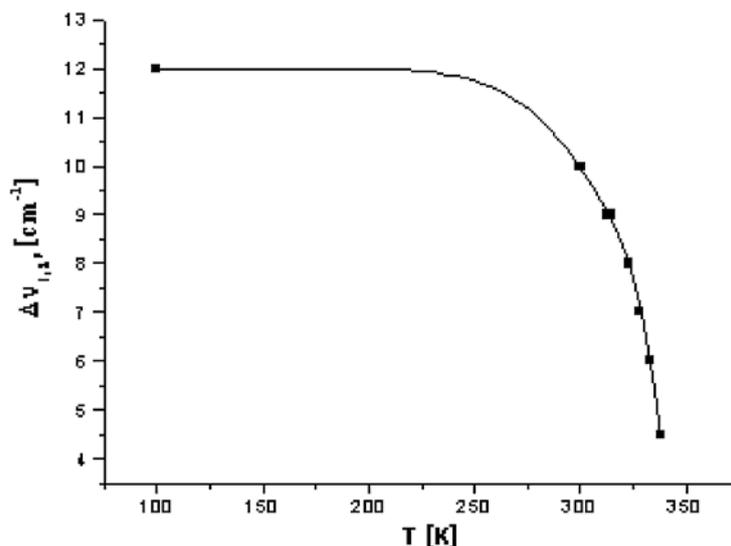


Fig. 3 – Computer simulation for temperature dependence of Davydov splitting value $\Delta\nu_{1,2}$ for CH_2 in-phase rocking vibrations of the molecules in cholesteryl myristate (CholC_{14}) crystal (dots – experiment, curve – theory).

the crystals in the ordered low-temperature monoclinic phase; ΔS_1 , ΔE_1 are, respectively, variations of entropy and activation energy at phase transition SC-Sm; ΔS_2 , ΔE_2 – corresponding energetic parameters at phase transition Sm-Chol.

The results of our computer simulation by formula (3) (line) for observed (dots) Davydov splitting value temperature dependency presented on Fig. 3. Good agreement between the experimental data and the results of such dependence computer simulation is observed. Theoretical estimations of corresponding energetic parameters presented in Table 1.

Table 1

The theoretical estimations of energetic parameters for SC-Sm and Sm-Chol liquid crystalline phase transitions of cholesteryl myristate (CholC_{14}) crystal

ΔE_1 , kJ/mole	ΔS_1 , kJ/mole·K	ΔE_2 , kJ/mole	ΔS_2 , kJ/mole·K
27.9 ± 5.1	0.0797 ± 0.016	177.0 ± 4.8	0.524 ± 0.013

4. CONCLUSIONS

1. In FTIR-spectra for the region of the “order-orientation and position disorder” phase transitions the temperature dependence of Davydov splitting

value for the in-phase CH₂ rocking vibrations of crystalline cholesteryl myristate (CholC₁₄) methylene chain has been observed.

2. A statistic and dynamic model is used, which provides an adequate description of this effect. In the frameworks of this model, the damping of vibrational excitons on defects of different nature takes place. Genesis of such defects is caused by the SC-Sm and Sm-Chol liquid crystalline phase transitions.

3. The theoretical analysis of the effects of resonance dynamical intermolecular interactions on the spectra of intramolecular vibrations of the crystals was performed in the terms of stochastic equations, taking into account the SC-Sm and Sm-Chol disordering of the crystalline lattice. Computer simulations of such dependence were performed and theoretical estimations of corresponding energetic parameters of liquid crystalline phase transitions were obtained. Good agreement between the experimental and computer simulation results was obtained.

4. For the first time, this theory has been applied to the description of the mobility of the long-chain methylene (ether) fragments in CholC₁₄ molecules. The first phase transition (SC-Sm) is assigned to the appearance of orientational disordering, and the second one (Sm-Chol) – to the changes in the molecule conformations.

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