
OPTICAL
PROPERTIES

Fourier Transform Infrared Spectroscopic Study of the Kinetics of a First-Order Phase Transition in Tridecanoic Acid $\text{CH}_3(\text{CH}_2)_{11}\text{COOH}$

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Abstract—The structural changes in crystalline lamella cores of tridecanoic acid $\text{CH}_3(\text{CH}_2)_{11}\text{COOH}$ during heating in the range from the temperature $T_1 = 13.5^\circ\text{C}$ to $T_2 > T_m = 41.6^\circ\text{C}$ have been investigated using Fourier transform infrared spectroscopy. The behavior of the bands of rocking (in the region of 720 cm^{-1}) and bending (in the region of 1470 cm^{-1}) vibrations of CH_2 groups in tridecanoic acid methylene segments has been analyzed. It has been shown that, in the first-order phase transition region ($T_{s-s} \sim 36^\circ\text{C}$) within a narrow temperature range ($\Delta T_1 \leq 1\text{ K}$), there is a gradual transformation of the initial triclinic subcell into the hexagonal subcell. The mechanism of this transition has been considered in terms of the theory of diffuse first-order phase transitions.

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1. INTRODUCTION

It is known [1, 2] that, during heating–cooling cycles of different long-chain molecular crystals (LCMC) (*n*-alkanes, *n*-alkane alcohols, α , ω -alkane diols, mono- and dicarboxylic alkane acids, and others), there can occur two types of phase transitions:

(1) a first-order solid phase (structural) transition (PT-1) at temperatures significantly below the melting temperature T_m , and

(2) a second-order phase transition (PT-2) of the order–disorder type due to the melting of crystals at the temperature T_m .

The differential scanning calorimetry (DSC) investigations demonstrated [2–4] that, in long-chain molecular crystals, first-order phase transitions occur within very narrow temperature ranges ΔT , but different from zero, as it should be in the case of perfect single crystals [5]. Such transitions with $\Delta T \geq 1\text{ K}$ are called the diffuse first-order phase transitions and denoted as the Λ transitions [6–8].

For the description of diffuse phase transitions, it was proposed to use the self-consistent field theory [7], according to which the first-order structural phase transition is considered as the fluctuation formation of nanosized nuclei of a new phase in the volume of the initial phase, followed by the growth of nuclei during

short periods of time. As a result, the new phase extends throughout the volume of the initial phase with a variation in the temperature within a narrow range $\Delta T \geq 1\text{ K}$.

For the purpose to prove the validity of this approach in the study of long-chain molecular crystals, in the present work, the structural transformations in the first-order phase transition region during heating of molecular crystals of monocarboxylic tridecanoic acid $\text{CH}_3(\text{CH}_2)_{11}\text{COOH}$ have been investigated using Fourier transform infrared (FTIR) spectroscopy.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

We investigated commercial tridecanoic acid products without further purification. For FTIR measurements, thin films were prepared by drying a 5% solution of tridecanoic acid in chloroform on the surface of KBr plates at room temperature. Further, the films in the gap between two KBr plates were placed in a thermo cuvette, heated to a temperature above the melting point (for our samples of the acid, $T_m = 314.6\text{ K}$ [3]), and then slowly cooled to room temperature. The thickness of the samples was equal to 10–20 μm . The FTIR spectra in the frequency range from

400 to 5000 cm^{-1} were recorded on a Bruker IFS-88 spectrometer (Bruker, Germany) under a stepwise increase in the temperature with a step of 0.2 K before the approach to the first-order phase transition region and with a step of 0.1 K within the first-order phase transition region. The temperature was measured on a differential chromel–copel thermocouple with an accuracy of 0.05 K.

Before recording the spectrum, the sample was kept for 10 min at a specified temperature until the thermal equilibrium was reached. The number of signal acquisitions was 50.

3. RESULTS AND DISCUSSION

It was established using the optical and electron microscopy investigations [9, 10] that macroscopic long-chain molecular crystals, including those of monocarboxylic acids, consist of stacks of thin lamellar (plate-like) crystals laminated on each other, the thickness (in nanometers) of which is comparable to the length of the acid molecule. Three-dimensionally ordered crystalline cores of a single lamella are formed from methylene sequences. Alternating layers between the crystalline cores in stacks consist either of two contacting terminal methylene groups of the adjacent lamellae connected to each other by van der Waals forces or of cyclic dimers that arise due to the formation of hydrogen bonds between the terminal carboxyl groups of the molecules in the adjacent lamellae [11]. X-ray diffraction investigations performed in the ranges of small and large diffraction angles make it possible to reveal specific features in the stacking of lamellae with respect to each other, types of mutual arrangement of molecules with respect to each other, and types of mutual arrangement of molecules in crystalline cores of individual lamellae.

In molecular crystals, there are two types of crystal cells:

(1) the main cell (main cell), which characterizes the way of stacking of lamellae with respect to each other [12];

(2) the subcell, which describes the character of the packing of molecules with respect to each other in the crystalline core of an individual lamella [13].

The main cells, as well as the subcells, can be orthorhombic, monoclinic, or triclinic, but not necessarily belong to the same crystal system simultaneously, because in all long-chain molecular crystals containing an odd number of carbon atoms in a chain, the molecules in the core are arranged at an angle with respect to the surface of lamellae.

Information about the type of main cells is usually obtained from comparison of small-angle X-ray diffraction data taking into account geometrical dimensions of the molecules [1, 2]. Experimental data on the type of subcells can be obtained not only on the basis of large-angle X-ray diffraction data, but also from the

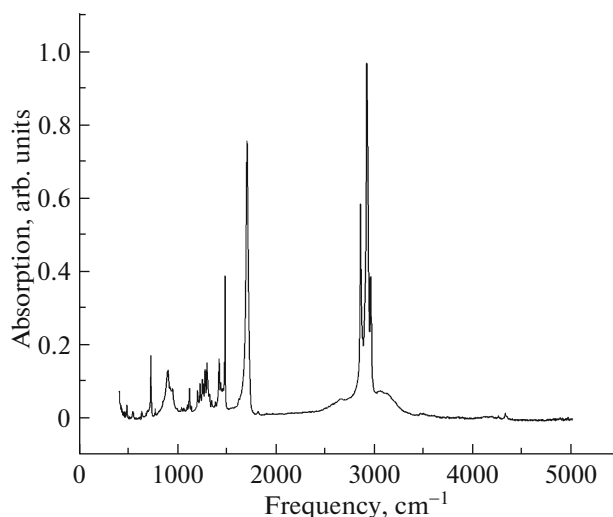


Fig. 1. IR absorption spectrum of tridecanoic acid at room temperature over the entire frequency range (400–5000 cm^{-1}).

analysis of IR absorption spectra corresponding to different types of vibrational modes of extended methylene sequences in crystalline cores of lamellae [14–16]. Moreover, important information about the structure of interlamellar layers can be obtained from analysis of specific IR absorption bands that correspond to vibrational modes of terminal CH_3 groups, as well as to different vibrational modes of carboxyl groups combined into cyclic dimers.

Thus, the analysis of the behavior of IR absorption bands with a variation in the temperature will make it possible to trace the transformations of the lamellar structure, including those upon the first-order phase transitions, which occur in the cores of lamellae and in their surface layers.

In this paper, we have considered changes in the crystalline part of the lamellae of tridecanoic acid during heating of samples in the range from the temperature of 13.5°C to the melting point. The structural changes occurring in the surface layers will be considered in subsequent papers.

The FTIR spectrum of tridecanoic acid at room temperature in the frequency range of 400–5000 cm^{-1} is shown in Fig. 1. It can be seen from this figure that, in the spectrum, there are intense characteristic absorption bands corresponding to different vibrational modes of methylene sequences, as well as to the vibrations of terminal groups. The frequencies of the absorption bands observed in this spectrum are in agreement with the data available in the literature (see [17, 19] and numerous references therein).

In this paper, we will analyze the thermal behavior of only the absorption bands that correspond to the rocking (in the region of 700–720 cm^{-1}) and bending (in the region of 1460–1480 cm^{-1}) vibrations of the

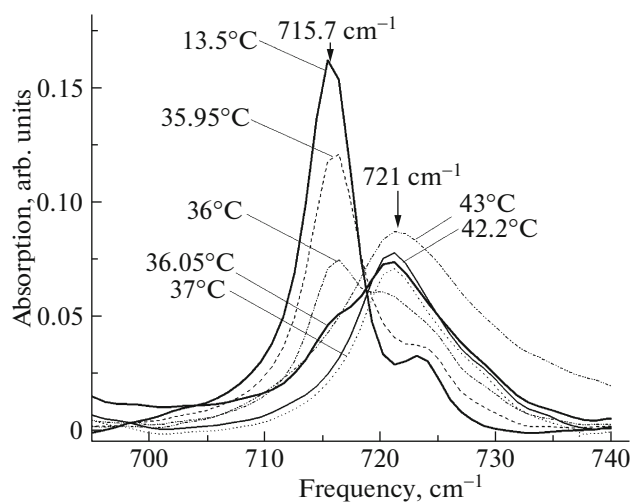


Fig. 2. Temperature dependences of the absorption spectrum of tridecanoic acid in the region of rocking vibrations.

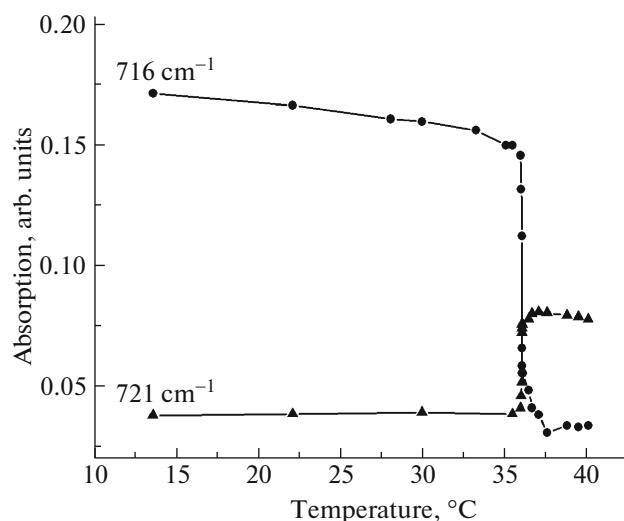


Fig. 3. Temperature dependence of the optical density of tridecanoic acid at maxima of the absorption bands of rocking vibrations.

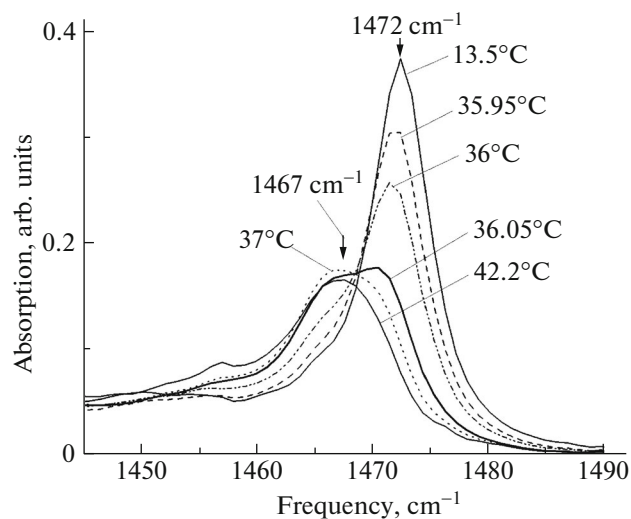


Fig. 4. Temperature dependences of the absorption spectrum of tridecanoic acid in the region of bending vibrations.

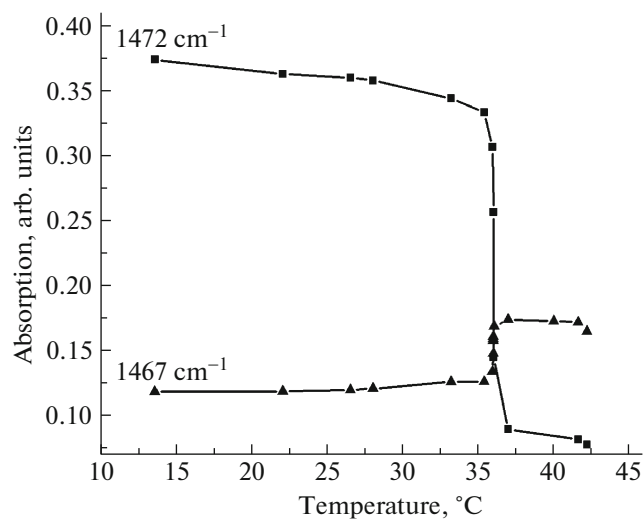


Fig. 5. Temperature dependence of the optical density of tridecanoic acid at maxima of the absorption band of bending vibrations.

CH_2 groups in methylene sequences in the crystalline cores of the lamellae. These data will allow us to analyze the character of structural transformations occurring in subcells of tridecanoic acid crystals during the development of the first-order phase transition, because all the absorption bands observed in the commonly used frequency range ($400\text{--}5000\text{ cm}^{-1}$) are attributed only to local variations in fairly short methylene sequences [20].

Figures 2–5 show the temperature changes of the IR absorption spectrum, which correspond to the bands of the rocking (Figs. 2, 3) and bending (Figs. 4,

5) vibrations of the CH_2 groups in the crystalline cores of the tridecanoic acid lamellae.

It is known [14–20] that, based on the analysis of the specific features in the behavior of the absorption bands in frequency ranges of the rocking and bending vibrations of the CH_2 groups, it is possible to draw a conclusion about the character of the mutual stacking of methylene segments, i.e., about the type of symmetry of the crystal subcells and the symmetry changes both in the process of crystallization and during the first-order and second-order phase transitions of different long-chain molecular crystals.

The presence of single intense absorption bands at room temperature in the IR spectrum at frequencies $\nu = 715.7 \text{ cm}^{-1}$ (rocking vibrations of CH_2 groups, Fig. 2) and $\nu = 1472 \text{ cm}^{-1}$ (bending vibrations of CH_2 groups, Fig. 4) suggests that, in the crystalline cores of the lamellae formed in our samples, which were prepared by cooling of the tridecanoic acid melt to room temperature, the methylene sequences form subcells with the triclinic symmetry.

In [21], based on the X-ray diffraction investigations, it was shown that the crystallization of tridecanoic acid from the melt and from solutions in different solvents, in contrast to many homologs of monocarboxylic acids, always leads to the formation of crystals of the *A'* type (according to the classification proposed in [22]), in which both the main cell and the subcell have the triclinic symmetry.

In triclinic subcells, the axes and planes of methylene trans-zigzags of all the molecules are parallel to each other. Since, in the triclinic primitive cell, there is one effective centrosymmetric molecule containing two methylene groups, the symmetry of IR vibrations in this case will be approximately the same as for the individual straightened molecule with the C_{2h} symmetry. Therefore, for each of the fundamental vibrations, including the rocking and bending vibrations, there should be only one component (the Davydov splitting observed in the orthorhombic subcell is absent [20]).

In the literature, there are no IR spectroscopic data for tridecanoic acid in the region of bending and rocking vibrations of CH_2 groups. In [18], the author investigated only the region of the spectrum, which includes absorption bands assigned to carboxyl groups combined into dimer rings.

Earlier studies of other homologs of *n*-monocarboxylic acids ($\text{C}_{18}\text{H}_{35}\text{O}_2$ [23] and $\text{C}_{16}\text{H}_{33}\text{O}_2$ [24]), as well as a series of methyl-branched octadecanoic acids [25, 26] and an unsaturated *trans*-8-octadecanoic acid [27], revealed triclinic subcells, for which the frequencies corresponding to single peaks in the region of rocking and bending vibrations are listed in the table. This table also presents data on the frequencies of the rocking and bending vibrations for a series of odd *n*-alkanes, which crystallize with the formation of triclinic subcells from methylene sequences [28–31]. Noteworthy is the wide variation in the values of the frequencies of both the rocking ($715\text{--}722 \text{ cm}^{-1}$) and bending ($1468\text{--}1475 \text{ cm}^{-1}$) vibrations in different compounds, in which the methylene sequences in the crystallized state form a triclinic subcell.

In [19, 20, 28, 32–34], it was noted that there is a good correlation between the position of the absorption band in the frequency region $\nu \sim 720 \text{ cm}^{-1}$ and the type of the subcell formed from methylene sequences. This is determined by the dependence of the potential energy of the molecules in the equilibrium crystal field, which, in long-chain molecular crystals, is

caused primarily by the intermolecular van der Waals attractive forces in subcells. In [12, 21, 34], it was shown that the densest packing is characteristic of triclinic subcells, because, in this case, the mutual displacement of the molecules can occur along all vectors of the subcell, which provides the strongest Van der Waals interaction.

The possibility of the formation of other polymorphic forms (orthorhombic, monoclinic, hexagonal, etc.) and polymorphic transformations, apart from the van der Waals interaction, depends on the symmetry of the molecule; the type of packing of terminal groups; the length of methylene sequences, the presence of polar groups, double bonds, and branches; crystallization conditions, external factors (temperature, pressure), etc.

The enhancement of the intermolecular interaction potential in triclinic subcells leads to a shift of the bands of the fundamental rocking vibrations toward lower frequencies. This effect is usually observed during transitions from the melt or solutions of long-chain molecular crystals to the triclinic crystal phase. In both cases, the IR spectrum is characterized by single bands, but the frequencies of vibrations at the maxima of these bands differ significantly from each other (see table). Usually, in the melts or solutions of *n*-alkanes, the frequencies of the rocking and bending vibrations have the values of $\nu_{\text{rock}}(\text{CH}_2) \cong 720\text{--}722 \text{ cm}^{-1}$ and $\nu_{\text{bend}}(\text{CH}_2) \cong 1467 \text{ cm}^{-1}$. According to our investigations of tridecanoic acid, these frequencies have the following values: $\nu_{\text{rock}}(\text{CH}_2) \cong 715.7 \text{ cm}^{-1}$ and $\nu_{\text{bend}}(\text{CH}_2) \cong 1472 \text{ cm}^{-1}$, which differ substantially (see table) from the results obtained in [23, 24] for *n*-monocarboxylic acids with an even number of carbon atoms.

The discrepancies between the data presented in the table can be explained by different degrees of packing density of methylene sequences in the studied samples, depending on the methods used for their preparation, as well as by the resolution capabilities of IR spectrometers used by the authors. The data presented in the table also demonstrate that, as expected, the weakening of the van der Waals interaction in triclinic cells due to the methyl branching [25, 26] or upon the introduction of double bonds [27] into methylene sequences (which is accompanied by a decrease in the melting temperature T_m in these samples) leads to a shift of the frequency $\nu_{\text{rock}}(\text{CH}_2)$ toward higher frequencies, i.e., toward the range $\nu_{\text{rock}}(\text{CH}_2) \cong 719\text{--}720 \text{ cm}^{-1}$.

The analysis of the data presented in Fig. 2 shows that the intensity in the maximum of the band at the frequency $\nu = 715.7 \text{ cm}^{-1}$ decreases only slightly during heating in the temperature range from 13.50 to 35.95°C (Figs. 2 and 3), but already at $T = 36.00^\circ\text{C}$, i.e., with a change in the temperature by only $\Delta T = 0.05^\circ\text{C}$, there are fundamentally important changes in

Frequencies of rocking and bending vibrations in different compounds with triclinic (nos. 1–13) and hexagonal (nos. 14–19) sub-cells

No.	Compound, chemical formula	References	ν CH ₂ -rock	ν CH ₂ -bend
Acids				
1	Tridecanoic acid CH ₃ (CH ₂) ₁₁ COOH	[Data of the authors of this paper]	715.7	1472
2	Octadecanoic acid CH ₃ (CH ₂) ₁₆ COOH	[23]	717	1468
3	Heptadecanoic acid CH ₃ (CH ₂) ₁₄ COOH	[24]	718	1468
4	Series of methyl-branched octadecanoic acids	[25, 26]	720	–
5	Unsaturated <i>trans</i> -8-octadecanoic acid	[27]	719	1469
<i>n</i> -Alkanes—solid				
6	C ₁₆ H ₃₄	[28]	715	–
7	C ₂₂ H ₄₆			
8	C ₂₄ H ₅₀			
9	C ₁₈ H ₃₈	[29]	718	1472
<i>n</i> -Alkanes—melt				
10	C ₂₁ H ₄₄	[19]	720	–
11	C ₂₃ H ₄₈	[32]	721	
<i>n</i> -Alkanes—low MW, liquid at T_{room}				
12	$n = 10\text{--}15$	[33], [9]	722	1469
<i>n</i> -Alkanes—liquids or solutions				
13	$n = 6\text{--}34$	[34], [10]	720	1469
<i>n</i> -Alkanes—hexagonal subcell				
14	C ₂₄ H ₅₀	[35]	720	1466
15	C ₂₈ H ₅₈			
16	C ₂₉ H ₆₀			
17	C ₁₉ H ₄₀			
18	C ₂₁ H ₄₄			
19	C ₁₇ –C ₂₇	[36, 37], [13, 14], [19]	720–721	1468

the shape of the band at $\nu = 715.7 \text{ cm}^{-1}$: the intensity in the maximum of the band at $\nu = 715.7 \text{ cm}^{-1}$ sharply decreases, and the band itself is split as a result of the appearance of a well-pronounced additional maximum at the frequency $\nu = 721 \text{ cm}^{-1}$ (Figs. 2, 3). With a further gradual increase in the temperature up to $T = 37^\circ\text{C}$, the band at $\nu = 715.7 \text{ cm}^{-1}$ completely disappears, and instead of it, there appears a broad band with a maximum at $\nu = 721 \text{ cm}^{-1}$.

In [19, 20, 35–37], it was shown that, for *n*-alkanes in the solid state, the single band at the frequency $\nu = 720 \text{ cm}^{-1}$ (see table) is characteristic of subcells with the hexagonal symmetry, which were considered for the first time in [38].

In this case, it is common practice to consider the dense packing of macromolecules approximated by effective cylindrical rods, because it is assumed that the planes of the chains can rotate with respect to their axis.

The uncorrelated oscillations with a limited amplitude relative to the middle position with the minimum displacement of the molecular axes lead to a statistical misorientation of the mutual arrangement of the planes of macromolecules in the matrix of the crystalline core of the lamellae. In this case, the van der Waals contacts between the neighbors are retained, which provides (primarily due to the attractive forces) the preservation of the sample in the solid phase.

The chains in the primitive hexagonal subcell are arranged in such a way that (as in the triclinic subcell) there is one effective molecule, i.e., each fundamental vibration has only one component (Davydov splitting of the vibrational bands is absent). In the hexagonal subcell, the interchain van der Waals interaction is significantly weakened as a result of the increase in the interchain distances due to the thermal expansion, which leads to a shift of the bands of rocking vibrations to the frequency $\nu = 720 \text{ cm}^{-1}$ and bending vibrations to $\nu = 1466\text{--}1468 \text{ cm}^{-1}$.

It is characteristic that the position of the maximum of the band at $\nu = 720 \text{ cm}^{-1}$ (Fig. 2), its intensity and half-width do not significantly change with further heating of the sample up to the melting temperature of tridecanoic acid ($T_m = 41.6^\circ\text{C}$), which apparently is caused by relatively small changes in the parameters of the hexagonal subcell in this temperature range.

The analysis of the behavior of the bands of bending vibrations of the CH_2 groups in the frequency range of $1450\text{--}1490 \text{ cm}^{-1}$ (Figs. 4 and 5) demonstrated that the character of the transformation of the IR spectrum in the first-order phase transition region is completely similar to that in the case of rocking vibrations. More specifically, with an increase in the temperature, the band at $\nu = 1472 \text{ cm}^{-1}$, which is characteristic of triclinic subcells, also gradually transforms into the band at $\nu = 1467 \text{ cm}^{-1}$, which indicates the formation and a gradual increase in the number of nuclei with the hexagonal packing of methylene sequences in the crystalline core of the lamellae. This transition also occurs quite rapidly in the same temperature range as in the case of rocking vibrations (compare Figs. 3 and 5).

At the same time, at temperatures significantly higher than the melting point T_m , in particular, at $T = 43^\circ\text{C}$ (Fig. 2), there is a further transformation of the band at $\nu = 720 \text{ cm}^{-1}$. This single band becomes substantially more broadened, but the position of its maximum remains virtually unchanged. The significant increase in the half-width of the bands at $T > T_m$ is caused by the enhancement of the rotational ability of the molecules, as well as by the increase in the number of irregular gauche defects of different types. However, in the liquid state, also, the interchain distances in the hexagonal cell are approximately equal to each other [19].

In [32, 39, 40], it was shown that, in n -alkanes with a variable number of CH_2 groups, which are in different phase states (in the liquid state with small values of $n = 6\text{--}15$; in melts or solutions with the values of n up to $n = 34$), the frequencies of the rocking and bending vibrations in all cases are equal to $\nu = 720\text{--}722 \text{ cm}^{-1}$ and $\nu = 1467 \text{ cm}^{-1}$, respectively (see table). Therefore, in all the cases under consideration, the effective potentials of intermolecular interactions, which are weakened in comparison with those for other subcells, prove to be approximately equal to each other. This explains the essential constancy of the frequency of rocking vibrations $\nu = 720 \text{ cm}^{-1}$, which is characteristic of methylene trans-sequences with the number of CH_2 groups $n \geq 4\text{--}5$ [14, 39].

4. CONCLUSIONS

It can be concluded that, using FTIR spectroscopy during the heating of tridecanoic acid samples, we

recorded the dynamics of a diffuse first-order structural phase transition, namely, a gradual transformation of the initial triclinic subcell into the hexagonal subcell within a very narrow temperature range $\Delta T \leq 1 \text{ K}$.

The mere fact that there is a transition from one type of subcell to another one was observed previously in numerous studies [1, 18] for many types of long-chain molecular crystals, beginning from the early works on X-ray diffraction [38].

In our investigations using FTIR spectroscopy, we revealed the fact not described previously in the literature that, in tridecanoic acid crystals within a narrow temperature range, two types of subcells can coexist simultaneously, namely, the initial triclinic and new, nucleating, hexagonal subcells, as well as the fact of increase in the number of hexagonal subcells due to the gradual "eating" of initial triclinic subcells, as it is considered in the theory of diffuse first-order phase transitions [7].

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