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## Specifics of n-Alkanes Polymorphism during Temperature Phase Transitions

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The differences in the kinetics of the polymorphic transformation of crystallographic phases of n-alkanes of different parities: tricosane C<sub>23</sub>H<sub>48</sub> and tetracosane C<sub>24</sub>H<sub>50</sub> were studied using Fourier transform infrared spectroscopy. It has been established that a first-order structural phase transition occurs with a change in the symmetry type of the initial orthorhombic or triclinic subcells to hexagonal ones through the formation of a number of intermediate rotator phases (*R<sub>I</sub>*, *R<sub>II</sub>*, *R<sub>V</sub>*) depending on the symmetry of the molecules (cis or trans).

**Keywords:** n-alkanes, lamellae, phase transitions, rotator phases, IR spectroscopy.

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### 1. Introduction

Normal alkanes (with the general formula C<sub>*n*</sub>H<sub>2*n*+2</sub>) are representatives of the family of long-chain molecular crystals (LCMCs) with the simplest chemical structure. Currently, it is possible to industrially synthesize n-alkanes with *n* from 10 to 60 with an unusually high degree of purity and monodispersity ≥ 95%, which indicates the preservation of a certain number of carbon atoms in the sample molecules with accuracy within one C–C-bond. Besides, the absence of structural and conformational defects allows us to consider such n-alkanes as convenient models for analyzing phase transitions (PTs) and establishing structure-property relationships at a quantitative level.

It is known [1,2] that when LCMC is heated during the transition from solid state to liquid state, two main temperature phase transitions are observed:

1) first-order solid-solid (structural) phase transition (PT-1) at temperature below the melting temperature *T<sub>m</sub>* associated with change in the symmetry of the molecular packing in the crystalline regions of the lamellae;

2) second-order phase transition (PT-2) of the order-disorder type, accompanied by the melting of polycrystals at *T<sub>m</sub>*. It is characteristic that when LCMC is heated, the crystal lattice first „loosens“ i.e. due to thermal expansion the distances between molecules in one lamella and between adjacent lamellae in stacks increase, but long-range order in the stack of molecules is maintained (PT-1); then the crystal lattice is completely destroyed, i.e. crystal melting occurs (PT-2).

The DSC method demonstrated that in n-alkanes PT-1 phase transition develops in fairly narrow temperature ranges  $\Delta T \approx 1\text{--}2^\circ\text{C}$ , but different from zero, as it should be in the case ideal single crystals [3]. Such transitions with

$\Delta T \geq 1^\circ\text{C}$  are called as diffuse phase transitions of the first order [4,5]. To analyze diffuse PT-1 a self-consistent field theory [5] was proposed, which considers the change in the phase state of the crystal according to a heterogeneous mechanism through the occurrence of fluctuation nuclei of a new phase of nanometer dimensions in the bulk of the initial phase on defects of various nature.

In addition to the main phase transitions in n-alkanes, there are also less energy-consuming transitions between low-studied intermediate states observed in temperature regions near PT-1. Identification of the features of the polymorphic rearrangement of the crystal structure of LCMC n-alkanes during temperature PTs raises the need for additional fundamental studies due to the lack of literature data. In this regard, to establish the step-by-step mechanism of structural transformations, studies are carried out on the kinetics of the development of the first-order solid-solid phase transition (PT-1) [6–8]. In this paper the main attention is paid to comparing the kinetics of PT-1 in n-alkanes of different parities due to the difference in the symmetry of molecular packing in the main structural elements lamellae with vertical and inclined chains.

Using optical and electron microscopy methods, it was established [9,10] that polycrystals of long-chain n-alkanes consist of spatially misoriented extended macroscopic stacks of numerous thin plate-like (lamellar) nanocrystals layered on top of each other, the thickness of which (units of nm) is comparable with the length of the n-alkane molecule. Three-dimensionally ordered crystalline cores of individual lamellae are formed by short trans-sequences of methylene CH<sub>2</sub> groups due to weak van der Waals forces. Alternating layers of slightly lower density between adjacent lamellae in stacks include end methyl CH<sub>3</sub> groups in contact with each other, also interacting due to van der Waals forces.

X-ray diffraction studies [6,7] in the regions of wide and small diffraction angles make it possible to reveal the nature of the relative arrangement of molecules in the crystalline cores of individual lamellae, as well as the features of the crystallographic arrangement of the lamellae relative to each other. In n-alkane crystals, two types of crystallographic cells are considered [11–13]: 1) the main cell, which characterizes the way the lamellae are stacked relative to each other in stacks, and 2) the subcell, which describes the nature of the stacking of the methylene trans-sequences in the crystalline cores of individual lamellae.

Further in the article the trans- or cis-symmetry of the individual molecule means the difference in the arrangement of the end methyl  $\text{CH}_3$  groups in n-alkanes of different parities: trans-symmetry is characterized by the end groups orientation on opposite sides of the trans-zigzag axis in even n-alkanes, cis-symmetry is characterized by the end groups orientation on one side in odd n-alkanes.

Depending on the symmetry (trans or cis) of individual n-alkane molecule, its length and the crystallization conditions of the sample, both main cells and subcells can be triclinic, orthorhombic, monoclinic or hexagonal, but not necessarily of the same symmetry at the same time. Under normal crystallization conditions n-alkanes with even number of methylene groups  $6 \leq n \leq 26$  form triclinic main cells and subcells, and with  $28 \leq n \leq 36$  — monoclinic main cells with orthorhombic subcells, while with odd  $9 \leq n \leq 45$ , 61, 65, 69 and even  $n \geq 38$  — structures with orthorhombic main cells and subcells [14,15]. Even-odd differences are associated with the type of symmetry of molecules (trans or cis), which is significantly manifested in the packing of end  $\text{CH}_3$  groups and leads to the appearance of inclined phases, which are more energetically favorable specifically for even chains. Thus, in n-alkanes containing an even number of carbon atoms in the chain, the molecules in the lamella cores are located at a certain angle to the base planes of the end groups, while with odd number they are perpendicular to them. Along with this, n-alkanes near the melting point exhibit either a true hexagonal phase, which was noticed already in the 30s of XX century [16,17], or its distorted modifications [18]. An important feature of the high-temperature hexagonal phase is the possibility of the occurrence of hindered discrete rotation of molecules around their main axes.

The parameters of subcells are determined based on the analysis of wide-angle X-ray diffraction patterns, while information about the type of the main cell is usually obtained by comparing wide- and small-angle X-ray diffraction data, taking into account the geometric dimensions of the molecules, the inclined or vertical arrangement of chains in individual lamellae as well as the presence of a slight displacement of the molecules relative to each other in adjacent lamellae, necessary to ensure the tightest contact of the end groups. Based on X-ray diffraction studies [6,7] of n-alkanes, it is shown that in most cases, during PT-1 a transition occurs from the initial crystallographic symmetry of elementary subcells in the crystalline cores

of nanolamellae to the rhombohedral (hexagonal) packaging of molecules.

The determination of the mechanism of the structural phase transition and the kinetics of its development are of particular interest, data on them can be obtained using Fourier transform infrared (FTIR) spectroscopy. IR spectroscopy makes it possible to monitor local structural transformations of n-alkanes during heating, since the frequencies of the IR absorption bands of fundamental vibrational modes from extended methylene trans-sequences in the crystalline cores of the lamellae depend on the type of symmetry of the subcells [19–22]. Besides, modern FTIR spectrometers make it possible to obtain spectra from n-alkanes with high-resolution in short periods of time.

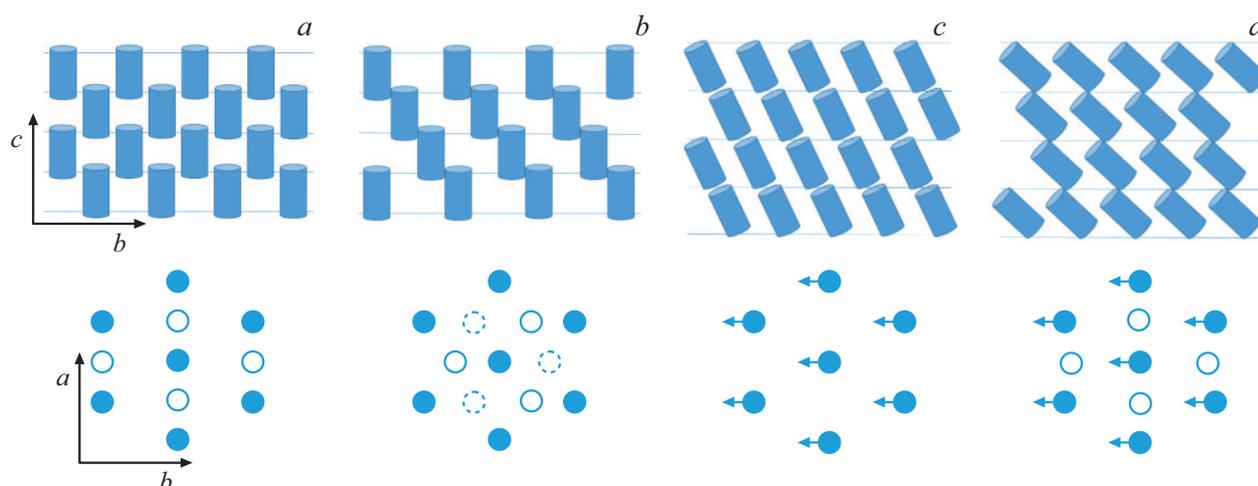
As noted earlier, in most cases, initial subcells with any type of symmetry transform into hexagonal ones when heated. The important task is to study the features of PT development depending on the initial structure of the crystal.

## 2. Structure of rotator-crystalline phase

In early papers [17] according to the structural polymorphism of n-alkanes, the concept of rotator phases ( $R$ ) was introduced. These phases make it possible to characterize various intermediate states between crystal and isotropic liquid associated with the occurrence of molecular rotation around their main axis. In further studies [23,24] the existence of five possible rotator  $R$  phases was determined, most fully observed during the cooling of n-alkanes from liquid state to completely crystallized state. It turned out that the process of rearrangement of n-alkanes during PT-1 is multistage process. With temperature increasing, any combination of several phases shall be realized in the following order: crystal  $\rightarrow R_V \rightarrow R_I \rightarrow R_{II} \rightarrow R_{III} \rightarrow R_{IV} \rightarrow$  liquid, but the complete sequence of phases was not yet experimentally observed for any n-alkane.

Note that during heating there are difficulties in temperature resolution of  $R$  phases, due to the presence of temperature hysteresis for solid-solid phase transition PT-1 in heating-cooling cycles. As a result, currently there is no reliable data on the structures of rotator-crystalline states that arise during heating.

The structural features of  $R$  phases can be characterized as follows (Table and Figure 1) [23–28]. For clarity, in Figure 1 the trans-sequences in the cores of the lamellae are presented in the form of rigid cylindrical rods. In the structure  $R_I$  the molecules are vertical, and the lattice is distorted hexagonal (with face-centered orthorhombic main cells and subcells) with a two-layer sequence of lamellae arrangement of ABAB-type (Figure 1, *a*). The phase  $R_{II}$  is also characterized by vertically arranged molecules in lamellae with a three-layer lamellae arrangement ABC and true hexagonal symmetry of the molecules packing (with rhombohedral main cells and subcells) (Figure 1, *b*). Phases  $R_{III}$  and  $R_{IV}$  have triclinic and monoclinic structures, respectively, with almost hexagonal packing of molecules in lamellae stacked one on top of the other (AAA) (Figure 1, *c*). Phase  $R_V$  has



**Figure 1.** Schematic image of arrangement of lamella layers in phases: (a)  $R_I$ , (b)  $R_{II}$ , (c)  $R_{IV}$  and (d)  $R_V$ . The linear trans-sequences of the molecules are presented in the form of cylindrical rods. Circles indicate a top view: filled circles represent molecules in the first layer of the structure, unfilled circles — in the second layer, dotted circles (b) represent the third layer of three-layer lamellar structure. Arrows indicate direction of molecules inclination in layers.

Basic characteristics of rotator phases

Rotator phase	$R_I$	$R_{II}$	$R_{IV}/R_{IV}$	$R_V$
Arrangement of lamellae	ABAB...	ABC...	AAA...	ABAB...
Subcell	FCO	RH	T/M	FCO
Cell	FCO	RH	T/M	M
Space group	$F_{mmm}$ (69)	$R\bar{3}m$ (166)	?	$Aa$ (9)
Number of equiprobable molecular orientations	4 ( $180^\circ$ turn + reflection)	6 ( $120^\circ$ turns + reflection)	?	2 ( $180^\circ$ turn)

Note \*: Designation of elementary cells: FCO — face-centered orthorhombic; RH — rhombohedral; T — triclinic, M — monoclinic.

the same subcell distortions as phase  $R_I$ , but the lamellae are arranged as in a monoclinic structure with ABAB arrangement (Figure 1, d).

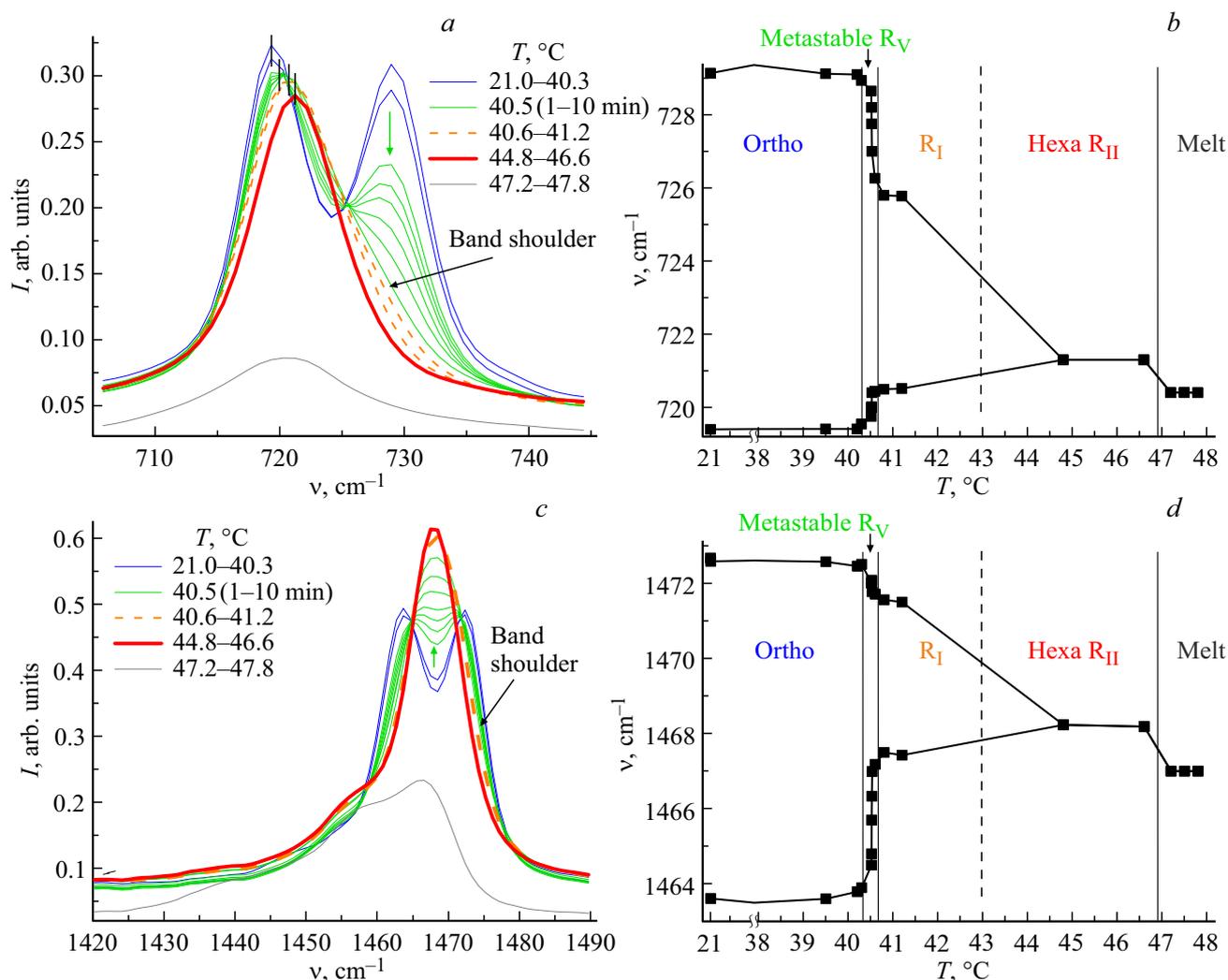
It is shown [23] that for *n*-alkanes with chain lengths  $n < 27$  carbon atoms, the common phases are crystal  $\rightarrow R_I \rightarrow R_{II} \rightarrow$  liquid. In chains with  $n \geq 27$  rearrangements are carried out according to the scheme: crystal  $\rightarrow R_{II} \rightarrow R_{IV} \rightarrow$  liquid. In alkanes with  $n = 23-27$  an additional phase  $R_V$  is isolated, which appears immediately after the transition from the crystalline state. *N*-alkanes with chain length  $n \geq 31$  form only one intermediate phase  $R_{II}$ . The emergence of one or another rotator  $R$  phase is determined by the energetic benefit of the reconstruction of the initial crystallographic cell of the *n*-alkane into a new one, which is the next step on the way to the melt.

Thus, when *n*-alkanes are heated, transitions between intermediate phases should occur while maintaining a spatially periodic lamella structure (long-range order). The potential barriers to the rotation of molecules around their axes in such phases turn out to be small compared to the lattice energy, therefore, even at small increases in temperature, states are possible in which molecules, well ordered in the

translational direction, become disordered in the azimuthal orientation due to a change in the relative position of the plane trans-zigzags in the initial subcells. This leads to more defective crystal ordering in  $R$  phases and the possibility of the appearance of conformational gauche defects at the ends of the chains  $gt_m$  [29]. Note that in rotator-crystalline  $R$  phases the rotation of molecules is hindered and limited to discrete turns around the chain axis. Thus, in the phase  $R_V$  the molecules make jump-like turns by  $180^\circ$  between two equally probable orientations (point group  $C_s$ ) [25], in the phase  $R_I$  four molecular orientations are possible ( $D_{2h}$ ) [26,27], and the most disordered phase  $R_{II}$  has sixfold rotational symmetry ( $D_{3d}$ ) [26,28]. It was impossible to study phases  $R_{II}$  and  $R_{IV}$  in details.

### 3. Experimental part

This paper examines the features of the kinetics of polymorphic transformation of crystallographic phases of *n*-alkanes of different molecular symmetries (different parities): tricosane  $n\text{-C}_{23}\text{H}_{48}$ (C23) (cis-symmetry) and



**Figure 2.** Temperature changes in the region of (a, b) rocking and (c, d) scissoring vibrations of CH<sub>2</sub> groups of tricosane C<sub>23</sub>H<sub>48</sub>. Green arrows (a, c) indicate sharp changes in the IR spectrum with temperature increasing.

tetracosane *n*-C<sub>24</sub>H<sub>50</sub>(C24) (trans-symmetry). Samples of monodisperse (with a purity of 99%) C23 and C24 from Sigma-Aldrich in the form of lamellar flake products of synthesis were studied.

It was C23 and C24 that were chosen for the study, since for these *n*-alkanes the solid-solid PT-1 and PT-2 of the order-disorder type (melting/crystallization) are separated by temperature upon heating [2], which makes it possible to study structural transformations of molecules in two main transitions independently.

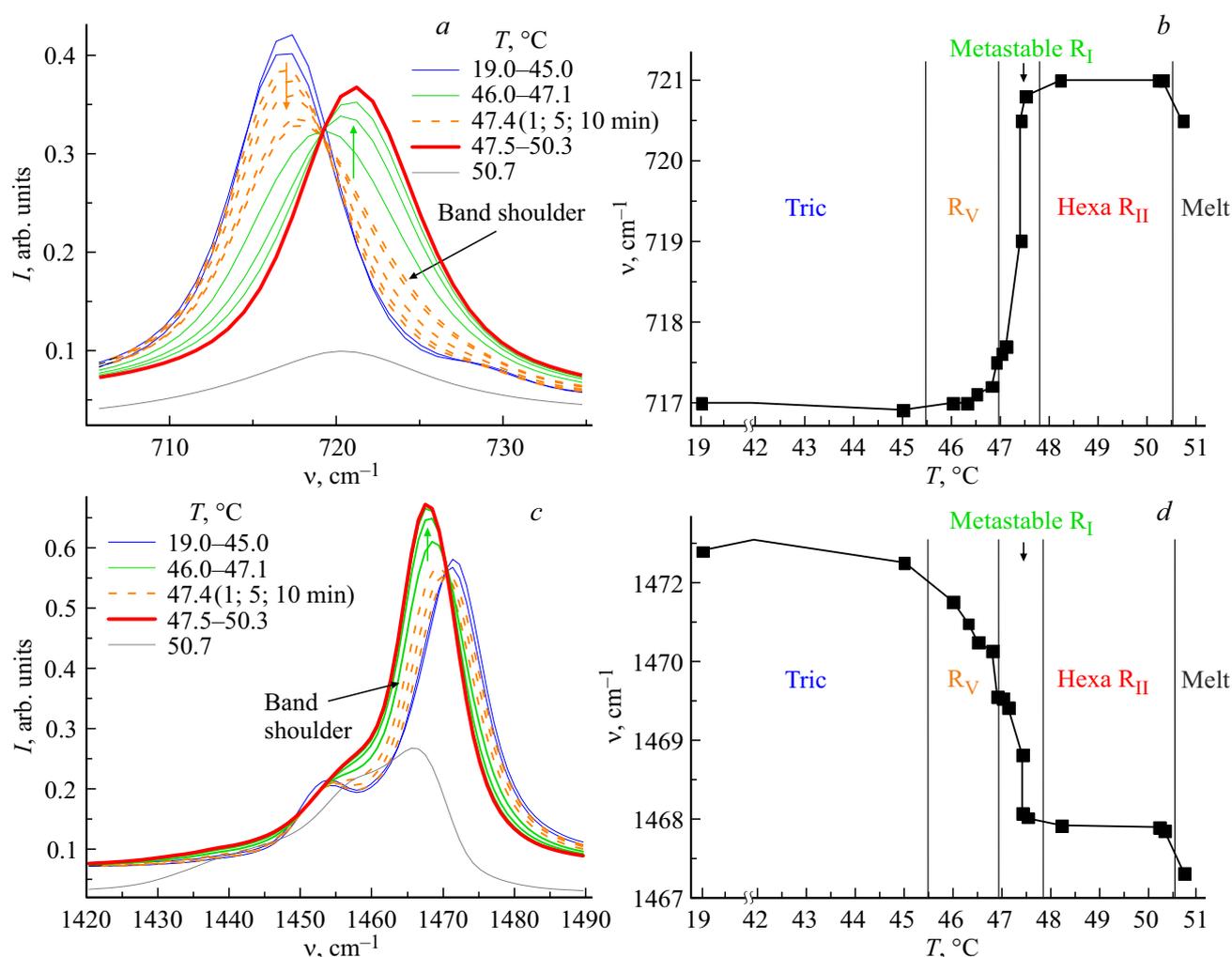
FTIR spectroscopy is highly sensitive to local structural transformations upon heating and to changes in the type of symmetry of elementary subcells in *n*-alkanes, since the frequencies and intensities of vibrations of various functional groups significantly depend on the magnitude of intermolecular interactions.

Micrometer-thick samples were prepared by depositing *n*-alkane flakes on NaCl plates. Then they were melted and

subsequently slowly cooled until an equilibrium crystalline structure was obtained.

Absorption spectra were recorded in the region  $\nu = 400\text{--}5000\text{ cm}^{-1}$  on Bruker IFS-88 FTIR spectrometer with a resolution of  $2\text{ cm}^{-1}$ . When recording the number of scans was 50. To eliminate possible distortion of the spectra, the spectra of atmospheric moisture and CO<sub>2</sub> were subtracted using the built-in software from Bruker. The separation of overlapping absorption bands in the IR spectra into individual components and their subsequent analysis were carried out using the Fityk 1.3.1 [30] program and Pearson VII function.

Scanning of the absorption spectra was carried out in the range of  $T_{\text{room}}$  to the melting temperature  $T_m$  of the samples with a stepwise increase by  $\Delta T = 2\text{--}3^\circ\text{C}$ . In the PT-1 temperature range determined based on the DSC data [2], measurements were carried out in more detail with a step  $\Delta T = 0.1\text{--}0.3^\circ\text{C}$ . Besides, at each step the samples were kept at a certain temperature for 10 min to achieve the



**Figure 3.** Temperature changes in the region of (a, b) rocking and (c, d) scissoring vibrations of CH<sub>2</sub> groups of tetracosane C<sub>24</sub>H<sub>50</sub>. Green and orange arrows (a, c) indicate changes in the IR spectrum with temperature increasing.

equilibrium state. When significant spectral changes were recorded, several (from 3 to 10) spectra were recorded at one temperature for 10 min in order to study the dynamics of changes over time. Temperature measurements were carried out with an accuracy of  $\Delta T = \pm 0.05^\circ\text{C}$  using a Chromel-Kopel differential thermocouple, one end of which was placed in close proximity to the sample, and the other one — in liquid nitrogen to stabilize the temperature difference and increase sensitivity.

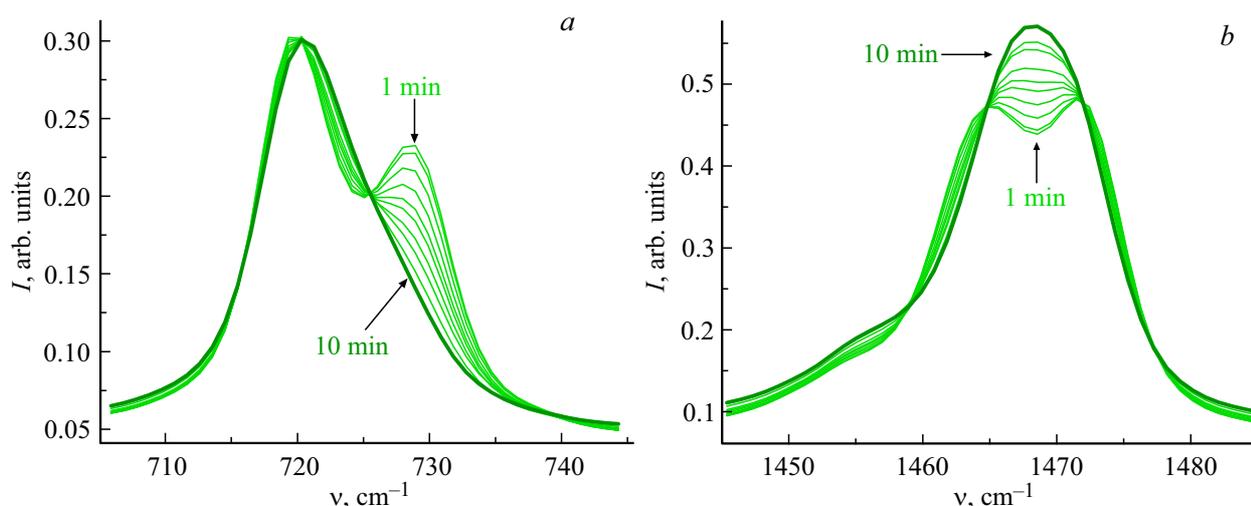
#### 4. Results and discussion thereof

It is known [19] that there is a correlation between the positions of fundamental absorption bands in the rocking ( $\nu \approx 720\text{ cm}^{-1}$ ) and scissoring ( $\nu \approx 1470\text{ cm}^{-1}$ ) (deformation) vibrations of CH<sub>2</sub> groups and the type of subcell formed from methylene trans-sequences in the crystalline cores of the lamellae. Since intermolecular interactions in *n*-alkanes are caused by weak van der Waals forces, changes

in the mutual arrangement of molecules in the crystalline cores of the lamellae lead to offsets in the frequencies of the deformation vibration bands in the IR spectra relative to their initial values. Thus, IR spectroscopy turns out to be very sensitive method for studying the kinetics of molecular transformations during PT-1.

Figures 2, a, c and 3, a, c show series of IR spectra in the region of deformation vibrations, demonstrating significant temperature changes during heating of the samples. In Figures 2, b, d and 3, b, d the temperature dependences of changes in the corresponding frequencies of absorption bands are plotted, which makes it possible to reveal the kinetics of polymorphic transformations in *n*-alkanes of different parity.

At  $T_{\text{room}}$  in the region of deformation vibrations of the IR spectrum of tricosane C<sub>23</sub> the intense doublets of characteristic bands  $\nu = 719.4/729.1$  and  $1463.6/1472.6\text{ cm}^{-1}$  are observed (Figure 2), indicating the formation of subcells of orthorhombic symmetry [19], including two effective molecules. Similar but single absorption bands



**Figure 4.** Temperature changes in the region of (a) rocking and (b) scissoring vibrations of  $\text{CH}_2$  groups of tricosane  $\text{C}_{23}\text{H}_{48}$  at constant temperature  $T = 40.5^\circ\text{C}$  for 10 min.

of tetracosane C24  $\nu = 717.0$  and  $1471.4\text{ cm}^{-1}$  (Figure 3) correspond to subcells of triclinic symmetry (with one effective molecule in the subcell) [19]. The appearance of multiplets in the spectra of molecular crystals is called Davydov splitting [31]. The observed effect is associated with the formation of molecular excitons in subcells containing identical molecules oriented at an angle  $\sim 90^\circ$  to each other. In this case, the number of corresponding bands in the spectrum is equal to the number of molecules in the subcell.

From Figure 2 it follows that with temperature increasing in the orthorhombic subcells C23 in a wide range  $\Delta T = 21.0\text{--}40.3^\circ\text{C}$ , the doublets of the bands are preserved with a slight decrease in intensity, which may be associated with weakening of intermolecular interaction due to thermal expansion. It turned out that in a very narrow temperature range  $\Delta T = 40.3\text{--}40.6^\circ\text{C}$  radical changes in the observed spectra occur: the initial bands in the doublets are shifted so that single asymmetric bands appear  $\nu = 720.4$  and  $1467.2\text{ cm}^{-1}$  with pronounced kinks at  $\nu = 726.3$  and  $1471.7\text{ cm}^{-1}$  (black arrows in Figure 2, a, c). Upon further increase in temperature  $\Delta T = 40.6\text{--}41.2^\circ\text{C}$ , the frequencies of the bands continue to shift, and hardly noticeable shoulders remain. In the range  $\Delta T = 44.8\text{--}46.6^\circ\text{C}$  the intense bands of symmetrical shape  $\nu = 721.3$  and  $1468.2\text{ cm}^{-1}$  are observed, characteristic of subcells of hexagonal symmetry ( $R_{II}$ ) [32]. Finally, at  $T = 47.2^\circ\text{C}$  melting of the n-alkane occurs, and the bands of deformation vibrations significantly expand and decrease in intensity.

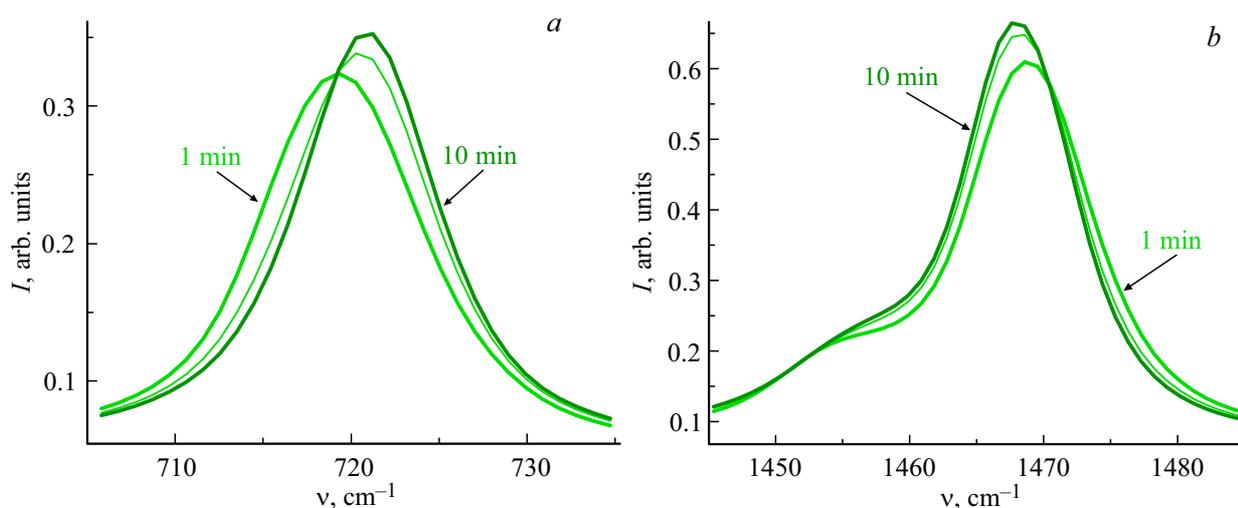
To identify the specific influence of the symmetry of n-alkane molecules (cis/trans) on the kinetics of temperature changes in deformation vibrations, similar studies were carried out using C24 (Figure 3). It turned out that the initial triclinic subcell is also preserved when heated in a wide temperature range  $\Delta T = 19.0\text{--}45.0^\circ\text{C}$ . Then, at  $\Delta T = 46.0\text{--}47.4^\circ\text{C}$ , single bands corresponding to the

triclinic subcell begin to shift and decrease in intensity, while weak shoulders appear (black arrows in Figure 3, a, c), increasing with temperature. And finally, at  $T = 47.5^\circ\text{C}$  there is transition to the true hexagonal phase  $R_{II}$ , which persists up to  $T = 50.3^\circ\text{C}$ , with symmetrically shaped bands  $\nu = 721.0$  and  $1468.0\text{ cm}^{-1}$ . Melting of C24 is observed at  $T = 50.7^\circ\text{C}$ , accompanied by a significant broadening of the bands and decrease in their intensity.

Besides, in our studies, for the first time, we were able to monitor the dynamics of transformations of the spectra of C23 when the sample was kept at constant temperature  $T = 40.5^\circ\text{C}$  for 10 min (Figure 4). 10 spectra were obtained with an interval of 1 min, showing that the doublets are characterized by different behavior: the high-frequency band in the doublet of rocking vibrations gradually disappears, leaving a shoulder (Figure 4, a), simultaneously with this, the doublet of scissoring vibrations merges into one asymmetric band (Figure 4, b). As in the case of C23, for C24 at constant temperature  $T = 47.4^\circ\text{C}$  it was also possible to identify the dynamics of changes in the phase state over time, at which large frequency shifts and a gradual decrease in the asymmetry of the bands with a corresponding increase in their intensity are observed (Figure 5, a, b). We assume that this effect is due to the relaxation of some intermediate phase to a more energetically favorable one at a given  $T$ .

When interpreting the data obtained, we believe that the appearance of weak shoulders near the bands of deformation vibrations of n-alkanes indicates the occurrence of specific doublets from new orthorhombic subcells in intermediate rotator phases  $R_I$  and  $R_V$  in temperature ranges:  $R_I$  at  $\Delta T = 40.6\text{--}41.2^\circ\text{C}$  for C23 and  $R_V$  at  $\Delta T = 46.0\text{--}47.1^\circ\text{C}$  for C24 (Figure 2, b, d and 3, b, d).

The splitting of vibrations into two components observed by us in  $R$  phases indicates the preservation of short-range correlation in the mutual orientations of trans-zigzags



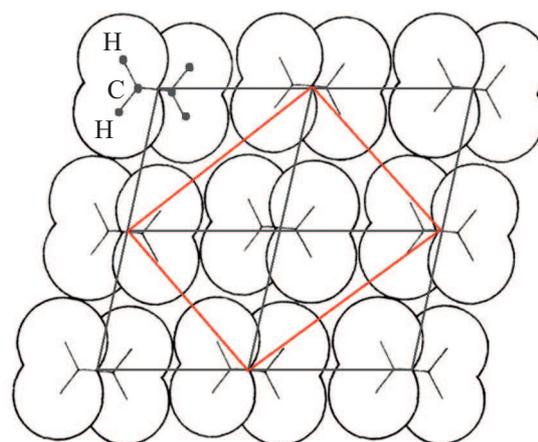
**Figure 5.** Temperature changes in the region of (a) rocking and (b) scissoring vibrations of  $\text{CH}_2$  groups of tetracosane  $\text{C}_{24}\text{H}_{50}$  at constant temperature  $T = 47.4^\circ\text{C}$  for 10 min.

of molecules even in the absence of long-range order. The data obtained allow us to state that the phases  $R_I$  and  $R_V$  consist of local domains with slightly distorted orthorhombic subcells. Two factors lead to distortions of subcells: 1) a decrease in intermolecular interaction during thermal expansion of crystals; 2) rotations of chains that change the angles between trans-zigzag planes (orientations) of molecules in subcells. As a result, with temperature increasing the magnitude of the Davydov splitting gradually decreases to zero, and all molecules turn out to be crystallographically equivalent (phase  $R_{II}$ ). These two effects determine the mechanism of the transition  $R_I \rightarrow R_{II}$ . Besides, data on the dynamics of changes in IR spectra at constant temperature made it possible for the first time to discover the possibility of the metastable rotator phases development over time:  $R_V$  at  $\Delta T = 40.3\text{--}40.6^\circ\text{C}$  for  $\text{C}_{23}$  and  $R_I$  at  $\Delta T = 47.1\text{--}47.5^\circ\text{C}$  for  $\text{C}_{24}$ , which especially emphasizes the differences in the kinetics of polymorphic transformations in *n*-alkanes of different symmetry. The existence of such metastable phases was considered in [33] for some other *n*-alkanes.

## 5. Conclusion

Based on the observed temperature changes in the IR spectra in the region of deformation vibrations, it was possible to identify significantly different kinetics of polymorphic transformations in *n*-alkanes of different parities (different molecular symmetries).

It turned out that for odd *n*-alkanes with initial orthorhombic symmetry of subcells, the magnitude of the Davydov splitting of the bands decreases with temperature increasing. As shown in [27], it is the decrease in the average sizes of domains of the true orthorhombic phase that leads to a sharp decrease in the bands splitting in



**Figure 6.** Non-primitive triclinic subcell.

the doublet of deformation vibrations. This is due to the appearance of domains of the metastable rotator phase  $R_V$  with distorted orthorhombic subcells (with different parameters and changed orientational order), the proportion of which increases when the sample is kept at constant temperature. With further transition to the phase  $R_I$ , the splitting decreases even more, since the degree of freedom of the molecules rotation around their main axis increases: instead of two equally probable orientations of molecules in the  $R_V$  phase, there are four in  $R_I$ . The subsequent increase in the freedom of rotation of molecules in the phase  $R_{II}$  leads to complete orientational disorder.

The comparison of triclinic and orthorhombic structures will be simplified if for even *n*-alkanes we consider not a primitive subcell, but one similar to the orthorhombic one (Figure 6). As the temperature increases due to the thermal expansion of the crystal, at a certain time the

librational energy of the molecule around its main axis will become sufficient to allow jumps between several positions (orientations) of the molecules. Moreover, we cannot exclude possible rototranslational (screw) movements of molecules, when molecules leave the lamella cores by one C–C-bond and at the same time turn by angle of  $180^\circ$  [34]. It is probably due to this mechanism that the initial triclinic structure transforms into a monoclinic structure  $R_V$  (similarly, the orthorhombic structure in odd n-alkanes acquires a slope). It can be assumed that distorted orthorhombic domains of  $R_V$  phase will also arise locally in the triclinic structure, and further metastable development of  $R_I$  facilitates the transition to the hexagonal phase.

Thus, for the first time, based on the method of FTIR spectroscopy, the differences in the kinetics of the polymorphic transformation of the initial crystallographic phase into true hexagonal phase for n-alkanes of different symmetries (parity effect) in a narrow temperature range  $\Delta T \leq 3^\circ\text{C}$  were described.

### Conflict of interest

The authors declare that they have no conflict of interest.

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