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# Conformational sensitivity of tricosane absorption band progressions to polymorphic transformations

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The polymorphic transformations of monodisperse tricosane $n$-$C_{23}H_{48}$ upon heating were studied using FTIR spectroscopy. A disruption of chain regularity in the lamellae cores was revealed based on temperature-induced changes in the progressions of rocking vibrations of $CH_2$ groups and stretching (skeletal) vibrations of C−C bonds. Thermal activation of various types of conformational defects, located predominantly at the chain ends, was observed. It was established that an increasing number of conformational defects facilitates crystal structure rearrangements upon heating, including transitions between intermediate rotator phases ($R_V$, $R_I$, $R_{II}$).

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

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## 1. Introduction

Starting from the mid XX century, and so far, the number of studies on identification of polymorphic transformations in various homologues of long-chain n-alkanes under the influence of temperature has been steadily growing [1–8]. However, it has not yet been possible to establish a single mechanism of structural rearrangements for all homologues during transition from a solid state to a liquid one and back in heating-cooling cycles. This uncertainty is due to a wide variety of polymorphic modifications that occur depending on the chain lengths of homologues, which makes it difficult to identify common patterns. In this regard, it is of particular importance to conduct such studies on commercially available long-chain n-alkanes $C_nH_{2n+2}$ with a high degree of purity ($\geq 95\%$) and monodispersity at various chain lengths ($16 \leq n \leq 60$ with an accuracy of one carbon atom in the molecule skeleton).

In most n-alkane homologues, one additional and often a number of intermediate solid phases appear during heating/cooling processes. Some of these intermediate phases have been called rotator phases (R) [9], because they are characterized by the presence of positional order in the absence of long-range orientation order. Rotator (or rotator-crystalline) R-phases are intermediate between the fully ordered crystalline state and the isotropic liquid in the long-chain n-alkanes. Their main difference from purely crystalline phases is the presence of discrete rotation of molecules around their axes, and each of the R-phases is characterized by a certain number of equally probable orientations of molecules in the lattice cells.

It is important to note that n-alkanes belong to the class of long-chain molecular crystals, during crystallization of which extended methylene trans sequences are stacked into lamellae — the lamellar formations comparable in thickness to the length of the homologue molecule (units nm) [10]. In the lamellar crystals of n-alkanes two types of lattice cells are identified: the main cell, which characterizes the way lamellae are arranged relative to each other in stacks, and the sub-cell, which describes the nature of the stacking of methylene trans-sequences in the crystalline cores of individual lamellae.

Long-chain n-alkanes are characterized by the division of homologues into even and odd ones, depending on the number of carbon atoms in the chain, since there are clearly two separate patterns in the development of the structure of crystals [10], as well as physical properties, with increasing chain lengths in two series of homologues [8]. The source of the parity effect is the symmetry of an individual n-alkane molecule with the end methyl groups located either on one side of the trans-zigzag axis — cis-shape of the molecule, or on different sides— trans-shape. As a result, even for the closest homologues, the pattern of the arrangement of regular trans-zigzags in the crystal cores of lamellae differs relative to the base planes of the end methyl groups $CH_3$. Thus, the structure of the ordered crystal phase of the n-alkanes homologue is determined by the trans- or cis-symmetry of the molecule and is characterized by either a vertical arrangement of chains in lamellae for odd homologues (orthorhombic main cell) or an inclined arrangement of chains (monoclinic/triclinic main cell) for even homologues. Symmetries of the main cell and sub-cell may differ. The appearance of an intermediate

R-phase upon heating is probably due to the symmetry of the preceding crystalline phase.

Using the methods of synchrotron X-ray diffractometry and differential scanning calorimetry [11], we managed for the first time to identify the kinetics of the development of a complete sequence of phase transitions of various nature when heated in odd n-alkane — tricosane $n$-$C_{23}H_{48}$, in particular, transitions between the following phases were found: low-temperature orthorhombic crystalline phase $O_i \rightarrow$ high-temperature orthorhombic crystalline phase $O_{dci} \rightarrow$ monoclinic rotator phase $R_V \Rightarrow$ orthorhombic rotator phase $R_I \rightarrow$ rhombohedral (hexagonal) rotator phase $R_{II} \rightarrow$ liquid. We were able to obtain additional information about the structural rearrangements of the crystal core of lamellae during polymorphic transformations of tricosane between rotator phases using IR-Fourier spectroscopy in the study of temperature changes in rocking and scissoring vibrations of $CH_2$ groups [12]. However, it is unlikely that based on the conducted studies, it is possible to reliably identify the transition between the crystalline orthorhombic phases $O_i$ and $O_{dci}$. Nevertheless, in the literature [13], it was using the IR spectroscopy method that the $O_i \rightarrow O_{dci}$ transition was first detected by the effect of an increase in the number of conformational defects in longer homologues of n-alkanes.

So far, it has been reliably proven that when tricosane is heated, three characteristic rotator phases emerge: $R_V$, $R_I$ and $R_{II}$, and their structures are outlined in [4]. $R_V$ and $R_I$ phases are characterized by orthorhombic sub-cells, while in $R_I$ phase the main cells are themselves the face-centered orthorhombic cells, and in $R_V$ phase — they are monoclinic. Both phases are characterized by a two-layer lamella stacking sequence (ABA...), the same is true for the low-temperature orthorhombic phase. The high-temperature phase of $R_{II}$ is described by rhombohedral main cells, hexagonal sub-cells, and three-layer lamellar stacking (ABCA...). At the same time, the obtained data from IR spectroscopy indicate significant stability of the solid hexagonal phase up to the melting point of the sample [12].

Note that the crystalline lamellar structure remains in R-phases (long-range order in the arrangement of macromolecule centers), however, during the transition from one R-phase to another, the number of possible equally probable orientations of molecules in sub-cells rises after heating (due to the discrete rotation of molecules in the lamellae). Thus, the hexagonal phase ($R_{II}$) is considered to exhibit complete orientation disordering of trans-zigzag planes in the sub-cells.

We believe that such a complex mechanism of polymorphic transformations of some rotator-crystalline phases into others is due to the thermal activation of various types of conformational defects (mainly end gauche defects and kinks), which, violating the symmetry of an individual molecule, lead to formation of ordered regions with a different crystalline symmetry. The corresponding results were obtained by analyzing the violation of the regularity of chains in the lamellae cores during polymorphic transformations for the nearest homologue of tricosane — tetracosane $n$-$C_{24}H_{50}$ with the initial triclinic symmetry of lattice cells [14].

For substances where the lamellae's crystalline cores are formed from extended methylene trans sequences, the characteristic feature is the progressions of various vibrational modes observed in IR spectra. Disruption of the regularity of methylene trans sequences, in particular, during heating, should affect the number of bands in the progressions and their intensity. In this regard, this study is focused on the temperature changes in IR spectra in the region of the most intense absorption band progressions characteristic of n-alkanes, in order to identify the relationship of structural transformations occurring at the molecular level with polymorphic transformations of n-alkanes upon heating, using tricosane as an example.

A detailed analysis of the progressions of rocking and skeletal Vibrations observed in the tricosane IR spectrum at room temperature was given in our previous article [15]. In this paper, the band changes in the region of the studied progressions caused by polymorphic transformations after n-alkane heating will be investigated.

Thus, the present study is intended to clear out the role of thermal activation of conformational defects at specific stages of structural rearrangements of the odd long-chain tricosane n-alkane upon heating, which will allow comparing the new results with those obtained earlier for tetracosane [14]. In addition, in this paper we will follow the changes in the concentration of conformers, not only those presented in previous work for tetracosane, but also those that are not clearly attributed to a specific type of defect in the literature. This will make it possible to monitor the structural transformations of tricosane with greater sensitivity.

The performed studies ensure supposition of the generalized model of progress of solid-solid phase transitions in the homologues of the long-chain n-alkanes.

## 2. Experimental

The paper investigates the specifics of the polymorphic transformation kinetics of crystalline phases of the odd n-alkane tricosane $n$-$C_{23}H_{48}$ (cis-symmetry of an individual molecule), monodisperse samples (with purity 99%) of which were prepared by company Sigma-Aldrich in form of plate flake synthesis products.

Micrometer-thick samples were prepared by depositing n-alkane flakes on NaCl polished plates. Then they were melted and subsequently slowly cooled until an equilibrium crystalline structure was obtained.

Absorption spectra were recorded in the region $\nu = 400-5000\,\mathrm{cm}^{-1}$ using Bruker IFS-88 Fourier transform spectrometer with a resolution of $2\,\mathrm{cm}^{-1}$, and 50 scans. To eliminate possible distortion of the spectra, the spectra of atmospheric moisture and $CO_2$ were subtracted using the built-in software from Bruker.

The absorption spectra were registered in range of $T_{\text{room}}$ to melt point of sample ($T_m = 47.2-47.8\,^\circ$C) during stepped increase by $\Delta T = 2-3\,^\circ$C, excluding temperature range of solid-solid phase transitions, measurements in them were performed in more details, with step of $\Delta T = 0.1-0.3\,^\circ$C, to determine kinetics of polymorphous transformations. Besides, samples at each step were held at definite temperature for 10 min to reach the equilibrium state. Temperature was measured with an accuracy of $\Delta T = \pm 0.05\,^\circ$C using specially manufactured Chromel–Kopel differential thermocouple (using 0.1 mm diameter wires), 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 of thermocouple.

The separation of overlapping absorption bands in the experimentally obtained IR-spectra into individual components and their subsequent analysis were carried out using Fityk software 1.3.1 [16] and Pearson VII function. To compare the integral intensities of the bands in the progressions, and to ensure that background contributions are taken into account correctly when changing the spectra, the baseline was subtracted uniformly over the entire spectral range $\nu = 670-1200\,\text{cm}^{-1}$ of each spectrum during heating. The work relating simultaneous analysis of $\sim 100$bands of each spectrum ensures comparison with large authenticity of the band of progressions both with each other at same temperature, and their transformation at each temperature step.

## 3. Analysis of progressions in IR-spectra of tricosane $C_{23}H_{48}$

To study the transformation of the trans-zigzag structure of an odd n-alkane tricosane molecule during heating, an IR spectral region containing the two most intense progressions of methylene trans sequence vibrations was selected. The band progression caused by rocking vibrations of $CH_2$ groups in n-alkanes is manifested in $\nu = 700-1100\,\text{cm}^{-1}$ region and is designated by Snyder as $P_k$ [17]. The high-frequency edge of this region is overlapped by another progression caused by stretching (skeletal) vibrations of C–C bonds and occupying the frequency range of $\nu = 950-1150\,\text{cm}^{-1}$. The designation $R_k$ is selected to denote this progression [17]. It should be noted that both progressions are strongly influenced by a rather intense band near $890\,\text{cm}^{-1}$ associated with the localized rocking in-plane vibration of the end methyl group $CH_3$ and denoted by $\beta$ (or $P_{CH_3}$) [17].

The spectrum of tricosane is shown in Figure 1, the bands were assigned in accordance with the work of [17,18].

Most of the selected vibration frequencies in the tricosane spectrum at room temperature (Figure 1) are slightly shifted towards lower values than those observed for the same molecule in its extended conformation (at $T = -180\,^\circ$C) [18]. This spectral behavior is due to a lower concentration of trans-conformers [19], which indicates the presence of irregular conformers already in a low-temperature ordered crystalline state. Nevertheless, the presence of all the expected members of the progression of rocking vibrations of $CH_2$ groups ($P_k$) suggests that most of the molecules in the lamellae are completely in trans-conformation without any conformational defects, and only a few molecules are likely to have one end gauche defect [14].

The detailed analysis and comparing the bands in the studied progressions $P_k$ and $R_k$ in the low-temperature orthorhombic modification of tricosane are given in paper [15] based on the model of linear chain of the coupled oscillators [20].

It is well known [21] that intense doublets of characteristic bands are observed in the area of deformation vibrations of the tricosane IR spectrum, including for rocking vibrations: $\nu(P_1) = 719.4/729.1\,\text{cm}^{-1}$ (Figure 1). Such splitting of bands is called factor-group splitting. A doublet occurs as a result of in-phase and out-of-phase vibrations of two unequally arranged molecules in a sub-cell [20,22]. The degree of splitting of such bands depends on the intermolecular interaction of [21], which varies with temperature [12]. Thus, the appearance of doublets of deformation vibration bands in the IR spectra indicates the formation of sub-cells of orthorhombic symmetry [21], comprising two molecules per cell. A more general consideration of this issue was presented by Davydov [23], therefore, the appearance of multiplets in the spectra of molecular crystals is called Davydov splitting. The observed effect is associated with the formation of molecular excitons in sub-cells containing identical molecules oriented at an angle of $\sim 90^\circ$ to each other, while the number of corresponding bands in the spectrum is equal to the number of molecules in the sub-cell.

The progressions of the IR absorption bands of rocking ($P_k$) and skeletal ($R_k$) vibrations observed by us (Figure 1) are characteristic of molecules that are completely in trans-conformation without any conformational defects in the lowest temperature polymorphic modification of tricosane (in the phase $O_i$). But significant interest relates to possible conformation changes of n-alkanes due to different polymorphous transformations occurred during heating up to their melt points $T_m$. Such transformations we observed in [12].

Figure 2 presents spectra of tricosane in $735-1150\,\text{cm}^{-1}$ region at temperatures corresponding to different phases specified by us in previous paper [12]. We may conclude that the progressions of $P_k$ and $R_k$ bands are clearly identified in the initial orthorhombic phase (up to $T < 40.3\,^\circ$C), as well as in rotator phases $R_V$ ($\Delta T = 40.3-40.6\,^\circ$C) and $R_I$ ($\Delta T = 40.6-41.2\,^\circ$C), yet with already lower intensities. In high-temperature hexagonal $R_{II}$-phase ($\Delta T = 43.7-46.6\,^\circ$C) intensity of all bands in progressions significantly decreases; but at that all bands are yet visible,

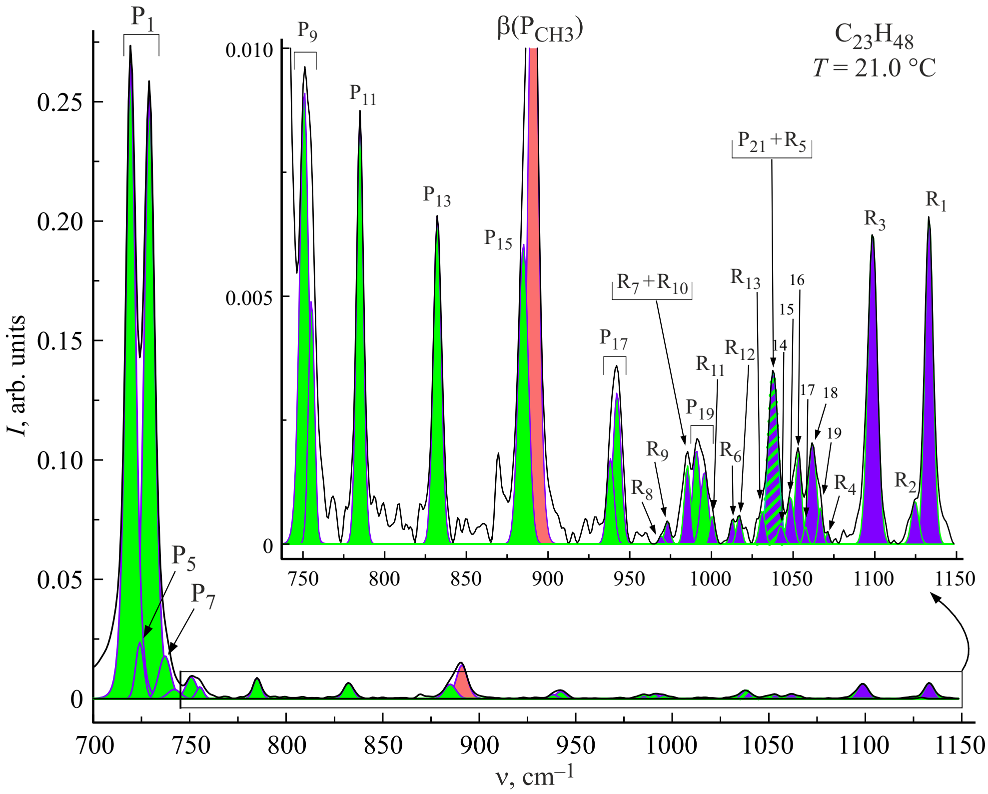

**Figure 1.** IR-spectra of tricosane $C_{23}H_{48}$ at $T = 21\,^\circ\mathrm{C}$. Absorption bands attributed to progressions of rocking vibrations of $CH_2$ groups ($P_k$) groups (green bands) stretching vibrations of C−C bonds ($R_k$) (violet bands) are marked, the characteristic rocking vibration of the methyl group $CH_3$ ($\beta$) is also highlighted (red band).

i.e. most of the molecules keep regular trans-conformation. In spectrum of melt (at $T = 47.2{-}47.8\,^\circ\mathrm{C}$) the number of bands in the progressions significantly decreases, and instead of them there remain several broad maxima, caused by the superposition of bands of large number of different conformers localized in certain parts of the chains. It should be emphasized that the band of the localized mode $\beta$ (near $890\,\mathrm{cm}^{-1}$) is clearly visible in the melt.

Figure 2 also shows the occurrence of constant frequency bands associated with localized vibration modes during heating. According to the data from publications [24], the marked bands should be associated with conformers localized at the ends of the chains, namely, with the end gauche defects $gt_m$. In this conformation the penultimate bond of the chain is located in gauche position (g or g*), while the rest $m$ of the bonds — in the trans position (t). In this case, $m$ indicates the degree of localization of the defect, its distance from other gauche bonds. It can be concluded that absorption bands of several types of the end gauche defects $gt_m$ are observed in the tricosane spectra, differing in the degree of localization in the trans chain and, accordingly, the associated vibration frequency: $\nu = 873.6\,\mathrm{cm}^{-1}$ ($m > 5$), $\nu = 956.2\,\mathrm{cm}^{-1}$ ($m > 8$) and $\nu = 1080.8\,\mathrm{cm}^{-1}$ ($m > 1$), which is fully consistent with the literature data [13,24].

In addition to the bands associated with conformers, weak bands also appear in tricosane spectra upon heating, located approximately in the middle between the $k$-odd bands of the rocking mode ($P_k$). They are marked by

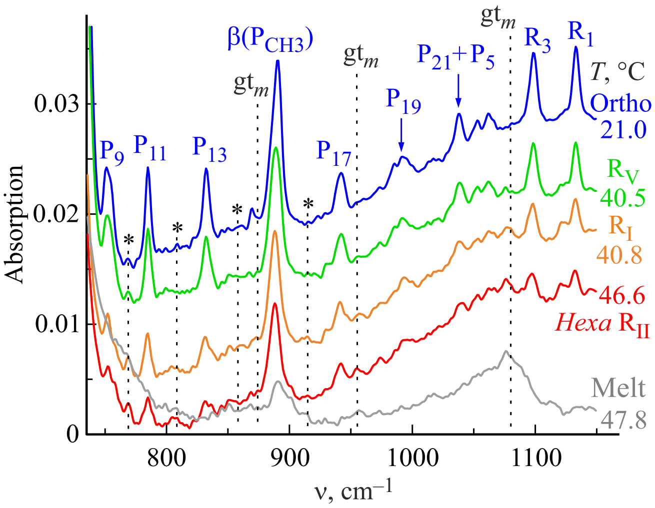

**Figure 2.** IR spectra in the range of progressions $P_k$ and $R_k$ of various phase states of tricosane upon heating. The asterisks indicate the appearance of bands $P_{\mathrm{even}}$, and the appearance of bands of constant frequency $gt_m$ associated with vibration modes localized on the chains' ends.

asterisks in Figure 2. These bands, presumably, are associated with non-localized vibration modes and belong to $k$-even rocking modes ($P_{even}$). As these modes in accordance with selection rules shall be IR-inactive for all-trans-chain, their appearance can indicate the occurrence of non-planar conformations. However, the coexistence of even and odd members of the progression with a clearly observed intensities ratio indicates slight deviation of the chain structure from the all-trans conformation, so it can be assumed that many of the end defects arise in planar chains ($< 1$ of defect per molecule). Same conclusions were made by authors of [13,24–27] during study of other homologue of n-alkanes. Moreover, the bands $P_{even}$ have measurable intensity even in the initial orthorhombic structure ($\nu(P_{10}) = 768.0\,cm^{-1}$, $\nu(P_{12}) = 805.0\,cm^{-1}$, $\nu(P_{14}) = 856.8\,cm^{-1}$, $\nu(P_{16}) = 915.3\,cm^{-1}$), i.e. small part of molecules is non-planar even in the most low-temperature solid phase at room temperature.

As noted earlier, during transition from the initial orthorhombic phase to the high-temperature hexagonal $R_{II}$ phase the intensity of bands $P_{odd}$ inherent to all-trans chain declines (Figure 3). We can state that all-trans molecules still remain the basic ones also in phase $R_{II}$, though non-planar molecules are clearly also present. However, the reduced intensity of the bands $P_{odd}$ is not a reliable quantitative indicator of the proportion of molecules that remain planar in the high-temperature phase, since the observed loss of intensity of these bands during the transition $R_I \rightarrow R_{II}$ is facilitated by other factors besides changes in the conformers concentration.

Figures 3, *a, c* and *e* show the temperature dependences of the position of maxima of $P_{odd}$ bands of the progression of tricosane rocking vibrations, with some exceptions. The analysis of the temperature variation (frequency and intensity) of $P_7$ band is difficult because the band is hidden by an intense doublet $P_1$. There is also no any dependence curve for the band $P_{19}$, i.e., because it remains almost constant when heated (similar to the band $P_{11}$). Based on the observed temperature changes, it can be concluded that most of the bands $P_{odd}$ in the interval $\Delta T = 40.3-40.6\,^\circ C$ (phase $R_V$) drastically shift towards lower frequencies at $\Delta\nu = 1-2\,cm^{-1}$ (Figure 3, *a, c* and *e*). The shifts in the vibration frequencies are associated with small changes in intermolecular interactions during the parameters transformation of crystallographic cells. Note that the magnitude of Davydov splitting of $P_9$ and $P_{17}$ bands weakly depends on temperature, however, the intensity of one of the bands in these doublets decreases more intensely when heated than the intensity of the other (Figure 3, *d* and *f*).

Figure 3, *b, d* and *f* show the temperature dependences of integral intensities for all observed progression bands ($P_{odd}$). It should be noted that during heating the doublet of bands $P_1$ ($\nu = 719.4/729.1\,cm^{-1}$), corresponding to the initial orthorhombic sub-cell transits to band $P'_1$ ($\nu = 721.3\,cm^{-1}$) standing for the hexagonal sub-cell (phase $R_{II}$), (Figure 3, *a* and *b*). At that, the band $P'_1$ occurs in a very narrow interval $\Delta T = 40.3-40.6\,^\circ C$ (phase $R_V$) as a single band of asymmetric shape $\nu = 720.4\,cm^{-1}$ with a clearly visible bend at $\nu = 726.3\,cm^{-1}$. With a further increase in temperature $\Delta T = 40.6-41.2\,^\circ C$ (phase $R_I$), the band $P'_1$ continues to approach its frequency value in phase $R_{II}$, becoming more and more symmetrical. The above-mentioned behavior of $P'_1$ band during structural reconstructions we associate with emergence of a specific doublet (some Davydov splitting of bands) from several distorted orthorhombic sub-cells in $R_V$ and $R_I$ phases and with weakening caused by molecular rotation in the rotator phases [12].

Reduction of integral intensities of progression bands $P_{odd}$ from $P_9$ to $P_{21}$ (that is to say, up to the combination of bands $P_{21} + R_5$, these bands are unambiguously separated at $T \geq 40.5\,^\circ C$) after heating is shown in Figure 3, *d* and *f*. At that, the most abrupt decline in the intensities occurs in very narrow temperature range $\Delta T = 40.5-40.6\,^\circ C$, near the transition $R_V \rightarrow R_I$. During transition $R_I \rightarrow R_{II}$ the progression of bands $P_{odd}$ declines again, though to a much lesser extent. It should be noted that for the even n-alkane tetracasane, a similar decrease in the intensity of bands in progressions was observed precisely during the transition to the high-temperature hexagonal phase [14], which underscores the difference in the structural transformations of molecules of different symmetry during the same polymorphic transformations [12]. However, in the melt, due to the violation of the regularity of the trans-zigzags, the intensity of all members of the progression reduced significantly, leaving only barely distinguishable bands against the background caused by the superposition of large number of different conformers.

Same analysis of temperature dependences in region of progression of skeletal vibrations ($R_k$) is presented in Figure 4. Figure 4, *a* shows the temperature dependences of the position of the maxima of the high-frequency terms of the progression $R_1$, $R_2$ and $R_3$, and Figure 4, *b* — illustrates changes in their integral intensities when tricosane is heated. The most strong terms of progression $R_1$ and $R_3$ demonstrate a slight decline of frequencies at $\Delta\nu \approx 1\,cm^{-1}$ again at a temperature of $T = 40.5-40.6\,^\circ C$, which is accompanied by a drastic twofold decline of these bands. The frequency of the band $R_2$ does not change so unambiguously with the temperature growth, especially during transitions between rotator phases. However, it should be noted that the intensity of this band increased slightly during the transition to $R_I$ phase and remained almost unchanged throughout the entire $R_{II}$ phase. It is likely that such intensification band may be due to the appearance of some kind of conformational defect that is not observed in the melt, and therefore is sufficiently localized. Similar, on the spectra of rotator phases $R_I$ and $R_{II}$ of tetracosane, the new bands $\nu \approx 1099$ and $1131\,cm^{-1}$ [14], emerge corresponding to the appearance of the new terms $R_3$ and $R_1$ which are not specific for the even homologs and indicating the formation of the end gauche defects.

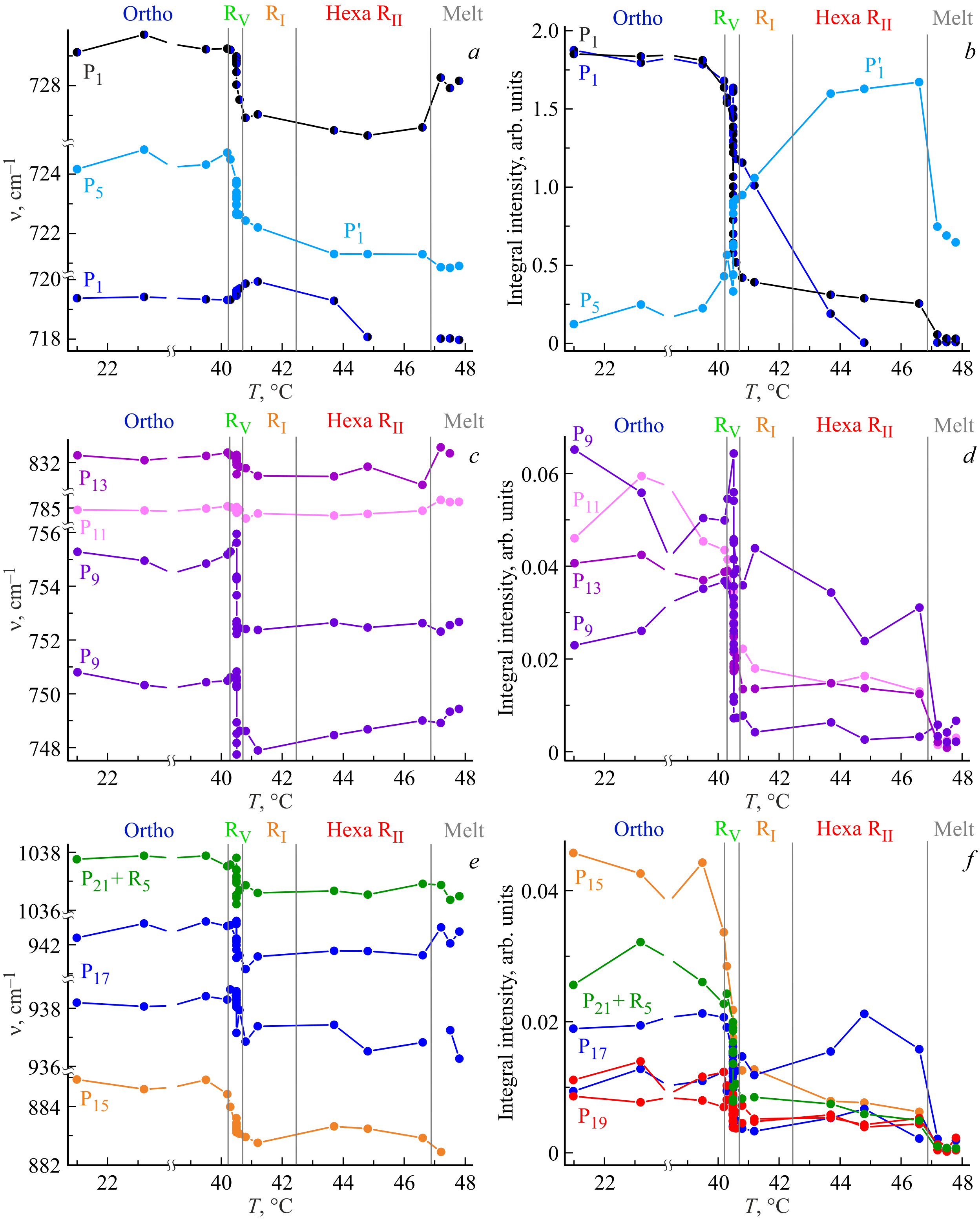

**Figure 3.** Temperature changes of tricosane IR-spectra in the range of rocking vibration progression ($P_k$): *a, c* and *e*) temperature dependencies of maxima position of the most strong band of progression; *b, d* and *f*) temperature dependencies of integral intensities of progression bands. The temperature ranges of the indicated phase states are taken according to [12] (same designations are also used in figures below).

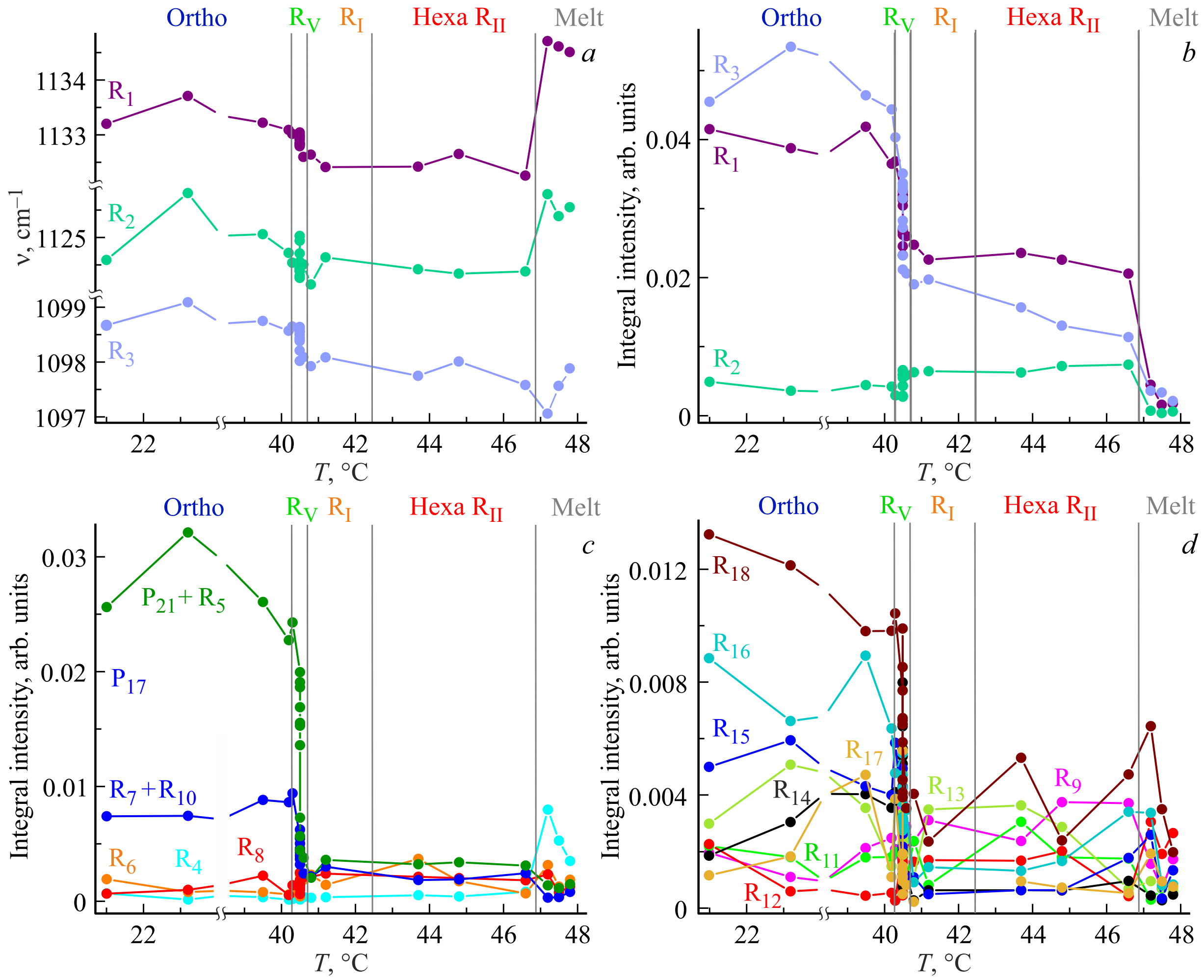

**Figure 4.** Temperature changes of tricosane IR spectra in the region of skeletal vibration progression ($R_k$): *a*) temperature dependences of the position of maxima of the high-frequency members of progression ($R_1$, $R_2$, $R_3$); *b, c* and *d*) temperature dependences of integral intensities for all bands of progression.

Figures 4, *c* and *d* show the temperature dependences of the integral intensities for the remaining bands of the progression $R_k$ (from $R_4$ to $R_{18}$), the intensity of which also decreases abruptly in a very narrow range $\Delta T = 40.5{-}40.6\,^\circ$C, however, they remain distinguishable even in the spectrum of phase $R_{II}$.

Thus, a decrease in the intensity of bands $P_{odd}$ and $R_k$ is observed with each change in the phase state of the n-alkane, including during intermediate transitions between rotator phases, which is clearly seen in Figure 2. Moreover, the abrupt decrease in the intensity of progressions occurs precisely near the transition $R_V \rightarrow R_I$ (Figures 3 and 4), which indicates the most significant violations of the trans-zigzag structure of molecules at this stage of structural transformations in tricosane. Note that the thermal activation of conformational defects at this transition is also indicated by a slight increase in the intensity of bands attributed to the modes $P_{even}$ of non-planar molecules that also react to the transition to phase $R_{II}$ (Figure 5). As the temperature rises, intermittent changes are observed in the IR spectra, corresponding to sharp jumps in the concentration of non-planar conformers during the transition $R_V \rightarrow R_I$ and in the hexagonal phase $R_{II}$.

Some of the simplest and low-energy irregular conformers are the end gauche defects. Figure 6 presents changes in the integral intensities of bands (concentration) detected in studied region of the studied spectrum of end gauche defects $gt_m$ during tricosane heating. It was mentioned above, that even in the initial orthorhombic phase there is small number of molecules with end defects. In particular, some minor concentrations of low-energy defects $gt_m$ are observed at frequencies $\nu = 873.6\,\text{cm}^{-1}$ ($m > 5$), $\nu = 956.2\,\text{cm}^{-1}$ ($m > 8$) and $\nu = 1080.8\,\text{cm}^{-1}$ ($m > 1$), nevertheless, the first defects are several times larger, based on data on the integral intensities of the corresponding absorption bands. As the temperature rises, the concentrations of all defects gradually increase with significant jumps during transitions between rotator phases (Figure 6). Thus, when transiting into phase $R_V$ the

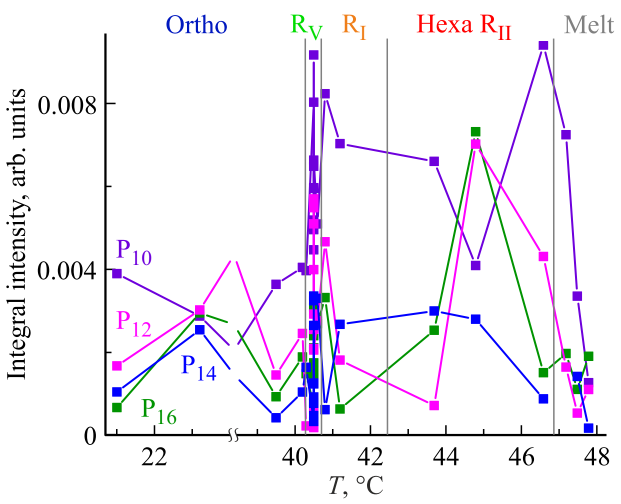

**Figure 5.** Temperature dependences of the integral intensities of the detected bands $P_{even}$ of the tricosane rocking vibration progression.

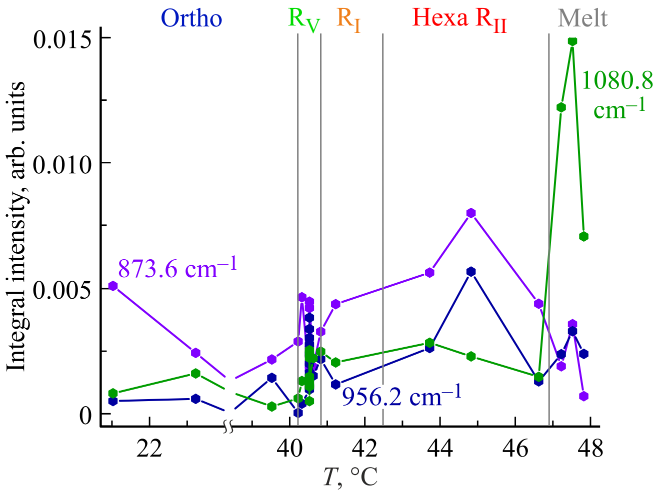

**Figure 6.** Temperature dependences of integral intensities of IR-bands of tricosane associated with the end gauche defects $gt_m$ found in the region of progressions $P_k$ and $R_k$.

amount of the end gauche defects from $\nu = 873.6\,\mathrm{cm}^{-1}$ jumps twofold, from $\nu = 1080.8\,\mathrm{cm}^{-1}$ — to 9 times, and then, throughout the phase $R_I$ these maximal defects persist. The concentration of defects from $\nu = 956.2\,\mathrm{cm}^{-1}$ grows by 11 times when transiting to $R_V$, yet, in phase $R_I$ their amount only twofold exceeds the initial amount. Upon further heating, the concentrations of defects from $\nu = 1080.8\,\mathrm{cm}^{-1}$ practically do not change throughout the entire phase $R_{II}$, whereas from $\nu = 873.6\,\mathrm{cm}^{-1}$ they jump 2 times, from $\nu = 956.2\,\mathrm{cm}^{-1}$ — 5 times. In the melt spectrum, the concentrations of strongly localized defects decrease, and the number of conformers with $\nu = 1080.8\,\mathrm{cm}^{-1}$ rises 10 times.

It can be concluded that the end defects with the highest degree of localization predominate in the solid phases of tricosane $(m > 8)$, which emphasizes the preservation of regular trans-conformations in the lamella cores by most molecules throughout all polymorphic transformations. The transition to the monoclinic phase $R_V$ is facilitated mainly by the activation of these same conformers. All types of end defects contribute to the further transition of $R_V \rightarrow R_I$, therefore, it can be concluded that already in the phase of $R_I$ molecules with more than one defect per chain appear (kinks probably appear among them in the cores of lamellae). To a large extent, only highly localized defects response to the transition to the hexagonal phase$R_{II}$, probably thereby increasing the total number of defective molecules. Finally, only defects with a small degree of localization remain in the melt, which increases the probability of the formation of several conformers in a single chain.

Note that the defects analyzed above and their corresponding absorption bands are unambiguously defined in the literature [13,24]. However, other weak bands are clearly present in the studied region of the spectrum (Figure 2), probably corresponding to other types of conformers. Thus, the bands at $\nu = 805.0$ and $856.8\,\mathrm{cm}^{-1}$, considered by us as odd terms of progression of the rocking vibrations $P_{12}$ and $P_{14}$, may, according to [19], also correspond to the thermal activation of the high-energy defects, significantly distorting the regular structure of the chain, $-t_m g t_n-$ $(m, n > 3)$ and $-t g_m t-$ $(m > 1)$ respectively. The identified band $P_{10}$ at $\nu = 768.0\,\mathrm{cm}^{-1}$ may also be attributed to the end defect $gt_m$ [25]. Similarly, the identified band $\nu = 776.0\,\mathrm{cm}^{-1}$ can be attributed to the end gauche defect [19]. In addition, there is information in the literature about other end defects in n-alkanes during heating, which otherwise occur in planar chains [28]. Among them, apart from the end $gt_m$, observed, as we expected, at $\nu = 873.6\,\mathrm{cm}^{-1}$ [19,25,28], also the end defects $tg-$ and $gg-$ are identified, which we observed at frequencies $\nu = 845.0$ [19,25,28,29] and $869.3\,\mathrm{cm}^{-1}$ [19,28] respectively. Such defects also lead to significant bends in the ends of the chains, and therefore are more energy-intensive.

Changes in the concentration of the end defects of the three mentioned types detected in the studied spectral region during heating of tricosane are shown in Figure 7. As can be seen, the number of defects $tg-$ at frequency $\nu = 845.0\,\mathrm{cm}^{-1}$ is practically the same when tricosane is heated. The concentration of $gt_m$ at $\nu = 776.0\,\mathrm{cm}^{-1}$ decreases slightly during the transition to the rotator phases, which may indicate a high degree of defect localization. The number of end double gauche defects $gg-$ at $\nu = 869.3\,\mathrm{cm}^{-1}$ noticeably reacts to polymorphic transformations, increasing by 5–8 times during transitions between rotator phases, while the concentration of these defects in the lowest-temperature solid phase of tricosane differs little from their concentration in the high-temperature hexagonal phase.

Despite the large amount of available literature on possible conformational defects in n-alkanes, we were unable

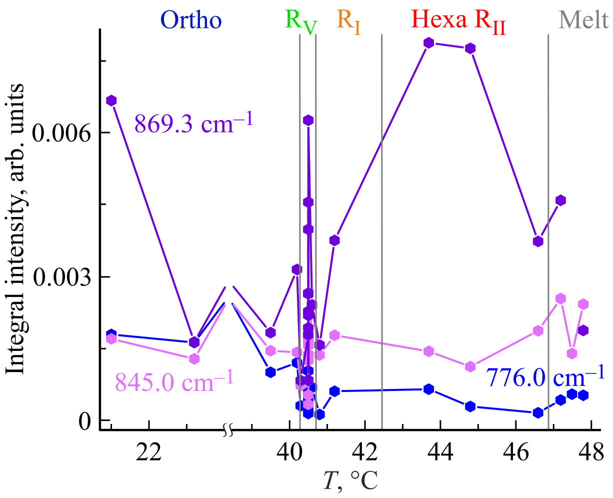

**Figure 7.** Temperature dependences of integral intensities of IR-bands of tricosane associated with the end gauche defects found in the region of progressions $P_k$ and $R_k$.

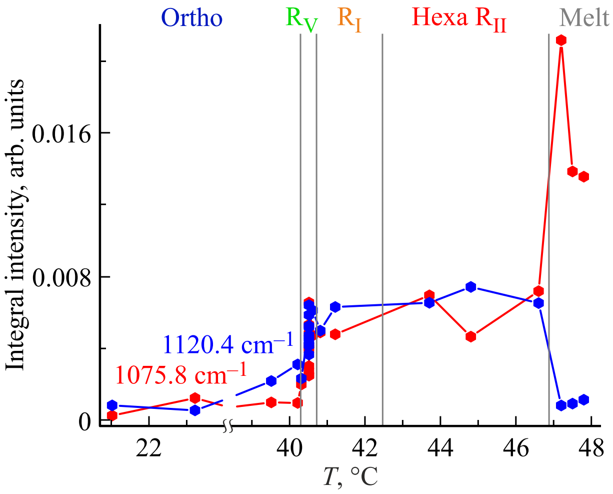

**Figure 8.** Temperature dependences of integral intensities of IR-bands of tricosane associated with some unknown conformation defects.

to find any information about defects corresponding to absorption bands at $\nu = 1075.8$ and $1120.4\,\mathrm{cm}^{-1}$, although these bands are characterized by a clear increase in integral intensities during the transition to the rotator phases (Figure 8). In this case, the first band behaves similarly to the band caused by the end defect $gt_m$ at the frequency $\nu = 1080.8\,\mathrm{cm}^{-1}$ $(m > 1)$, which suggests that this band is associated with some weakly localized defect. The second band, as noted earlier, is close in frequency to $R_2$ and has a significant effect on it. This band is probably caused by some highly localized conformational defect.

As it was mentioned earlier, the spectra of normal hydrocarbons clearly show rather intense absorption bands attributed to the rocking vibrations of the end methyl groups $CH_3$. The band of almost constant frequency near $890\,\mathrm{cm}^{-1}$ $(\beta)$ is attributed to the mixed skeletal vibrations and rocking in-plane vibrations of the methyl group, and these vibrations are localized at the ends of the molecule [17,30]. In the tricosane spectrum at $T = 21\,^\circ\mathrm{C}$, a strong absorption band of rocking in-plane vibrations of $CH_3$ groups at a frequency of $\nu = 891.0\,\mathrm{cm}^{-1}$ can be distinguished, and this mode refers to Vibrations of the ends of the chain in out of phase. In the spectrum of tetracosane [14], we managed to identify a weak low-frequency shoulder in this band associated with vibrations of the groups $CH_3$ in phase, however, in this case, for tricosane, a member of the progression of rocking vibrations $P_{15}$ appears in this region at a frequency of $\nu = 884.9\,\mathrm{cm}^{-1}$ (Figure 9, *a*), which significantly complicates the analysis of changes in these superimposed bands upon heating.

However, it was discovered that frequencies of these localized modes do not remain constant in the studied temperature range, and also demonstrate frequency offsets at temperatures corresponding to transitions between the rotator phases (Figure 9, *a*). Moreover, the number of bands in this area increases significantly when tricosane is heated. Thus, in the initial orthorhombic phase of tricosane $\beta$ vibration is observed at $\nu = 891.0\,\mathrm{cm}^{-1}$, however, already at $\Delta T = 40.2{-}40.3\,^\circ\mathrm{C}$ a significant low-frequency shoulder at $\nu = 887.5\,\mathrm{cm}^{-1}$ appears for this band with a significant decrease in intensity (Figure 9, *a*). We should emphasize that the vibration $\beta$ is considered surprisingly conformationally dependent [25], and therefore stands for the changes in the conformation of the ends of the chain. Based on the observed effects, it can be concluded that the initial structural changes during heating of tricosane occur precisely in the surface layers of the lamellae containing end methyl groups, while the ordered orthorhombic arrangement of molecules is still preserved in the lamellae cores. We came to similar conclusions when comparing the temperature changes of various modes of stretching vibrations of C$-$H bonds in tricosane [31].

Upon further heating in a very narrow temperature range $\Delta T = 40.3{-}40.5\,^\circ\mathrm{C}$, upon transition to the rotator phase $R_V$, the two studied bands are first compared in intensity, then the band with $\nu = 887.5\,\mathrm{cm}^{-1}$ becomes the main band, and the band at $\nu = 890.5\,\mathrm{cm}^{-1}$ turns out to be in the role of a high-frequency shoulder (Figure 9, *a* and *b*). In addition, the amplification of the $\nu = 887.5\,\mathrm{cm}^{-1}$ band is accompanied by the appearance of another high-frequency shoulder at $\nu = 893.5\,\mathrm{cm}^{-1}$. Upon further transition to $R_I$ phase, the three analyzed bands retain their intensities, with the exception of the progression member$P_{15}$, the influence of which is significantly weakened. When transiting into hexagonal phase $R_{II}$ the initial phase $\beta$ fully vanishes and only two bands $\nu = 887.8$ and $892.6\,\mathrm{cm}^{-1}$ remain.

When studying the tetracosane spectrum near $890\,\mathrm{cm}^{-1}$ $(\beta)$ [14] we obtained similar results. We found that during transition of $R_V \to R_I$ the frequency $\beta$ shifted from $\nu = 891.5\,\mathrm{cm}^{-1}$ to $\nu = 888.7\,\mathrm{cm}^{-1}$. Since a similar frequency shift $\beta$ during the solid-solid phase transition was also observed in [25], it was suggested

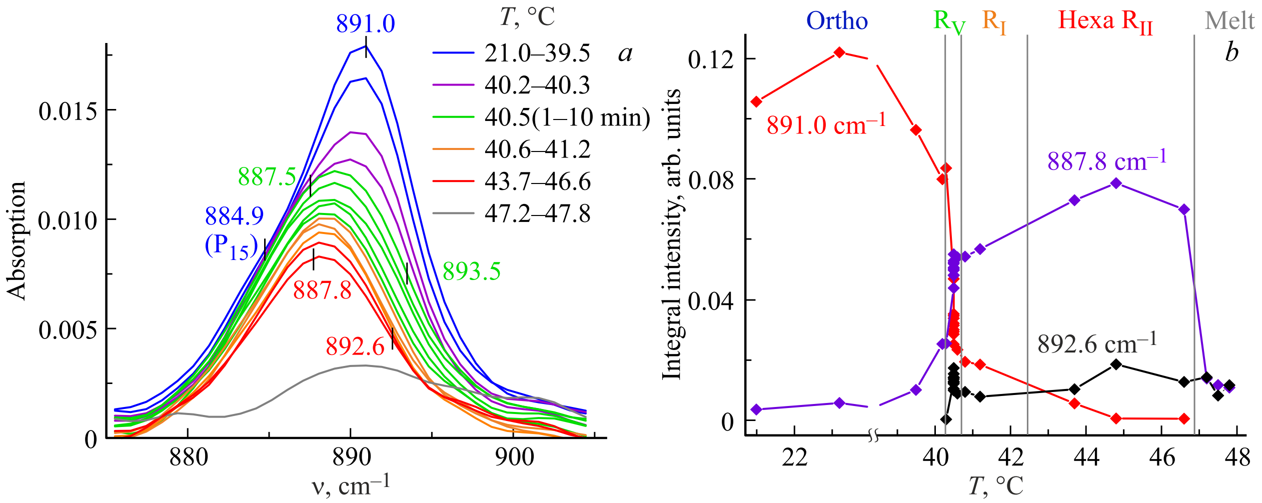

**Figure 9.** *a*) Temperature changes in the tricosane spectrum in 890 cm$^{-1}$ region, *b*) temperature dependencies of the integral intensities for the bands corresponding to the rocking in-plane vibrations of the methyl groups $CH_3$.

that this band for all n-alkanes is shifted towards lower frequencies as a result of an increase in conformational disorder.

In Snyder studies [17,18,21] the frequencies of the rocking vibrations $\beta$ of the methyl group for homologous series of n-alkanes were found, and based on their analysis it was found that frequency $\beta$ was different depending on the type of symmetry of the homologue crystal lattice: the triclinic structure is distinguished by a single band near 893 cm$^{-1}$, while the monoclinic and orthorhombic structures have doublets 888/893 and 891/894 cm$^{-1}$ respectively. The presented frequencies were determined at $T = -180\,°C$, so the differences with the results obtained at room temperature are not surprising. Yet, the frequencies of bands in $R_V$ and $R_I$ phases of tricosane are similar to the doublets described by Snyder. Since the frequencies $\beta$ depend on a certain type of interaction of the end methyl groups in neighboring lamellae, i. e., it is on the surface structure of the lamellae, and not on the structure of their cores [26], it is likely that the tilt of the molecules in the lamellae has some influence on frequency $\beta$.

We may conclude that significant transformations of frequencies and band intensities in the region of $\beta$ vibrations in case of tricosane with the initial orthorhombic symmetry of sub-cells are associated precisely with an increase in the of inter-lamellar space during transition to rotator phases ($R_V$ and $R_I$) and the possibility of some rotation of the end groups $CH_3$ relative to the rest of the chain. Similar results for tetracosane with the initial triclinic sub-cells were obtained during transition to the high-temperature phase $R_{II}$ [14], which highlights the differences in the kinetics of polymorphic transformations in homologues of different parity [12].

In conclusion, we'd like to highlight a significant decrease in the intensity of all absorption bands during transition from the solid phase to the liquid phase. The observed effect is explained by the change in electro-optical intermolecular interactions during transition from the ordered state to a „random" one [25].

## 4. Conclusion

Detailed analysis was performed concerning the conformation changes occurred during polymorphous transformations of tricosane $n$-$C_{23}H_{48}$ during heating, based on observed temperature changes of IR-Fourier-spectra in region $\nu = 700-1200\,cm^{-1}$ comprising progressions of the rocking vibrations of groups $CH_2$ ($P_k$) and stretching (skeletal) vibrations of bonds C$-$C ($R_k$), as well as rocking in-plane vibration of groups $CH_3$ ($\beta$).

Since the band progressions ($P_k$ and $R_k$) are caused by the presence of regular trans sequences in the cores of n-alkane lamellae, their temperature changes allow us to uniquely characterize which conformational transformations occur with trans molecules during heating. These results are complemented by the analysis of temperature changes in bands of localized vibration modes caused by vibrations in end methyl $CH_3$ groups or irregular conformers. The behavior of these bands reflects a change in the structure of a certain local section of the chain when the n-alkane is heated.

It should be noted that in IR-spectrum of n-alkane in all regular trans-conformation only $k$-odd terms of the rocking mode ($P_{odd}$) are active. It was found that under the influence of temperature, the selection rules are violated, and bands appear in the progressions corresponding to $k$-even rocking modes ($P_{even}$). Such bands can be IR-active, only if chains of n-alkanes contain at least one gauche conformer. Moreover, the simultaneous coexistence of even and odd terms of the progression (in such a proportion that the even terms are significantly weaker than the odd ones) indicates a slight deviation of the chain structure from a completely trans-conformation, which can only be due to the presence of conformers localized at the ends of the chains. As it turned out, even in the low-temperature orthorhombic structure $O_i$, a small part of the molecules are non-planar ($<1$ defects per molecule). Thus, thermally activated end gauche defects of various types do not disrupt the rest of the planar extended chains and, accordingly, do not noticeably deform the crystal structure in the lamella cores, as evidenced by the persistence of band progressions even in the high-temperature hexagonal phase.

The greatest interest belongs to increase in degree of conformation disorder during n-alkane heating. It has been found that the intensity of the bands $P_{odd}$ and $R_k$ decreases with each transition between the rotator-crystalline phases ($R_V \to R_I \to R_{II}$). Moreover, the most abrupt decrease in the intensity of progressions occurs precisely near the transition $R_V \to R_I$, which indicates significant violations of the trans-zigzag structure of molecules at this stage of structural transformations in tricosane. Since for the even n-alkane tetracosane, a similar decrease in the intensity of bands in progressions was detected precisely during transition of $R_I \to R_{II}$ [14], it can be assumed that the observed effects are associated with the relaxation of the metastable rotator phase to a more energetically beneficial one (for $C_{23}H_{48}$ the metastable phase is $R_V$, while for $C_{24}H_{50}$ — $R_I$ [12]). Probably, the relaxation process occurs due to the rapid appearance of end defects of various types in the near-surface regions of the lamellae [31]. Note that thermal activation of conformational defects during transition of $R_V \to R_I$ is also indicated by a slight increase in the intensity of bands attributed to $P_{even}$ modes of non-planar molecules that also response to transition to $R_{II}$ phase.

In addition, it was found for the first time that the end gauche defects $gt_m$ that occur during polymorphic transformations of tricosane differ in the degree of their localization in the chain. In this case, the concentrations of the end gauche conformers grow with increasing temperature, experiencing sharp jumps during transitions between the rotator phases $R_V \to R_I$ and $R_I \to R_{II}$, however, the thermal activation of a defect is clearly limited by the possibilities of its localization in the chain. It was found that the solid phases of tricosane are dominated by highly localized end gauche defects located in the surface layers of the lamellae, which emphasizes the preservation of regular trans-conformations by most molecules in the lamellae cores throughout all polymorphic transformations. Moreover, it can be assumed that molecules with more than one defect per chain appear in $R_I$ phase, while the total number of defective molecules increases significantly in the hexagonal phase $R_{II}$. The melt spectra are naturally dominated by the end defects with a low degree of localization, which makes formation of several conformers in a single chain a highly likely event.

We can state that the local conformation of the end gauche defect also impacts the rocking in-plane vibration ($\beta$) of $CH_3$ groups, with its frequency shifting towards lower frequencies with the rise in conformation disorder. It was found that in case of tricosane, the strongest changes in $\beta$ vibrations are characteristic of the transition to the rotator phase $R_V$, which may probably be due to transition to rotator phases with increased inter-lamellar space and the possibility of some rotation of the end groups $CH_3$ relative to the rest of the chain.

In our opinion, exactly the conformational disorder plays the key role in processes of re-arrangement of rotator-crystalline R-phases.

### Conflict of interest

The authors declare that they have no conflict of interest.

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