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Analysis of absorption band progressions in long-chain n-alkanes

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An analysis of absorption band progressions in the IR spectrum of monodisperse tricosane n-$C_{23}H_{48}$ was conducted. Dispersion curves were obtained for the absorption band progressions of the rocking vibrations of CH_2 groups and the stretching (skeletal) vibrations of C−C bonds. The interaction parameters of the studied vibrations were determined based on the coupled oscillator model in the selected regions corresponding to the approximation of interaction between the nearest neighbors. For the first time, it was established that the interaction parameters of the vibrations depend significantly on the magnitude of the phase shift.

Keywords: n-alkanes, IR spectroscopy, absorption band progressions, coupled oscillator model.

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1. Introduction

The model objects for various polymer materials may be selected as similar by their chemical composition, however, substantially lower molecular substances — long-chain n-alkanes C_nH_{2n+2}, commercially manufactured as monodisperse (with the accuracy of up to one C−C bond in the molecule skeleton) with various lengths of chains ($16 \leq n \leq 60$) and purity $\geq 95\%$. The study of such model objects will make it possible to answer questions at quantitative level regarding the features of structure formation in the processes of crystallization from melts and solutions, relationship between the structure and physical and chemical properties of arising supramolecular compounds, the mechanism of structural conversions with the change of the crystal phase state and etc.

The similarity of thermodynamic properties of long-chain molecular crystals (LCMCs), such as n-alkanes, and aliphatic polymers is based on the similar composition of crystalline cores of lamellae from methylene CH_2 trans-sequences [1,2]. The main structural difference of LCMCs from polymers consists in the fact that lamellar crystals are made from extended chains (ECC), i.e. lamellae surfaces are formed with terminal groups of molecules, and not their folds. In connection with the considerable effect of the terminal groups at the molecule packaging in the lamellae for LCMCs, effects arise that are not specific for the polymer materials, for example, so called „parity effect". Depending on even/odd number of carbon atoms in the chain, the symmetry of individual molecules of homologues (trans- or cis-form) changes, and, as a result, the nature of regular trans-zigzags location changes in the crystalline cores of lamellae relative to the base planes of terminal groups — vertical location for odd homologues and inclined location for even homologues [3].

Besides, a relevant area in the physics of polymers for many years remains the clarification of the mechanism of polymorphous transformations of long-chain n-alkanes when transitioning from a solid state to a melt and back [4–8]. In particular, using the combination of the methods of synchrotron X-ray diffractometry and differential scanning calorimetry [9], we managed for the first time to identify the kinetics of the development of a complete sequence of phase transitions of various nature in tricosane n-$C_{23}H_{48}$, in particular, kinetics of the transitions between the following phases: 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 $R \rightarrow$ liquid. It was possible to obtain more detailed information on the structural rearrangements in polymorphous transformations of tricosane at the level of molecular vibrations based on the method of IR Fourier spectroscopy [10].

We believe that the found complex mechanism of polymorphic transformations of some rotator-crystalline phases into others in n-alkanes 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-$C_{24}H_{50}$ [11].

This article is the continuation to the previously started paper [11] on the analysis of the conformation of molecules

of long-chain n-alkanes in a low-temperature polymorphous modification based on data of IR Fourier spectroscopy. This paper will be based on the study of the structure of molecular trans-zigzag in the lamellae cores of odd n-alkane tricosane n-$C_{23}H_{48}$ and comparison to the above results for even tetracosane n-$C_{24}H_{50}$ [11]. It is necessary to study the initial structure of the molecules for further analysis of its change in polymorphous transformations.

As is known [12,13], the presence of regular trans-sequences in the structure of long-chain n-alkanes results in appearance of progressions of absorption bands in IR spectra. Appearance of progressions in the spectra is caused by non-localized nature of vibrations covering many atoms in a molecule. The number of bands in a progression, their frequency and intensity depend both on the chain length and its conformation, therefore the progressions of bands turn out to be highly sensitive to the structural changes in the composition of regular trans-sequences in the lamellae cores.

One of the simplest methods of calculation of non-localized vibrations of long-chain molecules is based on model of linear chain of coupled oscillators, where each oscillator is an electrical dipole [12,14]. A simple coupled oscillator model for the chain of N parallel/antiparallel dipoles with fixed ends allows determining N possible discrete normal vibration frequencies [12]:

$$\omega_i^2 = \omega_0^2 + 2\omega^{*2}\left(1 \pm \cos\frac{i\pi}{N+1}\right),\ i = 1, \ldots N, \qquad (1)$$

where ω_0 — frequency of an unperturbed oscillator, ω^* — a parameter of interaction with frequency dimension, ω_i — frequency of oscillators of the ith vibration mode, N — number of monomer units in a chain or a number of bound dipoles. A set of frequencies with „+“ sign corresponds to vibrations of chain of parallel dipoles, with sign „–“ — chain of antiparallel dipoles. For the chain of parallel dipoles we obtain that at $i = N + 1$ the vibration occurs at frequency ω_0, and at $i = 0$ — at frequency equal to $\sqrt{\omega_0^2 + 4\omega^{*2}}$. Thus, all values ω_i^2 (at $i = 1, \ldots N$) are in range with width $4\omega^{*2}$ (similar for vibrations of antiparallel dipoles). Thus, the lowest frequency band of the series is shifted towards frequency ω_0 and approaches it asymptotically as the chain length increases to infinity. In case of infinite chain only one normal vibration turns out to be active in the IR spectrum, but for chains with finite length many of bands of series can be active [12]. In most cases the number of IR-active vibrations or observed bands in progressions is determined as $N/2$ or $(N + 1)/2$ depending on parity of value N. Since the progressions arise due to the difference in the value of the phase shift of vibrations in adjacent oscillators, frequencies of bands in the progressions are applied above phonon disperse curves designed for polymethylene chains in a trans-conformation [14–18].

Therefore, based on the model of coupled oscillators, the trans-structure of molecules of long-chain n-alkanes will be analyzed, using the example of tricosane, in a low-temperature polymorphous modification.

2. Experimental part

The paper studies low-temperature modification of odd n-alkane tricosane n-$C_{23}H_{48}$, monodisperse samples (with purity of 99 %) of which are made by Sigma-Aldrich as plate flake-like products of synthesis.

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 at room temperature in the region $\nu = 400-5000\,\mathrm{cm}^{-1}$ on Bruker IFS-88 Fourier-transform IR spectrometer with a resolution of $2\,\mathrm{cm}^{-1}$. When recording the number of scans was 50. 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 separation of overlapping absorption bands in the experimentally obtained IR-spectra into individual components and their subsequent analysis were carried out using Fityk 1.3.1 software [19] and Pearson VII function.

3. Analysis of progressions in absorption bands of tricosane $C_{23}H_{48}$

To analyze the trans-zigzag structure of odd n-alkane tricosane molecule in low-temperature polymorphous modification (orthorhombic crystalline phase O_i), an IR spectral region containing the two most intense vibration progressions of methylene trans sequences was selected. The band progression caused by the rocking vibrations of CH_2 groups in n-alkanes is manifested in $\nu = 700-1100\,\mathrm{cm}^{-1}$ region and is designated by Snyder as P_k [20]. 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 $\nu = 950-1150\,\mathrm{cm}^{-1}$. The designation R_k is selected to denote this progression [20]. It should be noted that both progressions are strongly influenced by a rather intense band near $890\,\mathrm{cm}^{-1}$ associated with the localized rocking in-plane vibration of the terminal methyl CH_3 group and denoted as β (or P_{CH3}) [20].

It is necessary to note that stretching vibration C–C of a trans-bond causes a very weak change in dipole moment as a result of local central symmetry of the bond. Actually, these vibrations must not be active in the IR spectrum. However, it is believed [21] that the observed intensities of n-alkane skeletal vibration bands in the rectified trans-conformation are almost fully caused by the contribution of rocking vibrations of terminal methyl CH_3 groups.

The spectrum of tricosane in phase O_i is shown in Figure 1, the bands were assigned in accordance with papers [20,22]. Experimental values of frequencies are presented in Table 1.

Most of the selected vibration frequencies in the tricosane spectrum at room temperature (Table 1) are slightly

Table 1. Experimental values of frequencies in progressions of bands of rocking (P_k) and skeletal (R_k) vibrations of tricosane n-$C_{23}H_{48}$ at $T = 21\,^{\circ}C$

Designation (according to [20])	Observed frequency, cm^{-1}
P_1	719.4/729.1
P_5	724.2
P_7	737.1/742.0
P_9	750.8/755.3
P_{11}	784.9
P_{13}	832.3
P_{15}	884.9
$\beta(P_{CH3})$	891.0
P_{17}	938.2/942.2
R_8	969.4
R_9	973.2
R_7+R_{10}	985.3
P_{19}	990.8/995.7
R_{11}	1000.4
R_6	1012.9
R_{12}	1017.0
R_{13}	1031.1
$P_{21}+R_5$	1037.8
R_{14}	1042.7
R_{15}	1048.4
R_{16}	1053.2
R_{17}	1057.5
R_{18}	1061.8
R_{19}	1066.7
R_4	1071.2
R_3	1098.7
R_2	1124.6
R_1	1133.2

shifted towards lower values compared to literature data for the same molecule in its elongated conformation (at $T = -180\,^{\circ}C$) [22]. This spectral behavior is due to a lower concentration of trans-conformers [21], 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 simplest terminal gauche defect [11].

It is well known [23] that intense doublets of characteristic bands are observed in the area of deformation vibrations of the tricosane IR spectrum, including for rocking vibrations: $\nu(P_1) = 719.4/729.1\,cm^{-1}$ (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 subcell [12,24]. The degree of splitting of such bands depends on the value of intermolecular interaction of [23], which varies with temperature [10]. Thus, the appearance of doublets of deformation vibration bands in the IR spectra indicates the formation of subcells of orthorhombic symmetry [23], comprising two molecules per cell. A more general consideration of this issue was presented by Davydov [25], 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 subcells 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 subcell.

Note that members of progression of rocking vibrations of CH_2 (P_1) groups at $k = 3$ and 5 are covered by an intense doublet of bands P_1 ($k = 1$). However, based on the expansion of the doublet area it was possible to separately identify a band P_5, which agrees with assignment of a similar band in shorter homologues n-$C_{17}H_{36}$ and n-$C_{19}H_{40}$ with orthorhombic subcells [20]. Besides, the identified frequency matches well with disperse dependence (see below).

In contrast to even n-alkanes, for odd homologues it is specific that odd members appear in the progression of skeletal vibrations. Probably, it is the cis-symmetry of the odd homologue molecule, when the terminal methyl groups are arranged at one side from the trans-zigzag axis, is the main cause of appearance of additional progression members. Note that even members of skeletal vibrations have very weak intensity, which is also the manifestation of the difference from the similar progression of the even n-alkane, having trans-symmetry of molecules [11]. It is difficult to insist on the precise compliance of the top members of progression (R_{17}, R_{18}, R_{19}), since in the literature these members were not identified or analyzed previously. At the same time, the frequencies of these bands agree perfectly with the disperse curve (see below).

The band at $\nu = 1134\,cm^{-1}$ in polyethylene corresponds to the stretching vibration of all C–C bonds in the phase [21], the corresponding bond in n-alkanes R_1 at $k = 0$ appears in the spectra of only odd members (note that justification of using here the $k = k - 1$ shift value is given in [20], and it is related to the presence of the minimum in the disperse curve). Sometimes, in the literature the skeletal vibrations are characterized as symmetrical and asymmetrical, and in the first case the vibrations of C–C bonds are in phase, and in the second one — out of phase [26]. For a polymethylene chain the corresponding frequencies are equal to $\nu_s(C{-}C) = 1131\,cm^{-1}$ and $\nu_a(C{-}C) = 1060{-}1070\,cm^{-1}$ [15,26,27]. The closest by frequency to the out of phase vibrations in the tricosane spectrum is the R_{19} band.

Figure 2 shows the frequencies of the observed progression bands of rocking vibrations of CH_2 (P_k) groups (a) and skeletal vibrations of (R_k) C–C bonds (b) in the form of dependences on φ/π, where the phase shift between two adjacent oscillators $\varphi = k\pi/(N+1)$, $k = 1, \ldots N$ (k — number of vibration mode $k = N - i + 1$, N — number of modes equal to the number of oscillators in the chain, i.e. for CH_2 groups $N = 21$, for C–C bonds $N = 22$).

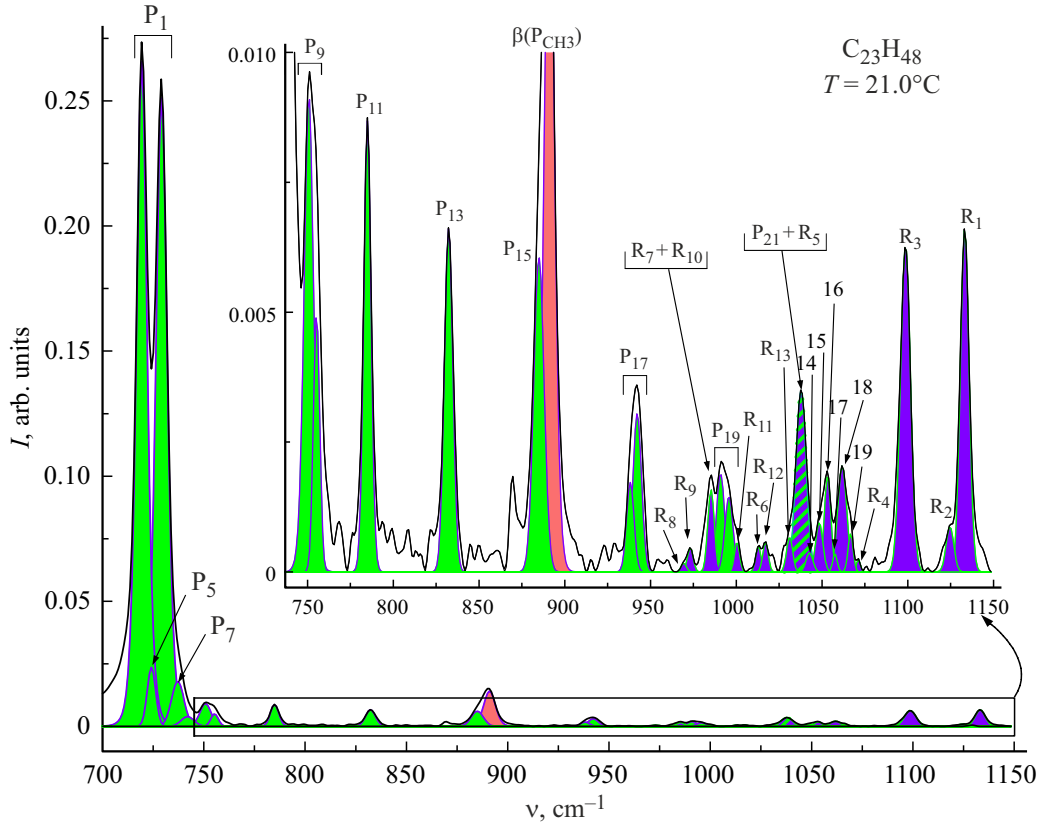

Figure 1. IR spectrum of tricosane n-$C_{23}H_{48}$ at $T = 21\,^{\circ}$C. Absorption bands attributed to rocking vibration progressions of CH_2 (P_k) groups (green bands) and valence vibrations of C−C (R_k) bonds (purple bands) are identified, the characteristic rocking vibration of the methyl CH_3 (β) group is also highlighted (red band).

The experimentally found frequency-phase dependences indicate correctness of the made assignment of progression bands [14–17,20,22]. Moreover, the results for tetracosane n-$C_{24}H_{50}$ from our previous article are also included on the obtained graphs in Figure 2 [11]. Note a very good agreement of the obtained disperse curves for two homologues.

In accordance with the literature data, let us accept for further analysis that the lowest frequency band ($719.4\,\mathrm{cm}^{-1}$) in the area of rocking vibrations n-$C_{23}H_{48}$ is the frequency of the unperturbed oscillator ω_0, and the highest frequency one ($1037.8\,\mathrm{cm}^{-1}$) corresponds to value $(\omega_0^2 + 4\omega^{*2})^{1/2}$. The assumed simplifications enable us to evaluate the mean value of oscillators interaction parameter $\omega^* = 374.0\,\mathrm{cm}^{-1}$. The obtained value is slightly lower than calculated similarly for n-$C_{24}H_{50}$ in [11] — $384.8\,\mathrm{cm}^{-1}$ or in [12] — $381\,\mathrm{cm}^{-1}$. Since the disperse curve for rocking vibrations fully corresponds to the one obtained previously for tetracosane (Figure 2, *a*), this paper makes it possible to confirm the values of parameters ω_0 and ω^* from paper [11] regarding the odd homologue.

Similarly the disperse curve obtained in this paper for skeletal vibrations (Figure 2, *b*) fully complies with the one found previously for tetracosane [11], and also contains twice more values of experimental frequencies. Therefore, this paper makes it possible to determine more accurate values of ω_0 and ω^* parameters for skeletal vibrations.

According to the model of related oscillators, the dependence of the square of rocking vibration frequencies of CH_2 groups representing parallel dipoles on parameter $\left(1 + \cos i\pi/(N+1)\right)$ may be presented as a linear function of (equation (1)), which corresponds to the red solid line in Figure 3, *a* for the experimentally obtained values ω_0 and ω^*. Note that CH_2 groups are a set of parallel dipoles $(\uparrow\uparrow)$ in case of rocking vibrations. As is known [11,12], squares of experimental frequency values of rocking vibrations (P_k) do not agree with the linear dependence (Figure 3, *a*), corresponding to the simple theory of interacting oscillators accounting only for the effect of closest neighbors. In case of rocking vibrations, the squares of experimental frequency values are found below the estimated direct dependence, and to eliminate this deviation, it is necessary to take into account the interaction of not only the nearest neighbors, but also the oscillators following them.

The square of frequencies of skeletal vibrations (R_k) shall linearly depend on parameter $\left(1 \pm \cos i\pi/(N+1)\right)$. As assumed in [11], the minimum presence on the dispersion dependence can mean transition from mode of antiparallel dipoles $(\uparrow\downarrow)$ to mode of parallel dipoles at $(\uparrow\uparrow)$ at $\varphi/\pi = 0.3-0.4$, so these regions shall be considered

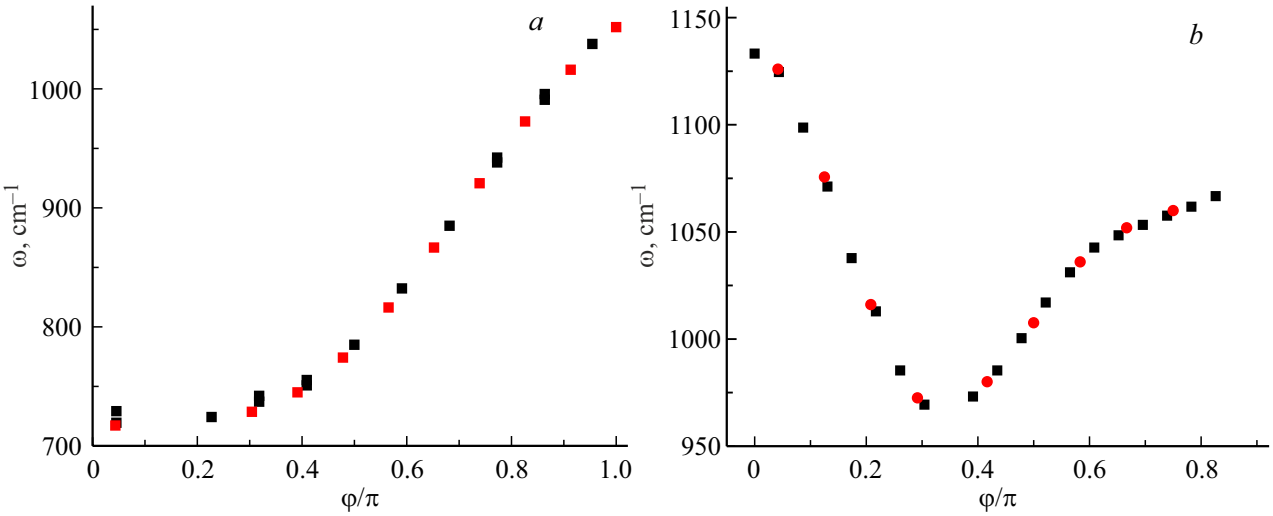

Figure 2. Experimental frequency-phase dependences for rocking vibrations (P_k) of methylene groups (a) and skeletal vibrations (R_k) of C−C bonds (b) of tricosane n-$C_{23}H_{48}$ at $T = 21\,^{\circ}$C (data obtained in this paper is marked black). The results are compared to the dependence for the even homologue of tetracosane n-$C_{24}H_{50}$ (red) [11].

individually. Such behavior of dipole moments in the chain is only possible for vibrations of C−C bonds, which is due to the feature of the disperse curve (Figure 2, b). As it is difficult to determine accurate boundary values of frequencies of two regions (except for band R_1 at $k = 0$, which corresponds to $i = N + 1$, i. e. high frequency boundary), then suppose that end points in both regions detected by experiments belong to the theoretical curve. Then it is possible to evaluate values of parameters in region of antiparallel dipoles: $|\omega_0'| = 586.0$ and $\omega^{*\prime} = 637.9\,\mathrm{cm}^{-1}$. At that ω_0' for antiparallel dipoles is purely imaginary quantity, this results in abrupt decrease in frequencies in this region and their transformation to zero at parameter value $\left(1 - \cos i\pi/(N+1)\right) \approx 0.42$. But this is not observed: vibrations do not stop, but transit to mode of parallel dipoles at parameter value $\left(1 + \cos i\pi/(N+1)\right) \approx 0.47$. In the region of parallel dipoles we get the following parameter values: $\omega_0'' = 916.7$ and $\omega^{*\prime} = 283.1\,\mathrm{cm}^{-1}$.

The performed theoretical calculation of dependence of squares of frequencies of skeletal vibrations (R_k) is presented in Figure 3, b in form of blue straight line for mode of antiparallel dipoles and red straight line for the mode of parallel dipoles (in both cases dependences are reduced to parameter $\left(1 + \cos i\pi/(N+1)\right)$). Note that similarly to results for rocking vibrations the squares of experimental values of frequencies R_k do not agree with the curve corresponding to the simple theory of interacting oscillators (Figure 3, b).

However, we would like to note that individual areas may be identified in the obtained experimental dependences for the squares of P_k and R_k vibration frequencies (Figure 3), which seemingly correspond more to the model of coupled oscillators. Therefore, it is possible to use a simple theory of interacting oscillators in a modified form for certain groups of vibration modes.

The area of skeletal vibrations in the mode of parallel dipoles may be divided into two areas (I and II) with different parameters: $\omega_0''(\mathrm{I}) = 898.8$ and $\omega^{*\prime\prime}(\mathrm{I}) = 323.4\,\mathrm{cm}^{-1}$, $\omega_0''(\mathrm{II}) = 978.3$ and $\omega^{*\prime\prime}(\mathrm{II}) = 220.7\,\mathrm{cm}^{-1}$. As you can see in Figure 3, b, the model of coupled oscillators perfectly describes the area of parallel dipoles of skeletal vibrations. Therefore, additional fragmentation of the area of parallel dipoles makes it possible to minimize the impact of interaction between remote oscillators and characterize the area corresponding to the approximation of interaction between the closest neighbors.

Similarly the additional areas can be considered for rocking vibrations and skeletal vibrations in the mode of antiparallel dipoles. Estimated values of ω_0 and ω^* parameters for various regions, which to a large extent comply with the simple theory of interacting oscillators, are presented in Table 2. Then for the skeletal vibrations it is possible to clarify the values of parameters, at which the vibrations of antiparallel dipoles change into the mode of parallel ones: $\left(1 - \cos i\pi/(N+1)\right) \approx 1.52$ and $\left(1 + \cos i\pi/(N+1)\right) \approx 0.48$, respectively.

Therefore, the experimentally obtained dependences of frequency squares of rocking (P_k) and skeletal vibrations (R_k) may be divided into several linear areas, which are described well by a simple model of coupled oscillators (Figure 3). For P_k there are areas — I, II, III; for R_k — III, IV, I, II. Based on the obtained results and taking into account that the parameter $\left(1 + \cos i\pi/(N+1)\right)$ may be presented in the form of $(1 - \cos\varphi)$, it can be concluded that the parameter of interaction ω^* of oscillators depends on phase shift φ, and substantially so.

The changes in the interaction parameter ω^* of vibrations in progressions P_k and R_k depending on the value of phase shift φ are presented in Figure 4. As can be seen from Figure 4, a, the force of interaction of rocking oscillators

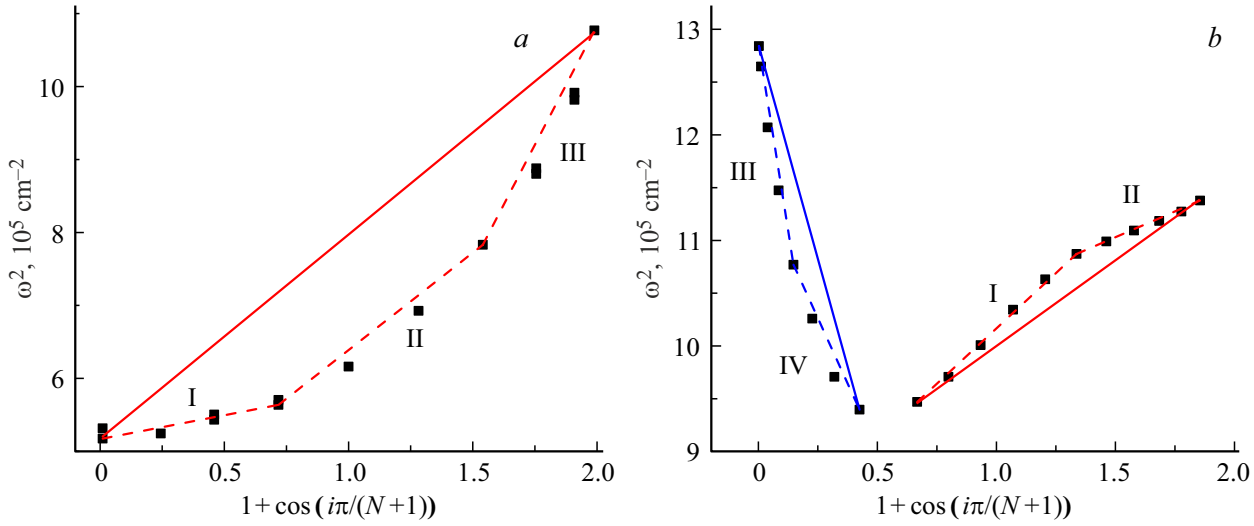

Figure 3. Dependences of squares of experimental frequency values for rocking vibrations (P_k) of methylene groups (a) and skeletal vibrations (R_k) of C−C bonds (b) of tricosane n-$C_{23}H_{48}$ at $T = 21\,^{\circ}$C on parameter $\left(1+\cos(i\pi/N+1)\right)$. Theoretically expected linear dependences for parallel dipoles are shown in red, and for antiparallel ones — in blue. Dotted lines show linear dependences corresponding to the additional splitting of areas of parallel and antiparallel dipoles.

Table 2. Values of ω_0, ω^*, $\varkappa$ and α parameters determined using the model of coupled oscillators for various regions of dependence of frequency squares in progressions of bands of rocking vibrations (P_k) of methylene groups and skeletal vibrations (R_k) of C−C bonds of tricosane n-$C_{23}H_{48}$ at $T = 21\,^{\circ}$C on $\left(1+\cos\frac{i\pi}{N+1}\right)$ parameter. For a set of parallel dipoles the designation ↑↑ is accepted, for antiparallel ones — ↑↓

Type of vibrations	Set dipoles	Region	ω_0, cm^{-1}	$\varkappa$, dyn/cm	ω^*, cm^{-1}	α, dyn/cm
Rocking vibrations CH_2 groups	↑↑		719.4	$4.28\cdot10^5$	374.0	$1.16\cdot10^5$
		I	718.9	$4.28\cdot10^5$	180.6	$0.27\cdot10^5$
		II	610.0	$3.08\cdot10^5$	365.2	$1.10\cdot10^5$
		III	474.0 i	$-1.86\cdot10^5$	571.9	$2.71\cdot10^5$
Skeletal vibrations C−C bonds	↑↑		916.7	$6.96\cdot10^5$	283.1	$0.66\cdot10^5$
		I	898.8	$6.69\cdot10^5$	323.4	$0.87\cdot10^5$
		II	978.3	$7.92\cdot10^5$	220.7	$0.40\cdot10^5$
	↑↓		586.0 i	$-2.84\cdot10^5$	637.9	$3.37\cdot10^5$
		III	1249.9 i	$-12.93\cdot10^5$	843.6	$5.89\cdot10^5$
		IV	400.3	$1.33\cdot10^5$	497.2	$2.05\cdot10^5$

increases with the increase of the phase shift value, and for the skeletal vibrations this dependence turns out to be inverse and significantly non-linear (Figure 4, b).

It may be assumed that the force of interaction of rocking oscillators increases to a large extent with the phase shift tending to $\varphi \approx \pi$, since the rocking vibrations are a set of parallel dipoles, and large phase shifts cause higher interaction energy. Similarly it can be explained that the maximum bond energy for the mode of antiparallel skeletal vibrations is achieved at $\varphi \approx 0$. Probably, the continued declining dependences in the mode of parallel skeletal vibrations as well with phase shift increase may be due to the specific nature of dipole moment change for this mode of C−C bond vibrations.

Based on the estimated values of parameters ω_0 and ω^* for the regions corresponding to the simple theory of interacting oscillators, the values of force constants of vibrations $\varkappa$ and bond constants α may be evaluated based on the following ratios: $\omega_0^2 = \varkappa/m$ and $\omega^{*2} = \alpha/m$, where the weight of the oscillator (CH_2 group) is determined as $m = m_C + 2m_H = 2.33\cdot10^{-23}$ g ($m_H = 1.674\cdot10^{-24}$ g, $m_C = 1.994\cdot10^{-23}$ g [28]). Estimated values of parameters $\varkappa$ and α are presented in Table 2. The order of the obtained values agrees well with the average values of valence and deformation force constants for C−C and C−H bonds in various substances [15,27,29–33].

Note that the negative force constant of $\varkappa$ vibrations (Table 2) may indicate system instability. In such cases

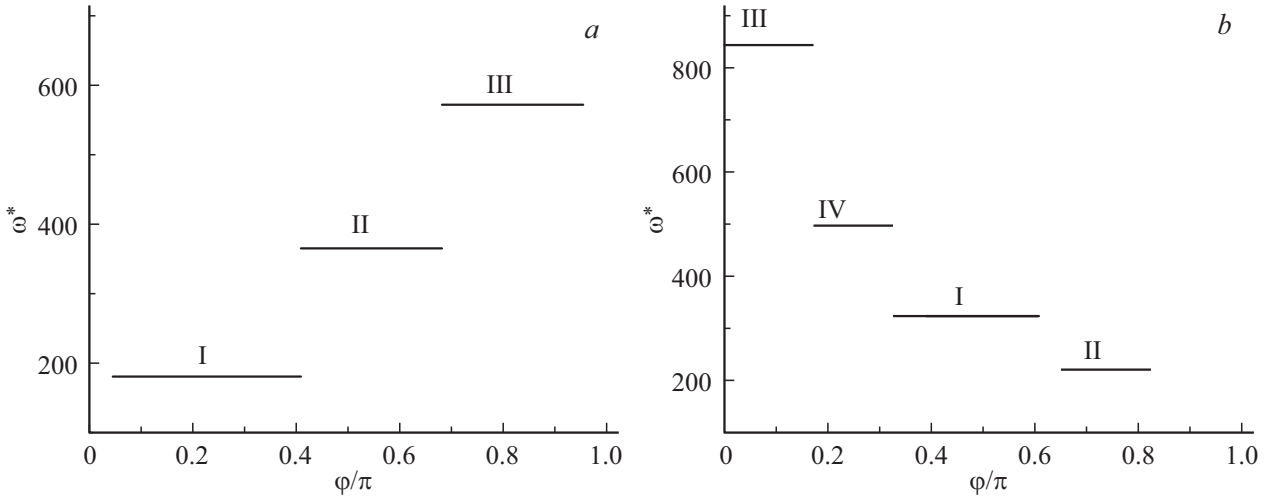

Figure 4. Dependences of interaction parameters of rocking vibrations (P_k) of methylene groups (a) and skeletal vibrations (R_k) of C−C bonds (b) of tricosane n-$C_{23}H_{48}$ at $T = 21\,^{\circ}C$ on phase shift φ.

any minor disturbance results in the fact that the system tends to leave the equilibrium position and not to return. If for the skeletal vibrations $\varkappa < 0$ is related to the transition from the mode $\uparrow\downarrow$ in $\uparrow\uparrow$, for the rocking vibrations (region IV), probably, $\varkappa < 0$ leads to the transition to twisting vibrations [34].

4. Conclusion

The detailed analysis was performed on two most intense progressions of vibrations of methylene trans-sequences in the area $\nu = 700{-}1200\,\mathrm{cm}^{-1}$ of IR Fourier-spectrum of odd n-alkane tricosane n-$C_{23}H_{48}$: progressions of rocking vibrations of CH_2 (P_k) groups and valence (skeletal) vibrations of C−C bonds (R_k).

Analysis of progressions of bands (P_k and R_k) was performed based on the widely used model of one-dimensional linear chain of coupled oscillators. Parameters were defined that described interaction of adjacent oscillators (ω_0, ω^*, $\varkappa$ and α). Moreover, it was possible to identify the areas in the band frequency square dependences in progressions on the parameter $\left(1 + \cos i\pi/(N+1)\right)$, which are described well by the linear dependence and correspond to the approximation of interaction only between the closest neighbors. For the first time on the basis of the obtained fragmentation of vibration modes into groups that to a large extent corresponded to the simple theory of interacting oscillators it was found that the parameter of interaction ω^* of vibrations in progressions P_k and R_k depends substantially on the phase shift value φ.

The presence of pronounced progressions P_k and R_k in the IR spectrum indicates a nearly defect-free trans-conformation of molecules of long-chain n-alkane tricosane at $T = 21\,^{\circ}C$ in the lowest temperature polymorphous (orthorhombic) modification. The patterns of polymorphous transformations when heating n-alkane n-$C_{23}H_{48}$ up to melting temperatures are studied in paper [35], which analyzed the thermal activation of conformation defects of different types and the corresponding lengths of trans-sequences in the lamellae cores in polymorphous transformations.

The numerical results obtained in the paper are useful to simulate the structure of long-chain n-alkanes, since specification of the accurate parameters of initial molecular structure of n-alkane was necessary to establish the kinetics of structural transformations in polymorphous transformations.

Conflict of interest

The authors declare that they have no conflict of interest.

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