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PHYSICAL PROPERTIES OF CRYOCRYSTALS

IR-spectroscopy of ethanol formed by recondensation from a nitrogen cryomatrix

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The processes of formation and the properties of ethanol recondensates, formed from a nitrogen cryomatrix during its evaporation, are investigated. Ethanol molecules create matrix-isolated polyagregates due to co-condensation with nitrogen. The matrix evaporation at 35 K is accompanied by recondensation of ethanol from the matrix onto a substrate. This leads to a formation of a highly-dispersive film (recondensate) consisting of aggregates of different size including dimers and monomers. IR-spectroscopic investigations of recondensed samples were performed. The condensation temperature was $T_c = 12$ K. The gas phase pressure in the cryodeposition process was $P = 10^{-5}$ Torr. The ethanol concentration in nitrogen was from 0.5 to 10%. The film thickness was varied from 1 to 30 μm . The spectral range of measurements was 400–4200 cm^{-1} . From a comparative analysis of oscillatory spectra of samples of ethanol cryocondensates, matrix-isolated ethanol in a nitrogen cryomatrix and ethanol recondensates, we concluded that both polyagregates located previously in a matrix and recondensed onto a substrate are in a glass state. A film heating near the glass point of ethanol (97 K) leads to transitions, which take place in a few steps at different temperatures. Such a character of a warming-up curve is explained by a highly-dispersive composition of recondensates and by a dependence of the glass point of polyagregates on their size. The character of warming-up curves of recondensates allows to speak about grouping of elements of recondensates by their size. In other words, in the process of recondensation and possible further coalescence, polyagregates with preferential sizes, which are energetically optimal for these conditions, are formed. In the considered case it is reasonable to speak about existence of three such sets, involved sequentially in a glass transition. © 2011 American Institute of Physics. [doi: 10.1063/1.3662482]

INTRODUCTION

Unique properties of solid ethanol are being kept under close watch of scientific groups from various countries for a long time. Not going deep into analysis of these investigations, we will confine ourself to indication of main, in our opinion, publications related to a subject of discussion.^{1–6} In doing so, we note that most of the works for last 20–30 years are focused on study of solid ethanol obtained by superfast cooling a liquid phase (quenching). This fact was mentioned by us previously and has inspired complex investigations of properties of solid-ethanol thin films obtained during cryovacuum condensation from a gas phase on substrates with different temperatures of cryodeposition.^{7–9} A substantial part of our investigations for last three years was focused on study of ethanol immobilized in a process of co-condensation in cryomatrices, in particular, in a nitrogen cryomatrix. An investigation of processes of cluster formation of ethanol molecules during the co-condensation with a matrix gas,⁹ but not study of ethanol molecules in a matrix, has been assumed. However, the question “What happens to ethanol immobilized at low temperatures in a nitrogen matrix, when the nitrogen evaporates after increasing the temperature?” remains unresolved until now. What are properties of a phase formed on a substrate?

FORMULATION OF THE PROBLEM AND EXPERIMENT

In Fig. 1, the formulation of the problem discussed in the paper is illustrated. Let us mention main steps of the experiment.

1. Cryocondensation of a mixture of nitrogen and ethanol for different concentration ratios is carried out on a substrate at $T = 12$ K. A cryocondensate, 25–30 μm thick film, is formed at a given concentration of ethanol in a nitrogen matrix (Fig. 1(a)). IR-spectra of the film are recorded, and the cluster composition of ethanol in the matrix is determined (for more details see Refs. 7 and 9).
2. The substrate temperature increases up to a sublimation temperature of nitrogen (38–40 K) (Fig. 1(b)). In the experiments discussed below, the temperature was risen up to 70–80 K. The nitrogen gas was pumped out of the chamber, and with that the ethanol structural elements, contained in the matrix, recondense from the matrix onto the substrate. For the sake of brevity, let us call the substance formed in this way as ethanol *recondensate*.
3. The substrate together with the sample of the ethanol recondensate located on it is cooled down to the temperature $T = 12$ K, and its IR-spectrum is recorded. IR-spectra of the matrix-isolated state of ethanol, the ethanol cryocondensate and the ethanol recondensate are compared.
4. At a fixed frequency of an IR-spectrometer the ethanol recondensate is warmed up to its complete evaporation. At the same time a signal from a laser interferometer is measured. The results are compared with the warming-up curves of pure ethanol samples.

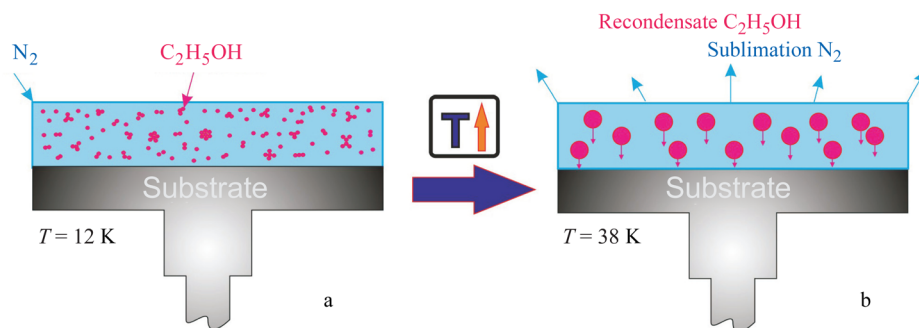


FIG. 1. A scheme of formation of an ethanol recondensate in the process of evaporation of a nitrogen matrix.

RESULTS AND DISCUSSIONS

In Fig. 2, vibrational spectra of ethanol for three different films are shown. The upper curve is for ethanol (3%) in a nitrogen matrix; the condensation temperature is $T = 12$ K. The middle curve is for pure ethanol, $T = 12$ K, the film thickness $d = 1$ μm . The lower curve is from the ethanol recondensate formed after evaporation of nitrogen at the temperature of 38 K, annealed up to 80 K and cooled again down to 12 K. As may be seen, the considered spectra retaining the main characteristic absorption lines have significant distinctions. For example, the main feature of the upper spectrum is the presence of characteristic absorption lines corresponding to different cluster states of ethanol molecules in a nitrogen matrix. In the work Ref. 9, a detailed analysis of these spectra for different concentration ratios, and its comparison with spectra of pure samples of ethanol, are given. The most evident manifestation of ethanol clusterization in the matrix is two absorption lines at the frequencies $\nu = 3658$ and 1258 cm^{-1} indicating a presence of monomers and dimers of ethanol in the matrix.^{10,11}

The warming-up of the sample and the nitrogen evaporation lead to recondensation of ethanol from the matrix onto the substrate surface (the lower spectrum). The change of a general character of the spectrum is a consequence of morphological changes in the sample, in particular, a combination of monomers and dimers into structural elements with larger size. It is assumed here that the process of combination of structural elements do not lead to final formation of a continuous film. It follows from the comparison of vibrational spectra of the ethanol recondensate with the spectrum

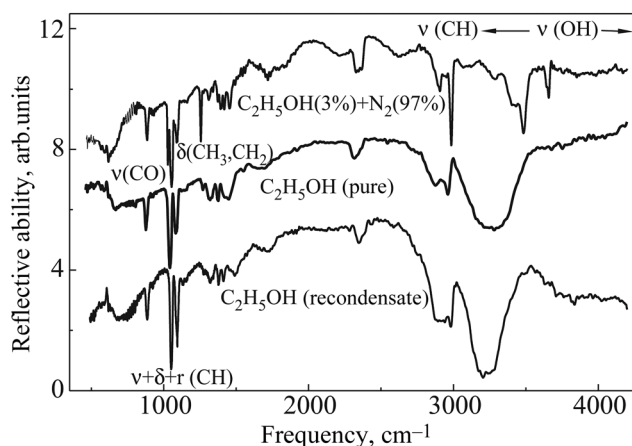


FIG. 2. IR-spectra: ethanol (3%) in a nitrogen matrix, $T = 12$ K; pure ethanol, $T = 12$ K, the film thickness $d = 1$ μm ; the ethanol recondensate formed after nitrogen evaporation, $T = 12$ K.

of the sample obtained during cryodeposition of pure ethanol (the middle curve). A clear shift of characteristic vibrations of the ethanol recondensate towards the short-wave frequency range in comparison with the cryocondensate is observed. In addition, an absorption line of O—H-bond of the recondensate is significantly narrower and has a fine structure that can indicate an inhomogeneity of the recondensed sample.

Among most evident differences of the considered spectra of the recondensate from the upper curves one can point out the following: the shift of characteristic frequencies, corresponding to valent vibrations $\nu(\text{CCO})$, from 877 to 886 cm^{-1} ; the shift to the short-wave region of absorption lines corresponding to the combination of valent $\nu(\text{CCO})$ vibrations and rotational vibrations of the methyl $r(\text{CH}_3)$ and methylene $r(\text{CH}_2)$ groups (the frequency range from 1000 to 1100 cm^{-1}); the presence of a fine structure in the absorption peak of the ethanol recondensate with a maximum absorption at the frequency $\nu = 1094$ cm^{-1} , that can indicate an inhomogeneous sample composition.

We will consider the spectral parts corresponding to one or other characteristic frequencies in more detail. In Fig. 3, the frequency range of vibrations of O—H-bond in free and bound states is shown. The oscillatory spectra of matrix-isolated, pure and recondensed ethanol obtained in accordance with the sample preparation procedure described above are demonstrated. An evident difference of the spectrum in Fig. 3(a) is caused by a much weaker degree of hydrogen bonding in the ethanol aggregates within a nitrogen matrix that leads to an appearance of characteristic lines corresponding to vibrations of quasi-free molecules. For example, the absorption line at 3658 cm^{-1} corresponds to O—H-bond vibrations of ethanol monomers and dimers. As may be seen in the figure, the line has local minima at the frequencies 3645 and 3658 cm^{-1} , that is related to a presence of two conformation states in an ethanol molecules: anti (3658 cm^{-1}) and gauche (3645 cm^{-1}).^{11,12}

In Fig. 3, it is seen that the difference in energies of the conformers is 13 cm^{-1} that agrees well with data of other authors.^{11,13} A fine-structure analysis of the absorption line of O—H-bond in the range 3000–3600 cm^{-1} indicates a presence of local minima corresponding to different cluster states of ethanol molecules in a nitrogen matrix. From calculations and experimental data of other authors, we conclude about existence of ethanol clusters with different size in a nitrogen matrix.⁹ The middle spectrum is attributed to an absorption line of O—H-bond in a thin film of pure ethanol. The line is practically symmetric with a maximum at the frequency of 3280 cm^{-1} and with a half-width $\Delta = 340$ cm^{-1} .

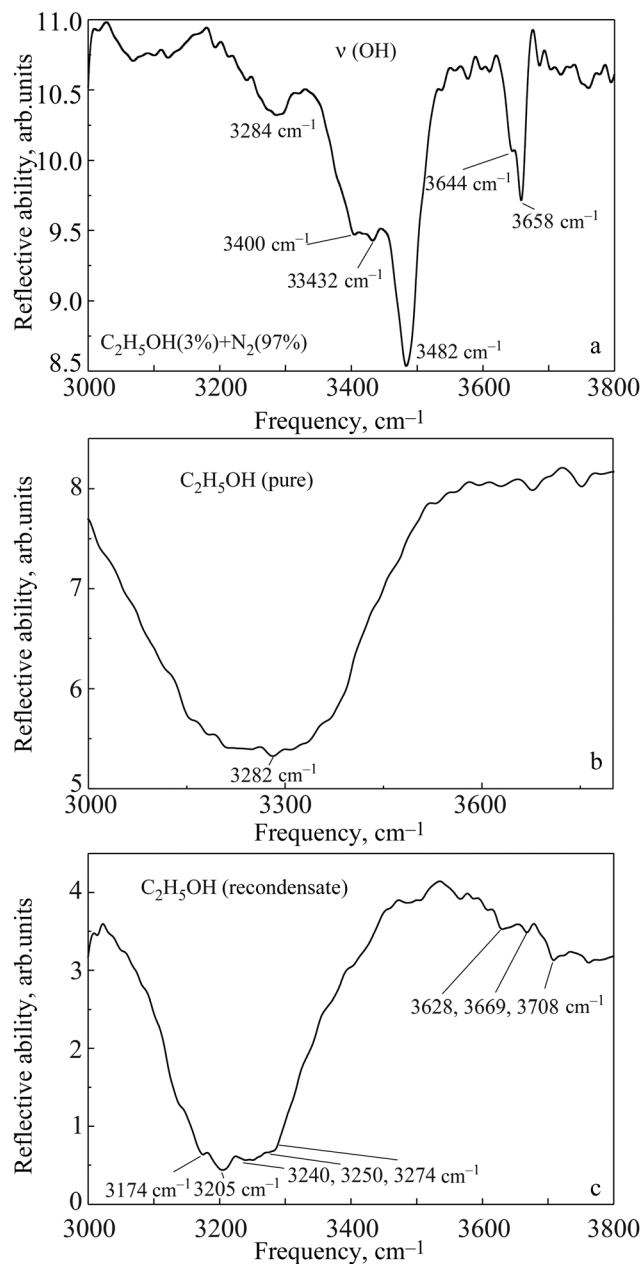


FIG. 3. Oscillatory spectra of matrix-isolated ethanol (a), pure ethanol (b) and recondensate of ethanol (c) in the frequency range of valent vibrations of O—H-bond in free and bound states.

The absorption spectrum of ethanol, recondensed from a nitrogen cryomatrix, retaining common features with the spectrum of pure ethanol has a series of peculiarities caused, in our opinion, by a difference in structural/morphological composition of condensate and recondensate of ethanol. First, the absorption line of the recondensate is shifted to the more long-wave spectrum range (the absorption maxima of the condensate and the recondensate are located at $\nu = 3280$ and 3205 cm^{-1} , respectively). Second, the absorption line of the recondensate becomes narrower and less symmetrical in comparison with that of the condensate. In particular, a half-width of the line of the recondensate is $\Delta = 220 \text{ cm}^{-1}$, whereas that of the continuous film of ethanol is $\Delta = 340 \text{ cm}^{-1}$. And third, the spectrum of the recondensate differs from that of the condensed film by presence of a fine structure. The mentioned features allows to make an assumption that after evaporating a nitrogen matrix, coalescence processes of ethanol aggregates

were not completed by formation of a continuous film, and the sample represents a polydisperse system with polyaggregates different in size, including, probably, also dimers (in particular, in the “blue” spectrum range in comparison with the curve in Fig. 3(a)).

In Fig. 4, the oscillatory spectra of matrix-isolated, pure and recondensed ethanol in the frequency range of valent vibrations of CH-bond of methyl and methylene groups. The evident difference is the presence of a fine structure of the spectrum, corresponding to a matrix-isolated state of ethanol. The pronounced narrow absorption peak at the frequency $\nu = 2985 \text{ cm}^{-1}$ corresponds to valent asymmetric oscillations of CH-bond of the methyl group $\nu_a(\text{CH}_3)$ of monomers and dimers.¹³ The weak line at the frequency $\nu = 2950 \text{ cm}^{-1}$ is associated with the same type of vibrations. The absorption line at the frequency $\nu = 2907 \text{ cm}^{-1}$ reflects

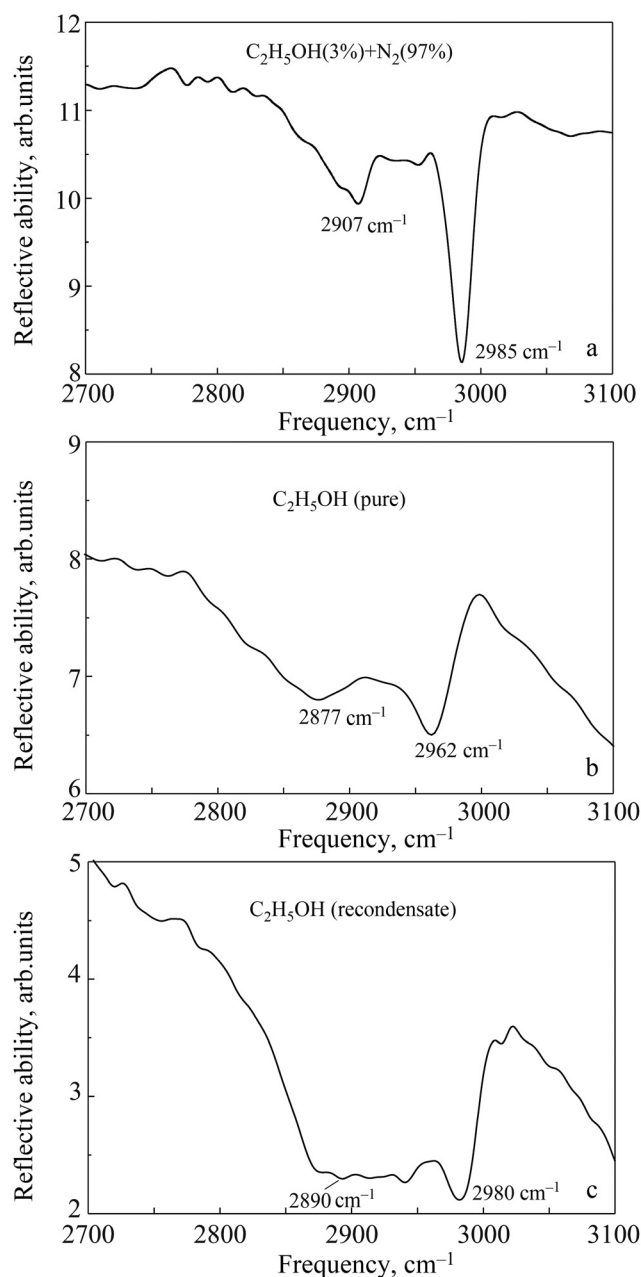


FIG. 4. Oscillatory spectra of matrix-isolated ethanol (a), pure ethanol (b) and recondensate of ethanol (c) in the frequency range of valent vibrations of CH-bond.

CH-valent asymmetric vibrations of the methyl group $\nu_a(\text{CH}_3)$, and local extrema at the frequencies 2894 and 2867 cm^{-1} correspond to a symmetric type of these vibrations.

A significant broadening of absorption lines that leads to disappearance of the fine structure caused by different types of vibrations of an ethanol molecule is observed in the absorption spectrum in the range of valent CH-vibrations of the cryocondensate of pure ethanol in comparison with the spectrum of matrix-isolated ethanol. Two wide lines with centers at the frequencies 2962 and 2875 cm^{-1} correspond to valent vibrations of CH-bond of the methyl and methylene groups, respectively.

Besides a broadening of the absorption lines, a significant shift of their centers to the low-frequency range is observed. This shift $\Delta\nu$ is 23 cm^{-1} for the methyl group and 32 cm^{-1} for the methylene group. The broadening of lines of CH-valent vibrations as well as their “red” shift are caused by intermolecular interactions in the film of pure ethanol and by an appearance of mean- and long-range order of a structure of cryocondensates.

A spectrum of CH-bond of the ethanol reconcondensate layer differs from that of both pure and matrix-isolated ethanol. The main differences are a spectrum broadening and an appearance of multiple pronounced local minima. We assume that this fact also means that the ethanol reconcondensate represents a polydisperse structure with elements of different sizes.

In Fig. 5, characteristic spectra of vibrations of ethanol molecules in the frequency range of strain (δ) and fan (W) vibrations of ethanol, and also their combinations, are shown.

As may be seen, a structure of the spectrum of a mixture of 3% ethanol with nitrogen is significantly more complicated than the spectrum of the cryocondensate. There is no line at the frequency $\nu = 1493 \text{ cm}^{-1}$, which corresponds to a strain vibration of the methylene group $\delta(\text{CH}_2)$ of anti-isomers. Two separated lines of symmetric strain vibrations of the methyl group $\delta(\text{CH}_3)_s$ with the central frequencies 1376 and 1395 cm^{-1} form one line at the frequency $\nu = 1376 \text{ cm}^{-1}$. The same happens with two separated frequencies (1315 and 1342 cm^{-1}) of combination of strain vibrations for the bond COH and fan vibrations of the methylene group $W(\text{CH}_2)$, resulting in an appearance of one broad line centered at the frequency $\nu = 1323 \text{ cm}^{-1}$. The absorption line corresponding to strain vibrations $\delta(\text{COH})$ of anti- and gauche-isomers with frequencies 1259 and 1276 cm^{-1} is transformed. The line from a vibration of the ethanol anti-isomer (1259 cm^{-1}) vanishes completely, whereas a gauche-isomeric vibration is retained and becomes more pronounced. It is related to the fact that by the bond $\delta(\text{COH})$ -anti the intermolecular formation of cyclic polyaggregates of ethanol with further damping of vibrations of this type is realized.

The mentioned arguments can be applied, in full measure, to the spectrum, which corresponds to the sample of the ethanol reconcondensate (Fig. 5(c)). Although it is similar, in general, to the spectrum of the ethanol cryocondensate (Fig. 5(b)) there are some distinctions, main of which is existence of local minima. As above, we explain this by a polydisperse character of the sample structure formed in the process of reconcondensation and interaction between ethanol aggregates. In Fig. 6, a more detailed fragment of the spec-

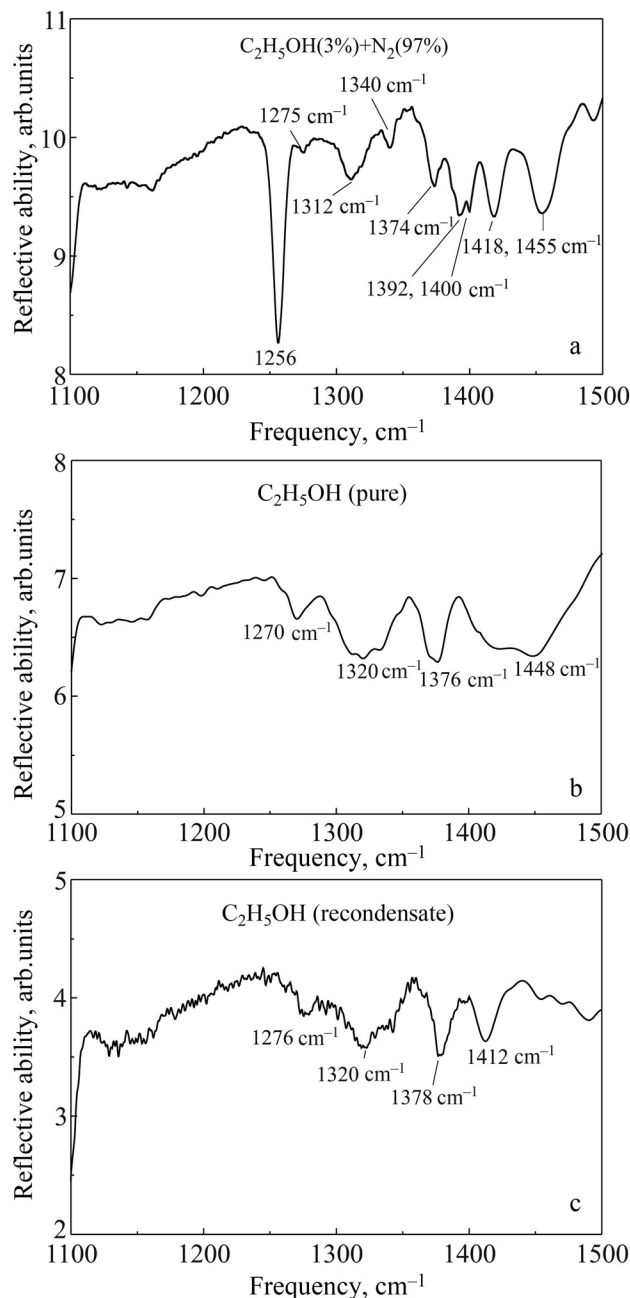


FIG. 5. Oscillatory spectra of matrix-isolated ethanol (a), pure ethanol (b) and reconcondensate of ethanol (c) in the frequency range of strain (δ) and fan (W) vibrations of ethanol, and their combinations.

trum of the reconcondensate in the frequency range under consideration is shown. It evidently demonstrates a presence of a fine structure.

The frequency range 1000–1150 cm^{-1} is presented in Fig. 7 by a set of absorption lines corresponding to combinations of valent $\nu(\text{CCO})$ vibrations with rotational vibrations of the methyl $r(\text{CH}_3)$ and methylene $r(\text{CH}_2)$ groups and with strain vibrations of $\delta(\text{OH})$ bond. As may be seen, for a mixture of ethanol and nitrogen the absorption spectrum has a significantly more complicated structure than that of pure cryocondensate of ethanol. Three broad pronounced absorption peaks as well as the sharp and narrow absorption line at the frequency $\nu = 1095 \text{ cm}^{-1}$ are to be noted in the first place. Based on an analysis made in the works Refs. 10 and 11, the nature of these vibrations can be determined with a fair degree of confidence.

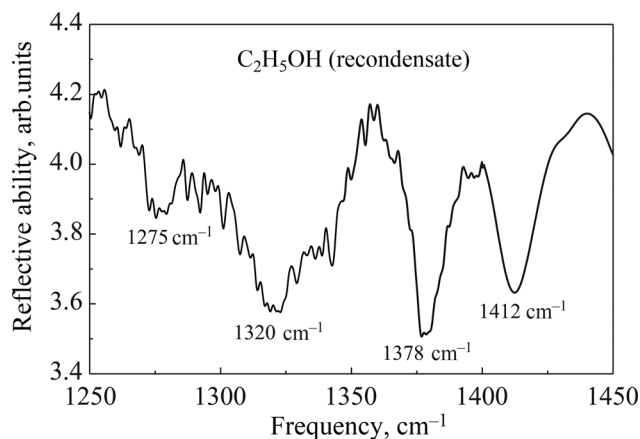


FIG. 6. A fine structure of spectrum of ethanol recondensate in the frequency range of strain vibrations.

The line with a absorption maximum at $\nu = 1028 \text{ cm}^{-1}$ corresponds to a combination of valent vibrations of the methyl group $\nu(\text{CH}_3)$. In the case of pure film of ethanol, this line broadens considerably with a simultaneous shift of a center to $\nu = 1042 \text{ cm}^{-1}$. Both are due to an interaction of an ethanol molecule with an internal field of a lattice. A broad and pronounced peak centered at $\nu = 1054 \text{ cm}^{-1}$ is related to a combination of valent $\nu(\text{CCO})$ vibrations with strain vibrations of $\delta(\text{COH})$ bond. And these vibrations are ascribed to gauche-conformers of ethanol. The line centered at $\nu = 1090 \text{ cm}^{-1}$ is attributed to a combination of valent vibrations $\nu(\text{CCO})$ with rotational vibrations of the methyl group $\nu(\text{CH}_3)$. It has two characteristic peaks corresponding to anti-dimers ($\nu = 1089 \text{ cm}^{-1}$) and anti-monomers ($\nu = 1095 \text{ cm}^{-1}$). At this concentration a fraction of the ethanol monomers in a nitrogen matrix is small.

Recondensation of ethanol from a matrix leads to formation of a sample with a significantly different spectrum (Fig. 7(c)) in comparison with both matrix-isolated and pure ethanol. First, as opposed to a cryocondensate of the pure ethanol, the line ascribed to a combination of valent vibrations $\nu(\text{CCO})$ with rotational vibrations of the methyl group $\nu(\text{CH}_3)$ becomes much narrower and shifts to the range of higher frequencies. In addition, it has at least two local minima at the frequencies $\nu = 1050$ and 1054 cm^{-1} . Second, the line centered at $\nu = 1090 \text{ cm}^{-1}$ (a combination of valent vibrations $\nu(\text{CCO})$ and rotational vibrations of the methyl group $\nu(\text{CH}_3)$) is also shifted to the region of higher frequencies. The line has two pronounced minima at the frequencies $\nu = 1094$ and 1097 cm^{-1} . A comparison with Fig. 7(c) allows to assume that the sample of the recondensate can contain dimers and monomers of ethanol. Third, a general character of the spectrum of the recondensate, namely a large number of local minima, allows once again to make an assumption about a highly-dispersed character of the sample structure.

The qualitative information about a degree of structural homogeneity of the ethanol recondensate can be found from an analysis of IR-spectra of samples obtained from matrices with different concentration ratios between ethanol and nitrogen. If a sample consists of polyaggregates of various dimensions, then taking into account a difference in pressures of a gas over the surface of elements with different size or corresponding melting temperature,^{14–16} one can expect more com-

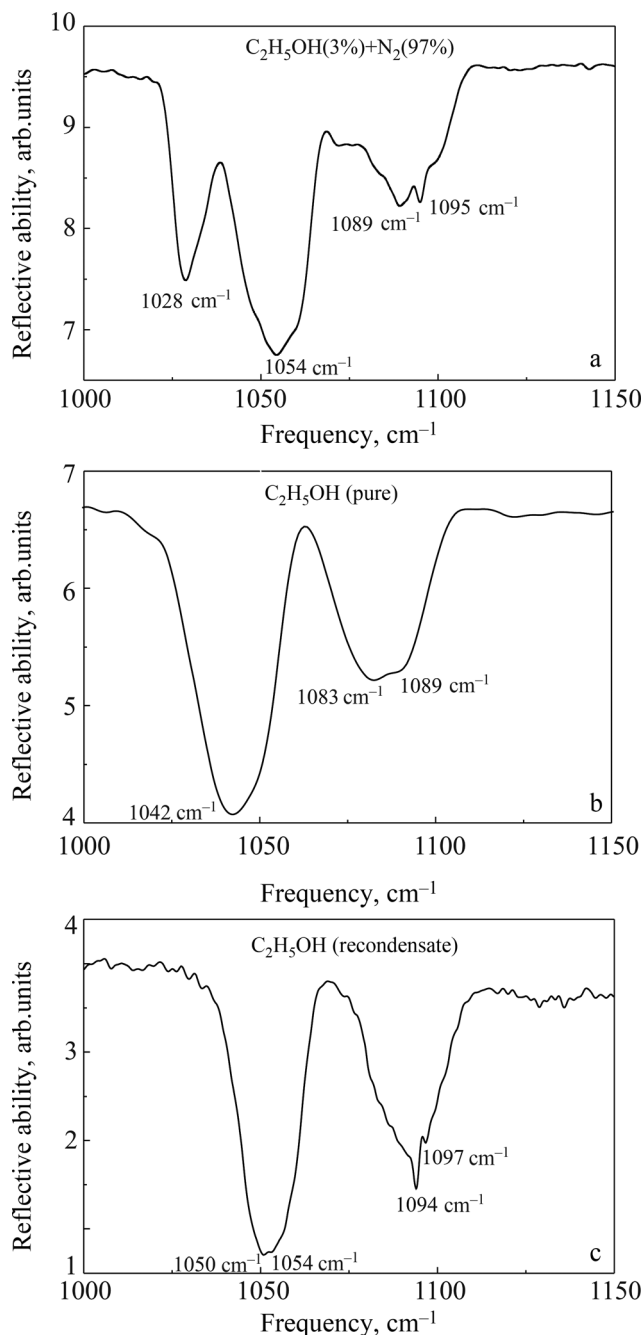


FIG. 7. Oscillatory spectra of matrix-isolated ethanol (a), pure ethanol (b) and recondensate of ethanol (c) in the frequency range of rotational (r) and strain (δ) vibrations of ethanol, and their combinations.

plex behavior of the ethanol recondensate with increasing the temperature then in the case of continuous films of cryocondensates. In other words, with slow increasing the temperature the different groups of polyaggregates unified by some average size will undergo one or the other structural phase transformations at different temperatures. In Fig. 8, the results of such experiments, namely, the warming-up curves of samples at fixed frequency of an IR-spectrometer, are shown.

Previously we have studied a process of structural phase transformations in pure ethanol^{7–9} in great depth, so here we will restrict our consideration by a short comment of Fig. 8(a) in order to have a some base for comparison with Figs. 8(b) and 8(c). An object under investigation is the $1.5 \mu\text{m}$ thick film of the ethanol cryocondensate created at the condensation temperature $T = 16 \text{ K}$ and the pressure of the

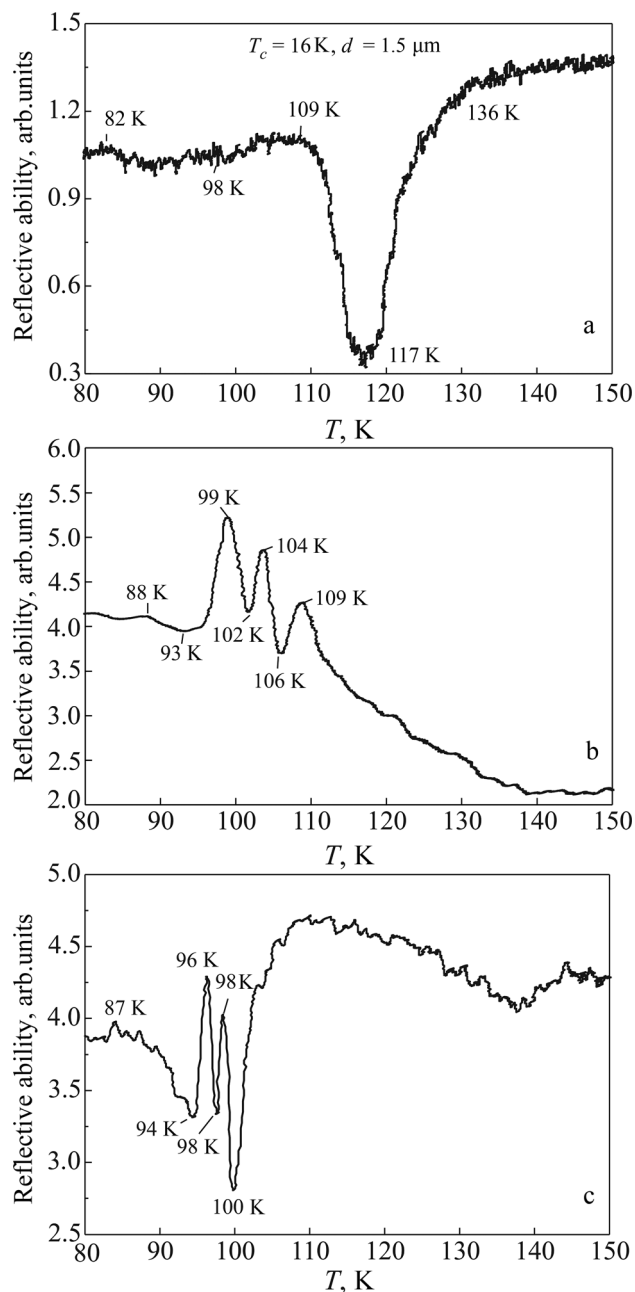


FIG. 8. Warming-up curves of samples of cryocondensates (a) and reconcondensates of ethanol at different concentrations in a nitrogen matrix in the frequency range of a glass transition: $c = 1.5\%$ (b) and 3% (c).

ethanol gas phase $P = 10^{-3}$ Pa. After cryodeposition, a slow heating of the film (at indicated in figures temperatures about 0.01 K/s) was performed with simultaneous registration of a signal from an IR-spectrometer at fixed frequency. In the case under consideration, $\nu = 3100$ cm^{-1} that corresponded to the frequency at a half-width of an absorption line of O—H-bond. A change of film structure led to a shift of this absorption line or to change of its parameters that was manifested in the signal value. Thus, the following characteristic temperatures are indicated in the figure: $T = 82$ K—the transition from amorphous ethanol to a glass state; $T = 98$ K—the ethanol glass point; $T = 109$ – 117 K—the transition to a state of supercooled liquid (SCL); $T = 117$ – 136 K—the crystallization of SCL to a plastic crystal.

A behavior of the ethanol reconcondensate in the process of heating differs significantly from that of the films of “pure”

ethanol. Moreover, an appearance of these features in the temperature range of a glass-transition allows to make an assumption that observed changes of the warming-up curves are related just to these processes. That is, one can propose that polyaggregates of ethanol located in a nitrogen matrix are in a glass state, and a process of their reconcondensation onto a substrate after nitrogen evaporation do not break down this state. Coalescence processes after reconcondensation are either absent completely or do not influence on structural properties of components. Thus, one can assume that the reconcondensate heating goes through a transition from a glass state to a state of supercooled liquid. It can also be affirmed that this process of the transition in reconcondensates starts at significantly lower temperatures then in the ethanol cryocondensates. And finally, a character of the warming-up curves allows to assume that reconcondensates are structurally grouped in some sets, a parameter of which is an averaged size of composed particles. Thus, the smaller is this parameter, at much lower temperatures for these particles a glass transition starts that leads to a step-like transformation process. The made conclusions applied to Figs. 8(b) and 8(c) allows to make hypotheses about both a relative number of supposed sets (from the number of extrema in the warming-up curve) and possible presence of much larger particles in previously formed supercooled liquid phase of ethanol and their interaction. However, these models are not confirmed by experiments yet.

CONCLUSIONS

From a comparative analysis of oscillatory spectra of samples of ethanol cryocondensates, matrix-isolated ethanol in a nitrogen cryomatrix and ethanol reconcondensates, the following conclusions can be derived.

1. Molecules of ethanol form matrix-isolated polyaggregates in a process of co-condensation with nitrogen. An evaporation of a matrix at the temperature of 35 K is accompanied by a process of reconcondensation of ethanol from the matrix onto a substrate. This leads to a formation of highly-dispersed film (recondensate), consisting of aggregates with various sizes, including dimers and, probably, monomers, that follows from results of comparison of relevant IR-spectra in Figs. 3, 5, and 7.
2. The features of warming-up curves of reconcondensates near the temperature of a glass transition in ethanol cryocondensates ($T = 97$ K) can be explained by the fact that polyaggregates located previously in a matrix as well as reconcondensed onto a substrate are in a glass state. A film heating leads to corresponding transformations, which occur in a few steps at different temperatures. Such a character of the warming-up curve is explained by a dependence of the transition temperature from a glass state to a state of supercooled liquid on size of polyaggregates. A significant shift of a beginning of the transition to the range of much lower temperatures allows to state that the glass-transition temperature is lower when a size of structural components is smaller.
3. A character of the warming-up curves of reconcondensates allows to speak about some grouping of elements of reconcondensates by size. In other words, in the process of reconcondensation and possible further coalescence, polyaggregates

with preferential sizes, which are energetically optimal for these conditions, are formed. In our case, it is reasonable to speak about existence of three such sets, involved sequentially in glass transformations.

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