

Analysis of Vibrational Spectra of Tetrafluoroethane Glasses Deposited by Physical Vapor Deposition

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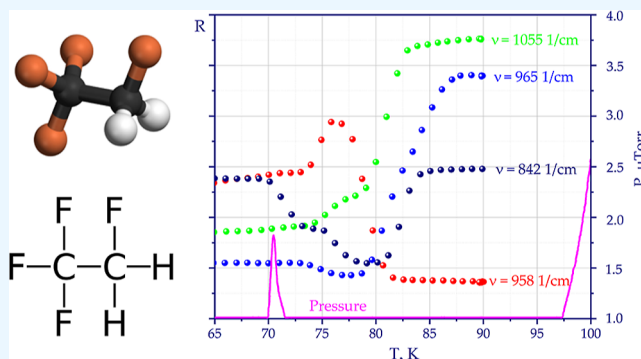
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ABSTRACT: This paper presents the results obtained in the study of structural phase transitions in thin films of R134A. The samples were condensed on a substrate by physical deposition of R134A molecules from the gas phase. Structural phase transformations in samples were investigated by observing the changes in characteristic frequencies of Freon molecules in the mid-infrared range with the help of Fourier-transform infrared spectroscopy. The experiments were carried out in the temperature range from 12 to 90 K. A number of structural phase states, including glassy forms, were detected. The changes in thermogram curves at fixed frequencies of half-widths of absorption bands of R134A molecules were revealed. These changes indicate a large bathochromic shift of these bands at frequencies of $\nu = 842 \text{ cm}^{-1}$, $\nu = 965 \text{ cm}^{-1}$, and $\nu = 958 \text{ cm}^{-1}$ and a hypsochromic shift of the bands at frequencies of $\nu = 1055 \text{ cm}^{-1}$, $\nu = 1170 \text{ cm}^{-1}$, and $\nu = 1280 \text{ cm}^{-1}$ at temperatures from $T = 80 \text{ K}$ to $T = 84 \text{ K}$. These shifts are related to the structural phase transformations in the samples.



1. INTRODUCTION

In recent years, researchers have started to focus their attention on fundamental studies of the molecular structure of liquids, amorphous semiconductors, polymer solutions, liquid metals (because of their optical and electrical properties), glassy states of substances, metal vapors, and many other systems.^{1–4} Despite the complexity of studying disordered systems at the microscopic level, so far, significant progress has been achieved in this field. General patterns for a wide class of objects have been identified, and the methods for the theoretical analysis of disordered systems have been improved.^{5–7}

Amorphous glassy solids have recently become of particular interest.^{8–11} Glasses are nonequilibrium, amorphous bodies that play a huge role in the current stage of technological development. Glass has no long-range order of atoms, like all materials with a non-crystalline structure. In other words, there is no ordering of molecules in glasses on a scale several times larger than the size of those molecules.^{12–15} Tammann was the first to attempt to characterize the glassy state by highlighting its characteristic physicochemical properties.¹⁶ He also developed a special approach to the thermodynamic and kinetic descriptions of the glassy state. Considering glass formation together with the problem of pronounced inhibition of crystallization processes in non-crystalline systems, an understanding of the structure of glassy materials and their bonds has been formed. Amorphous substances became even

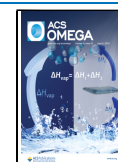
more attractive from a practical point of view later, when their microheterogeneous structure was discovered.¹⁷ Research results related to the properties of glass and attempts to interpret them have been described in many scientific works.^{18–21}

There are various methods for obtaining disordered structures. These methods include, for example, chemical deposition, affecting the crystal structure of high-energy radiation, and high-pressure destruction of ordered structures.^{22–25} One of the frequently used methods for obtaining such structures is physical vapor deposition (PVD).^{26,27} However, only recently, it has been found that under certain conditions of deposition, a stable glassy state with good thermodynamic characteristics can be achieved.²⁸ Glasses obtained through PVD have a higher density and modulus of elasticity in comparison with other glasses obtained using traditional liquid cooling methods.^{29,30} Glasses obtained through liquid-phase cooling of a substance have volatile properties that change over time, thus limiting their use in

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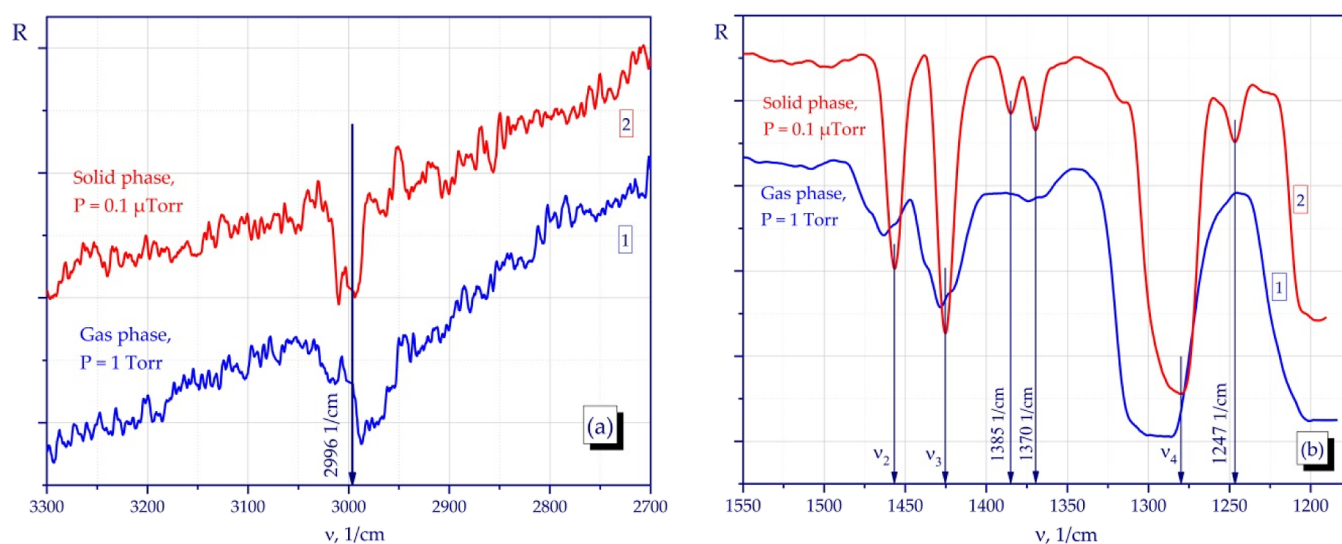


Figure 1. Infrared spectra of 1,1,1,2-tetrafluoroethane in the gas and solid phases. (a) Valence vibration frequency range and (b) deformation vibration frequency range.

applications. In contrast, PVD glasses demonstrate enhanced kinetic stability.

The physicochemical conditions of deposition that determine the properties of glassy states can be roughly divided into external and internal conditions. External conditions mainly include temperature and pressure during the process of deposition. These parameters determine the lifetime of molecules in the adsorption layer. This lifetime is needed to locate the minimum energy position on the condensation surface, ensuring the formation of a glass structure with improved packaging.³¹ As for the molecular kinetic (internal) conditions facilitating the formation of stable glasses, it is necessary to highlight the property of molecular anisotropy. The anisotropy of molecules affects the activation barrier to create a stable low-energy state of stable glass molecules in the process of deposition.³² These circumstances are, in our opinion, pre-requisites for thorough IR spectroscopic research on thermally stimulated transformations in $C_2H_2F_4$ samples. A 134A Freon molecule is an asymmetrical version of the 134 Freon molecule that demonstrates a symmetrical molecular structure. By analyzing the results obtained for these molecules, it will be possible to make certain assumptions regarding the influence of the structure of the molecules on the glass transition processes of these substances.

Thus, in this paper, we present the results of IR spectrometric research on 134A Freon molecules as a glass-forming substance with a kinetically stable structure. In addition, we note that, in contrast to the calorimetric method, studying samples via fixed-frequency IR spectrometer observation is a continuous method of tracking the formation of stable glass when heating the samples. Information on these structural changes cannot be obtained by Raman or X-ray scattering methods. Monitoring changes in IR intensity is a unique method for studying glass transition and related phenomena. It complements the information obtained using traditional methods such as calorimetry. In our opinion, this work is a useful “lens” through which the dynamics of the transformation of 134A Freon glasses in the experiments with periodic cooling and heating of the sample can be investigated.

2. MATERIALS AND METHODS

The subject of this study was 1,1,1,2-tetrafluoroethane produced by ClimaLife (UK). The gas purity was 99.5%, with a maximum water vapor content of not more than 10 ppm.

The apparatus used for studying amorphous structures was partially described in a number of our previous works.^{33,34} Therefore, we will not describe it in detail here. It is only worth noting that during this research, the operation of the PID controller was improved to increase its speed and speed of reaching the control temperatures, using a small program written in the LabView graphical programming environment (National Instruments, USA).³⁵

3. RESULTS AND DISCUSSION

The studies of thin films of cryovacuum condensate glasses of R134A were carried out in the temperature range from 12 to 90 K. The pressure during the vapor phase deposition was equal to $P = 10^{-5}$ Torr. The spectra were obtained for the films with thicknesses of 2.5 μm in the range of characteristic frequencies.

3.1. Comparative Analysis of the Solid and Gaseous Phases of R134A. In order to compare the spectra of a gaseous Freon with those of a condensed Freon, the IR spectra of gaseous R134A were measured at a pressure of 1.0 Torr in the chamber. The results of these measurements are shown in Figure 1 and 2. A Freon in the solid phase was condensed at a substrate temperature of 12 K and a pressure of $P = 10^{-5}$ Torr. Figures 1 and 2 show that in the IR spectrum of R134A, the main absorption bands corresponding to the characteristic vibrations of molecules are present.^{36,37} Figure 1a shows the absorption band of Freon molecules corresponding to the valence vibrations of the C–H bond at a frequency of $\nu = 2996 \text{ cm}^{-1}$. Figure 1b shows the IR spectra in the frequency range of the ν_2 , ν_3 , and ν_4 vibrational modes.³⁷

In Figure 1, it can be seen that the spectra of the gas and solid phases are different in their characteristics and in the location of the absorption bands in relation to each other. The absorption bands of the condensed phase of R134A are more pronounced, and their amplitudes exceed the amplitudes of the

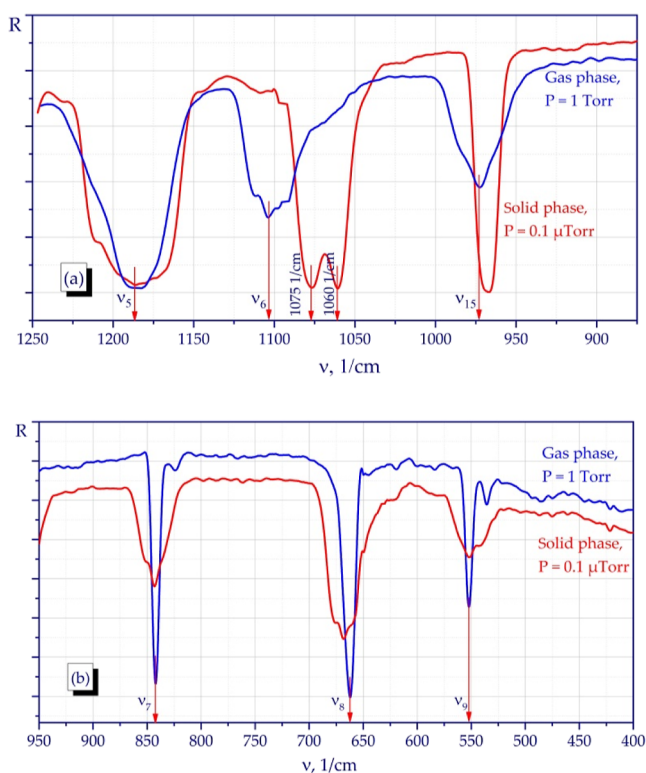


Figure 2. Absorption spectra of gaseous R134A and a 2.5 μm thick cryodeposited film. (a) Deformation vibration frequency range and (b) librational vibration frequency range.

absorption bands of the corresponding bands in the gas phase. In addition, there are peaks in the IR spectrum of the solid phase of the Freon that are absent in the gas phase (1247, 1364, and 1374 cm^{-1}). As can be seen, the observed bathochromic shift of the absorption bands of the solid Freon relative to the gas phase is typical of all the absorption peaks examined.

Significant differences in the IR spectra between the Freon gas and solid phases are observed in the frequency range of 400–1300 cm^{-1} as well (Figure 2). These differences are particularly evident for the absorption band of the ν_6 mode (Figure 2a) in which not only a bathochromic shift of the solid phase is observed but also a bifurcation of the absorption band at frequencies of 1059 and 1074 cm^{-1} is observed. Changes are also observed for the ν_{15} mode, which belongs to the A_1' group of symmetry and in which the bathochromic shift and constriction occur. The most striking manifestation of the changes in the phase state of the solid Freon for the ν_7 , ν_8 , and ν_9 vibrations (Figure 2b) is a drastic narrowing of the absorption band with a simultaneous increase in the amplitudes of these modes. A bathochromic shift of these bands is also observed here.

3.2. Structural Phase Transformations in the Solid Phase of R134A during Their Heating. This section describes the experiments aimed at studying the structural phase transformations in the solid phase of R134A during the heating of the samples. In the course of the experiment, the vibrational spectrum of the sample was obtained every 1 K. From the obtained series of infrared spectra of the sample, an array of data on the dependence of the intensity of infrared spectra on the temperature was created. The obtained array of data makes it possible to form the dependence of the IR

intensity on the temperature at the necessary fixed frequency. A thermogram of structural changes in the grown thin film was created using these data. The results of the experiment described are shown in Figure 3. The dependence of the IR

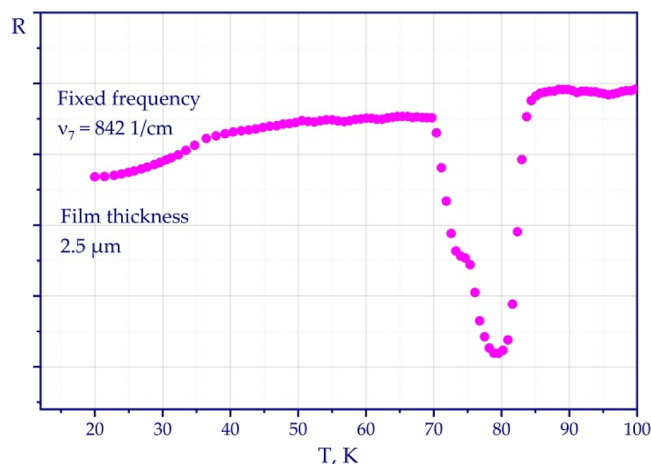


Figure 3. Temperature dependence of the spectrometer signal at the frequency $\nu_{\text{fix}} = 842 \text{ cm}^{-1}$ during heating.

intensity on the temperature at the fixed frequency of $\nu = 842 \text{ cm}^{-1}$ is shown here. This frequency corresponds to the half-width of the ν_7 absorption band on the left. This absorption band is sensitive to structural changes in the solid phase of R134A.

According to the thermogram shown in Figure 3, it is possible to draw a conclusion regarding the existence of different structural phase states. Let us consider the following separate temperature ranges corresponding to the characteristic changes in the thermogram.

3.2.1. Temperature Range of 12–50 K. In this temperature range, an increase in the intensity of the IR emission at the selected frequency is observed. Subsequently, IR spectra were obtained in the vicinity of the main vibrational frequencies of Freon molecules, shown in Figures 4 and 5. The absorption band that belongs to the A_1' group of symmetry is shown in Figure 4. Two spectrum curves are shown in each subfigure of Figures 4 and 5. The first curve is obtained immediately after the condensation at $T = 12 \text{ K}$. The second curve is obtained after the heating from $T = 12$ to 50 K. As can be seen from Figure 4a, the heating of the sample from $T = 12 \text{ K}$ to 50 K leads to a broadening and a bathochromic shift of the ν_9 vibration absorption band. The high-frequency part of the spectrum does not change its position. The ν_8 absorption band, shown in Figure 4b, follows a similar pattern. At the same time, the ν_7 vibrational absorption band, shown in Figure 4c, maintains its width but undergoes a bathochromic shift. In all subfigures of Figure 4, the arrow indicates the changes in the intensity of IR radiation at the selected frequency.

The data on the changes in the positions of the ν_6 , ν_5 , and ν_4 vibrational absorption bands are provided in Figure 5. It can be said that the heating of the sample does not affect the position of the absorption bands in the case of these types of vibrations (a slight bathochromic shift in the high-frequency region of the peak is observed at the ν_6 frequency).

3.2.2. Temperature Range of 70–90 K. The temperature range of 50–70 K was omitted since no changes in the intensity of the IR emission could be observed in this range. In the temperature interval of 70–90 K, the most significant and

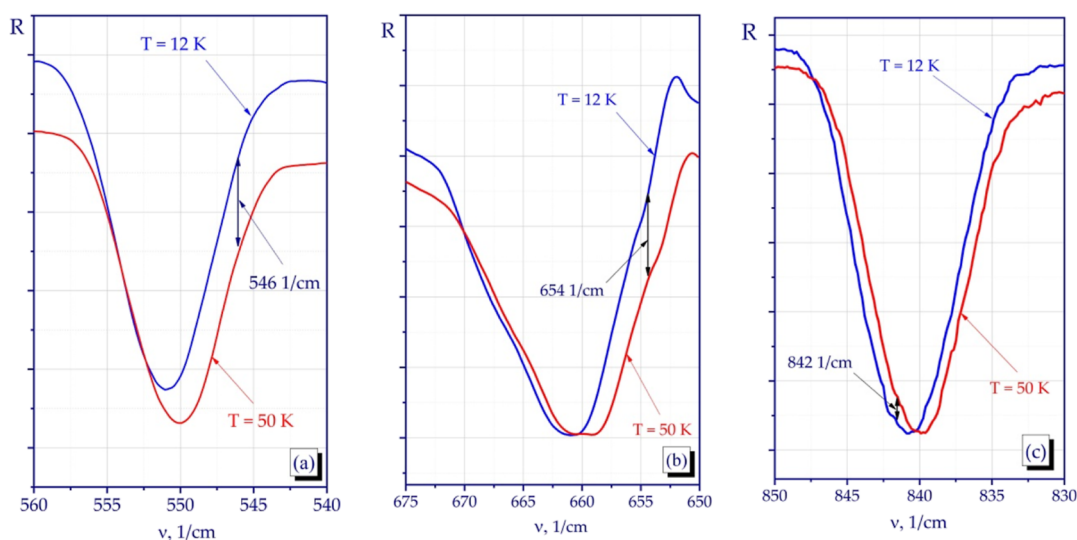


Figure 4. Absorption spectra of vibrational bands ν_9 (a), ν_8 (b), and ν_7 (c) in the process of heating the 1,1,1,2-tetrafluoroethane cryofilm from 12 to 50 K.

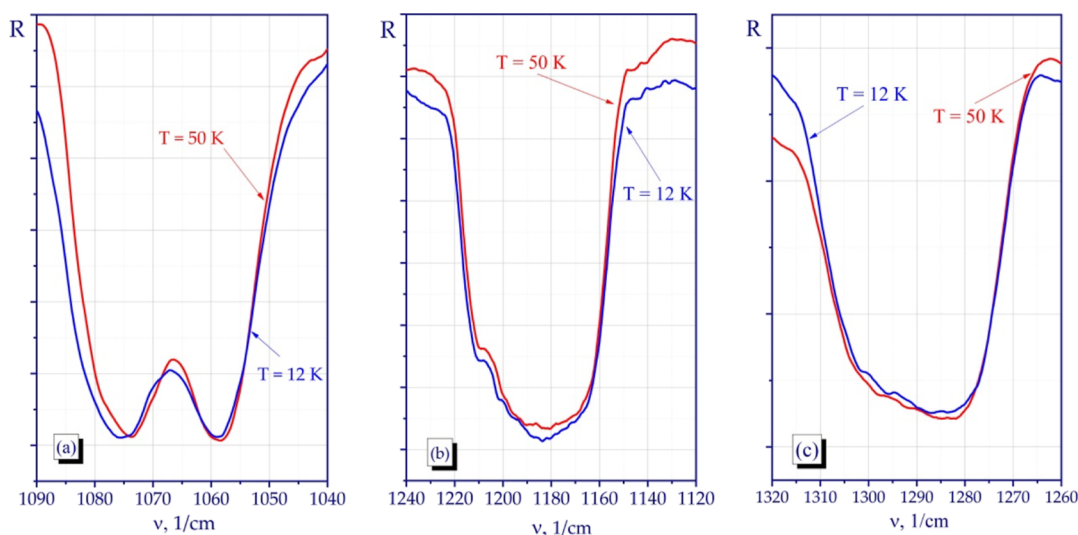


Figure 5. Absorption spectra of ν_6 (a), ν_5 (b), and ν_4 (c) vibrational bands in the process of heating the 1,1,1,2-tetrafluoroethane cryofilm from 12 to 50 K.

rapid changes in the state of the sample were observed. Figures 6 and 7 illustrate the influence of the temperature changes in this range on the absorption bands of different molecule vibrational modes. The spectra in this temperature range are compared with those obtained at $T = 12$ K. Thus, Figure 6 shows the absorption bands of a thin film of solid Freon at ν_9 (a), ν_8 (b), and ν_7 (c) frequencies.

As can be seen from Figure 6, the heating of the sample from 12 to 77 K initially leads to a hypsochromic shift of all absorption bands and the subsequent heating from 77 to 90 K leads to a dramatic bathochromic shift.

Figure 7 shows similar data for ν_6 , ν_5 , and ν_4 frequencies during successive heating of the Freon thin film from $T = 12$ K to $T = 77$ K and $T = 90$ K. Increasing the temperature leads to a hypsochromic shift on the left side of the band and a bathochromic shift on its right side.

The behavior of the absorption band of the vibrational mode ν_{15} (Figure 8), belonging to the A'' symmetry type of the Freon molecule, is particularly noteworthy. Figure 8 shows the

absorption band spectra of the ν_{15} vibrational mode obtained at temperatures of 12, 50, 77, and 90 K and the 90–12 K spectrum obtained after cooling from 90 to 12 K. As can be seen, heating the sample from 12 to 50 K results in a bathochromic shift of the entire band.

Further heating of the sample from 50 to 90 K leads to changes in the shape of the absorption band. As can be seen, during the heating in this temperature interval, the absorption band of the ν_{15} mode not only changes its position but also splits into two. This process is irreversible since cooling the sample back from 90 to 12 K does not cause the bands to form a merged peak again.

Thus, the results shown in Figure 8 demonstrate that a change in the sample temperature leads to a structural phase transformation that manifests itself through a bathochromic shift of the entire band and through a splitting of this band.

To determine if the processes of shifting and splitting are independent, the effect of the temperature at different frequency values was investigated. The frequency values were

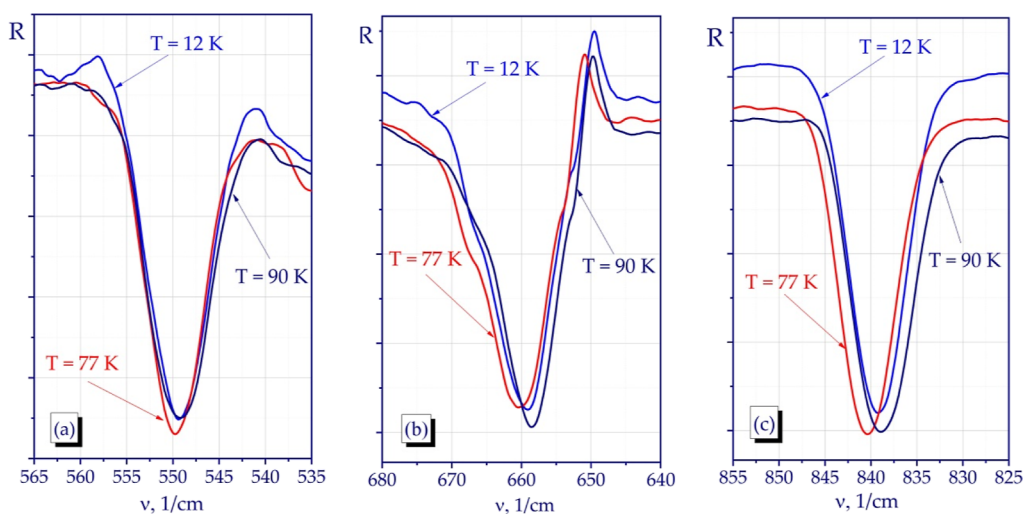


Figure 6. Absorption spectra of ν_9 (a), ν_8 (b), and ν_7 (c) vibrational bands in the process of heating the 1,1,1,2-tetrafluoroethane cryofilm from 12 to 77 K and $T = 90$ K.

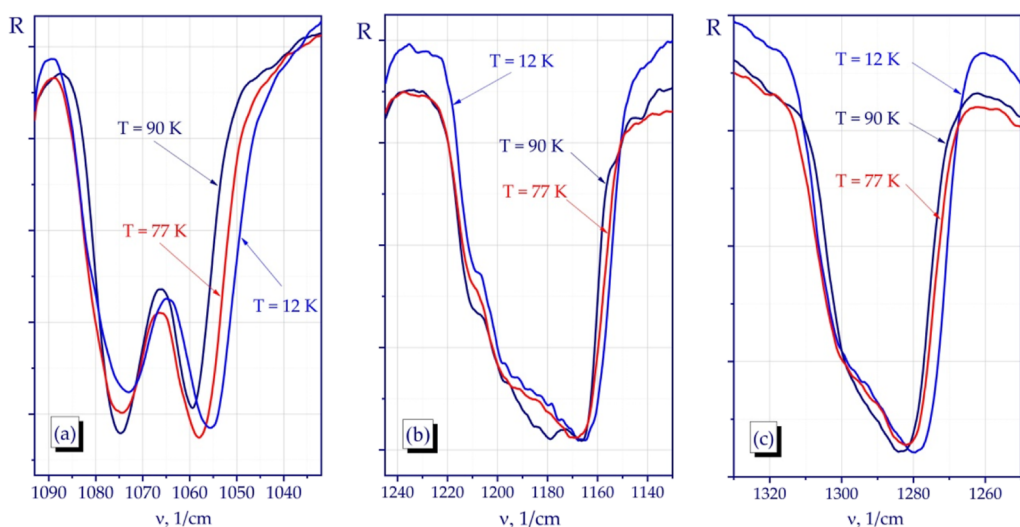


Figure 7. Absorption spectra of vibrational bands of ν_6 (a), ν_5 (b), and ν_4 (c) modes in the process of heating the 1,1,1,2-tetrafluoroethane cryofilm from 12 to 77 K and $T = 90$ K.

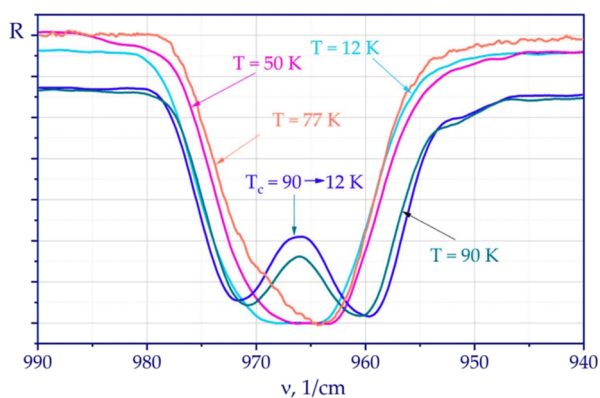


Figure 8. Absorption spectra of vibrational bands of the ν_{15} mode in the process of heating the 1,1,1,2-tetrafluoroethane cryofilm from 12 to 90 K and cooling it from 90 to 12 K.

chosen so that the change in the IR emission intensity at one of the frequencies corresponded to the band shift and the other frequency value corresponded to the process of its splitting

into two bands. These frequencies are $\nu_{\text{fix}} = 958 \text{ cm}^{-1}$ and $\nu_{\text{fix}} = 965 \text{ cm}^{-1}$. Thermograms of IR emission intensity at these frequencies during the process of heating the sample from 12 to 90 K are shown in Figure 9.

The heating of the sample from the temperature of $T = 12$ K to $T = 50$ K leads to a gradual bathochromic shift of the band (Figure 8) that corresponds to the data for the other vibrations presented in Figure 4. From the temperature of $T = 77$ K, the absorption band shifts abruptly to the high-frequency region, which is clearly illustrated by the thermograms at frequencies of $\nu_{\text{fix}} = 958 \text{ cm}^{-1}$ and $\nu_{\text{fix}} = 965 \text{ cm}^{-1}$ (Figure 9). This indicates structural phase transformations in the sample.

In the process of the subsequent temperature increase from 77 K, structural phase transformations in the sample lead to an abrupt shift of the band at the ν_{15} frequency to the low-frequency side of the spectrum (Figure 8), which is indicated by the sharp decrease in the IR reflection coefficient at the chosen frequency of $\nu_{\text{fix}} = 958 \text{ cm}^{-1}$ (Figure 9). The thermogram shows that the intensity of the IR radiation increases at a frequency of $\nu_{\text{fix}} = 965 \text{ cm}^{-1}$, which characterizes the splitting.

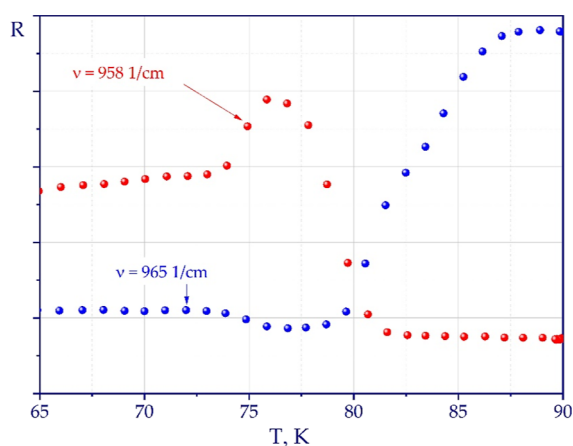


Figure 9. Thermograms of the changes in the IR reflection coefficient at $\nu_{\text{fix}} = 958 \text{ cm}^{-1}$ and $\nu_{\text{fix}} = 965 \text{ cm}^{-1}$.

The observed sudden changes in the IR emission intensity at a frequency of $\nu_{\text{fix}} = 958 \text{ cm}^{-1}$ occur up to the temperature $T = 81 \text{ K}$ and then stabilize up to a temperature of $T = 90 \text{ K}$. As for the bifurcation of the ν_{15} band, the sudden changes in the IR reflection coefficient at a frequency of $\nu_{\text{fix}} = 965 \text{ cm}^{-1}$ start occurring at a temperature of $T = 77 \text{ K}$ and stop at a temperature of $T = 87 \text{ K}$.

In order to understand the complex behavior of a solid Freon in the heating process, thermograms were obtained for the frequencies of $\nu = 842 \text{ cm}^{-1}$, $\nu = 958 \text{ cm}^{-1}$, $\nu = 967 \text{ cm}^{-1}$, and $\nu = 1055 \text{ cm}^{-1}$. The thermogram graphs are shown in Figure 10. It can be seen that the sample structure undergoes

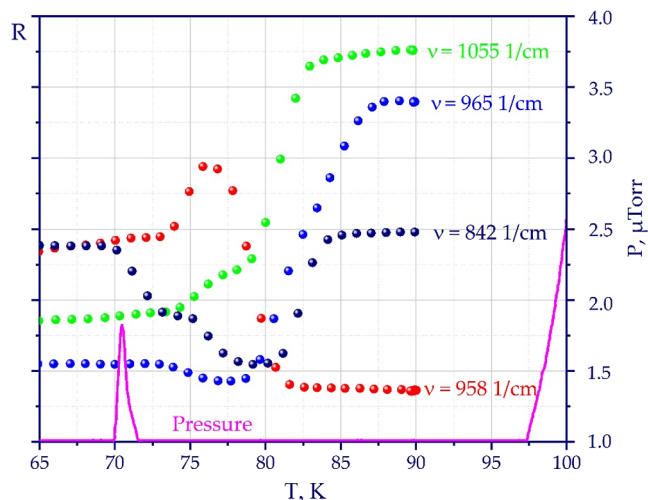


Figure 10. Thermograms of 1,1,1,2-tetrafluoroethane cryofilms at different fixed frequencies.

phase transformations at a temperature of $T = 70 \text{ K}$. The earliest changes are observed at a frequency of $\nu = 842 \text{ cm}^{-1}$. It is noticeable that the IR emission intensity decreases for this frequency in the temperature range from $T = 70 \text{ K}$ to $T = 80 \text{ K}$.

Figure 10 shows that the temperature around $T = 73 \text{ K}$ marks the beginning of changes for the vibrations at frequencies of $\nu = 958 \text{ cm}^{-1}$, $\nu = 965 \text{ cm}^{-1}$, and $\nu = 1055 \text{ cm}^{-1}$. The changes in the thermogram curve at a frequency of $\nu = 842 \text{ cm}^{-1}$ continue until 84 K , at a frequency of $\nu = 958 \text{ cm}^{-1}$ until 82 K , at a frequency of $\nu = 965 \text{ cm}^{-1}$ until 87 K , and at a frequency of $\nu = 1055 \text{ cm}^{-1}$ until 83 K . A further increase

in the temperature up to a temperature of $T = 90 \text{ K}$ does not cause any changes in the absorption bands in the spectra. This indicates the formation of a stable phase of solid R134A under these conditions.

4. CONCLUSIONS

On the basis of the obtained data, a conclusion was drawn that Freon thin films exist in amorphous states with different degrees of disorder in different time ranges.

The bathochromic shift of the absorption band occurs when the sample is heated from $T = 12 \text{ K}$ to $T = 50 \text{ K}$. When heating from $T = 12 \text{ K}$ to $T = 77 \text{ K}$, the absorption peak shifts to higher frequencies. A further increase in the temperature leads to a sudden shift of the ν_{15} vibrational band to the low-frequency region. It was also indicated by the decrease in the IR emission intensity at the chosen frequency of $\nu = 958 \text{ cm}^{-1}$ with a simultaneous increase in the IR emission intensity for a frequency of $\nu = 965 \text{ cm}^{-1}$. When the sample was cooled again from the temperature of $T = 90 \text{ K}$ to $T = 12 \text{ K}$, the absorption bands did not merge at a frequency of $\nu = 965 \text{ cm}^{-1}$. This may indicate that the process is irreversible.

The thermograms show that the glass structure undergoes some phase transformation at $T = 73 \text{ K}$. We assume that $T = 73 \text{ K}$ is the glass transition temperature.

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D.Y. and A.A.; and funding acquisition, A.S. and D.Y. All authors have read and agreed to the published version of the manuscript.

Notes

The authors declare no competing financial interest.

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