Applied Surface Science 446 (2018) 196-200

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Structure transformations in thin films of CF_3 - CFH_2 cryodeposites. Is there a glass transition and what is the value of T_g ?

Andrey Drobyshev, Abdurakhman Aldiyarov, Assel Nurmukan*, Dmitriy Sokolov, Ainura Shinbayeva

Al-Farabi Kazakh National University, al-Farabi ave. 71, Almaty 050040, Kazakhstan

A R T I C L E I N F O

Article history: Received 13 October 2017 Revised 22 January 2018 Accepted 29 January 2018 Available online 1 February 2018

Keywords: Cryocondensation Freon 134a Structural transformations IR spectrometry

1. Introduction

It is well-known that the method of cryovacuum condensation of samples is one of the effective ways of creating cryofilms in various and more important, well-controlled structural-phase states. As a result, the method of physical vapor deposition (PVD [1]) is widely used to study the properties of substance at low and superlow temperatures, such as density [2], polarizability [3,4], optical characteristics [5,6], to solve range of astrophysical and astrochemical research problems [7–9]. It is also important that the formed films of cryovacuum condensates of different substances have a number of unique properties, that cannot be obtained by freezing the same substances from the liquid phase even if the freezing rate is sufficiently high. In particular, it is related to the glass-forming materials, a number of properties of which depend crucially on the temperature of the cryodeposition, namely, on the degree of its distance from the temperature of the glass transition (T_g).

In the last decade the behavior of thin films of cryocondensates of elementary organic molecules, such as methane [10], ethanol [11], different composition of Freons [12] and others are receiving great attention. Realizing the important practical and ecological significance of studying the properties of such substances, at the same time, in this article, this study focuses on the fundamental issues of the formation of cryogenic films and the formation of their properties. In particular, the reason cause the formation of glass-like states of cryodeposits of organic molecules with different

ABSTRACT

In the temperature range 16–100 K, IR spectrometric studies of thermally stimulated transformations in cryocondensed Freon 134a films were carried out. It was found that Freon 134a cryofilms, formed at T = 16 K, under heating range from 70 to 90 K undergo multiple structural transformations of various nature. It was concluded that at a temperature of T_g = 72 K, takes place the glassy state transition to the supercooled liquid (G-SCL). At about T = 78 K, crystallization of SCL begins the state of an orientationally disordered plastic crystal. At a transition temperature T_{trans} = 80 K, a second quasi-glass transition occurs from the state of the orientation glass to a plastic crystal with an ordered rotational subsystem. Within temperature range 83–85 K, a plastic crystal-monoclinic crystal phase transition takes place.

© 2018 Elsevier B.V. All rights reserved.

kinetic stability. At the same time, those of the glass-like substances, the relaxation processes in which occur according to the Arrhenius law, refer to "strong" glassformers, while those whose relaxation times significantly exceed the "standard" values corresponding to the Arrhenius law, Refer to "fragile" glassformers. In this case, the relaxation times are described by the well-known Vogel-Fulcher-Tammann equation.

Physical and chemical parameters, which mainly determine the properties of cryovacuum condensates are external and internal conditions of cryogenic deposition. External temperatures include the cryogenic deposition temperature and the velocity of the gassolid interface separation, i.e. Pressure of the gas phase. It is clear that the temperature of the substrate determines the degree of mobility of the molecules and limits the time to search for the minimum energy position on the sample surface [13]. In this case, the pressure determines the time after which the molecules on the surface in the adsorption layer will be absorbed by the front of the growing monolithic sample [14] in its current state. However, it should be noticed, that too high supersaturation in pressure can lead to the heating of the condensation surface itself due to the release of the heat of condensation and the final value of the thermal conductivity of the layer.

As for the molecular-kinetic reasons that contribute to the formation of stable glasses. It should be highlighted, that the intramolecular degrees of freedom of organic molecules increase the activation barrier for transition to a more stable low-energy state in the process of cryo-precipitation. In addition, in accordance to the model S.L.L.M. Ramos [15] an important circumstance affecting the formation of stable organic glasses is the anisotropic molec-







^{*} Corresponding author. E-mail address: asel.nurmukan@inbox.ru (A. Nurmukan).

ular structure of glassformers. That is, the presence of additional features in the molecule such as the dipole moment, which increases the activation energy and shifts the glass transition temperature to a range of higher temperatures.

The above-mentioned circumstances were the impetus for carrying out complex studies of the processes of thermally stimulated transformations in organic glass-forming environs at low temperatures. The studied substances are Freons 134 and 134a, which differ in the structure of the molecules [16,17]. And if Freon 134 (CHF₂-CHF₂) is a symmetrical variant of the molecule, then its isomer Freon 134a (CF₃-CH₂F) demonstrates an anisotropic molecular structure. At this stage, the object of our research is Freon 134a, and the data presented in this article demonstrate the results of IR spectrometric studies of CF₃-CH₂F cryovacuum condensates.

2. Material and methods

The results proposed in this paper are a continuation of our IR spectrometric studies of Freon CF3-CH2F [18], in which the IR spectra of CF₃-CH₂F in the gas phase and in the condensed state were compared at low temperatures, and the effect of substrate temperature changes on the vibrational Spectra of thin-film cryocondensed samples. On the basis of the obtained IR spectrometric data, in [18] it is assumed that in the temperature range from T = 16 K to T = 90 K several structural modifications of solid Freon 134a, as well as thermostimulated transformations between them, are made. The most intensive transformations of vibrational spectra associated with structural transformations are observed in the temperature range 70-85 K. Moreover, a number of additional experimental factors made it possible to make the assumption that it is in this temperature range that the glass transition temperature is located. In particular, one of such factors is the thermodesorption effect, and it is known that this kind of phenomenon always accompanied the process of transition from a vitreous state to a supercooled liquid state of various cryocondensates, in particular water and ethanol [19.20].

The vibrational frequencies of the molecule, the results of which are given in this paper. The objects of investigation are thin films of Freon cryovacuum condensates condensed on a cooled metallic mirror in a range of deposition temperatures from 16 to 100 K and gas phase pressures from 10^{-4} to 10^{-6} Torr. The thickness of the films was measured by a two-beam laser interferometer and amounted to about $d = 2.5 \mu m$. At the same time, the refractive index of the condensed samples was measured. The vibrational spectra were measured by IR-spectrometer ICS 20 in the interval 400–4200 cm⁻¹. For continuous monitoring of the position of the absorption band, the value of the observation frequency of the spectrometer at the half-width of the absorption band was fixed and the corresponding thermogram was taken. This gives current information about the changes in the position of the absorption bands of the vibrational spectrum of Freon 134a during the thermovariation of the sample under study. In detail, the experimental setup and the measurement technique are described by us in earlier publications [19,20].

3. Theory and experiment

Below at Figs. 1–3 are the thermograms of the change in the position of the absorption bands, as well as the final positions of the absorption bands when these heating temperatures are reached.

Thus, Fig. 1 shows the data for the vibrational mode v_7 of the Freon 134a molecule. The sample was deposited at a condensation temperature T = 16 K and then warmed to T = 90 K. The figure contains the heating thermogram (lower curve) at the observation fre-



Fig. 1. The thermogram (lower curve) at the observation frequency $v_{obs} = 842 \text{ cm}^{-1}$ and the corresponding change in the position of the absorption band of the v_7 mode of the Freon 134a molecule when the sample is heated from 79 to 90 K.



Fig. 2. The thermogram at the observation frequency $\nu_{obs} = 1055 \text{ cm}^{-1}$ and the corresponding change in the position of the absorption band of the ν_6 mode of the Freon 134a molecule when the sample is heated from 60 to 90 K.

quency v_{obs} = 842 cm⁻¹ and the absorption bands at a temperature T = 79 and T = 90 K. The arrow indicates an abrupt increase in the spectrometer signal due to the "red" shift of the absorption band when the film is heated from 79 K to 90 K. These absorption bands reflect precisely the last stage of the transformation, corresponding, as we suppose [18] (in accordance with the data of [21]), to the transition from the state of the plastic crystal to the state of the monoclinic crystal structure. Analyzing the behavior of the thermogram in the entire indicated temperature range, it can be stated that the sample undergoes sharp transformations in the range 70-73 K, which correspond to the "blue" shift of the mode band v₇. Further, there is a narrow temperature range (73–75 K), in which a certain metastable phase of solid CF₃-CFH₂ is possible. Further in the interval 76–78 K again observe a sharp drop in the signal, which means a further "blue" shift of the band. The absence of changes in the 78-80 K temperature range may indicate the existence in this range of a quasi-stable structural modification



Fig. 3. (A) Thermally induced changes in the position and nature of the absorption of the v_{15} mode and the thermogram at the observation frequencies $v_{obs} = 967 \text{ cm}^{-1}$ and $v_{obs} = 958 \text{ cm}^{-1}$ when the sample is heated from 40 to 90 K. (B) Enhanced fragment of the thermogram 3 showing the change in the splitting rate of the absorption band v_{15} .

(plastic crystal), which is further transformed into a stable phase of the CF₃-CFH₂-monoclinic crystal.

Similar data for the v_6 mode are shown at Fig. 2. The curve marked as $v_{obs} = 1055 \text{ cm}^{-1}$ is a thermogram at the corresponding observation frequency, which covers the temperature change interval from 60 to 90 K. The arrow indicates a general change in the signal with a temperature change of 16–90 K. Analysis of the thermogram shows that in the interval 60–73 K there is a monotonic shift of the absorption band v_6 to the "blue" region of the spectrum with its simultaneous narrowing. In the interval 73–76 K, the velocity of the shift of the band increases, and further at temperatures from 76 to 79 K the rate of change of the position of the band decreases again, and at T = 79 K, a sharp increase in the signal of the spectrometer is observed, which, as we have already indicated, corresponds to a transition to a monoclinic modification of Freon 134a.

It can be noted that the data on the behavior of the thermogram shown at Fig. 2 and the corresponding changes in the position of the v_6 band correlate well with the results shown at Fig. 1. This concerns the temperature ranges 73–76 K, 76–79 K and, in particular, the temperature 79–80 K of the onset of an abrupt transition to the monoclinic modification. The partial mismatch of the tem-

perature values is explained by the fact that different types of vibrations of the CF₃-CFH₂ molecules are compared, which require different energies to activate the corresponding transformations.

Figs. 1 and 2 show absorption bands related to the A^{*l*}-symmetry group, for which the change in the dipole moment parallel to the plane of symmetry is characteristic [22]. At the same time, Fig. 3 shows the results obtained for the absorption band of the v₁₅ mode, whose mode of vibration belongs to the symmetry group $A^{/l}$, for which the perpendicular direction of the change in the dipole-moment vector with respect to the symmetry plane is characteristic. It can be assumed that it is this circumstance that is the cause of the complex behavior of this type of oscillation in the process of thermostimulation. Earlier we discovered [18] that as a result of sample heating the band v₁₅ not only changes its position, but also undergoes splitting into two components. These processes are clearly demonstrated at Fig. 3.

At Fig. 3, curves 1 and 2 represent the absorption bands of the v_{15} mode at the condensation temperature T = 16 K (1) and after heating to T = 90 K (2), curves 3 and 4 are thermograms at observation frequencies, respectively, v_{obs} = 967 cm⁻¹ and v_{obs} = 958 cm⁻¹. In this case, thermogram 3 monitors the beginning of the band splitting process, and the thermogram 4 "is responsible" for monitoring the position of this absorption band. Comparing these positions of the band v_{15} and thermograms 3 and 4, we can arrive at the following conclusions. An increase in the temperature of the film from T = 16 K to T = 70 K is accompanied by a gradual shift of the band v_{15} into the range of higher frequencies ("blue" shift). At a temperature in the vicinity of T = 71 K, this displacement acquires a sharp character, as evidenced by a jump upward of the thermogram 4 and a slight drop in the values of the thermogram 3. Further increase in temperature from 73 to 77 K is characterized by a relatively stable state of the film. Starting with T = 78 K, a sharp shift of the absorption band to the "red" area of the spectrum is observed (the drop in the values of thermogram 4, arrow 4 downward) with simultaneous initiation of the band splitting v15 (an increase in the signal of thermogram 3, arrow 3 upwards). At a temperature around T = 83 K. the state of the film stabilizes (the horizontal section of thermogram 4), while the band splitting continues up to T = 87 K (the horizontal section of thermogram 3). It is also interesting to note that the thermogram 3, during its growth, undergoes a break at T = 81 K (insertion), which can be interpreted as a change (slowing) in the dynamics of the band splitting v15. At a temperature of about 100 K, the sample begins to evaporate.

This difference in the behavior of thermograms 3 and 4 at Fig. 3 may indicate that isothermal relaxation processes are carried out in the temperature range 78-85 K, one of which leads to mixing of the position of the band v_{15} , and the other to a splitting of the position of the band v₁₅. The presence of such processes is indicated by the data shown at Fig. 4, the procedure for obtaining which is as follows. The sample was condensed at T = 16 K and then warmed to T = 76 K (thermogram 1), i.e. Up to the temperature of existence, as we assume, of a plastic crystal (Fig. 1). Then the temperature was set equal to T = 76 K, and at this temperature the sample was held for 20 min. As can be seen (the arrow marked as t = 20 min), during this time the signal decreased, which indicates isothermal relaxation in the sample. The question arises: if in this state we only have a plastic crystal (PC), then, by analogy with ethanol [23] and on the basis of general concepts [24], as a result of cooling, the sample can be transformed into a state with a frozen-out rotational subsystem-orientation glass (OG). In this case, the transition from PC to OG and back must be reversible. As can be seen at Fig. 4, cooling from T = 76 K to T = 16 K (thermogram 2) leads, as can be seen at Fig. 1, to an insignificant "blue" shift of the band v_7 . Re-heating (thermogram 3) differs from thermogram 2 and, in addition, exhibits residual relaxation phenomena at temperatures above T = 70 K. On the basis of what has been said,



Fig. 4. Thermograms of the change in the position of the absorption band ν_7 during thermal cycling.

it can be assumed that the sample in the final state of thermogram 1 and the initial state of thermogram 2 is a mixture containing, as we assume, a super-cooled liquid phase and a plastic crystal.

As for the glass transition temperature T_g , in 18 we assumed that its value lies within T = 71-72 K. The main reason for this was the thermodesorption effect accompanying the sample heating and showing itself also within the temperatures 71-72 K. In order to verify this assumption, we performed measurements at various cryoprecipitation temperatures of the samples in the vicinity of the presumed glass transition temperature. During the subsequent thermocycling at a fixed observation frequency, heating thermograms from T = 16 K to the evaporation temperature T = 102 K have been measured. The nature of the thermograms for different cryoprecipitation temperatures gives information on the states of the Freon 134a film that are realized during its heating. These data are shown at Fig. 5. Five different thermograms of the heating of samples deposited at cryocondensation temperatures of 16 K, 75 K, 77 K, 78 K, and 80 K are presented. The lower curve shows the pressure jump in the chamber corresponding to the onset of evaporation of the samples.

It seems reasonable to begin the analysis of the figure from the thermogram 5 relating to the temperature of cryogenic deposition T = 80 K. As can be seen, a film formed at T = 80 K does not undergo



Fig. 5. Thermograms of heating Freon 132a cryofilms, formed at different temperatures.

any changes in the process of thermovariation, which can mean that at a given temperature the sample is formed immediately in its most stable monoclinic modification [21]. In turn, the thermogram 1 (T_{dep} = 16 K) demonstrates the behavior that we interpret as: (1) the transition from the state of the glass to the supercooled liquid (SCL) at a temperature near T = 72-73 K (upward jump of the spectrometer signal); (2) the existence of SCL and its crystallization into a plastic crystal of PC in the interval from T = 75 to T = 78 K; (3) the transformation of a plastic crystal of PC into a monoclinic crystal of MC. It is interesting to note that at temperatures in the vicinity of T = 75 K the character of the change in the thermogram changes (Fig. 6). We assume that this is a reflection of the phase transition of a plastic orientationally disordered crystal (OG orientation glass) into a plastic PC crystal with an ordered rotational subsystem. With this assumption, the behavior of thermograms 2-4 can be explained as follows. At condensation temperatures in the range 75–77 K. a film is formed consisting of a mixture of OG and PC. At the same time, the concentration of PC increases with increasing temperature of film formation. Heating the film leads to a transition from the OG state to the PC. As can be seen at Fig. 6, this transition is completed in the vicinity of the temperature T = 79-80 K, and then the sample passes into the state of a monoclinic crystal. The behavior of thermogram 4 reflects the fact that at 78 K the Freon 134a film was condensed directly into the plastic phase, passing on to further heating into a monoclinic crystal.

Fig. 6 is an enlarged fragment of the thermogram 1 of Fig. 5. It clearly demonstrates our interpretation of the behavior of the cryovacuum condensate CF3-CFH2.

4. Results and discussion

The T_g icon indicates the expected transition temperature from the glass state (G) to the SCL state. The range of existence of the quasi-liquid SCL phase and the transition to the OG orientation glass are given below. The transition temperature from the OG state to the state of the plastic crystal of the PC is indicated by an arrow as T_{trans} . The arrow denoted as MC indicates the completion of the transition from the PC state to the MC. It is important to note the fact that the results shown at Figs. 5 and 6 are in good agreement with the information presented in the right-hand inset of Fig. 3, namely, the value of the temperature T = 80 K of the frac-



Fig. 6. Enlarged fragment of the thermogram 1 of Fig. 5. T_g – value of the transition temperature from the glass state (G) to the SCL state. SCL is the temperature range of the quasi-liquid phase and the transition to the OG orientation glass. T_{trans} is the temperature of the transition from the OG state to the state of the plastic crystal PC. MC-completion of the transition from the state of the PC to the MC.

ture of the thermogram of the splitting of the band v_{15} is consistent with the temperature T_{trans} (Fig. 6), also approximately equal to 80 K.

5. Conclusions

Data on the IR spectra of cryofilms in general, and Freon 134a in particular, cannot serve as a basis for categorical conclusions regarding the structure and structural-phase transformations in the objects under investigation. Nevertheless, based on the obtained results, our own experience of studying such systems, and also comparing our data with the results of structural studies of cryocondensates, we can make a number of assumptions indicating the approximate parameters and the possible nature of the transformations in the cryovacuum condensates CF_3-CFH_2 .

- (1) It is evident that the cryofilms of Freon 134a, formed at T = 16 K, experience multiple structural transformations of various nature in the temperature range from 70 to 90 K. At a temperature in the vicinity of 72 K, the classical transition is a glassy state-supercooled liquid (G-SCL). We believe that the value of the temperature of this glass transition is approximately equal to $T_g = 72$ K. The temperature range from 75 to 78 K is the area of the quasistable existence of SCL. At a temperature of about T = 78 K, crystallization of SCL into the state of an orientationally disordered plastic crystal-OG orientation glass begins. At a temperature of Ttr ans = 80 K, a second quasi-glass transition occurs from the state of the OG orientation glass, a plastic crystal with an ordered rotational subsystem of the PC. In the temperature range 83-85 K, a plastic crystal-monoclinic crystal phase transition is realized.
- (2) From the studies of Brunelli and FitchI [21] it follows that during the crystallization of Freon 134a from the liquid phase, the substance undergoes liquid-plastic orientationally disordered crystal stages during the cooling (T = 156 K) ; Plastic orientationally disordered crystal-plastic crystal (120 K), plastic crystal-monoclinic crystal (T = 108 K). It is in this sequence that transformations in the cryocondensed Freon 134a appear to us, with the difference that they are realized not with decreasing temperature, as in [21], but

with increasing temperature! The final state in both cases is a monoclinic crystal. The same state can be achieved in completely different ways! Or these states are not equivalent, as in the case of Water "A" and Water "B" [25].

Acknowledgement

The work was financially supported by the Ministry of Education and Science of the Republic of Kazakhstan, Grant No GF 17.

References

- [1] K.L. Kearns, S.F. Swallen, M.D. Ediger, T. Wu, L. Yu, J. Chem. Phys. 127 (15) (2007) 154702.
- [2] M.A. Satorre, M. Domingo, C. Millan, R. Luna, R. Vilaplana, C. Santonja, Planet. Space Sci. 56 (2008) 1748.
- [3] Perry A. Gerakines, Reggie L. Hudson, Astrophys. J. Lett. 805 (2) (2015) L20.
- [4] A. Aldiyarov, A. Drobyshev, D. Sokolov, A. Shinbayeva, J. LTP 187 (2017).
- [5] R.L. Hudson, M.J. Loeffler, P.A. Gerakines, J. Chem. Phys. 146 (2017) 024304.
- [6] Jeremy J. Harrison, J. Quant. Spectrosc. Radiative Transfer 151 (2015) 210.
- [7] Tetsuya Hama, Naoki Watanabe, Chem. Rev. 113 (2013) 8783.
- [8] G. Mulas, G.A. Baratta, M.E. Palumbo, G. Strazzulla, Astron. Astrophys. 333 (1998) 1025
- [1536] 1023.
 [9] R.B. Bohn, S.A. Sandford, L.J. Allamandola, D.P. Cruikshank, Icarus 111 (1994) 151
- [10] W.M. Grundy, Schmitt, E. Quirico, Icarus 155 (2002) 486.
- [11] A. Aldiyarov, M. Aryutkina, A. Drobyshev, et al., Low. Temp. Phys. 37 (2011) 524.
- [12] Y.Z. Chua, M. Tylinski, S. Tatsumi, M.D. Ediger, C. Schick, J. Phys. Chem. 144 (2016) 244503.
- [13] W. Zhang, C.W. Brian, L. Yu, J. Phys. Chem. B 119 (15) (2015) 5071.
- [14] S.F. Swallen, K.L. Kearns, M.K. Mapes, Y.S. Kim, R.J. McMahon, M.D. Ediger, T. Wu, L. Yu, S. Satija, Science 315 (5810) (2007) 353.
- [15] S.L.L.M. Ramos, A.K. Chigira, M. Oguni, J. Phys. Chem. B 119 (10) (2015) 4076.
 [16] A.D. Lopata, J.R. Durig, J. Raman Spectrosc. 6 (1977) 61.
- [17] L. Xu, A. Andrews, R. Cavanagh, G. Fraser, K. Irikura, F. Lovas, J. Grabow, W. Stahl, M. Crawford, Smalley, J. Phys. Chem. A101 (1997) 2288.
- [18] A. Drobyshev, A. Aldiyarov, A. Nurmukan, D. Sokolov, A. Shinbayeva, IR-studies of thermally stimulated structural phase transformations in cryovacuum deposited films of Freon 134a, Low Temp. Phys. 44 (5) (2018).
- [19] A. Aldiyarov, M. Aryutkina, A. Drobyshev, Low Temp. Phys. 37 (6) (2011) 524.
 [20] A. Drobyshev, K. Abdykalykov, A. Aldiyarov, Low Temp. Phys. 33 (8) (2007)
- 699
- [21] M. Brunelli, A.N. Fitchl, Z. Kristallogr. 217 (2002) 395.
- [22] L. Xu, A. Andrews, R. Cavanagh, G. Fraser, K. Irikura, F. Lovas, J. Grabow, W. Stahl, M. Crawford, Smalley, J. Phys. Chem. A 101 (1997) 2288.
- [23] A. Aldiyarov, M. Aryutkina, A. Drobyshev, Low Temp. Phys. 35 (4) (2009) 251.
- [24] M.D. Ediger, C.A. Angell, Sidney R. Nagel, J. Phys. Chem. 100 (1996) 13200.
- [25] V. Petrenko, R. Whitworth, Physics of Ice, Oxford Univ. Press Inc., Ny, 1999.