Refractive Index at Low Temperature of Tetrachloromethane and Tetrafluoroethane Cryovacuum Condensates

Abdurakhman U. Aldiyarov, Dmitriy Yurievich Sokolov, Assel Yerzhumayevna Nurmukan, and Miguel Angel Ramos

ABSTRACT: We present low-temperature measurements of the refractive index of cryofilms of tetrachloromethane and 1,1,1,2-tetrafluoroethane at different condensation and measurement temperatures between 16 and 130 K. Using cryovacuum condensation, we have been able to obtain thin films in an amorphous state for both substances despite them being very bad glass formers. Then, we have studied the evolution of the refractive index with an increasing temperature, including by transitions to ordered or partially disordered crystalline states.

1. INTRODUCTION

Molecular glasses and crystals, often obtained at low temperatures by cooling organic substances from their liquid state, are of great interest for physics and chemistry. In particular, they usually exhibit polymorphism and a rich phase diagram.1−3

Among them, 1,1,1,2-tetrafluoroethane (F3C−CFH2), which is a hydrofluorocarbon (HFC) type of freon known as Freon 134a, is particularly interesting given its practical applications. 1,1,1,2-tetrafluoroethane is nowadays widely used for domestic and industrial refrigeration systems, as well as air conditioning systems, liquid refrigeration systems, and heat pumps. Although the physical properties of tetrafluoroethane in the gas phase have been studied with some detail,4−7 its thermophysical and optical characteristics in the condensed state at low temperatures have seldom been studied.8,9

On the other hand, tetrachloromethane or carbon tetrachloride (CCl4) is a tetrahedral molecule, which has an interesting phase diagram as many other small-molecule organic materials. The phase diagram of CCl4 has been investigated thoroughly in the low-temperature range. Tetrachloromethane is reported to form several solid phases10−15 just below room temperature, and it finally freezes into a stable monoclinic crystal at 225 K. Given its nearly spherical structure, it is not surprising that CCl4 is a bad glass former.16 Nevertheless, Haida et al.16 reported for the first time the glass formation of tetrachloromethane after vapor deposition of CCl4 at a substrate temperature of 20 K. Furthermore, highly stable glasses of CCl4 have been recently obtained by physical vapor deposition (PVD).17 It is to be stressed that CCl4 has been the first reported ultrastable glass, which has been obtained from a substance with a nearly isotropic molecular structure, whereas it had been previously suggested that molecular anisotropy is a prerequisite for highly stable glass formation,18 although amorphous CH4 was made and reported one year earlier.3

Nevertheless, the stable monoclinic crystal of CCl4 has also been found to exhibit glassy relaxational dynamics19,20 and even glassy features in its thermal properties at low temperatures.21

In the present work, we have prepared amorphous thin films of both molecular solids mentioned above (F3C−CFH2 and CCl4) by employing a cryovacuum condensation technique. Then, their refractive indices as a function of the deposition temperature have been studied by means of a two-beam laser interferometer in the temperature range of 16−130 K, including the main structural transformation temperatures.8,22 The different numbers of translational and rotational degrees of freedom per molecule corresponding to their different solid phases will reflect on the value of the refractive index of these cryocondensates.
In Section 2, the experimental technique of cryovacuum condensation that we employ for obtaining the amorphous thin films of these molecular (bad glass former) solids and the experimental method used to determine the refractive index at any fixed deposition temperature are described. In Section 4, the measurements of the refractive index of both Freon 134a and tetrachloromethane are shown and discussed. Our conclusions are presented in Section 3.

2. RESULTS AND DISCUSSION

Depending on both the temperature of its deposition and the subsequent thermal history, Freon 134a cryofilms can exist in various states. Specifically, thin films of Freon 134a obtained by direct cryocondensation at $T = 16$ K from the gas phase have been observed to undergo multiple structural transformations of different natures in the temperature range from 70 to 90 K. In particular, a typical glass transition from a structural glass state (amorphous solid) to a supercooled liquid (SCL) state is observed. The glass transition temperature is found to occur approximately at $T_g = 72$ K. Then, in the temperature range from 75 to 78 K the SCL remains metastable. Increasing the temperature up to about $T = 78$ K, the SCL begins to crystallize into an orientationally disordered crystal, also known as “orientational glass” (OG). At a temperature of $T_{trans} = 80$ K, a second glass-like transition from the OG state to a rotationally disordered plastic crystal (PC) occurs. Finally, within 83–85 K, a plastic crystal–monoclinic crystal phase transition takes place.

By employing different condensation temperatures, the analysis of the correspondingly obtained samples allows to determine the temperature ranges for the formation of different states of 1,1,1,2-tetrafluoroethane (Freon 134a). Figure 1 shows data evidencing the influence of the condensation temperature at which the cryofilms is deposited on its refractive index for Freon 134a. Refractive index data vary with the deposition pressure, and the measurements were obtained as thin films. Deposition pressure was always $(1.3−1.4) \times 10^{-5}$ Torr except the point labelled as $4 \times 10^{-5}$ Torr.

![Figure 1. Refractive index as a function of condensation temperature for Freon 134a cryovacuum-condensated thin films. Deposition pressure was always $(1.3−1.4) \times 10^{-5}$ Torr except the point labelled as $4 \times 10^{-5}$ Torr.](image)

The influence of the degree of porosity of the samples on the value of the refractive index is considered to be as the main reason for this behavior. The value of the refractive index in our studies varies from $n = 1.17$ at $T = 16$ K to $n = 1.36$ at $T = 90$ K.

Thus, the following temperature ranges can be determined for stable molecular states of Freon 134a obtained as thin films at a given condensation pressure. When the deposition temperature is above $T = 80$ K, a monoclinic crystal is obtained. At 80 K, varying the condensation rate (condensation pressure) leads to different values of the refractive index $n$. So, at a condensation pressure of $4 \times 10^{-5}$ Torr, $n = 1.33$, and at $(1.3−1.4) \times 10^{-5}$ Torr, $n = 1.36$. When the deposition temperature lies between 60 and 80 K, a plastic crystal within the fcc lattice, with rotating molecules at the lattice points, is obtained. When the deposition temperature is below $T = 55$ K, one obtains an amorphous phase, as previously shown.

Therefore, a continuous increase in the refractive index is observed in the temperature range of the amorphous state from 16 to 50 K. Then, at temperatures below the glass transition temperature but above 50 K, a sharp change in the refractive index is observed, similar to what was observed for ethanol, methane, and nitrous oxide followed by another step at the monoclinic crystallization above 80 K.

In the future, we aim to compare the thermodynamic parameters of glass transition and the stability of Freon 134a (CF$_3$–CFH$_2$, asymmetric isomer) with those for Freon 134 (1,1,2,2-tetrafluoroethane, symmetric isomer) cryovacuum condensates so that one can obtain information on the influence of the structure of these molecules on cryofilm formation and the properties of the resulting states.

A different approach to the problem can be adopted for small molecules, attempting to ascertain the extent to which the size of a molecule can influence the nature of cryoprecipitation from the gas phase, bearing in mind both the fundamental possibility of the formation of glassy states and the properties of those presumably formed glasses. A model substance to address this matter is tetrachloromethane CCl$_4$. In the rather limited bibliography devoted to CCl$_4$...
Cryodeposition, there are different points of view regarding the parameters of glass transformation. The first reported production of tetrachloromethane in the glassy state by the method of gas phase cryocondensation was that by Haida et al.\textsuperscript{16} Using the calorimetric method, the glass transition temperature of an amorphous tetrachloromethane film condensed at \( T = 20 \text{ K} \) was determined. This temperature value was approximately equal to \( T_g = 61 \text{ K} \). The year before, Lesikar,\textsuperscript{26} based on indirect data, suggested a value in the vicinity of \( T_g = 130 \text{ K} \) as the temperature of the glass transition for tetrachloromethane. However, later and more accurate measurements questioned both of these values. Ediger,\textsuperscript{18} by using a differential calorimeter, investigated a 400 nm-thick tetrachloromethane film formed during condensation from the gas phase at a pressure of \( P = 10^{-6} \text{ Pa} \) \((7.5 \times 10^{-8} \text{ Torr})\) on a substrate at a temperature of \( T = 10 \text{ K} \). Based on the obtained dependence of the sample heat capacity on the heating temperature, the value of the transition temperature from the glass state to the supercooled liquid state was determined to be \( T_g = 78 \text{ K} \). The significant discrepancy between this value and that from Haida et al. could be explained by the possible uncertainty of the measurement technique and methods employed in those years, as well as the possible presence of impurities in the sample.

With this in mind, we carried out studies on the formation and structural transformations of cryovacuum condensates of tetrachloromethane under conditions similar to those implemented in the references.\textsuperscript{16,17} The reason for such studies is that calorimetric research methods are integral with respect to the degrees of freedom of the CCl\(_4\) molecule, while IR spectrometry studies can provide information about individual vibrations of the tetrachloromethane molecule and their reactions to thermally stimulated transformations in the samples under study. These data will help draw conclusions about the state of the film at different condensation temperatures.

Figure 2 shows data about the effect of condensation temperature on the refractive index of cryovacuum condensates of carbon tetrachloride. As can be seen, in the condensation temperature range from 16 to 50 K, an increase in the refractive index is observed with the increasing condensation temperature. The value of the refractive index in our studies varies from the value of \( n = 1.35 \) at \( T = 16 \text{ K} \) to \( n = 1.65 \) at \( T = 130 \text{ K} \). Out of the six substances studied by us earlier, carbon tetrachloride exhibits the highest refractive index for the corresponding condensation temperatures.

The obtained data at various condensation temperatures allow us to determine the temperature ranges for the formation of the different states of carbon tetrachloride. We assume, therefore, that at a condensation temperature of \( T = 16 \text{ K} \), tetrachloromethane condenses to an amorphous state. The upper temperature limit for the achievement of this amorphous state is determined to be approximately at \( T = 38 \text{ K} \). At the same time, the condensation of a film at a temperature \( T = 35 \text{ K} \) does not lead to the formation of an amorphous state.

In brief, when the deposition temperature is above \( T = 80 \text{ K} \), the usual monoclinic crystal of CCl\(_4\) is obtained. When the deposition temperature ranges between 50 and 80 K, an amorphous structure consisting of orientationally disordered crystallites with varying degrees of ordering is obtained. Only when the deposition temperature lies below \( T = 45 \text{ K} \) can the genuine amorphous state be achieved.

As can be seen from the data for CCl\(_4\) at 80 K, the effect of the condensation rate is also significant, as in the case of Freon 134a above. At a condensation pressure of \( 2 \times 10^{-5} \text{ Torr} \), \( n = 1.56 \), and at \((1.3-1.4) \times 10^{-5} \text{ Torr}, n = 1.62\).

### 3. CONCLUSIONS

The experimental technique of cryovacuum condensation has long been revealed as a very useful tool for preparing and studying films of solids (generally amorphous) at low temperatures made from molecules of the chosen substance in the gaseous state. Some structural, optical, or thermal properties of these amorphous solids can then be studied as a function of varying conditions of the physical vapor deposition. For instance, one can monitor the influence of the condensed molecular structure and of the employed deposition rate on several possible phase transitions or structural transformations observed when increasing the temperature.\textsuperscript{27}
This work has been devoted to assess the effect of deposition temperature on the refractive index of cryocondensed films of molecular materials that exist in different solid phases at low temperatures. The materials studied, 1,1,1,2-tetrafluoroethane (Freon 134a) and carbon tetrachloride, exhibit several solid phase transitions, leading to a change in the number of molecular degrees of freedom. In contrast to other preparation techniques, by cryovacuum condensation, we have been able to obtain and measure both substances in their different stable and metastable states, including the amorphous state, despite both of them being very bad glass formers.

4. EXPERIMENTAL TECHNIQUES AND MATERIALS

The main unit of the experimental setup (see Figure 3) is a high vacuum chamber, which routinely operates at $10^{-8}$–$10^{-6}$ Torr, by continuous evacuation with a turbomolecular pump Turbo-V-301 backed with a dry scroll vacuum pump SH-110. Pressure measurement is conducted using a converter FRG-700 with an AGC-100 controller.

A copper substrate covered with a planar silver film is used. This substrate with a diameter of 60 mm is put in thermal contact with a closed-cycle helium Gifford–McMahon refrigerator and placed inside a vacuum chamber. The double-stage cooling system cooled the substrate to 12 K. A resistor heater is connected to the end of the second stage. By the work of the refrigerator, the temperature can be varied in the range 12–200 K. The temperature is monitored by a TS 670-1.4 silicon diode connected to a M335/20 temperature controller, which kept the temperature constant to within 0.5 K.

By using a special protective shield (see Figure 4), we ensure that all the injected gas is deposited on the substrate when the pumping of the vacuum chamber is stopped. By using a metal cylinder (13) and shield (14), we can isolate the substrate (6) and all cold elements of the microcryogenic device from the main volume of the vacuum chamber. This isolation is not vacuum tight, but at operating pressures of $10^{-5}$–$10^{-6}$ Torr, it is effective due to the fact that the mean free path of molecules at these pressures is larger by several orders of magnitude than the distance between the protection shield and the substrate. Therefore, during our experiments, all the gas is deposited on the substrate when the pumping line is closed.

The experimental setup for laser-beam patterning during cryovacuum condensation is depicted in Figure 4. The laser light is divided into two beams, and through optical drives (7, 11, and 12), both beams converge in the center of the substrate. After reflection, the signal from the laser enters the two photoelectric multipliers P25a-SS-0-100 (Figure 5).

The thickness $d$ of the deposited film and its refractive index $n$ were measured by using two interference patterns (Figure 5) generated by a diode laser and two photomultiplier tubes. Measurements were performed at a frequency of 100 Hz, which makes it possible to determine the period of oscillation to within $\pm 0.05$ s.

Figure 3. Experimental setup for cryovacuum condensation: (1) vacuum chamber, (2) vacuum pump Turbo-V-301, (3) vacuum gate valve CFF-100, (4) pressure detector FRG-700, (5) Gifford-McMahon refrigerator, (6) substrate, (7) photo multiplier and laser interferometer, (8) light source and optical channel, (9) IR spectrometer, and (10) supply system.

Figure 4. Experimental setup for laser-beam patterning during cryovacuum condensation: (6) substrate, (11) photo multiplier, (12) laser, (1) vacuum chamber, (13) metal cylinder, and (14) shield. Number labelling follows that of Figure 3.

Figure 5. Interference curves for each laser beam during the deposition of 1,1,1,2-tetrafluoroethane (top) and tetrachloromethane (down). $\alpha_1 = 1^\circ$, $\alpha_2 = 45^\circ$.
For calculation of the refractive index, we use the following equation

\[ n = \sqrt{\frac{\sin^2 \alpha_2 - \left(\frac{t_1}{t_2}\right)^2 \sin^2 \alpha_1}{1 - \left(\frac{t_1}{t_2}\right)^2}} \]  

(1)

where \( t_1 \) and \( t_2 \) stand for the corresponding periods, and \( \alpha_2 = 1 \pm 0.1^\circ \) and \( \alpha_1 = 45 \pm 0.5^\circ \) are the angles of incidence of the laser beams.

Measurements of the dependence of the refractive indices on the deposition temperature were carried out using the experimental setup depicted in Figures 3 and 4. The experiments were performed in the temperature range of 16−130 K, thus including the structural transformations of the studied materials. In this work, the experiments were performed at the same deposition pressure \( P = 1.3 \times 10^{-3} \) Torr, except for a few complementary experiments, and the same sample thickness for each condensation temperature. The laser wavelength was (406 ± 0.5) nm. Refractive index measurements were carried out using a two-beam laser interferometer. Each point in Figures 1 and 2 is the result average of two to three measurements. The total measurement error of the refractive index was estimated to be no more than 1.5%.

It should be noted that each point representing the value of the refractive index in the diagrams below (Figures 1 and 2) corresponds to a separate experiment conducted at a given condensation temperature. After the completion of each experiment, the experimental setup was again prepared for a new experimental cycle.

■ AUTHOR INFORMATION

Corresponding Author

Dmitriy Yurievich Sokolov – Al-Farabi Kazakh National University Institute of Experimental and Theoretical Physics, Physico-Technical Faculty, Almaty 050040, Kazakhstan; orcid.org/0000-0001-7966-1140; Email: yasnyisokol@gmail.com

Authors

Abdurakhman U. Aldiyarov – Al-Farabi Kazakh National University Institute of Experimental and Theoretical Physics, Physico-Technical Faculty, Almaty 050040, Kazakhstan; orcid.org/0000-0002-5091-7699

Assel Yerzhumayevna Nurmukan – Al-Farabi Kazakh National University Institute of Experimental and Theoretical Physics, Physico-Technical Faculty, Almaty 050040, Kazakhstan; orcid.org/0000-0002-4231-0766

Miguel Angel Ramos – Física de la Materia Condensada, Francisco Tomas y Valiente, Universidad Autónoma de Madrid, Madrid E-28049, Spain; orcid.org/0000-0002-2157-9774

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c00969

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors of this work are deeply indebted to Prof. Andrey S. Drobyshev who has recently passed away. He was the head of this cryovacuum condensates research line and the laboratory for many years, and he is very much missed. This paper is dedicated to him. These studies have been carried out with the financial support of the Ministry of Education and Science of the Republic of Kazakhstan under grants AP05130123 and AP06851270.

■ REFERENCES

(1) Hudson, R. L.; Gerakines, P. A. Molecular Identifications in Experiments with Astronomical Ice Analogues: New Data, Old Strategies, and the N\(_2\) + Acetone System. Mon. Not. R. Astron. Soc. 2019, 485, 861−871.

(2) Jiménez-Ruiz, M.; González, M. A.; Bermejo, F. J.; Miller, M. A.; Birge, N. O.; Cendoya, I.; Alegria, A. Relaxational Dynamics in the Glassy, Supercooled Liquid, and Orientationally Disordered Crystal Phases of a Polymorphic Molecular Material. Phys. Rev. B: Condens. Matter Mater. Phys. 1999, 59, 9155−9166.

(3) Gerakines, P. A.; Hudson, R. L. Infrared Spectra and Optical Constants of Elusive Amorphous Methane. Astrophys. J., Lett. 2015, 805, L20.

(4) Chen, S. S.; Rodgers, A. S.; Chao, J.; Wilhoit, R. C.; Zwolinski, B. J. Erratum: Ideal Gas Thermodynamic Properties of Six Fluoroethanes. J. Phys. Chem. Ref. Data 1977, 6, 309−309.

(5) Cappellani, F.; Restelli, G. Infrared Band Strengths and Their Temperature Dependence of the Hydrohalocarbons HFC-134a, HFC-152a, HCFC-22, HCFC-123 and HCFC-142b. Spectrochim. Acta, Part A 1992, 48, 1127−1131.

(6) Newnham, D.; Ballard, J.; Page, M. Infrared Band Strengths of HFC-134a Vapour. J. Quant. Spectrosc. Radiat. Transf. 1996, 55, 373−381.

(7) Saar, B. G.; Steeves, A. H.; Thoman, J. W.; Howard, D. L.; Schofield, D. P.; Kjaergaard, H. G. CH-Stretching Overtone Spectroscopy of 1,1,1,2-Tetrafluoroethane. J. Phys. Chem. A 2005, 109, 5323−5331.

(8) Drobyshev, A.; Aldiyarov, A.; Nurmukan, A.; Sokolov, D.; Shinaibayeva, A. Structure Transformations in Thin Films of CF\(_3\)C\(_2\)H\(_2\) Cryodeposits. Is There a Glass Transition and What Is the Value of T\(_g\)? Appl. Surf. Sci. 2018, 446, 196−200.

(9) Drobyshev, A.; Aldiyarov, A.; Nurmukan, A.; Sokolov, D.; Shinaibayeva, A. IR Studies of Thermally Stimulated Structural Phase Transformations in Cryovacuum Condensates of Freon 134a. Low Temp. Phys. 2018, 44, 831−839.

(10) Hicks, J. F. G.; Hooley, J. G.; Stephenson, C. C. The Heat Capacity of Carbon Tetrachloride from 15 to 300°K. The Heats of Transition and of Fusion. The Entropy from Thermal Measurements Compared with the Entropy from Molecular Data. J. Am. Chem. Soc. 1944, 66, 1064−1067.

(11) Arenszen, J. G.; Van Miltenburg, J. C. Carbon Tetrachloride. Determination of the Enthalpy of Transition from Metastable Face-Centered Cubic Carbon Tetrachloride to the Stable Rhombohedral Modification. J. Chem. Thermodyn. 1972, 4, 789−791.

(12) Morrison, J. A.; Richards, E. L. Thermodynamic Study of Phase Transitions in Carbon Tetrachloride. J. Chem. Thermodyn. 1976, 8, 1033−1038.

(13) Nishikawa, K.; Tohji, K.; Murata, Y. The Intramolecular Arrangement in the Plastic Crystal (Phase Ia) of Carbon Tetrachloride Studied by x-Ray Diffraction. J. Chem. Phys. 1981, 74, 5817−5824.

(14) Takei, T.; Onoda, Y.; Fujii, M.; Watanabe, T.; Chikazawa, M. Anomalous Phase Transition Behavior of Carbon Tetrachloride in Silica Pores. Thermochim. Acta 2000, 352−353, 199−204.

(15) Li, X.; Zheng, Y.; Chen, J.; Grabow, J.-U.; Gou, Q.; Xia, Z.; Feng, G. Weak Hydrogen Bond Network: A Rotational Study of 1,1,1,2-Tetrafluoroethane Dimer. J. Phys. Chem. A 2017, 121, 7876−7881.

(16) Haida, O.; Suga, H.; Seki, S. Preparation of Glassy Carbon Tetrachloride. J. Non-Cryst. Solids 1976, 22, 219−221.
(17) Chua, Y. Z.; Tylinski, M.; Tatsumi, S.; Ediger, M. D.; Schick, C. Glass Transition and Stable Glass Formation of Tetrachloromethane. J. Chem. Phys. 2016, 144, 244503.

(18) Ediger, M. D. Perspective: Highly Stable Vapor-Deposited Glasses. J. Chem. Phys. 2017, 147, 210901.

(19) Zuriaga, M.; Pardo, L. C.; Lunkenheimer, P.; Tamarit, J. L.; Veglio, N.; Barrio, M.; Bermejo, F. J.; Loidl, A. New Microscopic Mechanism for Secondary Relaxation in Glasses. Phys. Rev. Lett. 2009, 103, No. 075701.

(20) Zuriaga, M. J.; Perez, S. C.; Pardo, L. C.; Tamarit, J. L. Dynamic Heterogeneity in the Glass-like Monoclinic Phases of CBrClCl₄ₙ, n = 0,1,2. J. Chem. Phys. 2012, 137, No. 054506.

(21) Moratalla, M.; Gebbia, J. F.; Ramos, M. A.; Pardo, L. C.; Mukhopadhyay, S.; Rudić, S.; Fernandez-Alonso, F.; Bermejo, F. J.; Tamarit, J. L. Emergence of Glassy Features in Halomethane Crystals. Phys. Rev. B 2019, 99, No. 024301.

(22) Aldiyarov, A.; Nurmukan, A.; Sokolov, D.; Korshikov, E. Investigation of Vapor Cryodeposited Glasses and Glass Transition of Tetrachloromethane Films. Appl. Surf. Sci. 2020, 507, 144857.

(23) Drobyshev, A.; Aldiyarov, A.; Sokolov, D.; Shinbayeva, A. Refractive Indices and Density of Cryovacuum-Deposited Thin Films of Methane in the Vicinity of the α-β-Transition Temperature. Low Temp. Phys. 2017, 43, 724–727.

(24) Drobyshev, A.; Aldiyarov, A.; Sokolov, D.; Shinbayeva, A.; Tokmoldin, N. Refractive Indices vs Deposition Temperature of Thin Films of Ethanol, Methane and Nitrous Oxide in the Vicinity of Their Phase Transition Temperatures. Low Temp. Phys. 2017, 43, 1214–1216.

(25) Loeffler, M. J.; Moore, M. H.; Gerakines, P. A. The Effects of Experimental Conditions on the Refractive Index and Density of Low-Temperature Ices: Solid Carbon Dioxide. Astrophys. J. 2016, 827, 98.

(26) Lesikar, A. V. Glass Transitions of Organic Solvent Mixtures. Phys. Chem. Glasses 1975, 16, 83–90.

(27) L. M. Ramos, S. L.; Chigira, A. K.; Oguni, M. Devitrification Properties of Vapor-Deposited Ethylcyclohexane Glasses and Interpretation of the Molecular Mechanism for Formation of Vapor-Deposited Glasses. J. Phys. Chem. B 2015, 119, 4076–4083.