Refractive indices vs deposition temperature of thin films of ethanol, methane and nitrous oxide in the vicinity of their phase transition temperatures

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This paper presents results of an experimental study of the dependence of deposition temperature on the refractive in dices of ethanol, methane and nitrous oxide, in the form of cryovacuum deposited thin films, in the vicinity of their structural transformation temperatures. The measurements were made using a two-beam laser interferometer in the temperature range 14–130 K. The refractive indices of ethanol, methane and nitrous oxide demonstrate clear non-monotonic dependence on deposition temperature in the vicinity of their structural phase transformation temperatures. It is speculated that the observed abrupt changes in the refractive indices are due to a difference in the number of translational and rotational degrees of freedom of the molecules existing in different phase states of these cryocrystals.

1. Introduction

In recent years, renewed interest has been noticed in the studies of thin films of ethanol [1,2], nitrogen oxide [3,4] and methane [5–7] deposited from the gas phase at cryogenic temperatures, specifically as part of astrophysical investigations. This paper aims at a more detailed study on deposition temperature dependence of the refractive indices in the vicinity of phase transition temperatures of the mentioned materials. The latter are often associated with abrupt changes in the number of translational and rotational degrees of freedom of the molecules in cryofilms. For example, phase transitions in solid N_2, CO, N_2O, C_2H_5OH up on decrease in temperature may result in partial or complete freeze-out of orientational ordering of rotational subsystem in these cryocrystals. The influence of these processes on mechanical and optical properties of thin films, such as refractive index, density and polarizability, is not yet fully clarified. This relationship becomes even more intricate due to the role of deposition temperature on the structural and phase state of these materials. This report focuses on the study of thin films of solid ethanol, methane and nitrous oxide in the temperature range between 12 and 130 K in which the mentioned structural phase transitions are observed.

2. Results and discussion

The measurements of influence of deposition temperature on the refractive indices of ethanol, methane and nitrous oxide were performed using the experimental setup described in detail elsewhere [9]. The experiments were conducted in the temperature range 14–130 K, comprising temperatures of structural transformations of the studied materials. All experiments were performed by same deposition pressure of $P = 1.2 \cdot 10^{-4}$ Torr and sample thickness of $d = 1.5$ μm. The refractive index was measured using a two-beam laser interferometer. The main source of error was associated with measurement of the period of interference during the film growth, whereas the random error was 0.3%. As such, the total error of the refractive index measurements was estimated to be no more than 1%. It must be noted that each point representing a refractive index value in the diagrams below corresponds to an individual experiment conducted at a given deposition temperature. After completion of each experiment the setup was prepared again to a new experimental cycle.

It is well known that cryofilms of ethanol, methane and nitrous oxide exist in various states depending on both their deposition temperature and consequent thermal history [10–12]. For example, following rapid quenching

to 80–90 K liquid ethanol exhibits transition into the glassy state [13], which upon annealing transforms sequentially in to the super-cooled liquid (SCL) at temperatures in the vicinity of $T = 97$ K, plastic crystal (PC) at temperatures above 110 K and monoclinic crystal at temperatures above 140 K. Cooling of ethanol in the plastic crystal state below 95–97 K results in its reversible transition into the orientational glass (OG) state. A similar behavior is observed for thin films deposited at cryogenic temperatures from the gaseous phase. However, in contrast to monolithic samples, a transition from the amorphous state (ASE) to the glassy state is observed in the region of 70–80 K [14]. Thus, the following characteristic temperature intervals can be identified for stable molecular states of ethanol deposited as thin films at lower temperatures.

— Deposition temperature above $T = 145$ K — monoclinic crystal.

— Deposition temperature between 120 and 90 K — plastic crystal, cubic face-centered lattice with rotating molecules in lattice points. Cooling below $T = 90$ K results in "freezing-out" of the rotational component and formation of structural glass.

— Deposition temperature below $T = 90$ K — amorphous phase comprising orientationally disordered crystallites with various degrees of ordering [15].

Figure 1 demonstrates the influence of deposition temperature on the refractive index of ethanol. Gradual rise in the refractive index value with deposition temperature is observed in the range between 12 and 60 K, which agrees with results of other authors for similar materials [5,6,8]. The influence of sample porosity on the refractive index is considered to be the main cause of this behavior. In our measurements the refractive index values for ethanol varied between $n = 1.250$ at $T = 16$ K and $n = 1.352$ at $T = 60$ K. In the range of 60–90 K the refractive index remains practically constant.

Further increase in deposition temperature above 90 K leads to an abrupt rise of the refraction index value from around $n = 1.352$ at 90 K to $n = 1.430$ at 98 K. Between100 K and 130 K the refractive index of ethanol is again practically independent of deposition temperature having an average value of $n = 1.430$. This is consistent with the given interval corresponding to the range of existence of the plastic crystal phase only [13].

The influence of deposition temperature on the refractive index of nitrous oxide is shown in Fig. 2. As reported by us earlier [16,17], at $T = 40$ K this material undergoes transition from the crystalline cubic face-centered state ($T > 40$ K) to the partially orientationally disordered $Pa3$ state ($T < 40$ K). It is therefore of interest how the refractive index of nitrous oxide is influenced by this transition. As seen in the diagram, the refractive index of nitrous oxide gradually rises with temperature from $n = 1.254$ at 16 K to $n = 1.310$ at 40 K. In the vicinity of 45 K, it undergoes an abrupt increase in value from $n = 1.315$ at $T = 45$ K to $n = 1.410$ at $T = 52$ K. Further increase in the deposition temperature from 50 K to 70 K results in continuation of the gradual rise pattern.

For comparison, we include into Fig. 2 the refractive index values of carbon dioxide measured experimentally using a technique similar to ours [5]. In this case, a monotonous rise is observed between 10 K and 55 K before plateauing at higher temperatures.

The influence of deposition temperature on the refractive index of methane deposited under high vacuum at cryogenic temperatures is demonstrated in Fig. 3. In this case, in the interval between 14 K and 20 K the refractive index rises monotonously with deposition temperature going from $n = 1.280$ at $T = 14$ K to $n = 1.291$ at $T = 19$ K. In the vicinity of $T = 20$ K the refractive index undergoes an abrupt increase jumping from 1.291 to 1.310. Further increase in deposition temperature results in recovery of the monotonous rise with n reaching the value of 1.342 at $T = 30$ K.

The quantum nature of CH_4 molecules, intramolecular spin-nuclear conversion processes in methane and peculiarities of the intermolecular interactions related to these
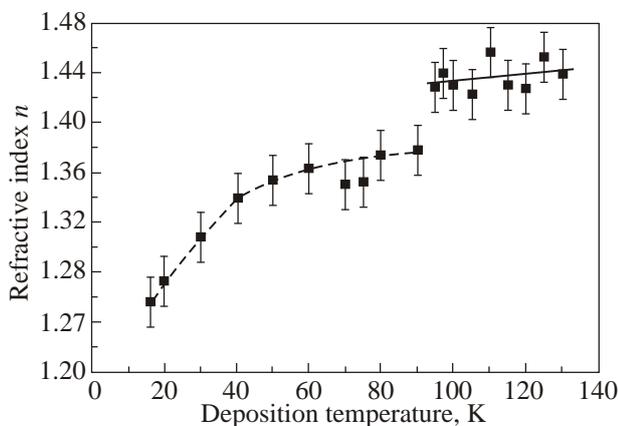

Fig. 1. Influence of deposition temperature on the refractive index of ethanol.
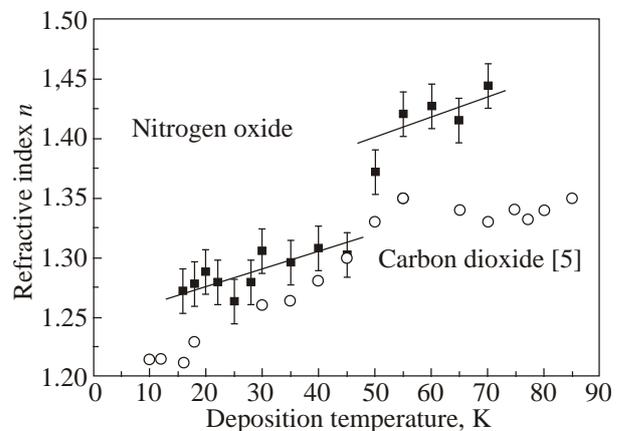

Fig. 2. Influence of deposition temperature on the refractive indices of nitrous oxide. For comparison, data for carbon dioxide are shown [5].
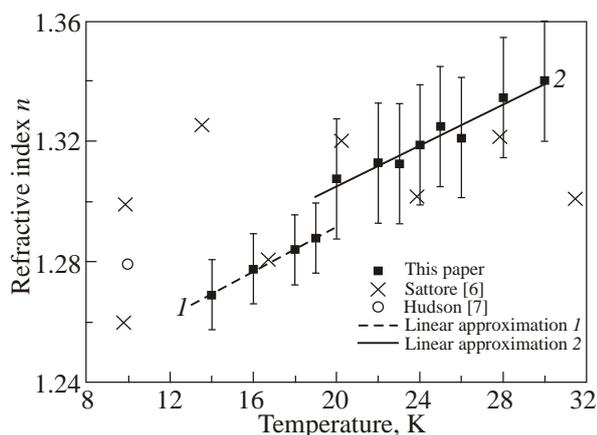
Fig. 3. Influence of deposition temperature on the refractive index of methane.

processes may act as some of the factors affecting the refractive index behavior at low temperatures [18–20]. For example, it is known that the solid methane undergoes transition from the orientationally disordered α-phase phase (at higher temperature) to the partially ordered β-phase phase (at lower temperature) at $T = 20.4$ K [21], which coincides with the temperature of the abrupt change in the refractive index observed in Fig. 3.

For comparison we include into Fig. 3 data points obtained dynamically using a two-beam laser interferometer and reported by other authors [6,7]. Our results are in satisfactory agreement with these data, particularly taking into account relatively high scattering in Ref. 6.

3. Conclusions

This study is dedicated to elucidation of the influence of deposition temperature on the refractive indices of cryovacuum deposited films of molecular materials existing in a variety of solid phases at low temperature. All materials under study: ethanol, methane and nitrous oxide, exhibit transitions resulting in changes in the number of molecular degrees of freedom. It must be noted that this study does not consider thermally stimulated transformations, but rather focuses on measurements at fixed deposition temperatures in the intervals of existence of stable and quasi-stable states of the studied films.

Based on the correlation between our data and the phase diagram of ethanol [13], the following characteristic temperature regions corresponding to its various states can be distinguished (Fig. 1):

Between 14 K and 65 K. This interval corresponds to amorphous solid ethanol (ASE). Rise in deposition temperature results in increasing of the refractive index, potentially due to reduction in sample porosity.

Between 65 K and 90 K. This interval corresponds to amorphous glassy state (GS) with the refractive index remaining constant. ASE and GS appear to represent to different phases which is confirmed by IR-spectrometric studies [9].

Between 90 K and 100 K. This interval corresponds to three different phases of ethanol obtained in various ways: 1) plastic crystal (PC) with cubic face-centered lattice having freely rotating ethanol molecules in lattice points (librations); 2) orientational glass (OG) obtained by rapid quenching of PC below $T = 97$ K, suggesting that this state cannot be realized in our experiments; this results in freezing out of the rotational subsystem and formation of an orientationally disordered cubic lattice; 3) super-cooled liquid (SCL) obtained by annealing of GS, suggesting that this state also cannot be realized in our experiments. Abrupt increase in the refractive index between 90 K and 100 K correlates with transition from ASE to PC with the freely moving rotational subsystem.

Between 100 K and 130 K. The refractive index shows weak temperature dependence. This range is associated with existence of the PC phase.

A similar jump-like dependence of the refractive index on deposition temperature is observed for nitrous oxide (Fig. 2). As we reported earlier [16,17] cryovacuum deposited films of nitrous oxide undergo a structural transition at temperatures below 40–45 K interpreted as amorphization of the samples. Thus, upon annealing to 37–42 K partially or fully amorphous films deposited at cryogenic temperatures become unstable and transform into the *Pa*3 structure. The interval between 14 K and 40 K corresponds to a cubic phase of nitrous oxide with an orientationally disordered rotational subsystem. Gradual rise in the refractive index in this interval is most likely related to an increase in porosity of the samples.

Transition from the amorphous state of nitrous oxide to the *Pa*3 structure occurs in the range of 40–50 K which is accompanied by an abrupt increase in the refractive index from $n = 1.310$ at $T = 40$ K to $n = 1.405$ at $T = 50$ K. Above 50 K the refractive index exhibits a gradual rise with deposition temperature reaching $n = 1.425$ at $T = 70$ K. In the vicinity of 70 K significant scattering of data points is observed which is explained by the proximity of the deposition pressure to the equilibrium vapor pressure at this temperature, which in turn makes it challenging to maintain given thin film deposition conditions.

The observed dependence of the refractive index of methane on deposition temperature (Fig. 3) correlates with the α–β-transition at $T = 20.4$ K reported elsewhere [18–20]. As such, a distinct gap in the n–T data is observed in the vicinity of the phase transition temperature. It may therefore be speculated that the data points lying in the range of 16–19 K relate to the partially ordered β-phase of methane, whereas the temperature interval 20.4–30 K corresponds to the α-state with freely rotating methane molecules located in the crystal lattice sites. In this case, one can argue that the α–β-transition resulting in orientational ordering of as many as three quarters of molecules [19,20] in the system is also reflected in a substantial and abrupt change in the refractive index of methane.

Results presented herein are in good agreement with the above studies and may find use in further astrophysical research

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