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On the existence of an intermediate liquid state of water and ethanol in the phase transition gas-solid

Abstract. Investigated thermally stimulated trans formations in thin films cry vacuum condensates water and ethanol. The values of the glass transition temperature, equal to water Tg=137±2 K and ethanol Tg=97±2K. Cryomatrix isolation method shows that the cry condensation process in both water and ethanol in a nitrogen cryomatrix formed nanoscale objects of different composition. Based on a comparison with the quantum-chemical calculations of other authors suggest that nano-objects are clusters of water and ethanol in the form officers, trimers, pen tamers, hexamers, and polymers.

Based on the data obtained by isolation cry matrix is assumed that the cryocondensation process in pure ethanol and water components in an intermediate step in the adsorption layer is the formation of clusters having a short-range order, similar to the liquid state of water or ethanol. This explains the fact that the values of glass transition temperature Tg of water and ethanol cry condensates coincide with the corresponding values for the samples obtained by other authors directly from the liquid phase by the method of ultrafast cooling.

Key words: cryomatrix polyaggregates, hydrogen bond, polymorphic, cryocondensates.

Introduction

The solid phase of water, perhaps more than any other solid, has a variety of structural modifications of the solid phase-polymorphic forms. This structural diversity of the solid phase of water is largely due to the emergence of a specific interaction between its molecules in the condensed state. Today we know13 [1] (some14 [2]) ice crystal modifications. All they occupy certain areas of the phase diagram. Change in the symmetry of the ice structure occur during phase transitions, which are accompanied by changes in the angular and linear dimensions of the lattice, and sometimes changing the coordination number.

One of the stable states of the ice is hexagonal ice, or ice I. It can be in a metastable crystalline (cubic) state and in the amorphous state. Figure 1 shows the phase states of the ice I and the transitions between them. The figure shows the following notation: ASW-A morph Solid Water - amorphous solid water; HGW - Hyper quenched Glass Water – tempered over the glassy water; LDA- Low Density A morph-low density amorphous; HAD- High Density A morph – amorphous high density.

Amorphous states are similar to liquid lack long-range order of symmetry, while differing from them by the presence of a partial structural order. They are meta stable with respect to the crystalline phases, provided that their temperature is low enough that it can not be implemented molecular rearrangement. Amorphous materials formed in various ways, may respectively have different properties, in contrast to the liquid whose properties are strictly determined result of establishing a dynamic equilibrium between all possible configurations of the molecules.

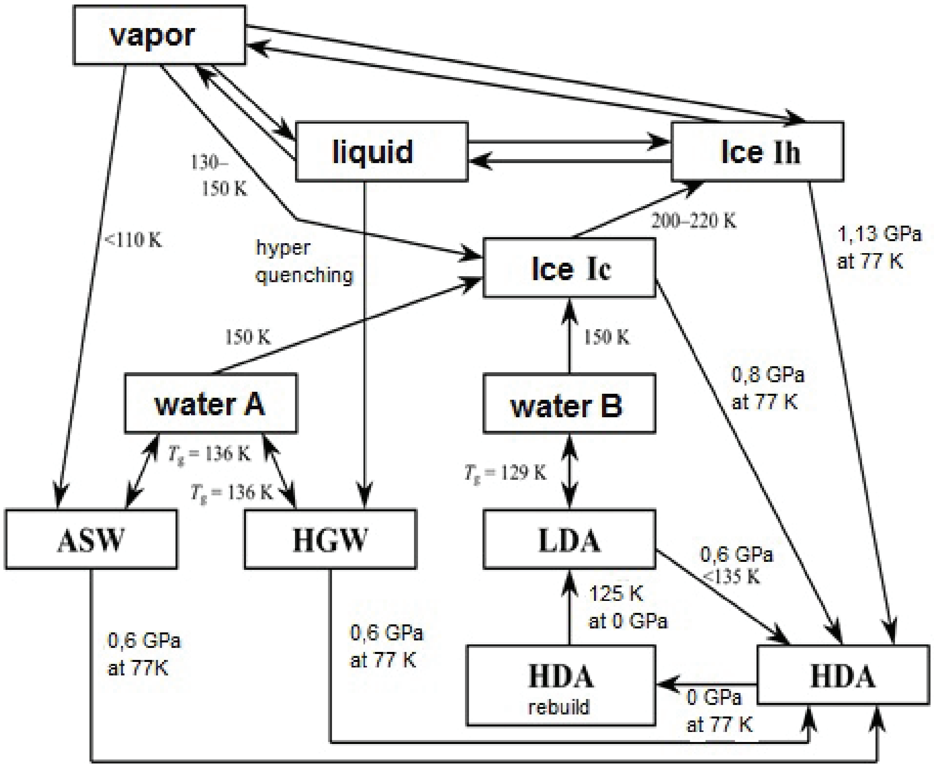

Figure 1 – Diagram of education and transitions of crystalline and non-crystalline forms of ice I.

Solid ethanol also has unique properties, showing a narrow temperature range, amorphous, crystalline and liquid properties. At temperatures below its melting point (Tm = 159 K) ethanol exists in different states: the vitreous state (structural glass SG), are formed during rapid cooling of the liquid phase to a temperature below the glass transition temperature Tg = 97 K; plastic crystal PC (bcc), which is formed through an intermediate liquid phase Super cooling (SCL) by heating above the T g SG; orientation-disordered crystal (ODC), which is formed during the cooling of the plastic crystal PC to a temperature below T = 97 K; monoclinic crystal MS, which is the main steady state solid ethanol.

The current state of research and polyamorphous polymorphic states of ice water and ethanol is a huge array of experimental and computational and theoretical data, often in a specific conflict with each other. Common is clear recognition of the fact that the properties of the resulting ice is rigidly dependent on the conditions of their formation and existence, such as substrate temperature and morphology, rate of condensation and heating the samples, the condition of gas phase - directional growth or condensation of a spatially homogeneous gas phase film thickness [3, 4].

However, much less attention is given to the study of the formation and properties of the crystalline and amorphous states of water and ethanol produced from the gas phase. It is known that the condensation at low temperatures leads to the formation of amorphous solid water and ethanol amorphous with a very large surface area, which play a crucial role in the processes of mass transfer in the universe. Furthermore, studies [5, 6] found an interesting fact of coincidence behavior over a super cooled liquid water and ethanol with the properties cry vacuum condensates thereof. In particular, almost completely coincide Tg of ethanol and water obtained in different ways - from the liquid phase of the gas and by cryo condensation. We assume that in the process gas from the cryo condensation on a substrate to form an intermediate layer adsorbed to the extent that the water and ethanol molecules form clusters polyaggregates and short-range order corresponding to a quasi-liquid state. Thus, the phase transition gas-solid transition is transformed into a gas-liquid-solid.

Results and Discussion

For experimental evidence assumption above, we used the method cry matrix isolation. The basis of this technique is the process of co-condensation of the gaseous phase of the mixture of the matrix gas (nitrogen) and the test substance (water or ethanol). As experimental setup and technique of these studies have been previously described in detail [7]. We believed that if the process of condensation of water or ethanol clusters emerge, they may be immobilized in cryomatrix nitrogen. Figure2 shows the results of such an experiment for the water-nitrogen mixture. From the methodological point of view, we are important absorption bands corresponding to oscillations of quasi-molecules in the nitrogen matrix. The most typical in this respect are the following bands with the corresponding frequencies of maximum absorption.

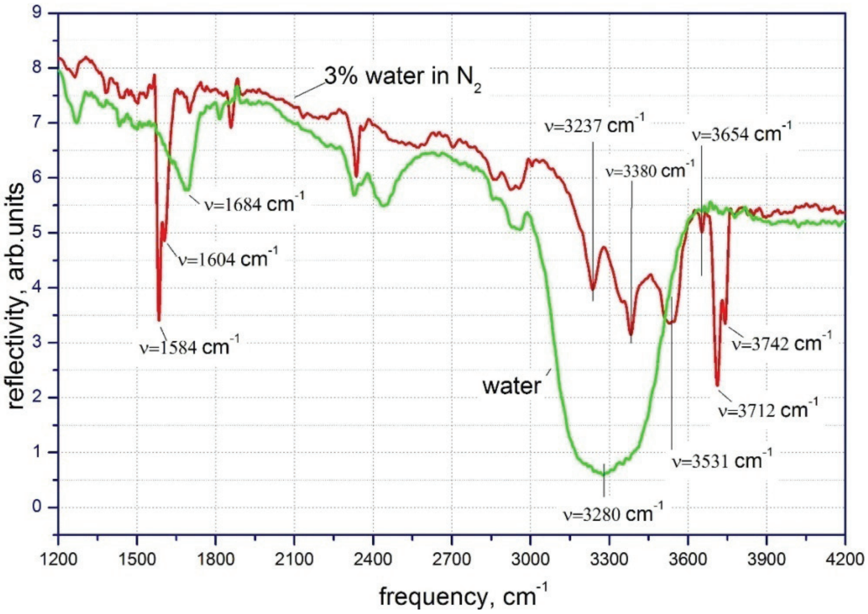

Figure 2 – The vibrational spectra of pure water film(bottom spectrum) and 3% solids solution in water of nitrogen cryomatrix (upper spectrum).

Band with a maximum at a frequency v = 1584 cm^{-1} in accordance with [8, 9], probably relates to quasi-free deformation vibrations of water molecules. Additional peak at the frequency v = 1604 cm-1 reflects, in our opinion, the deformation vibrations of the cluster, which brings together some of the water molecules. Peak at v = 1684 cm^{-1} belongs to the lower range of the bending vibration of water molecules in pure cryocondensate film in an amorphous state.

Band with a maximum at the frequency v = 3654 cm-1 may refer to quasi-free valence vibrations of linear dimers or monomers. Absorption at frequencies v = 3712 cm-1 and v = 3742 cm-1 are assigned to the symmetric and asymmetric stretching vibrations of monomers. Series minima most prominent at frequencies v = 3237 cm-1, v = 3380 cm-1 and v = 3531 cm-1 are a manifestation of the existence of clusters in the sample trimers and higher. Their transformation may be indicative of self-organization processes in the nitrogen matrix polyaggregates. All these bands are absent in the monolithic water condensate. Thus, fixing the condition of these peaks in the process of external influences on the sample can draw conclusions about the ongoing processes in the matrix. In particular, it can be concluded that in the condensation process to form clusters and polyaggregates cubic and hexagonal symmetry.

Similar measurements were carried out for a mixture of nitrogen and ethanol. These data are shown in Figure 3. The figure shows the comparison of the spectra of the two samples - absolute ethanol and the film sample consisting of 3% ethanol and 97% nitrogen. Selected ethanol concentration = 3% C contains all the characteristic features of the spectrum of ethanol in a nitrogen matrix as compared with an authentic sample. The film thickness of pure ethanol is 1 micron film thickness of ethanol and a mixture of nitrogen is 10 microns. Viewed frequency interval 4200-1200 cm-1 characteristic of the stretching vibrations of OH bonds in the free and the bound state, symmetric and asymmetric stretching vibrations of CH bond of methyl and methylene CH2 CH3 groups, and holds a frequency of deformation and wagging vibrations of CH3 and CH2 groups.

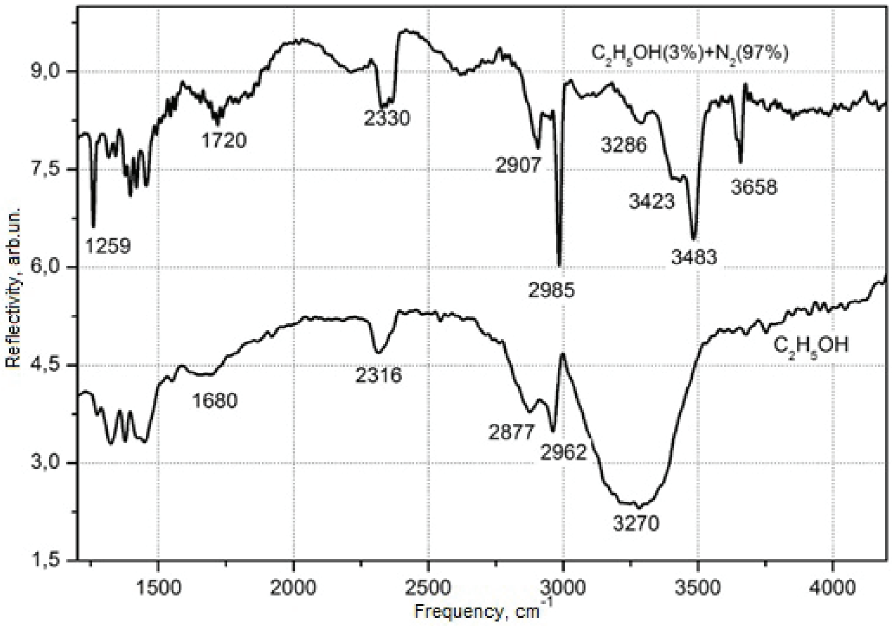

Figure 3 – Comparison of the vibrational spectra of thin Films cryo condensates pure ethanol and ethanol-nitrogen.

By comparing the data of the quantum-chemical analysis [10] it can be concluded that, as was the case with the water sample to nitrogen in the film in question also forms ethanol clusters polyaggregates cubic and hexagonal symmetry. In particular the absorption band with the frequency of 3658 cm-1 corresponds to the existence of dimers. Absorption frequencies at 3483 cm-1, 3423 cm-1 and 3286 cm-1 correspond to the existence of trimers and hexamers of ethanol respectively.

From of our research it can be concluded that in the cryoprecipitated water and ethanol in a mixture with nitrogen and polyaggregates form clusters of different sizes. Based on this, it can be assumed that during the cryo condensation pure components of water and ethanol on the substrate at low temperatures may be formed polyaggregates. It is these polyaggregates can play the role of nuclei of the solid phase. Ie we have reason to believe that the phase transition of gas - solid through the intermediate quasi-liquid phase. This may explain the overlap of glass transition temperatures for samples of water and ethanol produced by the method of ultrafast cooling liquid and low temperature gas-phase condensation.

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