

On thermal stability of cryovacuum deposited CH₄+H₂O films

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Whereas stable homogenous states of aqueous hydrocarbon solutions are typically observed at high temperatures and pressures far beyond the critical values corresponding to individual components, the stability of such system may be preserved upon transition into the region of metastable states at low temperatures and low pressures. This work is dedicated to the study of the thermal stability of a water–methane mixture formed by cryogenic vapor phase deposition. The obtained thin films were studied using vibrational spectroscopy in the temperature range of 16–180 K. During thermal annealing of the samples, characteristic vibrational C–H modes of methane were monitored alongside the chamber pressure to register both structural changes and desorption of the film material. The obtained results reveal that upon the co-deposition of methane and water, methane molecules appear both in non-bound and trapped states. The observed broadening of the characteristic C–H stretching mode at 3010 cm⁻¹ upon an increase in temperature of the sample from 16 to 90 K, followed by narrowing of the peak as the temperature is reduced back to 16 K, indicates localization of methane molecules within the water matrix at lower temperatures.

Keywords: molecular crystals, water-methane films, vibrational spectroscopy, low temperature, methane localization.

1. Introduction

The evolution of complex systems consisting of various chemical compounds co-existing under non-equilibrium conditions is an important topic in the condensed state research. Such systems can be readily obtained, for example, using vacuum deposition at cryogenic temperatures. Upon variation of intensive thermodynamic parameters (temperature, pressure) individual sub-systems of such complex dynamic systems may undergo chemical reactions and phase transitions. Of particular interest is the problem of describing complex systems whose components exhibit properties of polymorphism and conformational disorder. Among such systems, a combination of water and methane represents an interesting case both in terms of fundamental research and industrial application. The multitude of structural modifications of solid water makes it an excellent polymorphic model system to study the above-mentioned processes. In its turn, the single solid phase of methane

represents a combination of molecules with different spin states (A, T, and E with total nuclear spins of $I = 2, 1,$ and $0,$ respectively), whose equilibrium distribution depends on temperature [1, 2]. Transitions between these states in the solid phase take place via spin-nuclear conversions.

Under certain thermodynamic conditions, the interaction of water with methane results in formation of clathrate compounds of methane hydrates. These compounds may be classified as supramolecular formations, possessing unique structural, conformational, thermodynamic, and dynamic properties [3]. Clathrates of methane hydrates represent three-dimensional dodecahedral and tetra-decahedral water cages with one methane molecule located at the center of each cage. The thermodynamic stability of the methane molecule within the clathrate structure is determined by interaction of the “guest” molecule with the cage of the “host” molecules. In the natural environment, methane clathrates are expected to form and exist at high pressure and low-temperature conditions generally above 150 K,

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with very few studies conducted on the study of the stability of these systems at very low, cryogenic temperatures and low pressures [4–6]. At the same time, the earlier studies have indicated that a fraction of CH₄ retains in water ices at temperatures as high as 60 K in a distorted structure [6]. It has also been found that the sticking probability of methane is improved in porous amorphous solid water in comparison to other water structures, such as crystalline ice and non-porous amorphous solid water [7]. Previously, we performed infrared (IR) studies of the samples containing various amounts of methane in water (10, 25, and 50 %) deposited at 16 K and annealed up to complete sublimation [8]. The observation technique involved monitoring the IR signal at a fixed frequency corresponding to the maximum absorbance of the C–H bending vibrations as well as the pressure inside the chamber to notice any material sublimation. As a result, it was concluded that methane molecules remained in the sample up to 140 K. This paper follows up on the previous study focusing on measurements of molecular spectra in the whole IR range to investigate the evolution of characteristic absorption bands of the CH₄+H₂O mixture.

2. Experiment

The experimental setup represents a high-vacuum chamber equipped with a cryogenically cooled substrate and IR spectrometer, as described in detail elsewhere [8]. The experimental procedure of sample preparation was as follows. The gas-phase mixture of water and methane was prepared at room temperature immediately prior to injection into the chamber in order to prevent adsorption/condensation of water molecules on the internal walls of the gas mixture preparation antechamber. Between each use, the antechamber was evacuated and kept under vacuum in order to maintain the accuracy of setting the mixture composition. The amount and concentration of methane in water were calculated using the P – V – T data with a relative accuracy of 0.5 %. The samples were obtained by deposition from the gas phase at the pressure of $P = 1.0 \cdot 10^{-5}$ Torr onto a substrate held at 16 K. The thickness of the films was measured using a double-beam laser interferometer and varied between 1.0 and 1.5 μm [8]. The IR spectra of the samples were measured upon annealing and thermal cycling between 16 and 150 K.

3. Results

Our previous study of low-temperature CH₄+H₂O mixtures with various concentrations of methane in water (10, 25, and 50 %) suggested that the optimum concentration, corresponding to the highest absorption signal of the characteristic methane bending mode above the sublimation temperature of pure methane, lay in the range between 10 and 25 % [8]. Therefore, for the present study the concentration of 15 % of methane in water was selected. Based on the same methodology as in the previous study, IR absorption

spectra were measured for the samples of pure water and 15 % mixture of methane in water deposited at 16 K and further annealed until fully sublimed. During annealing, the IR signal intensity was monitored at the fixed wavenumber corresponding to the absorption band maximum of methane C–H bending vibrations (Fig. 1). Additionally, changes in the chamber pressure were monitored to account for sublimation of the film material. As seen in Fig. 1, annealing results in step-like reduction in the intensity of the methane peak. This correlates with rises in the pressure of the chamber upon annealing and is consistent with gradual desorption of the methane molecules, as in the range of chamber operating pressures water remains in the solid state up to the temperatures of 160–170 K. Overall, three desorption ranges of the film material are observed in the P – T diagram (Fig. 1): 1 — at around 40 K — corresponding to methane sublimation temperature at the working pressure, 2 — at around 140 K, and 3 — beyond 160 K — corresponding to complete sublimation of the sample, as expected for water.

Figure 2 compares the IR spectra of pure water and the 15 % methane solution in water recorded at 16, 60, 90, 130, and 150 K in the spectral range of 400–4200 cm^{-1} . The thickness of both samples was made to ensure that the amount of water in them remained equal. Well-known characteristic vibrations corresponding to water ices include librations observed in the figure in the range of 600–900 cm^{-1} , representing hindered rotations of the water molecules and corresponding to intramolecular proton transitions, H–O–H bending vibrations in the range of 1600–1750 cm^{-1} and stretching O–H vibrations in the range of 3000–3600 cm^{-1} [9–11]. The specific vibration modes of methane observed in the “methane+water” spectrum include H–C–H bending vibrations at around 1303 cm^{-1} and C–H stretching vibrations at 3014 cm^{-1} .

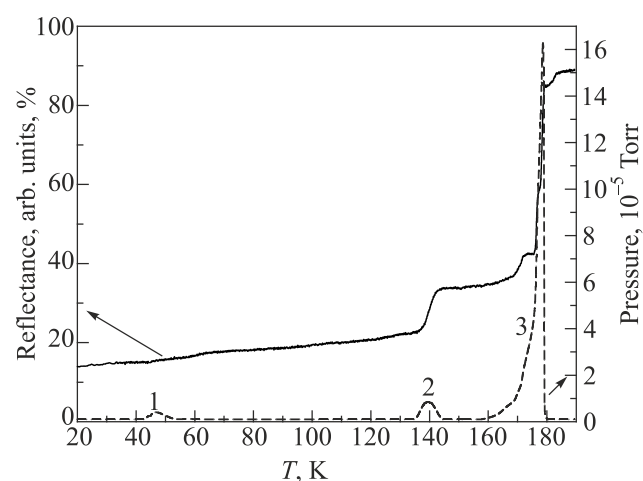


Fig. 1. Variation in reflectance at 1303 cm^{-1} (left scale, solid line) and chamber pressure (right scale, dashed line) depending on annealing temperature of the film obtained from the 15 % mixture of methane in water.

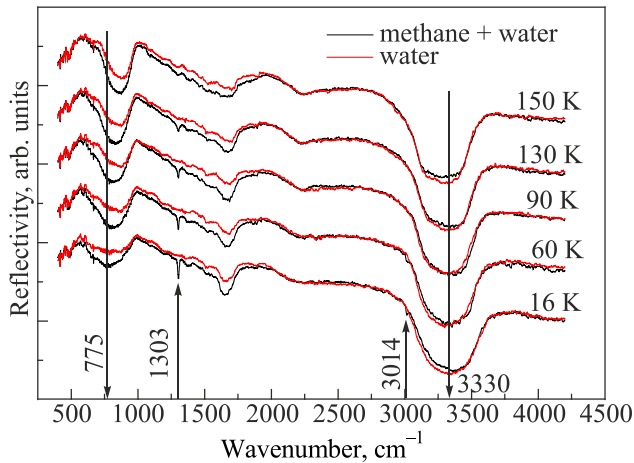


Fig. 2. (Color online) Evolution of IR absorption spectra of pure water (black lines) and the 15 % mixture of methane in water (red lines) at 16, 60, 90, 130, and 150 K.

Thermal annealing leads to gradual narrowing and shifting of the water libration band (centered at 775 cm^{-1}) towards higher wavenumber. This is observed both for water and water–methane samples with the latter showing significantly higher absorption intensity. At the same time, the shapes and intensities of the O–H stretching band (centered at 3330 cm^{-1}) remain relatively similar for both samples across the whole range of observation temperatures, with noticeable narrowing of the band upon annealing consistent with earlier observations of structural transformations in water ices [12].

Thermal cycling was employed to investigate the evolution of the characteristic methane absorption band corresponding to C–H stretching vibrations (Fig. 3). The methane-specific spectra were obtained by subtracting the baseline corresponding to the water O–H band in Fig. 2. Thermal cycling involved annealing of the “methane+water”

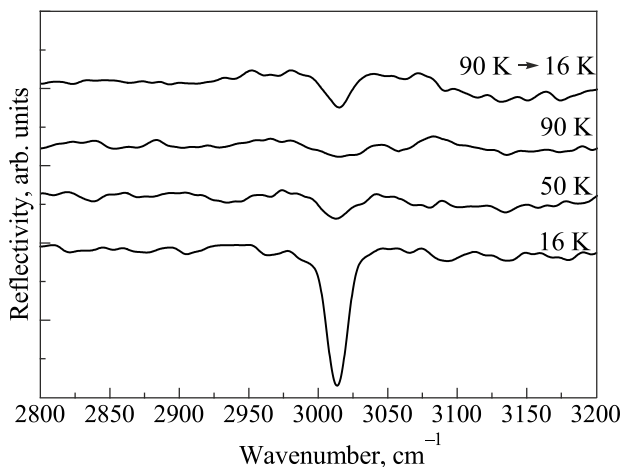


Fig. 3. Evolution of the IR absorption peak of C–H stretching vibrations upon thermal cycling of the film obtained from the 15 % mixture of methane with water.

sample from the deposition temperature of 16 to 90 K, followed by cooling back to 16 K.

4. Discussion

Our previous study of the methane–water cryogenic system both as a 20 % mixture of methane in water and bilayer samples, focusing on the analysis of the deformation band at 1300 cm^{-1} , associated a displacement in the absorption band minimum towards 1306 cm^{-1} with the processes of methane clathrate formation in the mixed sample [13]. It was also confirmed that binding between the water and methane molecules does not proceed in bilayer samples, irrespective of the order of the deposition of each layer. The measurements were performed in the temperature range from 16 to 32 K. Focusing mainly on binding between the water and methane molecules, this work extends the thermal annealing range to higher temperatures up to 200 K.

At the working pressure of 10^{-5} – 10^{-6} Torr, the equilibrium temperature of methane lies between 36 and 38 K. Therefore, annealing of the “methane+water” sample above these temperatures must result in complete sublimation of non-bound methane molecules. Indeed, as seen in Fig. 1, desorption of the film is observed around 40 K, accompanied by reduction in the intensity of the characteristic absorption peak of methane. Remarkably, according to Fig. 2, this desorption does not result in the complete disappearance of the characteristic methane features. The bending and stretching vibration peaks at around 1303 and 3014 cm^{-1} , respectively, can still be seen in the IR spectra of the sample at 60 K and even higher temperatures of 90 and 130 K. The absence of these peaks in the IR spectra of pure water confirms their correspondence to methane, whereas their observation at temperatures significantly higher than the equilibrium values, alongside the water absorption bands, suggests that these methane molecules are bound within the water matrix. The desorption peak 2 in Fig. 1 at around 135–140 K coincides with the glass transition temperature in pure water ($T_g = 136\text{ K}$) and is, therefore, likely to correspond to the release of residual methane captured within the solid water matrix as water molecules become more mobile [14].

The phenomenon of methane capturing within a network of water molecules is widely known in relation to clathrate hydrates, which are expected to occur under high pressure, resulting in formation of polyhedral water cages around individual methane molecules [15]. Under the employed experimental conditions, with pressures as low as 10^{-5} – 10^{-6} Torr and cryogenic temperatures, methane clathrate hydrate has not yet been widely reported.

In the earlier study by Dartois and Deboffe, a characteristic C–H stretching mode of methane clathrate hydrate at 3010 cm^{-1} was observed to reversibly broaden and reduce in intensity upon sample annealing from 7 to 80 K [16]. Figure 3 here demonstrates a similar behavior: temperature evolution of the peak at 3014 cm^{-1} from 16 to 90 K results

in its disappearance, whereas cooling of the sample back to 16 K recovers the absorption peak. Although it may be argued whether this observation is due to the formation of methane clathrate hydrate or, simply, capturing of methane inside water ice pores, without losing generality, one may conclude that the observed behavior is associated with broadening of the band corresponding to methane trapped in the water matrix [16, 17]. Irrespective of the specific type of coupling of methane within the water matrix, broadening of the characteristic C–H stretching mode at 3010 cm⁻¹ upon thermal annealing of the 15 % mixture sample suggests the presence of a landscape of localized sites for methane molecules which becomes accessible upon an increase in temperature from 16 to 90 K or a coupling between the vibrations of the localized methane molecules and the surrounding ice-like water lattice [18, 19]. In both of these cases, localization of the methane molecules within the water matrix plays a major part in elucidating the nature of the observations. The mechanism of capturing of methane molecules by the water matrix at low pressures and temperatures is the subject of further investigation, with potential models including interaction of methane with water molecules within the adsorption layer during film deposition or methane diffusion during structural transformations of ice [7].

The presence of methane in the water matrix appears to have an effect on characteristic water vibration modes as seen in Fig. 2. Specifically, the intensity of libration and bending bands is increased for the “water+methane” sample relative to the intensity of the stretching mode. This observation may be related to the increase in the coordination number of the water molecules due to interaction with the embedded molecules of methane. Our results in Fig. 2 also demonstrate that both of the samples obtained by cryodeposition from the gas phase exhibit an increase in the librational frequency with rising temperature. This is consistent with reduction in the moments of inertia of the water molecules and, hence, with the samples being more densely packed upon annealing [20]. As was shown in the past, at 16 K water is deposited in the amorphous glassy state with water molecules forming a continuous network of around four hydrogen bonds per each molecule [21]. Thus, whereas insertion of the methane molecule in the vicinity of the hydrogen bond network may change the coordination number of the water molecules, thermal annealing results in reduction in the average length of the hydrogen bond.

5. Conclusion

Our observations of low-temperature vacuum deposited films of water and the water–methane mixture show that annealing of the samples influences the positions, intensities and shapes of the absorption bands of characteristic vibrational modes, corresponding to both water and methane, indicating structural changes within the samples.

Release of the methane molecules from the water matrix takes place at various temperature ranges: near the equilibrium temperature for non-bound methane molecules, and near the glass transition temperature of pure water for the molecules trapped in pores and, possibly, clathrate structures. This is confirmed by observation of methane-specific vibrational modes at temperatures as high as 130 K, far beyond the methane equilibrium temperature, and also by the reversible disappearance and reappearance of the C–H stretching vibration band upon heating to 90 K and returning the system to 16 K. The presence of methane in the water matrix appears to influence its coordination number, as confirmed by the relative increase in the intensities of libration and bending bands in the “methane+water” sample.

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Термостабільність кріовакуумних конденсованих плівок $\text{CH}_4 + \text{H}_2\text{O}$

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У той час як стабільні гомогенні стани водних розчинів вуглеводнів зазвичай спостерігаються при високих температурах і тисках, що набагато перевищують критичні значення, які відповідають окремим компонентам, стабільність такої системи може зберігатися при переході в область метастабі-

льних станів при низьких температурах та низьких тисках. Вивчено термічну стійкість водно-метанової суміші, утвореної кріогенним осадженням з газової фази. Отримані тонкі плівки досліджено методом коливальної спектроскопії в інтервалі температур 16–180 К. В процесі термічного відігрівання зразків, поряд з тиском в камері, відстежувалися характерні коливальні С–Н моди метану для реєстрації як структурних змін, так і десорбції матеріалу плівки. Отримані результати показують, що при спільному осадженні метану й води молекули метану виявляються як в незв'язаному, так і в захопленому стані. Спостережуване розширення характерної моди коливання С–Н при 3010 cm^{-1} при підвищенні температури зразка від 16 до 90 К з подальшим звуженням піку при зниженні температури до 16 К вказує на локалізацію молекул метану всередині водної матриці при більш низьких температурах.

Ключові слова: молекулярні кристали, водно-метанові плівки, коливальна спектроскопія, низькі температури, локалізація метану.