

Facile Crystallization of Ice I_h via Formaldehyde Hydrate in Ultrahigh Vacuum under Cryogenic Conditions

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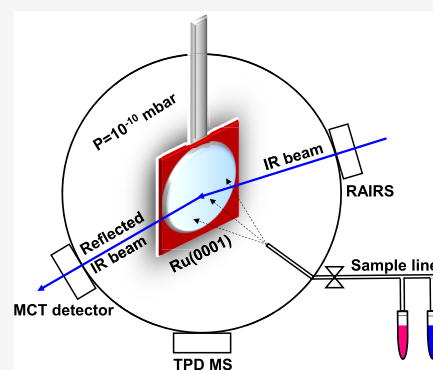


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ABSTRACT: Although hexagonal ice (ice I_h) is the most common and highly studied crystalline form of ice, its nucleation from clathrate hydrates is poorly understood. Here, we report the formation of ice I_h through the dissociation of formaldehyde hydrate, prepared under ultrahigh vacuum (UHV) in the temperature window of 130–135 K. This unique route for crystallization is highly facile, and it occurs below the usual crystallization temperature of ice I_h of 155 K in UHV; the associated activation energy is also lower. Time-dependent reflection absorption infrared spectroscopy was used to detect the formaldehyde hydrate and to determine the crystallization kinetics of ice I_h . The dissociation of formaldehyde hydrate is found to be a diffusion-controlled process, which reduces the activation barrier of crystallization. This study provides evidence that formaldehyde hydrate can exist in extremely low (P , T) conditions without forming the geminal diol or its polymer in the presence of water. This new and facile route of crystallization in the context of interstellar environments may have implications for cometary and prebiotic science.



INTRODUCTION

Ice is one of the most abundant solids found in comets,¹ interstellar medium (ISM),^{2,3} and the universe.⁴ The structure of ice is crucial to an understanding of its physical and chemical properties, which have significant importance in planetary science, astrochemistry, and physical chemistry. There are several amorphous and crystalline forms of ice at different conditions of pressure and temperature, leading to the rich polymorphism of water.^{5,6} Among these various forms, hexagonal ice (ice I_h) is the most abundant, and it occurs naturally on the surface of Earth. In the astrophysical or interstellar environment, in vacuum, ice is commonly found in an amorphous form as a result of the extremely low-temperature conditions present there.⁷ This amorphous ice, upon annealing, first crystallizes into metastable cubic ice (ice I_c) and further converts into more stable ice I_h at ~ 155 K.⁷

Several studies^{8–15} have been carried out to determine the kinetics and mechanisms associated with ice crystallization. In addition, the effect of guest molecules on ice crystallization has also been studied. Strong acids like HNO_3 ¹⁶ and HCl ¹⁷ are known to promote crystallization of amorphous solid water (ASW) to ice I_h . Here, excess protons (H^+) provided by the acids facilitated crystallization. However, NaCl ¹⁷ shows the opposite effect and hinders crystallization. In another study,¹⁸ the effect of methanol and butane on the crystallization of ASW was investigated. Methanol reduces the ASW crystallization temperature to 152 K by enhancing the crystallization, whereas butane¹⁸ and propane¹⁹ do not show such an effect.

The presence of guest molecules has various effects on ice, and the formation of clathrate hydrates (CHs) is one such

example.^{20–22} CHs are solid, crystalline host–guest complexes, where different gases (guests) are trapped inside the hydrate network made of water molecules (host).^{23,24} Previous reports^{25–28} suggest that CHs act as precursors for the formation of ice I_c . Neon hydrate is known to transform into a crystalline ice XVI when it is kept under a prolonged vacuum.⁶ Moreover, we have shown recently that ice I_c can be formed by the dissociation of acetone hydrate in ultrahigh vacuum (UHV) at 130–135 K.²⁹ In our previous study, the existence of CHs in the interstellar environment was also confirmed experimentally.²² Therefore, CHs can be an ideal precursor, which can transform into ice I_h under extremely low pressures and temperatures, conditions relevant to the interstellar medium (ISM).

Herein, we have formed formaldehyde hydrate, which acts as the precursor for ice I_h under UHV at 130–135 K. Formaldehyde is prone to undergo polymerization when it comes in contact with water, and this polymerization can be prevented only when it forms formaldehyde hydrate.³⁰ In addition, formaldehyde also likes to form geminal diol in the presence of water at ambient conditions.³⁰ Therefore, the normal terrestrial condition is not suitable for the formation of

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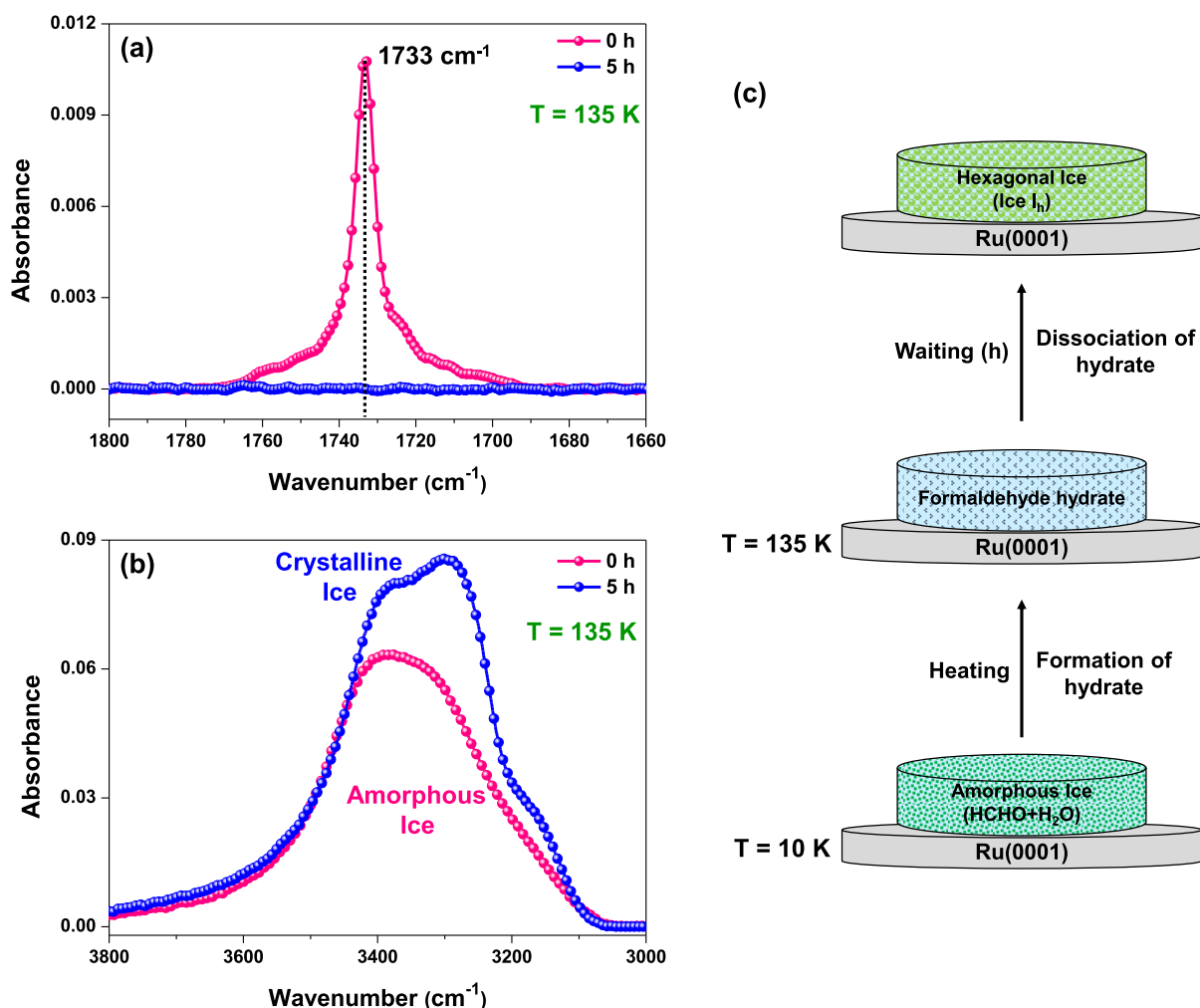


Figure 1. Time-dependent RAIR spectra of 300 MLs of formaldehyde:H₂O (1:1) at 135 K in the (a) C=O and (b) O–H stretching regions. The mixture was codeposited on Ru(0001) substrate at 10 K and annealed at a rate of 2 K·min⁻¹ to 135 K. The O–H band changed due to the dissociation of formaldehyde hydrate which resulted in ice crystallization. The schematic illustration in (c) shows the formation of formaldehyde hydrate and its dissociation, stepwise. Dissociation of formaldehyde hydrate leads to the formation of hexagonal ice (ice I_h).

formaldehyde hydrate. It was suggested that it could only be formed at low-temperature conditions present in space or ISM.³⁰ This study provides direct evidence of the earlier claim that it is indeed possible to create formaldehyde hydrate in astrophysical environments without undergoing polymerization or formation of geminal diol in the presence of water. Moreover, formaldehyde is known to exist in ISM,^{31–34} cometary ice,^{32,35,36} and extraterrestrial environment,³⁷ and its linear polymer was the first polymeric compound found in space.³⁸ The high abundance of formaldehyde and the inherent temperature of comets (120–140 K) suggest that the presented transformation route may occur in comets in regular intervals. Moreover, this unique process of ice crystallization is facile with respect to the conventional process as it occurs at a lower temperature. Here, the high mobility of water molecules during the dissociation of hydrate acts as the driving force. Hama et al.³⁹ have reported the formation of crystalline ice by subliming a water/neon matrix (1/1000 ratio) at 11–12 K under UHV, where matrix sublimation makes water molecules highly mobile.³⁹ It helps to overcome the kinetic barrier for rearrangement of the H-bonding network, which makes crystallization possible even at a lower temperature. In a nutshell, we have found a unique and facile mechanistic route

for ice crystallization, which links the existence of ice I_h and CH in comets. This study does give some directions to the ice composition and structure possible in many astrophysical bodies like comets, which may have further implications from the cometary and prebiotic science perspective.

EXPERIMENTAL METHODS

All the experiments were performed in a custom-built ultrahigh vacuum (UHV) instrument (base pressure of $\sim 5 \times 10^{-10}$ mbar). The instrument was discussed in detail elsewhere.⁴⁰ Briefly, it has three UHV chambers (namely ionization chamber, octupole chamber, and scattering chamber) made of stainless steel, equipped with reflection absorption infrared (RAIR) spectroscopy and temperature-programmed desorption (TPD) mass spectrometry. Each vacuum chamber was pumped by turbomolecular pumps (TMPs), which were backed by oil-free diaphragm pumps (Pfeiffer Vacuum). The pressure of the experimental chamber was measured by a Bayard–Alpert (B–A) gauge (Pfeiffer Vacuum) controlled by the “MaxiGauge” vacuum gauge controller (Pfeiffer, Model TPG 256 A).

Here, a ruthenium single crystal, Ru(0001), with 1.5 cm diameter and 1 mm thickness was used as the substrate. A thin

film of ice was grown layer by layer on this substrate at a low temperature (10 K). The substrate was mounted on a copper holder, which in turn was connected at the tip of a closed-cycle helium cryostat (Coldedge Technologies). The temperature of the substrate was monitored with the help of a K-type thermocouple sensor and a platinum sensor attached to the copper holder near the substrate. The substrate temperature could be varied in a wide temperature window of 8–1000 K. Before the sample deposition, the substrate was heated to 400 K multiple times to ensure surface cleanliness. Temperature ramping was controlled and monitored by a temperature controller (Lakeshore 336).

For the current study, formaldehyde vapor was obtained by thermolysis of solid paraformaldehyde (95% pure) purchased from Sigma-Aldrich. Here, paraformaldehyde was used as a precursor for the formation of formaldehyde vapor.⁴¹ The solid paraformaldehyde was taken in a vacuum-sealed test tube, and it was connected to the sample line of the instrument through a glass-to-metal seal. The test tube was heated at $\sim 120^\circ\text{C}$ in a silicone oil bath to generate the formaldehyde vapor upon thermolysis.⁴¹ The generated vapor of formaldehyde was then introduced into the UHV chamber through a high-precision all-metal leak valve. Millipore water (H_2O of $18.2\text{ M}\ \Omega$ resistivity) was taken in a separate test tube connected to the sample line through a glass-to-metal seal. The water was further purified through several freeze–pump–thaw cycles before introduction into the UHV chamber. Here, it must be noted that out of the two sample inlet lines, one was exclusively used for formaldehyde while the other line was used for water deposition. During the exposure of these samples to the substrate, mass spectra were recorded to check the purity as well as to measure the ratio of the mixtures with the help of a residual gas analyzer, attached near the sample inlet line. The substrate was kept at a perpendicular position near the sample inlet tubes for consistent growth of ice. The deposition of molecular solids was controlled through leak valves and represented in terms of monolayers (MLs), assuming that $1.33 \times 10^{-6}\text{ mbar}\cdot\text{s} = 1\text{ ML}$, which was estimated to contain $\sim 1.1 \times 10^{15}\text{ molecules}\cdot\text{cm}^{-2}$. The inlet pressures for sample deposition were decided based on the coverage required at the time of the experiment. Importantly, the substrate does not play any significant role during the experiment as these experiments were carried out under multilayer conditions.

Here, 300 MLs of formaldehyde: H_2O (1:1) were prepared by backfilling the UHV chamber at a total pressure of $\sim 5 \times 10^{-7}\text{ mbar}$ (where formaldehyde inlet pressure = $2.5 \times 10^{-7}\text{ mbar}$ and water inlet pressure = $2.5 \times 10^{-7}\text{ mbar}$), and the mixture was exposed to the surface for 10 min. After deposition, the mixed ice was heated at a rate of $2\text{ K}\cdot\text{min}^{-1}$ to the experimental temperatures. The ice sample was monitored by RAIR spectroscopy at different temperatures. The experimental conditions were kept the same such as the position of the substrate and external IR detector during the time-dependent study.

RAIR spectra were recorded using a Bruker FT-IR spectrometer, Vertex 70. The external IR beam was focused onto the substrate using gold-plated mirrors through ZnSe windows (transparent to the IR beam) attached to the vacuum chamber. The reflected IR beam from the substrate was refocused using another gold-plated mirror to a liquid N_2 cooled external IR detector (mercury cadmium telluride; MCT). The spectra were collected in the $4000\text{--}550\text{ cm}^{-1}$ range with a 2 cm^{-1} resolution. Each spectrum was an average

of 512 scans to get a better signal-to-noise ratio. The IR beam path outside the UHV chamber was purged with dry N_2 .

RESULTS AND DISCUSSION

Here, we report a unique and facile transformation route for the formation of hexagonal ice (ice I_h) via formaldehyde hydrate, relevant to astrophysical environments. The interstellar-like environment was mimicked in an UHV chamber, and more details of this chamber are discussed in the [Experimental Methods](#) section. Three hundred monolayers of formaldehyde: H_2O (1:1) were codeposited on Ru(0001) substrate at 10 K and heated at a rate of $2\text{ K}\cdot\text{min}^{-1}$ to 135 K. The mixture was kept at 135 K for 5 h under UHV. [Figure 1a](#) and [1b](#) show the RAIR spectra obtained immediately after the codeposited film was annealed at 135 K (0 h trace) and after 5 h (5 h trace) in the C=O and O–H stretching regions, respectively. In [Figure 1a](#), the C=O stretching peak at 1733 cm^{-1} is due to the formaldehyde hydrate, which was obtained by heating the formaldehyde: H_2O mixture. To understand the origin of this peak, which is assigned to formaldehyde hydrate, temperature-dependent RAIRS measurement of the formaldehyde: H_2O mixture was carried out separately, as shown in [Figure S1](#). The C=O stretching region in [Figure S1a](#) suggests that formaldehyde hydrate starts to form at 110 K during continuous heating. Here, the other features (1731 , 1722 , and 1716 cm^{-1}) come from the irregular crystallite formation of formaldehyde in the amorphous ice pores. These IR features of the formaldehyde crystallites are assigned based on the temperature-dependent RAIR study of pure formaldehyde, which undergoes crystallization at $\sim 90\text{ K}$ ([Figure S2](#)). It is clear that the IR feature of formaldehyde hydrate (1733 cm^{-1}) is entirely new as compared to the other features of formaldehyde. Moreover, previous reports^{20–22} suggest that the vibrational signature of the guest molecules trapped in hydrate cages usually falls in between their vapor (1746 cm^{-1})⁴¹ and condensed (1723 cm^{-1})⁴¹ phase frequencies. This clearly suggests that the 1733 cm^{-1} peak is due to hydrate since it also falls between the IR peak positions of vapor and condensed phases of formaldehyde. Moreover, a full-range IR spectrum of the formaldehyde:water mixture is shown in [Figure S3](#) along with the assignments.

On the other hand, the O–H stretching region in [Figure S1a](#) shows a profound change due to heating. At low temperature ($<90\text{ K}$), the O–H stretching band has three broad shoulders, positioned at 3510 , 3422 , and 3275 cm^{-1} . These features are due to the formation of H-bonding interaction between water and formaldehyde. These shoulders gradually disappeared as the ice mixture was heated beyond 90 K , eventually becoming a broad peak, which is the characteristic feature of ASW. Similar H-bonded features and their disappearance with heating were also observed with the acetonitrile and water mixture.⁴² Here, the breaking of H-bonds occurs due to heating, and they are completely broken at 90 K , the crystallization temperature of formaldehyde. At this point, most of the formaldehyde gets phase-separated and desorbed as the system is heated further. However, a small amount of formaldehyde, which was buried into the ASW pores, could not escape, leading to the formation of formaldehyde hydrate. It must be noted that although clathrate hydrates are crystalline in nature, the unit cells of hydrates are complex, and the water molecules reside in several inequivalent sites; therefore, the O–H stretching band of the host ice network is broadened.^{20,43,44} Moreover, we have confirmed the structure of the

resultant ice system left after the dissociation of formaldehyde hydrate. In this regard, we have compared the characteristic O–H stretching bands of pure crystalline ice I_h film and the resultant ice system left after the dissociation of formaldehyde hydrate at 135 K, as shown in Figure S4. Both of these experiments were carried out separately, and they produced similar O–H stretching bands, which again proved that the dissociation of formaldehyde produces nothing but ice I_h . Moreover, time-dependent studies of pure 150 MLs of H_2O were carried out at 120 and 130 K (Figure S5), and self-crystallization of ice was not observed. In addition, the time-dependent RAIR spectra of pure water at 135 K (Figure S6) clearly suggest that the crystallization is only due to the dissociation of formaldehyde hydrate at this condition. It is clear that the dissociation of formaldehyde hydrate alone produced ice I_h , even at a lower temperature.

To present more clear evidence for the 1733 cm^{-1} peak, being the characteristic feature of formaldehyde hydrate, we have done an isothermal time-dependent RAIR study of 150 MLs of pure formaldehyde at 95 K, as shown in Figure 2. This

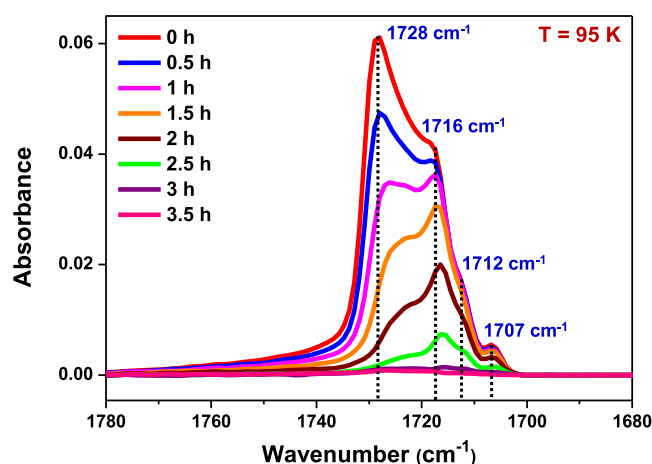


Figure 2. Isothermal time-dependent RAIR spectra of 150 MLs of pure formaldehyde film at 95 K in the C=O stretching region. Formaldehyde vapor was deposited on Ru(0001) substrate at 10 K, and then it was heated from 10 to 95 K at a rate of $2\text{ K}\cdot\text{min}^{-1}$.

particular temperature (95 K) is chosen as formaldehyde undergoes crystallization above this temperature. Figure 2 shows multiple C=O stretching features, which are attributed to the crystalline phase of formaldehyde. The intensity of these IR features gradually reduced with time, which accounts for the desorption of formaldehyde. Moreover, the temperature desorption-mass spectrum (TPD-MS) of pure formaldehyde also shows a desorption peak at $\sim 97\text{ K}$, as shown in Figure S7. It must be noted that these multiple features do not match with the 1733 cm^{-1} peak. It is entirely a new feature, which further supports our earlier claim that it arises only because of formaldehyde hydrate and not because of bulk formaldehyde or its aggregates. Moreover, it was observed that ice I_h crystallization via formaldehyde hydrate was associated with time-dependent kinetics. This was confirmed by conducting isothermal time-dependent RAIRS measurements at 130, 132, 135, and 137 K, where gradual changes of both C=O and O–H stretching bands are displayed (Figure S8–S11).

CRYSTALLIZATION KINETICS

The crystallization kinetics and associated thermodynamic properties of ice are of paramount importance not only in basic science but also in planetary science, astrochemistry, and physical chemistry. In this regard, RAIRS was found to be a useful tool to determine the crystallization kinetics of ice by monitoring the change in O–H stretching^{13,14,17} and decoupled O–D stretching bands^{15,45} of H_2O during crystallization. In this study, both these spectral bands were used to evaluate the kinetics of ice I_h crystallization.

Time-dependent RAIRS studies of formaldehyde:HDO (5% D_2O in H_2O) were conducted for the evaluation of the crystallization kinetics and its parameters (rate constants, Avrami exponent values) at 130, 132, 135, and 137 K (Figures S12–S15). In Figure S14a at 135 K, the 0 and 5 h spectra show pure ASW behavior and complete crystallization, respectively. The fraction crystallized with time t was calculated by subtracting the spectrum obtained at time zero from the spectrum at time t at a fixed wavenumber (3302 cm^{-1} in Figure S14b indicated by the vertical dashed line) for each temperature. Similarly, in Figure S14a, the crystallization fraction ($x(t)$) was calculated at a fixed wavenumber, 2427 cm^{-1} (indicated by the vertical dashed line), where a broad, amorphous spectrum ($t = 0$) changed into a relatively sharp crystalline spectrum ($t = 5\text{ h}$). Here, differences in the integrated peak area between the completely ASW and (partly) crystalline films at each time interval were considered. However, changes in the absorbance (ΔA) at a fixed wavenumber ($\sim 2427\text{ cm}^{-1}$ in Figure S14b, indicated by a vertical line) produced almost the same result for $x(t)$ as that obtained from the integrated peak area. A similar approach was adopted in several previous reports.^{13,14,17,29} The crystallization fraction, $x(t)$, was calculated by eq 1

$$x(t) = \frac{\Delta A(1)}{\Delta A(2)} \quad (1)$$

where $\Delta A(1)$ is the difference in the absorbance at a particular time t and that at time zero, and $\Delta A(2)$ is the difference in the absorbance of a completely crystallized film and that at time zero.

Figure 3a and 3b demonstrate the change in crystallization fraction at different temperatures with time as obtained from the O–H and decoupled O–D stretching bands at a fixed wavenumber. The change of the shape of the curve from sigmoidal to exponential with temperature shows that the rate of crystallization increases with increasing temperature. Now, the nucleation and growth mechanism of ASW crystallization was predicted by fitting the crystallization fraction $x(t)$ to the Avrami equation at different temperatures.

$$x(t) = 1 - \exp[-k(T) \cdot t]^n \quad (2)$$

Here $k(T)$ is the rate constant, t is time, and n is the Avrami exponent. For all temperatures, n held an integer value between 1 and 4, which reflected the nature of the transformation, whether it is diffusion or interface-controlled, and dictated the geometry of the growing particles.^{7,46} Thus, the Avrami exponent, n , can be used to predict the nature of the transformation process. After rearrangement and simplification, eq 2 becomes

$$\ln(-\ln[1 - x(t)]) = n \ln(t) + n \ln k(T) \quad (3)$$

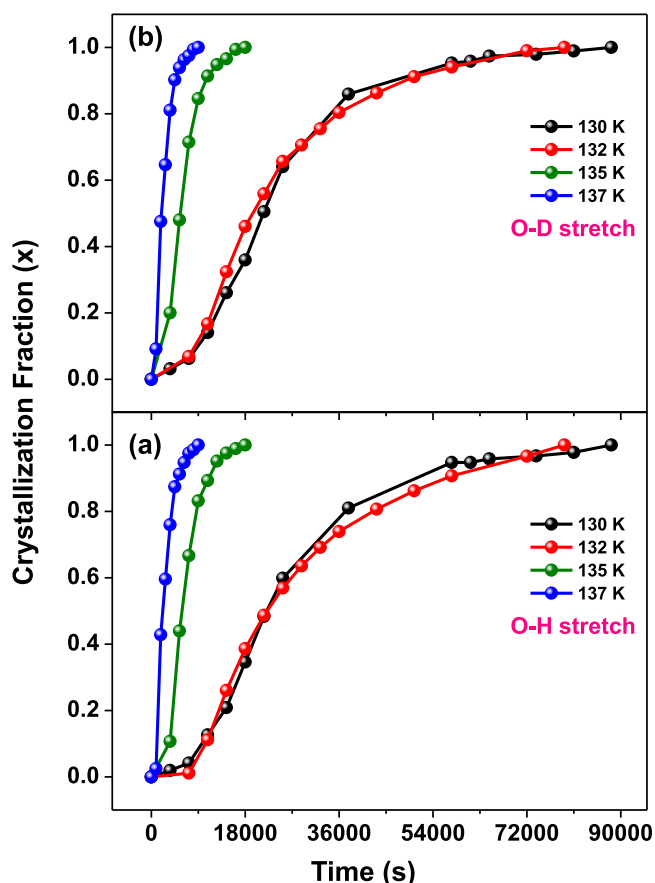


Figure 3. Crystallization fraction of 300 MLs of formaldehyde:HDO (5% D₂O in H₂O) obtained from isothermal RAIRS measurements at 130, 132, 135, and 137 K. The crystallization fraction was estimated from (a) the 3302 cm^{−1} peak in the O–H stretching region and (b) the 2427 cm^{−1} peak in the decoupled O–D stretching region.

Figure 4a and 4b demonstrate a plot between $\ln[-\ln(1-x(t))]$ vs $\ln(t)$ using eq 3. The slope and intercept of the linearly fitted lines were used to determine the values of n and $k(T)$ for different temperatures. Values of n and $k(T)$ obtained

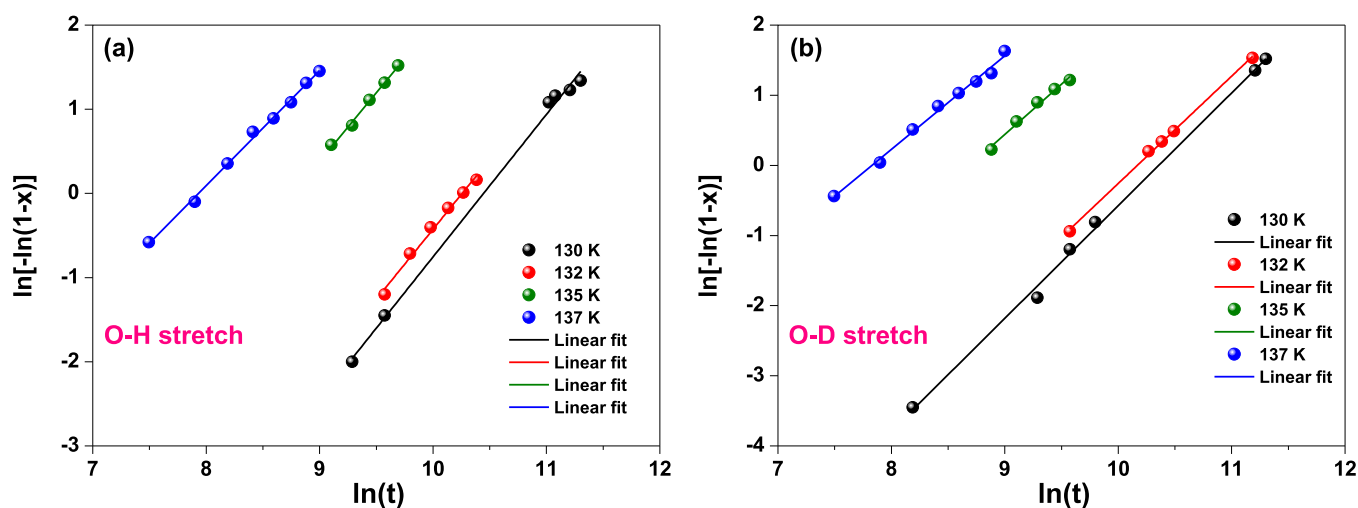


Figure 4. Plot of $\ln[-\ln(1-x(t))]$ vs $\ln(t)$ at different temperatures of 130, 132, 135, and 137 K. These data points are obtained from the analysis of (a) the O–H and (b) the O–D stretching regions and fitted using the Avrami equation.

from the analysis of O–H and decoupled O–D stretching bands for different temperatures are listed in Table S1.

The evaluated value of n (1.65–1.34, in Table S1) reflects that crystallization kinetics is diffusion-controlled with particles growing into a predominantly spherical geometry^{46–48} as the theory of phase transformation by nucleation and growth also suggests that the crystallization kinetics is diffusion-controlled with particles growing into a predominantly spherical geometry for n having fractional values.^{13,14,29} Here we propose that the dissociation of formaldehyde hydrate can enhance the diffusion or mobility of H₂O molecules which in turn prompt the crystallization of ice.²⁹ Moreover, for the ASW films thicker than 20 MLs, n is about 4, and the crystallization proceeds via homogeneous nucleation followed by three-dimensional growth as reported in previous studies.^{9,10,13} All these reports involve pure solid water film, and the only driving force for crystallization is annealing to higher temperatures. However, our study involves mixed film of formaldehyde and H₂O in a 1:1 ratio, where formaldehyde is desorbing from bulk as well as from the interface simultaneously. So, there is random generation of crystalline domains throughout the ice mixture which grow and soon reach the surface/interface of the films and would inhibit the three-dimensional growth, and therefore the decrease in the value of n is reasonable.^{49–52} Figure 5a and 5b demonstrate that all of the crystallization rates at different temperatures were fitted in an Arrhenius plot obtained from the O–H and decoupled O–D stretching regions, respectively. The activation energy (E_a) was evaluated from the slope of the linearly fitted lines. Activation energy obtained in this study was ~ 53.65 and ~ 56.70 kJ mol^{−1}, and it is comparable with the previously reported values for the crystallization of pure ASW evaluated by different experimental techniques.^{10,11,13,15,17} Here, crystallization occurred at a lower temperature than the usual crystallization temperature, which can be attributed to the high mobility of water molecules after hydrate dissociation.

CONCLUSIONS

In this study, we have observed experimentally the formation of hexagonal ice (ice I_h) at 130–135 K, which is lower than its usual crystallization temperature in UHV. This facile

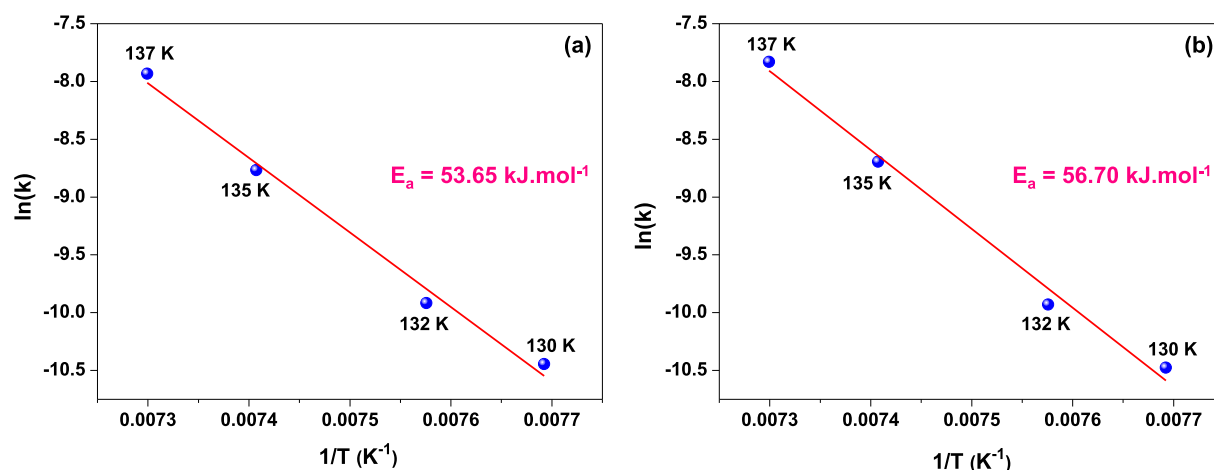


Figure 5. Plot of $\ln k(T)$ vs inverse temperature ($1/T$), obtained from the analysis of (a) the O–H and (b) the O–D stretching regions, respectively. The data points were fitted to obtain a straight line. Activation energy (E_a) can be calculated from the slope of the straight line.

crystallization happens due to the dissociation of formaldehyde hydrate, which acts as a precursor. The experiments were carried out in UHV and cryogenic temperatures and have direct relevance to the astrophysical environments or ISM. Formaldehyde is known to form geminal diol or undergo polymerization by reacting with water under ambient conditions. However, formaldehyde in its clathrate hydrate form does not show such an effect. This study shows that formaldehyde hydrate can exist in the extremely low-pressure conditions present in astrophysical environments or ISM without undergoing polymerization or reaction leading to geminal diol. Moreover, formaldehyde hydrate dissociated to form ice I_h after keeping for extended periods under UHV. Since formaldehyde and water are present in space, it is likely that a hydrate of it is formed. We believe that we have found a mechanistic route for the formation of ice I_h , which links the existence of ice I_h and formaldehyde hydrate in astrophysical environments/ISM.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c10367>.

Isothermal time-dependent RAIR spectra of pure formaldehyde, formaldehyde:H₂O, and formaldehyde:HDO at different temperatures, crystallization fractions, and different crystallization parameters of formaldehyde:HDO at different temperatures (PDF)

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Author Contributions

J.G., G.V., and S.D. designed and performed the experiments. J.G. and G.V. analyzed the results. T.P. proposed the project and supervised the progress. The manuscript was written through contributions of all authors.

Author Contributions

†J.G. and G.V. contributed equally.

Notes

The authors declare no competing financial interest.

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