Formation of Cubic Ice via Clathrate Hydrate, Prepared in Ultrahigh Vacuum under Cryogenic Conditions

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Supporting Information

ABSTRACT: Cubic ice (ice Ic) is a crystalline phase of solid water, which exists in the earth’s atmosphere and extraterrestrial environments. We provide experimental evidence that dissociation of acetone clathrate hydrate (CH) makes ice Ic in ultrahigh vacuum (UHV) at 130–135 K. In this process, we find that crystallization of ice Ic occurs below its normal crystallization temperature. Time-dependent reflection absorption infrared spectroscopy (RAIRS) and reflection high-energy electron diffraction (RHEED) were utilized to confirm the formation of ice Ic. Associated crystallization kinetics and activation energy (Ea) for the process were evaluated. We suggest that enhanced mobility or diffusion of water molecules during acetone hydrate dissociation enabled crystallization. Moreover, this finding implied that CHs might exist in extreme low-pressure environments present in comets. These hydrates, subjected to prolonged thermal annealing, transform into ice Ic. This unique process of crystallization hints at a possible mechanistic route for the formation of ice Ic in comets.

Ices are ubiquitous in the universe, planets, and interstellar medium (ISM) and can exist in different amorphous and crystalline forms. At ambient conditions, only hexagonal ice (ice Ih) can be obtained,除外 of more than 17 known crystalline ice polymorphs. Recently, in 2019, a new crystalline superionic ice phase was discovered, termed ice XVIII, which indicates the diverse and exciting nature of this field. Cubic ice (ice Ic), a metastable ice phase, was discovered by König in electron diffraction experiments. Subsequently, many experiments were performed to produce ice Ic. Such studies include vapor deposition on cooled substrates, freezing of water in confined geometries, supercooling of water droplets, freezing of high-pressure ice phases (phase II to IX) followed by annealing to 120–170 K, annealing of amorphous ices, dissociation of clathrate hydrates (CHs), etc.

Formation of ice Ic by dissociation of CHs is intriguing among the several methods mentioned above. It was shown that dissociation of CO2 hydrates can lead to ice Ic. The dissociation experiments were carried out at 6 mbar and 170–190 K, simulating the Martian surface and subsurface conditions. However, the applicability of this unique transformation route in more exotic environments (comets and ISM), where the pressure is extremely low (<10−10 mbar), is still an open question. Note that ice Ic is predicted to exist in comets. This is possible as CH, the precursor of ice Ic, in the transformation, can exist in cometary conditions. Moreover, ice Ic is also known to form in the earth’s atmosphere. Calculation of dissociation pressures of different hydrates suggests their stability at low pressures and low temperatures. We have shown recently that methane and CO2 can form CHs at ∼10−10 mbar and ∼10 K, conditions relevant to ISM. However, there has been no experimental evidence to our knowledge for the formation of ice Ic upon dissociation of CHs in ultrahigh vacuum (UHV) conditions.

Comets are assumed to be the most primitive bodies of the solar system and impart essential information on its formation. The nuclei of comets are mostly composed of rock, dust, and water-ice along with other volatile substances. The structures and phases of ice in comets play crucial roles in the entrapment of volatile gases, as well as in different cometary activities such as cometary outbursts, heat balance of the cometary nuclei, etc. Patashnick et al. proposed that the heat evolved during crystallization (amorphous to ice Ic) may be the driving force for these outbursts. Again, it was speculated that the change of thermal conductivity during this crystallization may alter the heat balance of the cometary nucleus. Amorphous ice is a poor heat conductor in comparison to ice Ic, and thermal conductivity rises by a factor of 10 upon phase transition. The comets composed of ice Ic show low volatile outburst activity in comparison to comets with amorphous ice. Enhanced thermal conductivity of ice Ic increases the overall temperature of the cometary nucleus, resulting in the escape of volatile species at one time. In contrast, the comets with amorphous ice continuously show outburst activity every time the surface is sufficiently heated by solar radiation. This phenomenon may occur in an erratic manner until all the ice is transformed into the cubic state.

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Letter
Acetone, a precursor of prebiotic species, was found on comet 67P/Churyumov-Gerasimenko, for the first time, in 2015. Recent measurements by the ROSINA (Rosetta Orbiter Spectrometer for Ion and Neutral Analysis) instrument onboard Rosetta suggested the possible existence of CHs in this comet. Here, we have shown that acetone could form CH because of its interaction with amorphous solid water (ASW) in conditions analogous to those of the comets. Extensive studies on the interactions of acetone with ASW or crystalline ice film exist in the literature. At higher temperatures, acetone can escape the hydrate cage to form empty hydrate. The empty hydrate is usually regarded as unstable because the guest species stabilize the host framework. Falenty et al. reported the formation of an "empty" hydrate after 5 days of continuous vacuum pumping of neon hydrate at 110–145 K, which they attributed to ice XVI. Here, we demonstrate that acetone hydrate formed in UHV can transform into ice Ic upon in situ dissociation of the former at 130–135 K.

Ice Ic via acetone hydrate was prepared by annealing a codeposited ∼300 MLs acetone:H₂O (1:1) film to 135 K and maintaining it there in UHV for 3 h (additional experimental details are given in the Supporting Information). Figure 1 shows the RAIR spectra obtained immediately after annealing the codeposited film at 135 K (blue trace; 0 h) and after 3 h (orange trace; 3 h). The inset of Figure 1 shows the time-dependent RAIR spectra of the same system in the C=O stretching region. In Figure 1, only the O–H (2800–4000 cm⁻¹) and C=O (1650–1770 cm⁻¹) stretching regions are displayed as these two regions are important for the acetone:H₂O system where major changes were observed. At 135 K, the O–H bending band became featureless, and therefore, it was neglected in the spectra. The C=O stretching band at 0 h shows two features at ∼1721 and ∼1709 cm⁻¹, which are attributed to acetone hydrate and ASW-trapped acetone, respectively, based on previous IR studies. These two features were deconvoluted to predict the actual amount of acetone in the hydrate form with respect to the total acetone present. Taking the area under the 1721 cm⁻¹ peak, the amount of acetone in the hydrate form was estimated to be 32.59% of the total acetone. Isothermal time-dependent RAIR spectra of 150 MLs of pure acetone (Figure S1), measured at different temperatures (115, 120, and 125 K), showed a major feature at ∼1718 cm⁻¹ due to bulk acetone. This confirmed that the 1721 cm⁻¹ peak is entirely a new feature and arises only because of acetone hydrate and not because of bulk acetone or its aggregates. Temperature-dependent RAIR spectra of 150 MLs of pure acetone (Figure S1), measured at different temperatures (115, 120, and 125 K), showed a major feature at ∼1718 cm⁻¹ due to bulk acetone. This confirmed that the 1721 cm⁻¹ peak is entirely a new feature and arises only because of acetone hydrate and not because of bulk acetone or its aggregates. Temperature-dependent RAIR...
solutions shown in Figure S2 suggest that acetone hydrate starts to form at 130 K.

However, it is not stable in this condition and dissociated within 3 h. The inset of Figure 1 shows the reduction of C=O stretching band with time and resulted in a weak feature at ∼1702 cm⁻¹. This feature is assigned to a dilute mixture of acetone and water (1:20), which was separately examined (Figure S3).

Acetone is a relatively less abundant molecule in the cometary environment. We have performed time-dependent RAIR spectra for dilute mixtures (1:10 and 1:20) of acetone:H₂O at 135 K (Figure S4). They also resulted in ice Ic in processes as described. Therefore, it is confirmed that acetone hydrate could be formed even with a very dilute mixture of acetone:H₂O, which may have direct relevance from the cometary science perspective. However, to present the results in a clear and consistent way, a 1:1 mixture was used, which allowed us to obtain better quality spectra and monitor the changes distinctly in the spectra.

The O–H stretching band also underwent a profound change with time. The featureless broad O–H stretching band at 0 h is a characteristic feature of ASW (blue trace in Figure 1). However, this particular band is red-shifted with respect to the O–H stretching band of an ASW film, reflecting the increase in the order and number of H-bonded water molecules with time. The unit cells of hydrates are complex, and the water molecules reside in several inequivalent sites, which results in the broadening of the O–H stretching band of the host ice network. This band became sharp and split partially after 3 h (orange trace in Figure 1). Splitting and sharpening of O–H stretching of the IR spectrum are associated with the crystallization of the ice film. This O–H band was deconvoluted to three distinct features as shown in Figure 1. The features at 3164, 3284, and 3395 cm⁻¹ correspond to ν₁ in-phase band, ν₃ TO band, and the overlapped ν₄, LO and ν₁ out-of-phase bands of ice Ic. These assignments were made based on the previous IR studies of ice Ic. It is evident that acetone hydrate in UHV slowly (within 3 h) dissociates at 135 K, leading to ice Ic. We carried out a similar time-dependent RAIR study of the same system at 130 and 120 K. These results are shown in Figures S5 and S6, respectively. We see that acetone hydrate formed at 130 K (Figure S5) got converted to ice Ic after 9 h. However, the formation of acetone hydrate and subsequent crystallization to ice Ic were not observed at 120 K, even after 48 h (Figure S6). This observation indicates that the thermal motion of acetone molecules is responsible for the formation of acetone CH. At low temperature (≤120 K), these motions are restricted; however, they became significant near the acetone desorption temperature (~130 K) in UHV. Earlier studies also suggest that molecular mobility plays a vital role in the entrapment of guest molecules into the hydrate cages; therefore, the temperature near the desorption of guest species used here is crucial for the observed phenomenon.

A similar time-dependent study was carried out with 300 MLs of acetone:D₂O (1:1) at 140 K, and cubic D₂O ice was formed upon dissociation of acetone hydrate (Figure S7). The requirement of a slightly higher temperature of 140 K is understandable because D₂O is a heavier molecule than H₂O, whose rearrangement required a higher temperature.

Thin films of ASW (<30 MLs) grown by vapor deposition below 110 K are known to have intrinsic ferroelectricity and negative surface potential. However, in our study, the contribution of these effects of ice may be disregarded, because all the experiments were performed with higher coverage of ice (300 MLs) and above 120 K when such properties disappear. Time-dependent studies of pure 150 MLs of H₂O were carried out at 120 and 130 K (Figure S8), and self-crystallization of ice was not observed. It proved that dissociation of acetone hydrate alone produced the ice Ic, even at a lower temperature.

The structure of the ice formed is crucial to be investigated by more direct measurements. Figure 2 shows the time-dependent reflection high-energy electron diffraction (RHEED) images of 300 MLs of acetone:H₂O (1:1) at different temperatures as indicated. These experiments were conducted in a separate chamber by depositing 300 MLs of mixed ice on a Ni(111) substrate at 20 K by following a method similar to that in a RAIRS study. After deposition, the mixtures were annealed at 2 K·min⁻¹ to reach the required temperatures. RHEED images were collected at 135 K for (a) 0 h and (b) 5 h, 130 K for (c) 0 h and (d) 12 h, or 120 K for (e) 0 h and (f) 24 h.
IR measurement. The RHEED pattern indicates that the water film is ordered; that is, this is a crystalline ice film which is cubic, as the observed diffraction patterns match with the earlier diffraction studies of ice Ic. Time-dependent RHEED experiments were carried out at 130 and 120 K as well. We observed in Figure 2d that after 12 h at 130 K, the ice became cubic. However, at 120 K, the ice Ic diffraction patterns were not observed, even after conducting the study for 24 h (Figure 2e,f). These observations are in accordance with the RAIR spectra presented in Figure 1. From an analysis of the diffraction patterns in Figure 2, it is evident that ice Ic was formed only through the dissociation of acetone hydrate.

Figure 3 shows the TPD-MS spectra of 300 MLs of acetone:H2O (1:1). Here, the ice film was heated at 30 K/min to obtain the TPD spectra. In Figure 3a, for the desorption trace of acetone, the intensity of CH3CO+ (m/z = 43) and H2O+ (m/z = 18) are plotted. (a) Desorption trace of acetone (m/z = 43) shows a sharp peak at 134 K, which is attributed to the untrapped acetone desorption. The shoulder labeled S is due to acetone hydrate desorption. The peak labeled # is attributed to acetone desorption due to premelting of ice upon annealing, and that labeled $ is due to desorption of acetone along with the processes in ice. (b) The desorption trace of water (m/z = 18) shows a sideband, which is due to the amorphous-to-crystalline ice transition. It coincides with the shoulder labeled S. The peak at 155 K is due to the complete desorption of ice.

min⁻¹ to obtain the TPD spectra. In Figure 3a, the desorption trace of acetone, the intensity of CH3CO+ (m/z = 43) is shown as a function of temperature. It shows a sharp desorption feature at 134 K due to the dissociation of untrapped acetone which exists outside the hydrate cage. It was further confirmed by the TPD of pure acetone, which shows a desorption peak at 132 K (Figure S9). It is to be noted that acetone starts to form a hydrate just by annealing to 130 K, as shown in Figure S2. In TPD, the shoulder marked with $ is due to acetone hydrate dissociation. This feature of acetone (Figure 3a) may have a contribution from the molecular volcano (MV) of acetone as it coincides with the transition of ASW to crystalline ice (Figure 3b). Upon deconvoluting the desorption trace of acetone (Figure S10), the amount of desorption due to acetone hydrate is estimated to be 24.26% of the total acetone at this condition, and it is correlated to the amount of acetone in hydrate form calculated from the IR data (Figure 1). Note that the shoulder peak is indeed narrow, much like the feature at 134 K (Figure S10). The feature marked with * is due to the premelting of ice, which releases some amount of trapped acetone, whereas the # feature is due to release of still smaller amounts of acetone, which desorb along with ice at 155 K. This smaller amount of acetone is also observed in the RAIRS study as shown in Figure 1 where a weak feature at ~1702 cm⁻¹ was observed even after hydrate dissociation, which was further confirmed in a separate experiment shown in Figure S3. The desorption trace of H2O+ (m/z = 18) consists of two features as shown by spectral deconvolution. The vapor pressure (desorption rate) of ASW is higher than that of crystalline ice, which resulted in a bump indicated by pink shading. Interestingly, this bump occurs right at the same temperature when acetone hydrate dissociated. Therefore, this is additional evidence to suggest that dissociation of acetone hydrate resulted in the crystallization of ice.

Kinetic parameters of ice Ic crystallization were evaluated by conducting time-dependent RAIRS studies at different temperatures. Previous reports suggest that the crystallization kinetics of ASW can be evaluated by monitoring the change in O−H stretching band during crystallization. The decoupled O−D stretch in HDO was also found to be effective in predicting the crystallization kinetics. Here, both these methods were adopted for a conclusive evaluation of the kinetics.

The time-dependent RAIR spectra of acetone:HDO (5% D2O in H2O) at different temperatures (130, 132, 135, and 137 K) are shown in Figures S11–S14. In Figure S13a, the bottom most spectrum (0 h trace) indicates a pure ASW film which was crystallized with time. We have evaluated the crystallization fraction, x(t), from changes in the absorbance (ΔA) at a fixed wavenumber (3307 cm⁻¹ in Figure S13a, indicated by the vertical line) for each temperature. A similar approach was adopted in several previous reports. Also in Figure S13b, the initially broad amorphous spectrum (0 min trace) eventually was transformed into a relatively sharp crystalline spectrum with a peak at ∼2427 cm⁻¹. 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 (∼2427 cm⁻¹ in Figure S13b, indicated by a vertical line) produced almost the same result for x(t) as that obtained from the integrated peak area. The crystallization fraction was calculated by eq 1

\[ x(t) = \frac{\Delta A(1)}{\Delta A(2)} \]

where ΔA(1) is the difference in the absorbance at a particular time “t” and that at time zero; ΔA(2) is the difference in
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absorbance of a completely crystallized film and that at time zero.

Panels a and b of Figure S15 illustrate the changes in the crystallization fractions as measured from the O–H and decoupled O–D stretching bands, conducted at different temperatures as shown. It was evident that the rate of crystallization was increased with rise in temperature. This change was reflected in the change of the curve shape from sigmoidal to exponential with temperature.69 Next, the crystallization fraction at different temperatures was fitted to the Avrami equation72,73

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

where \( t \) is time, \( k(T) \) the rate constant, and \( n \) the Avrami exponent. For all temperatures, \( n \) is a parameter whose value indicates the geometry of the growing particles and the type of nucleation, whether it is diffusion- or interface-controlled.74,75 Thus, the nature of the crystallization process can be predicted from the knowledge of Avrami exponent, \( n \). After rearranging, this equation becomes

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

Panels a and b of Figures S16 show linearly fitted straight lines using eq 3, for different temperatures as shown. The values of \( n \) are determined from the slopes. Using the values of \( n \) and intercept of the straight lines for each temperature, the rate constants, \( k(T) \), are estimated. Values of \( n \) and \( k(T) \) obtained from the analysis of O–H and O–D stretching bands at different temperatures are summarized in Table S1.

The obtained values of \( n \) (2.59–1.62, in Table S1) suggest that the crystallization kinetics is diffusion-controlled with particles growing into a predominantly spherical geometry.74–76 Previous studies also suggest that the crystallization kinetics of water to ice \( I_6 \) at \( T < 150 \) K is diffusion-controlled with predominantly spherical growth.74 Here, we suggest that dissociation of acetone hydrate can promote the diffusion or mobility of H\(_2\)O molecules which essentially trigger the formation of crystalline ice. Panels c and d of Figure S16 show the Arrhenius plot obtained from the analysis of O–H and O–D stretching bands at different temperatures as shown. The

\[ Ea = 60–77 \text{ kJ mol}^{-1} \]

Here, the high mobility of the water molecules during hydrate dissociation can overcome the kinetic barrier to form crystals even at a lower than usual ice-crystallization temperature.

In conclusion, we found that dissociation of acetone hydrate leads to the formation of ice \( I_6 \) under UHV. CHs are known to dissociate under prolonged exposure to vacuum and result in an entirely different crystalline structure of ice.51 The nucleation of ice \( I_6 \) occurs below the crystallization temperature, and molecular rearrangement during hydrate dissociation favors it. It is known that water-ice exists in comets, and acetone has also been found there recently.45 This study shows that acetone hydrate can exist in the extreme low-pressure conditions present in comets. Here, we believe that we present a missing piece of the puzzle linking the existence of ice \( I_6 \) and CH in comets. We suggest that this may be the mechanistic route for the formation of ice \( I_6 \) in such environments. This study may hint at the ice composition of a comet (amorphous or crystalline), which have implications from the cometary science perspective.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcllett.9b03063.

Experimental methods; crystallization kinetics; isothermal time-dependent RAR spectra of pure acetone, acetone:H\(_2\)O, and acetone:HDO at different temperatures; TPD-MS spectra of pure acetone; crystallization fractions and different crystallization parameters of acetone:HDO at different temperatures (PDF)

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REFERENCES


