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

Jyotirmoy Ghosh, Radha Gobinda Bhuin,[‡] Gaurav Vishwakarma, and Thalappil Pradeep*®

DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

Supporting Information

THE JOURNAL OF

ABSTRACT: Cubic ice (ice I_c) 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 I_c in ultrahigh vacuum (UHV) at 130–135 K. In this process, we find that crystallization of ice I_c 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 (E_{a}) 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 I_c. This unique process of crystallization hints at a possible mechanistic route for the formation of ice I_c in comets.



ces are ubiquitous in the universe, planets, and interstellar medium $(ISM)^1$ and can exist in different amorphous and crystalline forms.^{2,3} At ambient conditions, only hexagonal ice (ice I_h) can be obtained, out of more than 17 known crystalline ice polymorphs.⁴⁻⁶ 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 I_c), a metastable ice phase, was discovered by König⁸ in electron diffraction experiments.³ Subsequently, many experiments were performed to produce ice Ic, 9,10 Such studies include vapor deposition on cooled substrates,^{9,11-13} freezing of water in confined geometries,^{14–16} supercooling of water droplets, ^{17–20} freezing of high-pressure ice phases (phase II to IX) followed by annealing to 120–170 K, ^{3,21–24} annealing of amorphous ices, ^{25,26} dissociation of clathrate hydrates $(CHs)^{27-30}$ etc.

Formation of ice I_c by dissociation of CHs is intriguing among the several methods mentioned above. It was shown that dissociation of CO₂ hydrates can lead to ice I_c.^{27,29} The dissociation experiments were carried out at 6 mbar and 170-190 K, simulating the Martian surface and subsurface conditions.²⁷ However, the applicability of this unique transformation route in more exotic environments (comets and ISM), where the pressure is extremely low ($\sim 10^{-10}$ mbar), is still an open question. Note that ice Ic is predicted to exist in comets.^{31,32} This is possible as CH, the precursor of ice I_c in this transformation, can exist in cometary conditions.³³ Moreover, ice I is also known to form in the earth's atmosphere. $^{19,34-36}$ Calculation of dissociation pressures of different hydrates suggests their stability at low pressures and low temperatures.³⁷ We have shown recently that methane and CO_2 can form CHs at ~10⁻¹⁰ mbar and ~10 K, conditions

relevant to ISM.³⁸ However, there has been no experimental evidence to our knowledge for the formation of ice I_c 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,³⁹ as well as in different cometary activities such as cometary outbursts, heat balance of the cometary nuclei, etc.³⁹ Patashnick et al.⁴⁰ proposed that the heat evolved during crystallization (amorphous to ice I_c) 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.^{39,41-43} Amorphous ice is a poor heat conductor in comparison to ice I_{ct} and thermal conductivity rises by a factor of 10 upon phase transition.³⁹ The comets composed of ice I_c show low volatile outburst activity in comparison to comets with amorphous ice.³⁹ Enhanced thermal conductivity of ice I_c 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.³⁹

Received: October 24, 2019 Accepted: December 5, 2019 Published: December 5, 2019

0.12

0.08

0.04

0.00

4000

Absorbance (arb. units)



1800

1750

1750

1650

1600

1650

1700

1702 cm⁻¹

1700

Figure 1. RAIR spectra of 300 MLs of acetone: H_2O (1:1) at 135 K in the O–H and C=O 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 C=O stretching band was deconvoluted to show the concentration of acetone trapped in the hydrate cage and ASW pores. The inset focuses on the change in C=O stretching band upon dissociation of acetone hydrate over time. The O–H band changed after crystallization, and different features were resolved upon deconvolution.

Wavenumber (cm⁻¹)

3000

Acetone, a precursor of prebiotic species,⁴⁴ was found on comet 67P/Churyumov-Gerasimenko, for the first time, in 2015.45 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.⁴⁶ 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 studies⁴⁷⁻⁵⁰ 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.⁵¹ 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.⁵¹ Here, we demonstrate that acetone hydrate formed in UHV can transform into ice I_c upon in situ dissociation of the former at 130-135 K.

3500

Ice I_c via acetone hydrate was prepared by annealing a codeposited ~300 MLs acetone: H_2O (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 timedependent 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 \sim 1721 and \sim 1709 cm⁻¹, which are attributed to acetone hydrate 52-54 and ASW-trapped acetone,⁵⁵ 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.^{49,55,56} 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

27

spectra 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 \sim 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: H_2O at 135 K (Figure S4). They also resulted in ice I_c in processes as described. Therefore, it is confirmed that acetone hydrate could be formed even with a very dilute mixture of acetone: H_2O , 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.⁵⁷ 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.58 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 ν_1 in-phase band, ν_3 TO band, and the overlapped ν_3 LO and ν_1 out-of-phase bands of ice I_c. These assignments were made based on the previous IR studies of ice I_c .^{59,60} It is evident that acetone hydrate in UHV slowly (within 3 h) dissociates at 135 K, leading to ice I_c. 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 I_c after 9 h. However, the formation of acetone hydrate and subsequent crystallization to ice I_c 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 studies³⁸ 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: D_2O (1:1) at 140 K, and cubic D_2O ice was formed upon dissociation of acetone hydrate (Figure S7). The requirement of a slightly higher temperature of 140 K is understandable because D_2O is a heavier molecule than H_2O , whose rearrangement required a higher temperature.⁶¹

Thin films of ASW (<30 MLs) grown by vapor deposition below 110 K are known to have intrinsic ferroelectricity⁶² and negative surface potential.⁶³ 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 H_2O 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 I_{cr} 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-



Figure 2. Time-dependent RHEED images of 300 MLs of acetone:H₂O (1:1) at 120, 130, and 135 K. Here, a codeposition was done on the 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.

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. After deposition, the mixture was annealed (heating rate = 2 $K \cdot min^{-1}$) to the experimental temperatures and kept for the required time, as shown in the figure. Here, it must be noted that all of the experiments were performed under multilayer deposition conditions, and therefore, the substrate does not play a role in the morphology of the deposited ice systems.^{64,65} The RHEED image in Figure 2a, which was taken immediately after annealing the acetone:H₂O system at 135 K, does not show any pattern indicating the amorphous nature of the mixture. However, after 5 h, several diffraction rings were observed (Figure 2b). Notably, these diffraction patterns originate from the water ice film. In this particular condition, most of the acetone molecules desorb from the mixture as indicated by the

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^{66,67} of ice I_c. 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 I_c 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 I_c was formed only through the dissociation of acetone hydrate.

Figure 3 shows the TPD-MS spectra of 300 MLs of acetone: H_2O (1:1). Here, the ice film was heated at 30 K·



Figure 3. TPD-MS spectra of 300 MLs of acetone: H_2O (1:1). The ramping rate was 30 K·min⁻¹. Here, the intensities of CH_3CO^+ (m/z = 43) and H_2O^+ (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 \$\$ 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 \$\$. The peak at 155 K is due to the complete desorption of ice.

min⁻¹ to obtain the TPD spectra. In Figure 3a, for the desorption trace of acetone, the intensity of CH_3CO^+ (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 H_2O^+ (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.⁶⁸ 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 I_c crystallization were evaluated by conducting time-dependent RAIRS studies at different temperatures. Previous reports^{61,68,69} 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.^{70,71} 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.^{61,68,69} 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 (\sim 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

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

where $\Delta A(1)$ is the difference in the absorbance at a particular time "t" and that at time zero; $\Delta A(2)$ is the difference in

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 equation^{72,73}

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

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.^{2,74} Thus, the nature of the crystallization process can be predicted from the knowledge of Avrami exponent, n. After rearranging, this equation becomes

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

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_c 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 H₂O 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 the O-H and the O-D stretching regions, respectively. The slope of these linearly fitted lines gave the values of the activation energy (*E*₂), which were estimated to be ~57.92 and ~57.58 kJ mol⁻¹, respectively. This is comparable to the previously reported activation energy values ($E_a = 60-77$ kJ mol⁻¹) for the crystallization of pure ASW obtained by different experimental techniques.^{69,70,77–79} 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_c 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_c 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_c and CH in comets. We suggest that this may be the mechanistic route for the formation of ice I_c 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

S Supporting Information

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

Experimental methods; crystallization kinetics; isothermal time-dependent RAIR spectra of pure acetone, acetone:H₂O, 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)

AUTHOR INFORMATION

Corresponding Author

*E-mail: pradeep@iitm.ac.in.

ORCID

Thalappil Pradeep: 0000-0003-3174-534X

Present Address

[‡]R.G.B.: Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

J.G. thanks the University Grants Commission (UGC) for his research fellowship. We thank the Department of Science and Technology (DST), Government of India, for supporting our research. We thank Dr. Ryutaro Souda for helping us with the RHEED studies.

REFERENCES

(1) Jenniskens, P.; Blake, D. F. Structural Transitions in Amorphous Water Ice and Astrophysical Implications. *Science* **1994**, *265*, 753–756.

(2) Jenniskens, P.; Blake, D. F. Crystallization of Amorphous Water Ice in the Solar System. *Astrophys. J.* **1996**, 473, 1104–1113.

(3) Petrenko, V. F.; Whitworth, R. W. Physics of Ice; OUP: Oxford, 2002.

(4) Chou, I. M.; Blank, J. G.; Goncharov, A. F.; Mao, H.-k.; Hemley, R. J. In Situ Observations of a High-Pressure Phase of H_2O Ice. *Science* **1998**, 281, 809–812.

(5) Kohl, I.; Mayer, E.; Hallbrucker, A. The Glassy Water-Cubic Ice System: A Comparative Study by X-Ray Diffraction and Differential Scanning Calorimetry. *Phys. Chem. Chem. Phys.* 2000, *2*, 1579–1586.
(6) Lobban, C.; Finney, J. L.; Kuhs, W. F. The Structure of a New Phase of Ice. *Nature* 1998, *391*, 268–270.

(7) Millot, M.; Coppari, F.; Rygg, J. R.; Correa Barrios, A.; Hamel, S.; Swift, D. C.; Eggert, J. H. Nanosecond X-ray diffraction of Shock-Compressed Superionic Water Ice. *Nature* **2019**, *569*, 251–255.

(8) König, H. A Cubic Modification of Ice. Z. Kristallogr. - Cryst. Mater. 1943, 105, 279–286.

(9) Kuhs, W. F.; Sippel, C.; Falenty, A.; Hansen, T. C. Extent and Relevance of Stacking Disorder in "ice I_c . *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 21259–21264.

(10) Thürmer, K.; Nie, S. Formation of Hexagonal and Cubic Ice during Low-Temperature Growth. *Proc. Natl. Acad. Sci. U. S. A.* 2013, 110, 11757–11762.

(11) Honjo, G.; Kitamura, N.; Shimaoka, K.; Mihama, K. Low Temperature Specimen Method for Electron Diffraction and Electron Microscopy. J. Phys. Soc. Jpn. **1956**, *11*, 527–536.

The Journal of Physical Chemistry Letters

(12) Blackman, M.; Lisgarten, N. D. The Cubic and Other Structural Forms of Ice at Low Temperature and Pressure. *Proc. R. Soc. London A* **1957**, 239, 93–107.

(13) Shallcross, F. V.; Carpenter, G. B. X-Ray Diffraction Study of the Cubic Phase of Ice. J. Chem. Phys. **1957**, 26, 782–784.

(14) Steytler, D. C.; Dore, J. C.; Wright, C. J. Neutron Diffraction Study of Cubic Ice Nucleation in a Porous Silica Network. *J. Phys. Chem.* **1983**, 87, 2458–2459.

(15) Dore, J. C.; Dunn, M.; Chieux, P. Neutron Diffraction Studies of Ice Nucleation in Porous Silica. J. Phys. Colloques **1987**, 48, C1-457.

(16) Baker, J. M.; Dore, J. C.; Behrens, P. Nucleation of Ice in Confined Geometry. J. Phys. Chem. B **1997**, 101, 6226–6229.

(17) Malkin, T. L.; Murray, B. J.; Brukhno, A. V.; Anwar, J.; Salzmann, C. G. Structure of Ice Crystallized from Supercooled Water. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 1041–1045.

(18) Mayer, E.; Hallbrucker, A. Cubic Ice from Liquid Water. *Nature* **1987**, 325, 601–602.

(19) Murray, B. J.; Knopf, D. A.; Bertram, A. K. The Formation of Cubic Ice under Conditions Relevant to Earth's Atmosphere. *Nature* **2005**, 434, 202–205.

(20) Murray, B. J.; Bertram, A. K. Formation and Stability of Cubic Ice in Water Droplets. *Phys. Chem. Chem. Phys.* **2006**, *8*, 186–192.

(21) Bertie, J. E.; Calvert, L. D.; Whalley, E. Transformations of Ice II, ice III, and Ice V at Atmospheric Pressure. *J. Chem. Phys.* **1963**, *38*, 840–846.

(22) Handa, Y. P.; Klug, D. D.; Whalley, E. Energies of the Phases of Ice at Low Temperature and Pressure Relative to Ice I_h. *Can. J. Chem.* **1988**, *66*, 919–924.

(23) McMillan, J. A.; Los, S. C. Vitreous ice: Irreversible transformations during warm-up. *Nature* **1965**, *206*, 806–807.

(24) Yamamuro, O.; Oguni, M.; Matsuo, T.; Suga, H. Heat Capacity and Glass Transition of Pure and Doped Cubic Ices. *J. Phys. Chem. Solids* **1987**, *48*, 935–942.

(25) Dowell, L. G.; Rinfret, A. P. Low-Temperature Forms of Ice as Studied by X-Ray Diffraction. *Nature* **1960**, *188*, 1144–1148.

(26) McMillan, J. A.; Los, S. C. Vitreous Ice: Irreversible Transformations During Warm-Up. *Nature* **1965**, *206*, 806–807.

(27) Falenty, A.; Hansen, T. C.; Kuhs, W. F. Cubic Ice Formation and Annealing During CO_2 Clathrate Hydrate Decomposition at Low Temperatures. *Physics and Chemistry of Ice* **2010**, 2010, 411.

(28) Falenty, A.; Kuhs, W. F. Self-Preservation" of CO₂ Gas Hydrates-Surface Microstructure and Ice Perfection. *J. Phys. Chem. B* **2009**, *113*, 15975–15988.

(29) Kuhs, W. F.; Genov, G.; Staykova, D. K.; Hansen, T. Ice Perfection and Onset of Anomalous Preservation of Gas Hydrates. *Phys. Chem. Chem. Phys.* **2004**, *6*, 4917–4920.

(30) Takeya, S.; Uchida, T.; Nagao, J.; Ohmura, R.; Shimada, W.; Kamata, Y.; Ebinuma, T.; Narita, H. Particle Size Effect of CH₄ Hydrate for Self-Preservation. *Chem. Eng. Sci.* **2005**, *60*, 1383–1387.

(31) Gronkowski, P. The Search for a Cometary Outbursts Mechanism: A Comparison of Various Theories. *Astron. Nachr.* 2007, 328, 126–136.

(32) Prialnik, D.; Bar-Nun, A. Crystallization of Amorphous Ice as the Cause of Comet P/Halley's outburst at 14 AU. *Astron. Astrophys.* **1992**, 258, L9–L12.

(33) Blake, D.; Allamandola, L.; Sandford, S.; Hudgins, D.; Freund, F. Clathrate Hydrate Formation in Amorphous Cometary Ice Analogs in Vacuo. *Science* **1991**, *254*, 548–551.

(34) Riikonen, M.; Sillanpää, M.; Virta, L.; Sullivan, D.; Moilanen, J.; Luukkonen, I. Halo Observations Provide Evidence of Airborne Cubic Ice in the Earth's Atmosphere. *Appl. Opt.* **2000**, *39*, 6080– 6085.

(35) Whalley, E. Scheiner's Halo: Evidence for Ice I_c in the Atmosphere. *Science* **1981**, 211, 389–390.

(36) Whalley, E. Cubic Ice in Nature. J. Phys. Chem. 1983, 87, 4174-4179.

(37) Miller, S. L. The occurrence of gas hydrates in the solar system. *Proc. Natl. Acad. Sci. U. S. A.* **1961**, 47, 1798–1808.

(38) Ghosh, J.; Methikkalam, R. R. J.; Bhuin, R. G.; Ragupathy, G.; Choudhary, N.; Kumar, R.; Pradeep, T. Clathrate Hydrates in Interstellar Environment. *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116*, 1526–1531.

(39) Klinger, J. Extraterrestial ice. A review. J. Phys. Chem. 1983, 87, 4209-4214.

(40) Patashnick, H.; Rupprecht, G.; Schuerman, D. W. Energy Source for Comet Outbursts. *Nature* **1974**, *250*, 313–314.

(41) Klinger, J. Influence of a Phase Transition of Ice on the Heat and Mass Balance of Comets. *Science* **1980**, 209, 271–272.

(42) Smoluchowski, R. Amorphous Ice and the behavior of Cometary Nuclei. *Astrophys. J.* **1981**, 244, L31–L34.

(43) Klinger, J. Some Consequences of a Phase Transition of Water Ice on the Heat Balance of Comet Nuclei. *Icarus* **1981**, *47*, 320–324.

(44) Almeida, G. C.; Pilling, S.; Andrade, D. P. P.; Castro, N. L. S.; Mendoza, E.; Boechat-Roberty, H. M.; Rocco, M. L. M. Photodesorption and Photostability of Acetone Ices: Relevance to Solid Phase Astrochemistry. *J. Phys. Chem. C* **2014**, *118*, 6193–6200.

(45) Goesmann, F.; Rosenbauer, H.; Bredehöft, J. H.; Cabane, M.; Ehrenfreund, P.; Gautier, T.; Giri, C.; Krüger, H.; Le Roy, L.; MacDermott, A. J.; McKenna-Lawlor, S.; Meierhenrich, U. J.; Caro, G. M. M.; Raulin, F.; Roll, R.; Steele, A.; Steininger, H.; Sternberg, R.; Szopa, C.; Thiemann, W.; Ulamec, S. Organic Compounds on Comet 67P/Churyumov-Gerasimenko Revealed by COSAC Mass Spectrometry. *Science* **2015**, *349*, aab0689.

(46) Luspay-Kuti, A.; Mousis, O.; Hässig, M.; Fuselier, S. A.; Lunine, J. I.; Marty, B.; Mandt, K. E.; Wurz, P.; Rubin, M. The Presence of Clathrates in Comet 67P/Churyumov-Gerasimenko. *Sci. Adv.* **2016**, *2*, No. e1501781.

(47) Schaff, J. E.; Roberts, J. T. Structure Sensitivity in the Surface Chemistry of Ice: Acetone Adsorption on Amorphous and Crystalline Ice Films. *J. Phys. Chem.* **1994**, *98*, 6900–6902.

(48) Schaff, J. E.; Roberts, J. T. Toward an Understanding of the Surface Chemical Properties of Ice: Differences between the Amorphous and Crystalline Surfaces. *J. Phys. Chem.* **1996**, *100*, 14151–14160.

(49) Schaff, J. E.; Roberts, J. T. The Adsorption of Acetone on Thin Films of Amorphous and Crystalline Ice. *Langmuir* **1998**, *14*, 1478– 1486.

(50) Souda, R. Adsorption, Diffusion, Dewetting, and Entrapment of Acetone on Ni(111), Surface-Modified Silicon, and Amorphous Solid Water studied by Time-of-Flight Secondary Ion Mass Spectrometry and Temperature Programmed Desorption. *J. Chem. Phys.* **2011**, *135*, 164703.

(51) Falenty, A.; Hansen, T. C.; Kuhs, W. F. Formation and Properties of Ice XVI Obtained by Emptying a type sII Clathrate Hydrate. *Nature* **2014**, *516*, 231–233.

(52) Monreal, I. A.; Devlin, J. P.; Maşlakcı, Z.; Çiçek, M. B.; Uras-Aytemiz, N. Controlling Nonclassical Content of Clathrate Hydrates Through the Choice of Molecular Guests and Temperature. *J. Phys. Chem. A* 2011, *115*, 5822–5832.

(53) Consani, K. Infrared Bands of Acetone in Solid Argon and the Structure II Clathrate 2-Acetylene/Acetone/17-Water. *J. Phys. Chem.* **1987**, *91*, 5586–5588.

(54) Mitlin, S.; Leung, K. T. Surface Chemistry of OH Dangling Bonds in Vapour-Deposited Ice Films at 128–185 K: Hydrogen-Bonding Interactions with Acetone. *Surf. Sci.* **2002**, *505*, L227–L236.

(55) Shin, S.; Kang, H.; Kim, J. S.; Kang, H. Phase Transitions of Amorphous Solid Acetone in Confined Geometry Investigated by Reflection Absorption Infrared Spectroscopy. *J. Phys. Chem. B* 2014, *118*, 13349–13356.

(56) Hudson, R. L.; Gerakines, P. A.; Ferrante, R. F. IR Spectra and Properties of Solid Acetone, An Interstellar and Cometary Molecule. *Spectrochim. Acta, Part A* **2018**, *193*, 33–39.

(57) Backus, E. H. G.; Grecea, M. L.; Kleyn, A. W.; Bonn, M. Surface Crystallization of Amorphous Solid Water. *Phys. Rev. Lett.* **2004**, *92*, 236101.

The Journal of Physical Chemistry Letters

(58) Buch, V.; Devlin, J. P.; Monreal, I. A.; Jagoda-Cwiklik, B.; Uras-Aytemiz, N.; Cwiklik, L. Clathrate Hydrates with Hydrogen-Bonding Guests. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10245–10265.

(59) Whalley, E. A Detailed Assignment of the O-H Stretching Bands of Ice I. Can. J. Chem. 1977, 55, 3429-3441.

(60) Hagen, W.; Tielens, A. G. G. M.; Greenberg, J. M. The Infrared Spectra of Amorphous Solid Water and Ice I_c between 10 and 140 K. *Chem. Phys.* **1981**, *56*, 367–379.

(61) Smith, R. S.; Matthiesen, J.; Knox, J.; Kay, B. D. Crystallization Kinetics and Excess Free Energy of H_2O and D_2O Nanoscale Films of Amorphous Solid Water. J. Phys. Chem. A **2011**, 115, 5908–5917.

(62) Su, X.; Lianos, L.; Shen, Y. R.; Somorjai, G. A. Surface-Induced Ferroelectric Ice on Pt(111). *Phys. Rev. Lett.* **1998**, *80*, 1533–1536.

(63) Bu, C.; Shi, J.; Raut, U.; Mitchell, E. H.; Baragiola, R. A. Effect of Microstructure on Spontaneous Polarization in Amorphous Solid Water Films. *J. Chem. Phys.* **2015**, *142*, 134702.

(64) Ghosh, J.; Bhuin, R. G.; Ragupathy, G.; Pradeep, T. Spontaneous Formation of Tetrahydrofuran Hydrate in Ultrahigh Vacuum. J. Phys. Chem. C 2019, 123, 16300–16307.

(65) Ghosh, J.; Hariharan, A. K.; Bhuin, R. G.; Methikkalam, R. R. J.; Pradeep, T. Propane and Propane-Water Interactions: A Study at Cryogenic Temperatures. *Phys. Chem. Chem. Phys.* **2018**, *20*, 1838– 1847.

(66) Lisgarten, N. D.; Blackman, M. The Cubic Form of Ice. *Nature* **1956**, *178*, 39–40.

(67) Kouchi, A.; Kuroda, T. Amorphization of Cubic Ice by Ultraviolet Irradiation. *Nature* **1990**, 344, 134–135.

(68) Smith, R. S.; Petrik, N. G.; Kimmel, G. A.; Kay, B. D. Thermal and Nonthermal Physiochemical Processes in Nanoscale Films of Amorphous Solid Water. *Acc. Chem. Res.* **2012**, *45*, 33–42.

(69) Lee, D. H.; Kang, H. Acid-Promoted Crystallization of Amorphous Solid Water. J. Phys. Chem. C 2018, 122, 24164-24170.

(70) Yuan, C.; Smith, R. S.; Kay, B. D. Communication: Distinguishing between Bulk and Interface-Enhanced Crystallization in Nanoscale Films of Amorphous Solid Water. *J. Chem. Phys.* 2017, 146, No. 031102.

(71) Xu, Y.; Petrik, N. G.; Smith, R. S.; Kay, B. D.; Kimmel, G. A. Growth Rate of Crystalline Ice and the Diffusivity of Supercooled Water from 126 to 262 K. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 14921.

(72) Avrami, M. Kinetics of Phase Change. I General Theory. J. Chem. Phys. 1939, 7, 1103–1112.

(73) Avrami, M. Kinetics of Phase Change. II Transformation-Time Relations for Random Distribution of Nuclei. *J. Chem. Phys.* **1940**, *8*, 212–224.

(74) Hage, W.; Hallbrucker, A.; Mayer, E.; Johari, G. P. Crystallization Kinetics of Water below 150 K. J. Chem. Phys. **1994**, 100, 2743–2747.

(75) Rao, C. N. R.; Rao, K. J. In Phase Transitions in Solids: An Approach to the Study of the Chemistry and Physics of Solids; McGraw-Hill: New York, 1978; pp 81–173.

(76) Doremus, R. H. Rates of Phase Transformations; Academic Press, Inc.: Orlando, FL, 1985.

(77) Kondo, T.; Kato, H. S.; Bonn, M.; Kawai, M. Deposition and crystallization studies of thin amorphous solid water films on Ru(0001) and on CO-precovered Ru(0001). *J. Chem. Phys.* 2007, *127*, No. 094703.

(78) Safarik, D. J.; Mullins, C. B. The nucleation rate of crystalline ice in amorphous solid water. J. Chem. Phys. 2004, 121, 6003–6010.

(79) Smith, R. S.; Matthiesen, J.; Knox, J.; Kay, B. D. Crystallization Kinetics and Excess Free Energy of H_2O and D_2O Nanoscale Films of Amorphous Solid Water. J. Phys. Chem. A **2011**, 115, 5908–5917.