Formation and Transformation of Clathrate Hydrates under Interstellar Conditions

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CONSPECTUS: Continuing efforts by many research groups have led to the discovery of ~240 species in the interstellar medium (ISM). Observatory- and laboratory-based astrochemical experiments have led to the discovery of these species, including several complex organic molecules (COMs). Interstellar molecular clouds, consisting of water-rich icy grains, have been recognized as the primordial sources of COMs even at extremely low temperatures (~10 K). Therefore, it is paramount to understand the chemical processes of this region, which may contribute to the chemical evolution and formation of new planetary systems and the origin of life.

This Account discusses our effort to discover clathrate hydrates (CHs) of several molecules and their structural varieties, transformations, and kinetics in a simulated interstellar environment. CHs are nonstoichiometric crystalline host–guest complexes in which water molecules form cages of different sizes to entrap guest molecules. CHs are abundant on earth and require moderate temperatures and high pressures for their formation. Our focus has been to form CHs at extremely low pressure and temperature as in the ISM, although their existence under such conditions has been a long-standing question since water and guest molecules (CH₄, CO₂, CO, etc.) exist in space. In multiple studies conducted at ~10⁻¹⁰ mbar, we showed that CH₄, CO₂, and C₂H₆ hydrates could be formed at 30, 10, and 60 K, respectively. Well-defined IR spectroscopic features supported by quantum chemical simulations and temperature-programmed desorption mass spectrometric analyses confirmed the existence of the S¹2 (for CH₄ and CO₂) and S¹26² (for C₂H₆) CH cages. Mild thermal activation for long periods under ultrahigh vacuum (UHV) allowed efficient molecular diffusion, which is crucial for forming CHs. We also explored the formation of THF hydrate (a promoter/stabilizer for binary CHs), and a spontaneous method was found for its formation under UHV. In a subsequent study, we observed a binary THF-CO₂ hydrate and its thermal processing at 130 K leading to the transportation of CO₂ from the hydrate cages to the matrix of amorphous water. The findings imply that such systems possess a dynamic setting that facilitates the movement of molecules, potentially accounting for the chemical changes observed in the ISM.

Furthermore, an intriguing fundamental phenomenon is the consequences of these CHs and their dynamics. We showed that preformed acetone and formaldehyde hydrates dissociate to form cubic (Ic) and hexagonal (Ih) ices at 130–135 K, respectively. These unique processes could be the mechanistic routes for the formation of various ices in astrophysical environments.

Other than adding a new entry, namely, CHs, to the list of species found in ISM, its existence opens new directions to astrochemistry, observational astronomy, and astrobiology. Our work provides a molecular-level understanding of the formation pathways of CHs and their transformation to crystalline ices, which sheds light on the chemical evolution of simple molecules to COMs in ISM. Furthermore, CHs can be potential candidates for studies involving radiation, ionization, and electron impact to initiate chemical transformations between the host and guest species and may be critical in understanding the origin of life.

KEY REFERENCES

- 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, 1526−1531.¹ This work reported the experimental evidence of CH₄ and CO₂ clathrate hydrates (CHs) at extremely low pressure (10⁻¹⁰ mbar) under cryogenic conditions, relevant to the interstellar medium (ISM).
- Ghosh, J.; Bhuin, R. G.; Vishwakarma, G.; Pradeep, T. Formation of Cubic Ice via Clathrate Hydrate, Prepared in Ultrahigh Vacuum under Cryogenic Conditions. J. Phys. Chem. Lett. 2020, 11, 26−32.² This work reported a unique crystallization process of cubic ice (Ice Ic) involving the dissociation of preformed acetone hydrate in UHV.

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1. INTRODUCTION

The interstellar medium (ISM) is not empty but contains diffuse clouds, composed of gaseous species, particulate matter, and dust particles. To date, ~240 different molecules have been found in these clouds, making ISM exceedingly diverse and a host to rich chemistry. Molecular H₂ is the most abundant species found in ISM along with common terrestrial molecular species, molecular ions, radicals, complex organic molecules (COMs), and polycyclic aromatic hydrocarbons (PAHs). ISM is extremely cold (~10 K); therefore, most of these gaseous species get accreted onto the dust surfaces to form icy grain mantles. Ice in the ISM context refers to all condensed molecular solids. Such interstellar icy dust particles are considered to be the birthplace of COMs even at such low temperatures; therefore, it is important to study the associated chemistry. Several studies involving absorption IR spectroscopy were used to characterize the compositions of interstellar ice, and water is found to be the major constituent, followed by CO₂, CO, CH₃OH, NH₃, and CH₄. This interstellar ice is known to have two different phases, namely, water-rich and water-poor analogs. The water-rich phase consists of mostly water and CO₂, alongside small amounts of...
NH₃ and CH₄ ices, whereas the water-poor phase contains mostly CO, CO₂, and CH₃OH. In interstellar environments, the coexistence of all of these molecules along with water in the condensed phase presents a perfect recipe for clathrate hydrates (CHs), a unique molecular species yet to be detected in ISM, and this Account addresses that gap.

CHs are nonstoichiometric crystalline host–guest complexes, where water molecules form a cage–like structure to entrap different guest species to gain stabilization by the host–guest interaction. Their structures are dependent on the nature of guest species, and the most commonly occurring structures are referred to as structure I (sI), structure II (sII), and structure H (sH). CHs are also abundant on earth and generally found in permafrost regions, ocean floors, and outer continental shelves as marine sediments. CHs are known to serve as important materials as a sustainable source of energy and for the storage of natural gases with huge entrapment capability, CO₂ sequestration, and sea-water desalination. It is also important to understand the nucleation and decomposition behaviors of CHs for flow assurance in subsea pipelines and global climate change, respectively.

In general, high pressure and moderate to low temperature are the stabilizing conditions for the nucleation and growth of CHs. However, CHs can also form at low pressures and temperatures as per the $P-T$ phase diagram, and their existence was predicted in the outer solar system temperatures as per the Bayard–Alpert type were used in the UHV range. The base pressure below $\approx 5 \times 10^{-10}$ mbar was achieved after the bake-out. A closed-cycle helium cryostat cooled the Ru(0001) substrate over which ice layers were grown.

2. INSTRUMENTATION AND METHOD

2.1. Experimental Setup

Herein, the experimental details and description of the custom-built UHV instrument for studying CHs are presented, as shown in Figure 1. More details about the instrument can be found in recent papers. The instrument has a cylindrical UHV chamber fitted with turbomolecular pumps backed by oil-free diaphragm pumps. Ionization gauges of the Bayard–Alpert type were used in the UHV range. The base pressure below $\approx 5 \times 10^{-10}$ mbar was achieved after the bake-out. A closed-cycle helium cryostat cooled the Ru(0001) substrate over which ice layers were grown.

2.2. RAIRS Instrumentation

The general experimental procedure of forming CHs is either co-deposition or the sequential deposition of water and CH-forming gases. A high-precision leak valve was used to control the deposition pressure, where water and other gaseous species were deposited by using two separate inlet lines. Millipore water (18.2 MΩ) was used by purifying with freeze–pump–thaw cycles to deposit 300 monolayers (MLs) of ice; therefore, the substrate does not affect the formation of CH. The monolayer (ML) coverage was calculated by assuming that $1.33 \times 10^{-5}$ mbar s = 1 ML.

For the deposition of 300 MLs of 1:1 mixed ice, the chamber was backfilled starting from a base pressure of $\approx 5 \times 10^{-10}$ mbar to a total pressure of $\approx 5 \times 10^{-7}$ mbar (the pressure of the specific gas as well as water was $2.5 \times 10^{-7}$ mbar, individually) and deposited for 10 min. Moreover, a residual gas analyzer was used during the deposition of these molecules,
and the MS intensities of these species were utilized to determine the molecular ratio. The mixed ice was heated at 2 K min$^{-1}$ to the desired temperature. RAIR spectra were obtained to monitor CH formation. Identical experimental conditions were maintained throughout the spectral measurement.

3. CLATHRATE HYDRATES UNDER INTERSTELLAR CONDITIONS

3.1. IR Spectroscopic Evidence

We started our quest for CHs in the ISM with CH$_4$ hydrate, the most common gas hydrate found on earth. At first, 300 MLs of 1:1 CH$_4$ and water were codeposited at 10 K. Time-dependent RAIR spectra were recorded in the C–H antisymmetric stretching region of CH$_4$ at 10, 20, and 30 K for different annealing times (0 and 25 h) as shown in Figure 2a. The spectra showed an IR feature of solid CH$_4$ at 3009 cm$^{-1}$, which remained constant at 10 and 20 K even after 25 h. However, a new peak at 3017 cm$^{-1}$ appeared after 25 h of annealing at 30 K, which was blue-shifted in comparison to the spectral band for solid CH$_4$ (3009 cm$^{-1}$). This new peak (3017 cm$^{-1}$) was assigned to CH$_4$ hydrate, and the experimental blue shift of 8 cm$^{-1}$ was due to the entrapment of CH$_4$ in the hydrate cage. Previous study$^{40}$ had suggested that the trapped guest molecules in CH cages have more

Figure 2. Formation of CHs is studied by RAIR spectroscopy and quantum chemical calculations. RAIR spectra of 300 MLs (1:1) codeposited ice systems, namely, (a) CH$_4$ + H$_2$O, (b) CO$_2$ + H$_2$O, and (c) C$_2$H$_6$ + H$_2$O at different temperatures and annealing times, as indicated. Here, only the C–H and C=O antisymmetric stretching regions are shown for hydrocarbons and CO$_2$, respectively. DFT-optimized structures of hydrate cages are shown for (d) CH$_4$ hydrate, (e) CO$_2$ hydrate, and (f) C$_2$H$_6$ hydrate. Adapted with permission from ref 1. Copyright 2019 the authors. Published by the National Academy of Sciences under Creative Commons Attribution-NonCommercial-NoDerivatives License 4.0 (CC BY-NC-ND) and adapted with permission from ref 43. Copyright 2022 American Chemical Society.
vibrational freedom and behave like gaseous species; therefore, their vibrational frequency stays in between their gaseous- and condensed-phase frequencies. Another study also showed a blue-shifted IR feature due to CH trapped in a hydrate cage. The prolonged annealing (25 h) at 30 K, near the desorption temperature of CH₄, was crucial to forming the hydrate cage. Primarily due to the application of UHV at these temperatures, CH₄ molecules gained enhanced mobility, which led to the mixing of CH₄ and codeposited water, which results in enhanced interaction and CH₄ insertion into the hydrate cages. A time-dependent RAIR study of pure condensed CH₄ in the absence of water at 25 K did not show the peak at 3017 cm⁻¹, which confirmed its assignment to CH₄ hydrate. In addition, quantum chemical calculations using density functional theory (DFT) also confirmed the formation of CH₄ hydrate. It revealed the preferential formation of stable, small S₁² cages (Figure 2d) under the simulated condition. The calculated vibrational shift with the formation of CH₄ hydrates nearly matches the experimentally obtained spectral shift (8 cm⁻¹). A microsecond molecular dynamics (MD) simulation study of CH₄ hydrate nucleation predicted the preferential formation of smaller S₁² cages during the initial stages of nucleation, which supports our result.

The existence of CHs in ISM was further supported by the experimental evidence of two other hydrates, namely, CO₂ and C₂H₆ hydrates. An earlier report suggested that CO₂ hydrate can be formed at 1.33 × 10⁻⁵ mbar and 120 K. Figure 2b shows the RAIR spectra of 300 MLs of a CO₂:H₂O (1:1) codeposited mixture in the C=O antisymmetric stretching region. The peak at 2346 cm⁻¹ was attributed to CO₂ hydrate, entrapped in the S¹² cage as suggested by the DFT calculations (Figure 2e). The other peak at 2353 cm⁻¹ was due to the remaining untrapped solid CO₂, which exists outside the hydrate cages in the amorphous ice matrix. The 2346 cm⁻¹ peak was the characteristic feature of CO₂ hydrate as reported before. The gradual decrease in intensity for the 2353 cm⁻¹ peak and the simultaneous emergence of the 2346 cm⁻¹ peak with temperature suggested that annealing helps in better mixing of ice and CO₂, which favors the formation of CO₂ hydrate. The results suggested that CO₂ hydrate can be formed at 10 K, and it is quite stable at 120 K for 6 h. This is attributed to the stronger interaction of CO₂ with water than with CH₄, although both are weak. The formation of C₂H₆ hydrate in ISM was also explored. As per an earlier study, C₂H₆ hydrate can be formed at 10⁻⁵ mbar and 90 K but only in the presence of oxirane, which helped in the nucleation of ethane-oxirane mixed hydrate. Figure 2c shows the RAIR spectra of 300 MLs C₂H₆:H₂O (1:1) codeposited mixture in the C=H antisymmetric stretching region at different temperatures. Three distinct peaks appeared at 60 K, positioned at 2972, 2976, and 2982 cm⁻¹ corresponding to the crystalline, amorphous, and CH forms of C₂H₆ hydrate, respectively. The 2982 cm⁻¹ peak is the characteristic IR feature of C₂H₆ hydrate as observed in earlier reports. Again, the blue-shifted nature of the 2982 cm⁻¹ peak as compared to the amorphous and crystalline IR features of C₂H₆ indicates its assignment to C₂H₆ hydrate. A comparison of DFT-calculated vibrational and experimental shifts suggested that C₂H₆ is trapped in the S¹² cage as shown in Figure 2f.

3.2. Mass Spectrometric Evidence

Temperature-programmed desorption-mass spectrometry (TPD-MS) also supported the formation of CHs in ISM. TPD-MS is an MS-based analytical technique routinely utilized in surface science and laboratory astrochemical experiments.
Here, the continuous desorption of adsorbed species from the substrate upon thermal stimulation is analyzed by a mass spectrometer, and the resultant mass intensities are plotted as a function of the substrate temperature. Porous amorphous ice can entrap guest molecules, which are released during the crystallization of ice at 140 K due to the collapse of these pores. This results in an abrupt release of the trapped species, which produces a “molecular volcano (MV)”.

Figure 3a represents the comparative TPD spectra before and after the formation of CH$_4$ hydrate, which were monitored using the intensity of the CH$_4^+$ peak (m/z = 15). CH$_4$ hydrate was formed by annealing a codeposited mixture at 30 K for 25 h as mentioned before. The other peaks at 38 and 46 K correspond to multilayer CH$_4$ and CH$_4$ trapped in the ASW pores, respectively. The intensity of the MV peak before the formation of the hydrate is due to the trapped CH$_4$ in ASW, whereas the intensity of the MV peak was enhanced upon the formation of the hydrate due to the simultaneous release of trapped CH$_4$ from ASW pores as well as from the hydrate cages (Figure 3a). Note that the amounts of gases deposited are the same in both cases. The slight distortion in the MV peak is attributed to the modification of ASW pores due to CH$_4$ formation (Figure 3a). Figure 3b shows the TPD spectra of 300 MLs of CO$_2$ + H$_2$O at two ratios, 1:1 and 1:5, and they were annealed at 120 K for the complete formation of CO$_2$ hydrate. Then the samples were cooled back to 10 K, and TPD spectra were recorded. The peak at 140 K corresponds to the MV of CO$_2$, and its intensity increased as the ratio of CO$_2$ to H$_2$O was changed from 1:1 to 1:5. Experiments suggested that the extent of formation of CO$_2$ hydrate was greater for the ASW matrix. The peak was shifted from 60 to 80 K to the MV peak before hydrate formation. The enhanced intensity of the MV peak for the hydrate was due to the release of multilayer CH$_4$ from ASW pores and the MV peak, respectively.

Figure 3c shows the TPD profiles for C$_2$H$_6$ hydrate before and after formation. Two sets of TPD-MS experiments were performed; in the first, we deposited 300 MLs of an C$_2$H$_6$:H$_2$O (1:1) ice mixture at 10 K and heated it to 200 K at a ramping rate of 30 K min$^{-1}$. The desorption of C$_2$H$_6$ was monitored by the intensity of the C$_2$H$_6^+$ peak (m/z = 28). The peaks at 60 and 140 K were attributed to the desorption of multilayer C$_2$H$_6$ from ASW pores and the MV peak, respectively. In the second experiment, a C$_2$H$_6$:H$_2$O (1:1) ice mixture was annealed at 60 K for 18 h to create C$_2$H$_6$ hydrate. After the hydrate was formed, the sample was cooled to 10 K and the TPD spectrum was recorded (red trace), which showed two peaks at 80 and 140 K. The peak at 80 K was assigned to the desorption of trapped C$_2$H$_6$ (amorphous or crystalline) from the ASW matrix. The peak was shifted from 60 to 80 K primarily due to the formation of CH as well as a more compact ice network as a result of prolonged annealing.

The MV peak of C$_2$H$_6$ hydrate showed a higher intensity compared to the MV peak before hydrate formation. The enhanced intensity of the MV peak for the hydrate was due to the release of trapped C$_2$H$_6$ from the ASW pores and the dissociation of the CH cage, as explained before. Note that the peak marked by an asterisk around 125 K was due to the predissociation of hydrate cages.

4. TRANSFORMATIONS OF CLATHRATE HYDRATES

4.1. Formation of Cubic Ice (Ice Ic) from CH

The dissociation behavior of CHs is also important to understand since it leads to different crystalline phases of ice. An earlier study suggested that emptying neon from its hydrate cages led to the formation of ice XVI, a new crystalline phase of ice. The dissociation of CO$_2$ hydrates led to cubic ice...
In our study, we showed that acetone hydrates could be prepared by codepositing acetone:H₂O (1:1) mixtures and annealing them to 135 K. However, keeping acetone hydrate at 135 K for 3 h led to its dissociation, which resulted in ice I冕. Figure 4 shows the RAIR spectra of the codeposited film at 135 K (blue trace; 0 h) and after 3 h (orange trace; 3 h). The inset shows the C≡O stretching band, and at 0 h, it shows two features at 1721 and 1709 cm⁻¹ which were attributed to acetone hydrate and ASW-trapped acetone, respectively. The peak intensity was reduced with time and resulted in a peak at 1702 cm⁻¹, which was assigned to a dilute mixture of acetone and water (1:20). The profound change in the O–H stretching band with time indicates the change in the overall structure of ice due to the dissociation of acetone hydrate. In Figure 4, the broad O–H stretching band (blue trace) is a characteristic feature of ASW, which eventually became sharp and developed three shoulder features after 3 h (orange trace). Ice crystallization is generally associated with the splitting and sharpening of the O–H stretching band, and it was deconvoluted to three distinct features at 3164, 3284, and 3395 cm⁻¹, corresponding to the ν₁ in-phase band, the ν₂ TO band, and the overlapped ν₃ LO and ν₁ out-of-phase bands of ice I冕. Isotopic experiments with an acetone:D₂O (1:1) system also led to the formation of cubic D₂O ice due to the dissociation of acetone hydrate (not shown). Note that, in similar studies at 130 K, the ice I冕 conversion took 9 h, whereas the ice I冕 was not observed at 120 K, even after 48 h. The thermal motion of acetone molecules is likely to be responsible for the formation of acetone hydrate and subsequently ice I冕. In a similar study, the dissociation of acetaldehyde hydrate leads to the formation of ice I冕.

We have also provided more direct structural evidence to support the claim of forming ice I冕 via hydrate dissociation. Figure 5 shows the time-dependent reflection high-energy electron diffraction (RHEED) images of acetone:H₂O (1:1) at different temperatures. In Figure 5a, the RHEED image does not show any pattern, indicating the amorphous nature of the mixture. However, several diffraction rings were observed after 5 h (Figure 5b). Here, most of the acetone molecules desorb from the mixture, as indicated by the IR spectra. Note that these diffraction patterns originate from the ice I冕 and match the earlier diffraction studies of ice I冕. Time-dependent RHEED studies at 130 K showed an ice I冕 pattern after 12 h (Figure 5d). However, the diffraction patterns were not observed at 120 K, even after 24 h (Figure 5e,f). These observations support the RAIR spectral interpretation, which suggests that ice I冕 was formed only through the dissociation of acetone hydrate.

### 4.2. Formation of Hexagonal Ice (Ice h) from CH

Among several polymorphs of ice, hexagonal ice (ice h) is the most common, and it occurs naturally on earth. However, the formation of ice h from CH precursors was not studied. We found that formaldehyde hydrate dissociated to form ice h under UHV at 130–135 K. Figure 6a,b shows the time-dependent RAIR spectra of the codeposited formaldehyde–H₂O (1:1) film at 135 K in the C≡O and O–H stretching regions, respectively. The IR feature at 1733 cm⁻¹ is attributed to the C≡O stretching band of formaldehyde hydrate (Figure 6a). This assignment was performed by comparing formaldehyde vapor (1746 cm⁻¹) and condensed phase (1723 cm⁻¹) frequencies. The hydrate phase frequencies fall in between them. Besides, the O–H stretching region showed a profound change after 5 h with the disappearance of the formaldehyde hydrate IR peak. This O–H stretching band (blue trace) is the characteristic feature of ice I冕 as confirmed by comparing pure crystalline ice I冕 spectra, recorded independently. The control study also suggested that water by itself cannot form ice I冕 at 135 K in the absence of formaldehyde hydrate since its usual crystallization temperature is 150–155 K under UHV. The existence of formalddehyde and water in space suggests the possibility to form hydrates and their subsequent transformation to ice I冕, which constitutes a mechanistic route for its formation in ISM.

### 5. Structural Dynamics of Clathrate Hydrates

The structural dynamics in CHs are important to study, which reveals that the reorientation of water and the diffusion of guest molecules are the driving forces for these structures. Furthermore, the presence of a second guest species provides extra thermodynamic stability to the hydrate framework, and they are termed binary CHs. THF hydrate is known to be a stabilizer for such binary CHs. THF being a larger molecule occupies the larger cages (5–6), whereas the other guest species occupy the smaller ones (5–5). Here, we have studied the formation of THF hydrate by codepositing a THF:H₂O mixture (1:5) and annealing it to 130 K. Figure 7a,b shows the time-dependent spectra of the same system in the asymmetric C≡O and O–H stretching regions. The peaks at 1034 and 1053 cm⁻¹ were assigned to THF trapped in different sites of ASW, whereas the other peak at 1074 cm⁻¹ is the characteristic feature of THF hydrate. Continuous...
annealing (6 h) of the system increased the intensity of the THF hydrate peak and decreased the intensity of the other two peaks. The 1074 cm\(^{-1}\) peak serves as a convenient indicator of THF hydrate since it lies well above the IR peak positions of other likely condensed phases of THF. In Figure 7b, the O–H stretching band is also red-shifted with time, which was an indication of ice crystallization. Results suggested that the gradual transformation of THF hydrate also changes the structure of ice from amorphous to crystalline.\(^4\) Furthermore, the crystallization kinetics suggested that the formation of THF hydrate was a diffusion-controlled process.\(^4\) In addition, this study has the potential to explore a certain number of binary CHs. To explore this possibility, we conducted a study with a CO\(_2\)@(THF + H\(_2\)O; 1:5) composite ice film, where a THF + water mixture was sequentially deposited on a predeposited CO\(_2\) film and this system was annealed at 130 K for 6 h.\(^57\) Figure 7c,d shows the corresponding time-dependent RAIR spectra in the C=O and C–O antisymmetric stretching regions of CO\(_2\) and THF, respectively. The IR peaks at 2352, 2346, and 2340 cm\(^{-1}\) were assigned to CO\(_2\) in the ASW matrix and that CO\(_2\) in S\(^{12}\) cages remained mostly unperturbed.\(^57\) In Figure 7c, a new peak arose at 1074 cm\(^{-1}\) while the peaks at 1054 and 1032 cm\(^{-1}\) decreased with time, as shown in Figure 7c,d. The peak at 1074 cm\(^{-1}\) was the characteristic peak for THF hydrate encased in S\(^{12}\) cages, whereas the peaks at 1054 and 1032 cm\(^{-1}\) were assigned to THF trapped in ASW pores.\(^4,27,50\) The formation of stable binary THF-CO\(_2\) hydrate is a possibility, which is confirmed by the IR features of individual guest species (2346 and 1074 cm\(^{-1}\) of CO\(_2\) and THF), and computationally optimized structures also supported this observation.\(^57\) The higher mobility of CO\(_2\) in comparison to THF favors the formation of CO\(_2\) hydrate, kinetically. However, upon annealing at higher temperatures for a longer time, the formation of THF hydrate is triggered. The larger size of THF makes it a preferred guest over CO\(_2\) in large (S\(^{12}\)4) cages. This leads to partial dissociation of CO\(_2\) cages and rearrangement of the hydrate structure resulting in the increase in CO\(_2\) in the ASW matrix, as shown schematically in Figure 7e.\(^57\)

From the foregoing, it is evident that several CHs can be formed under UHV if subjected to certain key experimental conditions such as the annealing temperature, time, and stoichiometric ratio. The extreme low-temperature conditions in ISM result in a mass transfer limitation, primarily due to limited natural convection (and mixing of species), which may
hinder the nucleation process of CHs. Achieving sufficient molecular mobility is key to forming the hydrates, which is obtained by prolonged annealing of the system near their respective desorption temperatures, irrespective of the type of guest. As per our understanding based on the experimental results, the mechanism of CH formation involves the solvation or mixing of guest molecules with water molecules as the first step. It is followed by the formation of hydrate cages around the solvated guest molecules in a stochastic manner. On the other hand, the formation of different crystalline forms of ice upon dissociation of hydrate is possibly due to the orientational defects (Bjerrum defects). However, these defect-induced structural changes are only partially understood, and computational studies involving MD simulations on the formation and dissociation behavior of CHs may provide additional insights.

6. PHOTOCHEMICAL EFFECTS ON CLATHRATE HYDRATES

Light irradiation is known to initiate photochemistry in ISM ices, which is suggested to be a path to chemical complexity in space. These experiments involve single, binary, or multi-component ice mixtures with a range of radiation (MeV electrons/protons to high-energy UV photons). Upon radiation exposure, water–ice dissociates to produce highly reactive radicals and initiates radical chemistry. However, high diffusion barriers of radicals in ice present restricted photochemistry. On the contrary, CHs were shown to act as a host for unique hydrogen transfer reactions involving radicals. Furthermore, the CH cages were demonstrated to store...
stabilize the free radicals under high-pressure conditions. Given this, the photochemistry of CHs would be interesting under UHV and cryogenic conditions, where the guest molecule AB could dissociate to form A and B radicals. Depending on the size and kinetic energy, the fate of these radicals may vary such as recombination, stabilization upon entrapment, movement to the adjacent cage, and reaction with AB, A, or B.

So far, ice photochemical experiments resulted in racemic mixtures of the photolyzed products and not the homochiral form found on earth, which remains an unsolved puzzle in chemistry. The entrapped species in CH cages may interact with radiation asymmetrically to produce either left- or right-handed molecules. The proposed study can shed light on the origin of enantiomeric excess on earth.

7. FUTURE PERSPECTIVES

In this Account, the investigation of different CHs and their several important aspects such as nucleation conditions, mechanism, stability, and transformation to other ice structures are presented in the context of interstellar processes. The results suggested that the temperature and annealing time are crucial parameters in deciding the formation and structural changes of CHs. The key outcome of these studies is that it provides conclusive evidence that several CHs are formed at extremely low pressures and temperatures, conditions analogous to the ISM. This finding may open several possibilities for future explorations. While the formation of CHs of simple molecules such as methane, ethane, and carbon dioxide in interstellar-like environments is already established in the current study, many other guest molecules such as H₂, CO, N₂O, O₂, NH₃, and C₂H₂ are known to form CHs, which are also found in space or the ISM along with water in solid form. Therefore, we believe that this Account will provide a direction to investigate several other CHs under suitable conditions. Furthermore, the fate of CHs upon their dissociation could be an exciting area to explore since CHs can transform into different polymorphs of ice, as highlighted in this Account. The nucleation mechanism, stability, and structure of several polymorphs of ice are intriguing. Formation and detailed studies of binary CHs under interstellar-like conditions would be another direction. Our studies have provided an early hint that binary CHs could be formed in the presence of appropriate stabilizers such as THF. In addition, these binary CHs can be utilized as precursors for interguest chemical interactions under extreme conditions of ISM such as UV and particle impact.

Apart from these possibilities, the ultimate goal of the astrochemistry community is to understand the origin of life. Understanding the chemical evolution of simple molecules to COMs has been a long-standing question. CHs can be an ideal precursor to trap several simple guest species that can undergo chemical reactions. The presence of cosmic radiation could be the driving force in such exotic environments. More experimental studies in this direction are necessary for a complete understanding of the phenomena involved. The utilization of the direct structural interpretation of CHs through extensive diffraction data under such extreme conditions will provide important insights. There is also a need to understand the dynamics of the formation of CHs in UHV starting from ice mixtures, which will require detailed computational studies. Despite these challenges, we hope that the present investigations have provided new insights into the fascinating area of CHs and suggest exciting new directions for the future.

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Notes

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REFERENCES


