Clathrate hydrates in interstellar environment

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Clathrate hydrates (CHs) are ubiquitous in earth under high-pressure conditions, but their existence in the interstellar medium (ISM) remains unknown. Here, we report experimental observations of the formation of methane and carbon dioxide hydrates in an environment analogous to ISM. Thermal treatment of solid methane and carbon dioxide–water mixture in ultrahigh vacuum of the order of 10^{-6} mbar for extended periods led to the formation of CH hydrates at 30 and 10 K, respectively. High molecular mobility and H bonding play important roles in the entrapment of gases in the in situ formed 12 CH cages. This finding implies that CHs can exist in extreme low-pressure environments present in the ISM. These hydrates in ISM, subjected to various chemical processes, may act as sources for relevant prebiotic molecules.

Significance

Formation of clathrate hydrate (CH) requires high pressures and moderate temperatures, which enable their existence in marine sediments and the permafrost region of earth. The presence of CHs in interstellar medium (ISM) is still in question due to the extreme high vacuum and ultracold conditions present there. Here, we conclusively identified methane and carbon dioxide hydrates in conditions analogous to ISM. We found that molecular mobility and interactions play crucial roles in the formation of CHs, even though there is no external pressure to force cage formation. Various chemical processes on these hydrates in ISM may lead to relevant prebiotic molecules.


The authors declare no conflict of interest.

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like gaseous CH$_4$ as expected. It is known that vibrational frequency of free guest molecules in CH fall in between their vapor and condensed phase frequencies (14). The IR peak was deconvoluted to show the actual concentration of CH$_4$ trapped inside the hydrate cages and pores of amorphous solid water (ASW). The peak widths were calculated upon deconvolution, and the values were 14.1 and 4.2 cm$^{-1}$ for the peaks at 3,009 and 3,017 cm$^{-1}$, respectively. Note the reduced width (4.2) of 3,017 cm$^{-1}$ for the hydrate peak, characteristic of a unique structure. Taking the IR intensity, the extent of CH$_4$ in the hydrate form was estimated to be 12.71% of the total CH$_4$ at this condition. As the annealing temperature is close to that of desorption, about 6/7 of the adsorbed CH$_4$ desorbs during annealing. Furthermore, we confirmed the formation of CH$_4$ hydrate by quantum chemical calculations. Density functional theory (DFT) calculations of the CH$_4$ hydrate revealed that the small cage (5$^{12}$) as shown in Fig. 1C is favorable to form at this particular condition. Our computationally determined shift in the C–H antisymmetric mode during hydrate formation closely matches with the experimental value (SI Appendix, Table S1). A microsecond molecular dynamics simulation of CH$_4$ hydrate nucleation predicts preferential formation of smaller 5$^{12}$ cages in the initial stages of CH$_4$ hydrate nucleation, supporting our observation (2).

Keeping the CH$_4$ and water ice mixture at 30 K for more than 25 h results in the formation of CH$_4$ hydrate. The long experimental time scale and the temperature (30 K), very near to the desorption temperature of CH$_4$, are two crucial factors for the formation of CH$_4$ hydrate under UHV conditions. We propose that prolonged subjugation of CH$_4$–water mixture at 30 K enhances the mobility of CH$_4$ molecules and leads to its insertion within the cages formed simultaneously. In a time-dependent study of 150 MLs of pure solid CH$_4$ at 25 K (SI Appendix, Fig. S2), the additional peak (3,017 cm$^{-1}$) was not observed. This is again a piece of evidence that the above peak is due to CH$_4$ hydrate.

To support our claim of the formation of CH in ISM, we have chosen a more stable hydrate, namely that of CO$_2$, which is already known to form CH at 120 K and 10$^{-6}$ torr (12). Fig. 24 represents the temperature-dependent RAIR spectra of 300 MLs of the codeposited mixture (1:5 ratio) of CO$_2$ and water in the C = O antisymmetric stretching region. The figure shows two IR peaks for the C = O antisymmetric stretching band of solid CO$_2$ at 10 K. The peak at 2,353 cm$^{-1}$ is attributed to the untrapped CO$_2$ that exists...
outside of the CH cage, and in the amorphous pores of water ice. The other peak, positioned at 2,346 cm\(^{-1}\), is due to the CO\(_2\) entrapped in the CH cage (15, 16). Now, as the system was annealed further to 50 K (heating rate = \(2\) K min\(^{-1}\)), the intensity of the CO\(_2\) hydrate peak (2,346 cm\(^{-1}\)) increased and that of the free CO\(_2\) peak (2,353 cm\(^{-1}\)) decreased. At 120 K, the untrapped CO\(_2\) peak vanished completely and only the CO\(_2\) hydrate peak remained. It indicates that the annealing of CO\(_2\) mixed ice leads to the gradual formation of CO\(_2\) hydrate and the transformation is complete at 120 K. Furthermore, no change in CO\(_2\) hydrate peak position (2,346 cm\(^{-1}\)) was observed when the system was kept at 120 K for 6 h (Fig. 2A). This confirms that the CO\(_2\) hydrate is quite stable in these analogous astrochemical conditions. It is also clear that CO\(_2\) hydrate forms even at 10 K during deposition itself.

The stoichiometric ratio of water and guest molecules is an essential aspect of controlling the formation of CH (12). The ideal ratio of water and guest molecules is 20:1 for CH\(_3\)OH hydrate formed at 130 K and at 10\(^{-6}\) torr pressure (12). Fig. 2B shows the comparative formation of CO\(_2\) hydrate at different ratios of CO\(_2\):H\(_2\)O at 10 K under UHV. The figure clearly indicates that the intensity of 2,346 cm\(^{-1}\) peak is maximum for a 1:90 mixture compared with the other ratios. This suggests the optimum ratio needed for CO\(_2\) hydrate formation at 10 K, which is a very diluted mixed ice. The shoulder at 2,353 cm\(^{-1}\) vanished upon keeping the ice at 10 K for over 48 h as shown in Fig. 2B, suggesting that all of the remaining free CO\(_2\) forms hydrate structure over time.

We confirmed the formation of CO\(_2\) hydrate by quantum chemical calculations. These calculations revealed that the small cage (512), as shown in Fig. 2C, is favorable to form. Our computationally determined shift in the C = O antisymmetric mode closely matches with the experimental vibrational shift upon hydrate formation. Here, CO\(_2\) is interacting with the water cage through hydrogen bonding, and consequently, there is a red shift. This result agrees well with the experimental shift (SI Appendix, Table S1). Other possible cages computed (51262 and 51264) have reduced or opposite shift, respectively (SI Appendix, Table S1). In SI Appendix, Table S2, we have presented the coordinates of optimized geometries of CH\(_4\) and CO\(_2\) in 512, 51262, and 51264 CH cages. In SI Appendix, Table S3, we have added the harmonic frequencies calculated for different cages of CH\(_4\) CH and CO\(_2\) CH.

The rapid formation of CO\(_2\) hydrate compared with the slow kinetics seen for CH\(_4\) hydrate is because of the induced polarity of CO\(_2\). Nucleation mechanism of CH formation varies for different guest molecules and can depend on their chemical nature (17). During the nucleation of CO\(_2\) hydrate structure, it interacts...
with water through stronger interaction, whereas CH₄ is unable to interact similarly. We extended the analysis using Bader’s theory of atoms in molecules (AIM) to confirm the nature of interaction of guest molecules with hydrate cages. The electron density \( \rho(r_C) \) values obtained for the critical points between a particular atom of the guest species and the hydrate cage along with the corresponding Laplacian of the electron density \( \nabla^2 \rho(r_C) \) are listed in SI Appendix, Table S4. The higher value of electron density \( \rho(r_C) \) for the critical point between the O atom of CO₂ and the hydrate cage (0.01563 a.u.) compared with that between the H atom of CH₄ (0.00598 a.u.) and the hydrate cage suggests that the interaction for CO₂ is stronger than that for methane.

In the previous experiments, codeposition of CO₂ and water results in CH. Sequential deposition was also carried out. Annealing of this sequentially deposited system, CO₂@H₂O (1:5 ratio), did not result in CO₂ hydrate and the 2,346 cm \(^{-1} \) peak was not observed (SI Appendix, Fig. S3). Here, the peak at 2,381 cm \(^{-1} \) is attributed to pure multilayer CO₂. This phenomenon strongly supports the fact that proper mixing of water and CO₂ is a crucial step for the formation of CO₂ hydrate. The codeposition method allows better mixing of CO₂ molecules with water, whereas sequential deposition does not. Sequential deposition of water over CO₂ may result in diffusional mixing, but this does not lead to the formation of CH.

About 1% of \(^{13}\)CO₂ is present along with \(^{12}\)CO₂ naturally as shown (SI Appendix, Fig. S4). During the \(^{12}\)CO₂ hydrate experiment, \(^{13}\)CO₂ also shows CH upon annealing to 120 K. Temperature-dependent RAIR spectra in the \(^{13}\)C = O antisymmetric stretching region (SI Appendix, Fig. S5), where the 2,282 cm \(^{-1} \) peak is due to untrapped \(^{13}\)CO₂ and that at 2,278 cm \(^{-1} \) is due to \(^{13}\)CO₂ hydrate (15).

The formation of CHs in ISM condition is further confirmed by temperature programmed desorption-mass spectrometry (TPD-MS). The trapped guest molecules within ASW are released when amorphous to crystalline ice transition occurs at 140 K. Fig. 3A represents the comparative TPD spectra before and after the formation of CH₄ hydrate. The spectra correspond to CH₄ desorption and were monitored using the intensity of CH₃⁺ alone. Peaks at 38 and 46 K correspond to multilayer CH₄ and CH₄ trapped in ASW (CH₄·ASW), respectively. These TPD peaks are assigned by a control study as shown (SI Appendix, Fig. S6). The CH₄ hydrate was formed by annealing a codeposited mixture at 30 K for 25 h, and during this course, most of the free CH₄ got desorbed, as observed from TPD. Desorption of CH₄ in trapped ASW got shifted to 53 K after the formation of CH. The abrupt release of trapped gases from ASW at 140 K is termed as

![Fig. 3](image-url)

**Fig. 3.** TPD mass spectra of 300 MLs of codeposited ice systems at different ratio (heating rate = 30 K · min \(^{-1} \)). Here, the intensities of CH₃⁺ (m/z = 15), and CO₂⁺ (m/z = 44) are plotted. (A) Desorption of CH₄ after hydrate formation (magenta line) and before hydrate formation (blue line). MV peaks are shown in the Insets. *, peaks are attributed to desorption due to structural transitions of ASW upon annealing. (B) Desorption of CO₂ after hydrate formation at different ratios, as indicated. #, the peak is due to the predissociation of CO₂ hydrate cage. (C) Schematic representation of MV upon crystallization of ice.
molecular volcano (MV) (18, 19). The intensity of MV peak (at 140 K) increases, upon the formation of CH₄ hydrate. Before the formation of CH₄ hydrate, the MV peak is due to the trapped CH₄ in ASW. The reason for the enhancement of MV peak intensity is the simultaneous release of trapped CH₄ from ASW pores as well as from the CH₄ hydrate cage (Fig. 3C). Note that the amount of gases deposited is the same in both the cases. Slight distortion in the MV peak is attributed to the modification of ASW pores due to CH formation (Fig. 3D). The amount of desorption due to CH is estimated to be 14.53% of the total CH₄ at this condition, and it is correlated to the amount of CH calculated from the IR data (Fig. 1B).

In Fig. 3B, we compared the TPD spectra of 300 MLs of CO₂+H₂O at two ratios, 1:1 and 1:5, which were deposited at 10 K. Then, these two systems were annealed at 120 K for the complete formation of CO₂ hydrate. After that, they were cooled back to 10 K, and TPD mass spectra were taken. The heating rate for TPD was 30 K·min⁻¹. The peak at 140 K corresponds to MV of CO₂. Fig. 3B shows that the intensity of MV increased as the ratio of CO₂ and H₂O was changed from 1:1 to 1:5. Taking the area under the MV peaks, the amount of CH formed was found 1.7 times higher for (1:5) than the former. As previously explained, the enhancement of CO₂ hydrate is greater for the latter ratio (Fig. 2). Here again, the enhancement agrees with the IR data. Additional desorption of CH₄ and CO₂ above this temperature suggest that the hydrates have been decomposed.

Conclusion
We have shown that CHs can form in UHV and they can exist in the ISM conditions down to 10 K and 10⁻¹⁰ mbar. The anomalous eruption of volatile gases in ISM could be explained by the existence of hydrates. Enclathration of these gases and additional processing (e.g., irradiation, heating, etc.) may result in complex organic or prebiotic molecules. We believe that the present report may have an impact on both astronomy and chemistry.

Materials and Methods

Experimental Setup. Experiments were conducted in an ultrahigh vacuum instrument (base pressure 10⁻¹⁰ mbar), which was described elsewhere (20, 21). Briefly, the instrument consists of a UHV chamber made of stainless steel, equipped with RAIR spectroscopy and TPD mass spectrometry. The spectrometer can also perform low energy ion scattering and secondary ion mass spectrometry, which have not been used in the present work (20). Vacuum of the order of 10⁻¹⁰ mbar is an essential condition for simulating the condition of ISM. Vacuum was maintained by three oil-free Turbo molecular pumps backed by diaphragm pumps (Pfeiffer Vacuum). The system has a collective pumping speed of 400 Ls. The UHV system is fully covered with a heating jacket, which allows an easy bake out over the weekend. The pressure of the experimental chamber is monitored by a Bayard-Alpert gauge (Pfeiffer Vacuum), controlled by a “MaxiGauge” vacuum gauge controller (Pfeiffer, Model TPG 256 AO).

A thin film of ice was grown on top of a Ru(0001) single crystal that was mounted on a copper holder, which in turn was attached at the tip of a closed cycle helium cryostat (Cohlection Devices). The substrate temperature could be controlled from 8 to 1,000 K. Comprehensive heat shielding and excellent thermal contact between the substrate holder and the cryofinger allowed us to achieve 8 K in 2 h. For the present study, the temperature was measured by a thermocouple sensor attached to the substrate. Repeated heating to 300 K before vapor deposition ensured surface cleanliness, adequate for the present experiments. Temperature ramping was controlled and monitored by a temperature controller (Lakeshore 336) (20).

Sample Preparation. For the formation of methane hydrate, ~99.99% pure methane gas, purchased from Rana Industrial Gases & Products, was used. The gas lines were connected to the experimental chamber through a high-purity glass sample line through which the flow rate or deposition pressure of different gases was controlled. These two deposition tubes or gas lines were directed to the center of the substrate. Out of the two sample inlet lines, one was used exclusively for methane or carbon dioxide while the other line was used exclusively for water vapor deposition. Here, Millipore water (H₂O of 18.2 MΩ resistivity), taken in a test tube, connected to the sample line through a glass-to-metal seal was used for the experiment. The Millipore water was further purified through several freeze-pump-thaw cycles before introduction into the UHV chamber. During the exposure of different samples into the UHV chamber, mass spectra were recorded with a residual gas analyzer (RGA) attached near to the sample inlet line. Recorded mass spectra were used as an indication of the purity of the samples as well as to measure the ratio of the mixtures. The ratio of the mixed ice was achieved by using the proper adjustment of flow or inlet pressure of the gases by regulating the leak valves. The substrate was kept at a perpendicular position for the uniform growth of ice. Here, most of the experiments were performed using 300 MLs coverage of the mixed ice. One point to be noted is that all of the experiments were performed under multilayer deposition conditions, and therefore, the substrate does not play any significant role in the formation of hydrate. The deposition of molecular solids was controlled through leak valves, and ML coverage was calculated (18, 22) assuming that 1.33 × 10⁻¹⁰ mbar·s = 1 ML, which was estimated to contain ~1.1 × 10¹⁵ molecules cm⁻². Surface coverages mentioned were quantitative by following a similar deposition method adopted elsewhere (23). The inlet pressure during the sample deposition was decided based on the coverage desired at the time of the experiment.

Typical Experimental Protocol. For the deposition of 300 MLs of 1:1 mixed methane and CO₂, the chamber was backfilled at a total pressure of ~10⁻⁷ mbar (where methane pressure was 2.5 × 10⁻⁹ mbar and water pressure was 2.5 × 10⁻⁷ mbar) and the mixture was exposed to the surface for 10 min. Evacuation of residual water from the experimental chamber is one of the most common issues with UHV experiments, particularly when we deposit large amounts of water. After deposition, we waited for a few minutes to reach the background pressure before starting the spectroscopic measurements. Periodic bake out of the chamber during weekends ensures the cleanliness of the chamber.

This 1:1 mixed methane and ice was slowly (heating rate = 2 K·min⁻¹) heated to 30 K, near the desorption temperature of methane. At this temperature, most of the methane sublimed, which was observed in the mass spectra recorded by the residual gas analyzer. After that, the remaining mixed ice was maintained at 30 K for over 25 h. The ice sample was constantly monitored by IR spectroscopy. In other words, time-dependent RAIRS were recorded over a period of 25 h. By using these measurements, a few monolayers of additional water could be deposited but this is rather negligible to be reflected in the spectra. Variation of a few monolayers in coverage does not change the observed phenomena. During the time-dependent measurements, we maintained identical conditions from the beginning to the end. The position of the substrate, the external IR detector (mercury cadmium telluride, MCT), and the environment (dry N₂) in the IR spectrometer were kept constant throughout the experiment. A similar RAIRS study was carried out at 10 and 30 K also, and the spectra were collected for over 25 h as a separate set of experiments. IR exposure over extended periods did not have an effect on CH formation as revealed by studies at lower temperatures.

For the CO₂ hydrate study, 300 MLs of mixed ice was made by the codeposition of a mixture of CO₂+H₂O at 10 K. Different ratios (1:5, 1:10, and 1:90) of CO₂+H₂O were used. For each of the ratios, the total inlet pressure was kept at ~5 × 10⁻⁸ mbar, whereas the inlet pressures of CO₂ and water were varied according to the desired ratio. For the temperature-dependent measurements, after deposition of 1.5 ratio of CO₂+H₂O at 10 K, the sample was slowly heated (heating rate = 2 K·min⁻¹) up to 160 K. In another set of experiments, sequential deposition of CO₂ and water was carried out, where at first 150 MLs of CO₂ were deposited, which was followed by the deposition of 150 MLs of water at 10 K. By this way, we generated a sequentially deposited (CO₂+H₂O) film of equal coverage. A similar temperature-dependent measurement was carried out as described before, with this sequentially deposited film to observe the formation of CO₂ CH.

RAIRS Setup. RAIIR 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 IR beam), attached to the vacuum chamber. The reflected IR beam from the substrate was focused using another gold-plated mirror to a liquid N₂ cooled external MCT IR detector. The spectra were collected in the 4,000–550 cm⁻¹ range with 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 N₂.
TPD-MS Setup. The clathrate hydrates were further characterized by TPD-MS analysis. For this, after ice deposition or clathrate hydrate formation (by following the method described earlier), the substrate was moved to a fixed position by using the sample manipulator to ensure that the surface is close to the mass spectrometer inlet. During TPD-MS measurements, the substrate was heated at a constant heating rate (30 K min⁻¹). Suitable mass of the desorbed species was selected by the RGA and the intensity of the desorbed species was plotted as a function of substrate temperature. Mass spectrometers were supplied by Extrel CMS (20). For TPD, the inlet of the mass spectrometer was positioned 50 mm from the center of the Ru substrate.

Computational Details. We examined the stability of clathrate hydrate cages and their CO₂, CH₄ inclusion complexes computationally. All of the considered cages of clathrate hydrates have been fully optimized at the B3LYP/6-311++G(d, p) level of theory using the Gaussian 09 program package (24). Frequency calculations characterize the obtained stationary points as minima on the potential energy surface. We sequentially added CO₂ and CH₄ molecules in 5₁², 5₁⁴₂, and 5₁⁶₄ clathrate hydrate cages and probed their cage occupancy. In general, the optimizations of clathrate hydrate cages were found to be quite challenging with the Gaussian programs. Normally, most optimizations of clathrate cages take a large number of steps and it was difficult to reach convergence. The B3LYP/6-311++G (d, p) level of theory was found to be reasonable for optimizations of clathrate hydrates and various other water clusters (14). The quantum theory of atoms in molecules methodology (25) was capable of revealing bonding interactions between individual functional groups and atoms in a molecule by the electron density distribution analysis. All possible cages were considered in the present study. It was found that the 5₁² clathrate hydrate cage was more stable; stability also depended on the size of the guest molecule. These results were also compared with the computational studies reported (14).

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