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In their letter, Choukroun et al. (1) caution against our results (2) as definitive evidence for the formation of clathrate hydrates (CHs) in the interstellar medium (ISM). We show the emergence of an infrared (IR) feature at 3,017 cm⁻¹ in vapor-deposited CH₄-water mixture upon ~25 h of annealing, at 30 K in ultrahigh vacuum (2). We attribute the blue-shifted feature (with respect to the 3,009 cm^{-1} peak of condensed CH₄) to CH_4 hydrate of the 5¹² structure. Dartois et al. (3) also suggested a blue shift for CH_4 trapped in the 5¹² cage. A microsecond molecular dynamics simulation of CH₄ hydrate (4) predicted preferential formation of 5¹² cages during CH nucleation. In our experiment (2), the trapped CH₄ desorbs along with the collapse of 5¹² cages, increasing the intensity of molecular volcano of CH₄ at ~140 K in temperature programmed desorption (TPD). This is unexpected without CH being present. Thus, IR results, along with TPD and computations, support CH formation (2).

Because CO₂ forms CH at 120 K, confirmed by IR (5), we performed thermal annealing of the CO₂–ice mixture, and the characteristic 2,346 cm⁻¹ peak emerged corresponding to CO₂ trapped in the 5¹² cage (2). Devlin et al. (6) reported the formation of pure CO₂ CH by vapor deposition under vacuum, and the ν_3 (CO₂) due to 5¹² occupancy was seen at 2,346 cm⁻¹. In our work (2), only the 5¹² cage was formed as the 2,346 cm⁻¹ peak alone was observed, and not the double peak feature due to the s-I structure (6).

 CH_3OH is a CH inhibitor (7), although it forms CH under certain conditions (8). Blake et al. (5) used CO_2 as a local IR probe to sense CH_3OH hydrate. Additives

such as CH₃OH, tetrahydrofuran, etc., alter the rate of hydrate formation. However, our studies did not explore this aspect. It is unlikely that the presence of CH₃OH is absolutely necessary for the formation of CO_2 hydrate.

It is known that CO₂ interacts chemically with the 5¹² cage (9). However, this interaction is weak, although stronger than in CH₄ hydrate. We studied the nature of this interaction using atoms-in-molecules analysis, which confirmed it to be H bonding (2). The small cavity size (3.95 Å) of the 5¹² cage (7), comparable to the van der Waals diameter (2.32 Å) of CO₂, may be enabling this (10). However, this interaction is not strong enough to distort the overall structure of the host lattice (10). When we correlated the experimental shifts with computed values, the influence of neighboring cages on an isolated cage was not considered. Moreover, we did not make a comparison with the 2,353 cm⁻¹ peak, since CO₂ exhibits weak interaction with water of the ice matrix, while in CH₄, it is negligible.

The unit cells of hydrates are complex, and the water molecules reside in several inequivalent sites (11). For this reason, the O–H stretching band of the host ice network is broadened (11).

Ongoing investigations using other guest molecules by a similar method further support the existence of CHs under these conditions.

Although our experiments suggest the existence of CHs (primarily 5¹² cages) in ISM, further investigations with longer annealing time, supported by additional spectroscopic and diffraction data, are welcome to understand more details.

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