

REPLY TO CHOUKROUN ET AL.:

IR and TPD data suggest the formation of clathrate hydrates in laboratory experiments simulating ISM

Jyotirmoy Ghosh^a, Rabin Rajan J. Methikkalam^{a,1}, Radha Gobinda Bhui^{a,2}, Gopi Ragupathy^a, Nilesh Choudhary^b, Rajnish Kumar^{b,3}, and Thalappil Pradeep^{a,3}

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 $3,017\text{ cm}^{-1}$ in vapor-deposited CH_4 -water mixture upon ~ 25 h of annealing, at 30 K in ultrahigh vacuum (2). We attribute the blue-shifted feature (with respect to the $3,009\text{ cm}^{-1}$ peak of condensed CH_4) to CH_4 hydrate of the 5^{12} structure. Dartois et al. (3) also suggested a blue shift for CH_4 trapped in the 5^{12} cage. A microsecond molecular dynamics simulation of CH_4 hydrate (4) predicted preferential formation of 5^{12} cages during CH nucleation. In our experiment (2), the trapped CH_4 desorbs along with the collapse of 5^{12} cages, increasing the intensity of molecular volcano of CH_4 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 CO_2 forms CH at 120 K, confirmed by IR (5), we performed thermal annealing of the CO_2 -ice mixture, and the characteristic $2,346\text{ cm}^{-1}$ peak emerged corresponding to CO_2 trapped in the 5^{12} cage (2). Devlin et al. (6) reported the formation of pure CO_2 CH by vapor deposition under vacuum, and the $\nu_3(\text{CO}_2)$ due to 5^{12} occupancy was seen at $2,346\text{ cm}^{-1}$. In our work (2), only the 5^{12} cage was formed as the $2,346\text{ cm}^{-1}$ peak alone was observed, and not the double peak feature due to the s-l 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 CH_3OH , tetrahydrofuran, etc., alter the rate of hydrate formation. However, our studies did not explore this aspect. It is unlikely that the presence of CH_3OH is absolutely necessary for the formation of CO_2 hydrate.

It is known that CO_2 interacts chemically with the 5^{12} cage (9). However, this interaction is weak, although stronger than in CH_4 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 \AA) of the 5^{12} cage (7), comparable to the van der Waals diameter (2.32 \AA) of CO_2 , 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 $2,353\text{ cm}^{-1}$ peak, since CO_2 exhibits weak interaction with water of the ice matrix, while in CH_4 , 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 5^{12} cages) in ISM, further investigations with longer annealing time, supported by additional spectroscopic and diffraction data, are welcome to understand more details.

^aDepartment of Science and Technology (DST) Unit of Nanoscience and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India; and ^bDepartment of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600036, India

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¹Present address: Institute of Chemistry, The Hebrew University, Jerusalem 91904, Israel.

²Present address: Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany.

³To whom correspondence may be addressed. Email: rajnish@iitm.ac.in or pradeep@iitm.ac.in.

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