



REPLY TO CHOUKROUN ET AL.:

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

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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  $3,017\text{ cm}^{-1}$  in vapor-deposited  $\text{CH}_4$ -water mixture upon  $\sim 25$  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  $\text{CH}_4$ ) to  $\text{CH}_4$  hydrate of the  $5^{12}$  structure. Dartois et al. (3) also suggested a blue shift for  $\text{CH}_4$  trapped in the  $5^{12}$  cage. A microsecond molecular dynamics simulation of  $\text{CH}_4$  hydrate (4) predicted preferential formation of  $5^{12}$  cages during CH nucleation. In our experiment (2), the trapped  $\text{CH}_4$  desorbs along with the collapse of  $5^{12}$  cages, increasing the intensity of molecular volcano of  $\text{CH}_4$  at  $\sim 140$  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  $\text{CO}_2$  forms CH at 120 K, confirmed by IR (5), we performed thermal annealing of the  $\text{CO}_2$ -ice mixture, and the characteristic  $2,346\text{ cm}^{-1}$  peak emerged corresponding to  $\text{CO}_2$  trapped in the  $5^{12}$  cage (2). Devlin et al. (6) reported the formation of pure  $\text{CO}_2$  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).

$\text{CH}_3\text{OH}$  is a CH inhibitor (7), although it forms CH under certain conditions (8). Blake et al. (5) used  $\text{CO}_2$  as a local IR probe to sense  $\text{CH}_3\text{OH}$  hydrate. Additives

such as  $\text{CH}_3\text{OH}$ , tetrahydrofuran, etc., alter the rate of hydrate formation. However, our studies did not explore this aspect. It is unlikely that the presence of  $\text{CH}_3\text{OH}$  is absolutely necessary for the formation of  $\text{CO}_2$  hydrate.

It is known that  $\text{CO}_2$  interacts chemically with the  $5^{12}$  cage (9). However, this interaction is weak, although stronger than in  $\text{CH}_4$  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 ( $3.95\text{ \AA}$ ) of the  $5^{12}$  cage (7), comparable to the van der Waals diameter ( $2.32\text{ \AA}$ ) of  $\text{CO}_2$ , 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  $\text{CO}_2$  exhibits weak interaction with water of the ice matrix, while in  $\text{CH}_4$ , 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.

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The authors declare no conflict of interest.

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