DFT modeling of CO clathrate hydrates

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Clathrate hydrates (gas hydrates) are nanoporous crystalline solids composed of hydrogen-bonded water molecules forming cages within which gaseous molecules are encapsulated (see Fig. 1). Naturally present on Earth, gas hydrates can be observed on permafrost regions and on oceans floors, but also on comets and planets of the Solar System [1]. This natural occurrence makes them relevant for many geophysical and astrophysical applications.

Carbon monoxide (CO) hydrate might be considered an important component of the carbon cycle in the solar system since CO gas is one of the predominant forms of carbon. Intriguing fundamental properties have also been reported: the CO hydrate initially forms in the sI structure (kinetically favored) and transforms into the sII structure (thermodynamically stable) [2]. Understanding and predicting the gas hydrate structural stability then become essential. The aim of this work is, thereby, to study the structural and energetic properties of the CO hydrate using density functional theory (DFT) calculations. Performed on a complete unit cell (sI and sII), DFT-derived energy calculations lead indeed to the sII structure most thermodynamically stable. In addition, increasing the CO content in the large cages has a stabilizing effect on the sII structure, while it destabilizes the sI structure in agreement with recent experimental results [2,3].

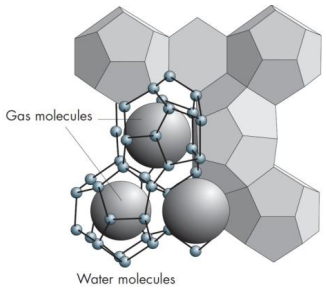

Figure 1: Clathrate hydrate

References

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