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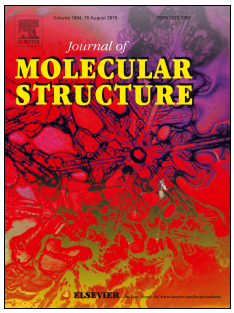

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Theoretical studies on microstructures, stabilities and formation conditions of some sour gas in the type I, II, and H clathrate hydrates

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ABSTRACT: Clathrate hydrates are well known for the water cage structures and the capability of encapsulating natural gas, generally considered as sour gas if containing appreciable amount of hydrogen sulfide. Using the *ab initio* calculations at the wB97X-D/6-311++G(2d,2p) level, we have investigated systematically the microstructures of five standard water cavities (ID, D, T, H and I) with single and multiple hydrogen sulfide inside. The interaction energies and deformation energies are predicted to ensure the stabilities and maximum occupancies of cages. In addition, the Gibbs free energies forming various water cavities enclosing CH_4 and H_2S molecules at temperature range 253K to 283K are also calculated to explore the selectivity on hydrate types and corresponding formation conditions. The results from this work may provide new insight into the theory for the replacement scheme in the exploitation of natural gas hydrate.

1. Introduction

Clathrate hydrate are a class of non-stoichiometric compounds formed by polyhedral water cages of different sizes and small molecules (such as H_2S, CO_2, CH_4) that are trapped inside under certain circumstances.[1] As a typical clathrate hydrate, the Natural gas hydrates (NGHs) are ice like inclusion compounds which are found mostly in the permafrost region and deep ocean sites.[1,2] These abundant resources are believed to be a new clean energy resource which may play as significant role as the fossil fuels in the future.[3]

The gas molecules in clathrate hydrates are vital in the formation of microscopic cage-like structures. For example, the hollow dodecahedral cage is energetically less stable than its cuboids counterpart, yet a guest molecule like methane can stabilize it.[4,5] Therefore, the accurate description of hydrogen bonding (H-bonding) energies and van der Waals (vdW) interactions which is usually dominant between host cages