Molecular modeling of carbon dioxide hydrates: comparison of different approaches

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Remarkable research efforts have been performed concerning the analysis of hydrates and organic clathrates using different theoretical approaches such as molecular equations of state, molecular simulations including both Molecular Dynamics and Monte Carlo techniques, and different ab initio Quantum Mechanics approaches[1-3]. In this work, CO_2 type I hydrates have been studied using Molecular Dynamics, electronic Density Functional Theory (DFT) and the Quantum Theory of Atoms in Molecules (QTAIM). First, the CO_2 hydrate three phase equilibrium line has been estimated using different existing rigid non polarizable molecular models and the direct coexistence Molecular Dynamics technique. Then, the energetic interactions between guest and host molecules have been evaluated from a different perspective, using DFT, allowing to evaluate the limitations of the hypothesis usually admitted within the thermodynamic modeling of gas hydrates. Several mechanisms for transport of guest molecules inside hydrates have been proposed so far in literature, and previous results have pointed out the apparent imposibility of some guests passing directly through faces connecting adjacent cages without destroying the water structure. Both types of cells included in the structure of type I hydrate were modeled as isolated double semi-flexible atomic systems. Interaction potentials of guest molecules with the enclathrating cell, when moving between neighbour cells were calculated using B3LYP/6-311+g(d,p) DFT approximation. The obtained results show that direct transitions are feasible through hexagonal and pentagonal faces without compromising the overall structure integrity in opposition to other results previously reported in literature. This stability has been explored using the QTAIM theory and reveals that even in the case that some bond may break during the transition, all of them are recovered because the face distorsion is absorbed locally by the hydrogen bond network. This technique allows also to determine the guest preferential orientations inside the hydrate cell, and in this case the usually neglected interaction among guests plays a key role to reproduce in detail available experimental results. The validity of the theory level selected has been stated, and the high anisotropy of the guest-cell interaction potential for the molecules analysed is shown, which may be considered in the formulation of hydrate thermodynamic models as equations of state, and also for the description of transport properties.

References:

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