

Density Functional Theory Calculation of the Potential Energy Landscape and Raman Spectra of Methane and Carbon Dioxide Hydrates

Ángel Vidal-Vidal and Martín Pérez-Rodríguez
Dpto. de Física Aplicada, Univ. de Vigo, Vigo, Spain

Jean-Philippe Torre
Lab. des Fluides Complexes et Leurs Réservoirs, UMR 5150, Univ. de Pau et des Pays de l'Adour, Pau, France

Manuel M. Piñeiro^{C,S}
Dpto. de Física Aplicada, Univ. de Vigo, Vigo, Spain
mmpineiro@uvigo.es

In this work, CO₂ and CH₄ type sl hydrates have been studied using electronic Density Functional Theory (DFT) and the Quantum Theory of Atoms in Molecules (QTAIM). Both types of cells included in the structure of type sl hydrate were modeled as isolated independent rigid cages, either empty or containing any of the two selected guest molecules, with single occupancy. Interaction potentials of guest molecules with the enclathrating cell, and the potential profiles when moving between neighbour cells were calculated using B3LYP/6-311+g(d,p) DFT approximation, considering the cases with and without long range Coulombic corrections. The selected theory level was validated by comparison of the estimated Raman spectra with the experimental ones, for both types of cells. Fermi resonance between vibrational bands of CO₂, resulting from anharmonic effects, was described using a perturbation procedure intended to estimate the theoretical non-mixed states. 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. In addition, the presented results suggest that the hydrate guest occupancy might be calculated from the comparison of experimental and predicted Raman spectra.