

DFT Study of Stability Limits and Mechanical Properties of Monocrystal Methane Gas Hydrates Under Extreme Pressure Conditions

Xiaodan Zhu, Alejandro Rey and Phillip Servio

Department of Chemistry, McGill University, QC, Email: xiaodan.zhu@mail.mcgill.ca

Density functional theory (DFT) is a widely used modelling methodology, which can provide general information on the material's structure from the electronic aspect. DFT can give a comprehensive insight into the material properties and performance and provide future applications under various conditions. For example, this theory can be applied to explore the gas hydrate's properties, which can be used for Carbon dioxide (CO₂) sequestration.

Carbon dioxide (CO₂) sequestration, one of the greenhouse gas mitigation technologies, has attracted public attention for several decades. CO₂ storage is still a big issue because the CO₂ storage in soil and ocean leads the sites to become acidic and threatens human life. On the other hand, the novel material, gas hydrate, is a potential material for CO₂ sequestration, but the stability is not well studied.

Gas hydrates, typical hydrogen systems, are guest-host crystalline materials formed by water cages and guest molecules such as methane and carbon dioxide. The CO₂ sequestration process is based on SI methane gas hydrates; methane is replaced by carbon dioxide. During this process, the surrounding pressures and temperatures change, making the hydrate structure unstable. Jendi et al. reported that material properties of gas hydrates associated with structural stabilities change along with pressures and temperatures. Jia, J. et al. demonstrated the role of the guest molecules (methane and carbon dioxide) on the gas hydrates' stability. However, although the performance of the gas hydrates under different pressures and temperatures was demonstrated, little attention has been paid to the description and characterization of their stability limits.

To fulfill this knowledge gap, DFT can be used to calculate the energies of the hydrate structures and, more importantly, the energy changes when the electrons and atoms move. It can present both the entire system's performance and the atoms' and electrons' positions, which provides a clear view of when the system approaches the stability limits. This contribution will present the pressure stability limits of monocrystal defect-free methane gas hydrates, using accurate density functional theory (DFT) to simulate the hydrate's performance under varying pressures. The effects of pressure on the geometric and atomic bonding feature of this guest-host crystal are presented and analyzed using various atomic angle and bond length distribution functions. Critical gaps or forbidden zones are identified and related to potential stability mechanisms as pressure increases. Locations of concentrated distortions in the crystal lattice are identified. Comprehensive characterization of the elastic properties with pressure is presented and related to the crystal geometry changes. Validation and accuracy are determined using available simulations, theory, and experiments. Taken together, these results, obtained from the DFT methodology, contribute to understand the methane gas hydrate stability under a great range of pressures and provide comprehensive predictions on the gas hydrate's applications such as CO₂ sequestration.