Molecular Simulations of Methane Hydrate: Crystal Structure and Spectroscopic Properties

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INTRODUCTION

Gas hydrates are crystalline compounds consisting of gas molecules encaged in cavities of a hydrogen-bonded network of water molecules. Gas hydrates are characterized by the general formula $X \cdot n H_2O$, where X is the guest molecule within a water cage, and *n* is the hydration number per guest molecule. Three different gas hydrate structures can be found: sI, sII and sH (Sloan, 1998). Cubic sI structure consists of 46 water molecules per unit cell, forming two dodecahedron (small 5^{12}) and six tetradecahedron (large $5^{12}6^2$) cages (Fig. 1) and is formed when small guest molecules such as methane are trapped. Methane hydrates are found in permafrost regions and sediments of the ocean floor in outer continental margin regions where medium pressures and low temperatures can be reached (Kvenvolden and Rogers, 2005). Gas Hydrates are important on Earth´s system because hydrate decomposition would cause the release of methane into atmosphere (high greenhouse gas) causing great impact on Earth´s climate, dramatically increasing the temperature of the planet. On the other hand, these natural gas hydrates are seen as a potential major energy resource.

Due to the complexity of experimental studies with hydrates, Computational Mineralogy can be very helpful. Vibrational spectroscopy is a useful tool in determining many aspects of guest-host relationships. Molecular simulations can also provide vibration frequencies of methane in hydrates (Greathouse et al., 2006). The aim of this work is to contribute to a better understanding of the crystalline structure of methane hydrate and the guest-host interactions in the hydrate by comparing different theoretical approaches.
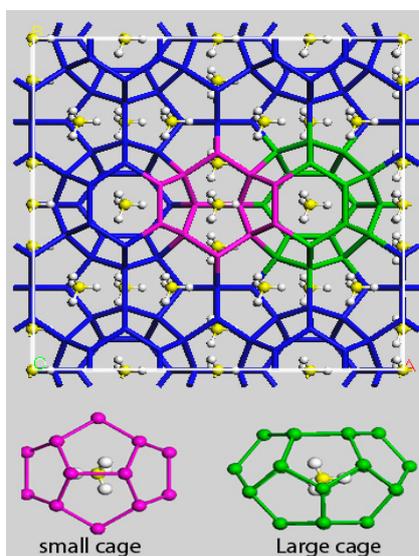

fig 1. *Schematic framework of cages extracted from the crystal lattice of methane hydrates. Pink and green balls represent O atoms from water molecules in small and large cage respectively. White and Yellow balls: H and C atoms from methane molecules. H atoms of water molecules are not represented for a better understanding.*

COMPUTATIONAL METHODOLOGY

In order to evaluate the liability of results obtained, different calculations methods were used: methane gas and methane hydrate small cage cluster were analyzed by quantum chemical calculations using HF/6-311G** levels with GAUSSIAN03; Ab initio total energy calculations of the periodic crystal model were performed using DFT methods GGA/PBE/DZP level with SIESTA and GGA/PBE and LDA/CA-PZ levels with CASTEP; Simulations of Methane hydrate periodic crystal mode by empirical interatomic potentials were performed within a Force Field (FF) based on CVFF (consistent valence force field) and we named it CVFFH. For these CVFFH calculations, we employed the Discover program within the Material Studio package (Accelrys, 2009). A periodic model of the crystal structure of methane hydrate was generated based on experimental atomic coordinates and lattice cell parameters (Klapproth et al., 2003). A cluster model of methane hydrate was also generated by extracting one hydrate cage with methane from the crystal lattice. In all cases the adsorption energy has been calculated in the usual way: $U_{adsorption} = U_{molecule\ in\ hydrate\ cage} - (U_{empty\ hydrate\ cage} + U_{molecule})$, where U is the internal energy of the each system fully optimized at constant volume.

RESULTS AND DISCUSSION

Methane Hydrate Crystal Structure

In methane hydrate crystal structure optimized at variable volume, X-Ray Diffraction (XRD) patterns were calculated and compared with experimental XRD (Klapproth et al., 2003) (Fig. 2). XRD comparison shows similar characteristics in all cases, meaning that crystalline structure of methane hydrate can be successfully reproduced using these methods.
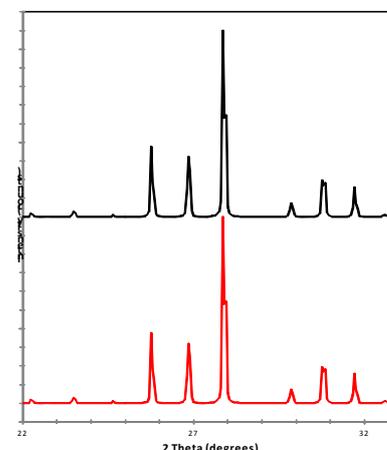

fig 2. *XRD profiles of methane hydrate crystal. Comparison obtained from geometry optimization with CVFFH (Black line) and experimental data (red line) (Klapproth et al., 2003).*

Adsorption Energies

Adsorption energy of one methane molecule inside the 5^{12} cage yields values of -5.38 Kcal/mol (HF), -5.19 Kcal/mol (CVFFH) and -7.59 Kcal/mol (LDA). Adsorption energies for the whole hydrate crystal calculated with CASTEP/LDA and CVFFH yielding values of -5.90 kcal/mol and -6.11 kcal/mol per methane molecule respectively. All values obtained are negative, indicating an exothermic formation process.

Molecular Dynamics Simulations

For these simulations a 2 x 2 x 2 supercell of the crystal lattice of hydrate was generated with periodic boundary conditions with full occupancy and with only one methane molecule in one small cage. NPT ensemble molecular dynamics (MD) simulations were performed with CVFFH force field at different conditions: At pressure P = 40 bar and temperature T = 273 K for hydrate fully occupied under stable conditions (S-MH); at P = 1 bar and T = 726.85 K for hydrate fully occupied under unstable conditions (U-MH); and at P =1 bar and T = 400 K for hydrate with only one methane molecule in small cage (1M-MH). All simulations were carried out during 100 ps with a time step of 1 fs (Fig. 3).
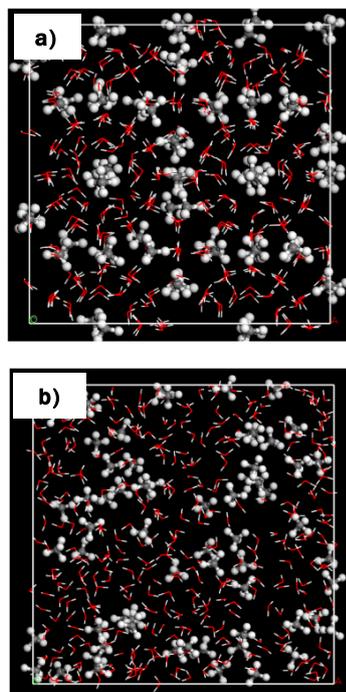
fig 3. Snapshots of the MD simulations of methane hydrate S-MH (a), and U-MH (b).

S-MH trajectory shows that methane hydrate structure keeps stable without significant distortions of hydrogen bonding network. However, in U-MH the hydrogen bonding network is collapsed and can be observed that methane molecules tend to form aggregates. In 1M-MH, it can be observed that during the trajectory the hydrogen bonding network is completely amorphized, when methane molecule tries to diffuse from the small cage to another cage.

Vibrational Spectroscopy

Experimentally it was observed that the $v(CH)_s$ mode of the methane in the large cage shifts to lower frequency than that in small cage (Tulk et al., 2000; Ohno et al., 2007) observation based on peak intensities. However, some discrepancies have appeared in the assignments of these bands, where Hester et al. (2007) reported the opposite assignments.

In agreement with experimental Raman studies (Ohno et al., 2007), our results with HF and CVFFH calculations shows a high frequency peak corresponding to small cages, and a low frequency peak that corresponds to large cages of methane hydrate.

Phase	Method[a]	v_{as} (C-H)	v_s (C-H)
Methane gas	Exp.	3019	2917
	HF	3007	2911
5^{12} Cluster	HF	3021	2920
$5^{12}6^2$ Cluster	HF	3008	2901
Crystal Lattice Hydrate	Exp.	3026[b]	2914[c,d] 2901[c,e]
	CVFFH	3078[d] 3070[e]	2914[d] 2903[e]

Table 1. Calculated and scaled frequencies of the main vibration modes of the methane molecules at gas phase and within the clathrate comparing with experimental values. [a]Exp. means experimental data (Lide, 1990), HF is HF/6-311G** level., [b] Raman spectroscopy (Tulk et al., 2000). [c] Raman spectroscopy (Ohno, 2010). [d] Assigned to the methane in small (5^{12}) cages. [e] Methane in large ($5^{12}6^2$) cages.

CONCLUSIONS

Crystalline structure of methane hydrate can be successfully reproduced using computational methods based on DFT and using empirical interatomic potentials.

Calculated adsorption energies yield negative values proving that methane hydrate formation is an exothermic process. Molecular Dynamics simulations show that under conditions of stability, crystalline structure of methane hydrate remains, but rising temperature methane hydrate decomposes, disordering the hydrogen bonding network, and methane molecules tend to aggregate. The vibrational stretching peaks of C-H at 2915 and 2905 cm-1 are due to small (5^{12}) and large ($5^{12}6^2$) cages respectively, matching the experimental behavior.

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