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Citation: Chin. Phys. B . 2018, 27(4): 043103. **doi:** 10.1088/1674-1056/27/4/043103

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Density functional theory study of structural stability for gas hydrate*

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(Received 6 December 2017; revised manuscript received 23 January 2018; published online 10 March 2018)

Using the first-principles method based on the density functional theory (DFT), the structures and electronic properties of different gas hydrates (CO_2, CO, CH_4, and H_2) are investigated within the generalized gradient approximation. The structural stability of methane hydrate is studied in this paper. The results show that the carbon dioxide hydrate is more stable than the other three gas hydrates and its binding energy is −2.36 eV, and that the hydrogen hydrate is less stable and the binding energy is −0.36 eV. Water cages experience repulsion from inner gas molecules, which makes the hydrate structure more stable. Comparing the electronic properties of two kinds of water cages, the energy region of the hydrate with methane is low and the peak is close to the left, indicating that the existence of methane increases the stability of the hydrate structure. Comparing the methane molecule in water cages and a single methane molecule, the energy of electron distribution area of the former is low, showing that the filling of methane enhances the stability of hydrate structure.

Keywords: first principles, gas hydrate, binding energy, stability

PACS: 31.15.es **DOI:** 10.1088/1674-1056/27/4/043103

1. Introduction

Gas hydrate is a kind of clathrate that is formed by water and gas molecules under certain pressure, temperature, salinity and chemical composition conditions.[1] The natural gas hydrate reservoirs are outstanding for their huge reserve, extensive distribution, high energy density and high caloric value.[2] The energy efficiency of the gas hydrate is ten times that of coal.[3] It is thought that it is going to be an important potential source of energy in the future.

With the development and innovation of molecular simulation technology, the structures and properties of gas hydrate have been extensively investigated by using molecular dynamics (MD), Monte Carlo (MC) and density functional theory (DFT) methods.[4–6] Duan *et al.*[7] chose the constant-pressure and constant-temperature (NPT) ensemble, the consistent valence force field and the Ewald method for molecular dynamics simulation of sI methane hydrate supercell system. They also analyzed the changes of system conformation, radial distribution function, system potential energy and mean square displacement under different pressure conditions have been analyzed. Tang *et al.*[8] employed the DFT-D method to study the phenomenon of water cage merging in the process of methane hydrate nucleation. They analyzed the structures, stabilities and Raman spectra of double cages and multi cages under the lowest energy. Song *et al.*[9] calculated the initial structure of methane hydrate without a single or two water molecules and optimized the unrestricted structure at a B3LYP /6-31 + G(d, p) level. The BSSE method was used to calculate the interaction energy between water and methane. They also studied the relationship between the cage structure and stability of methane hydrate without water molecules. Cao *et al.*[10] systematically calculated the stabilities of 18 alkane guest molecules in two kinds of water cages ($5^{12}6^2$ and $5^{12}6^4$) by density functional theory at a B97-D/6-311 ++ G(2d, 2p) level. They simulated Raman spectra of nine kinds of alkane hydrates to study the stability between the large guest alkane molecule and the water cage. They also studied the change of the vibrational frequency of the guest molecule in the hydrate with the object molecular category. According to the first principles based on the density functional theory method, Xu[11] analyzed the interaction between the guest molecules and water cage architecture. The binding energies of methane hydrate and ethane hydrate under the structure of sI and sII were calculated respectively. They also studied the stability of each system and the influence of tetrahydrofuran (THF) on the system structure.

Through the above investigation, we could see that the structural properties of methane hydrate and the change of the system energy have been calculated. Our work is based on these previous researches. In this paper, we calculate the binding energies of several common gas hydrates, and also analyze the methane hydrate structural stability from the view of density of states(DOS). In this paper, we not only calculate the partial electronic density of states (PDOS) of a water cage

*Project supported by the National Key Research and Development Program of China (Grant No. 2016YFC0304008).

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with/without the inner methane molecule, but also analyze the PDOS of single methane and methane in a water cage, to further verify the structural stability of methane hydrate. Among all kinds of gas hydrates, methane hydrate is outstanding for the huge reserve and extensive distribution. Therefore, we choose methane hydrate as the main research object in this paper. Through this research we hope that the mechanism can be revealed for quantum mechanics of gas hydrate structure stability, especially methane hydrate, and the theoretical guidance can be provided for the research and utilization of gas hydrate.

2. Calculation method and process

Based on the first principle method of DFT,[12,13] the geometric structure and electronic properties of different gas hydrates are calculated by the quantum mechanical program CASTEP which is developed by the condensed matter physics research group of the University of Cambridge. The program reliability has been verified by a large number of practical calculations. The calculation of the CASTEP program is based on the total energy pseudo potential method and the plane wave expansion,[14] which requires the system to be periodic.

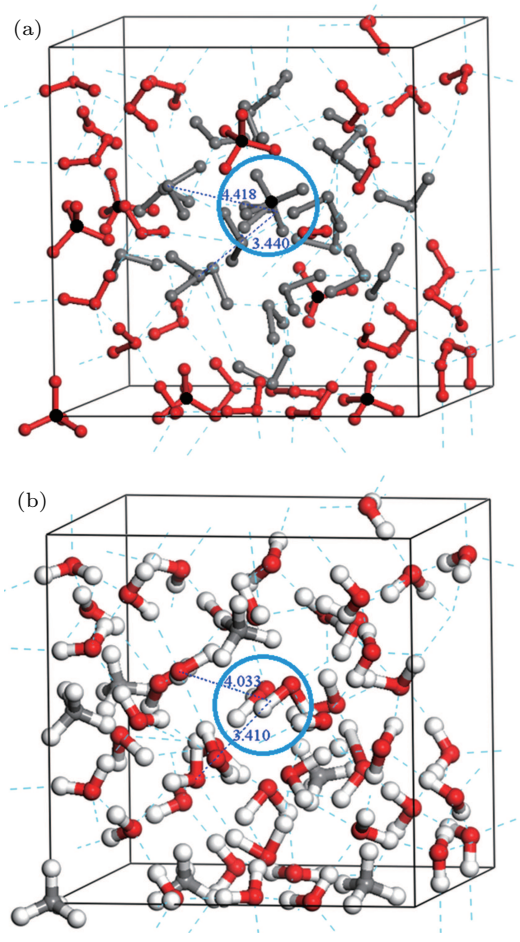


Fig. 1. (color online) (a) Structure model of methane hydrate(surrounding molecules are fixed); (b) structure model of non-inner methane hydrate (molecules are free).

In this paper, the initial structure of gas hydrate is derived from the x-ray diffraction experiment.[15] The space group of methane hydrate is $PM3N$, and the lattice constant is $a = b = c = 1.162$ nm. The calculation is carried out in the reciprocal space, so the volume of real space needs to be converted into the inverted lattice space. The exchange correlation function is based on the generalized gradient approximation (GGA-PBE).[16] The K point[17] grid size is $2\times2\times2$. Self-consistent field cycle converges to 1.0×10^{-5} eV. The BFGS[18] optimization algorithm is used to optimize the geometry. After geometry optimization of the gas hydrate structures, the parameters of the crystal structure at ground state are obtained. The total energy (E_T) of methane hydrate is -21275.69 eV. The forces acting on each atom are less than 0.1 eV/nm. The value of plane wave cut-off energy is 100 eV. The convergence test is carried out by changing the cut-off energy. The results show that these settings are sufficient to ensure the accuracy of the calculation. The structures of gas hydrate with/without an inner methane molecule are shown in Figs. 1(a) and 1(b), respectively. The carbon atoms of the methane molecules have been labeled in black (Fig. 1(a)).

3. Results and discussion

In this paper, we use $1\times1\times1$ periodic super cells as the initial structure. The study is divided into two cases, one is the water cage with an inner methane molecule (Fig. 1(a)), and the other is the middle water cage without an inner methane molecule (Fig. 1(b)). Both fixed and unfixed surrounding molecular structure models of gas hydrates are calculated. The average deviation of the distances from the water cage center to the oxygen atoms are all less than 0.3%. The result verifies that the effect of fixing surrounding molecules of the water cage is negligible. To reduce the computation load and improve efficiency in further case studies, we fix molecules outside the water cage.

In order to quantitatively reflect the difference between the two structures, the distances from the cage center to the oxygen atoms of the water cage are calculated (Table 1). As can be seen in Figs. 1(a) and 1(b), $R_1 = 0.3410$ nm, $R'_1 = 0.3440$ nm, $R_{10} = 0.4033$ nm, and $R'_{10} = 0.4418$ nm. When the inner methane molecule exists, the water cage experiences the repulsion from it and the repulsion makes the water cage more stable while it is squeezed by surrounding molecules. When the inner methane is missing, the repulsion disappears and the structure instability increases, the distance from the oxygen atoms to the water cage center becomes shorter and the volume of the water cage becomes smaller.

Table 1. Distances from the water cage center to the oxygen atoms without/with inner methane (R/R').

Distance	R/nm	R'/nm	ΔR/nm
R_1	0.3410	0.3440	0.0030
R_2	0.4282	0.4887	0.0605
R_3	0.3168	0.3351	0.0183
R_4	0.3503	0.3865	0.0335
R_5	0.3844	0.4212	0.0328
R_6	0.4617	0.4685	0.0068
R_7	0.3308	0.3358	0.0050
R_8	0.3392	0.3441	0.0049
R_9	0.3491	0.3698	0.0207
R_{10}	0.4033	0.4418	0.0385

To analyze the stability of gas hydrate, we calculate the binding energies of different gas hydrates. The formula is as follows:

$$E_{\mathrm{b}} = E_{\mathrm{T}} - \left(E_{\mathrm{gas}} + E_{\mathrm{cage}}\right), \tag{1}$$

where E_{T} represents the total energy of the gas hydrate structure, E_{gas} denotes the energy of the single molecule, and E_{cage} means the energy of the water cage without inner methane. The binding energies of carbon dioxide hydrate, carbon monoxide hydrate, methane hydrate and hydrogen hydrate were -2.36 eV, -1.57 eV, -0.58 eV, and -0.36 eV, respectively (see Table 2). This indicates that the structure stability of carbon dioxide hydrate is higher than that of methane hydrate, while hydrogen hydrate is the most unstable one among them. It may also provide a theoretical basis for developing the methane hydrate with CO_2 replacement from the view of energy.

Table 2. Energies of different gas hydrates.

Gas	E_{T}	E_{cage}	E_{gas}	E_{b}
CO	–23935.5104	–23392.3474	–541.587149	–1.57
CO_2	–26963.9443	–26027.2151	–934.369641	–2.36
H_2	–19751.1993	–19720.7215	–30.1200797	–0.36
CH_4	–21186.7291	–20976.9016	–209.246310	–0.58

Figure 2 shows the electronic DOSs of different gas hydrates. The x axis (i.e., horizontal axis) represents the energy. The energy that sets to zero in the electronic density of states of different gas hydrate is the "Fermi level". The electron distribution shifting to the left of the x axis means that more electrons occupy lower energy states, reflecting the energy reduction of the system. In Fig. 2, the minimum peaks of energy of carbon monoxide hydrate and carbon dioxide hydrate are between -36.5 eV and -31.5 eV, while the minimum peaks of energy of methane hydrate and hydrogen hydrate are between -30 eV and -23.5 eV. The energy distributions of carbon dioxide and carbon monoxide hydrate structure are lower than those of methane and hydrogen hydrate structure. The distribution of the peak shifts to the left and the energy is reduced, which shows that the stabilities of carbon dioxide and carbon monoxide hydrate are higher than those of methane and hydrogen hydrate.

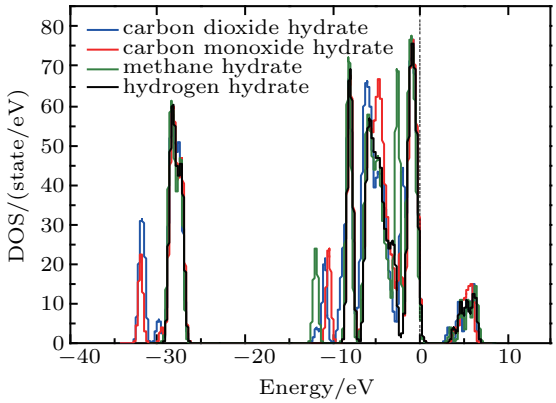


Fig. 2. (color online) Electronic densities of states of different gas hydrates.

Then we study the difference between water cages with/without the inner methane molecule from the view of DOS. As shown in Fig. 3, the energy distribution of the hydrate structure in the presence of inner methane (blue curve) is lower than that of non-methane (red curve). The distribution of the peak shifts to the left and the energy is reduced, which indicates that the stability of the hydrate structure is improved in the presence of inner methane. In order to better illustrate this point, we further analyze the PDOSs (partial electronic densities of states) of water cage with/without an inner methane molecule as well as the PDOSs of single methane and methane in a water cage.

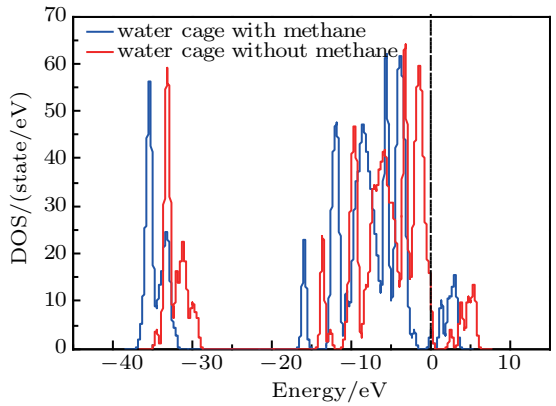


Fig. 3. (color online) Electronic densities of states of water cage with/without inner methane.

On the one hand, we compare the PDOSs of the water cage with/without the inner methane. As shown in Fig. 4, the PDOS of the water cage with inner methane is mainly contributed by p electrons. The s electron (blue curve) of the water cage with inner methane is continuously distributed in the energy ranges from -37.5 eV to -31.3 eV and from -11.2 eV to $+5$ eV, and there are nine peaks. The s electron (red curve) of the water cage without inner methane is continuously distributed in the energy ranges from -35 eV to -30 eV and from -7.3 eV to $+5.5$ eV, and there are eight peaks. The p electron

(green curve) of the water cage with inner methane is continuously distributed in the energy range from −12.5 eV to 4.5 eV. The p electron (black curve) of the water cage without inner methane is continuously distributed in the energy range from −11.3 eV to −5.4 eV. Therefore, the distribution of all electrons shifts to the left and the energy is reduced, which proves that the stability of the hydrate structure is enhanced by the filling methane molecules.

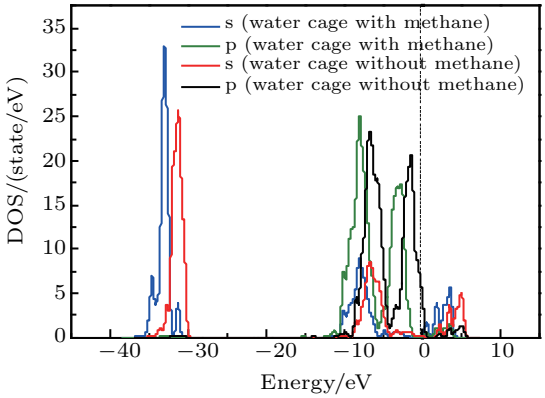


Fig. 4. (color online) Partial electronic densities of states of water cage of methane and non-methane.

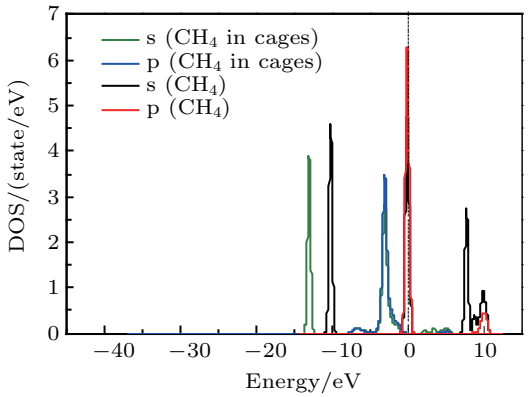


Fig. 5. (color online) Partial densities of states of methane in water cage and single methane.

On the other hand, we conduct a comparison of PDOS between single methane and methane in a water cage (Fig. 5). It shows that the electron density of methane is mainly contributed by s and p electron. The s electron (green curve) of methane in the water cage is continuously distributed in the energy ranges from −13.75 eV to −12.5 eV and from −7.5 eV to +6.5 eV. The s electron of a single methane molecular (black curve) is continuously distributed in the energy ranges from −11.5 eV to −9.5 eV and from −0.15 eV to +11.5 eV. The p electron (blue curve) of methane in the water cage is continuously distributed in the energy range from −7.5 eV to 5.75 eV. The p electron of a single methane molecular (red curve) is continuously distributed in the energy range from −0.15 eV to 11.5eV. As shown in this figure, the distributions of all electrons shift to the left and the energy decreases, demonstrating that the filling of methane enhances the stability of the hydrate structure.

4. Conclusions

Using the first principles method based on density functional theory, we have studied the structural stabilities of different gas hydrates, the binding energy, ground-state structures and electronic properties of different gas hydrates. A comparison of the two kinds of structures shows that water cages experience the repulsion from inner gas molecules, which makes the hydrate structure more stable. The analyses of the electronic properties of the two water cages show that the energy region of hydrate with inner methane is lower, and the peaks are closer to the left, indicating that the existence of methane increases the stability of the hydrate structure. The analysis of the density of states shows that when the methane exists, the distribution of s/p electrons of the water cage shifts to the left and the energy is reduced. In addition, the electron distribution of methane shifts to the left and the energy decreases after binding to the water cage, which further illustrates that hydrate structure is stable in the presence of methane. The binding energy of methane hydrate is −0.58 eV, which is higher than that of carbon dioxide hydrate (−2.36 eV) and lower than that of hydrogen hydrate (−0.36 eV), showing that the structure stability of carbon dioxide hydrate is higher than that of methane hydrate, while hydrogen hydrate is the most unstable among them.

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