Methane adsorption on graphite(0001) films: A first-principles study*

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Using first-principles methods, we have systematically investigated the electronic density of states, work function, and adsorption energy of the methane molecule adsorbed on graphite(0001) films. The surface energy and the interlayer relaxation of the clean graphite(0001) as a function of the thickness of the film were also studied. The results show that the interlayer relaxation is small due to the weak interaction between the neighboring layers. The one-fold top site is found most favourable on substrate for methane with the adsorption energy of −133 meV. For the adsorption with different adsorption heights above the graphite film with four layers, the methane is found to prefer to appear at about 3.21 Å above the graphite. We also noted that the adsorption energy does not dependent much on the thickness of the graphite films. The work function is enhanced slightly by adsorption of methane due to the slight charge transfer from the graphite surface to the methane molecule.

Keywords: first-principles calculations, graphite, methane molecule, adsorption

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1. Introduction

Methane in coal seams is referred to natural gas accumulated in coal beds. Over 90 percent of it consists of CH_4, and it has many advantages such as shallow burial and exploration easily. Developing methane in coal seams is important for changing the energy source structure and decreasing mine gases and green house gases.[1,2] However, the asphyxiation and explosive of methane are often the root causes of major accidents in the coal mining. When the methane emits directly into the air, it also causes a tremendous waste of resources and serious environmental pollution.[3,4] Therefore, the study of methane adsorbed on carbon is very necessary because of its practical and theoretical importance.[5–8] Two basic forms of bulk carbon are diamond and graphite,[9] which are the most important carbon materials. Many investigators have experimentally studied the nature of the methane-graphite interaction.[10–13] However, the microscopic mechanism of adsorption of CH_4 molecules on the graphite, as well as influences of the adsorption height and the layer film thickness, on the adsorption were not detailed in these studies. They have not been achieved in experiments, for example, the adsorbed methane structures and bonding properties. Computer simulation based on the density-functional theory (DFT) has been proven to be a powerful and reliable tool to study methane–semisolid interfaces at the molecular level.[14,15] The (0001) surface of graphite is the basal plane and the plane which graphite crystals predominately expose. Thus, the hydroxylated (0001) surface is the surface of primary interest in adsorption studies. In addition, a deeper insight into the methane on graphite(0001) surface through detailed first-principles calculations can be desirable, which is addressed in this paper.

2. Methods

Our first-principles total energy calculations are based on the DFT and the Vienna *ab initio* simulation package (VASP)[16] using the local density approximation (LDA)[17–19] for the exchange correlation potential and the projector augmented wave (PAW) method.[20,21] Previous studies showed that using the LDA can give better results of the electronic structures and adsorption properties of CH_4 adsorbed on graphite film than using the generalized gradient approximation (GGA).[14] We also adopt the LDA in all the calculations. The electron wave function is expanded in plane waves up to a cutoff energy of 500 eV. In the present study, we construct the calculated model with free-standing graphite(0001) films in periodic slab geometries with p(2×2) periodicities and the periodic slabs are separated by a vacuum region of 20 Å. For comparison, we consider the graphite film from 1 to 7 layers. The Brillouin zone integration is performed using the Monkhorst–Pack method with $6 \times 6 \times 1000$ mesh points. A Fermi broadening of 0.2 eV is chosen to smear the occupation of the bands around the Fermi energy (E_f) by extrapolating a finite-T Fermi function to $T = 0$ K. During geometry optimizations, two layers at the bottom of the clean graphite(0001) films are fixed, while other atoms are free to relax until the forces acting on them are less than 0.02 eV/Å. The calculated lattice parameters $a = 2.45$ Å and $c = 6.67$ Å, are used throughout the study, which are in good agreement with the theoretical[12,13] and experimental[22] lattice parame-

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ters reported previously. The C–H bond length and the CH internal angle of a free methane molecule are 1.10 Å and 109.5°, respectively. In order to calculate the electronic structure of methane, we put the methane molecule into a cubic box with a size of 16×16×16 Å and only gamma (Γ) point for k-point sampling. The energy cutoff is also set to be 500 eV and the structure is relaxed until the force is lower than 0.001 eV/Å.

The central quantities tailored for the present study are the surface energy and the adsorption energy of the adsorbed CH_4 molecule on graphite substrate. The surface energy of graphite is defined as

$$\sigma = \frac{1}{2}\left(E_{\text{surf}} - \frac{1}{4}N_{\text{atom}}E_{\text{bulk}}\right), \tag{1}$$

where N_{atom} is the total number of the atoms of the clean film, and E_{surf} and E_{bulk} are the total energies of the clean film and the bulk graphite unit cell containing 4 atoms, respectively.

The adsorption energy of the adsorbed CH_4 molecule on graphite substrate is described as

$$E_{\text{ab}} = E_{\text{graphite/CH}_4} - E_{\text{graphite}} - N_{\text{CH}_4}E_{\text{CH}_4}, \tag{2}$$

where N_{CH_4} is the total number of the CH_4 molecule adsorbed on the graphite films. Additionally, $E_{\text{graphite/CH}_4}$, E_{graphite}, and E_{CH_4} are the the total adsorption system, the clean graphite surface, and the total energies of the CH_4 molecule, respectively. According to this definition, a negative value of E_{ads} indicates that the adsorption is exothermic (stable) with respect to a free CH_4 molecule, while a positive value indicates endothermic (unstable) reaction.

3. Results and discussion

The interlayer relaxation and the surface energy of the clean graphite films were firstly studied before considering the interaction between methane molecules and graphite films. To describe more clearly the changes, here the interlayer relaxation $\Delta d_{i,i+1}$ is given in percentage with respect to the unrelaxed interlayer spacing d_0, i.e., $\Delta d_{i,i+1} = 100(d_{i,i+1} - d_0)/d_0$, where d_{i+1} is the interlayer distance between two adjacent layers calculated by minimizing the forces, and $d_0 = c/2$ is the bulk interlayer distance along the (0001) direction. Obviously, the signs + and − of $\Delta d_{i,i+1}$ indicate expansion and contraction of the interlayer spacing, respectively. The interlayer relaxation of graphite(0001) films as a function of the film thickness (from 1 to 7 layers) are summarized in Table 1, from which one can see the following trends: (i) the outmost layers is more relaxed than the innermost layers, which are almost not relaxed with $\Delta d_{i,i+1} \sim 0$; (ii) in the whole range of layers that we considered, the topmost interlayer relaxation is always inward ($\Delta d_{1,2} < 0$), while the second interlayer relaxation is always outward ($\Delta d_{2,3} > 0$); (iii) the graphite film with 4 layers is an exception of the above trends. All the interlayer relaxations are outward ($\Delta d_{i,i+1} > 0$) and significantly larger than those of other films with different layers. Furthermore, the innermost layer relaxation $\Delta d_{2,3}$ (0.42) is larger than the outmost layer relaxation $\Delta d_{1,2}$ (0.11) and $\Delta d_{3,4}$ (0.11). In the present study, we have thoroughly investigated the behavior of methane on the graphite film with 4-layers (0001) surface as a typical example. As for the surface energy listed in last column in Table 1, it is obvious that the surface energy is small indicating that the relaxation is small for the graphite films. Compared with the metal Be[23] or Cu[24] films, the interlayer relaxation and surface energy are smaller. This is thought to be because of the weaker van der Waals interaction between the adjacent layers.

Table 1. Interlayer relaxations$\Delta d_{i,i+1}$ (%) and surface energy σ (meV) of graphite (0001) as a function of the thickness (N) of the film.

N	$\Delta d_{1,2}$	$\Delta d_{2,3}$	$\Delta d_{3,4}$	$\Delta d_{4,5}$	$\Delta d_{5,6}$	$\Delta d_{6,7}$	σ/meV
1							90
2	–0.01						80
3	–0.01	–0.01					80
4	+0.11	+0.42	+0.11				60
5	–0.01	0	0	–0.01			60
6	–0.01	0	0	0	–0.01		40
7	–0.01	0	0	0	0	–0.01	10

For adsorption, two different coverages of $\sqrt{3} \times \sqrt{3}R(30°)$ and $2\sqrt{3} \times 2\sqrt{3}R(30°)$ have been studied recently.[8] In this paper, we have considered one coverage of methane, p(2×2), corresponding to an adsorption of 0.25 monolayer (ML) of methane. Three kinds of high-symmetry adsorption sites for CH_4 were considered, including one-fold top site, two-fold bridge site, and three-fold hcp site. The C atom of methane was initially placed on the precise high-symmetry sites with various orientations of methane with respect to the substrate. We put the methane molecule above the topmost graphite layer 4 Å at the three chosen sites above, then allowed the CH_4/graphite to fully relax. After relaxation, the methane molecule located above the topmost graphite layer at 3.21, 3.21, and 3.25 Å with the adsorption energy of −135, −133, and −126 meV calculated by Eq. (2) for top, bridge, and hcp sites, respectively. At the preference adsorption sites the CH_4 monomer sits upright. In the plane parallel to the surface, three C–H bonds of CH_4 point to the surface carbon atoms, respectively, while the other one C–H bond of CH_4 is perpendicular to the surface. The top site is the most stable and for all the following calculations and discussions, the methane is always adsorb on the top site, as shown in Fig. 1. The C–H bond in CH_4 is elongated to 1.1 Å from a calculated gas phase value of 1.0 Å. The bond angle between the top site H and the bottom H increases from 109.4° to 109.5°.

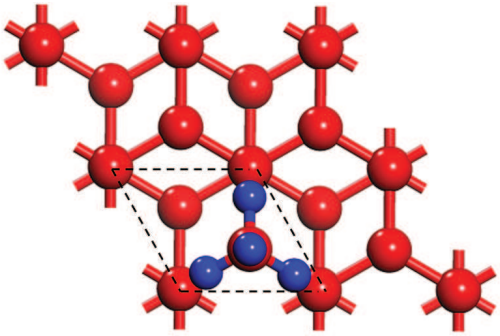


Fig. 1. (color online) The methane molecules adsorb on the top sites of the graphite(0001) surface. Red spheres and blue spheres represent carbon and hydrogen, respectively.

In order to gain more insights into the precise nature of the chemisorbed molecular state, the electronic total density of state (TDOS) and partial density of state (PDOS) of the free and adsorbed methane molecule, clean and after adsorption graphite film were calculated, as shown in Figs. 2 and 3, respectively. As a typical example, here we plotted the TDOS and PDOS for the most stable adsorption configuration of one-fold top site. Comparing the TDOS and PDOS for free and adsorbed methane molecule in Fig. 2, one can clearly see that all the bonding orbitals of the adsorbed CH_4 molecule are shifted to a much lower energy and the amplitude of all the bonding orbital are much weaker than that in free CH_4. Furthermore, as shown in the PDOS, the peak of the s and p components shifted downwards in energy from -8.9 and -1.4 eV to -12.5 and -4.9 eV, respectively. The results are essentially caused by different electronegativities of graphite and methane molecule, which induce charge redistribution and thus build a global electrostatic attraction between the methane and substrate. Another small peak at -12.0 eV appears in the DOS for methane after adsorption. Thus, during the molecule–solid interaction, the total electron densities of the CH_4 rearrange.

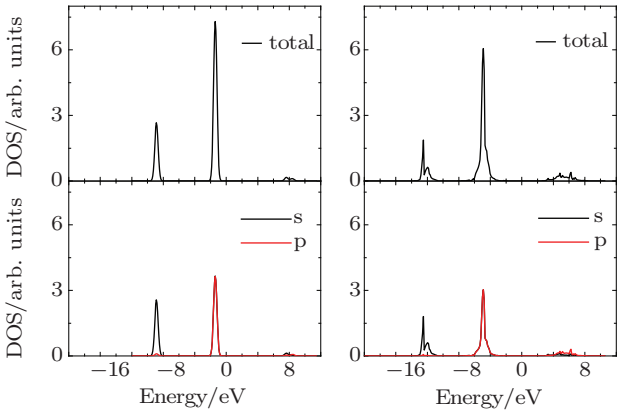


Fig. 2. (color online) The TDOS and PDOS for the CH_4 molecule at the stable fold top adsorption site on surface of (a,c) free CH_4 molecule, and (b,d) adsorbed CH_4 molecule. The Fermi energy is set at zero.

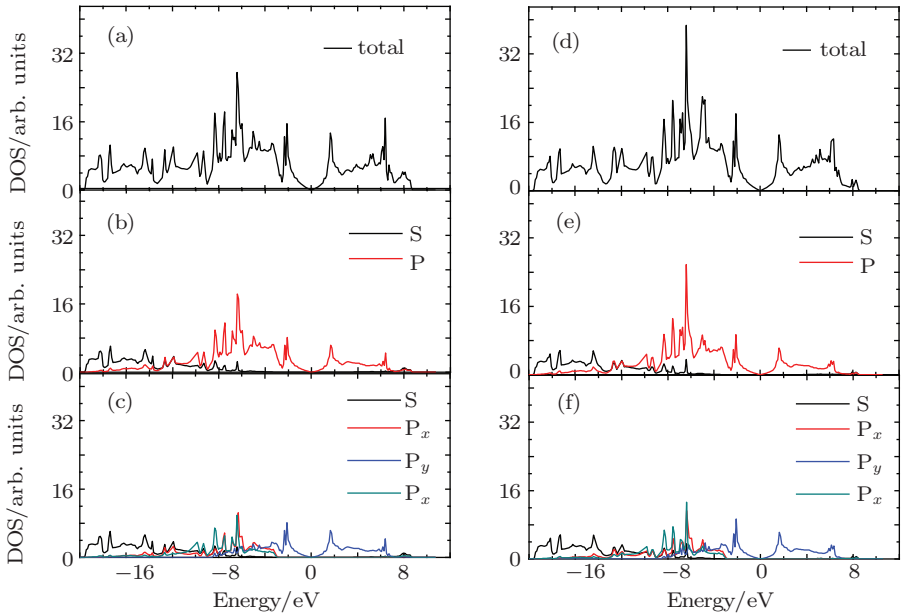


Fig. 3. (color online) The TDOS and PDOS for the top-layer C ions bonded to CH_4 at the one fold top adsorption site on surface of (a,c,e) clean graphite film, and (b,d,f) adsorbed graphite film. The Fermi energy is set to be zero.

For comparison, the electronic total and partial density of state of the clean and after adsorption graphite films were also shown in Fig. 3. For the clean graphite film, there is strong hybridization between the s, p_x, and p_y states in the large energy region from about -16 to -4 eV. Graphite is the typical of sp^2-bonded material, and our study of the PDOS of graphite (see Fig. 3) has verified this, which are consistent with other studies.[8] After adsorption, we also noted that

the DOS for graphite film is slightly affected by the adsorbed methane molecule and only the intensity of some peaks is enhanced. The peak at about −5 eV is enhanced significantly which is mainly composed of p states, as shown in the PDOS in Fig. 3. In addition, the results shown that both of the p states of graphite film and of the methane molecule locate at about −5 eV and they are strongly hybridized. The intensity of p states for graphite film and graphite/CH_4 system is enhanced, while the intensity of p states for methane is weakened after adsorption, as showed in the PDOS. Finally, the overlap between adsorbed CH_4 and the graphite surface electrons in the energy range from −8 to −4 eV implies a covalent coupling between the adsorbed mathane and substrate.

In the following, we investigated the dependence of adsorption energy upon the adsorption height of methane and the thickness of the graphite film. We calculated the adsorption energy in two cases: (i) methane molecule locates at different heights on graphite film with 4 layers; (ii) methane molecule locates at the same height on graphite films with different layers. The calculated results are shown in Tables 2 and 3, respectively. For the former case, we noted that the methane has the lowest adsorption energy of −133 meV when it is located at 3.21 Å (after relaxation). Our results are in good agreement with the theoretical and experimental results.[6,9] If we fixed the methane at 3.20 and 3.23 Å above the topmost layer, after relaxation the adsorption energy of the methane are −132 and −127 meV, respectively. The corresponding adsorption energy becomes larger from −30 to −23 meV as the adsorption height becomes higher from 4 to 8 Å. Meanwhile, the stability of adsorption for methane on graphite film is also reduced.

Table 2. Adsorption energy of methane on graphite(0001) surface (with four graphite layers) as a function of the adsorption height. The d_{C-C} is the distance between the methane and the graphite directly right downward. The d_{C-H} is the bond length of methane.

d_{C-C}/Å	d_{C-H}/Å	E_{ab}/meV
3.20	1.10	–132
3.21	1.10	–135
3.23	1.10	–127
3.50	1.10	–67
4.00	1.10	–30
5.00	1.10	–29
6.00	1.10	–24
7.00	1.10	–23
8.00	1.10	–23

Table 3. Adsorption energy of methane on graphite(0001) surface as a function of the thickness (N) of the film. The d_{C-C} is the distance between the methane and the graphite right downward.

N	d_{C-C}/Å	E_{ab}/meV
1	3.21	–134
2	3.21	–135
3	3.21	–135
4	3.21	–133
5	3.21	–134
6	3.21	–135
7	3.21	–135

For the latter case, the methane molecule is located at 3.21 Å above the film (after relaxation). It is clear that the thickness of the graphite films from 1 to 7 layers have a little effect on the adsorption energy as we expected because of the unique interactions exist in graphite films discussed above. As shown in Table 3, the methane reached the converged adsorption energy of −135 meV as the thickness of the films increases.

Finally, we investigated the work function of the clean and after adsorption graphite films. The work function, defined as the minimum energy required to emit an electron from the surface to the vacuum, is one fundamental physical quantity for surface reactivity. An elementary picture of the work function involves a surface dipole layer that a valence electron must overcome in order to escape. Our calculated work function of clean graphite film with 4 layers is 4.14 eV, which is in good agreement with the experimental values in the range of 4.4–4.7 eV for the graphite(0001) surface. After relaxation, the work function is 4.35 eV, which is slightly larger than that of the clean film, indicating that there is a slight charge transfer from the graphite film to the methane molecule. We also calculated the case of the symmetrical adsorption for methane adsorbed on the double surfaces of the graphite film. The corresponding work function is 4.60 eV, larger than those of the clean film and of the single adsorption system as we expect. The calculated results are shown in Fig. 4 with the relaxed structures. It is clear that the work function is enlarged after methane adsorption.

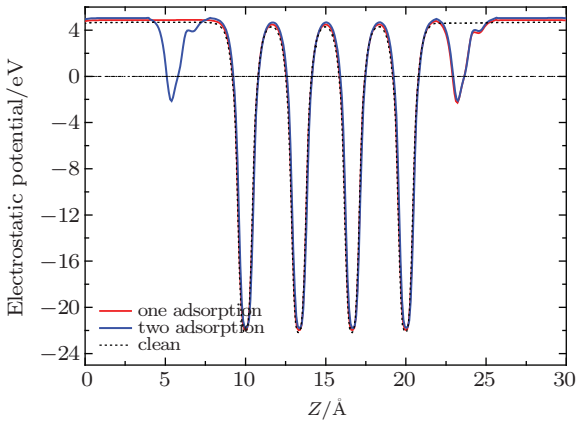


Fig. 4. (color online) The work functions of clean surface, one CH_4 molecule adsorption on graphite, and two CH_4 molecules adsorption on graphite systems with the relaxed structures.

4. Conclusion

In conclusion, the electronic density of states, work function, and adsorption energy of the methane molecule adsorbed on graphite(0001) films has been examined with the plane-wave pseudopotential formalism of DFT. The results showed that the interlayer relaxation, the surface energy of the film are small due to the unique chemical bonding properties of graphite. We have found that CH_4 adsorbs preferentially

at onefold top sites on surface with the adsorption energies −135 meV. Moreover, the methane prefers locating at 3.21 Å above the film and the adsorption energy is not dependent on the thickness of the substrate. Finally, the work function have been calculated. After methane adsorption, the work function is enlarged. The results indicate that there is a slight charge transfer from the graphite film to the methane molecule. We expect that the present results are helpful to researchers deeply and fundamentally understand the mechanism of interaction between methane and graphite in mining.

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