

Theoretical investigation of methane adsorption onto boron nitride and carbon nanotubes

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Abstract

Methane adsorption onto single-wall boron nitride nanotubes (BNNTs) and carbon nanotubes (CNTs) was studied using the density functional theory within the generalized gradient approximation. The structural optimization of several bonding configurations for a CH₄ molecule approaching the outer surface of the (8,0) BNNT and (8,0) CNT shows that the CH₄ molecule is preferentially adsorbed onto the CNT with a binding energy of $-2.84 \text{ kcal mol}^{-1}$. A comparative study of nanotubes with different diameters (curvatures) reveals that the methane adsorptive capability for the exterior surface increases for wider CNTs and decreases for wider BNNTs. The introduction of defects in the BNNT significantly enhances methane adsorption. We also examined the possibility of binding a bilayer or a single layer of methane molecules and found that methane molecules preferentially adsorb as a single layer onto either BNNTs or CNTs. However, bilayer adsorption is feasible for CNTs and defective BNNTs and requires binding energies of -3.00 and $-1.44 \text{ kcal mol}^{-1}$ per adsorbed CH₄ molecule, respectively. Our *first-principles* findings indicate that BNNTs might be an unsuitable material for natural gas storage.

Keywords: methane, BNNTs, SWCNTs, adsorption, *ab initio* calculations

1. Introduction

Natural gases as an environmentally friendly energy source and bulk transportation fuel are considered to be one of the best substitutes for fossil fuels in the future. However, their storage remains problematic. Recently, interest has shifted towards the use of nanoporous materials as a promising alternative to compressing natural gas to high pressures ($\sim 30 \text{ MPa}$) [1, 2]. Methane is one of the major components of natural gases therefore its adsorption behavior in confined pores is of practical and theoretical interest [3–13]. Several experimental and theoretical studies addressed the adsorption of methane on carbon-based nanoparticles. The focus remains on carbon nanotubes (CNTs) [10, 14–16] because of their unique properties including uniform porosity, high tensile strength and relative inertness. However, despite their promising results CNTs showed poor gas adsorption.

Since the discovery of boron nitride nanotubes (BNNTs) [17], much attention has been paid to this novel

material, particularly to its suitability to gas storage [18–22]. Their very high chemical reactivity, stability and mechanical strength have made BNNTs an important material in nanotechnology.

The main purpose of this study is to inspect the methane adsorption capability of BNNTs using density functional theory (DFT) calculations, to elucidate their adsorption mechanisms and develop adsorption models. To examine methane adsorption, we have calculated binding energies E_b for different configurations of a methane molecule approaching the exterior surface of a nanotube.

2. Computational methods

The results presented in this paper were obtained using self-consistent DFT calculations with the *ab initio* simulation package SIESTA [23, 24]. This state-of-the-art package employs a numerical atomic orbital basis and a periodic

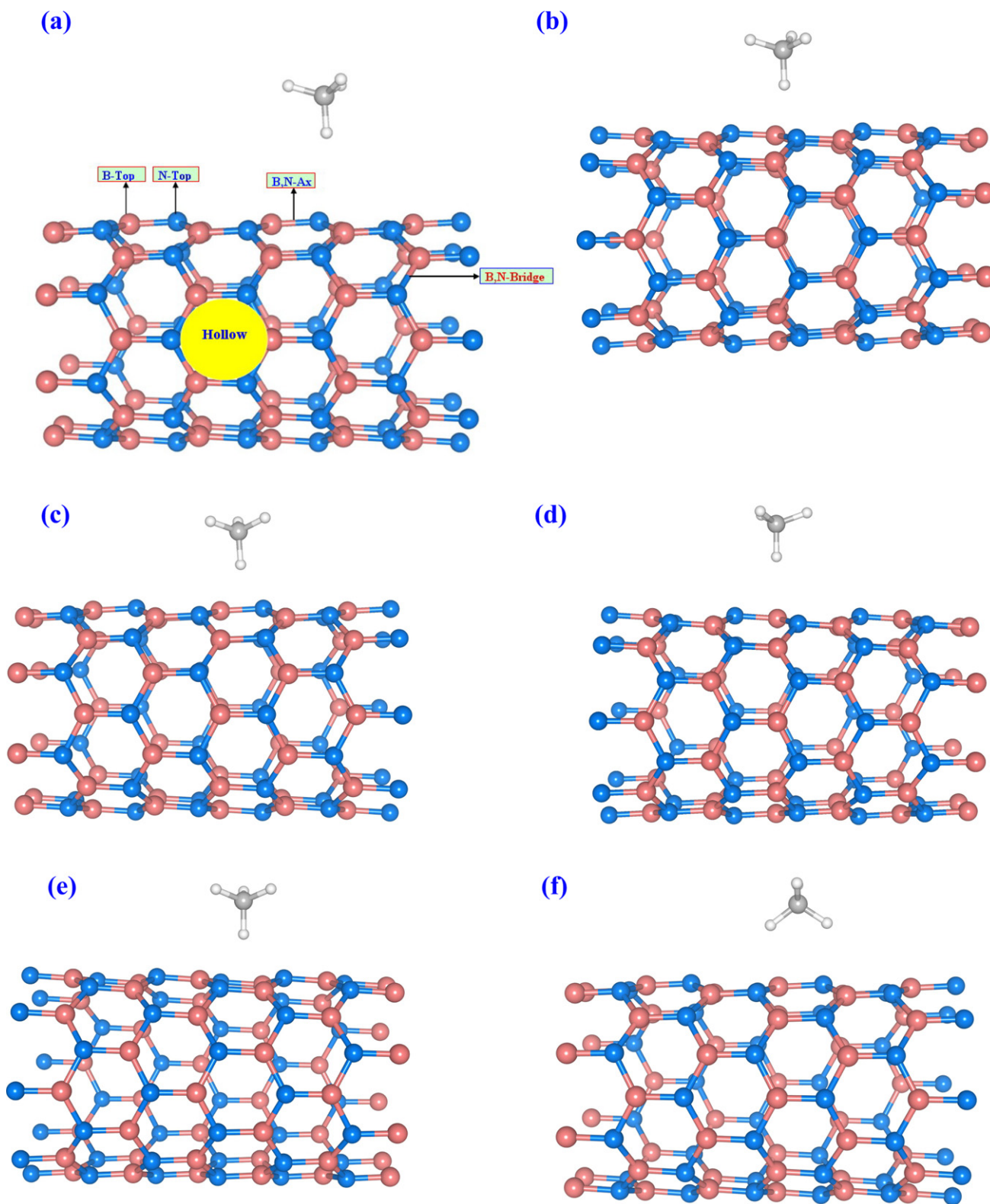


Figure 1. Different configurations of CH₄ molecule approaching the (8,0) BN nanotube via its –CH group over (a) nitrogen atom, (b) boron atom, at the centers of two nonequivalent B–N bonds (c) parallel and (d) nonparallel to the nanotube axis and (e) above the center of a hexagon of B and N atoms. Similar selected configurations for the CH₄ molecule approaching the tube via its –CH₂ and –CH₃ groups are represented in (f)–(j). Panel (a) presents the hollow site (Hol) above the center of the hexagon, the bridge (B, N-Ax) and zigzag (B, N-Zig) sites above the B–N bonds, and the top site directly above the boron atom (B-Top) and nitrogen atom (N-Top). Atom colors: grey–carbon, white–hydrogen, blue–nitrogen and red–boron.

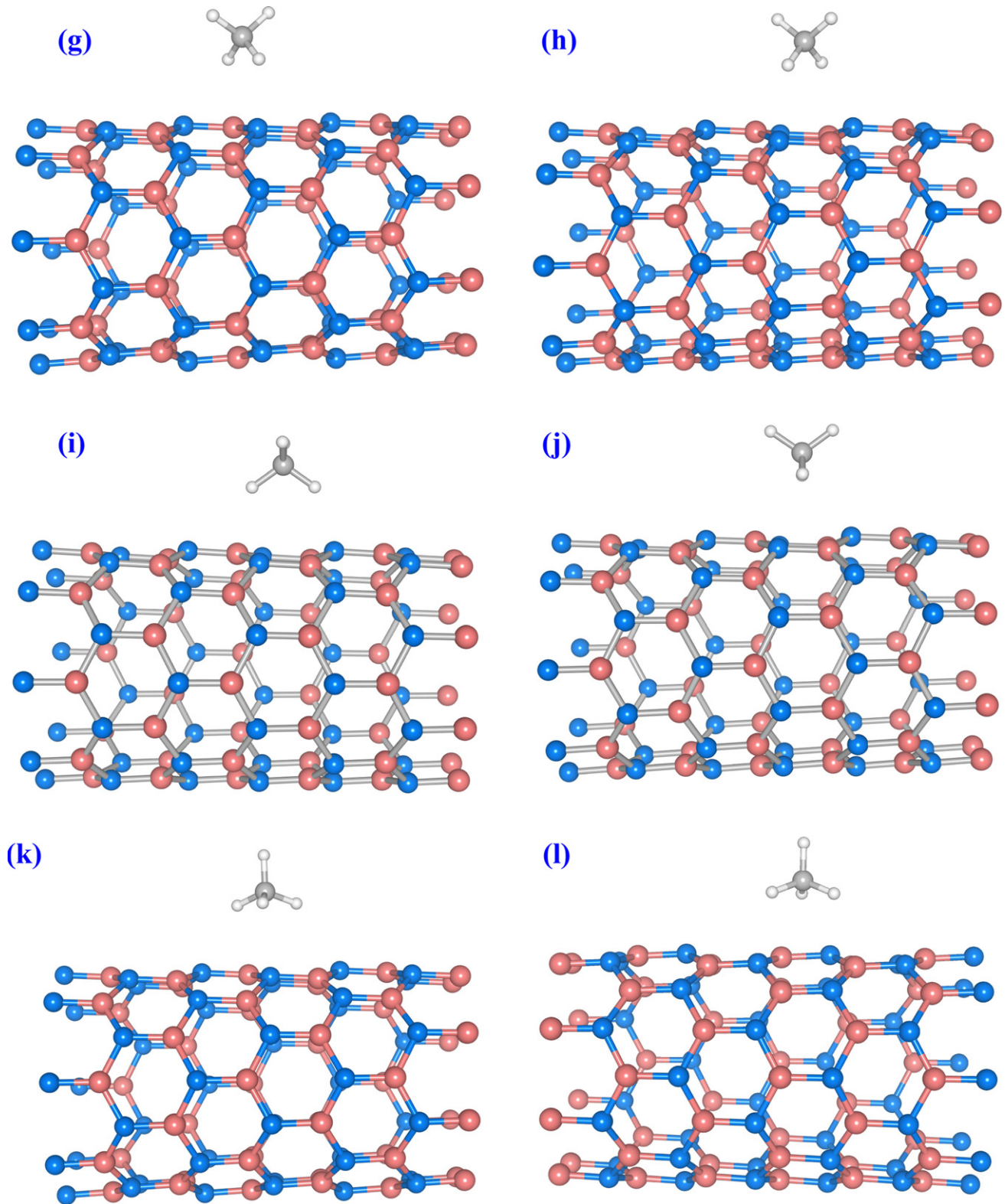


Figure 1. Continued.

supercell method. Direct diagonalization of the Kohn–Sham Hamiltonian is performed for Γ -point electronic structure calculations. For the exchange and correlation terms, the generalized gradient approximation (GGA) was used as described by Perdew *et al* [25]. Core electrons were

represented by the improved Troullier–Martins pseudo-potentials [26], and a numerical atomic orbital basis with polarization was used for valence electrons. All the calculations were performed with a double- ζ plus polarization basis set. A cut-off energy of 125 Ryd was set for grid integration.

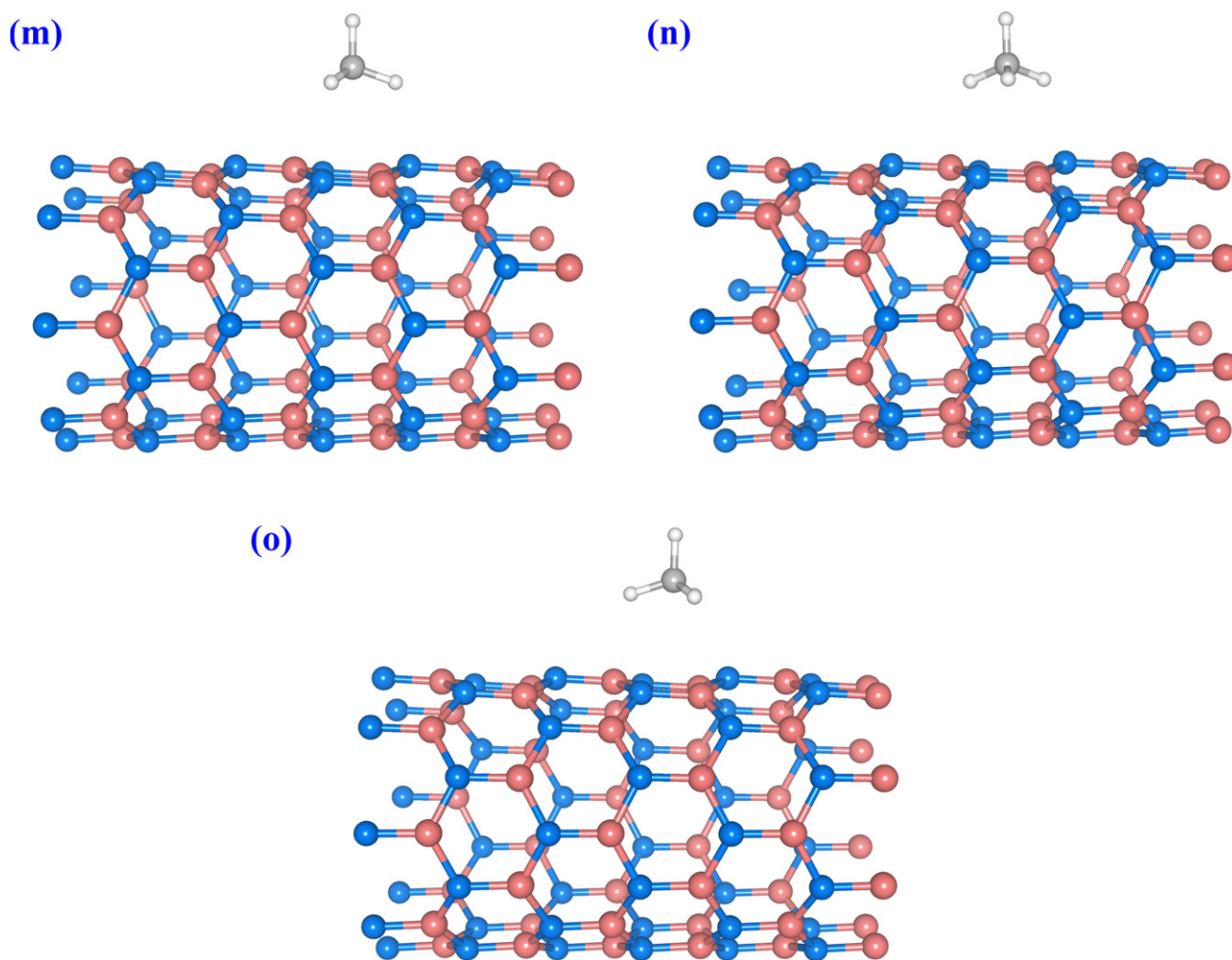


Figure 1. Continued.

Infinite one-dimensional (8,0) and (10,0) single-wall boron nitride and carbon nanotubes were simulated. We applied periodic-boundary conditions and supercell approximations with a lateral separation of 40 Å between the tube centers, which were large enough to neglect the interaction between the nanotube and methane and its periodic images. The supercells had 96 boron–nitrogen (carbon) atoms with tube lengths of 11.938 and 11.992 Å for the (8,0) BNNT and (8,0) CNT and 120 boron–nitrogen (carbon) atoms for the (10,0) BNNT and (10,0) CNT with tube lengths of 12.044 and 12.088 Å, respectively. The structural optimization was terminated when the forces due to displacements of an atom in the unit cell converged within 0.02 eV Å⁻¹.

The molecular binding energy, E_b , was obtained using

$$E_b = E_{\text{NT+Methane}} - E_{\text{NT}} - E_{\text{Methane}},$$

where E_{NT} , $E_{\text{NT+Methane}}$ and E_{Methane} are the total energies of a free nanotube, NT with adsorbate and a single methane molecule, respectively. Thus, a negative binding energy indicates that the adsorption process is exothermic and that the addition of methane leads to a stable complex. Binding energy was estimated for different methane configurations; its significance is discussed in the next section.

3. Results and discussion

To examine the adsorption behavior of methane molecules on BNNTs, we considered several orientations of the methane molecule (i.e. –CH, –CH₂ and –CH₃ groups) relative to the respective BNNT rings near the three symmetry sites on a BNNT. Figure 1(a) shows these sites: the hollow site (Hol) above the center of the hexagon, the bridge (B, N-Ax) and zigzag (B, N-Zig) sites above the B–N bonds and the top site directly above the boron atom (B-Top) and nitrogen atom (N-Top). Figures 1(a)–(o) also show the adsorption of methane at these sites with different orientations. The interaction of the CH₄ molecule with the exterior wall of the BNNT was studied by performing optimization calculations for several orientations of the molecular axis. The system included 60 B atoms, 60 N atoms and one methane molecule. The optimized (8,0) BNNT and methane molecule were used for adsorption. After full structural optimization of all the considered configurations we found that the methane molecule is preferentially adsorbed, through its –CH₃ groups, on the hollow site above the center of a nanotube hexagon. The calculated binding energy for the energetically most favorable state is –2.79 kcal mol⁻¹ and the equilibrium

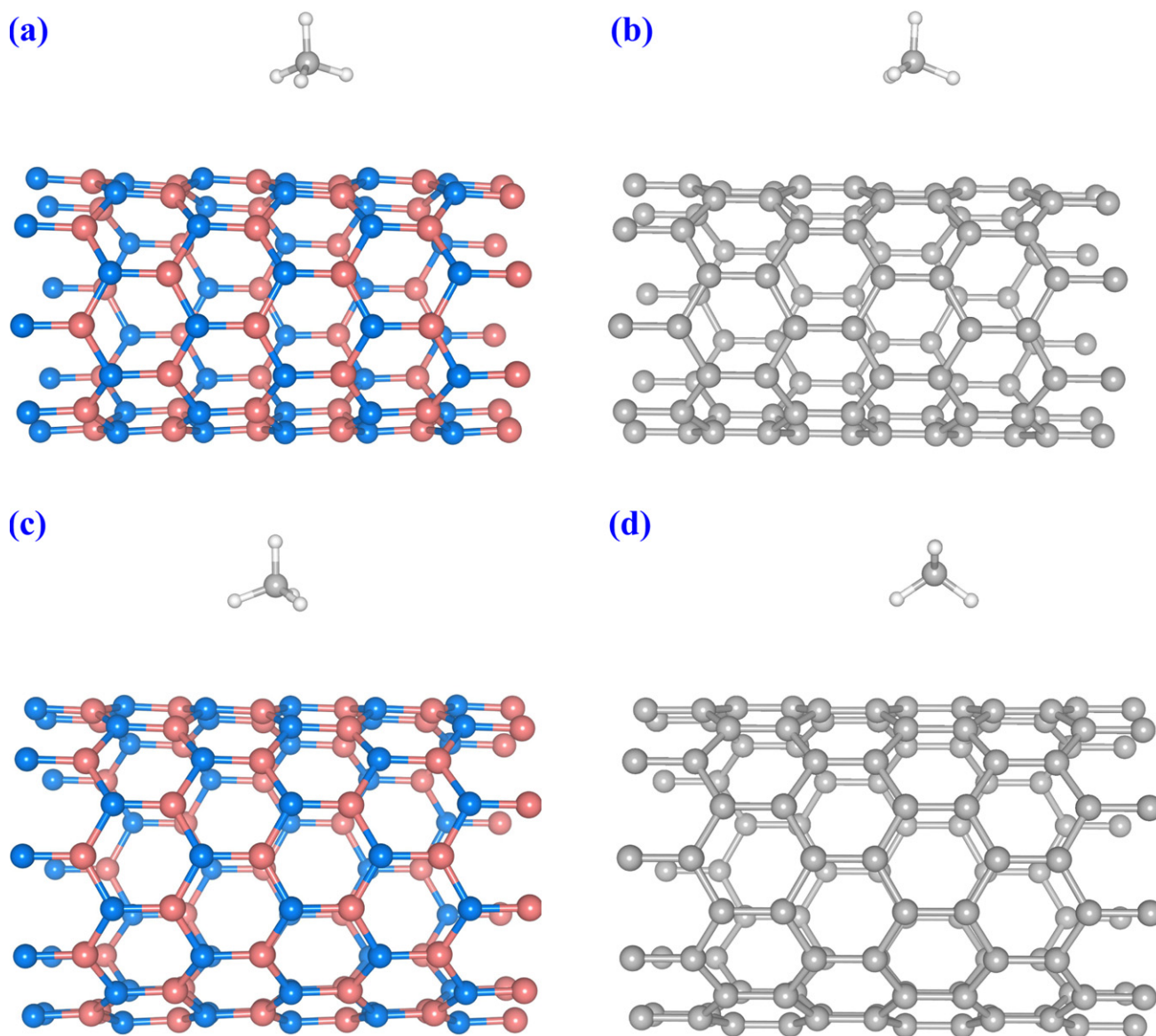


Figure 2. Optimized geometric structures for the most stable state of a methane molecule interacting with the (a) BNNT (8,0), (b) CNT (8,0), (c) BNNT (10,0) and (d) CNT (10,0).

distance between the closest atoms in the nanotube and methane (H atom from the methane molecule and N atom from the nanotube) is 3.044 Å. Our *first-principles* calculation results also yield an average C–H bond length of 1.102 Å in methane, which is basically the same as that in the isolated molecule (1.101 Å). Figure 2 shows the optimized geometric structure of the most stable methane/BNNT complex. The relatively large equilibrium CH_4 –substrate separation and small binding energy suggest the involvement of only noncovalent interactions in the adsorption. The present results also show that the methane molecule is weakly bound to the outer surface of the nanotube, with an adsorption energy comparable to those for amino acids, nucleic acid bases and gas molecules on carbon-based nanostructures [27–34].

For comparison, we have also examined methane adsorption onto carbon nanotubes using a similar calculation procedure for a methane molecule approaching the exterior surface of the (8,0) CNT. Optimization calculations for several

selected orientations reveal that methane is preferentially adsorbed at the center of a six-membered carbon ring via its $-\text{CH}_3$ group. The binding energy for the energetically most favorable complex is $-2.84 \text{ kcal mol}^{-1}$ and the equilibrium distance between the closest atoms of the methane molecule (H) and the carbon atom of the tube is 2.857 Å. Comparing these results with those obtained for the CH_4 /BNNT system reveals that methane is preferentially adsorbs onto the exterior surface of the CNTs.

To study the effect of the nanotube curvature (diameter), we investigated the adsorption of methane molecules onto the large-diameter (low-curvature) single-walled BNNTs and CNTs. For this purpose, we first selected the (10,0) BNNT and performed similar calculation procedures for the molecule attached to the various active sites of the tube. After full structural optimization of the considered configurations, the respective binding energies were found positive (about 5 kcal mol^{-1}) for all the considered sites

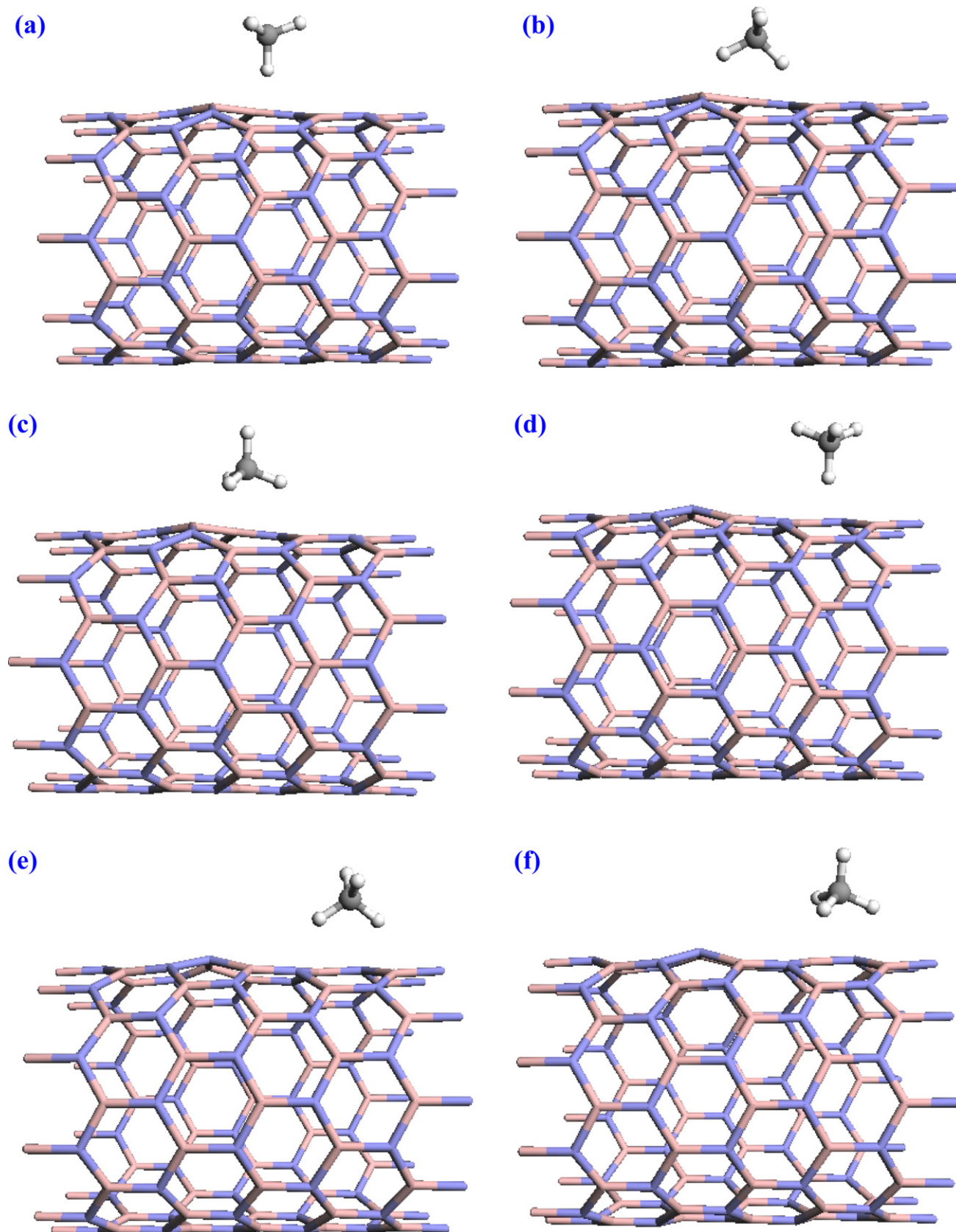


Figure 3. Model for nine different adsorption states of a methane molecule on a defective (10,0) BNNT above a defect heptagon site via its (a) $-CH$, (b) $-CH_2$ and (c) $-CH_3$ groups. Similar adsorption states for a methane molecule approaching the defective nanotube surface with respect to the hexagon and defect pentagon rings are represented in (d)–(i).

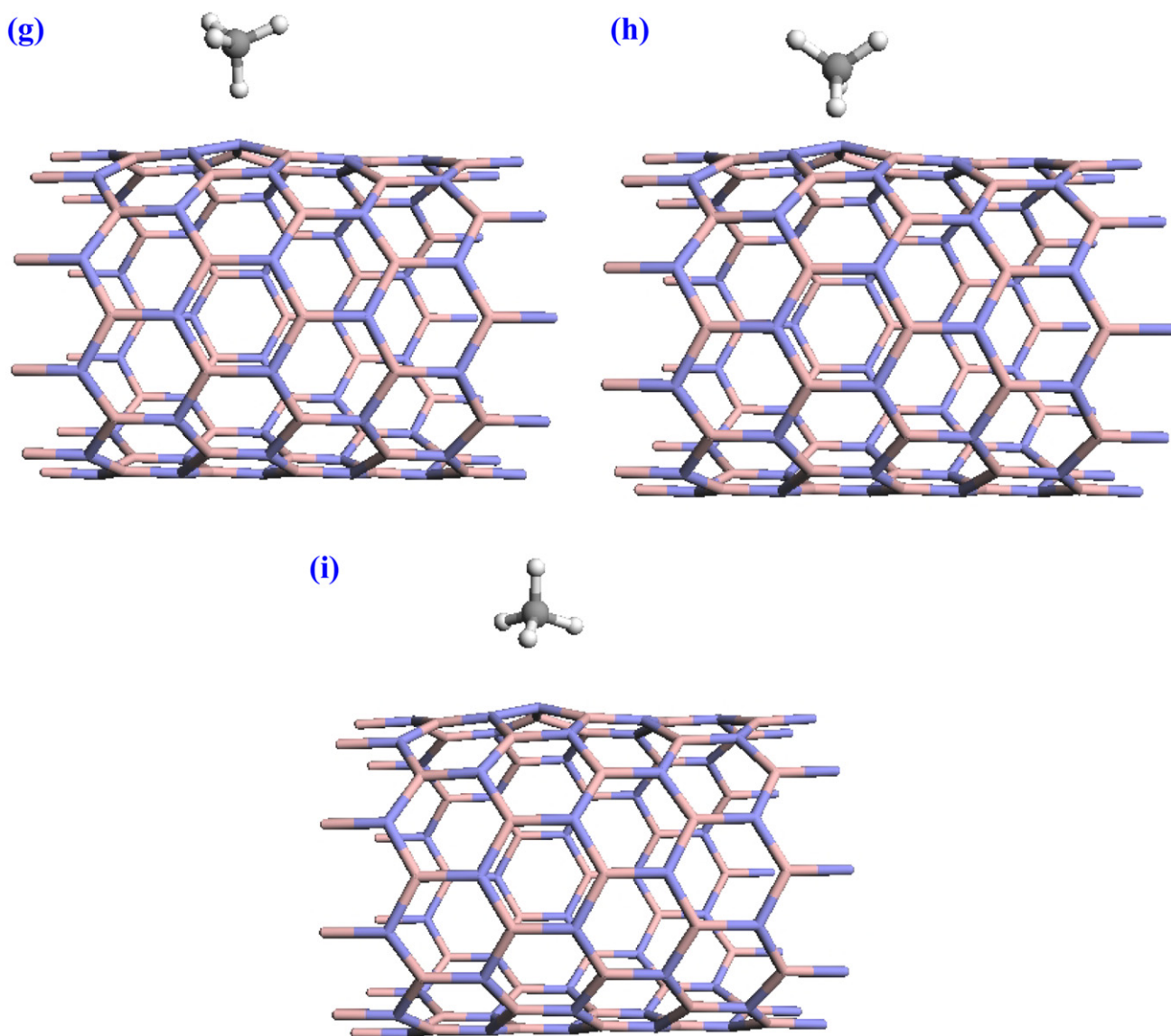


Figure 3. Continued.

indicating that methane adsorption onto the (10,0) BNNT is an endothermic and thermodynamically unfavorable process (metastable state).

We then evaluated the methane adsorption capability of the (10,0) CNT and found that the hollow site of a carbon hexagon is the most stable adsorption site for the methane molecule approaching the tube via the $-\text{CH}_2$ group, with the binding energy of $-2.97 \text{ kcal mol}^{-1}$ and a C–H binding distance of 2.803 \AA . Figure 2 schematically shows the optimized geometric structures of the most stable states for the methane molecule at the surface of the (8,0) and (10,0) CNTs and BNNTs. Comparing the results obtained for the (8,0) and (10,0) nanotubes, we conclude that the binding energy of methane increases for adsorption onto wider CNTs and decreases for adsorption onto wider BNNTs.

We now determine the effect of structural defects on the interaction of methane with BNNTs. Following a conventional procedure, we started by carrying out the optimization process

for the methane molecule approaching a defective (10,0) BNNT. Nine possible configurations were selected for a methane molecule approaching the center of the heptagon, hexagon and pentagon of B and N atoms via its $-\text{CH}$, $-\text{CH}_2$ and $-\text{CH}_3$ groups. Figure 3 shows the orientation schemes employed in the modeling. After full structural optimization of the considered systems, we found that the adsorption of methane molecules via its $-\text{CH}_3$ group is preferred on the pentagon of a defective nanotube. The corresponding binding energy is relatively large at $-2.22 \text{ kcal mol}^{-1}$ meaning that structural defects assist methane absorption onto BNNTs.

Finally, to further evaluate the methane adsorption capability for BNNTs and CNTs, we compared the methods of forming additional layers around these nanotubes. For this purpose, we selected two configurations for methane molecules attached to the nanotubes as shown in figure 4. The first one consists of two methane molecules set at different distances with respect to the nanotube wall, in such a way

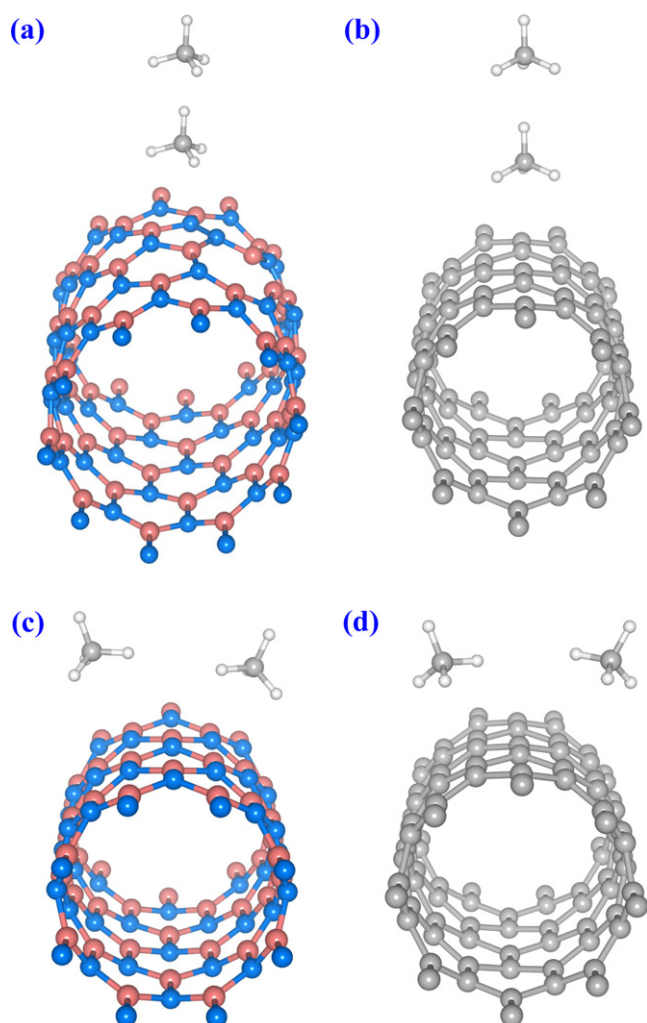


Figure 4. Model of two methane molecules set at different distances to the (a) defective (10,0) BNNT and (b) (8,0) CNT in such a way that only the first molecule is directly adsorbed on the tube surface; (c) and (d) schematically represent a single layer of two methane molecules situated on the active sites of the (8,0) BNNT and (8,0) CNT, respectively.

that only the first molecule is directly attached to the active adsorption site of the nanotube. In the second configuration, two methane molecules are positioned at adjacent active sites of the nanotube surface as a single layer of adsorbed molecules. We find that methane molecules prefer to adsorb as a single layer with binding energies of -3.13 and $-4.37 \text{ kcal mol}^{-1}$ per adsorbed CH_4 molecule for the (8,0) BNNT and (8,0) CNT, respectively. Our results indicate that the bilayer adsorption of methane is possible for the (8,0) CNT and defective (10,0) BNNT with binding energies of -3.00 and $-1.44 \text{ kcal mol}^{-1}$ per CH_4 molecule, respectively. Thus, we conclude that wide CNTs and BNNTs are more suitable for methane adsorption than narrow ones, and that CNTs can adsorb more than one methane layer. However, our *first-principles* calculation results for methane adsorption onto the zigzag CNTs and BNNTs contradict the Grand Canonical Monte Carlo (GCMC) simulations by Xiu-Ying *et al* [35] for hydrogen adsorption onto armchair CNTs and BNNTs.

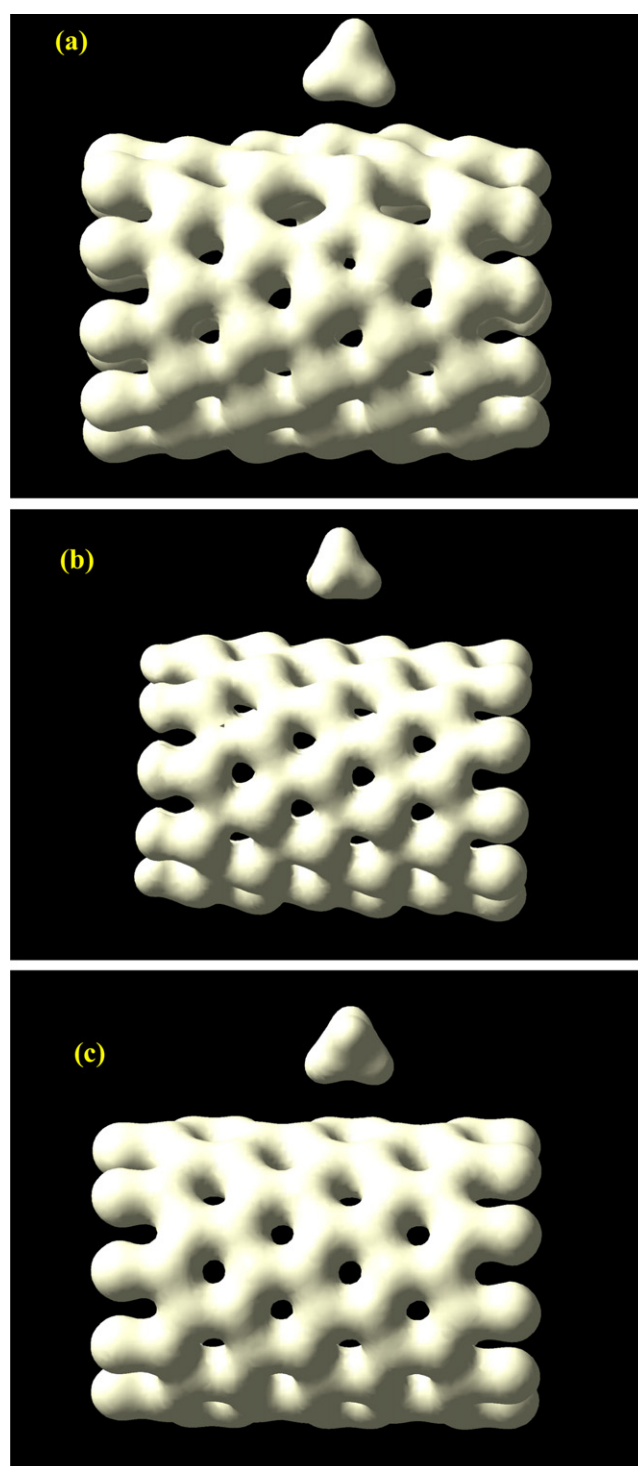


Figure 5. Isosurface of the total electron density for the (a) defective (10,0) BNNT/ CH_4 , (b) perfect (10,0) BNNT/ CH_4 and (c) (10,0) CNT/ CH_4 complexes, where 0.05 eV \AA^{-3} was used as an isovalue of total electron density.

To elucidate the adsorption of methane onto the considered nanotubes, we obtained the total electron density maps of electronic density. Figure 5 shows isosurface maps for the energetically most favorable complexes of the methane molecule and a (10,0) BNNT or CNT. The figure shows that the physically adsorbed methane, which

is far from the tubes, has almost no effect on the electronic charge distribution of B, N or C atoms of the tubes; thus, no significant charge transfer occurs between the methane molecule and the nanotubes. We further evaluated this charge transfer by Mulliken charge analysis. Negligible charge ($0.002 e$) is transferred from the (10,0) BNNT to the methane molecule, whereas $0.03 e$ is transferred from the (10,0) CNT. These results emphasize that the interaction is weak (physisorption) between the methane molecule and BNNTs or CNTs.

4. Conclusions

We theoretically investigated methane adsorption onto the exterior surface of single-walled carbon nanotubes and BNNTs to evaluate their methane storage capability. The structural optimization of several different bonding configurations for methane molecules approaching the outer surface of the (8,0) BNNT was computed using *ab initio* DFT calculations to determine the most stable state of methane adsorption onto such nanotubes. The *first-principles* total energy analysis revealed that the CH_4 molecule adsorbs through its $-\text{CH}_3$ group just above the hollow site of a nanotube hexagon, with corresponding binding energy of $-2.79 \text{ kcal mol}^{-1}$. This binding energy is 18% larger for the (8,0) CNT than for the (8,0) BNNT, which should affect the methane storage capacity of these nanotubes. The deduced energies and binding distances are typical for physisorption, for both CNTs and BNNTs.

We also investigated the effect of nanotube diameter (curvature) on methane adsorption and found that methane molecules bind more strongly to the exterior surface of wider CNTs, however, the adsorption capability decreases for wider BNNTs. Furthermore, the introduction of defects in BNNTs significantly enhances methane adsorption in comparison with the use of perfect BNNTs.

We also examined the possibility of binding more than one layer of CH_4 molecules and found that methane molecules preferentially adsorbed as a single layer on the (8,0) BNNT and (8,0) CNT. Our calculations indicate that the bilayer adsorption of methane is feasible for the (8,0) CNT and defective (10,0) BNNT with binding energies of -3.00 and $-1.44 \text{ kcal mol}^{-1}$ per adsorbed methane molecule, respectively. Thus, we conclude that BNNTs might be unsuitable for the storage of methane and thus of natural gases.

Results of the electronic structure and Mulliken analyses highlight that the methane molecule and BNNT or CNT interact rather weakly and that no significant hybridization takes place between their respective orbitals.

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