การศึกษาเชิงทฤษฎีของการดูดซับแก๊สบนท่อนาโนคาร์บอนแบบผนังชั้นเดียวที่เติมด้วยอะตอมคู่ซิลิกอน

Theoretical investigation of gas adsorption on SiSi co-doped single wall carbon nanotube

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บทคัดย่อ

ได้ศึกษาสมบัติเชิงโครงสร้าง สมบัติเชิงอิเล็กทรอนิกส์ และ สมบัติการดูดซับแก๊สบนผนังท่อนาโนคาร์บอนแบบผนังชั้นเดียวที่เติมอะตอมคู่ซิลิกอน โดยใช้ทฤษฎีฟังก์ชันนัลความหนาแน่นที่ระดับของทฤษฎี B3LYP/6–31G(d,p) ผลการคำนวณ แสดงให้เห็นว่าแก๊ส H_2, CO, CO_2 และ N_2O สามารถดูดซับกับท่อนาโนคาร์บอนแบบผนังชั้นเดียวที่เติมอะตอมคู่ซิลิกอนได้ โดยที่แก๊ส CO ดูดซับได้ดีที่สุดเมื่อเทียบกับแก๊สชนิดอื่น

คำสำคัญ: ท่อนาโนคาร์บอน, การเติมอะตอมคู่, ทฤษฎีฟังก์ชันนัลความหนาแน่น, การดูดซับแก๊ส

ว วทย เทคโน มมส

Abstract

The structural, electronic and gas adsorption properties on a SiSi co-doped single wall carbon nanotube (SWCNT) were investigated using the density functional theory at the B3LYP/6–31G(d,p) theoretical level. The computed results indicate that H_2, CO, CO_2 and N_2O can adsorb with SiSi co-doped SWCNT and that CO gas shows the strongest adsorption as compared to the other gases.

Key words: Carbon nanotubes, Co-doped, Density functional theory, Gas adsorption

J Sci Technol MSU

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Introduction

Carbon nanotubes (CNTs) comprised of sheets of carbon in a hexagonal lattice that are rolled into a cylinder and were first discovered by Sumo Iijima.[1] The CNTs have been used in a wide range of applications in material reinforcement, field emission panel display, chemical sensing, drug delivery, and nanoelectronics.[2] The CNTs belong to the family of fullerene structures. There are two types of nanotubes: single walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs).[3] The SWCNTs were also first discovered by Sumo Iijima and his team.[4] The SWCNT is only one graphene sheet which is rolled. Many recent studies focused on these nanotubes, finding applicability in molecular electronics,[5,6] nanomechanics,[7,8] optics,[9,10] and sensors.[11,12] The SWCNT can exhibit metallic or semiconducting properties,[13] depending on its diameter and chirality. This unique ability to be both metallic and semiconducting without doping has led to speculation that SWCNT might serve as a key building block for the construction and design of carbon-based electronics.[14] After doping SWCNT with intercalates species which can be located either in between the individual tubes or inside the tube.[15] Silicon doped carbon nanotubes for modifying electronic and structural properties of SWCNTs have been reported.[16] It was predicted that Si substitutional doping may impose changes in the chemical reactivity and hence in the interaction of the tube with foreign atoms and molecules through the Si sites. Another observed characteristic of the electronic structure is the strong localization on the Si sites of both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states. This would permit the creation of novel nanotube-related materials by modifying the functionality of CNTs themself by, first, substitutional doping of carbon by silicon atom and, subsequently, trapping of foreign atoms or molecules.[17] The adsorptions of small gas molecules on SWCNTs have been widely studied and reported. The adsorptions of H_2,[18-21] CO_2,[19, 22] N_2,[22, 23] CO,[22, 23] and O_2,[24] gases on SWCNTs were also studied. Gas adsorption on CNT is an important issue for both fundamental research and technical application of nanotubes.[24]

In the present work, the adsorptions of various gas molecules on SiSi co-doped armchair (5,5) SWCNTs have been investigated by using the density functional (DFT) method. Structural and electronic properties of pristine, SiSi co-doped SWCNT and their various gas molecule adsorption structures have been determined and reported.

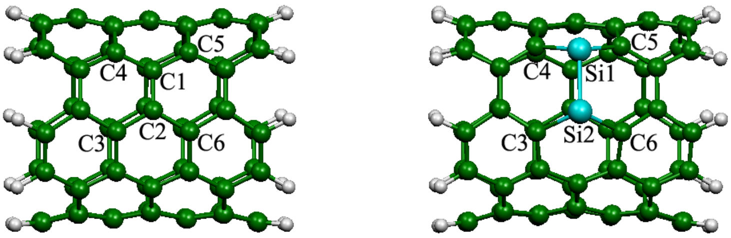
Computational details

The system of pristine SWCNT was composed 70 carbon atoms. The system of SiSi co–doped SWCNT was composed 68 carbon atoms and two Si atoms. H atoms were used to terminate the ends of both systems, resulting in systems with molecular formula $C_{70}H_{20}$ and $Si_2C_{68}H_{20}$. The structures of pristine and SiSi co–doped SWCNT, were optimized by using density functional (DFT) method at the B3LYP/6–31G(d,p) theoretical level.[25] Additionally, the adsorption abilities of various gas molecules on SiSi co–doped SWCNT were studied using the same theoretical level. All calculations were performed using the GAUSSIAN 03 program.[26] The electronic structure of bare SiSi co-doped SWCNT and gas-adsorbed SiSi co-doped SWCNT were plotted and analyzed by the GAUSSUM 2.1.4 program.[27] The partial charge transfer (PCT)[28] which is defined as a charge difference of a gas molecule before and after adsorption process was investigated by using natural bond orbital (NBO) analysis implemented in GAUSSIAN 03 program.

The adsorption energies (ΔE_{ads}) of various gas molecules adsorbed on SiSi co–doped SWCNT were calculated according to the following equations:

$$\Delta E_{ads} = E(\text{gas/SiSi-SWCNT}) - E(\text{SiSi-SWCNT}) - E(\text{gas})$$

Where *E*(gas/SiSi-SWCNT) and *E*(SiSi-SWCNT) are the total energies of gas molecule adsorbed on SiSi-doped SWCNT and SiSi co–doped SWCNT, respectively. And *E*(gas) is the total energy of a gas molecule.



(a) (b)

Figure 1 The B3LYP/6-31G(d,p) optimized structures of (a) pristine armchair (5,5) SWCNT and (b) SiSi co-doped SWCNT**.**

Results and discussion

Geometries of the SiSi co-doped SWCNT and its adsorptions with gas molecules

The B3LYP/6-31G(d,p) optimized structures of SWCNT and SiSi co-doped SWCNT are displayed in Figure 1, the selected geometrical parameters of all optimized structures are listed in Table 1. The Si1-Si2 (2.187 Å), C4—Si1 (1.788 Å), C5—Si1 (1.788 Å), C3—Si2 (1.788 Å) and C6—Si2 (1.788 Å) bond lengths of SiSi co-doped SWCNT are longer than C1—C2 (1.408 Å), C1—C4 (1.434 Å), C1—C5 (1.434 Å), C2—C3 (1.434 Å) and C2—C6 (1.434 Å) bond lengths of SWCNT. The C4—Si1—C5 (108.4^{o}), C4—Si1—Si2 (103.7^{o}), C5—Si1—Si2 (103.7^{o}), C3—Si2—C6 (108.5^{o}), C3—Si2—Si1 (103.7^{o}) and C6—Si2—Si1 (103.7^{o}) bond angles for SiSi doped SWCNT are smaller, compared to C4—C1—C5 (120.2^{o}), C4—C1—C2 (118.6^{o}), C5—C1—C2 (118.6^{o}), C3—C2—C6 (120.3^{o}), C3—C2—C1 (118.6^{o}) and C3—C2—C1 (118.6^{o}) bond angles of the undoped SWCNT.[22] Clearly, doping of the SiSi atoms cause the deformation of the six-membered rings in the doping site of the SWCNT and the SWCNT surfaces are protruding similarly to pyramidal structure. The optimized structures of H_2, CO, CO_2 and N_2O molecules adsorbed on the SiSi co-doped SWCNT computed at B3LYP/6-31G(d,p) level of theory are displayed in Figure 2, and the selected geometrical parameters are also listed in Table 1. For the various gas molecules adsorbed on SiSi co-doped SWCNT, the Si1-Si2, C4—Si1, C5—Si1, C3—Si2 and C6—Si2 bond lengths are longer than the corresponding bond lengths of bare SiSi co-doped SWCNT. The C4—Si1—C5, C4—Si1—Si2, C5—Si1—Si2, C3—Si2—C6, C3—Si2—Si1 and C6—Si2—Si1 bond angles of various gas molecules adsorbed on SiSi co-doped SWCNT are narrowered, compared to the corresponding bond angles without gas adsorptions. The results indicate that various gas molecule adsorptions have more affect on the geometrical structures at the adsorption sites of SiSi co-doped SWCNT than that of those without gas molecule adsorptions.

Table 1 Selected geometrical parameters of adsorption structures of the various gas molecules adsorbed on SiSi co–doped SWCNT. Distances and angles are given in angstrom (Å) and degree (°), respectively.

Species	Bond distance					Bond angles					
	Si1-Si2	C4-Si1	C5-Si1	C3-Si2	C6-Si2	C4-Si1-C5	C4-Si1-Si2	C5-Si1-Si2	C3-Si2-C6	C3-Si2-Si1	C6-Si2-Si1
SWCNT	1.408	1.434	1.434	1.434	1.434	120.2	118.6	118.6	120.3	118.6	118.6
SiSi-SWCNT	2.187	1.788	1.788	1.788	1.788	108.5	103.7	103.7	108.4	103.7	103.7
H_2/SiSi-SWCNT	2.193	1.887	1.888	1.771	1.771	99.6	84.2	84.2	110.2	120.6	120.6
$\underline{C}O$/SiSi-SWCNT[a]	2.203	1.895	1.895	1.779	1.779	98.8	83.7	83.7	109.6	120.5	120.5
$C\underline{O}$/SiSi-SWCNT[b]	2.192	1.888	1.888	1.771	1.772	99.5	84.3	84.3	110.3	120.5	120.5
$\underline{C}O_2$/SiSi-SWCNT[a]	2.193	1.888	1.888	1.771	1.771	99.6	84.2	84.2	110.3	120.6	120.6
$C\underline{O_2}$/SiSi-SWCNT[b]	2.193	1.886	1.885	1.771	1.771	99.7	84.4	84.4	110.3	120.6	120.5
$\underline{N_2}O$/SiSi-SWCNT[c]	2.193	1.887	1.887	1.772	1.773	99.6	84.5	84.5	110.2	120.3	120.3
$N_2\underline{O}$/SiSi-SWCNT[d]	2.194	1.888	1.888	1.774	1.774	99.5	84.4	84.4	110.1	120.4	120.4

[a] Pointing with its C atom toward adsorption site of SiSi co-doped SWCNT.

[b] Pointing with its O atom toward adsorption site of SiSi co-doped SWCNT.

[c] Pointing with its N atom toward adsorption site of SiSi co-doped SWCNT.

[d] Pointing with its O atom toward adsorption site of SiSi co-doped SWCNT.

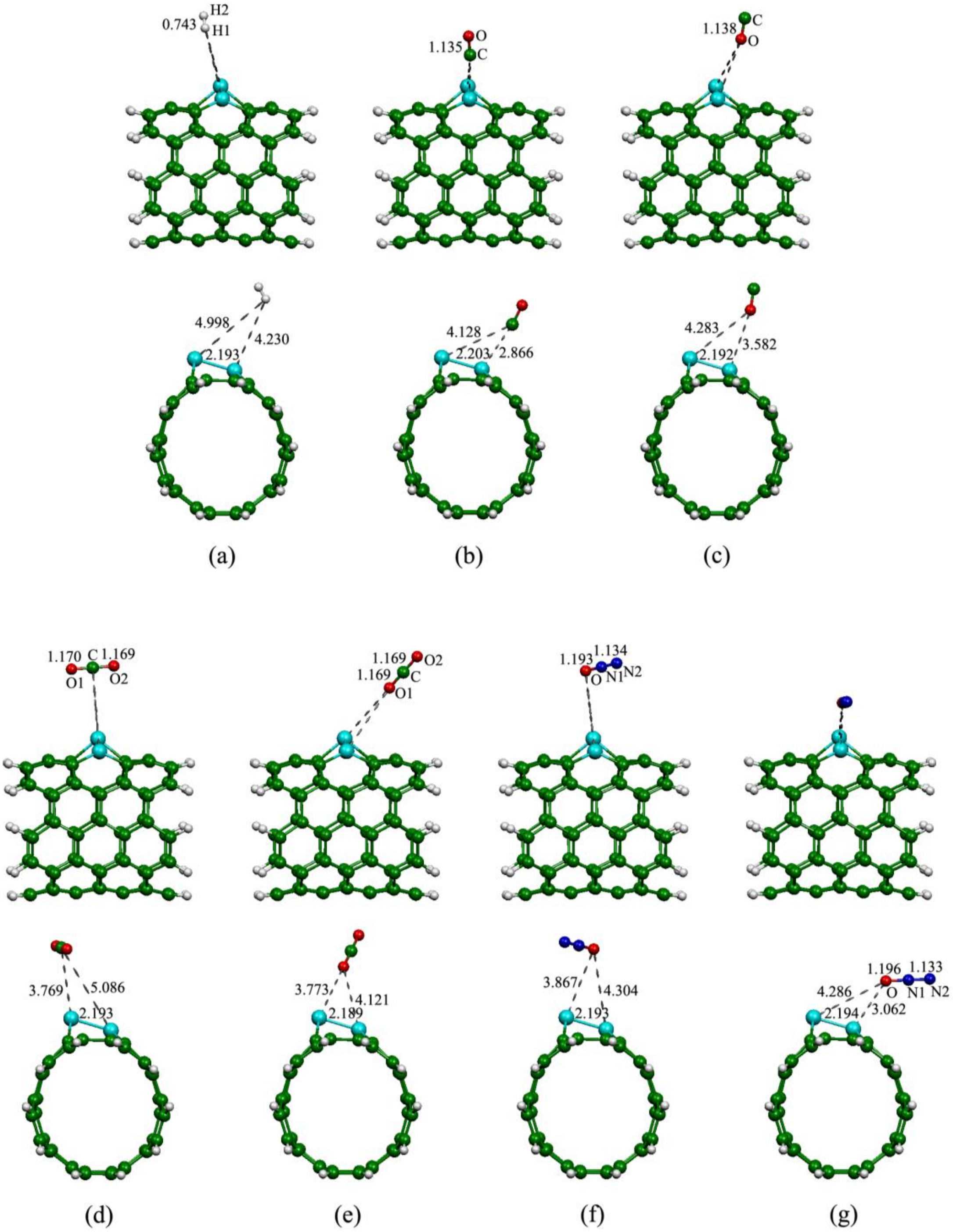


Figure 2 Adsorption configurations of (a) H_2, (b) CO pointing with C, (c) CO pointing with O, (d) CO_2 pointing with C, (e) CO_2 pointing with O, (f) N_2O pointing with N and (g) N_2O pointing with O to the SiSi co-doped SWCNT, computed at the B3LYP/6-31G(d,p) level. Top and bottom are side and front views, respectively.

Adsorption of various gas molecules on the SiSi co–doped SWCNT

The adsorption energies of various gas molecules (H_2, CO, CO_2, and N_2O) adsorbed on the SiSi co-doped SWCNT and partial charge transfer[28] during adsorption are shown in Table 2. It is found that the PCT for most of gases adsorbed on the SiSi co-doped SWCNT are positive which indicated that partial charges of gas molecules transfer to SiSi co-doped SWCNT. The adsorption ability of the CO, CO_2 and N_2O (Pointing with its O atom toward adsorption site of doped SWCNT) to the SiSi co-doped SWCNT is in the decreasing order: N_2O > CO > CO_2. The adsorptions of the CO and CO_2 (Pointing with its C atom toward adsorption site of doped SWCNT) on the SiSi co-doped SWCNT which are the highest strengths, are much higher than of the CO and CO_2 (Pointing with its O atom toward adsorption site of doped SWCNT) on the SiSi co-doped SWCNT. The adsorption ability of all studied gases adsorbed on the SiSi co-doped SWCNT is in the decreasing order: CO > N_2O > CO_2 > H_2.

Table 2 Adsorption energies and partial change transfers of the various gas molecules onto the SiSi co–doped (5,5) SWCNT, computed at the B3LYP/6–31G(d,p) level.

Species	ΔE_{ads}[a]	PCT[b]	Bond distance (Å)	
			Si1–gas[c]	Si2–gas[c]
H_2/SiSi-SWCNT	-3.23	0.000	4.998 (Si1-H1)	4.230 (SiSi-H1)
$\underline{C}O$/SiSi-SWCNT[c]	-5.49	0.103	4.128 (Si1-C)	2.866 (SiSi-C)
$C\underline{O}$/SiSi-SWCNT[d]	-3.98	0.006	4.283 (Si1-O)	3.582 (SiSi-O)
$\underline{C}O_2$/SiSi-SWCNT[c]	-4.25	0.001	3.769 (Si1-C)	5.086 (SiSi-C)
$C\underline{O}_2$/SiSi-SWCNT[d]	-3.57	0.003	3.773 (Si1-O1)	4.121 (SiSi-O1)
$\underline{N}_2O$/SiSi-SWCNT[e]	-4.04	0.003	4.733 (Si1-N1)	3.331 (SiSi-N1)
$N_2\underline{O}$/SiSi-SWCNT[f]	-4.55	0.026	4.286 (Si1-O)	3.062 (SiSi-O)

[a] In kcal/mol

[b] Defined as a change of adsorbate's charges of gases during adsorption, in *e*

[c] Pointing with its C atom toward adsorption site of SiSi co-doped SWCNT.

[d] Pointing with its O atom toward adsorption site of SiSi co-doped SWCNT.

[e] Pointing with its N atom toward adsorption site of SiSi co-doped SWCNT.

[f] Pointing with its O atom toward adsorption site of SiSi co-doped SWCNT.

The energies of the highest occupied molecular orbital (E_{HOMO}), the lowest unoccupied molecular orbital (E_{LUMO}), and the frontier molecular orbital energy gap (E_{gap}), for the SiSi co-doped SWCNT and it various gas adsorptions are listed in Table 3. In addition, their HOMO and LUMO plots are displayed in Figure 3. Table 3 shows that the relative reactivity by mean of energy gap of gases adsorbed on SiSi co-doped SWCNT is in the decreasing order: CO/SiSi-SWCNT > N_2O/SiSi-SWCNT > CO/SiSi-SWCNT $\approx$ CO_2/SiSi-SWCNT > CO_2/SiSi-SWCNT $\approx$ N_2O/SiSi-SWCNT > H_2/SiSi-SWCNT. The larger energy gap of the gas molecules adsorbed on SiSi co-doped

SWCNT, compared to pristine SWCNT indicates that the conductivity of SWCNT is changed by gas adsorptions. Interestingly, all of HOMO orbitals of gas molecules adsorbed on SiSi co-doped SWCNT are widely located all around the tubes whereas all of their LUMO orbitals are located nearby the adsorption sites.

Table 3 Chemical indices of the various gas molecules on the on the SiSi co–doped (5,5) SWCNT, computed at the B3LYP/6–31G(d,p) level.

Species	E_{LUMO} [a]	E_{HOMO} [a]	E_{gap} [a]
SWCNT	-0.113	-0.163	1.361
SiSi-SWCNT	-0.107	-0.165	1.578
H_2/SiSi-SWCNT	-0.098	-0.164	1.796
$\underline{C}O$/SiSi-SWCNT[b]	-0.106	-0.165	1.606
$C\underline{O}$/SiSi-SWCNT[c]	-0.108	-0.166	1.578
$\underline{C}O_2$/SiSi-SWCNT[b]	-0.106	-0.165	1.606
$C\underline{O_2}$/SiSi-SWCNT[c]	-0.105	-0.165	1.633
$\underline{N_2}O$/SiSi-SWCNT[d]	-0.104	-0.164	1.633
$N_2\underline{O}$/SiSi-SWCNT[e]	-0.113	-0.163	1.361

[a] In eV

[b] Pointing with its C atom toward adsorption site of SiSi co-doped SWCNT.

[c] Pointing with its O atom toward adsorption site of SiSi co-doped SWCNT.

[d] Pointing with its N atom toward adsorption site of SiSi co-doped SWCNT.

[e] Pointing with its O atom toward adsorption site of SiSi co-doped SWCNT.

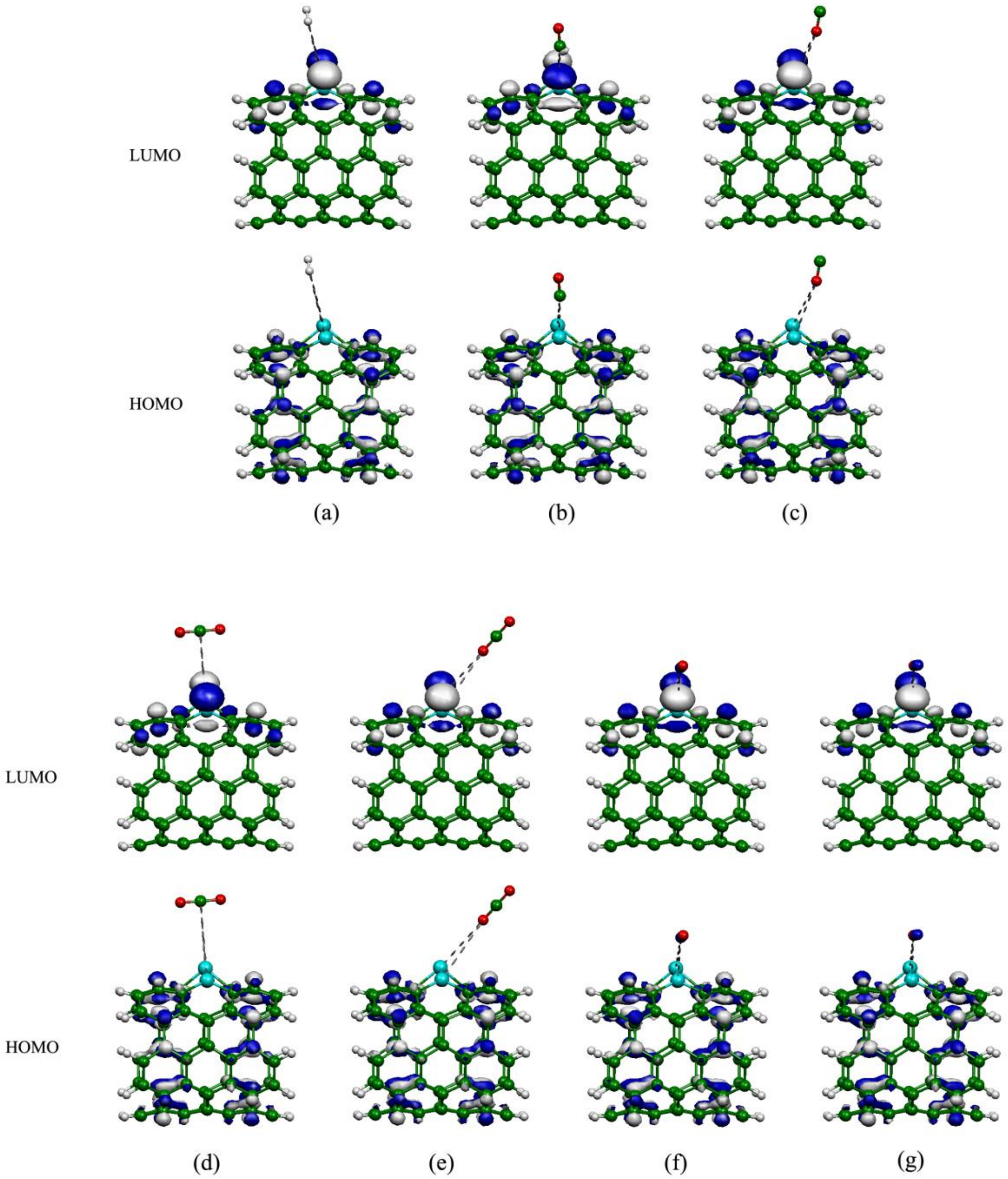


Figure 3 The plots of LUMOs (top) and HOMOs (bottom) of adsorption configurations of (a) H_2, (b) CO pointing with C, (c) CO pointing with O, (d) CO_2 pointing with C, (e) CO_2 pointing with O, (f) N_2O pointing with N and (g) N_2O pointing with O to the SiSi co-doped SWCNT, computed at the B3LYP/6-31G(d,p) level.

Conclusion

The adsorptions of various gas molecules on SiSi co-doped SWCNT were investigated by using the density functional theory method at the B3LYP/6-31G(d,p) theoretical level. The results indicate that all of the gas molecules can adsorb on the SiSi co-doped SWCNT via an exothermic process. The structural and electronic properties of the SWCNT, SiSi co-doped SWCNT and its gas adsorptions are reported. The present results will provide the useful guidance to develop a novel SWCNT-based gas storage applications.

Acknowledgements

The authors gratefully acknowledge the Research Affairs, Mahasarakham University, and the facility provided by Supramolecular Chemistry Research Unit and Department of Chemistry, Faculty of Science, Mahasarakham University.

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