

Can Silicon Carbide Nanotubes Sense Carbon Dioxide?

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Abstract: Detection of carbon dioxide (CO_2) is very important in environmental, biological, and industrial processes. Recent experiment showed that carbon nanotubes can act as chemical sensors for detecting certain gaseous molecules such as NH_3 , NO_2 , and O_2 . Unfortunately, the intrinsic stability of CO_2 makes its sensing by CNTs unsuccessful due to the rather weak adsorption energy on the tube surface. In the present Article, we study the CO_2 adsorption on various zigzag $(n,0)$ ($n = 6, 8, 10, 12$, and 18) single-walled SiC nanotubes to explore the possibility of the SiC tube as potential gas sensors for CO_2 -detection by density functional theory (DFT) calculations. It is found that tube diameter and CO_2 coverage play important roles in the tube– CO_2 interaction. A single CO_2 can be chemisorbed to the Si–C bonds of SiCNT with appreciable adsorption energy and can draw significant charge transfer from the SiCNT. The adsorption energy decreases gradually with increased tube diameter. The addition of more CO_2 molecules in different patterns has been considered for the exemplified $(8,0)$ tube, and CO_2 molecules prefer to be as far from each other as possible. With the increase of CO_2 coverage, the interaction between CO_2 molecules and tube becomes weaker, and up to eight CO_2 molecules can be adsorbed on the tube. In addition, we find that the band gap is lowered to a different degree due to the different adsorption. Because of the sufficient charge transfer and high concentration of CO_2 , SiCNT could be a perfect material for efficiently detecting the CO_2 molecule.

1. Introduction

Carbon dioxide (CO_2) is the focus of much current research activity. Millions of tons of CO_2 are used every year in the carbonated beverage industry and for the production of carbonates, carboxylic acids, carbon monoxide, and urea. It is also a natural byproduct of ammonia production, grain fermentation, and petroleum operations.^{1–3} The need for CO_2 sensors for medical applications, for atmospheric concentration control, and for indoor climate monitoring is the driving force in this area of analytical research.^{4–6} Thus, gas sensors for CO_2 -detection with high sensitivity and fast response time are highly desired. For the current nondispersive infrared (NDIR) sensors,^{7–9} many significant problems, such as direction detection, high cost, low power consumption, and room temperature operation, are still unsolved.

Recently, “sensing” has been a hot topic in carbon nanotube (CNT) research.^{10–12} The structural features, such as high aspect ratios, large surface area, as well as unique thermal and electronic properties, render CNT as a potential candidate for gas sensors. The sensing mechanism is to detect the conductance change of the CNT induced by charge transfer between adsorbates and CNT.^{10,11} So far, a few gas molecules, such as NH_3 ,¹⁰ NO_2 ,¹⁰ and O_2 ,¹¹ are shown to be sensible by pure CNT. However, CNT and even boron nitride nanotube (BNNT) cannot detect some important molecules such as CO_2 because they cannot be effectively adsorbed on the nanotube surface.¹³ Successful sensing of CO_2 via nanotubes has not been reported up to now, according to our literature survey.

The recently synthesized silicon carbide nanotube (SiCNT) has been found to be a semiconducting material of great technological interest for devices designed to operate at high

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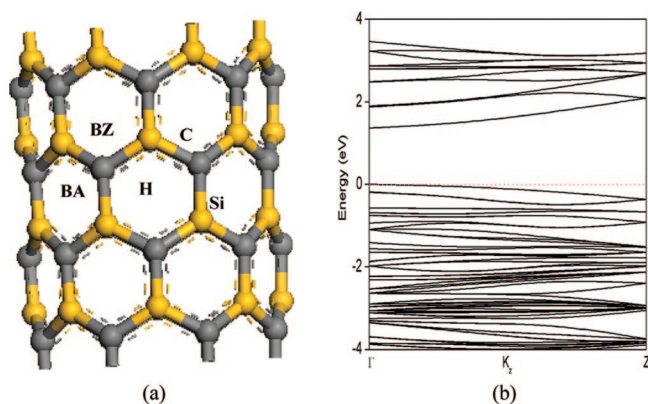


Figure 1. (a) Detailed description of different adsorption sites of a single CO₂ molecule on an (8,0) SiCNT. C, carbon; Si, silicon; H, hexagon; BA, axial Si–C bond; BZ, zigzag Si–C bond. (b) The band structure of the (8,0) SiCNT. The Fermi level is set as zero.

temperatures, high power, and in harsh environments.¹⁴ An attractive point is that SiCNT has higher reactivity than carbon nanotube (CNT) or BNNT due to its great polarity.¹⁵ For example, our study of the functionalization of SiCNTs by transition metal (TM) has shown that the adsorption of an individual TM on SiCNTs is significantly stronger than that on CNTs.¹⁶ Kang et al. found that NO and N₂O molecules can be chemisorbed on SiCNTs, while this is not the case for CNTs.¹⁷ Additionally, Feng et al. studied the interaction between two toxic gases (CO and HCN) and SiCNTs and found that SiCNTs exhibit better reactivity toward the two adsorbates than do CNTs.¹⁵

Can SiCNT be used to detect the CO₂ molecule? Through the detailed density functional theory (DFT) calculations of the CO₂ adsorption with different coverage on a series of zigzag (*n*,0) SiCNTs, we showed that the answer is “yes”. To our knowledge, no prior theoretical investigations have been reported on this issue.

2. Computational Methods and Models

We performed all-electron ab initio DFT calculations using the double numerical basis sets plus polarization functional (DNP basis set) implemented in the DMOL³ package.¹⁸ The generalized gradient approximation (GGA) with the Perdew Burke Ernzerhof (PBE)¹⁹ was used to obtain all of the results given below. We chose a series of zigzag (*n*,0) SiCNTs in a periodically repeating tetragonal supercell with lattice constants of $a = b = 30$ Å and c taken to be twice the one-dimensional lattice parameter as the studied systems. For example, the supercell of an (8,0) SiCNT includes totally 32 silicon and 32 carbon atoms. The Brillouin zone is sampled by $1 \times 1 \times 5$ special k -points using the Monkhorst–Pack scheme.²⁰ No symmetric constraints are considered when carrying out calculations in the present work.

The adsorption energy of n CO₂ molecules on SiCNT is defined as $E_{\text{ads}} = [E_{\text{total}}(\text{SiCNT} + n\text{CO}_2) - E_{\text{total}}(\text{SiCNT}) - nE_{\text{total}}(\text{CO}_2)]/n$, where E_{total} is the energy of the system per supercell and n is the number of the adsorbed CO₂ molecules. A negative E_{ads} corresponds to a stable structure.

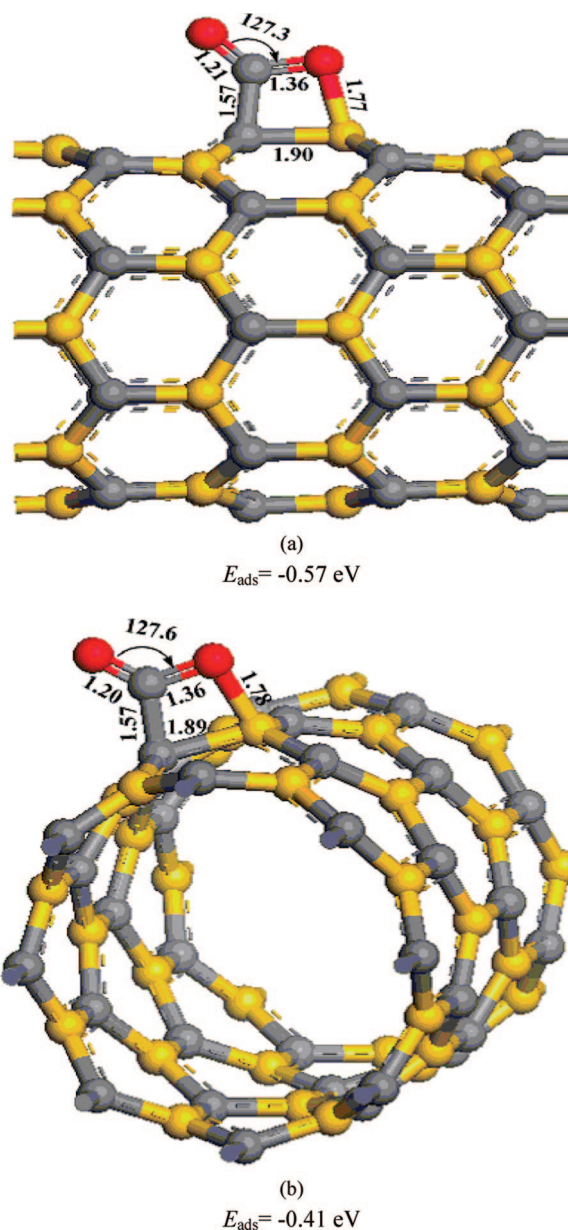


Figure 2. The optimized structures of an individual CO₂ molecule on the (a) BA site and (b) BZ site. The bond distances and angles are in angstroms and degrees, respectively.

Table 1. Structural Optimization Results and Calculated Adsorption Energy (E_{ads}) Values of a Single CO₂ Adsorbed on Various Zigzag (*n*,0) SiCNTs for Model BA

SiCNT	diameter (Å)	$d(\text{Si}-\text{O})$ (Å)	$d(\text{C}-\text{O})$ (Å)	$\angle\text{O}-\text{C}-\text{O}$ (deg)	E_{ads} (eV)
(6,0)	6.18	1.76	1.56	126.8	-0.80
(8,0)	8.11	1.77	1.57	127.3	-0.57
(10,0)	10.07	1.77	1.58	127.4	-0.39
(12,0)	12.03	1.78	1.59	127.5	-0.25
(18,0)	17.95	1.79	1.60	127.7	-0.09

3. Results and Discussion

3.1. Pure Single-Walled SiC Nanotubes. First, taking the (8,0) SiCNT as an example, we study the stable structures of pure SiCNTs. As shown in Figure 1a, two types of Si–C bonds can be found: one has the bond

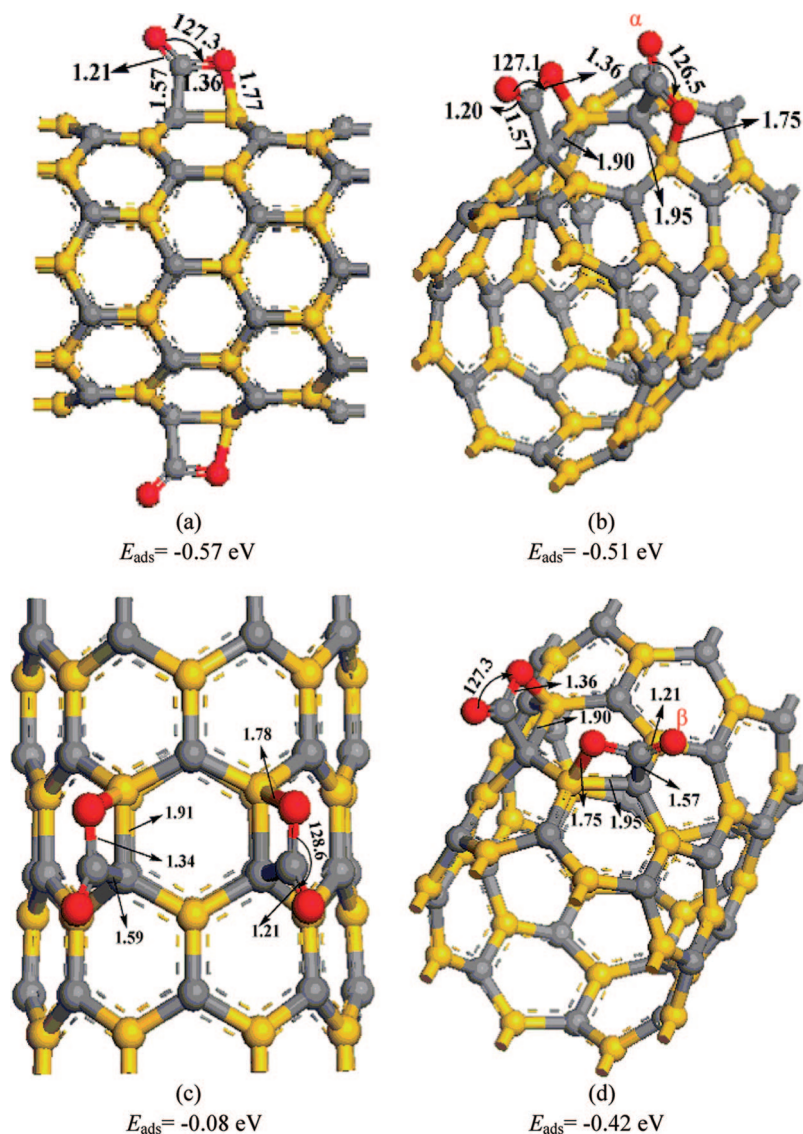


Figure 3. The optimized structures of (a–f) a second CO_2 adsorbed on the (8,0) SiCNT. Various adsorption sites are examined. The bond distances and angles are in angstroms and degrees, respectively.

Table 2. Structural Parameters,^a Adsorption Energies (E_{ads} ,^b eV), Band Gap (E_{b} , eV), and Charge Transfer^c (Q , e) for Adsorption of More CO_2 Molecules on an (8,0) SiCNT

$m\text{CO}_2$	$d(\text{Si}-\text{C})$	$d(\text{Si}-\text{O})$	$d(\text{C}-\text{C})$	$d(\text{C}-\text{O})$	$\angle\text{O}-\text{C}-\text{O}$	E_{ads}^b	E_{b}	Q
3	1.83	1.77	1.57	1.29	127.6	-0.50	1.29	0.26
4	1.85	1.77	1.58	1.28	127.8	-0.48	1.22	0.26
5	1.87	1.78	1.60	1.27	128.4	-0.31	1.17	0.24
6	1.88	1.79	1.61	1.27	129.2	-0.19	1.11	0.23
7	1.89	1.80	1.62	1.27	129.7	-0.09		0.22
8	1.91	1.80	1.64	1.26	130.7	-0.02		0.21

^a Only average values of the bond lengths and angles are listed. The units of the bond distance and angle are in angstroms and degrees, respectively. ^b Adsorption energy per CO_2 molecule. ^c The positive value denotes the charge is transferred from the tube to molecule.

length of 1.78 Å and is in parallel with the tube axis (labeled BA bond), and another has the bond length of 1.80 Å, but is not in parallel with the tube axis (labeled BZ bond). The structural parameters are in good agreement with previous reports.^{16,21–25} Furthermore, the charge analysis using the Hirshfeld method suggests that about 0.34 e charges are transferred from the Si atom to its nearest carbon atoms in the tube, which are much larger than those of carbon nanotubes (CNTs: 0 e) or boron nitride nanotubes (BNNTs: 0.21 e).²⁶ The continuous

charge transfer from Si to C in SiCNTs^{15,27} makes the tube possess higher reactivity of SiCNTs than of CNTs or BNNTs. The calculated band structure of the exemplified (8,0) SiCNT is shown in Figure 1b. The result indicates that the (8,0) SiCNT is a direct semiconductor with a band gap of 1.36 eV, in good agreement with previous reports.¹⁶

3.2. Adsorption of an Individual CO_2 on SiCNT. We take the (8,0) SiCNT as an example to study the stable configuration for a single CO_2 adsorption on zigzag SiCNT.

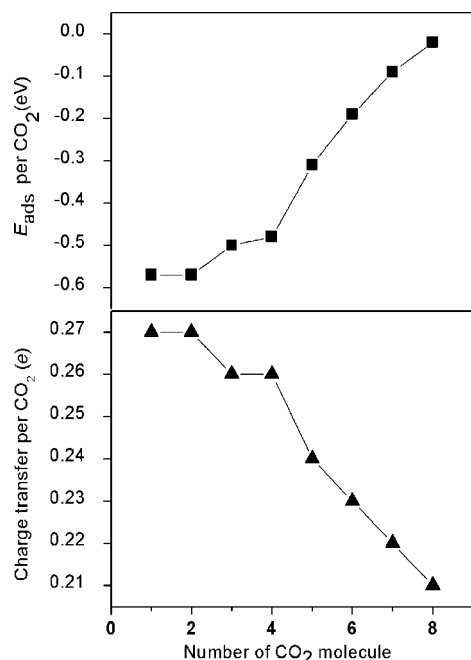


Figure 4. Variation of adsorption energy and charge transfer (per CO₂) as a function of the number of adsorbed CO₂ molecules on an (8,0) SiCNT.

We initially consider three typical possible configurations for CO₂ adsorption on the (8,0) SiCNT, including (1) oxygen-attacking, (2) 3 + 2 cycloaddition, and (3) 2 + 2 cycloaddition types. In type (1), the linear CO₂ molecule is almost vertically attached to the active sites (i.e., carbon atom (C), silicon atom (Si), or center of the hexagon (H)); see Figure 1a) of the tube. In type (2), the CO₂ molecule uses its two O-atoms to bond with Si- and C-atoms, forming a five-membered ring. In type (3), the C–O bond of CO₂ attacks the Si–C bond of either BA or BZ sites of the tube, forming a four-membered ring. After careful structural optimization, we find that both the oxygen-attaching configuration (type (1)) and the 3 + 2 cycloaddition configuration (type (2)) are collapsed to the 2 + 2 cycloaddition one (type (3)), which is the only energetically stable adsorption type.

The optimized structures and the corresponding adsorption energies of the 2 + 2 cycloaddition configuration are displayed in Figure 2. The most stable configuration (Figure 2a, labeled as BA configuration) is such that the C–O bond of CO₂ is closer to a BA bond of SiCNT and the oxygen atom of CO₂ is located directly above the Si atom of SiCNT. This configuration has an E_{ads} of -0.57 eV and a charge transfer of 0.27 e from the tube to the molecule. The bond lengths of C–C and Si–O bonds are 1.57 and 1.77 Å. Furthermore, the CO₂ adsorption induces a locally structural deformation to both the CO₂ molecule and the SiCNT (Figure 2a). The bond angle of O–C–O of CO₂ is significantly decreased from 180° in free CO₂ to 127.3° in the adsorbed form, and the CO₂-adsorbed Si–C bond is pulled outward from the tube wall with the bond length increasing from 1.78 (pure tube) to 1.90 Å. Such structural deformation is attributed to the change from sp^2 to sp^3 hybridization of the Si and C atoms, suggesting that the adsorption is covalent. Similar radical deformation is also observed in covalently functionalized CNT²⁸ or BNNT.^{26,29} On the other hand,

the CO₂ molecule can also be chemisorbed on the top of the BZ site in the SiCNT as shown in Figure 2b. For the configuration, the adsorption energy is -0.41 eV, much weaker than that on the BA site (Figure 2a). Moreover, about 0.27 electrons are transferred from the tube to molecule.

In addition to the (8,0) SiCNT, we also explore the adsorption of a single CO₂ on other zigzag ($n,0$) ($n = 6, 10, 12$, and 18) SiCNTs and for simplicity only consider the adsorption on the BA site. Table 1 summarizes the results of the adsorption energy and optimized Si–O distance for the adsorption of a single CO₂ molecule on various zigzag SiCNTs. For all of the studied tubes, CO₂ molecule is adsorbed to the tube stably. Because of the curvature effects, the adsorption energies significantly decrease with the increase of the tube diameters. For example, the adsorption energy on the (6,0) tube is -0.80 eV, while it decreases sharply to -0.09 eV when adsorbed on the (18,0) tube. Obviously, a transformation from the chemisorption to physisorption for CO₂ molecules on SiCNTs is found as the tube diameter increases. Additionally, the change in the Si–O distance increases with the increase of the tube diameter, further testifying that the CO₂–tube interaction becomes much weaker.

3.3. Adsorption of More CO₂ Molecules on an (8,0) SiCNT. With each Si–C bond on the SiCNT being a potential chemisorption site, the possibility for multiple adsorption should have interest for consideration to evaluate the concentration of CO₂ molecule on SiCNT. In this section, taking the (8,0) SiCNT as an example, we explore the adsorption of multiple CO₂ molecules on tube. On the basis of the results of a single CO₂ molecule adsorption, we only focus on the cycloaddition configurations (Figure 2a) for the adsorption of more CO₂ on an (8,0) SiCNT.

As shown in Figure 3, four initial models are considered when the second CO₂ molecule is adsorbed on the (8,0) SiCNT on which the first CO₂ molecule is located. Each structure is fully relaxed. The most stable configuration (labeled as BA–BA) is that two CO₂ molecules are located on the top of two symmetric BA bonds far from each other on the opposite sides of the circumference of the tube (Figure 3a). The adsorption energy of this configuration is -0.57 eV per CO₂ molecule with a charge transfer of 0.27 e, which is equal to that of the most stable configuration of the adsorption of individual CO₂ molecule. Additionally, three other metastable adsorption configurations are obtained as shown in Figure 3b–d. In the three metastable configurations, the second CO₂ molecule is adsorbed on the same hexagonal ring on which the first CO₂ is located. The adsorption energies of the metastable configuration are -0.51 (Figure 3b), -0.08 (Figure 3c), and -0.42 eV (Figure 3d). The steric repulsion between two CO₂ molecules in the same hexagon may be responsible for their adsorption energies being lower than that of Figure 3a. It should be pointed out that two ortho BZ bonds at the same hexagonal ring are not equivalent to each other because the nanotube is rolled up.³⁰ Hence, the configuration in Figure 3b and d is different. Also, we can observe the difference according to the orientations between CO₂ molecules: the α -oxygen (Figure 3b) is neighboring to

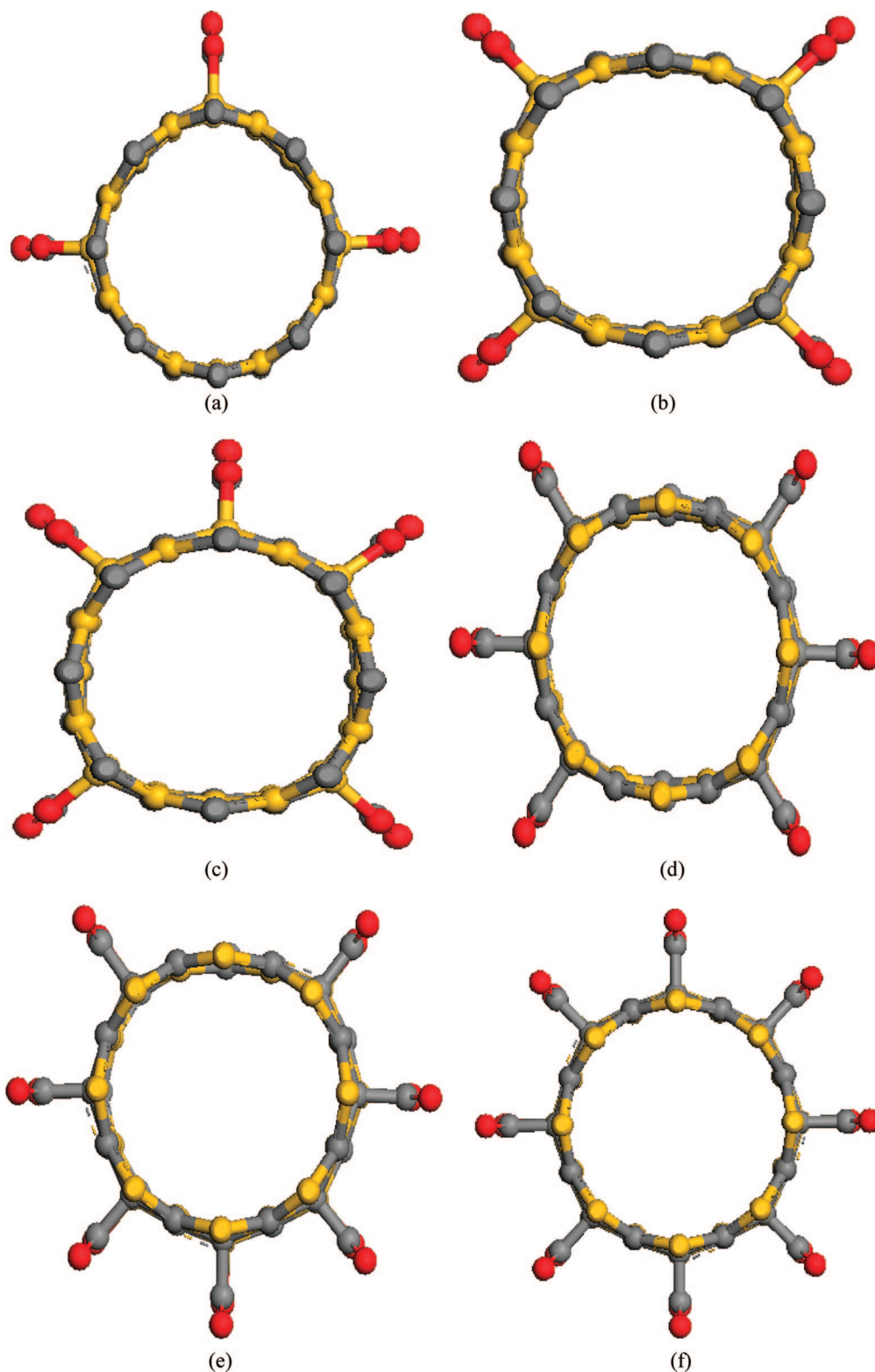


Figure 5. The optimized structures of m_{CO_2} ($m = 3-8$) molecules adsorbed on the (8,0) SiCNT.

the first adsorbed CO_2 molecule, while the β -oxygen (Figure 3d) is far from the first adsorbed CO_2 molecule.

Based on the results of the adsorption of two CO_2 molecules on an (8,0) tube, more CO_2 molecules (m_{CO_2}) are added to the tube by increasing the number of the adsorbed molecules from $m_{\text{CO}_2} = 3$ to $m_{\text{CO}_2} = 8$. It should be pointed out that the adsorption of more CO_2 molecules on the tube is deduced from configuration BA–BA, in which other CO_2

molecules are bound to the tube in the sequence that successive CO_2 is adsorbed at the BA bonds far away relative to the previous CO_2 on the circumference of the tube. The calculated adsorption energy, charge transfer, band gap, and distance between the adsorbed molecule and the tube wall per CO_2 molecule are summarized in Table 2 and displayed in Figure 4. It can be seen that the adsorption of all eight CO_2 molecules on the tube results in the formation of a CO_2

ring structure around the circumference of the (8,0) tube (Figure 5a–f). Because of the structural deformation upon adsorption of CO₂ molecules, the tube diameter is increased from 7.92 to 8.50 Å when eight CO₂ molecules are bonded to the surface of the (8,0) tube (Figure 5f). Moreover, we can find from Figure 4 that the adsorption energy per CO₂ molecule decreases gradually when increasing the number of adsorbed CO₂ molecules. For example, in the case of $m_{\text{CO}_2} = 8$, due to the steric repulsion between CO₂ molecules, it is slightly exothermic (−0.02 eV) relative to the tube and CO₂ molecules. When the ninth CO₂ molecule is adsorbed on the SiCNT, it leaves from the tube surface. In other words, the maximum number of CO₂ molecules that can be bound to an (8,0) SiCNT is eight ($m_{\text{CO}_2} = 8$).

Because up to eight CO₂ molecules can be adsorbed to the (8,0) SiCNT with appreciable adsorption energy, now we examine the possibility of SiCNTs as a potential gas sensor for CO₂ detection. The sensing mechanism is to detect the conductance change of SiCNT induced by charge transfer from gas molecules adsorbed on nanotube surface. Thus, we calculate the charge transfer between SiCNTs and CO₂ molecules by the Hirshfeld method and present the variation of charge transfer per CO₂ as a function of number of CO₂ molecules on the (8,0) tube as shown in Figure 4. We can see that more than 0.21 electrons are transferred from the tube to the molecule, which renders SiCNTs suitable for CO₂ detection. Additionally, we also study the changes of band gaps of an (8,0) SiCNT adsorbed with CO₂ at different coverage. From our computations, the pure (8,0) SiCNT shows a typical semiconducting feature with a band gap of 1.36 eV. The band gap gradually reduces with the increase of the adsorbed number of CO₂. When one or two CO₂ molecules are adsorbed on the (8,0) tube, the band gap slightly decreases by 0.03 or 0.05 eV, respectively. When eight CO₂ molecules are adsorbed on the tube, the band gap of the tube is decreased to 0.77 eV. We can see that the variation of the band gap is generally correlated with the charge transfer from the tube to the adsorbates.

Collins et al. have reported experimentally that CNT is a perfect gas sensor for O₂ detection by examining the conductance changes of CNT before and after the adsorption of O₂ molecules.¹¹ Sequential calculations by DFT suggest that the chemisorption of O₂ on the (8,0) CNT is possible with E_{ads} of −0.25 eV and a charge transfer of about 0.10 e from CNT to the adsorbate, which results in the changes of conductance of CNT.³¹ As compared to the well-established case, the adsorption energy per CO₂ is moderate to allow the CO₂ to be chemisorbed on the SiCNT. Meanwhile, the charge transfer is larger than that of the adsorption of O₂ molecule on CNT, which is enough to induce the conductance change of SiCNT, although a small change in band gap is found. In short, SiCNTs exhibit high reactivity toward CO₂ molecules, and thus it can be expected to be an excellent candidate for the design of CO₂ sensors.

4. Conclusion

To examine the possibility of SiCNT as a potential gas sensor for CO₂ detection, we for the first time studied the interaction between an (8,0) SiCNT and CO₂ molecules with different

concentration by DFT calculations. The results indicate that up to eight CO₂ molecules can be adsorbed at the BA bonds in the SiCNT with appreciable adsorption energies and charge transfer, which would lead to the significant changes of conductance of SiCNTs. Therefore, SiCNTs can serve as efficient sensors for detecting the presence of CO₂ molecules. This represents the first report on the successful sensing of CO₂ by nanotubes. We believe that the present results will provide helpful guidance to develop effective nanoscale sensors for the detection of CO₂ molecules, even in harsh environments.

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