

# Highly Sensitive Single-Walled Carbon Nanotube (5,0) for Adsorptions Gases CO<sub>2</sub>, CO and N<sub>2</sub> : A DFT Study

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**Abstract:** Adsorbed various CO<sub>2</sub>, CO and N<sub>2</sub> gases on the open-ended semiconducting single-walled carbon nanotube (SWCNT) (5, 0) zig-zag were studied using density functional theory (DFT) calculations. Geometric optimizations were performed at the B3PW91 level of 6-311++G\*\* method standard basis set using GAUSSIAN 98 package of program<sup>1-2</sup>. We studied in terms of absorption energy and charge transfer and the nuclear quadrupole resonance (NQR) spectroscopy parameters in (5, 0) SWCNT. For the first time, calculated adsorption energies  $E_{ads}$  (eV), Bond gap (eV), Charge (DFT) and dipole momentum (Debye) of the CO<sub>2</sub>, CO and N<sub>2</sub> adsorbed on the open end of zigzag (5,0) nanotube<sup>3</sup>. DFT calculations were performed to calculate 13-Carbon interaction of quadrupole moment with EFG in the representative considered model of the (CO<sub>2</sub>-SWCNT, CO-SWCNT and N<sub>2</sub>-SWCNT). Due to the physisorption, NQR parameters of molecular CO<sub>2</sub>, CO and N<sub>2</sub> are also altered. The DFT methods very well reproduce the correlation between spectroscopic parameters. Comparison of adsorption energies show that adsorption of CO<sub>2</sub> molecule over open-end of nanotube zigzag (5, 0) model is stronger than the adsorption of CO and N<sub>2</sub> molecules.

**Keywords:** single-walled carbon nanotube, DFT, NMR, chemical-shielding.

## Introduction

Carbon nanotubes (CNTs)<sup>3</sup> have distinctive properties in mechanical, chemical and electronic aspects due to its one dimensional structure ushered in a new and very amazing research field in compacting gases by physisorption methods. The changes in electrical resistance by adsorption of certain gas molecules are considerable, for example by adsorption of CO<sub>2</sub>, CO and N<sub>2</sub><sup>4</sup>. Figure 1 depicts a C<sub>53</sub>H<sub>10</sub> tube modeling a zig-zag (5, 0) SWCNT which demonstrates the stated effect on the electronic structure of single-walled carbon nanotube (SWCNT). Comparing the

adsorption of gases on the open end, using computational methods substantially reduces costs and thus NQR were used in related investigations. Even at low concentration, due to the charge transfer between gases and tube, gas physisorption can change the conductivity of SWCNT. The enhanced surface area and modified morphological feature result in increased ability of these SWCNTs to adsorb the target gas molecules and hence be suitable for a wide range of sensor applications. However, exhibiting semiconducting behavior depending

on the tubular diameter and chirality, it is very difficult to synthesize SWCNT for desired purposes<sup>5</sup>. Global analysis of electron density distribution in the whole molecule was made by the theoretical methods of density functional theory (DFT). The detailed analysis of the results obtained by each of the resonance methods separately.  $E_{ads}$ , NQR and Bond gap, has been performed by us in<sup>6-8</sup>. The NQR measurable asymmetry parameter ( $\eta$ ) is also reproduced by quantum chemical calculations of the electric field gradient (EFG) tensors<sup>9</sup>. Considering that the gas adsorption on carbon nanotubes modifies sensibly, their electronic properties proposed the use of SWCNT as gas sensors. According to the electron-transmission mechanism on the open ended of SWCNT, the detected gas can be classified in the reducing or oxidizing range of gaseous species. By adsorption of reducing gaseous species (such as  $NH_3$ <sup>10</sup>,  $CO_2$ <sup>11-12</sup>,  $N_2$ <sup>13</sup> and ethanol<sup>14</sup>), the electrical resistance of CNTs was found to increase, whereas by absorption to oxidizing ones such as  $O_2$  and  $NO_2$  the electrical resistance decrease<sup>15-16</sup>. These show that the electrical conductance of the SWCNT can change obviously upon adsorption of  $O_2$ ,  $NO_2$ , or  $NH_3$  gases. Even though experimental techniques have advanced, theoretical calculations have preserved their significant role in predicting geometries and energy levels and interpreting spectroscopic data.

### Computational Method

In this study, geometry optimizations, the natural bond orbital (NBO) and density of states (DOS) analyses were performed on a model of the zig-zag (5, 0) SWCNT with tube lengths of 7.06 nm and is considered in the quantum chemical calculations. The first model is the (5,0) SWCNT consisting of 53 C atoms where the two ends of the tube are capped by 10 H atoms (see Fig. 1). The atoms at the open ends of the nanotube were saturated by hydrogen atoms to avoid the boundary effect. Firstly, the considered model systems were allowed to fully relax during the geometrical optimization by the B3PW91 exchange-functional method<sup>17-18</sup> and the 311++G\*\* standard basis set to evaluate the  $E_{ads}$  and 13C NQR parameters (see Tables 1 and 2).

We define the adsorption energy ( $E_{ads}$ ) of  $CO_2$ ,  $CO$  and  $N_2$  molecular as (Table1)

$$E_{ads} = E_{tot}(\text{molecule} + \text{SWCNT}) - E_{tot}(\text{SWCNT}) - E_{tot}(\text{molecule})$$

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Where,  $E_{tot}$  (SWCNT),  $E_{tot}$  ( $CO_2$ ,  $CO$  and  $N_2$ ) and  $E_{tot}$  (SWCNT+  $CO_2$ ,  $CO$  and  $N_2$ ) are the energies of the optimized tubes, which are adsorption systems. By this explanation,  $E_{ads} < 0$  corresponds to exothermic adsorption which leads to local minima stable for adsorption of gas molecules on the open ended of nanotube.

For non-magnetic dielectrics, this response gives information about coordination and geometry around each nucleus with spin  $I > 0$ . It is known that when nuclei with spin  $> 1/2$  are put in an electric field gradient (EFG)<sup>19</sup>, decayed spin energy levels are created. NQR methods are applied to produce high external magnetic fields and some kind of internal interaction in order to form a non decayed energy spectrum. However, the field has recently started to produce good products and an increasing amount of experimental and theoretical data is becoming available. Dependence of these parameters on length and diameter of CNTs are also considered. Hence, the diameter of the tube at both ends are the same but in the zigzag (5,0) model the ends of the tube are elliptically oriented, meaning that at each end, the C-C diameter is 3.73 Å. The NQR measurable asymmetry parameter ( $\eta$ ) both are also reproduced by quantum chemical calculations of the electric field gradient (EFG) tensors. Geometry optimizations and EFG calculations were performed using 311++G\*\* basis set with B3PW91 functional. In quadrupolar spin system, the electric field gradient (EFG) tensor at 13-carbon nuclear sites has axial symmetry (asymmetry parameter  $\eta = 0$ ). The existence of the zero asymmetry parameter was one of the reasons why this compound is considered to present such interest<sup>20-21</sup>. The interaction between nuclear electric quadrupole moment and EFG at quadrupole nucleus is described with Hamiltonian:

$$\hat{H} = \frac{eQq_{zz}}{4I(2I-1)} [3\hat{I}_z^2 - \hat{I}^2] + y_Q (\hat{I}_x^2 - \hat{I}_y^2)$$

where  $eQ$  is the nuclear electric quadrupole moment,  $I$  is the nuclear spin and  $q_{zz}$  is the largest component of EFG tensor. The principal axis system (PAS) components of the EFG tensor,  $q_{ii}$ , are computed in atomic unit ( $1 \text{ au} = 9.717365 \times 10^{21} \text{ V m}^{-2}$ ), with

$$|q_{xx}| \leq |q_{yy}| \leq |q_{zz}| \quad \text{and} \quad q_{xx} + q_{yy} + q_{zz} = 0.$$

These diagonal elements are related by a symmetry parameter

$$y_Q = \left| \frac{q_{yy} - q_{xx}}{q_{zz}} \right| \quad \text{and} \quad 0 \leq y_Q \leq 1, \quad \text{that}$$

measures the deviation of EFG tensor from axial

symmetry. Cluster model is proved to be valid for nanotubes<sup>22, 23</sup>. The computed  $q_{zz}$  component of EFG tensor is used to obtain nuclear quadrupole coupling constant from the equation  $C_Q = e^2 Q q_{zz} / h$ <sup>24</sup>. Recently, Lim and Lin have explored the CO<sub>2</sub>, CO and N<sub>2</sub> molecular physisorption of single-walled CNT (5, 0) using density functional theory (DFT)<sup>25</sup>. In this work, we report DFT study of SWCNT (5, 0) functionalized with CO<sub>2</sub>, CO and N<sub>2</sub> molecular. Our study can help in applications of SWCNT in gas sensor or biosensor industry or their purification and processing.

## Results and Discussion

In the present work, model of zigzag (5, 0) SWCNT with specified tube lengths are studied using quantum chemical calculations (fig.1 - 4). Geometries, adsorption energies and NQR (5, 0) SWCNT interacted with CO<sub>2</sub>, CO and N<sub>2</sub> molecules species have studied in this work. The calculated geometry parameters and adsorption energies, dipole momentum and EFG tensors have shown in Tables 1 and 4. In the following sections, molecular geometries,  $E_{ads}$ , HOMO-LUMO gap and EFG tensors and the data obtained from CO<sub>2</sub>, CO and N<sub>2</sub> molecules adsorptions are discussed.

**Molecular geometries and Electronic properties:** In this study, the efficacy on electronic properties of SWCNT by CO<sub>2</sub>, CO and N<sub>2</sub> physisorption have been established to appear field of spin-electronics, a field that influences the electron's spin degree of freedom for transfer and storage of information and communication. The optimized geometries of calculated configurations of CO<sub>2</sub>, CO and N<sub>2</sub> molecule adsorbed on zigzag (5, 0) SWCNT are schematically displayed in Fig. 1. reported the characteristic behaviour of a field effect transistor based on an individual Fig. 2-4. Electronic density of states for (a) CO<sub>2</sub>-SWCNT (5, 0) (D<sub>1&2</sub>), CO-SWCNT (5, 0) (D<sub>1&2</sub>) and N<sub>2</sub>-SWCNT (5, 0) (D) systems. Obtained values show that as the dipole moment gets bigger, the absolute value of adsorption energy increases. We can interpret this fact as following: the big dipole moment depends to the big distance between electron clouds, then, as the distance becomes bigger the absolute value of adsorption energy will become higher [26]. The calculated band gap of nanotube model CO<sub>2</sub>-SWCNT (5,0) (D<sub>1&2</sub>) is about (0.77)eV, CO-SWCNT (5,0) (D<sub>1&2</sub>) about (1.74) eV and N<sub>2</sub>-SWCNT (5,0) (D) is about (1.69) eV, which is very close to

DFT simulated for the other small diameter nanotube<sup>27-28</sup>. The electron conduction mechanism is expected to be tunneling when the Fermi levels of contacts lie within the HOMO-LUMO gap of a short length molecule, as for the case of these SWCNT<sup>29</sup>. The effect of CO<sub>2</sub>, CO and N<sub>2</sub> molecules physisorption on zigzag (5, 0) SWCNT decreases the bond gap energy. Such a big decrease of the band gap of the zigzag (5, 0) nanotube upon CO<sub>2</sub>, CO and N<sub>2</sub> physisorption on seat gases may originates from the changes of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of these systems. For chemisorptions model CO<sub>2</sub>-CNT (5, 0) (D<sub>2</sub>), we found that band gaps below electric field become narrow and new local energy levels occur near the Fermi level, which result in the nearly continuous local density of state (DOS) peaks below electric field. Moreover, the oxidizing characteristic of CO<sub>2</sub>, CO and N<sub>2</sub> molecules and transfer of its non-binding pairs of electrons to neighbor carbon atoms over carbon rings on open-ended nanotube, cause increase in its resistance and also increase in nanotube diameter. Since this effect induces a bond-gap at the Fermi level, the resistivity is enhanced. Mainly the electron-electron interactions give rise to magnetic field independent conductivity corrections. Geometry calculations of distortion caused by the CO<sub>2</sub>, CO and N<sub>2</sub> molecules on the (C) bond on the open ended are changed partly. Two different types of adsorbed CO<sub>2</sub> and CO molecules were recognized (Fig.2&3. SWCNT (5, 0). The calculated adsorption energies were predicted to be -2.3620 -2.3684eV for CO<sub>2</sub> -SWCNTs-D<sub>1&2</sub>(5, 0) and -1.3760 and -1.3775 eV for CO -SWCNT-D<sub>1&2</sub>(5, 0) and N<sub>2</sub> -SWCNT-(5,0) -1.4844, respectively. Comparison of adsorption energies show that adsorption of CO<sub>2</sub> molecule over open-end of nanotube zigzag (5, 0) model is stronger than the adsorption of CO and N<sub>2</sub> molecules.

## The C-13 NQR spectroscopic parameters:

The evaluated NQR parameters reveal that the EFG tensors of 13-Carbon are influenced and show particular trends from gas molecules in the SWCNT due to the contribution of CO<sub>2</sub>, CO and N<sub>2</sub> gas molecules in SWCNT interactions. Semiconducting SWCNT are ballistic conductors with two and one spin degenerate conducting channel<sup>30-31</sup>. The channels belong to the first and \*-band of the delocalized -electron system. The C-13 NQR parameter  $\gamma_Q$  in the geometrically optimized SWCNT model zig-zag (5, 0) is estimated by EFG tensors calculations at the B3PW91 level of the DFT method and the

311++G\*\* standard basis set. Since the electric field gradient (EFG) tensors are very sensitive to the electrostatic environment at the sites of quadrupole nuclei, the most possible interacting molecules with the target one were considered in a five carbon atoms in the open end of SWCNT (5,0) zig-zag model with the optimal diameter of 4.03 Å and the length of 7.07 Å. Tables 2 shows the calculated NQR and EFG tensors for SWCNT(5,0)  $\gamma$  parameter of CO<sub>2</sub>, N<sub>2</sub> and CO adsorption on the SWCNT open ended has a remarkable effect on EFG tensors. A glimpse to  $\gamma_Q$  values presented in table 2 reveals that for 13-carbon changes in EFG tensor for molecular

adsorptions are quite significant which is in complete agreement with calculations. The B3PW91/311++G\*\* calculations indicate that all three principal components of the EFG tensor ( $q_{ii}$ ) and associated asymmetry parameter are affected due to adsorption of CO<sub>2</sub>, N<sub>2</sub> and CO molecules. For the (CO<sub>2</sub>-SWCNT-D<sub>2</sub>)

systems, the EFG tensors of SWCNT (5, 0) is more significantly affected compared to CO<sub>2</sub>-SWCNT (5, 0)- D<sub>1</sub>, CO-SWCNT (5, 0)-D<sub>1&2</sub> and N<sub>2</sub>-SWCNT (5, 0)-D, respectively.

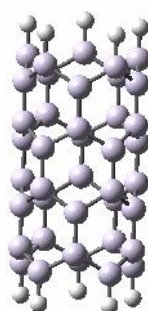


Figure.1. (5,0) SWCNT



Figure.2. (D<sub>1</sub>) and (D<sub>2</sub>) adsorption configurations of dioxide carbon molecules



Figure.3. (D<sub>1</sub>) and (D<sub>2</sub>) adsorption configurations of monoxide carbon molecules

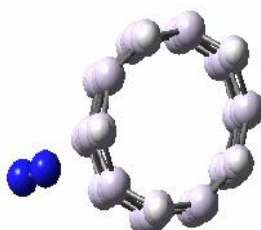


Figure.4. (D) adsorption configurations of nitrogen molecule

**Table1.** Calculated adsorption energies  $E_{ads}$ (eV), Bond gap(eV), Charge(DFT) and dipole momentum(Debye) of the CO<sub>2</sub>, CO and N<sub>2</sub> adsorbed open ended zigzag(5,0) nanotube.

Model	Atoms	HOMO(eV)	LUMO(eV)	Bond gap	Charge (DFT)	$E_{ads}$ (eV)	Dipole momentum (Debye)
SWCNT(5,0) D	C <sub>1</sub>	-6.7292	-3.1568	3.6251	-0.358165	-	1.1498
	C <sub>2</sub>				-0.358819		
	C <sub>3</sub>				-0.268999		
	C <sub>4</sub>				-0.268306		
	C <sub>5</sub>				-0.199846		
CO <sub>2</sub> -SWCNT(5,0) D <sub>1</sub>	C <sub>1</sub>	-3.9533	-3.1808	0.7725	-0.705896	-2.3620	1.3058
CO <sub>2</sub> -SWCNT(5,0) D <sub>2</sub>	C <sub>2</sub>	-3.8826	-3.1163	0.7663	-0.184042	-2.3684	1.5229
CO-SWCNT(5,0) D <sub>1</sub>	C <sub>1</sub>	-4.9904	-3.2406	1.7497	-0.832881	-1.3760	1.6660
CO-SWCNT(5,0) D <sub>2</sub>	C <sub>2</sub>	-4.9123	-3.1674	1.7448	-0.308488	-1.3775	1.4925
N <sub>2</sub> -SWCNT(5,0) D	C <sub>1</sub>	-4.8461	-3.1495	1.6965	-0.791139	-1.4844	1.4631

**Table 2.** Calculated Carbon-13 EFG parameters for the SWCNT, CO-SWCNT(5,0), CO<sub>2</sub>-SWCNT(5,0), N<sub>2</sub>-SWCNT(5,0) and O<sub>2</sub>-SWCNT(5,0) systems.

Model	Atoms	$q_{xx}$	$q_{yy}$	$q_{zz}$	$Y_Q$
SWCNT(5,0) D	C <sub>1</sub>	0.113721	0.050131	-0.163852	0.3880
	C <sub>2</sub>	0.114492	0.050880	-0.165372	0.3846
	C <sub>3</sub>	0.187547	0.140698	-0.328245	0.1427
	C <sub>4</sub>	0.228188	0.187883	-0.416071	0.0968
	C <sub>5</sub>	0.186403	0.139176	-0.325578	0.1450
CO <sub>2</sub> -SWCNT(5,0) D <sub>1</sub>	C <sub>1</sub>	0.090608	0.011426	-0.102034	0.7760
CO <sub>2</sub> -SWCNT(5,0) D <sub>2</sub>	C <sub>2</sub>	0.227720	0.168225	-0.395945	0.1502
CO-SWCNT(5,0) D <sub>1</sub>	C <sub>1</sub>	0.215851	0.165585	-0.381435	0.1317
CO-SWCNT(5,0) D <sub>2</sub>	C <sub>2</sub>	0.090105	0.011374	-0.101480	0.7758
N <sub>2</sub> -SWCNT(5,0) D	C <sub>1</sub>	0.218326	0.162828	-0.381154	0.1456

## Conclusion

In summary, our theoretical studies show that SWCNT (5, 0) can be used as mechanical sensors. We found the electronic properties of SWCNT (5, 0) are sensitive to the adsorptions of oxygen, nitrogen and carbon monoxide gases on the surface. According to DFT theory and hybrid functional B3PW91/311++G\*\* are applied to study NQR of CO<sub>2</sub>, CO and N<sub>2</sub> calculations the electronic structure properties of (5, 0) SWCNT. We calculated Carbon-13 EFG tensors in the various structures of thymine an optimized isolated gas-phase, gas monomer and the target molecule in X-SWCNT (X= CO<sub>2</sub>, CO and N<sub>2</sub>).

The calculated results have different effects on the EFG tensor at Carbon-13 nuclei. Theoretical calculations are performed to characterize the behavior of CO<sub>2</sub>, CO and N<sub>2</sub> molecules adsorption on external open ended zigzag(5, 0), SWCNT. Results show that as the diameter of zigzag tubes increases, the binding energy of N<sub>2</sub> and CO molecules decreases. The equilibrium N<sub>2</sub>-SWCNT and CO-SWCNT on the open ended distance exhibits considerable sensitivity to the type of tube.

The calculated, CO<sub>2</sub>-SWCNT, CO-SWCNT and N<sub>2</sub>-SWCNT bond gap are (0.7725- 0.7663 Å), (1.7497-1.7448Å) and (1.6965Å) on the open ended of zigzag(5, 0), respectively.

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