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Adsorptions Gas CO_2 on the Surface and Open-Ended Single-Walled Carbon Nanotube: A NQR Study

A.S. Ghasemi[1]*, M. Molla[2], M. Mostashregh[3]

[1]Dept. of Chem. Payame Noor University, Tehran, Iran
[2]Dept of Petroleum, Science and research Branch, Islamic Azad University, Tehran, Iran.
[3]Department of Biotechnology, chemical Engineering biotechnology, Islamic Azad University, Shahrood, Iran.

***Corres.author: ashraf.ghasemi@gmail.com**
Iran. Tel.: +98 9111570503; Fax: +98 1513258960;

Abstract: Background: Adsorbed various CO_2 gas on the surface and open-ended semiconducting single-walled carbon nanotube (SWCNT) (5, 0) zig-zag were studied using density functional theory (DFT) calculations. Methods: Geometric optimizations were performed at the B3PW91 level of 6-311++G** method standard basis set using GAUSSIAN 98 package of program [1-2]. We studied in terms of adsorption energy and charge transfer and the nuclear quadrupole resonance (NQR) spectroscopy parameters in (5, 0) SWCNT. For the first time, calculated adsorption energies ΔE_{ads} (eV), Bond gap (eV), Charge (DFT) and dipole moment (Debye) of the CO_2 adsorbed on the surface and open-ended of zigzag (5, 0) nanotube. DFT calculations were performed to calculate 13-Carbon interaction of quadrupole moment with EFG in the representative considered model of the (CO_2-SWCNT). Due to the physisorption, NQR parameters of molecular CO_2 are also altered. The DFT methods very well reproduce the correlation between spectroscopic parameters. Results: Comparison of adsorption energies show that adsorption of CO_2 molecule over open-ended of nanotube zigzag (5, 0) model is stronger than the adsorption of on the surface molecule. Conclusions: In the following sections, molecular geometries, E_{ads}, HOMO-LUMO, bond gap and EFG tensors and the data obtained from CO_2 molecule adsorptions are discussed.

Keywords: gas sensors, single-walled carbon nanotubes, NQR, Gaussian98 software.

Introduction

Carbon nanotubes (CNTs)[3] 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_2 [4]. Figure 1 depicts a $C_{53}H_{10}$ 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 gas on the surface and open-ended, using computational methods substantially reduces costs and thus NQR were used in related investigations. Even at low concentration, due to the charge transfer between gas 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 molecule 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[5]. 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[6–8].The NQR measurable asymmetry parameter (η_Q) is also reproduced by quantum chemical calculations of the electric field gradient (EFG) tensors[9]. Considering that the gas adsorption on carbon nano tubes modifies sensibly, their electronic properties proposed the use of SWCNT as gas sensors.

According to the electron-transmission mechanism on the surface and 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 NH3[10], CO_2[11-12], N_2[13] and ethanol[14]),the electrical resistance of SWCNTs was found to increase, whereas by adsorption to oxidizing ones such as O_2 and NO_2 the electrical resistance decrease[15-16].

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.

Materials And Methods

Software

GAUSSIAN 98 package program

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_2 molecule species have studied in this work. The calculated geometry parameters and adsorption energies, dipole momentum and EFG tensors have shown in Tables 1 and 2.

Materials and Methods

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[17-18] and the 6-311++G** standard basis set to evaluate the E_{ads} and C -13 NQR parameters (see Tables 1 and 2).

We define the adsorption energy (E_{ads}) of CO_2 molecular as (Table1)

$E_{adS} = E_{tot}(\text{moleculeCO}_2 + \text{SWCNT}) - E_{tot}(\text{SWCNT}) - E_{tot}(\text{moleculeCO}_2)$

Where, E_{tot} (SWCNT), E_{tot} (CO_2) and E_{tot} (SWCNT+ CO_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 molecule on the surface and 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) [19], 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 SWCNTs 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 3.73A˚.The NQR measurable asymmetry parameter (η_Q) both are also

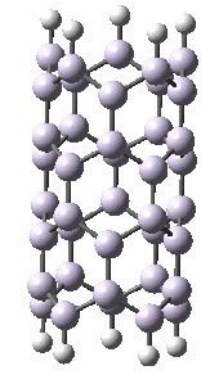
reproduced by quantum chemical calculations of the electric field gradient (EFG) tensors. Geometry optimizations and EFG calculations were performed using 6-311++G** basis set with B3PW91 functional. In quadrupolar spin system, the electric field gradient (EFG) tensor at 13-carbon nuclear sites has axial 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[20-21]. The interaction between nuclear electric quadrupole moment and EFG at quadrupole nucleus is described with Hamiltonian:

$\hat{H} = \frac{e^2 Q q_{ZZ}}{4I(2I-1)}[3\hat{I}_Z^2 - \hat{I}^2) + \eta_Q(\hat{I}_X^2 - \hat{I}_Y^2)]$ 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 $|q_{xx}| \le |q_{yy}| \le |q_{zz}|$ and $q_{xx} + q_{yy} + q_{zz} = 0$. These diagonal elements are related by a symmetry parameter $\eta_Q = \left|(q_{yy} - q_{xx})/q_{zz}\right|$ and $0 \le \eta_Q \le 1$, that measures the deviation of EFG tensor from axial symmetry. Cluster model is proved to be valid for nanotubes [22, 23]. The computed q_{zz} component of EFG tensor is used to obtain nuclear quadrupole coupling constant from the equation $C_Q = e^2 Q q_{ZZ} / h$ [24]. Recently, Lim and Lin have explored the CO_2 molecular physisorption of single-walled CNT(5,0) using density functional theory (DFT) [25]. In this work, we report DFT study of SWCNT (5,0) functionalized with CO_2 molecular. Our study can help in applications of SWCNT in gas sensor or biosensor industry or their purification and processing.

Molecular geometries and Electronic properties: In this study, the efficacy on electronic properties of SWCNT by CO_2 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_2 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_2-SWCNT (5, 0) ($D_{1\&2}$) and CO_2-SWCNT (5,0) ($A_{1\&2}$) 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_2-SWCNT (5,0) ($D_{1\&2}$) is about (0.77)eV and CO_2-SWCNT (5,0) ($A_{1\&2}$) about (0.7464 & 0.8036) eV, which is very close to DFT simulated for the other small diameter nanotube [27-28]. The electron conduction mechanism is expected to be tunnelling when the Fermi levels of contacts lie within the HOMO-LUMO gap of a short length molecule, as for the case of this SWCNT [29]. The effect of CO_2 molecule 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_2 physisorption on seat gas may originates from the changes of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of these systems. For physisorption model CO_2-CNT (5, 0) (D_2), we found that band gaps below electric filed 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 filed. Moreover, the oxidizing characteristic of CO_2 molecule and transfer of its non-binding pairs of electrons to neighbour carbon atoms over carbon rings on surface and 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_2 molecule on the (C) bond on the open ended are changed partly. Two different types of adsorbed CO_2 on the Surface and open ended molecule were recognized (Fig.2&3) SWCNT (5, 0).The calculated adsorption energies were predicted to be -2.3620, -2.3684eV for CO_2 -SWCNTs-$D_{1\&2}$(5, 0) and -0.0335and -0.0338eV for CO_2-SWCNT-$A_{1\&2}$(5,0), respectively. Comparison of adsorption energies show that adsorption of CO_2 molecule over open ended of nanotube zigzag (5, 0) model is stronger than the adsorption of over surface CO_2 molecule.

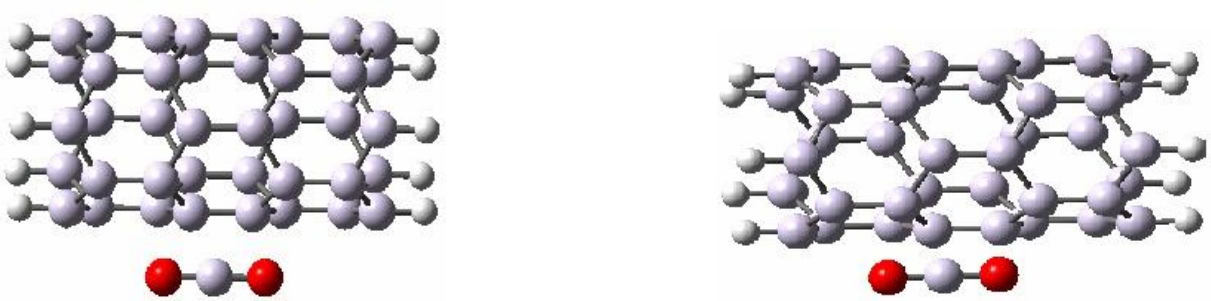
The C-13 NQR spectroscopic parameters: The evaluated NQR parameters reveal that the EFG tensors of 13-Carbon are influenced and show particular trends from gas molecules in the SWCNT due to the contribution of CO_2 gas molecule in SWCNT interactions**.** Semiconducting SWCNT are

ballistic conductors with two and one spin degenerate conducting channel [30-31].The channels belong to the first π and π*-band of the delocalized π-electron system. The C-13 NQR parameters (C_Q and ¦) 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 6-311++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 on the Surface and open ended 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) ¦ parameter of CO_2 adsorption on the Surface and open ended SWCNT has a remarkable effect on EFG tensors. A glimpse to ¦ 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 B3PW91/6-311++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_2 molecule. For the (CO_2–SWCNT-D_2) systems, the EFG tensors of SWCNT (5, 0) is more significantly affected compared to CO_2-SWCNT (5, 0)- D_1 and CO_2-SWCNT (5, 0)-$A_{1\&2}$, respectively.



Scheme 1. (5,0) SWCNT

Scheme 2. (D_1) and (D_2) adsorption configurations of dioxide carbon molecules.



Scheme 3. (A_1) and (A_2) adsorption configurations of dioxide carbon molecules.

Table. 1. Calculated adsorption energies ΔE_{ads}(eV), Bond gap(eV), Charge(DFT) and dipole moment (Debye) of the CO_2 adsorbed surface and open-ended zigzag (5,0) nanotube.

Model	Atoms	HOMO(eV)	LUMO(eV)	Bond gap (eV)	Charge (DFT)	ΔE_{ads}(eV)	Dipole moment (Debye)
SWCNT(5,0)	C_1 C_2 C_3 C_4 C_5	-6.7292	-3.1568	3.6251	-0.358165 -0.358819 -0.268999 -0.268306 -0.199846	-	1.1498
CO_2-SWCNT(5,0) D_1	C_1	-3.9533	-3.1808	0.7725	-0.705896	-2.3620	1.3058
CO_2-SWCNT(5,0) D_2	C_2	-3.8826	-3.1163	0.7663	-0.184042	-2.3684	1.5229
CO_2-SWCNT(5,0) A_1	C_1	-3.9182	-3.1718	0.7464	-0.284412	-0.0335	1.2989
CO_2-SWCNT(5,0) A_2	C_2	-3.9487	-3.1451	0.8036	-0.076469	-0.0338	1.2414

Table 2. Calculated Carbon-13 EFG parameters for the SWCNT, CO_2–SWCNT(5,0)-$D_{1\&2}$ and CO_2-SWCNT(5,0)$A_{1\&2}$, systems.

Model	**Atoms**	$\mathbf{q_{xx}}$	$\mathbf{q_{yy}}$	$\mathbf{q_{zz}}$	$\mathbf{\eta_Q}$
SWCNT(5,0)	C_1 C_2 C_3 C_4 C_5	0.050131 0.050880 0.140698 0.187883 0. 139176	0.113721 0.114492 0.187547 0.228188 0.186403	-0.163852 -0.165372 -0.328245 -0.416071 -0.325578	0.3880 0.3846 0.1427 0.0968 0.1450
CO_2-SWCNT(5,0) D_1	C_1	0.011426	0.090608	-0.102034	0.7760
CO_2-SWCNT(5,0) D_2	C_2	0.168225	0.227720	-0.395945	0.1502
CO_2-SWCNT(5,0) A_1	C_1	0.031568	0.148028	-0.179596	0.6484
CO_2-SWCNT(5,0) A_2	C_2	0.023655	0.179709	-0.203363	0.7673

[a] Calculated adsorption energies ΔE_{ads}(eV), Bond gap(eV), Charge(DFT) and dipole momentum(Debye) of the CO_2 adsorbed surface and open-ended zigzag (5,0) nanotube

Conclusions

In the following sections, molecular geometries, E_{ads}, HOMO-LUMO,bond gap and EFG tensors and the data obtained from CO_2 molecule adsorptions are discussed.

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