

CO₂ adsorption on the surface and open ended of single wall carbon nanotubes (SWCNTs): A comparative study

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Abstract

Adsorption of CO₂ on the surface of Single-wall zigzag (5, 0) and armchair (4, 4) carbon nanotubes (SWCNTs) were studied through using density functional theory (DFT) calculations. Optimizations of geometric were performed at the B3PW91 level of 6-311++G** method standard basis set using GAUSSIAN 03 package of program. Structural models were optimized and adsorption energies, band gap, charge transfer and dipole momentum were obtained to investigate the nuclear magnetic resonance (NMR) and Nuclear Quadrupole Resonance (NQR) spectroscopy parameters for (CO₂-CNTs) model of zigzag (5, 0) and armchair (4, 4) SWCNTs. Comparison of the results of the zigzag and armchair models with calculated chemical shielding, electric field gradient tensors at the sites of carbon on the surface and open ended revealed that CO₂ adsorption has a dramatic effect on the electronic structure of SWCNTs and adsorption on the surface is about -1.5747eV SWCNT-S (5, 0) nanotube.

Key words: GAUSSIAN 03; NMR; NQR adsorption; SWCNTs, MWCNTs

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INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) by Iijima, CNTs have attracted great interest owing to their extraordinary structural, mechanical, chemical, physical, and electronic properties [1, 2]. Carbon nanotubes are categorized in two types: Single cylinder known as SWCNTs and more concentric cylinders known as multi wall carbon nanotubes (MWCNTs) [3]. SWCNT properties are highly structure-size-dependent and are influenced by an atomic arrangement (chirality), nanotube diameter, length and morphology or its nanostructure. Depending on their diameter and chirality, carbon nanotubes can either be semiconductors [4]. One possible way to modify the electronic and vibration properties is a charge transfer during their intercalation [5]. CNTs were first theoretically investigated in 1994 and then experimentally were synthesized in 1995 as mainly semiconductor materials with wide band

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gaps [6-9]. The changes in electrical resistance by adsorption of certain gas molecules such as CO₂ are considerable [10]. The absorption of various gas molecules like NO₂, O₂, NH₃, N₂, CO₂, CH₄, H₂O, H₂ and Ar on both single SWCNT and SWCNT bundles using first principles method were studied [11]. The Self-Consistent Field (SCF) electronic structure calculations were performed based on density functional theory (DFT) [12-15]. The calculation of nuclear magnetic resonance (NMR) spectroscopy parameters using DFT techniques have become a major and powerful tool for investigation of molecular structure [16]. The chemical-shielding (σ_{ii}) tensors originating at the sites of half-spin nuclei, magnetic nuclei, reveal important trends about the electronic properties at the sites of these nuclei. The (σ_{ii}) tensors are either measured experimentally or reliably reproduced by high-level quantum chemical calculations [17, 18]. Nuclear experimental techniques such as Nuclear

Quadrupolar Resonance (NQR) are widely used to study the geometry and electronic structure of molecules [19]. 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 $I > 1/2$ is put in an Electric Field Gradient (EFG); decayed spin energy levels are created [20, 21]. 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. In this research, we expect that our studies can provide suitable information in the application of SWCNTs a sensor for detection of CO_2 .

EXPERIMENTAL

This study was performed in Payame Noor University, Tehran, Iran, as a research project over carbon nanotubes adsorption property in 2014.

Computational details

In this approach, we used a single-wall zigzag (5, 0) and an armchair (4, 4) carbon nanotubes.

The atoms at the open ends of the nanotube were saturated by hydrogen atoms to avoid the boundary vibration. Frequencies were also calculated at the same level to confirm that all the stationary points correspond to true minimum on the potential energy surface. Geometry and density of states (DOS) and analyses of the optimized tube are shown in Figs. 1 and 2 which indicate that the tube is semi-conductive with HOMO (electropositive density), LUMO (electronegative density) and energy gap (E_g) on the surface and an open ended armchair (4,4) and a zig-zag (5,0) a nanotube of 0.08269, 0.08269, 0.05588 and 0.03104 eV, respectively. From DOS analyses of Table 1, it is found that CNTs captured CO_2 effectively at ambient conditions. However, reports in literature show that the pristine CNTs with a wide band gap are almost inert to many gas molecules [22, 23]. The diameters of nanotubes are 4.24 and 5.67 Å, the lengths of the nanotubes are 10.02 and 7.61 Å, respectively, and the average bond length is 1.42 Å. The (5, 0) SWCNT containing 50 carbon atoms and 10 hydrogen atoms and the (4, 4) SWCNT containing 80 carbon atoms and 16 hydrogen atoms were selected for this purpose. DFT is used to study the structural and electric properties of the tube-molecule systems

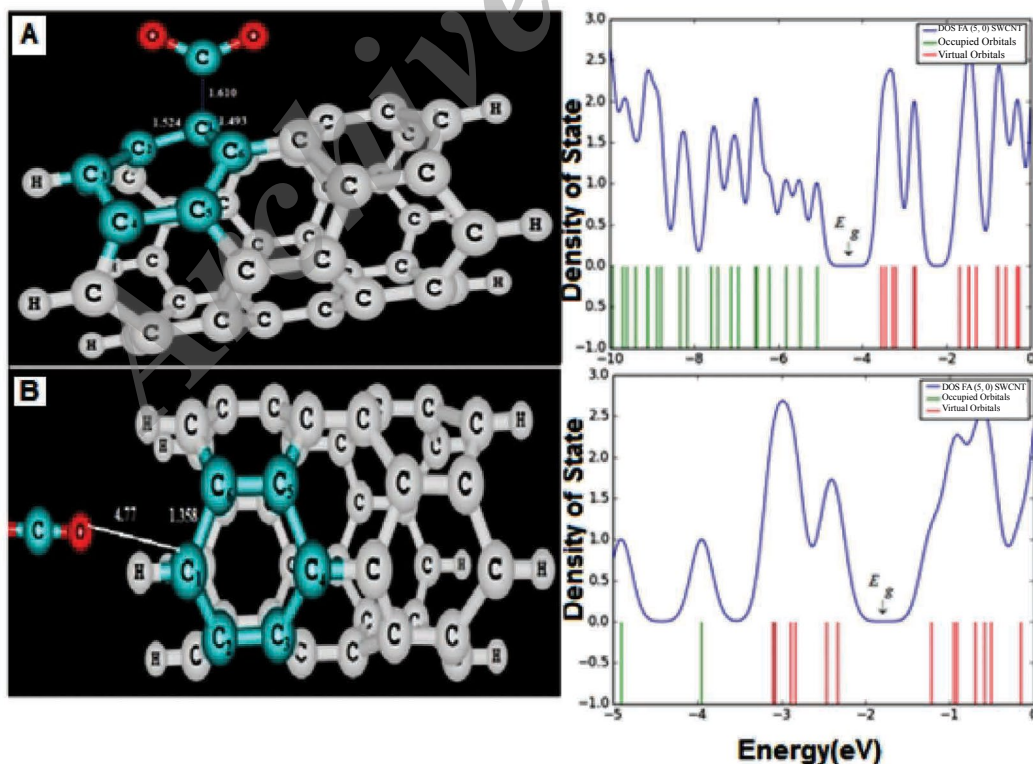


Fig. 1: The A: (5, 0) SWCNT(S) and B: (5, 0) SWCNT(D) adsorption configurations and the electronic density of states of CO_2 molecule (sites on the surface and on the open ended, respectively)

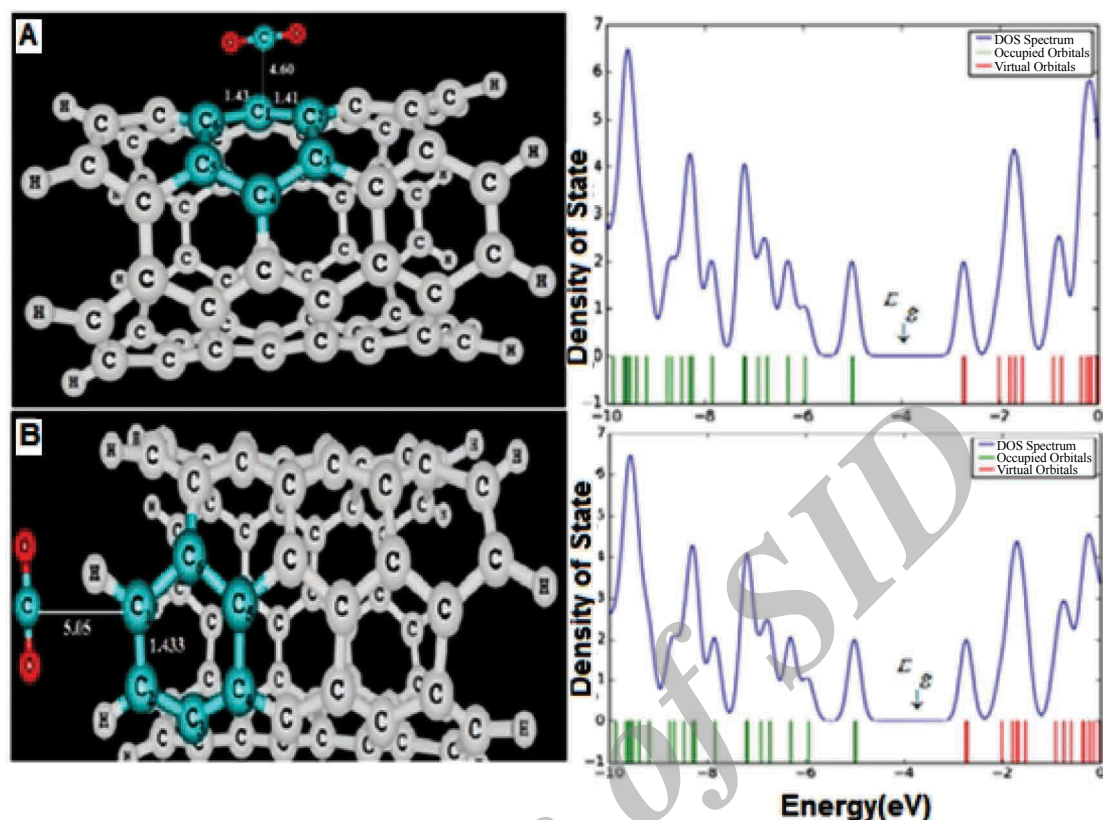


Fig. 2: The A: (4, 4) SWCNT(S) and B:(4, 4) SWCNT(D) adsorption configurations and the electronic density of states of CO₂ molecule (sites on the surface and on the open ended, respectively).

during adsorption of CO₂ molecule on the SWCNTs. The calculations are performed by hybrid functional B3PW91/ DFT based method and 6-311++G (d, p) standard basis set by GAUSSIAN 03 package of program. We used the NMR including chemical shielding isotropic (σ_{iso}), chemical shielding anisotropic ($\Delta\sigma$) and asymmetric (η_Q) parameters [24, 25] and NQR including C_Q [26] spectroscopy for the electronic structured properties of materials by quantum calculations.

NMR ¹³C chemical shielding calculations were computed at B3LYP/6-311G* level of theory using Gauge Including Atomic orbital's (GIAO) approach [27]. The NMR parameters of ¹³C nuclei for the investigated a model of the zigzag (5, 0) and an armchair (4, 4) single-walled CO₂-CNTs are summarized in Table 4. Quantum chemical calculated tensors at the Principal Axes System (PAS) ($\sigma_{33} > \sigma_{22} > \sigma_{11}$) is converted to a diagonal matrix with (σ_{11}), (σ_{12}) and (σ_{33}) components, measurable NMR parameters, $\Delta\sigma$ and η_Q are used, respectively [28, 29]. They have been converted to σ_{iso} , $\Delta\sigma$ and η_Q using Eqs. 1-3, respectively.

$$\sigma_{iso} (ppm) = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (1)$$

$$\Delta\sigma (ppm) = \sigma_{33} - \frac{1}{2}(\sigma_{11} + \sigma_{22}) \quad (2)$$

$$\eta_Q = \frac{3}{2} \left(\frac{\sigma_{22} - \sigma_{11}}{\Delta\sigma} \right) \quad (3)$$

The NQR measurable asymmetry parameter (η_Q) is also reproduced by quantum chemical calculations of the electric field gradient (EFG) tensors [30-33]. Geometry optimizations and EFG calculations were performed using 6-311++G** basis set with B3PW91 functional. In quadrupolar spin system, the EFG tensor at ¹³-carbon nuclear sites has an 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 [34]. The interaction between nuclear electric quadrupole moment and EFG at quadrupole nucleus is described with Hamiltonian:

$$\hat{H} = -\frac{e^2 Q q_{zz}}{4I(2I-1)} [3\hat{I}_z^2 - \hat{I}^2] + \eta_Q (\hat{I}_x^2 - \hat{I}_y^2) \quad (4)$$

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 ($1\text{au}=9.717365\times 10^{21}\text{Vm}^{-2}$), with $|q_{xx}|\leq|q_{yy}|\leq|q_{zz}|$ and $q_{xx}+q_{yy}+q_{zz}=0$; these diagonal elements are related by a symmetry parameter $\eta_Q=|(q_{xx}-q_{yy})/q_{zz}|$ and $0\leq\eta_Q\leq 1$ measures the deviation of EFG tensor from axial symmetry. Cluster model is proved to be valid for nanotubes [35] computed q_{zz} component of EFG tensor is used to obtain nuclear quadrupole coupling constant from the equation $C_Q=e^2Qq_{zz}/h$ [36].

RESULTS AND DISCUSSION

In this work, geometries, binding energies, ^{13}C NMR and NQR chemical shielding tensors of zigzag (5, 0) and armchair (4, 4) SWCNT interacted with molecule CO_2 , have studied. The calculated geometry parameters and binding energies, Chemical potential (μ), hardness (η), softness (S), ΔN_{max} (a.u.), and electrophilicity (ω), ^{13}C chemical shielding and EFG parameters tensors have shown in Tables 1 - 4. In the following sections, molecular geometries and binding energies, NMR and NQR chemical shielding tensors, the data obtained from CO_2 molecule adsorption are discussed, separately. The net charge-transfer (Q_T) from the CO_2 molecule to the zigzag (5,0) and armchair (4,4) SWCNT is calculated by using Mulliken population analysis, which is defined as the charge difference between the CO_2 molecule adsorbed on the doped nanotube and an isolated CO_2 molecule.

Molecular geometries and binding energies

In this study, the use of the electronic properties of single-walled carbon nanotubes has 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) and armchair (4,4) SWCNTs are schematically displayed in Figs. 1 and 2. Geometrical parameters, adsorption energies and dipole moment are summarized in Table 1. The nature of stationary points are confirmed by vibrational frequency calculations at the B3PW91/6-311++G** level.

For CO_2 molecule, we have considered distinct adsorption sites, marked as SWCNTs, CO_2 -SWCNTs

adsorption energies, (Table 1) are calculated using:

$$E_{\text{ads}} = E_{\text{tot}}(\text{molecule } \text{CO}_2 + \text{SWCNT}) - E_{\text{tot}}(\text{SWCNT}) - E_{\text{tot}}(\text{molecule } \text{CO}_2) \quad (5)$$

Where, E_{tot} (SWCNTs), E_{tot} (CO_2) and E_{tot} (SWCNTs+ CO_2) are the energies of the optimized tubes, which are adsorption systems, respectively. The electrophilicity concept was stated for the first time in 1999 by Parr *et al.* [37,38]. μ is defined according to the following equation:

$$\mu = -\chi = -\frac{I+A}{2} \quad (6)$$

χ is defined as the negative of μ , as follows: $\mu = -\chi$. Furthermore, η can be approximated using the Koopmans' theorem [39] I ($-E_{\text{HOMO}}$) is the ionization potential and A ($-E_{\text{LUMO}}$) the electron affinity of the molecule. Where E_{HOMO} is the energy of the Fermi level and E_{LUMO} is the first given value of the conduction band.

$$\eta = (I-A)/2 \quad (7)$$

S and ω are defined as the following equations, respectively.

$$S = 1/2 \eta \quad (8)$$

$$\omega = \mu^2/2 \eta \quad (9)$$

The maximum amount of electronic charge, ΔN_{max} , that the electrophone system may accept is given by Eq. (10) as [40]:

$$\Delta N_{\text{max}} = -\frac{\mu}{\eta} \quad (10)$$

By this explanation, $E_{\text{ads}} < 0$ corresponds to exothermic adsorption which leads to local minima stable for adsorption of gas molecules on the open ended and surface. In Fig. 1, nanotube(5, 0) has (C-C₁) $S = 1.610 \text{ A}^\circ$, (C₁-O) $D = 4.77 \text{ A}^\circ$, and in Fig. 2, CO_2 SWCNT- D & S (4, 4) nanotube has two different CNT- CO_2 bonds (C-C₁) $D = 5.05 \text{ A}^\circ$ and (C-C₁) $S = 4.60 \text{ A}^\circ$, that show increased adsorption of CO_2 molecule on the surface SWCNT-D (5, 0) nanotube and has different C-C bond length on the open ended (5,0) (C₁-C₆) $= 1.358 \text{ A}^\circ$, on the open ended (4, 4) (C₁-C₂) $= 1.433 \text{ A}^\circ$, and on the surface (5, 0) (C₁-C₂) $= 1.524 \text{ A}^\circ$ and (C₁-C₆) $= 1.493 \text{ A}^\circ$ and on the surface (4, 4) (C₁-C₂) $= 1.41 \text{ A}^\circ$, and (C₁-C₆) $= 1.43 \text{ A}^\circ$ thus suggests two distinct adsorption sites, respectively. The increased bond length (C₁-C₂) and diameter SWCNT-(S) (5, 0) on the surface after adsorbing the molecular CO_2 on the (5,0) SWCNT systems, CO_2 seemed to place the outer surface (5, 0) tube in parallel. Density functional

calculations of SWCNTs, efficient process of charge transfer between the CO₂ molecule and the nanotube, is found to substantially reduce the susceptibility of the π-electrons of the nanotube to modification through CO₂ while maintaining stable doping. Diagrammatic view of this form is shown in Figs. 1 and 2 SWCNTs and CO₂-SWCNTs-(S) and (D). Geometry calculations of distortion caused by the carbon dioxide molecule on surface and open ended the (C-C) bond of zig-zag (5, 0) and armchair

(4, 4) SWCNTs are partly changed.

Two different types of adsorbed CO₂ molecules were recognized (Figs. 1 and 2) CO₂-SWCNT-S, CO₂-SWCNT-D model (5, 0) and (4, 4). The calculated adsorption energies were predicted to be -1.868 and -1.869 eV on surface and open ended CO₂-SWCNTs-S and D(4, 4) and -1.574 and -1.885 eV for CO₂-SWCNTs-S and D (5, 0), respectively. The length of nanotube have selected with regard to the length of unit cell of nanotube. The geometry

Table 1: Calculated adsorption energies (E_{ads}), Band gap (E_g), QT (DFT) and dipole moment (Debye) of the CO₂ adsorbed surface and open-ended zigzag (5, 0) and armchair (4, 4) nanotubes. All energies are in units of eV.

System	atoms	E _{ads} (eV)	Dipole moment (Debye)	E _{HOMO} (eV)	E _{LUMO} (eV)	Band gap (eV)	QT
CNT (5, 0)	C	-	1.1498	-6.7292	-3.1568	3.6251	-
CNT (4, 4)	C	-	0.0049	-0.23157	-0.10058	0.13099	-
CO ₂ -CNT (4, 4)-D	C	-1.8691	0.0484	-0.18353	-0.10084	0.08269	-0.581286
CO ₂ -CNT (5, 0)-D	C	-1.8859	1.3712	-0.14503	-0.11399	0.03104	-0.353004
CO ₂ -CNT (4, 4)-S	C	-1.8685	0.0484	-0.18353	-0.10084	0.08269	-0.0686652
CO ₂ -CNT (5, 0)- S	C	-1.5747	9.5506	-0.18668	-0.13080	0.05588	-1.235756

Table 2: Chemical potential (μ), hardness (η), softness (S), ΔN_{max} (a.u.), and electrophilicity (ω) of CO₂ adsorption on CNT surfaces at the B3PW91/6-311++G** level. The parameters are in units of eV.

Property	CNT(4,4)	CNT(5,0)	CNT(4,4)-CO ₂ -S	CNT(4,4)-CO ₂ -D	CNT(5,0)-CO ₂ -S	CNT(5,0)-CO ₂ -D
[I=-E _{HOMO}] (eV)	2.737	3.139	2.744	2.744	3.559	3.946
[A=-E _{LUMO}] (eV)	4.986	3.982	4.994	5.015	5.080	3.102
[η=(I-A)/2](eV)	-1.125	-0.422	-1.125	-1.136	-0.761	0.422
[μ=-(I+A)/2] (eV)	-3.862	-3.561	-3.869	-3.880	-4.320	-3.524
[S=1/2 η] (eV)	-0.445	-1.186	-0.444	-0.440	-0.657	1.185
[ω=μ ² /2η] (eV)	-6.630	-15.038	-6.653	-6.627	-12.267	14.714
ΔN _{max} = -μ/η (a.u.)	-3.434	-8.447	-3.439	-3.417	-5.680	8.351

Table3: Calculated of chemical shielding and chemical shift tensors adsorption on the surface 13-C parameters for CNT (4, 4), CNT (5, 0), CNT (4, 4) – CO₂ and CNT (5, 0) – CO₂ system.

Model	Atoms	σ ₁₁	σ ₂₂	σ ₃₃	σ _{iso}	Δσ	η _σ
CNT (5, 0)	C ₁	-45.2511	154.2238	334.2732	147.7486	279.78685	-1.0694
	C ₂	-45.2511	154.2238	334.2732	147.7486	279.78685	-1.0694
	C ₃	-115.1751	60.2234	103.6177	16.2220	-197.0956	131.0935
CNT (4,4)	C ₁	0.9584	40.6177	131.4106	57.6662	110.6316	0.5377
	C ₂	22.1907	26.0307	126.3909	58.2041	102.2802	0.0563
	C ₃	1.6784	87.2017	87.2244	58.7045	42.7798	2.9984
CNT (5, 0)-CO ₂ -S	C ₁	74.4312	77.7044	155.3112	102.4823	79.2434	0.0620
	C ₂	74.6323	77.7154	155.0228	102.4568	79.2720	0.0637
CNT (4,4)-CO ₂ -S	C ₁	1.6000	19.0380	154.1514	58.2631	143.8324	0.1818
	C ₂	1.8314	73.0690	101.9763	58.9582	64.5281	1.6560
	C ₃	0.2349	3.1759	171.1831	58.1980	169.4776	0.0260
CNT (5, 0)-CO ₂ -D	C ₁	42.8507	97.3469	149.1738	96.4571	79.0751	1.0338
	C ₂	47.6078	104.8761	127.8227	93.4355	51.5808	1.6654
CNT (4,4)-CO ₂ - D	C ₁	-8.9800	-8.9800	103.1800	28/4067	98.6900	0.0000
	C ₂	-8.9700	-8.9700	103.2000	103/2000	112.1700	0.0000

Table 4: NQR parameters of the (4, 4) armchairSWCNT and (5, 0) zigzagSWCNT [20]

Sait	13- C Atoms	q_{xx}	q_{yy}	q_{zz}	η_Q
CNT (5, 0)	C ₁	0.050131	0.113721	-0.163852	0.3880
	C ₂	0.050880	0.114492	-0.165372	0.3846
	C ₃	0.140698	0.187547	-0.328245	0.1427
	C ₄	0.187883	0.228188	-0.416071	0.0968
	C ₅	0.139176	0.186403	-0.325578	0.1450
CNT (4,4)	C ₁	0.104304	0.129776	-0.234079	0.1088
	C ₂	0.104235	0.129456	-0.233691	0.1079
	C ₃	0.104324	0.129658	-0.233983	0.1082
	C ₄	0.088491	0.173612	-0.262104	0.3247
	C ₅	0.088333	0.173564	-0.261897	0.3254
CNT(5,0)-CO ₂ -A	C ₁	0.031568	0.148028	-0.179596	0.6484
	C ₂	0.023655	0.179709	-0.203363	0.7673
CNT(4,4)-CO ₂ -A	C ₁	0.000053	0.000203	0.000792	0.1893
	C ₂	-0.000099	-0.000435	0.000831	0.4043
CNT(5, 0)-CO ₂ -D	C ₁	0.011426	0.090608	-0.102034	0.7760
	C ₂	0.168225	0.227720	-0.395945	0.1502
CNT(4,4)-CO ₂ - D	C ₁	0.000472	-0.000590	0.000860	1.2348
	C ₂	-0.000185	-0.000730	0.000933	0.5841

of zig-zag (5, 0) on the open ended and armchair (4, 4) on the surface and open ended tubes are considerably modified when such oxidation occurs and physisorbed product is formed and the geometry of zig-zag (5, 0) on the surface tubes chemisorbed product is formed. The electron can not enter into CO₂ molecule binding orbital because the binding orbital is filled. This arrives to either sp³ hybridization for two carbon atoms or breaking of one C-C bond. Two different types of adsorbed CO₂ species were identified (Figs. 1 and 2, Tables 1 and 2). The dipole moments were calculated by Gaussian software and have shown in Table 1. The results of the dipole moment for single species and most stable configurations of considered complexes demonstrate that during CO₂ adsorption for all systems, total dipole moments increase. We considered that dipole moments for (5, 0) CO₂-CNTs and (4, 4) CO₂-CNTs on the surface and open ended are 9.55, 1.37 and 0.05 Debye, respectively. (See Table 1).

CONCLUSIONS

Geometries, E_{ads} , HOMO-LUMO, NMR and EFG tensors and the data obtained from CO₂ molecule adsorptions are discussed. In this investigation, it was concluded that the NMR and EFG tensors of 13-C nuclei in the SWCNTs are appropriate parameters to characterize the property of these interactions. Results indicated that the calculated NMR and NQR parameters change via carbon bonding interactions to the CO₂ molecule.

Considering the available theoretical errors in determining the chemical shift and EFG tensors, the calculated σ_{iso} and η_Q values of 13-C nucleus at C-C bond on CNT (5,0) -CO₂-A model is about 102.48 and 0.6484 MHz, respectively. Decrease in global hardness, ionization potential and energy gaps during adsorption of CO₂ molecule on SWCNTs is due to the increase of chemical reactivity and also leads to the reduction of stability in the systems.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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