CO$_2$ adsorption on the surface and open ended of single wall carbon nanotubes (SWCNTs): A comparative study

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Abstract
Adsorption of CO$_2$ 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 (CO$_2$-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 filed gradient tensors at the sites of carbon on the surface and open ended revealed that CO$_2$ 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

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 gaps [6-9]. The changes in electrical resistance by adsorption of certain gas molecules such as CO$_2$ are considerable [10]. The absorption of various gas molecules like NO$_2$, O$_2$, NH$_3$, N$_2$, CO$_2$, CH$_4$, H$_2$O, H$_2$, and Ar on both single SWCNT and SWCNT bundles using first principles method werestudied [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 ($\sigma$) 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 ($\sigma$) 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 CO₂.

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 (electro-positive 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 0.03104eV, respectively. From DOS analyses of Table 1, it is found that CNTs captured CO₂ 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 5.67Å, 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 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 (σ₁₁), chemical shielding anisotropic (Δσ) and asymmetric (η₁) parameters [24, 25] and NQR including CQ [26] spectroscopy for the electronic structured properties of materials by quantum calculations.

NMR 13-C 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) (σ₃₃>σ₂₂>σ₁₁) is converted to a diagonal matrix with (σ₁₁), (σ₂₂) and (σ₃₃) components, measurable NMR parameters, Δσ and η₁ are used, respectively [28, 29]. They have been converted to σiso, Δσ and η₁ using Eqs. 1-3, respectively.

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

(1)

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

(2)

\[ \eta_1 = \frac{3}{2} \left( \frac{\sigma_{33} - \sigma_{11}}{\Delta \sigma} \right) \]  

(3)

The NQR measurable asymmetry parameter (ηQ) 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 η=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:

\[ \hat{H} = \frac{e^2 Q_q}{4I(2I-1)} (3\hat{l}_z^2 - \hat{l}_z^2) + \eta_0 (\hat{l}_z^2 - \hat{l}_x^2 - \hat{l}_y^2) \]  

(4)
RESULTS AND DISCUSSION

In this work, geometries, binding energies, 13C 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 ($\mu$), hardness ($\eta$), softness (S), $\Delta N_{max}$ (a.u.), and electronegativity ($\omega$), 13C 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 ($\Delta q$) 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 vibrationfrequency 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:

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

Where, $E_{tot}$ (SWCNTs), $E_{tot}$ (CO$_2$) and $E_{tot}$ (SWCNT+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]. $\mu$ is defined according to the following equation:

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

$\chi$ is defined as the negative of $\mu$, as follows: $\mu = -\chi$. Furthermore, $\eta$ can be approximated using the Koopmans’ theorem [39] $I (E_{HOMO})$ is the ionization potential and $A (E_{LUMO})$ 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.

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

$S$ and $\omega$ are defined as the following equations, respectively.

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

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

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

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

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 and surface. In Fig. 1, nanotube(5,0) has (C-C1) S = 1.610 Å, (C1-O) D = 4.77 Å, and in Fig. 2, CO$_2$-SWCNT-D & S (4, 4) nanotube has two different CNT-CO$_2$ bonds (C-C$_2$) D = 5. 05 Å and (C-C$_2$) S = 4.60 Å respectively. The increased bond length (C1-C6) = 1.433 Å, and in the surface(5, 0) (C1-C$_2$) = 1.524 Å and (C-C$_2$) = 1.493 Å 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) (C$_1$-C$_2$) = 1.358 Å, on the open ended (4, 4) (C$_1$-C$_2$) = 1.433 Å and on the surface(5, 0) (C$_1$-C$_2$) = 1.524 Å and (C-C$_2$) = 1.493 Å and on the surface(4, 4) (C$_1$-C$_2$) = 1.41 Å, and (C-C$_2$) = 1.43 Å thus suggests two distinct adsorption sites, respectively. The increased bond length (C$_1$-C$_2$) and diameter SWCNT-(S) (5, 0) tube in parallel. Density functional
calculations of SWCNTs, efficient process of charge transfer between the CO$_2$ molecule and the nanotube, is found to substantially reduce the susceptibility of the π-electrons of the nanotube to modification through CO$_2$, while maintaining stable doping. Diagrammatic view of this form is shown in Figs. 1 and 2 SWCNTs and CO$_2$-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 CO$_2$ molecules were recognized (Figs. 1 and 2) CO$_2$-SWCNT-S, CO$_2$-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 CO$_2$-SWCNT-D and D(4, 4) and -1.574 and -1.885 eV for CO$_2$-SWCNT-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>
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<tr>
<th>System</th>
<th>atoms</th>
<th>$E_{\text{in}}$ (eV)</th>
<th>Dipole moment (Debye)</th>
<th>$E_{\text{ads}}$ (eV)</th>
<th>$E_{\text{ads}}/I_{\text{chem}}$ (eV)</th>
<th>Band gap (eV)</th>
<th>QT (DFT)</th>
<th>$\mu$ (eV)</th>
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<td>CNT (5, 0)</td>
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<td>-6.729</td>
<td>-3.1568</td>
<td>3.625</td>
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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 chemisorbed product is formed and considerably modified when such oxidation (4, 4) on the surface and open ended tubes are considered complexes demonstrate that during CO adsorption for all systems, total dipole moments increase. We considered that dipole moments for (5, 0) CO\textsubscript{2}-CNTs and (4, 4) CO\textsubscript{2}-CNTs on the surface and open ended are 9.55, 1.37 and 0.05 Debye, respectively. (See Table 1).

CONCLUSIONS

Geometries, \(E_{\text{el}}\) HOMO-LUMO, NMR and EFG tensors and the data obtained from CO\textsubscript{2} 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 interaction to the CO\textsubscript{2} molecule.

<table>
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<tr>
<th>Suit</th>
<th>13-C Atoms (q_{xx})</th>
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<th>(q_{zz})</th>
<th>(\eta_{Q})</th>
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</table>

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

Considering the available theoretical errors in determining the chemical shift and EFG tensors, the calculated \(\sigma_{\text{Q}}\) and \(\eta_{Q}\) values of 13-C nucleus at C-C bond on CNT (5,0) -CO\textsubscript{2}-A model is about 102.48 and 0.6484 MHz, respectively. Decrease in global hardness, ionization potential and energy gaps during adsorption of CO\textsubscript{2} 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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CONFICT OF INTEREST

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

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