Study of Nuclear Quadrupole Resonance on CO-Doped Single-Walled Carbon Nanotubes: A DFT Computation

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Abstract: Carbon Monoxide (CO) gas adsorption on external surface of zig-zag (5, 0) and armchair (4, 4) semiconducting Single-Walled Carbon Nanotube (SWCNTs) were studied using Density Functional Theory (DFT) calculations. Geometry optimizations were carried out by B3LYP/DFT method at 6-311G* level of theory using the Gaussian98. SWCNTs have been proposed as ideal candidates for various applications of gas sensors due to their amazing physical adsorption properties. We studied the Nuclear Quadrupole Resonance (NQR) of the zigzag (5, 0) and armchair (4, 4) SWCNTs with the optimal length of 7.13 and 9.8 Å, respectively. For the first time, DFT calculations were performed to calculate the interaction of 13-Carbon quadrupole moment with EFG in the considered model of CO-SWCNTs. The evaluated NQR parameters reveal that the EFG tensors of 13-Carbon are influenced and show particular trends from gas molecules in the SWCNTs due to contribution of C-O gas molecule of SWCNTs.

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

INTRODUCTION

The discovery of carbon nanotubes produced by graphite, first reported by Iijima in 1991 (Iijima and Ichihashi, 1993), ushered in a new and very amazing research field in compacting gases by adsorption methods. The changes in electrical resistance, by adsorption of certain gas molecules are considerable, for example by adsorption of O₂, N₂ and CO (Odom et al., 1998). Figure 1 depicts a C₄₀H₁₀ and C₇₂H₁₆ tube modeling a zig-zag (5, 0) and armchair (4, 4) SWCNTs which demonstrates the stated effect on the electronic structure of SWCNTs. Comparing the adsorption of gases on the surface, using computational methods substantially reduces costs and thus NQR were used in related investigations. Due to the change transfer between gases and tube, even at low concentration, gas adsorption can change the conductivity of SWCNTs. Electronic properties of SWCNTs have been studied in a number of theoretical studies (van Houten et al., 1992; Aijiki and Ando, 1993; Wildoer et al., 1998) and optimized forms of nanotube can be designed by a precise positioning of CO gas on considered carbon atoms. Theoretical studies have found that this single-walled carbon nanotube has novel electronic properties, which can be semiconducting, depending on their radius or chiralities (Bezryadin et al., 1998; Mintmire et al., 1992; Rao et al., 1997). A new SWCNTs gas sensor would be fulfilled by utilizing such electrical characteristics. In this study CO adsorption mechanism on carbon nanotubes was investigated by the surface SWCNTs gas sensor. It was found that CO can be adsorbed on the surface of CO-SWCNT-A2, model (5, 0) that makes C-O bonds active.

In addition, comparison the adsorption rate between SWCNTs forcefully increases this viewpoint that present theoretical study on CO-SWCNT-A2 (5, 0) shows larger adsorption capacity. Nuclear computational techniques such as Nuclear Quadrupole Resonance (NQR) are widely used to study the geometry and electronic structure of molecules. 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) (Semin et al., 1975) 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.

The NQR measurable asymmetry parameter ($\eta_0$) is also reproduced by quantum chemical calculations of the Electric Field Gradient (EFG) tensors. The aim of this study is investigating adsorption properties of (5, 0) and (4, 4) Single-Walled Carbon Nanotube as a gas sensor and optimized adsorption rates by using DFT calculations.
MATERIALS AND METHODS

This study was performed in Payame Noor University, Sari center, Sari, Iran, as a research project over carbon nanotubes adsorption property in 2011 and 2012.

In this study CO molecule adsorption behaviors on surface of SWCNT zig-zag (5, 0) and armchair (4, 4) are taken in to consideration. Zig-zag (5, 0) and armchair (4, 4) SWCNTs containing 40 and 72 carbon atoms with length of 7.13 and 9.8 Å are selected for this purpose, respectively. Saturating carbon dangling bonds with 10 and 16 hydrogen atoms in zig-zag (5, 0) and armchair (4, 4) models are necessary because there is no periodic boundary conditions in molecular calculations and also due to limitation of nanotube length and lack of homogeneity for ending atoms, symmetry breaks down and some changes in geometrical properties are proved for ending atoms during optimization processes. Optimization of a sample system includes relaxation of atoms to lower forces from other constituents on each atom. Calculations were carried out with Gaussian98 (Catlow et al., 2010; Lynch and Hu, 2000a, b; Frisch et al., 1998) suite of programs at all-electron level (Barone et al., 2004). It has been established that DFT is able to accurately treat such systems due to incorporation of the exchange-correlation effects (Yim and Liu, 2004a, b). 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 (Lu et al., 2005; Osokin et al., 1969, 1992). Geometry optimizations and EFG calculations were performed using 6-311G* basis set with B3LYP functional. The interaction between nuclear electric quadrupole moment and EFG at quadrupole nucleus is described with Hamiltonian:

$$\hat{H} = \frac{e^2Q_xx}{4(2I-1)}(3Iz^2 - I^2) + \eta_q(I_x - I_y)$$

where, $eQ$ is the nuclear electric quadrupole moment, $I$ is the nuclear spin and $q_{xx}$ is the largest component of EFG tensor. The principal components of the EFG tensor, $q_{xx}$ are computed in atomic unit ($1 \text{ au} = 9.717365 \times 10^{-21} \text{ Vm}^2$), with $|q_{xx}| > |q_{yy}| > |q_{zz}|$ and $q_{xx} + q_{yy} + q_{zz} = 0$. These diagonal elements are related by a symmetry parameter $\eta_q = |q_{yy} - q_{zz}|/q_{zz} \leq 1$, that measures the deviation of EFG tensor from axial symmetry. Cluster model is proved to be valid for nanotubes (Furman and Naturforsch, 1994; Lucken, 1992). The computed $q_{xx}$ component of EFG tensor is used to obtain nuclear quadrupole coupling constant from the $C_Q = e^2Q_{xx}/h$ equation (Froudakis et al., 2003).

RESULTS AND DISCUSSION

In the present study, two models of zig-zag (5, 0) and armchair (4, 4) SWCNTs with specified tube lengths are studied using quantum chemical calculations (Fig. 1 and 2). Geometries, binding energies and NQR (5, 0) and (4, 4) SWCNTs interacted with CO molecules have studied in this study. The calculated geometry parameters and binding energies, dipole momentum and EFG tensors.
Molecular geometries and binding energy: adsorptions are discussed. EFG tensors and the data obtained from CO molecule (configuration) Atom $q_{xx}$ $q_{yy}$ $q_{zz}$

<table>
<thead>
<tr>
<th>Model (configuration)</th>
<th>$R_{cc}$ (Å)</th>
<th>$R_{cc}$ (Å)</th>
<th>$\Delta E_{ad}$ (eV)</th>
<th>Dipole moment (Debye)</th>
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</thead>
<tbody>
<tr>
<td>SWCNT (4, 4)</td>
<td>(C-C) = 1.424</td>
<td>-</td>
<td>-</td>
<td>0.4358</td>
</tr>
<tr>
<td></td>
<td>(C-C) = 1.419</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(C-C) = 1.438</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(C-C) = 1.405</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(C-C) = 1.437</td>
<td>-</td>
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<tr>
<td></td>
<td>(C-C) = 1.437</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>SWCNT (5, 0)</td>
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<tr>
<td></td>
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<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(C-C) = 1.519</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(C-C) = 1.465</td>
<td>-</td>
<td>-</td>
<td></td>
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<tr>
<td></td>
<td>(C-C) = 1.425</td>
<td>-</td>
<td>-</td>
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<tr>
<td>CO-SWCNT -A1(5, 0)</td>
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<td>(C-O) = 1.557</td>
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<tr>
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<tr>
<td></td>
<td>(C-C) = 1.582</td>
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<td>-0.3126</td>
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</table>

Table 1: Calculated adsorption energies $E_{ad}$ (eV), bond energies (Aº) and dipole momentum (Debye) of the CO adsorbed on surface armchair (4, 4) and zigzag (5, 0) nanotube.

$R_{cc}$ (Å) = $R_{cc}$ (Å) = 1.324 -0.3126 2.9150

$E_{tot}$ (SWCNTs) - $E_{tot}$ (molecule CO) = $E_{ad}$ (molecule CO) + $E_{ad}$ (SWCNTs)

$E_{ad}$ (molecule CO) + $E_{ad}$ (SWCNTs) = $E_{tot}$ (molecule CO) - $E_{tot}$ (SWCNTs)

$\Delta E_{ad}$ (Table 1) are calculated using:

$$E_{ad} = E_{ad}$$

where, $E_{ad}$ (SWCNTs), $E_{ad}$ (CO) and $E_{ad}$ (SWCNTs+CO) are the energies of the optimized tubes, which are adsorption systems, respectively. By this explanation, $E_{ad}$<0 corresponds to exothermic adsorption which leads to local minima stable for adsorption of gas molecules on the surface of nanotube. $E_{ad}$ (C-C) = 1.500 Aº, (C-C) = 1.519 Aº, (C-C) = 1.425 Aº and (C-C) = 1.488 Aº to CO-SWCNT-A1 (5, 0) nanotube has two different C-C bonds (C-C) = 1.500 Aº and (C-C) = 1.519 Aº increased to CO-SWCNT-A2 (5, 0) nanotube has four different C-C bonds (C-C) = 1.586 Aº, (C-C) = 1.496 Aº, (C-C) = 1.488 Aº and (C-C) = 1.488 Aº thus suggests two distinct adsorption sites. Armchair (4, 4) and zigzag (5, 0) tubes have different C-C bonds thus offers two distinct adsorption sites (Table 1) before and after the doping of CO atoms, the bond length of in SWCNT (4, 4) from (C-C) = 1.424 Aº and (C-C) = 1.419 Aº (C-C) = 1.438 Aº, (C-C) = 1.405 Aº and (C-C) = 1.437 Aº increased to 1.481 Aº in the SWCNT-A1 (4, 4) and bond length of in SWCNT-A4 (4, 4) increased to from (C-C) = 1.480 Aº, (C-C) = 1.480 Aº and (C-C) = 1.482 Aº. Density functional calculations of SWCNTs, efficient process of charge transfer between the CO molecule and the nanotube is found to substantially reduce the susceptibility of the π-electrons of the nano-tube to modification by CO while maintaining stable doping. A diagrammatic view of this form is showed in Fig. 1 and 2 SWCNTs and CO-SWCNTs-A1&2. Such a structure has also been observed for other SWCNTs (Soreasco et al., 2001; Ghasemi et al., 2010). For the molecular CO-SWCNT systems, CO seemed to place parallel to the outer surface of the tube. Geometry calculations of distortion caused by the carbon monoxide molecule on the (C1-C2) bond of zig-zag (5, 0) and armchair (4, 4) SWCNTs are changed partly. Two different types of adsorbed CO molecules were recognized (Fig. 1 and 2. SWCNTs (5, 0) and (4, 4), CO-SWCNT-A1, CO-SWCNT-A2 model (5, 0) and (4, 4). The calculated adsorption energies were predicted to be -3.126
and -4.165 eV for CO-SWCNTs-A1&2(5, 0) and -2.415 eV for CO-SWCNTs-A1&2(4, 4), respectively. The length of nanotube have selected with regard to the length of unit cell of nanotube. Such adsorptions of CO molecule are known as cycloaddition which is very similar to those found for larger diameter tubes (Walch, 2003; Krsic et al., 2002). The geometry of (5, 0) and (4, 4) tubes are considerably modified when such oxidation occurs and physisorbed product is formed. The electron can't enter into CO 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 CO species were identified (Fig. 1 and Table 1). Also, the dipole moments were calculated by Gaussian software and have shown in Table 1. Obtained values demonstrate that as the dipole moment increases, the absolute value of bond energy increases too. We can explain this reality as following: the big dipole moment relies to the large distance between electron clouds, then, as the distance becomes larger the absolute value of bond energy will become higher. By comparing the obtained results with Jordan's one (Collins et al., 2000). It is well known that the tendency for sp²-sp³ rehybridization upon CO adsorption is strong for thin nanotubes, because highly bent sp³ bonding of thin nanotubes is favored for the transition to sp³ bonding. According to adsorption energy and dipole moment parameters in Table 1, CO-SWCNT (5, 0) molecule shows the highest adsorption rate. This is a general reason for the binding in the performed studies, which shows that CO molecules energy values of adsorption on zig-zag (5, 0) and armchair (4, 4) SWCNTs models with determined diameter and length have about twice differences in grandeur.

The CO NQR parameters: Semiconducting SWCNTs are ballistic conductors with two and one spin degenerate conducting channel(s) (Kang et al., 2005; Yeung et al., 2010). The channels belong to the first π and π*-band of the delocalized π-electron system. The C-13 NQR parameters (C₀ and π) in the geometrically optimized SWCNTs models zig-zag (5, 0) and armchair (4, 4) were estimated by EFG tensors calculations at the B3LYP level of the DFT method and the 6-311G* standard basis set. Table 2 shows the calculated NQR and EFG tensors for SWCNTs π parameter of CO adsorption on the surface of zig-zag (5, 0) and armchair (4, 4) SWCNTs surface which has a remarkable effect on EFG tensors. A glimpse to π 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 B3LYP/6-311G* calculations indicate that all three principal components of the EFG tensor (q_0) and associated asymmetry parameter are affected due to adsorption of CO molecule. For the (CO-SWCNTs) systems, the EFG tensors of SWCNTs (4, 4) and SWCNTs (5, 0) are more significantly affected compared to CO-SWCNTs (4, 4) -A1&2 and CO-SWCNTs (5, 0) -A1&2, respectively. As previously mentioned, CO molecule adsorption at the CO-SWCNTs (5, 0) -A1 leads to the C-O bond cleavage and CO molecule adsorption at the CO-SWCNTs (5, 0) -A2 breaks C-O bond. CO adsorptions produce more EFG change at CO-SWCNT (5, 0) -A₂ which can be attributed to their hybridization effect (from sp² to sp³). The principle components of EFG tensor change significantly after CO adsorption at C₁ and C₂ atoms in CO-SWCNTs (5, 0) -A₁&₂.

DISCUSSION AND RECOMMENDATIONS

In summary, we studied the influence of substitutional CO on the single-walled carbon nanotubes conformation and a quantum-chemical calculation was performed. We found that the electronic properties of SWCNTs are sensitive to the adsorptions of carbon monoxide gas on the surface. DFT theory and hybrid functional B3LYP are applied to study NQR of CO, the GIAO calculation and the electronic structure properties of (4, 4) and (5, 0) SWCNTs. We calculated Carbon-13 EFG tensors in the various structures of single walled carbon nano tube optimized isolated gas-phase, the target molecule in CO-SWCNTs. The calculated results have different effects on the EFG tensor at 13-Carbon nuclei. Theoretical calculations are performed to characterize the behavior of CO molecule adsorption on external surface and adsorption on the surface of armchair (4, 4) and zigzag (5, 0) SWCNTs. Results show that as the diameter of armchair and zigzag tubes increases, the binding energy of CO molecule increases. The equilibrium CO-SWCNTs (4, 4) and (5, 0) on the surface distance exhibits considerable sensitivity to the type of tube. Adsorptions are also dependent upon the nanotube family and radius. Due to the adsorption, NQR parameters of CO molecule are also altered.

REFERENCES


