

A DFT Computation for Comparison of NQR of O₂, N₂ and CO over the Surface of Single-Walled Carbon Nanotubes

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Abstract: In this study we assumed Single-Walled Carbon Nano Tubes (SWCNTs) as ideal candidates for various applications of gas sensors due to their amazing physical adsorption properties. The adsorption behavior of selected nitrogen, oxygen and CO molecules on the surface of the Single-Walled Carbon Nano Tubes (SWCNTs) was studied by the Density Functional Theory (DFT) (B3LYP/6-311G*) using the Gaussian 98 software. We studied the Nuclear Quadrupole Resonance (NQR) of the armchair (4, 4) SWCNTs with the optimal diameter of 5.6 Å and the length of 9.8 Å. For the first time, DFT calculations were performed to calculate oxygen and nitrogen the interaction of quadrupole moment with Electric Field Gradient (EFG) in NQR in the representative considered model of the (N₂-CNTs), (O₂-CNTs) and (CO-CNTs). The evaluated NQR parameters reveal that the EFG tensors of Oxygen-17, Nitrogen-14 and Carbon-13 are influenced and show particular trends from gas molecules in the SWCNTs due to the contribution of N-N, O-O and C-O gas molecules of SWCNTs.

Keywords: DFT, electric field gradient, Gaussian 98, NQR, N₂-CNT, O₂-CNTs, CO-CNTs, SWCNTs

INTRODUCTION

Iijima was the first who has discovered carbon nanotubes which were produced by graphite and reported this (Ijima, 1993) ushered in a new and very amazing research field in compacting gases by physisorption methods. Electrical resistance changes considerable by adsorption of certain gas molecules such as O₂, N₂, NH₃ and H₂ (Chang *et al.*, 2001). Figure 1 depicts a C₇₂H₁₆ tube modeling an armchair (4, 4) SWCNT 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 charge transfer between gases and tube, even at low concentrations, gas adsorption can change the conductivity of SWCNTs. Electronic properties of SWCNTs have been studied in a number of theoretical works (Houten *et al.*, 1992; Aijki *et al.*, 1993; Wildoer *et al.*, 1998) and optimized forms of nanotube can be designed by a precise positioning of various gases 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 (Hertel *et al.*, 1998; Mintmire, 1992; Hamada, 1992; Saito *et al.*, 1992; Rao *et al.*, 1997; Wildoer, 1998; Kataura *et al.*, 1999). According to the electron-transmission mechanism on the surface of SWCNTs, the detected gas can be classified into reducing and oxidizing gaseous species. The electrical resistance of SWCNTs was found to increase when exposed to reducing gaseous species like N₂ (Zhao *et al.*, 2004), whereas being exposed to oxidizing ones

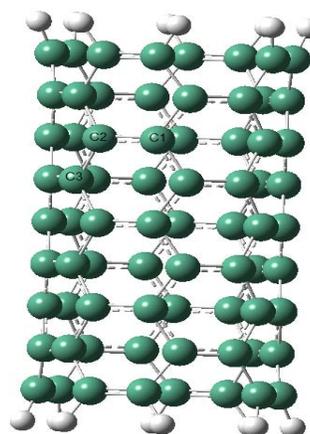


Fig. 1: CNTs (4, 4)

like O₂ decreased (Semin *et al.*, 1975). A new SWCNT gas sensor would be fulfilled by utilizing such electrical characteristics. In this study, N₂, O₂ and CO adsorption mechanism on carbon nanotubes was investigated by the surface Single-Walled Carbon Nano Tube (SWCNT) gas sensor. The adsorption of N₂, O₂ and CO at the open ended SWCNT has been investigated. It was found that N₂, O₂ and CO can be adsorbed at the surface site of armchair SWCNT that makes the N-N, O-O and C-O bonds active (Fig. 2). This can be attributed to the decisive effect of the local end carbon atoms arrangement of the open-ended SWCNT surface.

In addition, comparison of the adsorption amount on SWCNTs forcefully increases this viewpoint that present theoretical study on open-ended SWCNTs shows larger adsorption capacity. In this study, a

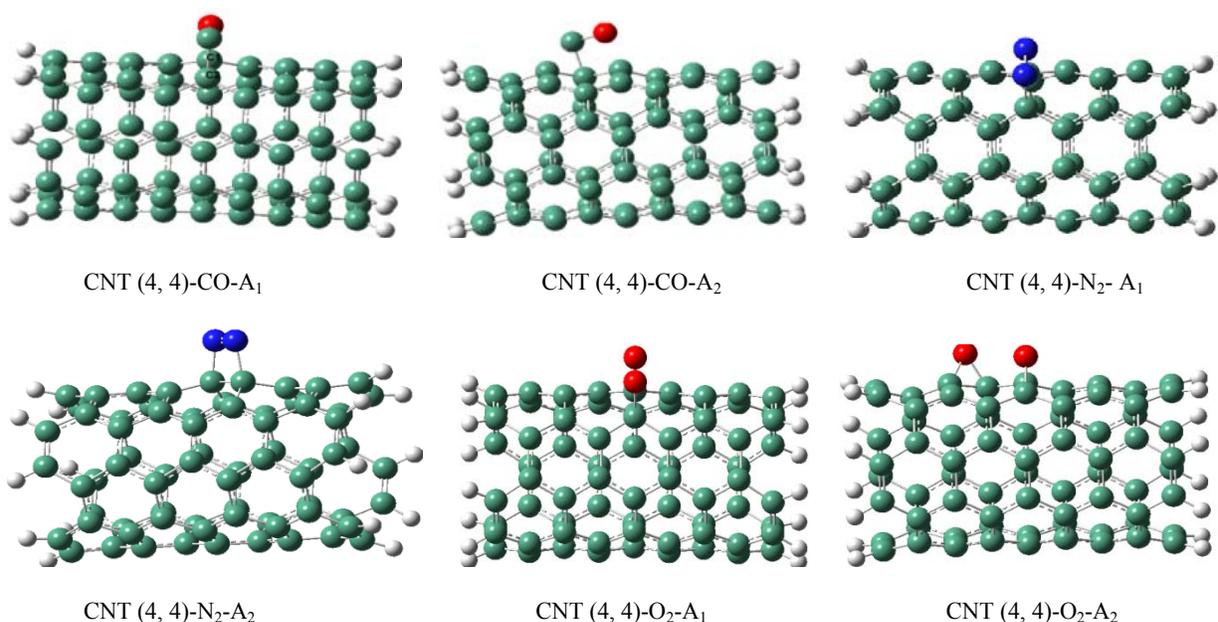


Fig. 2: (A₁) and (A₂) adsorption configurations of an oxygen, nitrogen and carbon monoxide molecule

computational study of the adsorption of N₂, O₂ and CO on the surface of the open-ended SWCNT is reported (Fig. 2). The esoteric adsorption and the binding energy were compared with adsorption on surface SWCNT. Nuclear experimental techniques such as Nuclear Quadrupolar Resonance (NQR) (Semin *et al.*, 1975) 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 $> 1/2$ is put in an Electric Field Gradient (EFG) (Kessel *et al.*, 1999; Khitrin *et al.*, 2001), 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. There are two naturally occurring isotopes for nitrogen-14 with natural abundance of 99.635% and nuclear spin $I = 1$ and N-15 with natural abundance of 0.365% and $I = 1/2$. Despite its rich natural plenty fullness, present N-14 applied an Electric Quadrupole moment (NQR) in our study. Dependence of these parameters on length and diameter of CNTs are also considered. The NQR measurable parameter is asymmetry parameter (η_Q) which is also reproduced by quantum chemical calculations of the Electric Field Gradient (EFG) tensors.

Nuclei with spin angular momentum $I > 1/2$ have the nuclear electric quadrupole moment, which interacts with the Electric Field Gradient (EFG) tensor originated at the site of quadrupole nuclei. For O-17, N-14 and C-13 spin angular momentums are $\frac{5}{2}$, $\frac{3}{2}$ and $\frac{1}{2}$, respectively. Therefore O-17 and N-14 are very sensitive to the electronic density at the sites of nuclei and feel changes by any disturbance.

The aim of this study is investigating, A DFT computation for Comparison of NQR of O₂, N₂ and CO over the Surface of Single-Walled Carbon Nano tubes as gas sensors and optimizing absorption rates by using DFT calculations.

MATERIALS AND METHODS

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

In this study O₂, N₂ and CO molecules adsorption behaviors on the end and surface of single-walled nanotube is taken in to consideration (Fig. 2). A (4, 4) CNT containing 72 carbon atoms with length of 9.8 Å and a diameter of 5.6 Å is selected for this purpose. Saturating carbon dangling bonds with 16 hydrogen atoms is necessary because there is no periodic boundary condition 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 Gaussian 98 suite of programs at all-electron level (Frisch *et al.*, 1998). It has been established that DFT is able to accurately treat such systems due to incorporation of the exchange-correlation effects (Barone *et al.*, 2004). In quadrupolar spin system, the Electric Field Gradient (EFG) tensor at nitrogen-14 and oxygen-17 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 (Osokin *et al.*, 1997; Osokin *et al.*, 1992; Furman *et al.*, 1994; Hill *et al.*, 1997; Abragam 1961; Frey *et al.*, 2005).

Geometry optimizations and EFG calculations were performed using 6-311G* basis set with B3LYP functional (Kang 2006; Hou *et al.*, 2004). The interaction between nuclear electric quadrupole moment and EFG at quadrupole nucleus is described with Hamiltonian (Hil *et al.*, 1997):

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

where,

Q = The nuclear electric quadrupole moment is the nuclear spin

q_{zz} = The largest component of EFG tensor

The principal components of the EFG tensor, q_{ii} , are computed in atomic unit ($1au = 9.717365 \times 10^{21} Vm^{-2}$, with $|q_{xx}|, |q_{yy}|, |q_{zz}|$ and $q_{xx} + q_{yy} + q_{zz} = 0$. These diagonal elements are related by a symmetry parameter $\eta_Q = |(q_{yy} - q_{xx})/q_{zz}|$ and $0 \leq \eta_Q \leq 1$, that measures the deviation of EFG tensor from axial symmetry (Frey *et al.*, 2005). Cluster model is proved to be valid for nanotubes (Kang, 2006; Hou *et al.*, 2004).

RESULTS AND DISCUSSION

Geometries, binding energies and NQR (4, 4) SWCNT interacted with O₂, N₂ and CO molecule species have studied in this study. The calculated geometry parameters and binding energies, dipole momentum and EFG tensors have shown in Table 1 and 2.

In the following sections, molecular geometries and binding energies, E_{ad} EFG tensors and the data obtained from O₂, N₂ and CO molecules adsorptions are discussed, separately.

Molecular geometries and adsorption energies: In this study, the use of the electronic properties of nano tubes 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 O₂, N₂ and CO molecules adsorbed on (4, 4) SWCNT are schematically displayed in Fig. 1. 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 B3LYP/6-311G* level. For nitrogen, oxygen and CO molecules we have considered distinct adsorption sites, marked as CNT, CNT-O₂, CNT-N₂ and CNT-CO adsorption energies, ΔE_{ad} , (Table 1) are calculated using:

$$E_{ad} = E_{tot}(mo1.O_2 + CNT_S) - E_{tot}(CNT_S) - E_{tot}(mo1.O_2) \quad (1)$$

$$E_{ad} = E_{tot}(mo1.N_2 + CNT_S) - E_{tot}(CNT_S) - E_{tot}(mo1.N_2) \quad (2)$$

$$E_{ad} = E_{tot}(mo1.CO + CNT_S) - E_{tot}(CNT_S) - E_{tot}(mo1.CO) \quad (3)$$

where, E_{tot} (CNT), E_{tot} (O₂), E_{tot} (CNT + O₂), E_{tot} (N₂), E_{tot} (CNT + N₂), E_{tot} (CO) and E_{tot} (CNT + 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. Armchair (4, 4) nanotube has two different C-C bonds ((C₁ - C₂) = 1.405 Å and (C₂ - C₃) = 1.438 Å) thus suggests two distinct adsorption sites. A diagrammatic view of this form is showed in Fig. 1 CNT, N₂-CNT-A_{1,2}, O₂-CNT-A_{1,2} and CO-CNT-A_{1,2}. Such a structure has also been observed for other SWCNTs (Duer, 2002; Walch, 2003). For the molecular O₂-CNTs, N₂-CNTs and CO-CNTs systems, O₂, N₂ and CO seemed to place parallel to the outer surface of the tube. Geometry calculations of distortion caused by the oxygen and nitrogen and carbon monoxide molecules on the (C₁ - C₂) bond are changed partially. Placing the oxygen molecule in CNT - A₁, CNT - A₂ sites doesn't change the bridge distance of

Table 1: Calculated adsorption energies E_{ad} (eV), bond energies (\AA) and dipole momentum (debye) of the O_2 and N_2 and CO adsorbed on surface armchair (n, n), n = 4 nanotube

Model (configuration)	R_{C-C} (\AA)	R_{C-X} (\AA) (X = O, N, C)	R_{O-O} (\AA)	R_{C-O} (\AA)	R_{N-N} (\AA)	ΔE_{ad}^a (eV)	Dipole momentum (debye)
CNT (4, 4)	(C-C) ₁ = 1.424						0.43258
	(C-C) ₂ = 1.419						
	(C-C) ₃ = 1.438	-	-	-	-	-	
	(C-C) ₄ = 1.405						
	(C-C) ₅ = 1.437						
	(C-C) ₆ = 1.437						
CNTs-N ₂ -A ₁	(C-C) ₁ = 1.481						3.54480
	(C-C) ₂ = 1.481	(C-N) ₁ = 1.515	-	-	1.250	-14.531	
	(C-C) ₃ = 1.481	(C-N) ₂ = 1.515					
	(C-C) ₄ = 1.481						
CNTs-N ₂ -A ₂	(C-C) ₁ = 1.504						1.61720
	(C-C) ₂ = 1.516	(C-N) ₁ = 1.521	-	-	1.255	-4.081	
	(C-C) ₃ = 1.517	(C-N) ₂ = 1.525					
	(C-C) ₄ = 1.500						
CNTs-O ₂ -A ₁	(C-C) ₁ = 1.487						3.17470
	(C-C) ₂ = 1.487	(C-O) ₁ = 1.436					
	(C-C) ₃ = 1.487	(C-O) ₂ = 1.436	1.485	-	-	-1.197	
	(C-C) ₄ = 1.487						
CNTs-O ₂ -A ₂	(C-C) ₁ = 1.500	(C-O) ₁ = 1.487	2.660	-	-	-2.112	3.44750
	(C-C) ₂ = 1.507						
	(C-C) ₃ = 1.563						
	(C-C) ₄ = 1.459						
CNTs-CO-A ₁	(C-C) ₁ = 1.481						3.47640
	(C-C) ₂ = 1.481	(C-C) ₁ = 1.584					
	(C-C) ₃ = 1.481	(C-O) ₂ = 1.501	-	1.315	-	-2.415	
	(C-C) ₄ = 1.481						
CNTs-CO-A ₂	(C-C) ₁ = 1.480						2.68880
	(C-C) ₂ = 1.480	(C-C) ₁ = 1.477					
	(C-C) ₃ = 1.461	(C-O) ₂ = 1.562	-	1.374	-	-0.135	
	(C-C) ₄ = 1.582						

a: These values of ΔE_{ad} are calculated for entire complex; The related values adsorptions on nanotube are indicated inside parenthesis

Table 2: (A₁) and (A₂) adsorption configurations of an oxygen, nitrogen and carbon monoxide molecule

Model (configuration)	Atoms	q_{xx}	q_{yy}	q_{zz}	η_Q
CNT (4, 4)	C ₁	0.095540	0.137945	-0.233485	0.18
	C ₂	0.115713	0.118493	-0.234206	0.01
	C ₃	0.115853	0.118548	-0.234401	0.01
CNTs-O ₂ -A ₁	C ₁	0.114913	0.217092	-0.332005	0.30
	C ₂	0.115191	0.217377	-0.332568	0.30
CNTs-O ₂ -A ₂	C ₁	0.056708	0.235503	-0.292211	0.61
	C ₂	0.134179	0.172331	-0.306510	0.12
CNTs-CO-A ₁	C ₁	0.131771	0.279074	-0.410845	0.36
	C ₂	0.026205	0.139259	-0.165464	0.68
CNTs-CO-A ₂	C ₁	0.002444	0.226654	-0.229098	0.98
	C ₂	0.201458	0.223643	-0.425101	0.05
CNTs-N ₂ -A ₁	C ₁	0.062574	0.226654	-0.229098	0.36
	C ₂	0.007669	0.136100	-0.143769	0.89
CNTs-N ₂ -A ₂	C ₁	0.046359	0.090398	-0.196494	0.32
	C ₂	0.037639	0.158783	-0.196422	0.62

(C₂ - C₃) considerably. Two different types of adsorbed O₂, N₂ and CO molecules were recognized (Fig. 1) CNT, N₂-CNT-A₁, N₂, -CNT-A₂, O₂-CNT-A₁, O₂, -CNT-A₂, CO-CNT-A₁ and CO-CNT-A₂). The calculated adsorption energies were predicted to be (-14.531) eV and (-4.081) eV for N₂, (-1.197) eV and (-2.112) eV for O₂ and (-2.415) eV and (-0.135) eV for CO, respectively. These values of ΔE_{ad} are calculated for entire complex, the related values adsorption on

nanotube is inside parenthesis (Zhao *et al.*, 2004; Sorescu *et al.*, 2001; Fereydoun *et al.*, 2012). The length of nanotube have selected with regard to the length of unit cell of nanotube. Such adsorptions of O₂ molecule are known as cycloaddition which is very similar to those found for larger diameter tubes (Duer, 2002; Zhang *et al.*, 2004). Nitrogen molecules adsorbed with a comparatively lower rate and almost never formed a chemical binding with the carbon nanotube.

The geometry of (4, 4) tube is considerably modified when such oxidation occurs and physisorbed product is formed. The electron configuration of O₂ is KK (σ_{2s}) (σ_{2s}^*)² (σ_{2pz})² (π_{2px})² (π_{2py})² (π_{2px}^*)¹ (π_{2py}^*)¹. The electron configuration of N₂ is KK (σ_{2s})² (σ_{2s}^*)² (π_{2px})² (π_{2py})² (π_{2pz})² and the transferred electron is placed in the half-filled anti-bonding orbital of O₂, thus weaken the O-O bond. The electron can't enter into N₂ 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 O₂, N₂ and 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 becomes bigger, the absolute value of bond energy increases. We can explain this reality as following: the big dipole moment relies to the large distance between electron clouds, then, as the distance becomes bigger the absolute value of bond energy will become higher. By comparing the obtained results with Jordan's one (Zhang *et al.*, 2004), It is well known that the tendency for sp²-sp³ rehybridization upon O₂ adsorption is strong for thin nanotubes, because highly bent sp² bonding of thin nanotubes is favored for the transition to sp³ bonding. According to adsorption energy and dipole moment parameters in Table 1, O₂ molecule shows the highest adsorption rate.

This is a general reason for the binding performed studies, which shows that nitrogen molecules energy values of adsorption on armchair model with determined diameter and length have about twice differences in grandeur. Based on performed calculations, we approach that the adsorption accomplishes over open ends of nanotubes has more advantages. In addition, all these energies are positive which demonstrate the reaction is improbable. Based on these results, we can conclude that the physical adsorption over the surface area of nanotube occurs very hard and so this is an appropriate case.

N₂, O₂ and CO NQR parameters: Semiconducting SWCNTs are ballistic conductors with two and one spin degenerate conducting channel(s) (Bachtold *et al.*, 2000; Fereydoun *et al.*, 2012). The channels belong to the first π and π^* -band of the delocalized π -electron system.

The N-14, O-17, C-13 NQR parameters η_Q in the geometrically optimized SWCNTs model 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 show the calculated NQR and EFG tensors for SWCNTs. η_Q parameter of O₂, N₂ and CO adsorption on CNTs surfaces has a remarkable effect on EFG tensors. A glimpse to η_Q values presented in Table 2 reveals that the changes in EFG tensor of N-14 and O-17, for molecular adsorptions are quite significant which is in compatible agreement with calculations.

The B3LYP/6-311G* calculations indicate that all three principal components of the EFG tensor (q_{ii}) and associated asymmetry parameter are affected due to adsorption of oxygen, nitrogen and CO molecules. For the (O₂-CNT) and (N₂-CNT) systems, the EFG tensors of CNT (4, 4) -O₂ (A₂) and CNT (4, 4) -N₂ (A₁) are more significantly affected compared to CNT (4, 4) -O₂ (A₁) and CNT (4, 4) -N₂ (A₂), respectively. As previously mentioned, oxygen molecules adsorption at the CNT (4, 4) -O₂ (A₂) leads to the O₁-O₂ bond cleavage and N₂ molecules adsorption at the CNT (4, 4) -N₂ (A₁) breaks C₁-C₂ bond. Therefore, a noticeable change in the field gradient, especially at the C₁ and C₂ is detected. O₂ adsorptions produce more EFG change at CNT (4, 4) -O₂ (A₂) which can be attributed to their hybridization effect (from sp² to sp³). This is consistent with the bond angle distortion from 120 to 109, induced by oxygen and nitrogen adsorption. The principle components of EFG tensor change significantly after CO adsorption at C₁ and C₂ atoms in CNT (4, 4) -CO (A₂).

CONCLUSION

In summary, our theoretical studies show that CNTs can be used as mechanical sensors. We found the electronic properties of CNTs are sensitive to the adsorptions of oxygen, nitrogen and carbon monoxide gases on the surface. According to DFT theory and hybrid functional B3LYP are applied to study NQR of N₂, O₂ and CO calculations the electronic structure properties of (4, 4) SWCNT. We calculated Oxygen-17, Nitrogen-14 and Carbon-13 EFG tensors in the various structures of thymine an optimized isolated gas-phase, gas monomer and the target molecule in X-CNTs (X = O₂, N₂ and CO). The calculated results have different effects on the EFG tensor at Oxygen-17, Nitrogen-14 and Carbon-13 nuclei. Theoretical calculations are performed to characterize the behavior of N₂ and O₂ molecules adsorption on external surface of armchair (4, 4), SWCNTs. Results show that as the diameter of armchair tubes increases, the binding energy of N₂ and O₂ molecules decreases. The equilibrium N₂-CNT and O₂-CNT on the surface distance exhibits considerable sensitivity to the type of tube.

The calculated N₂-CNT, O₂-CNT and CO-CNT bond lengths are (1.515-1.525 Å), (1.408-1.465 Å) and (1.477-1.584 Å) on the surface of armchair (4, 4), respectively. Adsorptions are also dependent upon the nanotube family and radius. Moreover, η_Q (Nitrogen-14 and Oxygen-17) of armchair nanotube increases as the diameter of tube decreases while in our study, the diameter of tube increased. The obtained η_Q parameters for Nitrogen-14 (A₁, A₂) and Oxygen-17 (A₁, A₂) are (4.148, 4.017) MHz and (4.466, 1.833) MHz, respectively. Due to the adsorption, NQR parameters of nitrogen and oxygen molecular are also altered.

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