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Optimization of adsorption of oxygen gas on Carbon nanotubes surface

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ABSTRACT

Carbon nanotubes have important applications in gas adsorption. Therefore the study of their properties for this application is very important. In this study the Density Functional Theory (DFT) and Hartree-Fock (HF) methods were used to investigate the adsorption of oxygen molecules on the surface of (5, 0) and (4, 4) carbon nanotubes. The electronic structure, and dipole moment of both oxygen and carbon nuclei are thoroughly studied. The computational results indicate that rich adsorption patterns may result from the interaction of oxygen with the carbon nano-tubes.; sometimes C-O bounds are formed via breaking C-C bounds and sometimes a carbon atom in the nano-tube is replaced with a oxygen atom. Sometimes oxygen atoms are attracted to a C-C bound. In summary, the optimized adsorption rates are calculated. Gaussian 98 software has been used to carry out quantum chemistry calculations.

Keywords: Carbon nano-tubes, Oxygen gas, Adsorption, DFT, HF.

INTRODUCTION

The discovery of carbon nanotubes by Sumiu Iijima [1], led him to an extensive domain of study and investigation for determination the properties and applications of carbon nanotubes [2, 3]. The fields of applications of carbon nanotubes are very wide domain. Due to their diameter and chirality, the carbon nanotubes can represent the properties of metallic and semiconductor materials which is the target of their synthesis for special purposes [6]. Carbon nanotube sensors can detect many much gases; for example O_2 [7], NH_3 [8, 9], NO_2 [10, 11] and SO_2 [12] and the change in electrical conductivity occurs after adsorption of molecules. These sensors have fast response time and high sensitivity to special gas molecules which is very favorable for certain applications [13].

The changes in electrical resistance, by adsorption of certain gas molecules are considerable, for example by adsorption of O_2, N_2, NH_3 and H_2 [14].

Small size and electrical characteristics of these materials make them incomparable for sensor utilities and pharmacy devices. Because of their biological agreements and high consistency, nanotubes have introduced in biomedicine and pharmacology [6 and 14].

Oxygen gas adsorption on the surface of semiconductor nanotubes, have a vast effect on its electrical characteristics, but haven't any effect on electrical characteristics of conductor nanotubes [15]. All armchair nanotubes (4, 4) are semiconductors, the zigzag nanotubes (5, 0), also, are semiconductors [16].

Impurity addition to semiconductor nanotubes with zigzag form (5, 0), causes energy gap decrease and tend to quasi-metallic state which results in increase of its conductivity.

The purpose of our approach is studying in adsorption of oxygen molecule on single-walled nanotube surface with both armchair (4, 4) and zigzag (5, 0) forms by Hartree-Fock (HF) and density functional theory (DFT) method. This study consists of: *a*) configuration of adsorption, *b*) determination of binding energy located on carbon nucleuses of nanotube which involve in chemical binding with oxygen molecules, and *c*) determination of bond length after oxygen molecule adsorption on nanotube which will optimize by calculation methods.

As we observe on figures (1 and 2) the total number of carbon atoms in a single-walled nanotube is many much, which causes long calculations even for one small wire of nanotube. For resolve this problem we have used based method and standard basis set and adequate calculations.

MATERIALS AND METHODS

This study was performed in Payame Noor University, Sari Center, Iran, as a research project over carbon nanotubes adsorption properly in 2009 and 2010. The calculations are performed by a GAUSSIAN 98 package program [17]. DFT and HF methods were used for studies.

RESULTS AND DISCUSSION

In this approach we use both DFT and HF methods for calculation over armchair (4, 4) and zigzag (5, 0) models. The calculations are performed by hybrid functional B3LYP density functional theory (DFT) based method and 6-311G* standard basis set by GAUSSIAN 98 package of program [17]. The choice of adequate model leads us to reasonable results which are comparable with experimental results. Minimum length of nanotube in SWCNTs model is unit cell's representative which characterizes the comportment of adsorption of this nanotube similar to a real nanotube. It is approved that, if the length of selected model is $\sqrt{3/2}$ and equal to unit cell, the model is convenient for calculation. Determination of the length of this unit cell with respect to its hexagonal rings is simple [18].

Adsorption energies

Primary structures of nanotubes have optimized in length and diameter by nanotube modeler software. The calculation was performed for a zigzag (5, 0) nano-tube of 7.10 Å length and 2.26 Å diameter and for an armchair (4, 4) model of nanotube of 4.18Å of length and 5.67 Å of diameter. The length of nanotube have selected with respect to the length of unit cell of nanotube. Then, after selection this length for nanotube, the carbon atoms situated in both ends of this length will have negative charge because of carbon bonds breaking. For saturation of carbon bond in two ends of nano wire and create a model similar to a real wire of nanotube, hydrogen atoms were added to the end links of nanotube.

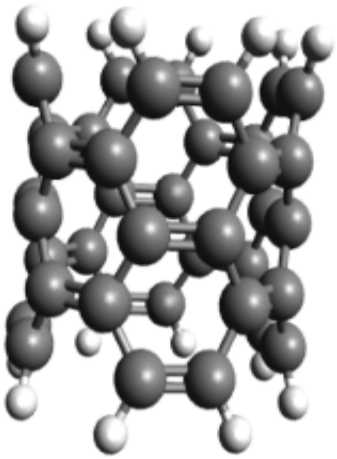

Figure 1. The structure of carbon nanotube, zigzag.

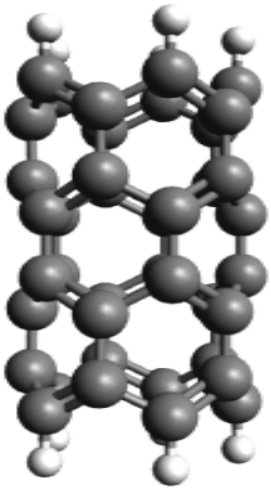

Figure 2. The structure of carbon nanotube, armchair.

In our zigzag (5, 0) nanotube, 10 hydrogen atoms were added to basic structure of nanotube (fig. 1) and 16 hydrogen atoms were added to the end links of nanotube wire, in armchair (4, 4) model of nanotube, for obtaining a model so similar to a real one (fig. 2). Optimization was performed by atoms were added to the end links of nanotube wire and by GAUSSIAN 98 software, calculation method of B3LYP and 6-311G* basis set.

After optimization the basic structure of nanotube, adsorption energy of oxygen molecule for both zigzag and armchair cases by DFT and HF methods was determined separately by studying the structures and the structure variations during oxygen adsorption (table 1, the units are in hartry and kcal mol^{-1}). The best proposed method for this study is DFT which gives the values approximately approach to real ones. The studies on structural variations during oxygen adsorption and comparing with studies performed on adsorption of small molecules and atoms on surface areas of graphite and nanotubes and present study was approved that the chemical adsorption over C-C bond is most probable C-C bond [19, 20]. With respect to geometric structure of armchair nanotubes (4, 4) there are two different sites for adsorption of oxygen molecule over external surface of nanotube [21]. Model 3 is the best model for discussion and is much similar to real model (table 1). The same study was performed for adsorption of oxygen molecule over external surface of zigzag form of nanotube (5, 0). The obtained results show that model 3 is favorable for this case (table 1).

Bond length

After oxygen molecule adsorption on external surface of nanotube the values of bond length has been shown in table2. By comparing the obtained results with Jordan's one [23] which includes oxygen molecule adsorption over (8, 0) nanotube and by considering the values of David Mann et al [24] for the bond length of C-O using AIMD method, we can conclude that our results may be suitable.

By observing table 2 and figure(1, 2) we can conclude that increase in bond length of C-C after adsorption of oxygen molecule on external surface of nanotube, is due to this fact that oxygen is more electronegative than carbon. During formation of C-O bond, this property cause partial positive charge on both carbon atoms of C-C bond and hence create electrostatic repulsion between two carbon atoms which results in C-C bond length increasing.

Table 1. Comparison the surface adsorption energies* of molecular oxygen for two zigzag (5, 0) and armchair(4, 4) nano tubes model

Site	Model	Structure	Energy(Hartry)	Energy (Kcal/mol)	E_{ab} (ev)	Energy Difference for comparison (Kcal/mol)
1	CNT(5,0)-O_2,A1		-1680.3734599	-1054450.31	-1111.6171	0.0000
2	CNT(5,0)-O_2,A2		-1680.341431	-1054430.21	-1110.7455	20.09788
3	CNT(4,4)-O_2,A1		-1684.4576623	-1057013.16	-1112.2774	0.0000
4	CNT(4,4)-O_2,A2		-1684.3753394	-1056961.52	-110.0383	15.63308

**The surface adsorption energy was obtained with $E_{ad} = E_{tot}(molecule\ O_2 + CNT_S) - E_{tot}(CNT_S) - E_{tot}(molecule\ O_2)$ formula that E_{ad} is the adsorption energy and the negative adsorption energies appear that the reactions are exothermic and the best case of adsorption is third model.*

Also, the dipole moments were calculated by Gaussian software and have shown in table 2. Obtained values show that as the dipole moment is bigger, the absolute value of bond 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 bond energy will become higher.

Table2. Comparison the bond length of oxygen molecule adsorption for two zigzag (5, 0) and armchair(4, 4) nano tubes model and quantities of dipole moments.

Site	Model	Dipole moment (Debye)	R(C-C) (Å)	R(C-C) (Å)	R(C-O) (Å)	R(C-O) (Å)
1	CNT50-O2A1	2.5970	1.51	1.51	1.456	1.456
2	CNT50-O2A2	2.5764	1.50	1.49	1.474	1.498
3	CNT44-O2A1	7.2966	1.47	1.47	1.228	1.228
4	CNT44-O2A2	3.4863	1.51	1.52	1.468	1.473

CONCLUSION

In this work the structures of nitrogen molecule adsorption over single-walled nanotube armchair (4, 4) and zigzag (5, 0) models were studied by using density functional theory (DFT) and Hartree-Fock (HF) methods. It is found that interaction of oxygen molecule with surface of nanotube is an exothermic chemical reaction in which the amount of liberated energy varies with the site which adsorbs oxygen molecule.

Absorption of oxygen molecule on nanotube increases the length of carbon bond which was involved in adsorption. Comparison of bonds length and adsorption energies show that adsorption of oxygen molecule over surface of nanotube armchair (4, 4) model is stronger than zigzag (5, 0) model. Because of curvature of nanotube surface, interactions over its surface are more probable. Moreover, the oxidizing characteristic of oxygen molecule and transfer of its non-binding pairs of electrons to neighbor carbon atoms over carbon rings on nanotube surface, cause increase in its resistance and also increase in nanotube diameter.

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