Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 7 (4) 213-219: Winter 2011
(J. Phys. Theor. Chem. IAU Iran)
ISSN: 1735-2126

Ab initio Calculations SWNTs and Investigation of Interaction Atoms of Oxygen with that by Computational Calculations

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Received November 2010; Accepted December 2010

ABSTRACT

In this work, theoretical investigations on carbon nanotube with oxygen atom have been carried out by first-principles calculations and density functional theory and hartree fock theory in 3-21G and 6-31G basis sets. The interaction energy of the oxygen atom to a CNT is calculated. The effects of this substitutions have been investigated on the during transplantation (10,0) single-walled carbon nanotube with 120 atoms and the effect of method and basis sets have been investigated on the reaction energy. We observe the interaction energy increase with increasing oxygen atoms.

Keywords: Nanotube; Ab initio; Gaussian 98; Oxygen; Reaction energy

INTRODUCTION

After first discovery, due to their excellent physical, chemical and mechanical properties, carbon nanotubes (CNTs) [1] continue to be one of the hottest research areas more than 18 years.[2] Such considerable interest reflects the unique behavior of CNT, including their remarkable electrical, chemical, mechanical and structural properties. CNT can display metallic, semiconducting and superconducting electron transport, possess a hollow core suitable for storing guest molecules and have the largest elastic modulus of any known material [3]. In addition to their interesting physical properties, carbon nanotubes are structurally well defined in terms of chirality and tube diameter, making them a unique nanoscale environment in which chemical reactions may be carried out. These properties support CNTs to be the suitable element for transistors, quantum dots, hydrogen storage devices, chemical and electromechanical sensors, field emission, etc.[2]Compared to the gas phase, reaction energetics, mechanism, and dynamics could be significantly altered inside of carbon nanotubes because of their large electronic polarizabilities and because of the severely reduced reaction volume. The use of carbon nanotubes as nanoscale reaction vessels is an exciting possibility [4]. CNT is known to be an agglomerated material that will bundle together and entangle, causing many site defects in the composite [5]. Functionalization of the CNT is one of several ways utilized to improve the compatibility of CNT and the host material. The solubility of CNT in common solvents can be improved by the presence of functional groups on the surface of the CNT [6].

Theoretical studies of the electronic structure and dynamics of carbon nanotubes have been successful in the prediction of their electronic, thermodynamic, and mechanical, properties, as well as their reactivity with gas phase molecules, the effects of confinement on molecular adsorption, and the electronic stabilization and enhancement of encapsulated chemical reactions.

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Much of this success is the result of improved algorithms for semi-empirical and ab initio electronic structure calculations of materials systems and their combination with classical trajectory techniques for the accurate simulation of chemical reaction dynamics [7]. The power of these computational techniques, as a viable alternative to expensive or complicated laboratory experiments, provides the theoretician with a tool for exploring and predicting potential novel uses for nanotube-based materials. Many recent experimental and theoretical studies have explored the potential use of carbon nanotubes as molecular sensors [8-9], where a dopant atom or molecular adsorbate can substantially perturb the electrical conductivity of semiconducting single-walled carbon nanotubes (SWNTs). Kong and co-workers [8] carried out conductance measurements of semiconducting SWNTs exposed to diluted NO_2 and found a 1000-fold increase in conductivity subsequent to NO_2 exposure.

First-principles calculations using density functional theory (DFT) predicted the conductance enhancement to be the result of charge transfer from the nanotube to NO_2. In separate experiments they found the opposite effect for NH_3 exposure (i.e., decreased conductance!) which they attributed to the possible binding of NH_3 to preadsorbed oxygen species. It has been shown that the electronic properties of SWNTs are extremely sensitive to oxygen exposure [10]. Collins and co-workers found an increase in conductance of SWNTs exposed to oxygen at room temperature and that oxygen-saturated SWNT's have a higher conductance than SWNTs with less adsorbed oxygen. This trend has been attributed to an increase in the local density of states (LDOS) available for electron transport subsequent to oxygen adsorption. In a separate theoretical study [11], Rochefort and Avouris examined the effects of conductance on oxygen atom substitutionally doped SWNTs where doping was modeled by substituting a carbon atom with an oxygen atom. Using the metallic (6,6) armchair nanotube as their model, they found a 30% decrease in conductance of a single oxygen atom doped nanotube. Similar effects may also exist for SWNTs with oxygen atoms confined inside the nanotube wall [12].

THEORY

Gaussian

A Gaussian 98 molecular modeling software package performs ab initio quantum mechanical and semi-empirical molecular orbital calculations [13]. Gaussian 98 was used to design and predict the properties of molecular-based magnets. Gaussian 98 enables to calculate magnetic moments on atoms and hyperfine coupling constantin ESR spectra close to experimental data. Also, Gaussian 98 can optimize structures, calculate single point energy and predict the stability of a molecule [14]. The calculations are performed in the gas phase or solution. Gaussian 98 methods include HF, MP2, MP3, GVB, DFT, Molecular Mechanics,…

Hartree Fock

Ab initio is described of non-relativistic and time-independent of Schrödinger equation.

$H\Psi = E\Psi$

H denotes the Hamiltonian that is the potential and kinetic energy function, Ψ is wave function and E is energy of molecule. The accurate solution of this is often difficult or impossible in practice, except for H atom, In order to be able to solve Schrödinger's equation for any system larger than an atom with one electron, various approximations need to be made. Each of these approximations contributes its own inaccuracies to the final result, which must be accounted for in reporting results [15].

Hartree-Fock theory is fundamental for the electronic structure theory. It is based on the molecular orbital (MO) theory, which posits that each electron's motion can be described by a single - particle function (orbital) which does not depend explicitly on the instantaneous motions of the other electrons. The ubiquity of orbital concepts in chemistry is a testimony to the predictive power and intuitive appeal of Hartree-fock MO theory [16].

In applied molecule orbital for making wave function and propositional determinant isn't existed any limitation and Slater determinant is made in terms of spin of orbital, that is product spatial orbital to α or β spin functional. If different orbital are used, we have unrestricted Hartree-Fock method. HF calculations with identical spatial orbitals for electrons with spins up/down are called restricted Hartree-Fock method [17].

Density Functional Theory

The DFT method is a kind of ab initio quantum chemistry method for determining the electronic structure of molecules. For a given basis set expansion, it is comparable in accuracy to the MP2 method (better than Hartree-Fock, but less accurate than more extensive electron correlation methods such as MP4 or CCSD). However, for systems with large numbers of basis functions it more efficient than any other methods that include electron correlation effects [18].

METHODS

The method used in this work is quantum mechanics study. First we built a fragment of the (10,0) SWCNT of 80 carbon atoms with 40 hydrogen atoms, $C_{80}H_{40}$. We chose zigzag-type (n,n) nanotubes to study the interaction between nanotubes and Oxygen atoms. We made these molecules using Nanotube modeler software. For adding Oxygen, Hyperchem software was used. Nanotube (10,0), Oxygen atom and Oxygen-nanotube are optimized by HF, DFT(B3LYP) methods and 3-21G, 6-31G basis sets, separately. Optimization was performed by Gview and GAUSSIAN 98 softwares. After optimization the basic structure of nanotube, interaction energy of Oxygen atom by both DFT and HF methods was determined separately, by studying the structures and the structure variations during Oxygen adsorption. These calculations, also were carrying out with addition 1 to 10 Oxygen atoms to nanotube. For the Oxygen-nanotube system we also obtained bond length using HF and DFT (B3LYP) methods and 3-21G, 6-31G basis sets. These basic sets are standard and widely used, because for large system with high basis set, super computers must be used.

Then, we can calculate Oxygen interaction energy with single walled nanotube by following relation:

$$E_{int} = E_{tot\,(O\ atoms\ +CNTs)} - E_{tot\,(O\ atoms)} - E_{(CNTs)}$$

Fig. 1. Zigzag carbon nanotube (10-0).

Fig. 2. Zigzag carbon nanotube (10-0) with five oxygen atoms.

Fig. 3. Zigzag carbon nanotube (10-0) with ten oxygen atoms.

RESULTS AND DISCUSSION

Table 1 clearly show the reaction energy increases linearly as the number of oxygen atoms increase (See fig 4 to 7).

Another case which is important importance in this research, that is for any oxygen atom, reaction energy increase. The subject can depends on the change of charge density and charge current of nanotube. In this research the effect of methods and basis sets on amount of reaction energy are studied. In other words, reaction energy is calculated by using of HF and DFT (B3LYP) methods. Results show the amount of reaction energy which is calculated in DFT (B3LYP) method is more than the amount of reaction energy which is calculated in HF method and both of them increased.

As shown in Table 2, the changes in length of O-SWNT are much small.

Table 1. The HF and B3LYP optimized values of interaction energies obtained for oxygen atoms given in kcal/ mol

Nanotube	**Method and basis set**	$(\frac{kcal}{mol})$ **Reaction energy**
$C_{80}H_{40}$	HF 3-21 G	-
$C_{80}H_{40}O$	HF 3-21 G	82.298
$C_{80}H_{40}O_2$	HF 3-21 G	163.362
$C_{80}H_{40}O_3$	HF 3-21 G	244.731
$C_{80}H_{40}O_4$	HF 3-21 G	326.395
$C_{80}H_{40}O_5$	HF 3-21 G	406.778
$C_{80}H_{40}O_6$	HF 3-21 G	482.946
$C_{80}H_{40}O_7$	HF 3-21 G	558.184
$C_{80}H_{40}O_8$	HF 3-21 G	633.594
$C_{80}H_{40}O_9$	HF 3-21 G	709.115
$C_{80}H_{40}O_{10}$	HF 3-21 G	783.688
$C_{80}H_{40}$	B3LYP/3-21 G	-
$C_{80}H_{40}O$	B3LYP/3-21 G	129.031
$C_{80}H_{40}O_2$	B3LYP/3-21 G	256.903
$C_{80}H_{40}O_3$	B3LYP/3-21 G	385.208
$C_{80}H_{40}O_4$	B3LYP/3-21 G	513.739
$C_{80}H_{40}O_5$	B3LYP/3-21 G	641.075
$C_{80}H_{40}O_6$	B3LYP/3-21 G	764.777
$C_{80}H_{40}O_7$	B3LYP/3-21 G	887.539
$C_{80}H_{40}O_8$	B3LYP/3-21 G	1010.769
$C_{80}H_{40}O_9$	B3LYP/3-21 G	1133.859
$C_{80}H_{40}O_{10}$	B3LYP/3-21 G	1256.385
$C_{80}H_{40}$	HF 6-31 G	-
$C_{80}H_{40}O$	HF 6-31 G	75.825
$C_{80}H_{40}O_2$	HF 6-31 G	150.458
$C_{80}H_{40}O_3$	HF 6-31 G	225.326
$C_{80}H_{40}O_4$	HF 6-31 G	300.428
$C_{80}H_{40}O_5$	HF 6-31 G	374.300
$C_{80}H_{40}$	B3LYP/6-31 G	-
$C_{80}H_{40}O$	B3LYP/6-31 G	121.140
$C_{80}H_{40}O_2$	B3LYP/6-31 G	241.080
$C_{80}H_{40}O_3$	B3LYP/6-31 G	361.312
$C_{80}H_{40}O_4$	B3LYP/6-31 G	481.762
$C_{80}H_{40}O_5$	B3LYP/6-31 G	600.734

Table 2. The HF and B3LYP optimized values of bond length O - SWNT obtained for oxygen atoms given in Å

Nanotube	HF/6-31G	HF/3-21G	B3LYP/6-31G	B3LYP /3-21G
$C_{80}H_{40}O$	1.478	1.484	1.523	1.523
$C_{80}H_{40}O_2$	1.478	1.484	1.523	1.523
$C_{80}H_{40}O_3$	1.478	1.484	1.523	1.523
$C_{80}H_{40}O_4$	1.478	1.483	1.523	1.523
$C_{80}H_{40}O_5$	1.478	1.483	1.523	1.523
$C_{80}H_{40}O_6$	-	1.483	-	1.523
$C_{80}H_{40}O_7$	-	1.483	-	1.523
$C_{80}H_{40}O_8$	-	1.483	-	1.525
$C_{80}H_{40}O_9$	-	1.482	-	1.525
$C_{80}H_{40}O_{10}$	-	1.482	-	1.526

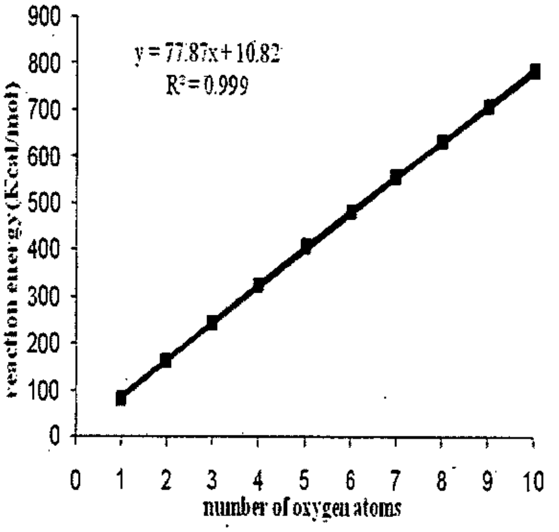

Fig. 4. Reaction energy curve for the adsorption of oxygen atoms with HF/3-21G.

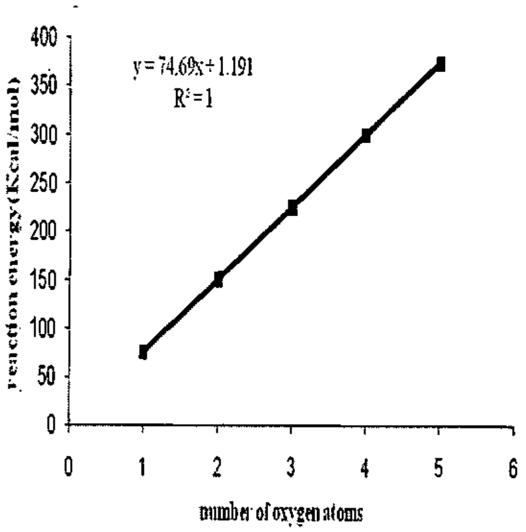

Fig. 6. Reaction energy curve for the adsorption of oxygen atoms with HF/6-31G.

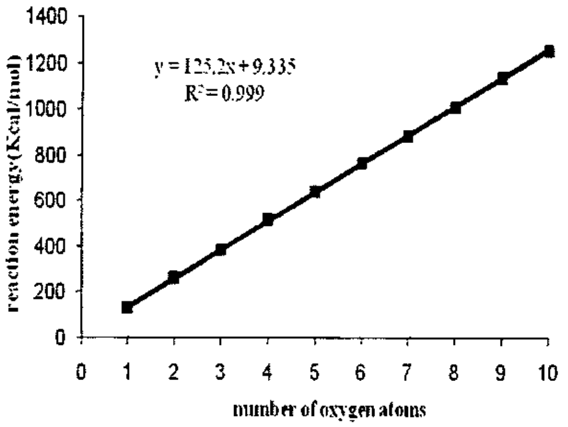

Fig. 5. Reaction energy curve for the adsorption of oxygen atoms with B3LYP/3-21G.

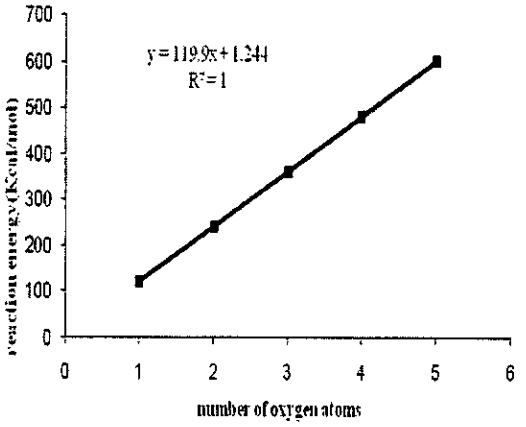

Fig. 7. Reaction energy curve for the adsorption of oxygen atoms with B3LYP/6-31G.

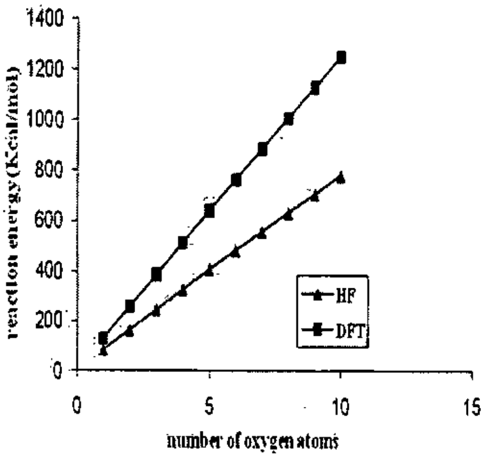

Fig. 8. The effect of HF/3-21G and B3LYP/3-21G on reaction energy of carbon nanotube(10-0) with oxygen atoms.

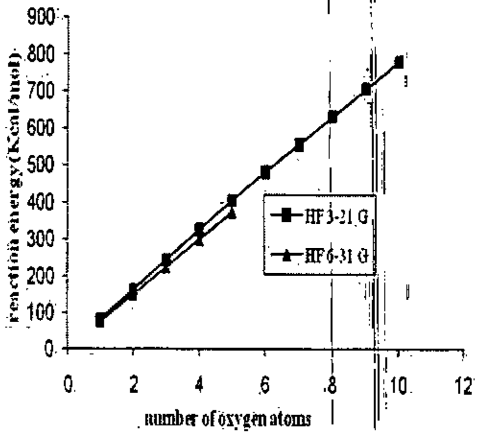

Fig. 10. The effect of 3-21G and 6-31G basis sets in HF method on reaction energy of carbon nanotube (10-0) with oxygen atoms.

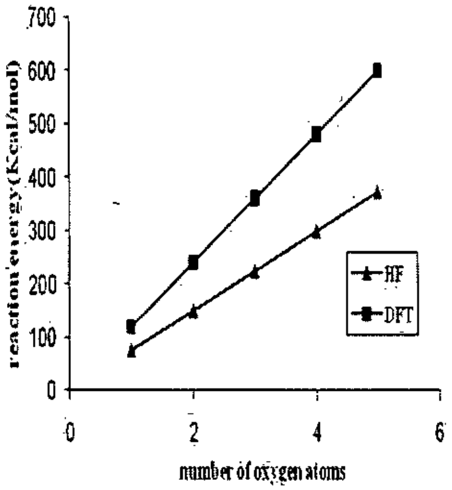

Fig. 9. The effect of HF/6-31G and B3LYP/6-31G on reaction energy of carbon nanotube (10-0) with oxygen atoms.

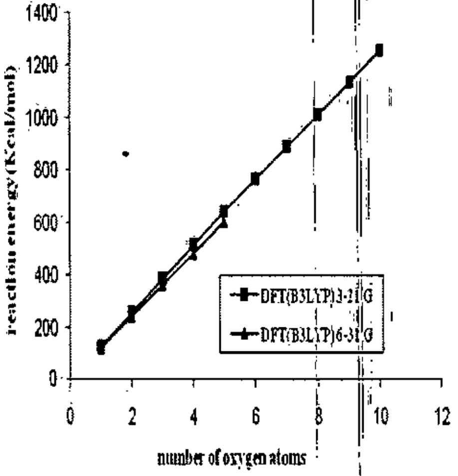

Fig. 11. The effect of 3-21G and 6-31G basis sets with DFT (B3LYP) method on reaction energy of carbon nanotube (10-0) with oxygen atoms.

Also the calculation of reaction energy by using of HF and DFT (B3LYP) methods are done in 3-21 G and 6-31G basis sets. The results of reaction energy for above methods are so close to each other and prove (see below).

CONCLUSION

In this study the structures of Oxygen atom adsorption over nanotube zigzag (10, 0) model were studied by using density functional theory (DFT) of electron and Hartree-Fock (HF) methods by 6-31G and 3-21G basis sets. It is found that interaction energy of Oxygen atom with surface of nanotube is increase proportional to the number of Oxygen atoms. Interaction energies were obtained with different method show that the amount of interaction energy in DFT method is more than HF method.

In general, in this research the electrical and mechanical properties and also storage property of carbon nanotube have been studied. Nanotube with their different properties can be used in many research in different fields as their synthesis, carrier molecules and drugs, …

ACKNOWLEDGMENTS

We gratefully acknowledge the support of this work by Islamic Azad University Rasht.

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