Adsorption of Carbon Monoxide on a (6, 6) Armchair Carbon Nanotube: Ab initio Study

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ABSTRACT

Perhaps the more interesting nanostructures with large application potential, from transistors to probes, are carbon nanotubes. One of the most widely uses of these nanostructures are their applications as gas detector, which is an important application in the field se of environmental technologies. The present work studies the adsorption of carbon monoxide on a (6, 6) armchair carbon nanotube .Two possible states were investigated; approaching CO from outside to the CNT and from inside of it. The results show that approaching the gas molecule has an exothermic nature which can be seen clearly when the CO molecule approaches toward CNT from outside. Investigation of NMR parameters showed that approaching CO from outside of the CNT has a general effect on all of the CNT atoms while there is no such an effect in the other case.

Keywords: CNT; Carbon Monoxide; Gas adsorption

INTRODUCTION

Nanotechnology refers broadly to using materials and structures with nanoscale dimensions, usually ranging from 1 to 100 nanometers (nm). To some extent, environmental scientists and engineers are already working with nano-scale materials [1]. Nano structures such as nanotubes, nanowires, nanomaterials and so on, are often arranged or self –assembled in to highly ordered layers arising from hydrogen bonding, dipolar forces, hydrophilic or hydrophobic interactions, gravity or other forces, like membrane, vesicles and DNA, form because of such self assembly.

More than a decade after the discovery of carbon nanotubes (CNT) by Iijima in 1991[2], they are still one of the hottest research areas in all of science and engineering. The interest is driven by the probability of several commercial applications [3, 4] including transistors, quantum dots, hydrogen storage devices (as clean fuel), structural reinforcement agents, chemical and electrochemical sensors, gas sensors, Nanoscale manipulators, and so many other applications.
At the same time the highly regular atomic structure of CNTs and the large degree of the structure purity makes it accessible to accurate

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computer modeling using a variety of theoretical techniques [5].

The most widely used consideration of atomistic modeling of a CNT is by reference to rolling up graphene sheet to form a hollow cylinder with end caps. The cylinder is composed of hexagonal carbon rings, while the end caps of pentagonal rings. The hexagonal pattern is repeated periodically leading to binding of each carbon atom to three neighboring atoms with covalent bonds. This covalent bond is a very strong chemical bond and plays significant role to the impressive mechanical properties of graphitic and as a consequence, of all carbon-related nano-structures. The atomic structure of nanotubes depends on tube chirality, which is defined by the chiral vector and the chiral angle. The chiral vector is defined as the line connected from two crystallographically equivalently sites on a two-dimensional graphene structure. The chiral vector can be defined in terms of the lattice translation indices (n, m) and the basic vectors of the hexagonal lattice (see Fig. 1) as respectively. These two types of nanotubes correspond to the two limiting cases. In terms of the roll-up vector, the armchair nanotubes are defined by (n, n) and the zigzag nanotubes by (n, 0) [6, 7] .

The present work performed in the area of gas (carbon monoxide) on a CNT. The studies aimed to determine the adsorption energy by approaching the gas inside the CNT and approaching from outer space of the CNT, and exploring the differences in magnetic properties of CNT through adsorption by use of theoretical methods (namely Density Functional Theory).

THEORETICAL METHODS

All the calculations have been carried out using Gaussian 03 software [8] and in vacuum. The model chemistry used for all calculations is B3LYP/6-311G*. This corresponds to the approximation method that makes use of Becke-style 3-parameter density functional theory with the Lee-Yang-Parr correlation functional [9, 10].NMR shielding tensors have been computed with the continuous set of the Gauge Independent Atomic Orbital (GIAO) method [11, 12, 13, 14 and 15].

RESULTS AND DISCUSSION

Carbon monoxide molecule was approached to a (6, 6) armchair carbon nanotube from two directions, out side and inside the nanotube. Distance scan and angle scan were performed to achieving relative energy for each movement of carbon monoxide to the CNT. Distance scanning calculated between 0-5 angstrom and the angle scanning between 0-180 degrees. The results are given in Table1. The CO molecule has a free rotation movement inside the nanotube .This confirms with the results of the angle scanning inside the CNT, which shows no difference during rotations.

The results showed that the most stable structure of CO during rotation movement outside the CNT at 180 degree and then by approaching CO molecule at this direction, the most stable structure were seen at 3 angstrom away from CNT (see Table1).The most stable structure of CO+CNT can be seen at 4.5 angstrom away from the inner wall of the CNT (see Table 1).
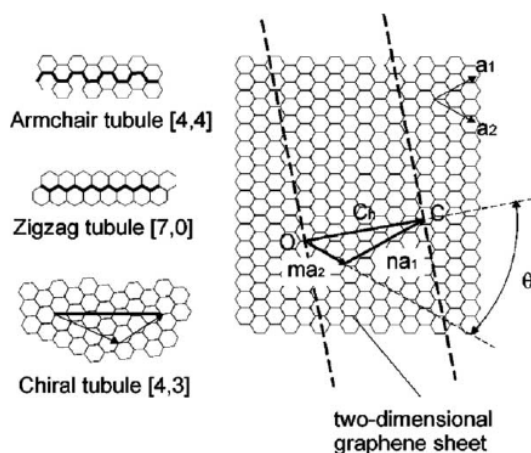

Fig.1. Schematic of the hexagonal lattice of graphene sheet including definition of basic structural parameters and explanation of Single Wall CNTs formation [7].

Table 1. Energy of the CNT-Gas structure with gas molecule inside and outside of the CNT

Energy (Hartree, 1Hartree=627.51Kcal/mol)			
CO molecule Approaching from out of the CNT			
Angle and Distance Scanning			
Angle(Degree)	E	distance (Angstrom)	E
0	-2413.9384	0.5	-2412.7893
30	-2413.9886	1	-2413.8428
60	-2414.0233	1.5	-2414.0359
90	-2414.0650	2	-2414.0826
120	-2414.0888	2.5	-2414.0933
150	-2414.0886	3	**-2414.0950**
180	**-2414.0892**	3.5	-2414.0931
		4	-2414.0928
CO molecule Approaching from inside of the CNT*			
Distance Scanning			
Distance (Angstrom)	E		
0	-2574.9483		
0.5	-2406.1405		
1	-2412.9053		
1.5	-2413.5825		
2	-2413.9201		
2.5	-2414.0590		
3	-2414.0871		
3.5	-2414.0936		
4	-2414.0934		
4.5	**-2414.0941**		
5	-2414.0933		

* Angle scanning showed no difference with changing the angles
E(angle scanning inside the CNT) =   -2414.079417

The adsorption energy (E adsorption) of CO is defined as the difference between the total energy of gas-host(CNT) and the sum of the energy of the separated host (CNT) and the energy of one gas molecule, and is calculated as follows [16]:

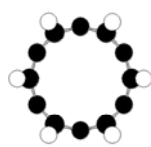$$E \text{ adsorption} = E(CNT\text{-}gas) - E(CNT) - E(gas). \quad (1)$$

By this definition, E(adsorption) < 0 in Eq. (1) corresponds to exothermic adsorptions leading to minima stable towards desorption into the CNT (Single Wall) and molecular CO. Endothermic energies, E(adsorption) > 0, correspond to minima of adsorbed species, which are unstable thermodynamically relative to the separated host model and molecular CO.

The gas adsorption energies were calculated by using Equation (1). The energies of gas adsorption and the stable structures are given in Table2. The results showed that the adsorptions are of type exothermic ones which leads to minimum stable towards desorption of CO on the CNT and also shows a stable thermodynamic model .Also, the adsorption energies have higher negative values when CO molecule approaches from outside the CNT relative to the inner wall of the CNT.

Calculation of the NMR shielding tensors shows no difference of NMR anisotropy chemical shift parameter in and out of the CNT but the comparison of the isotropic values between the CO state in the CNT and out of it, respectively, shows an increasing for C3 (the carbon atom of CNT in front of the C atom of CO molecule) while shows a periodic behavior in going CO from inside to outside of the CNT. In other words approaching CO from outside of the CNT has a general effect on all of the CNT atoms .The results are given in Fig.2.

Table 2. The Energies of Gas Adsorption*.

E ads.=[E(CNT-gas) - E (CNT) - E gas]

E(CNT-gas) : data from Table1

E(CNT) =   -2284.909158

E gas =   -113.3094543

Abs.Eads.(In)	Rel.Eads.(In)	Abs.Eads.(out)	Rel.Eads.(out)
-14.5707	1.3057	-176.7297	**0.0000**
-15.6242	0.2522	-7.9219	168.8078
-15.8172	0.0591	-14.6867	162.0431
-15.8640	0.0123	-15.3639	161.3658
-15.8747	0.0017	-15.7015	161.0282
-15.8764	**0.0000**	-15.8404	160.8893
-15.8745	0.0019	-15.8685	160.8612
-15.8742	0.0022	-15.8750	160.8547
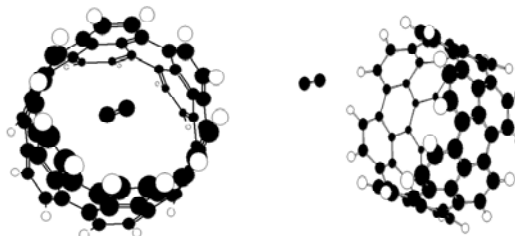
* Energies are given in Hartree, Absolute (Abs.) and Relative (Rel.) adsorption energies (Eads), are given in Hartree too.
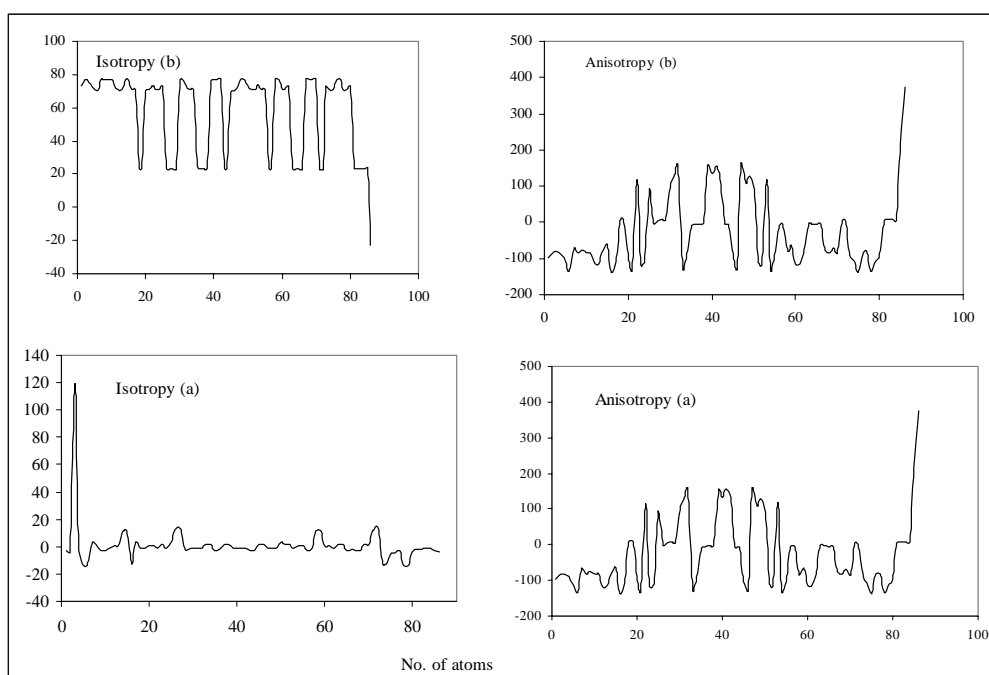
Fig.2. Isotropic and Anisotropic NMR tensor shielding values for (a) in the CNT and (b) out of CNT

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