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The Carbon Nanotubes as an Environmental Filter for carbon dioxide: The Semi-empirical approach

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Abstract
The nature of the quantum interaction properties between the carbon dioxide with the single walled carbon nanotubes surface is investigated by PM3 calculations. We have studied the effect of the CNTs diameter, the carbon dioxide's positions and its rotation characteristics inside the CNTs cavity. Our results suggest that the anti-binding energy is lower as the CNT diameter increases, and naturally the carbon dioxide can't enter inside the CNTs cavity without external operator. The axis of CO_2 molecules and the CNT parallel as CO_2 enter into the CNT.

Keywords: carbon dioxide, environment filter, CNT, semi-empirical, binding energy.

1. Introduction
The physicochemical properties and behavior of nanomaterials has been given a new field for science, which were discovered by Iijima [1]. The quantum nature comes back due to their atomic and molecular sizes. How the experiments can approach to the atomic dimensions to do nano-measurements? Carbon nanotubes (CNT) are a huge cylindrical large molecules consisting of a hexagonal arrangement of sp^2hybridized carbon atoms, and CNT can be synthesized by the techniques of electric arc discharge, laser ablation and catalytic decomposition of hydrocarbons [2-8]. Several applications due to their unique properties are employed in drug delivery, biosensor, antigen recognition, DNA hybridization without toxic effects[9-15].The penetration ability of the CNT into cells offers the potential of using CNT as vehicles for the delivery of drug and antibiotic molecules without toxic effects [16,22]. Azamian and co workers used a simple non covalent route to attach reactive molecules to sidewalls of CNT [23]. This related work is of interest to the development of biosensor based on nanotubes. Wong and his co workers have shown that CNTs are ideal probe tips for AFM due to their small diameter [24]. The CNTs will present potential technological advances in bioengineering [25]. The using the CNT filters over conventional membrane filters lies in the fact that they can be cleaned repeatedly after each filtration process to regain their full filtering efficiency and sufficient for cleaning these filters. In conventional cellulose nitrate/acetate membrane filters used in water filtration, however, strong bacterial adsorption on the membrane surface affects their physical properties preventing their reusability as efficient filters [26]. The typical filters used for virus filtration are not reusable. Because of the high thermal stability of the CNT filters can also be operated at temperatures of ~400 °C, which are several times higher than the highest operating temperatures of the conventional polymer membrane filters (~52 °C). The

nanotube filters, owing to their high mechanical and thermal stability, may compete with commercially available ceramic filters; furthermore, in the future, these filters may be tailored to specific needs by controlling the nanotube density in the walls and the surface character by chemical functionalization [27]. Up to now, there have been a lot of literatures on the functionalization of CNTs with various molecules [20, 28-31]. One way to study the interaction of CNT with other molecules is by means of theoretical modeling. The results of Ab initio calculation and density functional theory (DFT) gave good agreement between them [29,32-34]. Also, the semi-empirical results, the MINDO/3 (Modified Intermediate Neglect of Differential Overlap version 3) and PM3, gave good agreement with the ab initio and DFT methods in estimated the interaction energy [30,31].

In this work, we try to introduce a model to evaluate the CNT as an environmental filter for carbon dioxide by examining the interaction of the carbon dioxide with the internal cavity of single walled carbon nanotube (SWCNT), which is defined as bond-alternation patterns of an armchair [35].

2. Computational Method

In many cases the results of the experimental methods are unable to accurately describe small complex systems or it can be used to further investigations and to predict the physical nature of bonding energies. For that, the theoretical calculations can be used to investigate properties beyond the scope of current crystallographic methods and to bridge the gaps in understanding experimental results. To investigate the binding energy of CNTs decorated with the carbon dioxide, we used PM3 method. PM3, developed by Stewart [36,37], is a re-parameterization of AM1 (Austin Model 1 is a Modified Neglect of Diatomic Overlap method (MNDO)), which is based on the neglect of diatomic differential overlap (NDDO) approximation. NDDO retains all one-center differential overlap terms when Coulomb and exchange integrals are computed. PM3 differs from AM1 only in the values of the parameters. The parameters for PM3 were derived by comparing a much larger number and wider variety of experimental versus computed molecular properties. Typically, non-bonded interactions are less repulsive in PM3 than in AM1. PM3 is primarily used for organic molecules, but is also parameterized for many main group elements. PM3 can also be used to study transition metal compounds; new parameters include the following elements Ti, Mn, Fe, Co, Ni, Cu, Zr, Mo, Rh, Pd, Hf, Ta and W. The problem in quantum computational chemistry that arises is how to perform an accurate calculation for a nano-sized system without ending in a prohibitively large computation. The dangling bonds at the ends of the tubes were saturated by hydrogen atoms. The resolution of PM3, as implemented in the HyperChem Release 7.52 for Windows Molecular Modeling System program package [38], was employed for the geometry optimizations.

3. Results and Discussions

The present work involves the investigation of carbon dioxide CO_2 moving inside a cylinder of CNT, as shown in Figure 1. This study enabled us to determine the binding energy between the CO_2 and CNT as a function of the distance between them. The interaction binding energy BE of the carbon dioxide with the CNT was calculated by using the formula: $BE = E_{CO_2+CNT} - (E_{CO_2} + E_{CNT})$; where E_{CO_2+CNT} is the total energy of carbon dioxide and CNT. Two CNTs were adapted; one has a diameter and length of 7.064A° and 7.345A° respectively, and the second one has a diameter and length of 8.476A° and 7.345A°. Figure 2 shows the results of binding energy between carbon dioxide and CNTs. We try to scanning on the path from point, which it’s located outside the CNT, until the point that locates inside the CNTs center, see Figure 1.

As the carbon dioxide moves into the center of CNTs cavity, shows increase in the anti-binding energy. These anti-binding energies appear at distances of few Angstroms (~3.5A°) from the end of CNTs, and as the diameters of CNTs increase this effect decreases. This effect may be due to the lowering in the steric effect. Entering the carbon dioxide inside the CNTs is unusual procedure, where it needs an external force such as applying a pressure. Also, for defining the amount of pressure that is needed to be applied for entering the carbon dioxide into the CNTs cavity. Generally, the effect of diameter on the carbon dioxide entered inside the CNTs, can be as a good model for the nano-applications in the environment, where, empirically possible to make a nano-filter for carbon dioxide molecules. To examine the best geometry for the carbon dioxide inside the cavity of CNTs, we rotate it about axil perpendicular on CNTs axil and the result as shown in Figure 3.

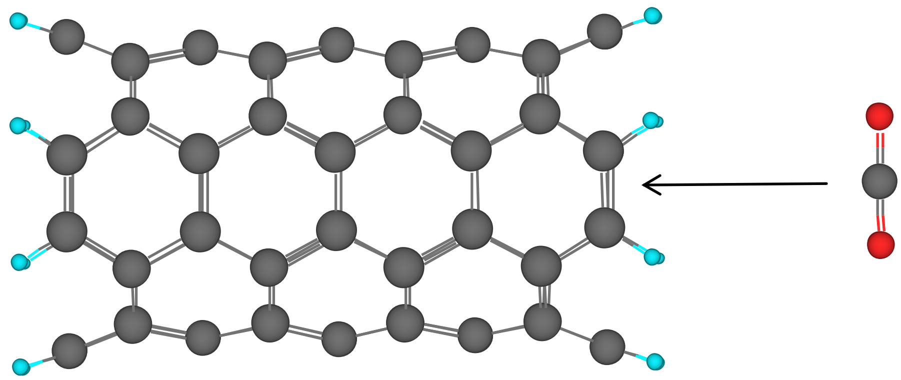

Figure 1. The direction of movement of the carbon dioxide to enter the cylindrical cavity for CNT.

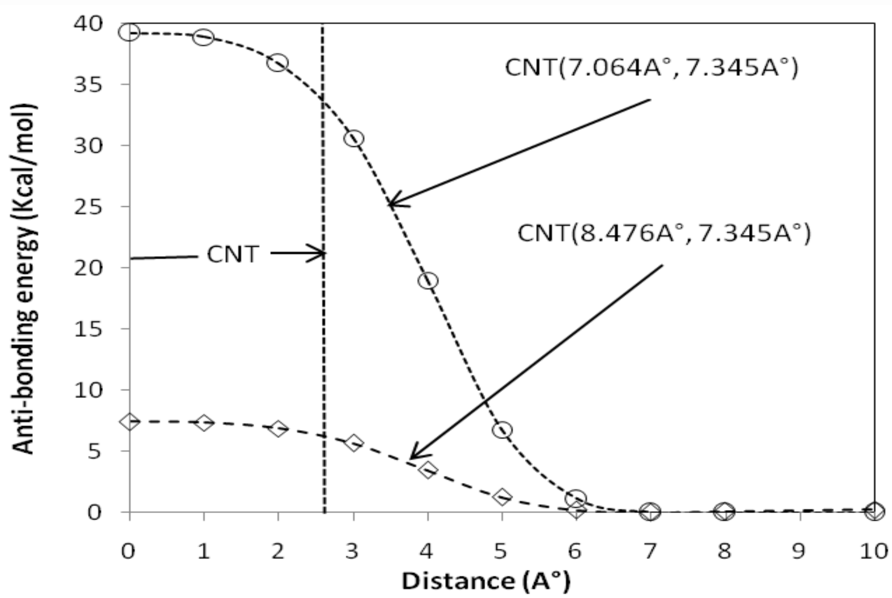

Figure 2: The binding energy of the carbon dioxide with CNTs as a function of the distance between them using PM3.

While the carbon dioxide rotates in side CNT, the anti-binding energy decreases to minimum value at rotation angle equal to 90^o. At this angle, the axis of the carbon dioxide conceding with axis of CNTs cylinder. There are little changes in the anti-binding energy to be dominant at these rotation angles. Therefore, that factor may help to enable the carbon dioxide to move into the CNT. When the carbon dioxide axis becomes perpendicular to the axis of CNT, the entering of the carbon dioxide becomes difficult. Hence, we expect the axis of CO_2 molecules during this process to be parallel to the axis of CNT.

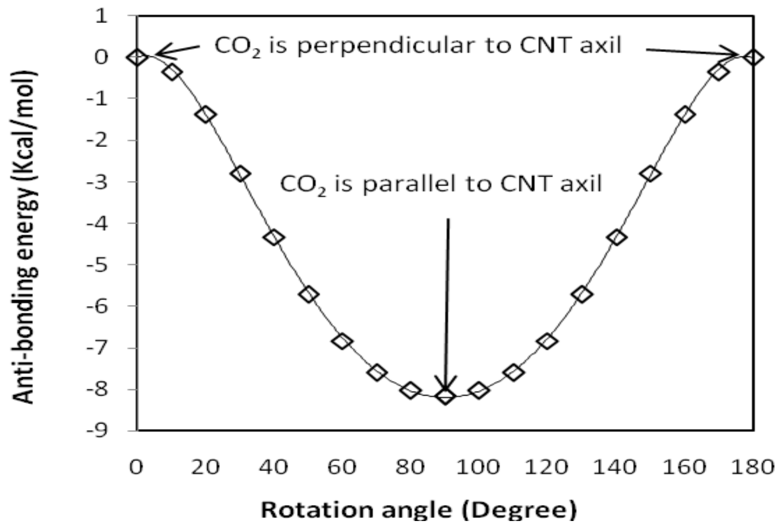

Figure 3. The change in anti-binding energy as a function of rotation angle of the CO_2 using PM3.

To confirm the stability of this system as a function of the carbon dioxide position shifting, inside the CNTs, the anti-binding energy was studied as a function of the position shift of the carbon dioxide from the CNTs axil forward the internal wall of CNT. Figure 4 shows that as the carbon dioxide shifted its position from the center of CNT, the stability decreases, so that the carbon dioxide will moves inside the CNT at the middle. The change in the energy with the position shifting of CO_2 is high, therefore only one carbon dioxide can move inside the cavity without increasing the CNT diameter. These steric effects that may be appear with this shifting for the CNTs may give a good idea about the fabricated filter for CO_2. According to Figure 4 we can notice that CO_2 can has shifted of ~3A^o toward the internal wall of CNT, so that it may move in a cylindrical path, which has diameter of ~3A^o inside CNT.

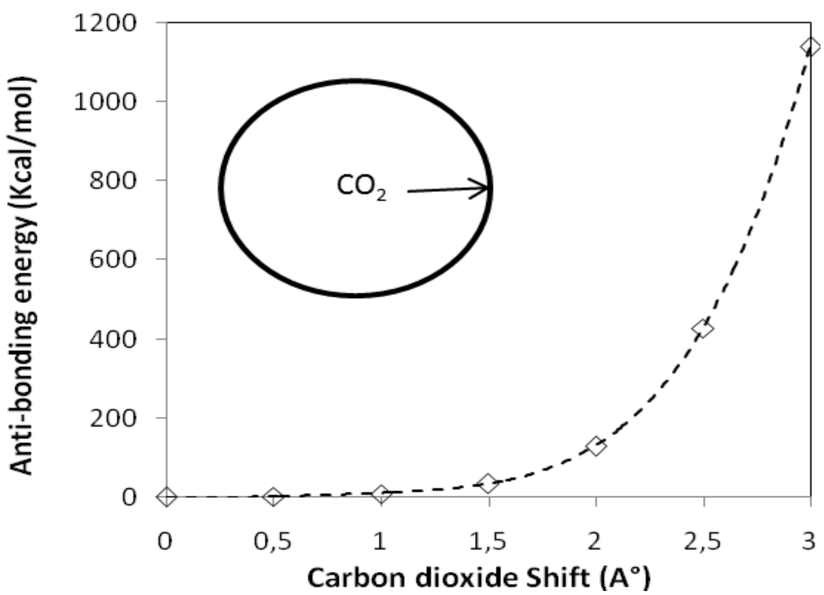

Figure 4. Anti-binding energy as a function of carbon dioxide shift from the CNTs axil using PM3.

Conclusions

We have performed PM3 calculations on the interaction nature between CNT with carbon dioxide. The effect of the CNTs diameter on the carbon dioxide entering inside the cavity of CNT was studied. Naturally the carbon dioxide can't enter inside the CNTs cavity without external operator. The axis of CO_2 molecules are parallel to the axis of CNT as them enter the CNT.

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