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Hydrogen Interaction with Single-Walled Carbon Nanotubes: A Combined Quantum-Mechanics/ Molecular-Mechanics Study

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ABSTRACT

A mixed quantum mechanics/molecular mechanics (QM/MM) model is used for investigating the nature of hydrogen adsorption in single-walled carbon nanotubes (SWNTs). For the QM part the B3LYP functional was used while for the MM we employ the universal force field (UFF). Our model includes up to 64 carbon and 32 hydrogen atoms in the QM region and up to 200 carbon atoms of a (4,4) SWNT in the MM region. Our results demonstrate that hydrogen atoms will bind to the tube walls and not enter in the tube interior. This binding will take place in zigzag rings around the tube walls and not in lines toward the tube axis, changing the tube shape and causing an enlargement of the tube volume by 15%. After the tube walls are half-filled with hydrogens, we obtained the energetically more favorable procedure of hydrogen insertion in the tube.

It is well-known that pores of molecular dimensions can adsorb large quantities of gases. In the past few years, carbon nanotubes, which have diameters of typically a few nanometers, have been suggested as suitable materials for gas storage.[1,2] Gases and especially hydrogen can condense to high-density inside narrow SWNTs even at room temperature.[3] The very high hydrogen uptake of these materials suggests that they can be used as hydrogen-storage material for fuel-cell electric vehicles.

A lot of experimental work has been done in the past few years trying to investigate the hydrogen adsorption in SWNTs and to improve the storage capacity of the tubes by doping them.[1−7] On the other hand, there is no sufficient theoretical explanation of this phenomenon but only guesses about the procedure of hydrogen adsorption in SWNTs. This effects badly both the understanding of the nature of these materials and the improvement of their storage capacity that end up in a random procedure.

Our aim in this work is to investigate the nature of the hydrogen adsorption in SWNTs. The problem that arises in such an attempt is how to compromise the large size of the system that you need to take into account and an accurate ab initio method without ending up in a prohibitively large calculation. Most of the previous attempts to study this phenomenon are using empirical approaches in order to treat a sufficient number of atoms.[8−10] On the other hand Jeloaica and Sidis used density functional theory (DFT) to investigate the hydrogen−graphite interaction,[11] while Bauschlicher used a QM/MM approach for studying the binding of up to 4 hydrogen atoms to a (10,0) SWNT.[12] In addition, models with periodic boundary conditions were also used for studding the sidewall functionalization of SWNTs with fluorine.[19,20]

In our study we apply the QM/MM approach in a 200-atom (4,4) SWNT, treating up to 64 carbons and 32 hydrogens with the higher level of theory. The small diameter of the tube together with the large number of atoms we consider allows our higher level model to include a cylindrical part of the tube. This is very critical for investigating the changes of the shape of the tube during the adsorption procedure.

As we can see in Figure 1, a two-level ONIOM[13] model was used. A 200-atom (4,4) tube was divided into three cylindrical parts. The inner one was treated with DFT, while the two outer parts were treated with molecular mechanics. The three-parameter hybrid functional of Becke using the Lee−Yang−Parr correlation functional (B3LYP)[17] was employed for the higher theoretical level. The atomic basis set that we use includes Gaussian functions of double-ζ quality augmented by d-polarization functions (6-31G*). The combination of method and basis (B3LYP/6-31G*) had already worked out in similar systems.[14−16] The two outer cylindrical parts were treated with the universal force field

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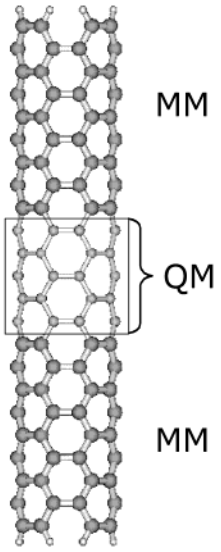

Figure 1. One of the QM/MM models simulating a (4,4) SWNT that was studied in this work. The total 200 atoms tube was separated into three cylindrical parts. The inner one was treated with DFT (40 open color carbon atoms) while the two outer parts with molecular mechanics (darker color carbon atoms). The dangling bonds at the ends of the tube were saturated with hydrogen atoms

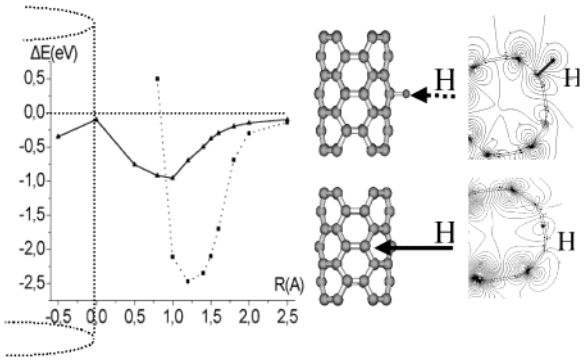

Figure 2. Potential curves during the hydrogen approach to a carbon nanotube in two different pathways. The first is toward a carbon atom that will lead to a C−H bond (doted line) and the second is toward the center of a C-hexagon that will lead to an H insertion in the tube (solid line). In the middle part of the figure we demonstrate schematically the approaching pathways, while in the right part we plot constant amplitude contours of the charge density in a cut vertical to the tube axis. In the upper part the hydrogen atom is boned to the tube while in the lower part the hydrogen atom is "caught" while entering the tube wall.

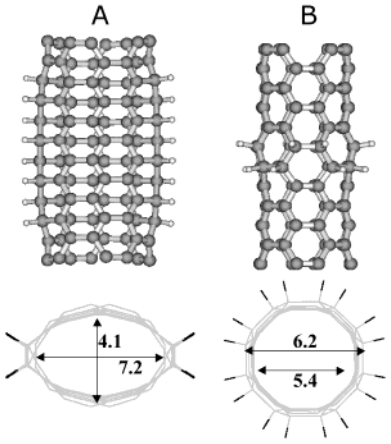

Figure 3. Optimized geometries of 16 hydrogen atoms bonded in the tube in the two different ways: (A) following two zigzag lines parallel to the tube axis and (B) following an "armed chair" ring vertical to the tube axis. In the lower part of the figure we see the tube toward its axis and we report the changing of its diameter in angstroms.

(UFF),[17] while the dangling bonds at the ends of the tube were saturated with hydrogen atoms. This two-level approach combines the high accuracy of the ab initio treatment of the central part of the tube, where the interaction with hydrogens will take place, with the relaxation accuracy that the large size of the tube guarantees. The energies that we report in this letter are computed with the ab initio B3LYP/6-311G* method concerning the higher level model, while the rest of the atoms in the lower level model were kept for constraining the shape of the higher level part. All the computations were performed with the Gaussian 98 program package.[17]

The first part of our study was the investigation of the potential that a hydrogen atom feels while approaching a carbon nanotube. There are basically two different approaching pathways. The first is toward a carbon atom that will lead to a C−H bond and the second is toward the center of a C-hexagon. The potential curves of these two approaches are plotted in Figure 2.

It is clearly demonstrated that the first way will end up with a binding of the H atom to the wall of the tube. According to our ab initio calculation this bonding will lead to a charge transfer of $0.25|e|$ from the H to the tube. In the second path the H will feel initially the attraction of the C atoms but afterward it has to pass over a barrier in order to enter the tube. The charge transfer from the H to the tube, when the H atom is placed in the center of the C-hexagon, is $0.31|e|$. This procedure of charging and discharging of the H atom together with an opening of the charge density of the tube (Figure 2) is responsible for the entrance barrier. A combined interpretation of these two curves shows that despite the approaching direction, the H will feel an attraction from the C atoms of the tube and finally will bind to the wall of the tube and not enter inside. The total energy of the QM region of the tube that contains 24 carbon and 1 hydrogen atom was found to be −913.754082 Hy at the lowest point of the binding curve.

As more hydrogens approach the tube, they will bind to neighboring C atoms in order to minimize the loss of C−C π bonds.[12] But there are two different ways of doing this: The first is to follow a zigzag line parallel to the tube axis, while the second is to follow an armed chair ring vertical to the tube axis. Our first principle calculations showed that the second procedure is energetically more favorable, as has been found also experimentally for similar systems.[18]

In the next step of our calculations we consider 16 hydrogen atoms bonded in the tube in the two different ways mentioned before in order to see how this will effect the tube shape. In Figure 3 we can see the optimized structures where we kept 64 C and 16 H atoms in the QM region. The C atoms that hydrogens are bonded to, pass from the sp^2 to sp^3 configuration. This effects drastically the bond lengths

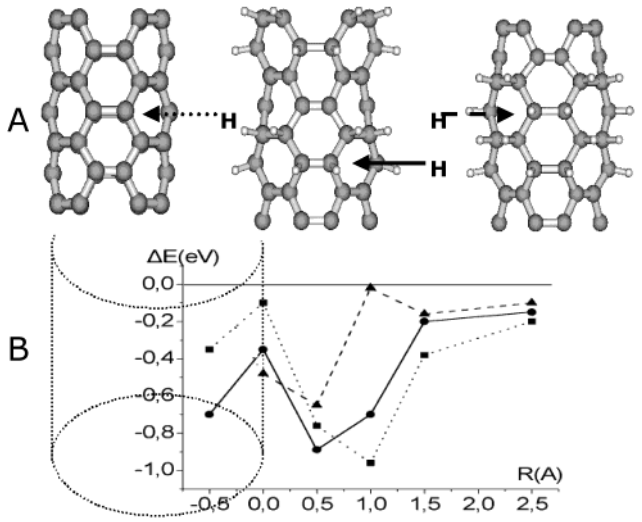

Figure 4. (A) Optimized geometries of 32 hydrogen atoms bonded in the tube in two different ways: "ring by ring" configuration (in the middle) and "all rings together" configuration (at the right part), as analyzed in the text. The geometry of the tube without hydrogens is also plotted for comparison (left part). (B) Potential curves during the hydrogen approach to the three different carbon nanotubes shown in (A): SWNT with no hydrogen atoms to its walls (dotted line); SWNT with walls half-filled with hydrogens (solid line); SWNT with walls full with hydrogens (dashed line).

and the size of the tube hexagons. The C−C bond length increases from 1.43 to 1.59 Å, while the diameter of the hexagons goes from 2.84 to 3.15 Å if 4 hydrogen atoms are attached in this hexagon (Figure 3b). These cause a strain that leads to a tube deformation.

In the case of the line orientation of the hydrogens, the shape of the tube changes from cyclic to elliptic (Figure 3a). The 5.4 Å diameter of the tube without hydrogens split to a 4.1 Å small and 7.2 Å large diameter of an ellipsis. In the case of the ring orientation, we see an enlargement of the tube diameter from 5.4 to 6.2 Å, but keeping the cyclic shape (Figure 3b). The second orientation is more favorable because the strain can be relaxed with the enlargement of one ring that does not effect the whole tube, while in the first case, an axial enlargement of the tube cannot take place only in one zigzag C line. This effect results in an energy difference of 2.6 eV between these two orientations. It is worth mentioning that in the line format we have no change in the volume of the tube while in the ring one we have a 30% enlargement of the volume.

Since the hydrogens "prefer" to form rings around the tube, the next question that arises is, how close can those rings be? For answering this question we perform two different calculations with two different zigzag ring orientations (48 carbons and 32 hydrogens in the QM region). In the first, the rings were separated and in the second they were close together, as can be seen in Figure 4a (middle and right upper part, respectively). After the geometries were optimized, the separated configuration showed a plus/minus changing of the tube diameter of almost 1 Å. On the other hand, when the rings were close together, the tube diameter was increased in the first ring by 1 Å and decreased to the normal value at the last ring. The total energy of "ring by ring" configuration was found to be −1847.550839 Hy, and it was favored energetically from the "all rings together" by 17 eV.

This energy difference can be explained from the nature of the hybridization of the carbon atoms. During the hydrogen addition the carbon atoms pass from sp^2 to sp^3 hybridization and a 3-dimensional-bond orientation is preferable. This 3-D orientation can be obtained by the continuous changing of the tube diameter in the "ring by ring" configuration. In this case the tube wall is not flat toward the tube axis but shows a zigzag shape (Figure 4a, middle). In the case of the "all rings together" configuration, the tube wall is changing shape only in the beginning and at the end, while between it stays flat (Figure 4a, right). The flat wall shape that was favorable when carbon atoms had sp^2 hybridization is not favored after the hydrogen adsorption because carbon atoms changed hybridization to sp^3. Extending this configuration to an *n*-atom tube will need *n*/2 hydrogens since one C-zigzag ring has hydrogens and the next does not, periodically. This procedure will cause a 15% enlargement of the tube volume (half of the rings gain 30% in volume).

The final and more interesting question we tried to answer is, what happens after the adsorption of hydrogens in the tube walls? Is it easier to fill up the tube with hydrogens? In Figure 4b we plot the potential curves of a hydrogen approach in the center of the hexagon of three different tubes. The first has no hydrogens (also plotted in Figure 2), the second is half-filled with hydrogens, and the third is full of hydrogens.

Analyzing these potential curves, we see two competing forces in the approaching procedure. On one hand, it is clear that the more hydrogens we have in the C-hexagon, the larger the hexagon is and the easier the outcoming H enters the tube. This can be easily observed by the lowering of the barrier at the tube wall as the number of hydrogens in the hexagon increases. On the other hand, the hydrogens in the hexagon are screening the attraction of the carbon atom to the external hydrogen. This screening, in the case of a fully hydrogenated hexagon, inserts a barrier to the outcoming hydrogen 1 Å from the tube wall (where actually the bonded hydrogens are located). As a result of these, the energetically favorable H approach is when the tube wall is half-filled with hydrogens. This happens because in the first part of the approach there is no barrier caused from steric repulsion of the bonded hydrogens, while in the entrance of the tube wall the barrier is smaller by almost 0.3 eV from the first case. The total energies of the QM region where the H atom is located at the center of the hexagon of the tube wall are C-hexagon without H's (C24+H), −913.666966 Hy; C-hexagon with 4 H's (C24H16+H), −923.603436 Hy; and C-hexagon full of H's (C24H24+H), −928.126147 Hy.

Comparing our results obtained with the QM/MM approach with those of Seifert et al.[19] and Kudin et al.[20] obtained with periodic boundary condition models, we find an agreement concerning the stoichiometry (2 C, 1 ligand) and the deformation of the tube that takes place during the adsorption. Nevertheless, there is a disagreement about the ligand orientation around the tube wall that can be explained

from the different approaches used (QM/MM versus periodic box) and/or form the different ligands (H versus F) and/or from the different tubes examined (4,4 versus 10,10 that have almost double diameter).

Summarizing, our work clearly shows that a mixed QM/MM model can successfully employa SWNT and provide a solution to the problem of making accurate calculations in large systems like nanotubes. Our results demonstrate that hydrogen atoms will bind to the tube walls and not enter into the tube interior. This binding will take place in zigzag rings around the tube walls and not in lines toward the tube axis, causing a ring by ring enlargement of the tube diameter. The changing of the tube shape during the hydrogen adsorption drives to an enlargement of the tube volume by 15%. After the tube walls are half-filled with hydrogens, we obtained the energetically more favorable procedure of hydrogen insertion in the tube.

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