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HYDROGEN STORAGE IN SWNTS. A MIXED QM/MM STUDY

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Abstract. A mixed Quantum Mechanics / Molecular Mechanics (QM/MM) model is used for investigating the nature of atomic and molecular hydrogen adsorption in pure and alkali metal doped single walled carbon nanotubes (SWNTs). The results demonstrate that hydrogen atoms will bind the tube wall in a ring-by-ring form, covering 50% of the wall. For the alkali-doped tubes the charge transfer from the alkali metal to the tube polarizes the H_2 molecule and this charge induced dipole interaction is responsible for the higher hydrogen uptake of the doped tubes.

1. INTRODUCTION

Hydrogen has been recognized as an ideal energy carrier but has not been used yet in long extent. One of the major problems is the difficulty of an efficient storage. In the beginning metal alloys were tested for storage tanks but even though they have sufficient storage capacity, they are expensive and heavy for commercial production focused on mobile applications. In the recent years, carbon based materials attracted attention due to the discovery of novel carbon nano-materials like fullerenes, nanofibers and nanotubes [1-3]. Especially SWNT's, which have diameters of typically a few nanometers, have been suggested as suitable materials for gas storage [4]. Since pores of molecular dimensions can adsorb large quantities of gasses, hydrogen can condense to high density inside narrow SWNT's even at room temperature [5]. The high hydrogen uptake of these materials suggests that they can be used as hydrogen-storage material for fuel-cell electric vehicle [6-8].

A lot of recent experiments are trying to investigate the hydrogen storage in SWNT's. First at 1997, Dillon *et al.* reported that SWNTs could store hydrogen [4]. Using Temperature-Programmed Desorption spectroscopy (TPD) they showed that hydrogen would condense inside SWNTs under conditions that do not induce adsorption within a standard mesoporous activated carbon.

Two years later Liu *et al.* found out that this storage can take place in room temperature [5]. They used SWNTs of 1.85 nanometers diameter, synthesized by semi-continuous hydrogen arc discharge method, and found storage capacity of 4.2 weight percent at room temperature and under modestly high pressure. The 78.3% of the adsorbed hydrogen can be released under ambient pressure and room temperature.

The same year Chen *et al.* report that Alkali-doped carbon nanotubes poses high hydrogen uptake [9]. They investigate lithium and potassium doped carbon nanotubes and found hydrogen absorption of 14 to 20 weigh percent between 400 ^{o}C and room temperature. These values are higher than those of metal hydride and cryoadsorption systems. The stored hydrogen could be released at higher temperatures and the sorption-adsorption cycle can be repeated with minor loss of the storage capacity.

After that a lot of experimental work has been performed trying to investigate the hydrogen adsorption in SWNTs and to improve the storage capacity of the tubes by doping them [10,11]. Nevertheless the experiments on hydrogen storage in nanotube

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samples have been controversial as reported by the recent review of Ding at al. [8].

2. THEORETICAL MODELING

On the other hand until recently, there was no sufficient theoretical explanation of H adsorption in SWNT but only guesses about this procedure. That was affecting badly both the understanding of the nature of these materials and the improvement of their storage capacity that was ending up in a random procedure.

One of the major *headaches* in the computational material science is how accurate theoretical techniques can be applied in large systems. By ‘accurate theoretical techniques’ we mean quantum the chemistry methods, called *ab-initio,* due to the fact that they do not enforce any parameters to the system but solve the Schrondinger equations from first principles. The grater advantage of the *ab-initio* methods is that they can provide structural, electronic and dynamic properties of the calculating system in high accuracy. On the other hand the computational cost increase dramatically with the number of the electrons in the system.

The problem that arises in polyatomic systems is how to compromise the relatively large size of the system and an accurate *ab-initio* method without ending up in a prohibitively large calculation. A possible solutions to this dilemma of treating with *ab-initio* methods, large systems is the mixed Quantum Mechanics / Molecular Mechanics model.

The mixed Quantum Mechanics / Molecular Mechanics (QM/MM) model is schematically presented in Fig. 1. The basic idea of this method is that the system is divided in two parts: one is treated by *ab-initio* methods while the other by molecular mechanics. The bordering of the two parts is arranged by introducing link atoms. More details for this model can be found in reference 12.

For the (4,4) SWNT presented in Fig. 1, the total 200 atoms tube was separated in three cylindrical parts. The inner one was treated with DFT (40 light grey carbon atoms) while the two outer parts with molecular mechanics (dark grey carbon atoms). The dangling bonds at the ends of the tube were saturated with hydrogen atoms.

The B3LYP functional was employed for inner part of the tube together with a double-ξ basis (6-31G*) that includes polarization functions. The two outer cylindrical parts were treated with the UFF while the dangling bonds at the ends of the tube were saturated with hydrogen atoms. All the computations were performed with the Gaussian 98 [12] program package under the ONIOM two level approach [13].

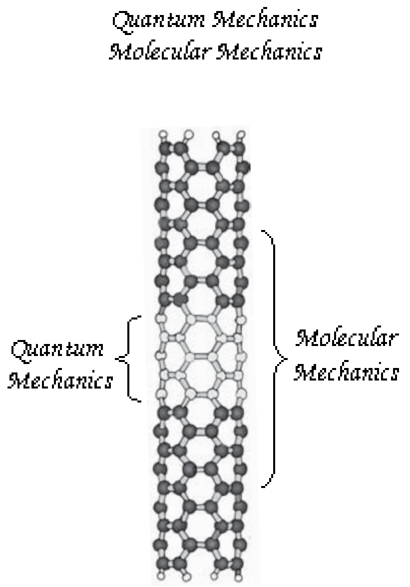

Fig. 1. The QM/MM model simulating a (4,4) SWNT. The total 200 atoms tube was separated in three cylindrical parts. The inner one was treated with DFT (40 light grey carbon atoms) while the two outer parts with molecular mechanics (dark grey carbon atoms). The dangling bonds at the ends of the tube were saturated with hydrogen atoms.

3. RESULTS AND DISCUSSION

In this study we mainly try to answer two questions: The first concern the coverage of SWNT’s by hydrogen atoms and the second deals with the difficulty of putting hydrogen atoms inside the tube. From the work of Bauschlicher [14] and ours [15] it is clear that the hydrogen atoms that approach the SWNT will be bound to the tube walls in neighboring C atoms for minimizing the loss of C-C π bonds. But there are many different ways of doing this: One is to follow a zigzag line parallel to the tube axis while an other is to follow an armed chair ring vertical to the tube axis. First principle calculations [14] showed that the second procedure is energetically more favorable as have been found also experimentally for similar systems [10].

In the case of the line orientation of the hydrogens the shape of the tube change from cyclic to elliptic. 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

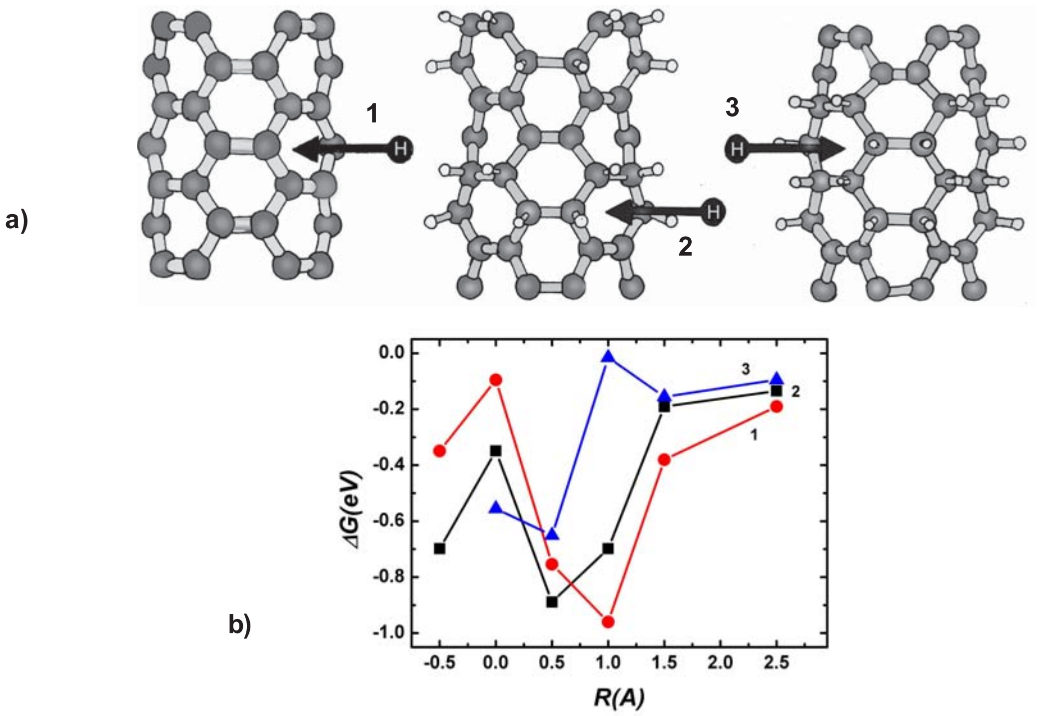

Fig. 2. (a) Optimized geometries of 32 hydrogen atoms bonded in the tube in the two different ways: ‘ring by ring’ configuration (in the middle) and ‘all rings together’ configuration (at the right part) as analyzed in the text. The geometry of the tube without hydrogens is also plotted for comparison (left part). (b) Potential curves during the hydrogen approach to the three different carbon nanotubes showed in A (SWNT with no hydrogen atoms to its walls: 1, SWNT with walls half field with hydrogens: 2 and SWNT with walls full with hydrogens: 3).

an enlargement of the tube diameter from 5.4 Å to 6.2 Å is obtained but keeping the cyclic shape. The second orientation is more favorable because the strain can be relaxed with the enlargement of one ring that doesn’t effect the whole tube, while in the first case, an axial enlargement of the tube can not take place only in one zigzag C line. This effect results 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 arise is how close those rings can be? For answering this question we performed 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 Fig. 2a (middle and right upper part respectively). After optimizing the geometries the separated configuration showed a repeatively increasing and decreasing of the tube diameter of almost 1 Å. On the other hand, when the rings were closed 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 favored energetically from the ‘all rings together’ by 17eV.

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 sp2 to sp3 hybridization and a 3-Dimentional (3-D) bond orientation is preferable. This 3-D can be obtained by the continue changing of the tube diameter in the ‘ring by ring’ configuration. In this case the tube wall is not flat towards the tube axis but shows a zigzag shape (Fig.2a-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 in between stays flat (Fig.2a-right). The flat wall shape that was favorable when carbon atoms had sp2 hybridization is not favored after the hydrogen adsorption because carbon atoms changed hybridization to sp3. Extending this configuration to an infinite atom tube will end up to 50% coverage since one C-zigzag ring has hydrogens and the next has not, periodically. This procedure will cause a 15% enlargement of the tube volume (half of the rings gain 30% in volume).

The second question we tried to answer is what happens after the adsorption of hydrogens to the tube walls. Is it easier to fill up the tube with hydrogens? In Fig. 2b we report the potential curves when atomic hydrogen approaches the center of three tube-wall hexagons that differs only in the adsorption rate. The first has no hydrogens, the second is half field with hydrogens, and the third is full with hydrogens. Analyzing these potential curves we see two competing forces in the approaching procedure. In one hand it is clear that the more hydrogen we have in the C-hexagon, the larger the hexagon is, the easier the out coming H pass. This can be easily observed by the lowering of the barrier at the tube wall as the number of hydrogens in the hexagon increase. 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 fully hydrogenated hexagon insert a barrier in the out coming hydrogen at a distance of 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 field 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 case of the bare tube.

Comparing our QM/MM with those of Seifert *et al.* [16] and Kudin *et al.* [17] obtained with periodic boundary condition models, we find an agreement concerning the stoichiometry (C: 2 ligand: 1) and the deformation of the tube that take place during the adsorption. Nevertheless there is a disagreement about the ligand orientation around the tube wall that could be a consequence of the different approach used (QM/MM versus periodic box) and/or from the different ligand (H versus F) and/or from the different tube examined (4,4 versus 10,10 that have almost double diameter).

After 1999 when Chen *et al.* [9] reported that Alkali-doped carbon nanotubes poses high hydrogen uptake a lot of experimental work has been performed trying to investigate the hydrogen adsorption in SWNTs and to improve the storage capacity of the tubes by doping them.

All the theoretical calculations reported so far can be divided in two categories. Either they are empirical [8,18,19] or they are based on first principle methods but deal only with atomic hydrogen [13,14,16,20]. The first category cannot give an understanding of the elementary steps in the adsorption process. Since these methods are not *ab-initio* but based on parameters, they cannot provide an insight of the chemical bond. The first principle methods can, but they deal only with atomic hydrogen while the most important interaction for the storage, which is the molecular hydrogen interaction with SWNTs, remains untouched. The reason why *ab-initio* studies of the H_2 interaction with SWNTs do not exist is obvious. The interaction is weak and the system is large.

With the use of QM/MM model we tried to investigate the nature of the H_2 adsorption in alkali doped SWNTs and to compare it with the adsorption in pure SWNTs [21]. Only in this way it is possible to answer the question 'why alkali doped carbon nanotubes have high H_2 uptake? '. We applied the QM/MM mixed model as described earlier in a closed (5,5) SWNT with 150 carbon atoms. K atoms dope the tube in a 2 x 2 pattern as suggested by Gao *et al.* [22]. In this pattern the K atoms were placed on 'hollow' positions above the center of the C hexagons of the tube in a way that if one hexagon has a potassium, all the neighboring doesn't have (Fig. 3a). A geometry optimization confirmed that these positions were optimum for our model, too. 24 carbon atoms together with two potassium atoms and all the H_2 molecules that were interacting with these two K atoms were kept in the QM region, while the rest of the atoms were treated by MM.

The first case considered (Fig. 3a left) was a doped tube where a single H_2 molecule was interacting with each K atom. After the geometry was optimized, the binding energy of the H_2 to the K was 3.4 Kcal/mol/H_2. The distance of the K atom from the center of the C_6-hexagon of the tube was 3.0 Å while the distance of the closer H of the H_2 molecule from the K was 3.0 Å, too. In the next case (Fig. 3a middle) two hydrogen molecules were interacting with each K and finally three (Fig. 3a right). The binding energies were 2.5 Kcal/mol/H_2 and 1.8 Kcal/mol/H_2 respectively. The H_2 distance from the K was found to be 3.3 Å and 3.5 Å while the K-tube distance remained the same (3.0 E).

From these results is clearly showed that at least three hydrogen molecules can bound each K atom of a doped tube even though the binding energy is

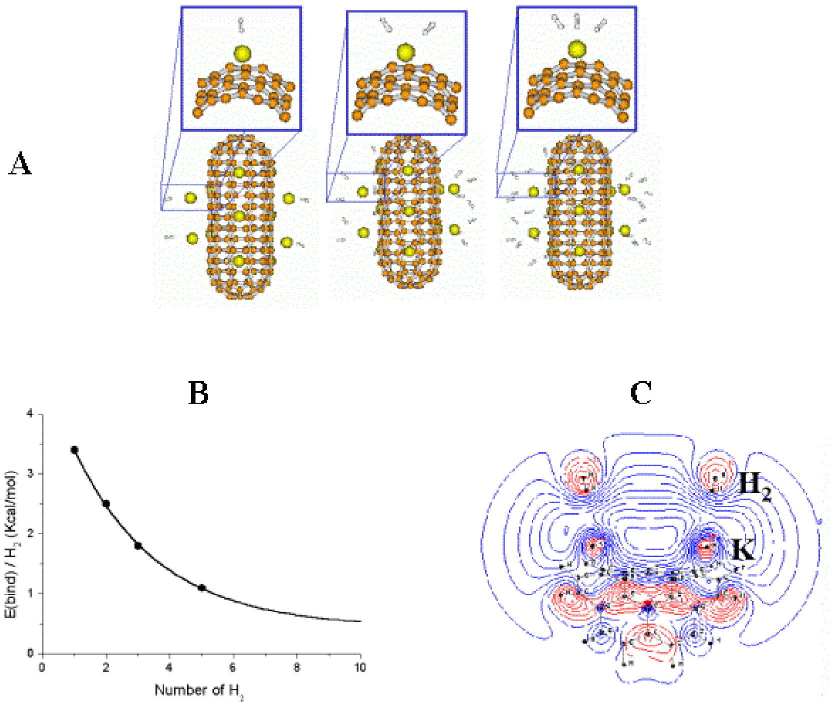

Fig. 3. (a) Three of the alkali metal doped (5,5) SWNT's that we to study the interaction with molecular hydrogen. The first has one H_2 per K, the second two and the third three. A magnifying part of all pictures is also presented. (b) Binding energy per hydrogen molecule with respect to the number of the H_2 molecules. The hexagons represent the calculated values where the line was fitted. (c) Constant amplitude contours presenting the HOMO of the (5,5) K-doped SWNT with one H_2 per K atom. The plotted area is also marked on the entire tube.

consistently decreasing with the number of ligands. The two questions that immediately arise are: How many H_2 can be accommodated to each alkali of the doped tube? And why the doped tubes have larger hydrogen uptake than the pure carbon nanotubes?

For answering the first question we also calculated the case where five H_2 molecules were attached at each K of the doped tube. The binding energy was 1.1 Kcal/mol/H_2. Then the binding energy per hydrogen molecule was plotted with respect to the number of the H_2 molecules. As can be seen from Fig. 3b the binding energy decays exponentially. This result has to be considered together with the geometrical constrains i.e. the space around the K atoms has a maximum number of H_2 molecules that can be introduced without having steric interactions. From this graph we can estimate the amount of the H_2 molecules that can be attached to a doped tube according to the temperature that plays the role of the energetic cut-off.

For the second question (why the doped tubes have larger hydrogen uptake?) we have to understand the nature of the H_2 interaction with the pure carbon and the alkali-doped nanotubes. In the case of the doped tube there is a charge transfer from the alkali metal to the tube. This charge was calculated by Mulliken population analysis to be 0.6 |e| for the K doped tube. The positively charged K atoms polarize the H_2 molecules. Even though there is no charge transfer from the H_2 to the K the charge induced dipole interaction gives the character of the bonding (Fig. 3c). In the case of the pure tube, where the H_2 interaction was calculated for comparison, there is neither charge transfer nor polarization of the H_2 molecule and these result in an extremely weak interaction, under the accuracy of our theoretical level.

Comparing our results with previous work for atomic hydrogen we can see *physisorption* of the molecular hydrogen to doped or not SWNT's while for the atomic hydrogen we have *chemisorption*. There is in agreement of our QM/MM results and the semi-empirical results of Dubot and Cenedese [20] indicating that the alkali metal is responsible for the adsorption of molecular hydrogen to doped tubes. Nevertheless they predict adsorption energy of 11.5 kcal/mol [20], while we found it 3.4 kcal/mol. The fact that we use K while they use Li for doping the tube is not explaining this large difference, which is probably due to empirical nature of their calculations. In addition, the explanation that the alkali metal act as a catalytic active center for the H_2 dissociative adsorption proposed by Chen *et al.* [9] doesn't seem very possible since the alkali metal – H_2 interaction is very weak to cause H_2 dissociation.

4. CONCLUSIONS

In this paper we review the existing *ab-initio* literature of atomic and molecular hydrogen interaction with carbon nanotubes. Specifically for the hydrogen adsorption, it is showed that the mixed QM/MM model can successfully be employed and provide a solution to the problem of making accurate calculations in large systems like Nanotubes. The results demonstrate that atomic hydrogen 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 will result an enlargement of the tube volume. After the tube walls are half field with hydrogens, the energetically more favorable procedure of hydrogen insertion in the tube is obtained.

Since the storage capacity is mostly obtained by molecular hydrogen, it is essential to answer the question why Alkali-doped carbon nanotubes poses high hydrogen uptake, forward by Chen *et al.* in 1999 [9]. Our results demonstrate a charge transfer from the alkali metal to the tube that polarizes the H_2 molecule. This charge induced dipole interaction characterize the H_2 physisorption on alkali metal doped tubes and is responsible for the higher hydrogen uptake of the doped tubes.

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