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Why Alkali-Metal-Doped Carbon Nanotubes Possess High Hydrogen Uptake

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ABSTRACT

A mixed quantum mechanics/molecular mechanics (QM/MM) model is used for investigating the nature of molecular hydrogen adsorption in pure and alkali-metal-doped single-walled carbon nanotubes (SWNTs). Our results demonstrate that 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.

Hydrogen has been recognized as an ideal energy carrier but has not been used yet. 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 past few years, single-walled carbon nanotubes, which have diameters of typically a few nanometers, have been suggested as suitable materials for gas storage.[1,2] But very soon it was also clear that pure carbon nanotubes do not present sufficient storage capacity for commercial use.

Since 1999, when Chen et al.[3] reported that alkali-metal-doped carbon nanotubes possess high hydrogen uptake, a lot of experimental work has been performed to investigate the hydrogen adsorption in SWNTs and to improve the storage capacity of the tubes by doping them.[4,5] An extended review appeared recently by Ding et al.[6] 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 affects badly both the understanding of the nature of these materials and the improvement of their storage capacity that end up in a random procedure.

All the previous theoretical calculations, as reported in a short review by Meregalli and Parrinello,[7] can be divided in two categories. Either they are empirical[8−11] or they are based on first principle methods but deal only with atomic hydrogen.[12−15] The first category cannot give an understanding of the elementary steps in the adsorption process. Since these methods are not ab initio but are based on parameters, they are not able to give insight into 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 there are no ab initio studies of the H_2 interaction with SWNTs is obvious. The interaction is weak and the system is large.

Our aim in this work is to investigate the nature of the H_2 adsorption in alkali-doped SWNTs and to compare it with the adsorption in pure SWNTs. Only in this way can we answer the question "why do alkali-metal-doped carbon nanotubes have high H_2 uptake?". To compromise the large size of the system together with an accurate ab initio method without ending up in a prohibitively large calculation, we apply a quantum mechanics/molecular mechanics (QM/MM) mixed model. The QM/MM model has been successfully used before for studying the interaction of atomic H[13−15] and F[13] with SWNTs.

The bulk of our calculations was performed at the density functional level of theory. The three-parameter hybrid functional of Becke using the Lee−Yang−Parr correlation functional[16] (B3LYP) was employed for the QM part. The atomic basis set that we use includes Gaussian functions of double-ζ quality augmented by d-polarization functions (6-31G*). The MM part was treated with the universal force field (UFF).[16] This two-level approach combines the high accuracy of the ab initio treatment in the QM part of the tube 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. The combination of methods and basis set (B3LYP/6-31G*: UFF) has already worked out in similar problems.[13−15] Furthermore, since the H_2 interaction with the tube was weak, we tested our methodology by performing single-point energy calculations with the second-order Moller−Plesset perturbation theory (MP2) at the B3LYP-optimized geometries (MP2/6-31G*//B3LYP/6-

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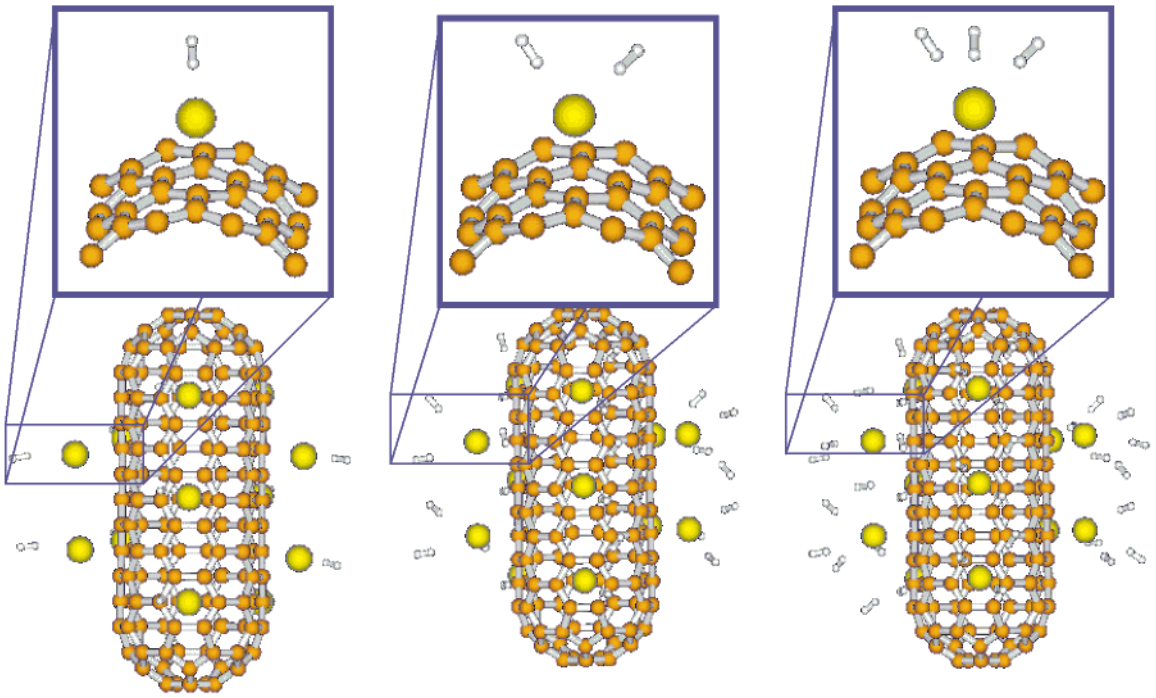

Figure 1. Three of the alkali-metal-doped (5,5) SWNT's that we used to study the interaction with molecular hydrogen. The first has one H_2 per K, the second two, and the third three. A magnifying part of all pictures is also presented.

Table 1. Energetic and Structural Characteristics for All the Different Cases of Molecular Hydrogen Adsorption in K-doped (5,5)-Carbon Nanotube

no. of H_2	E_{bind}/H_2 (kcal/mol)	d[K−C_{hex}] (Å)	d[K−H_2] (Å)
1	3.4	3.0	3.0
2	2.5	3.0	3.3
3	1.8	3.0	3.5
5	1.1	3.0	3.8

31G*), and the results were consistent. All the computations were performed with the Gaussian 98 program package[16] and under the ONIOM[17] two-level approach.

The system we chose was a closed (5,5) SWNT with 150 carbon atoms. K atoms dope the tube in a "2 × 2" pattern, as suggested by Gao et al.[18] 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 K, all the neighboring ones do not (Figure 1). A geometry optimization confirmed that these positions were optimum for our model, too. In the QM region we kept 24 carbon atoms, 2 K atoms, and all the H_2 molecules that were interacting with these two K atoms, while the rest were treated by MM.

The first case we consider (Figure 1 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. 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, as can be seen in Table 1. In the next case (Figure 1, middle) two hydrogen molecules were interacting with each K, and finally three (Figure 1 right). The binding energies (Table 1) were

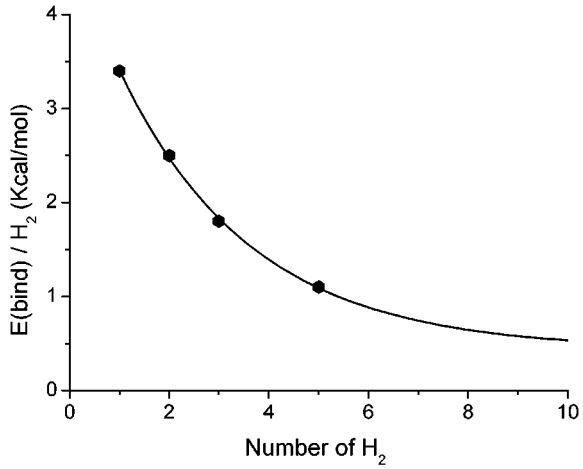

Figure 2. Binding energy per hydrogen molecule with respect to the number of the H_2 molecules. The hexagons represent the calculated values where the line was fitted.

2.5 and 1.8 (kcal/mol)/H_2, respectively. The H_2 distance from the K was found to be 3.3 and 3.5 Å, while the K−tube distance remained the same (3.0 Å).

From these results we can clearly see that at least three hydrogen molecules can be bound to each K atom of a doped tube even though the binding energy is consistently decreasing. The two questions that immediately arise are: How many H_2 can be accommodated to each alkali metal of the doped tube? And why do the doped tubes have larger hydrogen uptake that the pure carbon nanotubes?

For answering the first question we also calculate 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 we plotted the binding energy per hydrogen molecule with

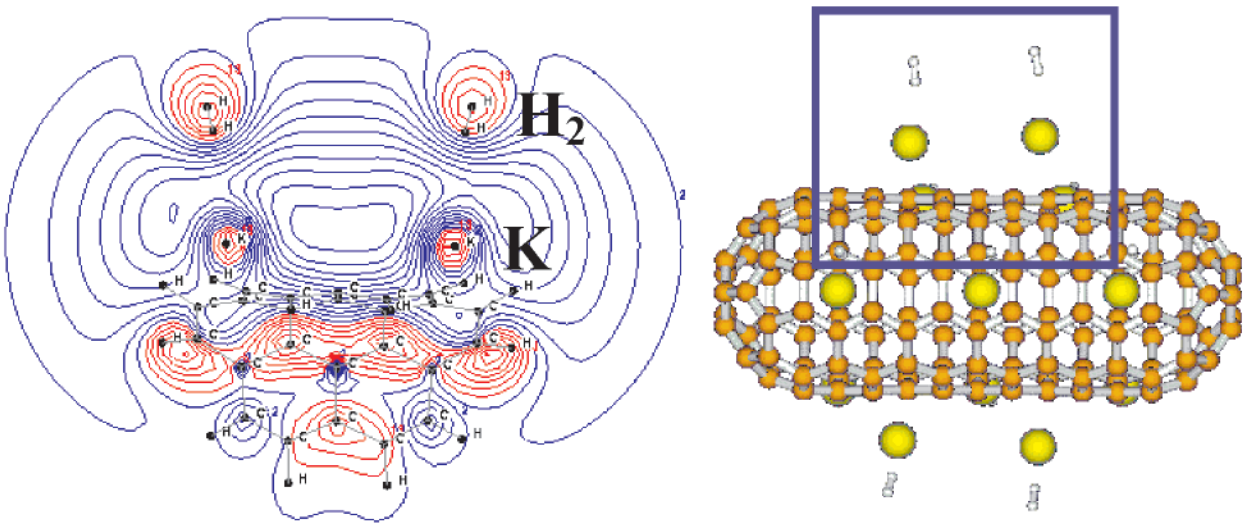

Figure 3. Constant amplitude contours presenting the HOMO of the (5,5) K-doped SWNT with one H_2 per K atom. The plotted area is also marked on the entire tube.

respect to the number of the H_2 molecules. As can be seen from Figure 2 the binding energy is exponentially decay. 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 cutoff.

For the second question we have to understand the nature of the H_2 interaction with the pure and the alkali-metal-doped carbon 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 (Figure 3). 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,[13−15] we can see a physisorption of the molecular hydrogen to doped or not SWNT's, while for the atomic hydrogen we have a chemisorption. In addition, the explanation that the alkali metal acts as a catalytic active center for the H_2 dissociative adsorption proposed by Chen et al.[3] does not seem very possible since the alkali metal−H_2 interaction is very weak to cause a H_2 dissociation.

Summarizing, our work clearly shows that a mixed QM/MM model can successfully be employed to SWNT's and provide a solution to the problem of making accurate calculations in large systems like nanotubes. 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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