Hydrogen interaction with carbon nanotubes: a review of *ab initio* studies

TOPICAL REVIEW

Hydrogen interaction with carbon nanotubes: a review of *ab initio* studies

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Abstract
In this paper we review the existing theoretical literature on hydrogen storage in single-walled carbon nanotubes. The importance of theoretical simulations for understanding the adsorption procedure and for improving the storage capacity of these nano-materials is underlined. We report two different categories of theoretical approach used for this purpose, i.e. classical modelling and *ab initio* calculations. For both, advantages and disadvantage are listed. For the *ab initio* simulations in particular, we present an analytical overview that gives insight into the storage procedures in different cases.

Contents

1. Introduction

Hydrogen has been recognized as an ideal energy carrier but has not been used as such yet to any great extent. One of the major problems is the difficulty of achieving efficient storage. In the beginning, metal alloys were tested for use as storage tanks but even though they have sufficient storage capacity, they are expensive and heavy for commercial production focused

on mobile applications. In recent years, carbon-based materials have attracted attention due to the discovery of novel carbon nano-materials like fullerenes, nanofibres, and nanotubes [1–3]. In particular, single-walled carbon nanotubes (SWNTs), which have diameters of typically a few nanometres, have been suggested as suitable materials for gas storage [4]. Since pores of molecular dimensions can adsorb large quantities of gas, hydrogen can condense to high density inside narrow SWNTs even at room temperature [5]. The high hydrogen uptake of these materials suggests that they could be used as hydrogen-storage materials for fuel-cell-powered electric vehicles [6–8].

2. A brief experimental overview

A lot of recent experiments have investigated the hydrogen storage in SWNTs. First, in 1997, Dillon *et al* [4] reported that SWNTs could store hydrogen. Using temperature-programmed desorption (TPD) spectroscopy 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* [5] found that this storage can take place at room temperature. They used SWNTs of 1.85 nm diameter, synthesized by a semi-continuous hydrogen arc discharge method, and found a storage capacity of 4.2 wt% at room temperature and under modestly high pressure. 78.3% of the adsorbed hydrogen can be released under ambient pressure and at room temperature.

In the same year, Chen *et al* [9] reported that alkali-doped carbon nanotubes show high hydrogen uptake. They investigated lithium- and potassium-doped carbon nanotubes and found hydrogen absorption of 14–20 wt% between 400 °C and room temperature. These values are higher than those for 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.

Subsequently a lot of experimental work was performed to investigate the hydrogen adsorption in SWNTs and with the aim of improving the storage capacity of the tubes by doping them [10–17]. However, experiments on hydrogen storage in nanotube samples have been controversial, as reported in the recent review by Ding *et al* [8].

3. The need for theoretical modelling—problems and solutions

On the other hand, until recently, there was no adequate theoretical explanation of the hydrogen adsorption in SWNT, only guesses about this procedure. This has adversely affected both the understanding of the nature of these materials and the improvement of their storage capacity— that has ended up being a random procedure. Theoretical modelling has become crucial, because even though the experiments can inform us *what* is happening, only theory allows us to find out *why* it is happening and what will happen in similar conditions. A short review on the theoretical calculation of hydrogen storage in carbon-based materials can be found in [18].

As regards hydrogen adsorption in carbon nanotubes, theoretical calculations can be extremely useful for understanding the elementary steps of the adsorption procedure and give insight into the phenomenon. The theoretical simulations in this field can be generally classified into two categories according to the theoretical approximation that they are based on. The first group employs Monte Carlo and molecular mechanics (MM) *classical* algorithms in order to investigate the physisorption of hydrogen in SWNTs, while the second uses *ab initio* or semi-empirical *quantum* techniques for studying mainly the chemisorption of atomic hydrogen in SWNTs.

4. Classical simulation of hydrogen physisorption in carbon nanotubes—a brief overview

First Darkrim and Levesque at late 1998, using a Lennard-Jones potential, performed a grand canonical Monte Carlo simulation of hydrogen storage in a cell of SWNTs and investigated the influence of the tube diameter on the storage capacity [19]. They found that adsorption decreases as the SWNT diameter increases due to the fact that a large part of the volume inside or outside the tube is out of the attractive force range of the solid–gas interaction. They also note the dependence of their results on the intermolecular potential used for the hydrogen–carbon interaction. This is the major disadvantage of classical simulations and shows the need for *ab initio* calculations in the field.

In 1999, Johnson and co-workers using the Silvera–Goldman potential for the H_2–H_2 interaction and the Crowell–Brown potential the H_2–tube interaction studied the hydrogen adsorption in neutral [20] and positively and negatively charged [21] SWNTs. Their results show that idealized graphitic nanofibres (slit pores) give significantly better performance for hydrogen storage than SWNT arrays. They also underline the importance of the packing geometry of the SWNTs in the storage capacity. In addition, a 0.1 e/C charging of the nanotubes increases the adsorption up to 30%.

In the year 2000, Williams and Eklund [22] simulated the H_2 physisorption in finite-diameter carbon nanotube ropes using grand canonical Monte Carlo simulation. Their simulation clearly shows that small-diameter ropes are preferable for hydrogen storage. They also point out an essential difference between models and experiments that has to do with the ideal and 'atomically clean' surface of the tubes in the simulation.

The great advantage of these classical approaches (in addition to the luxury of being able to take into account large systems) is the temperature dependence of the simulations. On the other hand, they are parameter dependent and they cannot provide insight into the chemical bond, as the *ab initio* methods do.

5. Quantum approaches

From 2001 the *quantum picture* was introduced into the molecular dynamics study of hydrogen in SWNTs either by quantum molecular dynamics algorithms [23] or by minimal *ab initio* calculations in parts of classically optimized tube geometries [24]. In the first case, Cheng *et al* [23] using the Vienna *ab initio* simulation package performed a quantum mechanical molecular dynamics simulation of H_2 absorption in a trigonal two-dimensional lattice of armchair (9, 9) SWNTs. The potential energy surface near the equilibrium point was found to be relatively flat, and significant changes of the lattice constants (>0.5 Å) resulted in only small changes in the lattice energy (<1 kcal mol^{-1}). Cheng *et al* [23] also investigated the site selectivity during the adsorption, since arrays of SWNTs with open ends may accommodate hydrogen inside the tube (endohedral adsorption) or inside the pores formed by different tubes (exohedral adsorption). According to their thermodynamical studies, the exohedral adsorption is energetically more favourable.

On the other hand Ma *et al* [24] first used a many-body Tersoff–Brenner potential to simulate low-energy collision of atomic H on the side-wall of an armchair (5, 5) SWNT. In addition to this, they performed minimal HF/STO-3G *ab initio* calculations on some selected snapshots of the molecular dynamics simulations. The interesting part of their work is the sorting of the collision results with respect to the hydrogen energy. Their results indicate that if the hydrogen energy is in the range 1–3 eV, the H will be adsorbed in the tube side-wall, while for energy between 4 and 14 eV, the H has a large probability of rebounding off the wall. With energy in the interval 16–25 eV, the hydrogens have a high probability of penetrating into

the tube and being trapped inside, forming hydrogen molecules and gradually condensing to produce liquid hydrogen inside the tube. Finally, for the energy range from 20 to 30 eV the H atom can enter the tube from one side and escape from the other or break a C–C bond [24].

Since only quantum chemistry calculations can give insight into the interaction of hydrogen with SWNTs, Dubot and Cenedese [25] used semi-empirical AM1 simulations to obtain the binding sites, energetics, and orbital pictures of lithium and molecular hydrogen adsorption in SWNTs. They found that Li can adsorb inside and outside a zigzag tube and that the most stable site is above the centre of a tube hexagon. After the Li adsorption, molecular hydrogen can be bound to the Li atom with a binding energy of 0.5 eV. Their AM1 calculation showed also that molecular hydrogen is repelled from the tube wall if the tube is not doped [25].

In 1999, Jeloaica and Sidis [26] used density functional theory (DFT) to investigate hydrogen adsorption on a graphitic cluster model, but it was only in 2000 that first-principles calculations of the hydrogen adsorption in SWNTs appeared in the literature [27–32].

The main reason that *ab initio* calculations for SWNTs have appeared only lately is the system size. In order to take into account a large enough model of a SWNT, you need approximately 200 atoms. The problem that arises in such an attempt is how to treat a large enough system using an accurate enough *ab initio* method without ending up with a prohibitively large calculation.

Up to now, there have been two different ways to deal with this dilemma. The first is to use the periodicity of the SWNTs and combine an *ab initio* method with periodic boundary conditions [27, 28]. The second is to use a two-level quantum mechanics/molecular mechanics (QM/MM) approach [29–32]. In the latter, the tube is divided into two different parts treated with different methods. The advantage of the former is that the total system is treated with *ab initio* techniques, while the obvious disadvantage is that an external periodicity is forced on the system. For the QM/MM model there is no periodic constraint. The disadvantage is that only a relatively small part of the system is treated quantum mechanically, while the rest is used for constraining the boundaries. In addition, both approaches have the disadvantage of excluding temperature from the calculations.

6. Atomic hydrogen interaction with carbon nanotubes

6.1. Periodic DFT models

Hydrogen chemisorption in SWNTs has been studied with both quantum chemistry models that we described earlier. Lee and Lee [27] first employed the periodic DFT approach for studying chemisorption sites of atomic hydrogen outside and inside a (5, 5) and a (10, 10) SWNT. They used supercells of eight layers along the tube axis and their results are presented in figure 1. Their periodic DFT calculations showed two hydrogen chemisorption sites in SWNTs. Both are *top* positions, inside (figure 1(*b*)) and outside (figure 1(*d*)) the tube walls. They predict also that hydrogen molecules can exist in the empty space inside the nanotube. The maximum storage capacity is mainly determined by the steric interaction between the H_2 molecules and between the H_2 and the tube wall. As a result, the capacity increases linearly with the tube diameter. Excessive hydrogen storage will result in large repulsion energies and eventually break down the tube wall [27].

6.2. QM/MM mixed models

The QM/MM mixed model has been employed for studying the hydrogen interaction with SWNTs by Bauschlicher [29, 30] and Froudakis [31]. In this approach the total system is divided into two different sections: the inner part that is treated with an accurate quantum chemistry method and the outer part where a MM force field is employed (figure 2). This
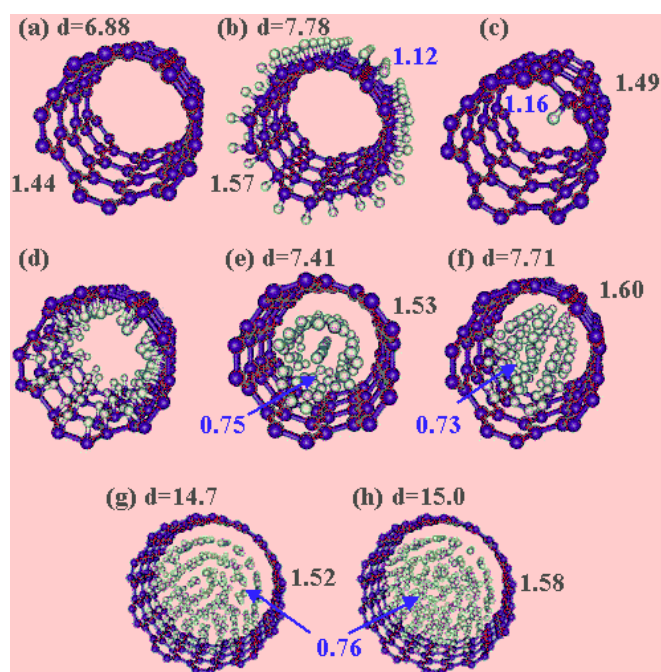
Figure 1. The calculations of Lee and Lee [27] for the chemical adsorption of H in SWNTs: (*a*) the (5, 5) SWNT before the storage; (*b*) hydrogens adsorbed on the outside of the tube wall; (*c*) adsorption of a single hydrogen atom on the inside of the wall; (*d*) the initial geometry; (*e*) the fully relaxed version of geometry (*d*); (*f*) molecular hydrogen inside the (5, 5) SWNT; (*g*) H_2 inside the (10, 0) SWNT with an allocation of two H per C atom and with 2.4 H per C atom (*f*). Bond lengths are in Å.
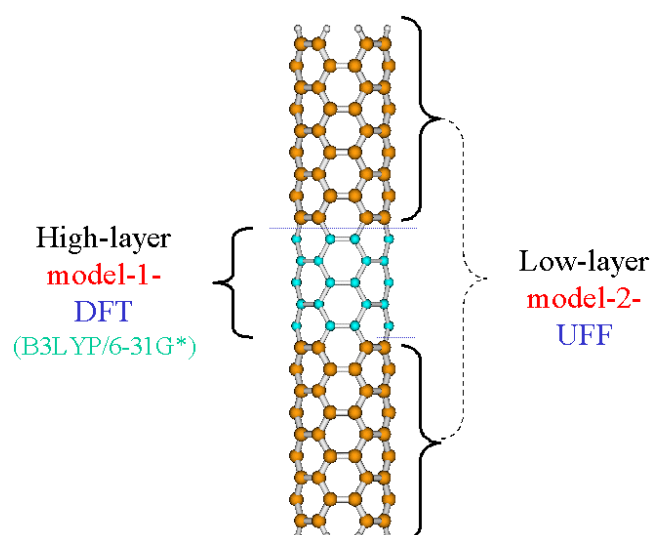

Figure 2. One of the QM/MM models simulating a (4, 4) SWNT that was studied in [31]. The total 200-atom tube was separated into three cylindrical parts. The inner one was treated with DFT (40 blue carbon atoms) while the two outer parts were treated using MM (brown carbon atoms). The dangling bonds at the ends of the tube were saturated with hydrogen atoms.

two-level approach combines the high accuracy of the *ab initio* treatment of the inner part of the tube where the interaction with hydrogens will take place with the relaxation accuracy that the large size of the tube guarantees.

Bauschlicher use a (10, 0) carbon nanotube for studying the hydrogen and fluorine binding to its wall [29] and for examining the maximum coverage of the tube wall [30]. The entire model uses 200 carbon atoms while the *ab initio* section includes 24 carbon atoms. The ONIOM two-level method of Morokuma and co-workers [32] was used for this purpose as it is implemented in the GAUSSIAN 98 program package [33]. The higher level was treated with DFT while the lower level was treated using MM. More specifically, the B3LYP hybrid functional together with the 4-31 G basis set was employed for the QM part and the universal force field (UFF) for the MM part. The preferred sites for the chemisorption of one, two, and four hydrogen atoms in the tube walls are reported together with the binding energies [29].

In [31] we applied the QM/MM approach to a 200-atom (4, 4) SWNT, treating up to 64 carbons and 32 hydrogens with the higher level of theory (figure 2). The small diameter of the tube together with the large number of atoms considered allow the higher-level model to include a cylindrical part of the tube. This is critical for investigating the changes of shape of the tube during the adsorption procedure.

In figure 2, we can see the two-level ONIOM [32] model that was used in [31]. The B3LYP functional was employed for the inner part of the tube, like in [29, 30]. However, a larger set with a double-ζ basis was employed (6-31 G*) that includes polarization functions. The two outer cylindrical parts were treated using 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 program package [33].

These studies [29–31] are mainly trying to answer two questions: the first concerns the coverage of SWNTs by hydrogen atoms and the second deals with the difficulty of putting hydrogen atoms inside the tube. From the work of Bauschlicher [29] and Froudakis [31] it is clear that the hydrogen atoms that approach the SWNT will be bound to the tube walls in neighbouring C atoms to minimize 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 another is to follow an armchair ring normal to the tube axis. First-principles calculations [31] showed that the second procedure is energetically more favourable, as has also been found experimentally for similar systems [10].

Furthermore, it is interesting to see the effect of the two different hydrogen chemisorption patterns mentioned before on the shape of the tube walls. In figure 3 we can see the optimized structures with 64 C and 16 H atoms in the QM region from [31]. The C atoms that hydrogens are bonded to pass from sp^2 to sp^3 hybridization. This affects the bond lengths and the sizes of the tube hexagons drastically. The C–C bond length increases from 1.43 Å to 1.59 Å while the diameter of the hexagons goes from 2.84 Å to 3.15 Å if four hydrogen atoms are attached in this hexagon (figure 3(*b*)). 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 circular to elliptic (figure 3(*a*)). The 5.4 Å diameter of the tube without hydrogens splits into a 4.1 Å small diameter and a 7.2 Å large diameter of an ellipse. 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 circular shape (figure 3(*b*)). The second orientation is more favourable because the strain can be relaxed with the enlargement of one ring, which does not affect the whole tube, while in the first case, an axial enlargement of the tube cannot take place in only 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.
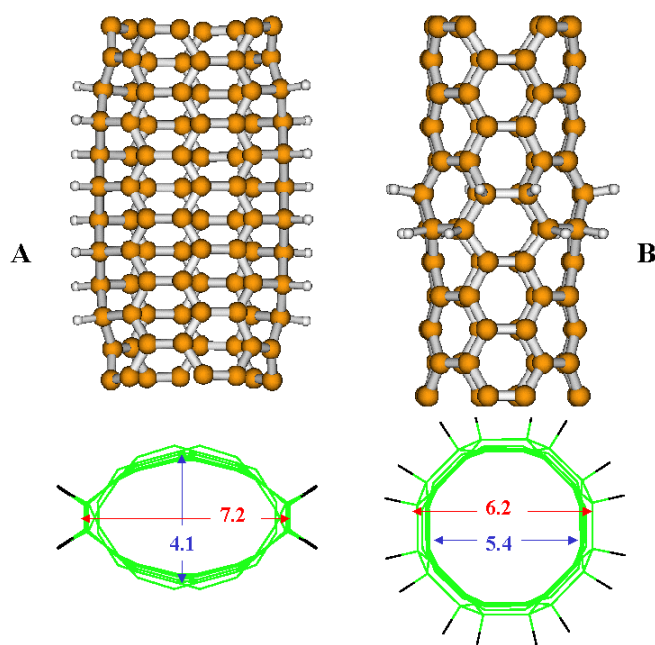
Figure 3. Optimized geometries from [31] showing 16 hydrogen atoms bonded in the tube in two different ways: (A) following two zigzag lines parallel to the tube axis; and (B) following an armchair ring normal to the tube axis. In the lower part of the figure we see the tube flattened toward its axis and we report the change in its diameter in Å (from [31]).

Since the hydrogens 'prefer' to form rings around the tube, the next question that arises is that of how close these rings can be. To answer this question, in [31] 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 figure 4(*a*) (middle and upper right parts respectively). After optimizing the geometries, the separated configuration showed repeated increasing and decreasing of the tube diameter by 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 in the last ring. The total energy of the 'ring by ring' configuration was favoured energetically above the 'all rings together' configuration by 17 eV.

This energy difference can be explained on the basis of 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 three-dimensional bond orientation is preferred. This three-dimensional orientation can be obtained by continued changing of the tube diameter in the 'ring by ring' configuration. In this case the tube wall is not flattened towards the tube axis but shows a zigzag shape (figure 4(*a*)—middle). In the case of the 'all rings together' configuration, the tube wall changes shape only at the beginning and at the end, while in between it stays flat (figure 4(*a*)—right). The flat wall shape that was favoured when the carbon atoms had sp^2 hybridization is not favoured after hydrogen adsorption, because the carbon atoms have changed in hybridization to sp^3. Extending this configuration to an infinite atom tube will lead to 50% coverage, since one C-zigzag ring has hydrogens and the next does not, periodically. This scenario will cause a 15% enlargement of the tube volume (half of the rings gain 30% in volume).
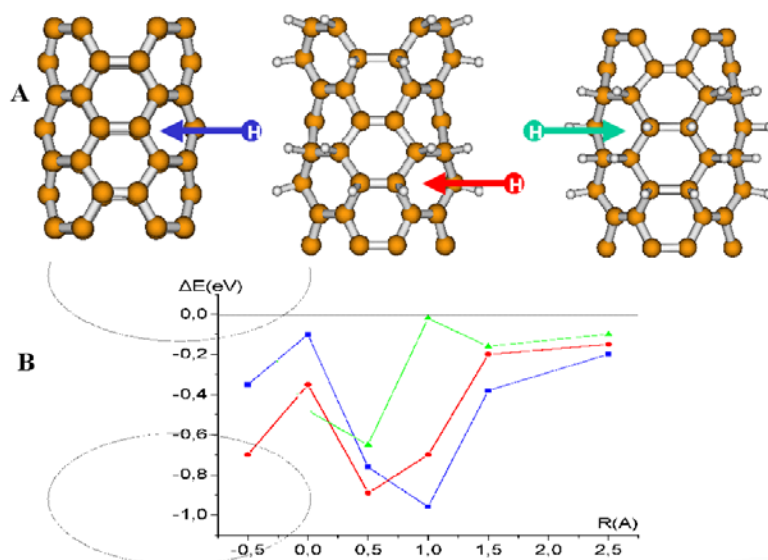
Figure 4. (A) Optimized geometries [31] of 32 hydrogen atoms bonded in the tube in two different ways: the 'ring by ring' configuration (in the middle) and the 'all rings together' configuration (on the right), as analysed in the text. The geometry of the tube without hydrogens is also plotted for comparison (on the left). (B) Potential curves during the hydrogen approach to the three different carbon nanotubes shown in A (SWNT with no hydrogen atoms on its walls: blue line; SWNT with walls half-covered with hydrogens: red line; SWNT with walls covered with hydrogens: green line). Also taken from [31].

　　　Bauschlicher [30] also reported 50% hydrogen coverage in a (10, 0) SWNT. He tested, with the ONIOM approach, a lot of random and prefixed bonding configurations of the hydrogen in the tube walls. The 'pairs of lines' configuration is presented in figure 5 and found to be energetically more favourable. This result is not in disagreement with the previous description of a (4, 4) SWNT by Froudakis [31] since the (10, 0) tube is significantly larger than the (4, 4) tube, and the curvature was found to play an important role in the adsorption procedure for SWNTs [34–36]. Furthermore, Froudakis did not make calculations for a 'pair of lines' configuration in the (4, 4) SWNT.

　　　The second question that we tried to answer in [31] is that of what happens after the adsorption of hydrogens on the tube walls. Is it easier to fill up the tube with hydrogens? In figure 4(b) we report the potential curves when atomic hydrogen approaches the centre of three tube-wall hexagons which differ only in adsorption rate. The first has no hydrogens, the second is half-filled with hydrogens, and the third is full of hydrogens. Analysing these potential curves, we see two competing forces in the approach procedure. On one hand, it is clear that the more hydrogen we have in the C hexagon, the larger the hexagon is, and the easier it is for the H to emerge. This can be easily observed from 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 fully hydrogenated hexagon, inserts a barrier to the emerging hydrogen at a distance of 1 Å from the tube wall (where the bonded hydrogens are actually located). As a result of this, the most energetically favourable 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 by steric repulsion of the bonded hydrogens, while in the entrance to the tube wall the barrier is smaller by almost 0.3 eV than in the case of the bare tube.
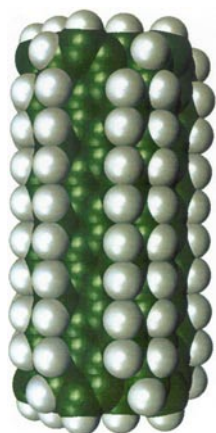
Figure 5. The most stable configuration for 50% hydrogen coverage in a (10, 0) SWNT calculated by Bauschlicher (from [30]).

Comparing the QM/MM results of Froudakis [31] with those of Seifert *et al* [28] and Kudin *et al* [37] obtained with periodic boundary condition models, we find an agreement concerning the stoichiometry (C: 2; ligand: 1) and the deformation of the tube that takes place during the adsorption. Nevertheless, there is disagreement about the ligand orientation around the tube wall that could be a consequence of the different approaches used (QM/MM versus periodic box) and/or of the different ligands (H versus F) and/or of the different tubes examined ((4, 4) versus (10, 10) that has almost double the diameter).

7. Molecular hydrogen interaction with alkali-metal-doped carbon nanotubes

Since 1999, when Chen *et al* [9] reported that alkali-doped carbon nanotubes show high hydrogen uptake, a lot of experimental work has been performed investigating the hydrogen adsorption in SWNTs and attempting to improve the storage capacity of the tubes by doping them [12]. On the other hand, there was no adequate theoretical explanation of this phenomenon.

All the theoretical calculations reported so far can be divided into two categories. Either they are empirical [19–25] or they are based on first-principles methods but deal only with atomic hydrogen [26–31]. 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 insight into the chemical bond. The first-principles methods can, but they deal only with atomic hydrogen, while the most important interaction for the storage, which is the interaction of molecular hydrogen with SWNTs, remains untouched. The reasons that *ab initio* studies of the H_2 interaction with SWNTs have not been made are obvious: the interaction is weak and the system is large.

In [38] 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. Only in this way is it possible to answer the question 'why do alkali-doped carbon nanotubes have high H_2 uptake?' In order to have a large enough system together with an accurate enough *ab initio* method without ending up with a prohibitively large calculation, we applied the QM/MM mixed model as described earlier [31] to 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* [39]. In this pattern the K atoms were placed at 'hollow' positions above
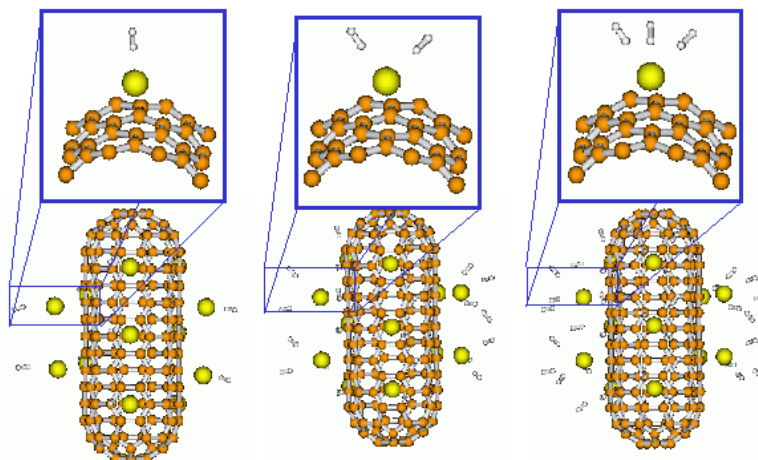
Figure 6. Three of the alkali-metal-doped (5, 5) SWNTs that were used by Froudakis [38] to study the interaction with molecular hydrogen. The first has one H_2 per K, the second two, and the third three. A magnified view of a part of each picture is also presented.

the centres of the C hexagons of the tube in such a way that if one hexagon has a potassium, all the neighbouring ones do not (figure 6). 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 using MM.

The first case considered (figure 6, 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 and the K was 3.4 kcal mol^{-1}/H_2. The distance of the K atom from the centre of the C_6 hexagon of the tube was 3.0 Å, and the distance of the closer H of the H_2 molecule from the K was 3.0 Å, too. In the next case (figure 6, middle), two hydrogen molecules were interacting with each K, and finally there were three (figure 6, right). The binding energies were 2.5 and 1.8 kcal mol^{-1}/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 it is clear that at least three hydrogen molecules can bond to each K atom of a doped tube even though the binding energy consistently decreases with the number of ligands. The two questions that immediately arise are: how many H_2 can be accommodated by each alkali of the doped tube and why do the doped tubes have larger hydrogen uptake than the pure carbon nanotubes?

To answer the first question we also made calculations in [38] for the case where five H_2 molecules were attached to each K of the doped tube. The binding energy was 1.1 kcal mol^{-1}/H_2. Then the binding energy per hydrogen molecule was plotted with respect to the number of H_2 molecules. As can be seen from figure 7, the binding energy decays exponentially. This result has to be considered together with the geometrical constraints, i.e. the space around the K atoms has a maximum number of H_2 molecules that can be introduced without there being steric interactions. From this graph we can estimate the number of H_2 molecules that can be attached to a doped tube according to the temperature that plays the role of the energetic cut-off.

In order to answer the second question (that of 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
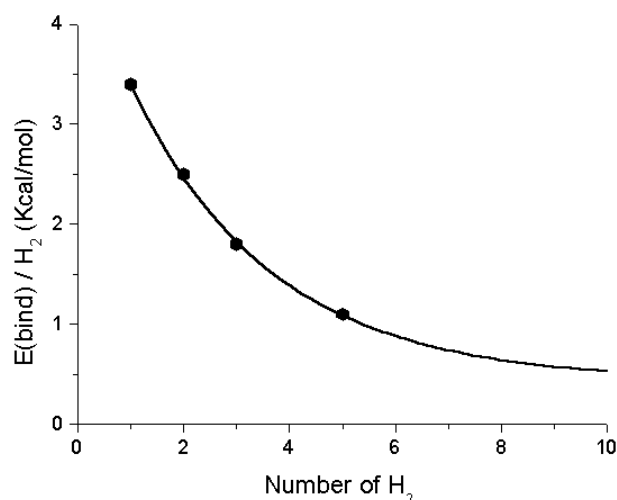
Figure 7. Binding energy per hydrogen molecule with respect to the number of H_2 molecules. The hexagons represent the calculated values where the line was fitted (from [38]).
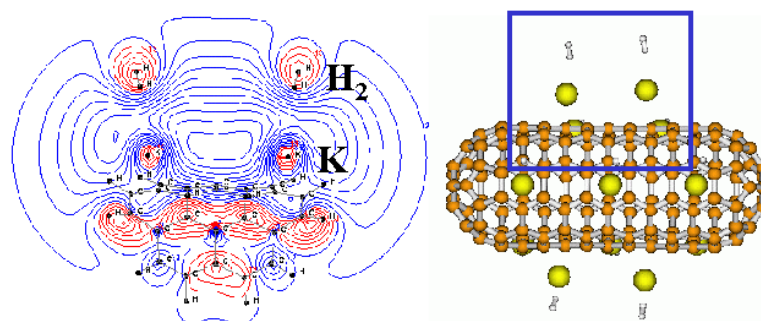

Figure 8. Constant-amplitude contours representing the HOMO of the (5, 5) K-doped SWNT with one H_2 per K atom. The area plotted is also marked on the whole tube (from [38]).

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 [38]. 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 8). 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, below the accuracy at our theoretical level.

Comparing these results [38] with previous work on atomic hydrogen, we can see *physisorption* of the molecular hydrogen to doped or undoped SWNTs, while for the atomic hydrogen we have *chemisorption*. There is agreement of our QM/MM results [38] and the semi-empirical results of Dubot and Cenedese [25], indicating that the alkali metal is responsible for the adsorption of molecular hydrogen onto doped tubes. Nevertheless, Dubot and Cenedese predict an adsorption energy of 11.5 kcal mol^{-1} [25], while we found it to be 3.4 kcal mol^{-1} [38]. The fact that we use K while they use Li for doping the tube does not explain this large

difference, which is probably due to the empirical nature of their calculations [25]. In addition, the explanation that the alkali metal acts as a catalytically active centre for the H_2 dissociative adsorption proposed by Chen *et al* [9] does not seem very plausible, since the alkali metal–H_2 interaction is very weak to cause a H_2 dissociation.

8. Conclusions

In this paper we review the existing theoretical literature on hydrogen storage in SWNTs. The importance of theoretical simulations for understanding the adsorption procedure and for improving the storage capacity of these nano-materials is underlined. We report two different categories of theoretical approach used for this purpose, i.e. classical modelling and *ab initio* calculations. The first deals with molecular hydrogen physisorption into the tube and has the advantage of the temperature dependence of the simulations. The second concerns mostly atomic hydrogen chemisorption into the tube walls and has the advantage of showing the nature of the interaction, which the quantum mechanical calculation guarantees.

Summarizing, it is shown that both periodic DFT and mixed QM/MM models can be successfully employed to address SWNT and provide a solution to the problem of how to make accurate calculations for large systems like nanotubes. The results of Bauschlicher [30] and Froudakis [31] demonstrate that atomic hydrogen will bind to the tube walls and not enter the tube interior. This binding can take place either in pairs of lines flattened toward the tube axis, as the former results suggest, or in zigzag rings around the tube walls, supported by the latter results. This will result in a changing of the tube shape during the hydrogen adsorption and an enlargement of the tube volume [31]. Both set of results indicate 50% to be the maximum coverage of the tube walls. After the tube walls are half-covered with hydrogens, the energetically more favourable procedure of hydrogen insertion in the tube is obtained [31].

Since the storage is mostly of molecular hydrogen, Froudakis [38] tried to answer the question of why alkali-doped carbon nanotubes show high hydrogen uptake (posed by Chen *et al* [9]). His results demonstrate a charge transfer from the alkali metal to the tube that polarizes the H_2 molecule. This charge-induced dipole interaction characterizes the H_2 physisorption on alkali-metal-doped tubes and is responsible for the higher hydrogen uptake of the doped tubes.

Closing this review, we can conclude that in the last couple of years the theoretical modelling of the hydrogen storage in carbon nanotubes has achieved only its first goal, i.e. of providing an understanding of what is going on in the laboratory experiments by explaining the elementary parts of the adsorption procedure. The second and most important goal, that is still to be achieved, is that of predicting how the storage capacity of carbon nanotubes can be improved and achieving a sufficient level for commercial use in fuel-cell-powered electric vehicles.

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