Interaction of molecular and atomic hydrogen with single wall carbon nanotubes

J.A. Alonso ^{a,b}, J.S. Arellano ^c, L.M. Molina ^d, A. Rubio ^b, and M.J. López ^a

a. Departamento de Física Teórica, Universidad de Valladolid, E-47011, Valladolid, Spain b. Donostia International Physics Center, 20018 San Sebastián, Spain

c. Area de Física Atómica Molecular Aplicada, Universidad Autónoma Metropolitana Azcapotzalco, 02200 México D.F., México

d. Institut of Physics and Astronomy, Aarhus University, DK-800 Aarhus C, Denmark

ABSTRACT

Density functional theory is used to study the interaction of molecular and atomic hydrogen with (5,5) and (6,6) single wall carbon nanotubes. Molecular physisorption is predicted to be the most stable absorption state, with the molecule at a distance of 5-6 a.u. from the nanotube wall. The physisorption energies outside the nanotubes are about 0.07 eV, and twice as large inside. This means that uptake and release of molecular hydrogen from nanotubes is a relatively easy process, as many experiments have proved. A chemisorption state with the molecule dissociated has also been found, with the H atoms much closer to the nanotube wall. However, this dissociative state is separated from the physisorption state by an activation barrier of 2 eV or more. The dissociative chemisorption weakens C-C bonds, and the concerted effect of many incoming molecules with sufficient kinetic energies can lead to the scission of the nanotube.

1. INTRODUCTION

The absorption of hydrogen by carbon materials, including nanotubes, has been investigated by several groups, but the reports on the absorption capacity are controversial ¹⁻⁵. Additional experiments on well controlled samples are required to resolve the discrepancies. Also, theoretical calculations have the potential of being very useful to understand the nature of the absorption and storage processes ⁶. Computer simulations of hydrogen absorption have been performed using effective model potentials to describe the interactions, but only first principles electronic structure calculations can give an accurate description of the interaction of hydrogen with carbon nanotubes and other graphitic materials.

The interaction of atomic hydrogen with single wall carbon nanotubes has been studied using the Density Functional Theory (DFT), and Gülseren and coworkers ⁷⁻⁹ found that the binding energy depends sensitively on the curvature of the nanotube. Although the chemisorption of atomic hydrogen is an important issue, the technologically relevant process is the absorption of molecular hydrogen. Early attempts of studying the absorption of molecular hydrogen on the nanotube walls failed because the Gradient Approximations employed to describe exchange and correlation between the electrons give a purely repulsive interaction potential between the closed shell molecule H₂ and the nanotube wall ¹⁰⁻¹², a prediction in disagreement with the experiments for adsorption on graphite pores, nanotube bundles and nanofibers. We have found that the Local Density Approximation (LDA) to exchange and correlation allows for an accurate unified treatment of the molecular and atomic absorption of hydrogen. Under normal conditions molecular physisorption is preferred. However if by energetic impact, or under high pressure, the H₂ molecules can approach sufficiently close to the nanotube wall, the molecules can dissociate and then atomic chemisorption becomes possible. The atomic chemisorption weakens substantially the C-C bonds.

2. COMPUTATIONAL METHOD

The calculations of the interaction between the hydrogen atom, or the hydrogen molecule, and the carbon nanotubes (or graphite) have been performed with the *ab initio* FHI96MD code¹³. The code uses a periodic supercell geometry and a plane wave expansion for the electronic wave functions. The $1s^2$ cores of the carbon atoms are replaced by the nonlocal norm-conserving pseudopotentials of Hamman et al.¹⁴⁻¹⁵. Below we present results for static calculations and dynamical simulations of the interaction of H and H₂ with (5,5) and (6,6) nanotubes. The supercell contains 20 carbon atoms in the case of (5,5) nanotubes, and 48 carbon atoms in the case of the (6,6) nanotubes. Several tests were performed to control the influence of the spacial cell dimensions and the cutoff of the plane waves basis. The results for nanotubes are complemented with the study of the interaction of H₂ with graphite.

3. PHYSISORPTION OF H₂ ON GRAPHITE AND NANOTUBES

The interaction potential between H₂ and a planar graphene layer is given in Figure 1. The calculations were performed maintaining frozen the bond length of the molecule at 1.48 a.u., the calculated bond length of the free molecule. This is a valid approximation, except at very close distances from the layer (a case that is studied in detail in Section 4 below). The deepest curve (A) represents the potential energy when the molecule approaches the graphene layer in a hollow position above the center of an carbon hexagon, with the molecular axis parallel to the layer plane. The other curve (B) is for the molecule on top of a carbon atom with the molecular axis perpendicular to the graphene layer.

Figure 1. Potential energy curves for the approach of H₂ to a planar graphene layer. The horizontal axis represents the distance between the center of mass of the molecule and the layer. The continuous curve represents the approach above the center of an hexagon, with the molecular axis parallel to the layer. The dashed curve stands for the approach above a carbon atom, with the molecular axis perpendicular to the layer.

The calculated binding energies are 0.070 eV (A) and 0.086 eV (B), respectively, and curves for other representative orientations lie in between those two plotted in the Figure¹⁶. In the first case (A), the distance from the center of mass

of the molecule to the layer is 5.1 a.u. The electron densities of pure graphene in a plane 5.1 a. u. above the layer are in the range $6-9 \times 10^{-5}$ e/a.u.³, so the H₂ molecule is in equilibrium in the tail of the graphene electron density. The binding is due to attractive exchange and correlation effects arising from the weak overlap between the electron densities of the graphene layer and the close-shell molecule. The graphene density is lower in the hollow sites above the hexagon centers, and these are the preferred positions for the molecule. Although the binding depends only weakly on the particular position (on top of an atom, bond or center of hexagon) and orientation of the molecular axis (parallel or perpendicular to the layer), only the hollow sites are true minima in the potential energy surface. All these features indicate a physisorbed state. The simulation of the diffusion of the molecule from one hollow site to another in a neighbor hexagon, allowing for the free reorientation of the molecular axis during the travel following the shortest path, predicts a diffusion barrier of 0.14 meV, the same number that one obtains from the two minima in Fig. 1. The weakly attractive LDA potential is in agreement with that obtained by Möller-Plesset perturbation theory (MP2)¹⁷.

The results of the static calculations are supported by dynamical simulations in which the molecule was placed in different orientations at distances of 4-6 a.u. from the graphene layer. The molecule was free to evolve under the influence of the forces on the H atoms, allowing the H-H distance to change in the process. At the end of the simulations the molecules end up in the hollow positions above carbon hexagons, at distances from the layer and with binding energies practically identical to those obtained in the static calculations.

After the optimization of the structure of a free (5,5) SWNT, which gives an average C-C bond length of 2.68 a.u. and a nanotube radius $R = 6.44$ a.u., a hydrogen molecule was placed in different sites and orientations relative to the nanotube, as shown in Figure 2, and the energy of the system was calculated as a function of the distance D_a from the center of mass of the molecule to the nanotube axis. The bond length of the molecule was maintained fixed at 1.48 a.u., and the coordinates of all the carbon atoms of the nanotube were kept frozen. From the experience with the planar graphene layer we know that this is enough in the region of the physisorption minimum.

Figure 2. Configurations of the H₂ molecule above a carbon-carbon bond, and above an hexagon with the molecular axis parallel and perpendicular to the nanotube wall.

In Figure 3 we show that weak physisorption wells are obtained outside the nanotube, but the absolute energy minimum occurs for the molecule at the center of the nanotube. The binding energies outside (for the most stable configuration) and inside are 0.068 eV and 0.17 eV, respectively, and this difference reflects the opposite curvature seen by the hydrogen molecule inside and outside the nanotube. Inside the nanotube the molecule is effectively sampling a larger nanotube area. The binding energy for the case of the planar graphene layer, 0.086 eV, is, in fact, intermediate between those two values. For the same reason the short-range repulsion between the molecule and the SWNT becomes stronger inside the nanotube. A comparison of the different curves for H₂ outside the nanotube indicates that physisorption on a hollow position is preferred over other sites, the same as for graphene. The calculated physisorption energy of 0.068 eV remarkably agrees with the experimental value of 0.062 eV obtained by Brown et al.¹⁸ by thermally activated H₂ desorption from nanotubes with a radius about 13 a.u.

We have also studied the interaction of the H_2 molecule with a (6,6) carbon nanotube. The optimized radius of the (6,6) nanotube is $R = 7.78$ a.u. The results confirm the picture found for the interaction with the (5,5) nanotube: the molecule is weakly physisorbed both outside and inside the (6,6) nanotube. The depths of the external and internal wells are 0.07 eV and 0.12 eV, respectively. The binding energy in the external well is nearly identical to that for the (5,5) SWNT. A minor difference is that the minimum for the molecule inside the (6,6) nanotube does not occur at the position of the tube axis; it is displaced, instead, 2.5 a.u. from that axis. The difference is due to the larger radius of the (6,6) nanotube. As a consequence, the depth of the inner minimum is smaller (0.12 eV, to be compared with 0.17 eV for the (5,5) nanotube).

Figure 3. Potential energy for the physisorption of the hydrogen molecule on a (5,5) carbon nanotube. The vertical line represents the nanotube wall. The curves joining the circles, crosses and diamonds correspond to the three approaching configurations shown in Figure 2, from top to bottom, respectively.

4. DISSOCIATIVE CHEMISORPTION

The preferred site for the absorption of a single hydrogen atom on a SWCN is on top of a carbon atom¹⁹⁻²³; in fact, the C-H stretching mode has been observed using Fourier transform infrared spectroscopy¹⁸. We have studied the radial approach of the hydrogen atom to the nanotube following a path on top of a C atom. The estimated binding energies are 0.9 eV and 1.3 eV for the (5,5) and (6,6) nanotubes, respectively. The binding energies of a H atom to the nanotube surface calculated previously using DFT show a wide range of values. Gülseren and coworkers^{7,9} predicted binding energies higher than 2 eV. Bauschlicher¹⁹ obtained $E_b = 0.93$ eV for a (10,10) nanotube. Lee and coworkers²² found $E_b = 1.64$ for absorption on a (5,5) nanotube. Our calculated binding energies fit within that range. The differences in binding energies can be ascribed to the different functionals describing exchange and correlation effects used in those works. In fact, the exchange–correlation functional has an influence even more drastic on the molecular absorption. The LDA gives the minimum shown in Fig. 1, while the gradient corrected (GGA) functionals fail to produce a minimum^{10,11,17}.

The interaction energy as a function of the distance between the H atom and a (6,6) SWNT is shown by the curve joining the diamonds in Figure 4. In the calculations the C-C bond distances were kept frozen. Another curve, joining the stars, corresponds to the the H atom approaching the nanotube over the midpoint of a C-C bond. The molecular

absorption is represented by the curve joining the triangles. In order to compare atomic and molecular absorption, the two absorption curves have been multiplied by a factor of 2, and have been displaced with respect to the molecular absorption curve by a constant shift of 4.76 eV, which is the experimental dissociation energy of the hydrogen molecule in two H atoms (the value calculated using the spin-polarized LDA is very close to this quantity). The figure clearly shows that two (or more) H atoms can be chemisorbed on the surface of the nanotube, provided that those two atoms are sufficiently far apart from each other. The C-H bond distance is 2.5 a.u. (or 2.6 a.u. for the (5,5) nanotube). However this is not the most stable state of the system. The calculations predict, instead, that physisorption of the bound molecule on the surface of the nanotube is preferred. One can see, nevertheless, that the molecular and atomic curves cross at a distance $D_c = 2.7$ a.u. from the nanotube wall (the nanotube wall is represented in the Figure by the vertical dashed line. This means that when the molecule is forced to approach the SWNT to a distance smaller than 2.7 a.u., the molecule will dissociate. Inside the nanotube the situation is similar. An estimation for the dissociation barrier is 2.5 eV. However, this has been obtained by introducing drastic assumptions in the calculation of the energies, namely, no relaxation of the C-C bond lengths has been permitted when the H_2 molecule, or the H atoms, approach closely the nanotube, and the H_2 bond length was also frozen during the approaching towards the nanotube.

Figure 4. Interaction energies of molecular (triangles) and atomic (diamonds and stars) hydrogen and a (6,6) SWNT. The atomic curves have been multiplied by 2 and shifted upwards 4.76 eV, the dissociation energy of the H_2 molecule. The vertical dashed line represents the nanotube wall.

Various static calculations were performed in which, for each separation between the molecule and a (5,5) SWNT, the H-H bond length was allowed to vary to minimize the total energy of the system, while still maintaining the nanotube structure frozen during the process. The orientation of the molecule in those calculations was taken parallel upon a C-C bond. For distances between the molecule and the nanotube wall higher than 3.05 a.u., bond length relaxation of the molecule was not observed and the picture drawn from the calculations reported in Section 3 is not altered. On the other hand, closer to the nanotube wall, the H-H bond becomes stretched, its length increases and the molecule dissociates (one can notice from Figure 3 that for separations $D_a = 3$ a.u. or smaller, the molecule samples the repulsive wall of the interaction potential). At the same time the total energy of the system decreases, but the total energy for the metastable dissociated configuration is still larger than the total energy of the molecule in the physisorption minimum, so the

relation between molecular physisorption and dissociative chemisorption, pictured in Figure 4 for the (6,6), nanotube remains valid.

5. DYNAMICAL SIMULATIONS

To gain further insight into the processes that occur at close distances from the nanotube wall we have performed damped molecular dynamics simulations, starting from several initial configurations and dynamically relaxing the system under the action of the forces on the atoms. First of all we have performed simulations with the H_2 molecule initially in the region of the physisorption well of the (5,5) and (6,6) nanotubes, although not at the minimum. In those cases the dynamical evolution drives the molecule towards the physisorption minimum. In the final configuration the nanotube shows no distortion, and the energy of the system is almost identical to that obtained in the static calculations discussed in Section 3. The simulations also show that the axis of the molecule easily changes its orientation in the physisorption configuration.

Then, simulations were performed starting with the molecule very close to the nanotube wall, at distances $D_a = 1.1$ - 2.1 a.u., with the two atoms in a dissociated configuration. This is a configuration of high potential energy, that could be achieved under high pressure conditions, or by injecting hydrogen atoms or molecules with high kinetic energies into the reaction cell. The analysis of the atomic configurations of the system as the simulation develops in time shows that the circular cross section of the nanotubes deforms substantially due to the bonding of the two hydrogen atoms to a pair of nearest carbon atoms. Typical C-H bond distances are $2.07 - 2.10$ a.u., values shorter than the $2.5 - 2.6$ a.u. found for the absorption of an isolated H atom (see Section 4), and the distance between those two particular carbon atoms increases substantially. A typical snapshot is shown in Figure 5 for the (6,6) nanotube. The nanotube is broken and the shortening of the C-H bond length seems itself a consequence of the scission of the C-C bond.

Figure 5. Snapshot of the broken nanotube for a dynamical simulation starting with the dissociated hydrogen molecule outside a (6,6) nanotube at a distance of 1.2 a.u. from the wall. Three views are shown.

Our interpretation is that the scission of the nanotube is due to the addition of contributions from three different effects. The first one is the weakening of the C-C bond by the concerted chemisorption of the two H atoms. This changes the bonding between each of those two carbon atoms and the environment from sp^2 to sp^3 . A second important contribution

is the excess potential energy initially deposited on the system, present in the configurations that we have used to start the dynamical simulations. Calculations of atomic chemisorption performed by other authors without the input of that extra potential energy do not lead to nanotube scission¹⁹⁻²⁰, so we conclude that the extra potential energy has a substantial influence on the breaking of the C-C bonds. As a final effect we stress that we have performed the simulations for a periodic superlattice with a relatively small supercell in the direction parallel to the nanotube axis. Because of the periodic repetition of the picture given in Figure 5, there is a strip of breaking C-C bonds along a line parallel to the nanotube axis. Scission suddenly opens a new region in the potential energy landscape where the broken nanotube follows a steep path towards the formation of a planar graphene sheet, but this process cannot be properly handled by our simulations because the dimensions of the simulation cell in the directions perpendicular to the nanotube axis are not big enough to accommodate the unfolding. We expect a similar breaking of C-C bonds if a larger supercell were used in the direction parallel to the nanotube axis, but in those cases the nanotube wall will be shattered only locally because of the lower hydrogen concentration. Those localized broken bond defects, or the grouping of some of them, could provide a door allowing foreign atoms or molecules to enter single wall nanotubes through their walls, and exploring this possibility may help experimentalists to fill nanotubes with different molecules.

Our simulations have analysed the effect of a strip of aligned dissociated H-H pairs. Attempts to study more complex configurations than the strip would require to enlarge the size of the simulation cell. Calculations performed by Bauschlicher^{19,20} for nanotubes with a high coverage of atomic hydrogen predict that some particular ordered patterns are favored over random coverages. For (10,0) nanotubes, a configuration of pairs of lines parallel to the nanotube axis, similar to the strip configuration, is favored with respect to others like single lines, rings or spirals. For (5,5) nanotubes, pairs of lines are again more stable than ring configurations, although a zig-zag pattern (related to the configuration of pair of lines) is preferred.

The weakening of C-C bonds could help in explaining the mechanism for the coalescence of SWNT in ropes and the doubling of SWNT diameters observed by Smalley and coworkers²⁴. In those experiments, SWNT ropes were annealed in a hydrogen atmosphere at temperatures up to 1773 K, and it was observed that some neighbor nanotubes coalesce, leading to the formation of tubes of larger diameters. According to our results, hydrogen could perhaps catalyze the coalescence of adjacent nanotubes by the weakening of C-C bonds.

6. CONCLUSIONS

This work was intended to provide insight on the competition between molecular and atomic absorption of hydrogen on carbon nanotubes. Static calculations and dynamical simulations of the interaction of molecular and atomic hydrogen with (5,5) and (6,6) single wall nanotubes provide the following picture: the lowest energy states of those systems are achieved for the H₂ physisorbed outside and inside the nanotubes. This is our main result, since molecular physisorption is relevant for the purposes of hydrogen storage in porous graphitic materials. However, when the molecule has enough kinetic energy to approach closely to the nanotube wall, then the molecule dissociates and the two hydrogen atoms bind strongly to two nearest neighbor carbon atoms, weakening that particular C-C bond. The weakening of the C-C bond, combined with an excess kinetic energy of the incoming molecule, can actually break the C-C bond, and the self-organization of those defects along a line parallel to the nanotube axis can lead to the scission of the single wall nanotube.

7. ACKNOWLEDGEMENTS

Work supported by MCYT of Spain (Grant MAT2002-04499-C02-01), Junta de Castilla y León (Grant CO01/102) and European Community (RTN-COMELCAN). We acknowledge the computational facilities provided by CESCA and CEPBA. One of us (JAA) is grateful for the hospitality and support of Donostia International Physics Center. MJL acknowledges support from MCYT of Spain under the “Ramón y Cajal” Program.

REFERENCES

1. A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D. S. Bethune and M.J. Heben, *Nature* **386**, 377 (1997).
2. .A. Chambers, C. Park, R. T. K. Baker and N. M. Rodriguez, *J. Phys. Chem. B* **102**, 4523 (1998).
3. P. Chen, X. Wu, J. Lin and K. L. Tan, *Science* **285**, 91 (1999).
4. R. T. Yang, *Carbon* **38**, 623 (2000).
5. U. Bünger and W. Zittel, *Appl. Phys. A* **72**, 147 (2001).
6. V. Meregalli and M. Parrinello, *Appl. Phys. A* **72**, 143 (2001).
7. O. Gülseren, T. Yildirim and S. Ciraci, *Phys. Rev. Lett.* **87**, 116802 (2001).
8. T. Yildirim, O. Gülseren and S. Ciraci, *Phys. Rev. B* **64**, 75404 (2001).
9. O. Gülseren, T. Yildirim and S. Ciraci, *Phys. Rev. B* **66**, 121401 (2002).
10. K. Tada, S.Furuya and K. Watanabe, *Phys. Rev. B* **63**, 155405 (2001).
11. P. Dubot and P. Cenedese, *Phys. Rev. B* **63**, 241402 (2001).
12. S. P. Chan, G. Chen, X. G. Gong and Z. F. Liu, *Phys. Rev. Lett.* **87**, 205502 (2001).
13. M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, *Comput. Phys. Commun.* **107**, 187 (1997).
14. G.B. Bachelet, D.R. Hamann, and M. Schlüter, *Phys. Rev. B* **26**, 4199 (1982).
15. D.R. Hamann, *Phys. Rev. B* **40**, 2980 (1989).
16. J.S. Arellano, L.M. Molina, A. Rubio and J.A. Alonso, *J. Chem. Phys.* **112**, 8114 (2000).
17. Y. Okamoto and Y. Miyamoto, *J. Phys. Chem. B* **105**, 3470 (2001).
18. C. M. Brown, T. Yildirim, D. A. Newmann, M. J. Heben, T. Gennett, A. C. Dillon, J. L. Alleman and J. E. Fischer, *Chem. Phys. Lett.* **329**, 311 (2000).
19. C. W. Bauschlicher, *Nano Lett.* **1**, 223 (2001).
20. C. W. Bauschlicher and C. So, *Nano Lett.* **2**, 337 (2002).
21. S. M. Lee and Y. H. Lee, *Appl. Phys. Lett.* **76**, 2877 (2000).
22. E. C. Lee, Y. S. Kim and K. J. Chang, *Phys. Rev. B* **66**, 073415 (2002).
23. J.S. Arellano, L.M. Molina, A. Rubio, M. J. López and J.A. Alonso, *J. Chem. Phys.* **117**, 2281 (2002).
24. P. Nikolaev, A. Thess, A. G. Rinzler, D. T. Colbert and R. E. Smalley, *Chem. Phys. Lett.* **266**, 422 (1997).