Eur. Phys. J. D **34**, 279–282 (2005)
DOI: 10.1140/epjd/e2005-00158-9

THE EUROPEAN PHYSICAL JOURNAL D

Adsorption of hydrogen on normal and pentaheptite single wall carbon nanotubes

I. Cabria[1], M.J. López[1], and J.A. Alonso[1,2,a]

[1] Departamento de Física Teórica, Universidad de Valladolid, 47005 Valladolid, Spain
[2] Donostia International Physics Center (DIPC), 20018 San Sebastián, Spain

Received 6 September 2004

Abstract. Density functional calculations of the physisorption of molecular hydrogen and the dissociative atomic chemisorption on the external surface of hexagonal and pentaheptite carbon nanotubes, have been carried out. Physisorption binding energies are near 100 meV/molecule and are similar on metallic and semiconducting nanotubes. Full coverage of the nanotube with one molecule per graphitic hexagon decreases the binding energy per molecule. Chemisorption binding energies per H atom are larger on pentaheptites than on hexagonal carbon nanotubes. The molecular physisorption and dissociative chemisorption states on pentaheptites have very similar total energies (some chemisorbed states are even slightly more stable than the physisorbed states), while on hexagonal carbon nanotubes molecular physisorption is more stable than dissociative chemisorption. However, a substantial energy barrier has to be overcome to go from physisorption to dissociative chemisorption in both types of nanotubes.

PACS. 68.43.-h Chemisorption/physisorption: adsorbates on surfaces – 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes and nanocrystals

1 Introduction

The general agreement, nowadays, of experiments and theoretical results is that the hydrogen storage capacity of carbon nanotubes is significant at very low temperatures but it becomes small (2–4 weight%) at room temperature and moderate pressures [1,2]. This is a result of the small physisorption energies, which are about 100 meV per molecule or smaller [3–8]. It has been argued that H_2 physisorption may be stronger on metallic than on semiconducting nanotubes, because of the higher polarizabilities of the former ones. Another suggestion is that physisorption would be more intense on defects on nanotubes, in particular on Stone-Wales defects, and there is a recent theoretical study of the physisorption and chemisorption of hydrogen on Stone-Wales defects in graphene [9]. Pentaheptite carbon nanotubes (PHNTs) can be generated by rolling up a two-dimensional three-fold coordinated carbon network composed of pentagons and heptagons [10], which in turn can be obtained by the creation of Stone-Wales defects on a graphene sheet. These PHNTs are metallic. In order to test the storage possibilities of these new materials we study the molecular physisorption and the dissociative atomic chemisorption of hydrogen on PHNTs and compare the results with those for adsorption on normal nanotubes. The calculations use the Density Functional Theory (DFT), with two different computational implementations, one that considers the helical symmetry of the nanotubes to calculate their electronic structure using a basis of Gaussian-type orbitals [11], and a second one with the DACAPO code [12], that utilizes plane-wave basis and ultrasoft pseudo-potentials. In both implementations the Local Density Approximation (LDA) is employed for exchange and correlation, since the generalized gradient (GGA) functionals fail to describe the physisorption of the hydrogen molecule on graphitic materials [13].

2 Physisorption in the dilute and concentrated limits

We have first studied the interaction of a single molecule with the external surface of metallic and semiconducting nanotubes (the geometry of the nanotubes was previously optimized). There are different configurations of a single physisorbed molecule, but the differences in binding energy are, in general, very small. In its most stable configuration, shown in Figure 1, the molecule is physisorbed above the center of a carbon hexagon with the molecular axis perpendicular to the nanotube surface. In this configuration the molecule is able to fit optimally into the electron density valley that exists around the hexagon

---

[a] e-mail: `jaalonso@fta.uva.es`

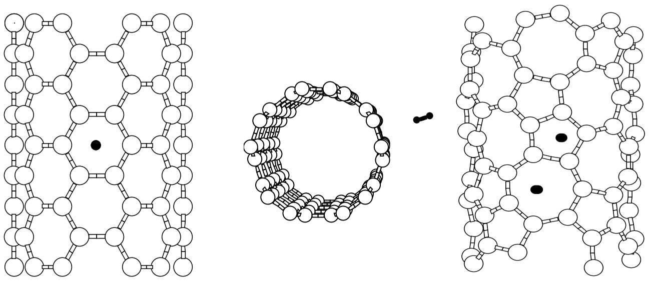

Fig. 1. Left panel: equilibrium physisorption configuration of a single hydrogen molecule on a normal (5,5) carbon nanotube. Center panel: the molecular axis is perpendicular to the nanotube wall. Right panel: physisorption on a (8,2) pentaheptite carbon nanotube.

Table 1. Calculated binding energies E_b (meV per adsorbed molecule), and equilibrium molecule-nanotube wall distances D_{eq} (in Å) for the physisorption of a H_2 molecule on the surface of hexagonal and pentaheptite (ph) carbon nanotubes whose radii (in Å) are indicated.

Nanotube	Radius	site	E_b	D_{eq}
		Single molecule		
(5,5)	3.43	hexagon	89	2.6
(6,4)	3.45	hexagon	101	2.8
(8,2)	3.63	hexagon	88	2.7
ph(8,2)	3.31	pentagon	78	2.7
ph(8,2)	3.31	heptagon	69	2.5
		Full coverage		
(5,5)	3.43	–	66	2.6
(6,4)	3.45	–	68	2.6
(8,1)	3.39	–	98	2.6
(8,2)	3.63	–	96	2.6
ph(8,2)	3.31	–	62	2.7

center [14]. In Table 1 we present the calculated binding energies E_b for adsorption on (5,5), (6,4) and (8,2) nanotubes and the corresponding equilibrium distances D_{eq} between the center of mass of the molecule and the nanotube surface. The calculated adsorption energies are near 100 meV and these results are consistent with those obtained in previous works [6,7]. There are only small differences between the adsorption energies on the metallic (5,5) and the semiconducting (6,4) and quasimetallic (8,2) nanotubes. In fact, the (5,5) and (6,4) nanotubes have practically the same radii and the binding energy to the semiconducting nanotube is marginally larger.

We have also studied the full coverage of the nanotubes with molecules adsorbed on all the hexagons. The binding energies per molecule for full coverage of the (5,5) and (6,4) nanotubes (66 and 68 meV/molecule, respectively; see Tab. 1) are lower than the binding energies for a single molecule because the distances between some neighbor molecules lie on the repulsive region of the H_2–H_2 potential and the net effect of the interaction between neighbor molecules contributes to decrease the binding to the nanotube. The present results are in agreement with the findings of Diep and Johnson [15]. They obtained an accurate H_2–H_2 interaction potential from first principles and have shown that there is a strong intermolecular repulsion when the distance between the centers of mass of the two molecules is less than 2.5 Å. For the single molecule adsorption discussed above, we found that the binding energies to metallic and semiconducting nanotubes were similar. For full coverage we find a more complex situation. The binding energies are again similar for the metallic (5,5) and semiconducting (6,4) nanotubes; however, those for the semiconducting (8,1) and quasimetallic (8,2) nanotubes are larger compared to (5,5) and (6,4). The reason is again the different distances between neighbor adsorbed molecules. The distances between a H_2 molecule and its six neighbor molecules in the (8,1) and (8,2) nanotubes lie in the attractive part of the H_2–H_2 interaction potential. Configurations with more than one adsorbed molecule per graphitic hexagon would imply higher storage densities, but also reduced intermolecular distances, which give rise to strongly repulsive interactions, and we have found that those configurations are not stable.

The optimized (8,2) PHNT ((8,2) in the usual notation of hexagonal carbon nanotubes and (4,1) if we follow the notation of Crespi et al. [10]) has a slightly buckled surface (the relative difference between the shortest and largest radius is 6%) and is the equivalent of the (8,2) hexagonal nanotube, which has a flat surface. The most favorable adsorption sites are above the centers of carbon pentagons and heptagons, with the molecular axis perpendicular to the surface. The physisorption energies of a single molecule on the (8,2) PHNT are slightly smaller than those on the hexagonal (8,2) nanotube (see Tab. 1). For full coverage of the PHNT, some intermolecular distances lie on the repulsive part of the intermolecular potential and contribute to a lowering of the binding energy (per molecule) with respect to the case of a single molecule.

3 Physisorption and chemisorption on pentaheptite and hexagonal carbon nanotubes

We have optimized the structure of a (6,6) PHNT, obtaining a slightly buckled surface (about 5%). The physisorption energies of hydrogen molecules above the center of heptagons (131 meV) are higher than above pentagons (78 meV), a behavior opposite to that found for the (8,2) PHNT, so a common trend does not exist. There are energy barriers for the motion of a molecule between those local minimum positions. The barriers for the motion between two neighbor heptagons (81 meV), or from a heptagon to a pentagon, are both large. On the other hand the barriers for motion between two neighbor pentagons (about 8 meV), or from a pentagon to a heptagon, are both very small.

To compare molecular physisorption and dissociative chemisorption on the PHNT we have optimized the structure of three chemisorption configurations of the dissociated molecule with the H atoms attached to two neighbor carbon atoms. In those configurations the bond between these two carbon atoms is shared by two pentagons, by two heptagons, and by a pentagon and a heptagon, respectively. Finally, a fourth configuration with the hydrogen atoms bonded to two non-adjacent carbon atoms has been studied. Total energies were then calculated using three different relaxation models for each configuration: (a) when the PHNT geometry is fixed and only the positions of the H atoms are allowed to vary, (b) when the positions of the C atoms bonded to the H atoms are also allowed to relax, and (c) when another four neighbor C atoms are also relaxed. Comparing the total energies we have found that molecular physisorption is clearly more stable if we consider model (a). Adopting the relaxation model (b) lowers the total energies of the chemisorbed states by about 1.4–1.7 eV, making its total energy very close to the total energies of physisorption configurations, or even slightly smaller (that is, more stable). Those two C atoms relax outwards the nanotube surface, adopting a tetrahedral sp^3 bonding configuration with the three C neighbors and the H atom. Relaxing the positions of additional C atoms according to model (c) lowers further the total energies by about 50 meV. Taking into account all the configurations and relaxation models, the most stable state of the system is achieved for the dissociated molecule with the H atoms attached to the carbon atoms of a pair between a pentagon and a heptagon. The binding energy of each H atom is 2.6 eV, and this chemisorbed state is about 150 meV more stable than the lowest physisorbed state. Duplock et al. [9] have studied physisorption and chemisorption on a Stone-Wales defect on a graphene sheet modulated to produce armchairlike curvature, and they also found that the difference between the total energies of physisorbed and chemisorbed states is very small, about 150 meV, although the physisorbed state was more stable in that case.

Although some chemisorbed states are slightly more stable than all the physisorbed states on a pentaheptite, an initially physisorbed hydrogen molecule must overcome a substantial energy barrier to turn into the dissociated state with two chemisorbed atoms. The calculated barrier is about 2.4 eV.

There are some studies of the chemisorption of a single H atom on hexagonal carbon nanotubes [16], and studies of the dissociation of a hydrogen molecule [17]. However, in order to have a meaningful comparison with our results on the (6,6) PHNT, we have studied molecular physisorption and dissociative chemisorption on a hexagonal (6,6) nanotube. The molecular physisorption energy is 81 meV per molecule, very similar to the physisorption energy on a pentagon of the (6,6) PHNT. The dissociated chemisorption state obtained by relaxing only the positions of the two H atoms is again less stable than the physisorption state. Relaxation of the two adjacent C atoms bonded respectively to the H atoms lowers the total energy of the chemisorbed state by 1.8 eV (this chemisorbed state is more stable than a chemisorbed configuration with the H atoms bonded to non-adjacent C atoms; in this configuration, the C atoms bonded to H atoms and the C atom between them were relaxed). Relaxation of more C atoms lowers additionally the total energy by about 90 meV. The binding energy per H atom in this chemisorbed state becomes 2.25 eV. However the most stable state of the system is still molecular physisorption, which is 0.48 eV more stable than the dissociative chemisorbed state. The result that the chemisorption binding energy per H atom is larger on pentaheptites (2.6 eV) than on hexagonal nanotubes (2.25 eV) is in agreement with the findings of Duplock et al. [9], who also obtained larger binding energies on a Stone-Wales defect on a graphene sheet with curvature than on a regular flat graphene sheet. The energy barrier separating molecular physisorption from dissociative chemisorption in this hexagonal carbon nanotube is 1.8 eV.

In summary, the physisorption binding energies of molecular hydrogen to hexagonal and pentaheptite single wall nanotubes are about 100 meV/molecule or less, substantially below the value of 300–400 meV/molecule that would be required for viable adsorption/desorption operation at room temperature and normal pressures [8]. It also appears that the presence of even large quantities of pentagonal and heptagonal defects in the nanotubes will not help to increase the adsorption energies. By comparing total energies we have found that molecular physisorption and dissociative atomic chemisorption are nearly equally stable on pentaheptites, but on hexagonal carbon nanotubes physisorption is more stable. However, substantial barriers exist to dissociate the physisorbed molecule both on the pentaheptites and hexagonal carbon nanotubes.

This work was supported by MCYT of Spain (Grant MAT2002-04499-C02-01) and Junta de Castilla y León (Grant CO01/102). IC is indebted to the University of Valladolid for a Research Contract, MJL acknowledges support from MCYT of Spain under the Ramón y Cajal Program, and JAA acknowledges the hospitality and support from DIPC (San Sebastián).

References

1. A. Züttel, Mat. Today **9**, 24 (2003)
2. S. Orimo, A. Züttel, L. Schlapbach, G. Majer, T. Fukunaga, H. Fujii, J. Appl. Cryst. **356**, 716 (2003)
3. C.M. Brown, T. Yildirim, D.A. Newmann, M.J. Heben, T. Gennett, A.C. Dillon, J.L. Alleman, J.E. Fischer, Chem. Phys. Lett. **329**, 311 (2000)
4. B.K. Pradhan, G.U. Sumanasekera, K.W. Adu, H.E. Romero, K.A. Williams, P.C. Eklund, Physica B **323**, 115 (2002)
5. D.G. Narehood, J.V. Pearce, P.C. Eklund, P.E. Sokol, R.E. Lechner, J. Pieper, J.R.D. Copley, J.C. Cook, Phys. Rev. B **67**, 205409 (2003)
6. J.S. Arellano, L.M. Molina, A. Rubio, M.J. López, J.A. Alonso, J. Chem. Phys. **117**, 2281 (2002)
7. J. Zhao, A. Buldum, J. Han, J.P. Lu, Nanotechnology **13**, 195 (2002)

8. J. Li, T. Furuta, H. Goto, T. Ohashi, Y. Fujiwara, S. Yip, J. Chem. Phys. **119**, 2376 (2003)
9. E.J. Duplock, M. Scheffler, J.D. Lindan, Phys. Rev. Lett. **92**, 225502 (2004)
10. V.H. Crespi, L.X. Benedict, M.L. Cohen, S.G. Louie, Phys. Rev. B **53**, R13303 (1996)
11. J.W. Mintmire, C.T. White, in *Carbon Nanotubes: Preparation and Properties*, edited by T.W. Ebbesen (CRC, Boca Raton, 1997), p. 191
12. B. Hammer, L.B. Hansen, J.N. Nørskov, Phys. Rev. B **59**, 7413 (1999)
13. Y. Okamoto, Y. Miyamoto, J. Phys. Chem. B **105**, 3470 (2001)
14. J.S. Arellano, L.M. Molina, A. Rubio, J.A. Alonso, J. Chem. Phys. **112**, 8114 (2000)
15. P. Diep, J.K. Johnson, J. Chem. Phys. **112**, 4465 (2000)
16. V. Barone, J. Heyd, G.E. Scuseria, J. Chem. Phys. **120**, 7169 (2004)
17. E.-C. Lee, Y.-S. Kim, Y.-G. Jin, K.J. Chang, Phys. Rev. B **66**, 73415 (2002)