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Density functional study of molecular hydrogen coverage on carbon nanotubes

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Abstract

Density functional calculations of the adsorption of molecular hydrogen on the external surface of (5,5), (6,4), (8,1) and (16,2) carbon nanotubes have been carried out. Binding energies of single molecules have been studied as a function of orientation of the molecules and type of nanotube. We have found weak adsorption, with binding energies near 100 meV/molecule in the most stable configurations. The binding energies on metallic and semiconducting nanotubes are similar. When the nanotube surface is fully covered with one molecule per graphitic hexagon, the binding energy per molecule decreases for some nanotubes due to repulsive interactions between neighbor molecules. For the same reason, direct adsorption of a single hydrogen layer with a coverage of more than one molecule per graphitic hexagon is not possible, even at low temperatures. However, adsorption of two layers (14.3 wt% hydrogen adsorbed when all the surface is covered) leads to binding energies between 40 and 80 meV/molecule, although the molecules of the outer layer are more weakly bound compared to those of the inner one. All the small calculated binding energies indicate that substantial adsorption is only possible at very low temperatures.

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1. Introduction

An economy based on hydrogen requires a high storage capacity and the reversibility of uptake and release of hydrogen at room temperature and moderate pressures. The US Department of Energy established that a hydrogen storage of, at least, 6.5% of the storage system weight is necessary for onboard automotive applications. One of the possible methods of hydrogen storage is the physisorption of hydrogen on materials with a large specific surface area, as carbon nanotubes (CNTs). Dillon et al. [1] reported in 1997 a significant adsorption of hydrogen on carbon nanotubes. However, since then, very different hydrogen storage capacities have been reported, leading to some controversy. Reviews of recent experimental work [2,3] conclude that the hydrogen storage capacity of CNTs is small (2–4 wt%) at room temperature and moderate pressures, that a significant hydrogen adsorption is only observed at very low temperatures, that the binding energies, E_b, per molecule are between 20 and 110 meV [4–6] and that CNTs are not superior to other carbon nanostructures for hydrogen storage.

Theoretical calculations yield binding energies of a single H_2 molecule on graphite [7–9] and CNTs [10–12] of approximately 100 meV or less, in reasonable agreement with experimental results of hydrogen adsorption

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on CNTs. A thermodynamic analysis of the adsorption/desorption process based on a comparison of the free energies of the free gas and adsorbed hydrogen phases has shown that a binding energy of about 0.15–0.20 eV/atom would be required for viable adsorption/desorption at room temperature and normal pressures [12]. Consequently, an accurate calculation of the binding energies for different adsorption configurations and degree of coverage is of high interest.

In this work we intend to extend our understanding of the interaction of molecular hydrogen with CNTs by means of Density Functional (DFT) calculations. We have first studied the interaction of a single molecule, placed on the center of an hexagon on the external surface of (5,5), (6,4) and (16,2) nanotubes. By comparing the results for (5,5) metallic nanotubes with those for (6,4) and (16,2) semiconducting chiral nanotubes we can study the effect that the different electronic character of the nanotubes has on the physisorption energy of the molecule. Our second objective, a question not considered in previous first principles calculations, is the study of the massive coverage of the CNT surface, in particular the surface of (5,5), (6,4), (8,1) and (16,2) CNTs. The calculations show that the direct low temperature coverage of the nanotube surface saturates at a concentration of one H_2 molecule per graphitic hexagon (because of the strong repulsion between H_2 molecules for intermolecular distances corresponding to higher coverages). However, we have found that a second layer of adsorbed molecules can be weakly adsorbed on top of the first one.

2. Physisorption in the dilute and concentrated limits

In the calculations we have applied the Density Functional method, with a computational implementation [13] that considers the helical symmetry of the nanotubes to calculate their electronic structure, using a basis of Gaussian-type orbitals [14]. We have used a 7s3p basis set for the carbon atoms and a 6s1p one for hydrogen. For exchange and correlation we have used the Local Density (LDA) functional of Perdew and Zunger [15]. Previous studies [7,8,10] have shown that the LDA predicts physisorption energies of H_2 on the surface of graphite and carbon nanotubes in substantial agreement with experiment. Furthermore, Okamoto and Miyamoto [8] compared LDA and second order Moller-Plesset (MP2) calculations of the physisorption of a hydrogen molecule on planar graphitic clusters, and they found an LDA interaction energy curve in very good agreement with the MP2 calculations. In contrast, DFT calculations using the Generalized Gradient Approximation (GGA) produced a purely repulsive interaction. Using a GGA functional, Tada et al. [16] obtained a repulsive interaction between H_2 and a graphene layer and also a (6,6) nanotube.

Before studying the physisorption of hydrogen on CNTs we have optimized the equilibrium geometries of the free H_2 molecule and the (5,5), (6,4), (8,1) and (16,2) single-wall nanotubes. We obtained a bond length of 0.77 ± 0.01 Å and a binding energy of 4.60 ± 0.01 eV for the hydrogen molecule (the experimental values are 0.74 Å and 4.8 eV, respectively). The optimized structure of the free (5,5), (6,4), (8,1) and (16,2) CNTs gave the same average C–C bond length of 1.42 Å and radii of 3.43, 3.45, 3.39 and 6.71 Å, respectively. We have used these equilibrium geometries in the study of the physisorption of hydrogen molecules, changing only the radial distance D_w between the center of mass of the molecules and the nanotube wall. The accuracy of the physisorption binding energies is 10 meV.

We have first calculated the binding energy of a single molecule in three different configurations, shown in Fig. 1 and labelled as A, B and C, respectively. The center of mass of the molecule is placed above the center of an hexagon and the energy of the system is computed as a function of D_w. Other possible configurations, on top of a carbon atom, or on top of a C–C bond, are less favorable [7]. In Table 1 we present the calculated binding energies E_b and equilibrium distances D_{eq} for adsorption on (5,5), (6,4) and (16,2) nanotubes. Configuration C, with the molecular axis perpendicular to the nanotube surface, is the most stable of the three configurations studied, because in this configuration the molecule is able to fit better into the electron density valley that exists on the center of the hexagons [7]. Our results are consistent with those obtained by Arellano et al. [10] with a different computational implementation of the DFT method. They obtained a binding energy of 68 meV in configurations A and C on the external surface of a (5,5) CNT, and equilibrium distances D_{eq} of 2.65 and 2.7 Å, respectively. DFT calculations performed by Zhao et al. [11] for a single molecule adsorbed on a (5,5) nanotube predicted a binding energy of 84 meV and an equilibrium distance of 3.2 Å.

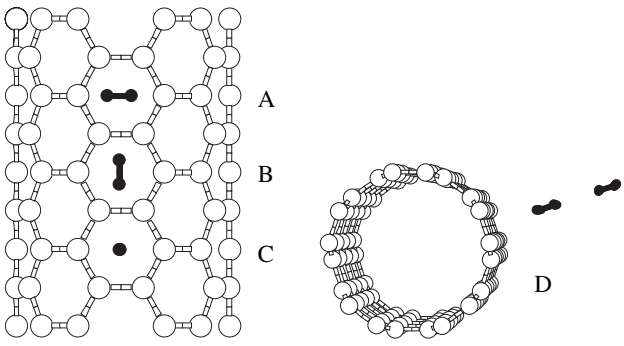

Fig. 1. Physisorption configurations A, B, C and D. In configurations C and D the molecular axis is perpendicular to the nanotube wall.

Table 1
Calculated binding energies E_b and equilibrium molecule-nanotube wall radial distances D_{eq} for the physisorption of a H_2 molecule on carbon nanotubes whose radii are indicated

Nanotube	Radius	Configuration	E_b	D_{eq}
Single molecule				
(5,5)	3.43	A	70	2.6
(5,5)	3.43	B	30	2.7
(5,5)	3.43	C	90	2.6
Single molecule				
(6,4)	3.45	A	80	2.5
(6,4)	3.45	B	50	2.5
(6,4)	3.45	C	100	2.8
Single molecule				
(16,2)	6.71	A	70	2.5
(16,2)	6.71	B	70	2.5
(16,2)	6.71	C	90	2.8
Full coverage				
(5,5)	3.43	A	30	2.5
(5,5)	3.43	C	70	2.6
(6,4)	3.45	C	70	2.6
(8,1)	3.39	C	100	2.6
(16,2)	6.71	C	100	2.7

The configurations A, B and C correspond to those shown in Fig. 1. Results for full coverage in configurations A and C are also reported. D_{eq} and nanotube radii are given in Å, and E_b in meV per adsorbed molecule.

The attractive interaction between the molecule and the nanotube arises from two sources. First, there is a small electron density redistribution in the system when the molecule approaches the nanotube wall. That density relaxation causes a lowering of the energy. On the other hand, the LDA exchange-correlation functional is a nonlinear functional of the density (the exchange part is just $-c_x \int \rho(\vec{r})^{4/3} d^3\vec{r}$, where c_x is a constant), which causes an attractive contribution even in the case of simple overlapping densities ($\rho_1 + \rho_2$). These points are discussed in more detail in [7].

The LDA does not account for the long-range van der Waals forces, due to the interaction between mutually induced dipoles in nonoverlapping density distributions. Consequently, our calculation does not describe accurately the interaction when the molecule is at a substantial distance from the nanotube wall, that is, the long-range part of the interaction potential. However, as discussed before, the main contribution to the interaction in the region of the attractive minimum comes from other sources well captured by the calculation [17].

It might be speculated that the binding energies are different on metallic and semiconducting nanotubes, because of their different polarizabilities. Our calculations detect only small differences between the binding energies of a single molecule adsorbed on the metallic (5,5) CNT and the semiconducting (6,4) and (16,2) nanotubes, in particular for configuration C, the most stable one (the (6,4) and (5,5) nanotubes have practically the same radii, and the radius of the (16,2) nanotube is about two times larger). To be precise, the binding energies to semiconducting nanotubes in configuration C are marginally larger. Although not relevant for H_2 physisorption, we think that the electronic character (metallic or semiconducting) of the CNTs will be much more important in the case of chemisorption of atomic H.

We have also calculated the zero-point vibrational energy of a hydrogen molecule physisorbed on the nanotube surface. The well of the interaction between the molecule and the nanotube wall is very shallow and the zero-point vibrational energy of the molecule in that well is about 10–15 meV, depending on the configuration of the physisorbed molecule and the nanotube. This energy should be substracted from all the physisorbed binding energies obtained in the present work.

We have also considered the full coverage of the nanotubes, with H_2 molecules adsorbed on all the hexagons of the external surface. The results are given in Table 1, where we report the calculated binding energy per adsorbed molecule. This is defined as

$$E_b = \frac{E(\mathrm{CNT}) + nE(\mathrm{H_2}) - E(n\mathrm{H_2} - \mathrm{CNT})}{n}, \qquad (1)$$

where E(CNT) is the energy of the CNT, $nE(H_2)$ is n times the energy of a free H_2 molecule and $E(nH_2 - CNT)$ is the energy of the nanotube with n hydrogen molecules adsorbed on its surface, in the appropriate configuration. Of course, the definition also applies to the case $n = 1$ discussed above.

The binding energy per molecule for full coverage of the (5,5) and (6,4) nanotubes is lower than the binding energy for a single H_2 molecule in the same configuration (A or C), due to repulsive interactions between some neighbor molecules. Diep and Johnson [18] have 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 a reference molecule in the fully covered (5,5) nanotube, four of its neighbor molecules on adjacent hexagons are at a distance of 3.92 Å and in the (6,4) nanotube are at 3.75 and 4.05 Å. However, the other two neighbor molecules in adjacent hexagons are at distances of only 2.46 and 2.49 Å in the (5,5) and (6,4) nanotubes, respectively, which 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 between the hydrogen molecules and the (5,5) and (6,4) CNTs. The present results are in agreement with the findings of Diep et al.

However, the binding energies of a single molecule and for full coverage on the (16,2) CNT are very similar, because some intermolecular distances between neighbor molecules adsorbed on these nanotubes lie in the weakly attractive region of the intermolecular potential (for full coverage on the (16,2) surface, the distances

between a molecule and its six nearest neighbor molecules are 2.65, 2.84 and 3.43 Å).

In the case of a single H_2 molecule discussed above, we found that the binding energy to metallic and semiconducting nanotubes was similar. However, for full coverage we find that the binding energy per adsorbed molecule is the same for the (5,5) and (6,4) nanotubes and larger for the semiconducting nanotubes (8,1) and (16,2), compared to the metallic one, (5,5). The reason is, as we have explained above, the different distances between neighbor hydrogen molecules on the surface of these nanotubes. The distances between a molecule and its six nearest neighbors on the fully covered (8,1) are 2.88, 3.24 and 4.29 Å.

We may notice that all the calculated binding energies are small compared to the estimated value (0.15–0.20 eV/atom) required for operational adsorption/desorption at room temperature and normal pressures. This means that the full coverage configurations studied here will be stable only at very low temperatures. At finite temperatures the equilibrium adsorption coverage will be reduced. A calculation of the free energies is necessary to predict the finite temperature adsorption.

Configurations with more than one molecule per graphitic hexagon would imply higher storage densities, but those higher coverage configurations are unfavorable because the reduced intermolecular distances give rise to strongly repulsive interactions between the hydrogen molecules. A configuration obtained by placing molecules on top of each carbon atom and on top of the center of each hexagon is not stable, because the intermolecular distances are too small.

3. Adsorption of additional hydrogen layers

Instead of trying to increase the storage capacity by increasing the hydrogen density on a single layer of adsorbed molecules, a possible alternative would be the formation of additional layers around the nanotube. To investigate this possibility we have first considered two hydrogen molecules in the configuration D shown on the right panel of Fig. 1. This consists of two hydrogen molecules in configuration C (that is, the molecular axis is perpendicular to the nanotube surface) at different distances to the nanotube wall, in such a way that only the first molecule is directly adsorbed on the nanotube surface.

As can be seen in Table 2, the binding energies per molecule for full covering of the external nanotube surface with two hydrogen layers are 20–40% smaller than those for a single layer (that is, for full covering in configuration C; see Table 1). This indicates that the outer hydrogen layer is more weakly bound than the inner layer. The molecules of the inner layer experience two types of interactions: with the nanotube and with other hydrogen molecules of the inner and outer layers. On the other hand the interaction between the molecules of the outer layer and the carbon nanotube is lower due to the increased separation, so the binding of the second layer arises mostly from intermolecular (H_2–H_2) interactions within the same layer and between the inner and outer layers. But, of course, the adsorption capacity has been increased by a factor of two. Covering the nanotube with more than one hydrogen layer could then provide a way to increase the storage capacity, although, as stressed above, this increased coverage will only be stable at very low temperatures (or high pressures).

Table 2
Calculated binding energies E_b (in meV per hydrogen molecule) for a single pair of molecules and for full coverage by two layers in configuration D

Nanotube	Coverage	E_b	D_{eq}
(5,5)	Single pair	60	2.6
(6,4)	Single pair	60	2.6
(16,2)	Single pair	50	2.7
(5,5)	Full	40	2.6
(6,4)	Full	50	2.6
(8,1)	Full	70	2.6
(16,2)	Full	80	2.7

The equilibrium radial distances D_{eq} (in Å) between the molecules of the first layer and the nanotube surface are also given.

In a bundle of parallel nanotubes adsorption can occur on the outer surface of the bundle and also in the channels (of triangular-like section) between nanotubes (of course, also inside the nanotubes, if their ends are open). Two layers of molecules can be adsorbed on the surface of the bundle, but the possibility of two layer adsorption in the interstitial channels or inside the nanotubes will depend on the available space, that is, on the nanotube radii. That is, only large radii will allow for multilayer adsorption. For instance, in the case of interstitial channels, the radius should be about 22 Å or larger.

4. Conclusions

We have performed density functional calculations for the adsorption of molecular hydrogen on the external surface of carbon nanotubes of different radii and chirality: (5,5), (6,4), (8,1) and (16,2) nanotubes. The physisorption energies of a single molecule adsorbed in the most stable configuration vary between 90 and 100 meV. The physisorption energies per molecule decrease when the surface of (5,5) and (6,4) nanotubes is fully covered. This is due to the repulsive interactions between some neighbor molecules. In other cases, like the (16,2) nanotube, such a lowering does not occur, and the adsorption energy even increases a little at high coverage because the distances between neighbor hydrogen

molecules lie in the weakly attractive region of the H_2–H_2 potential. The calculated adsorption energies are consistent with experimental binding energies, which lie between 20 and 110 meV [4–6]. Binding energies of a single molecule on metallic and semiconducting nanotubes are very similar, but they are different for full coverage, due to the different distances between neighbor molecules on the nanotubes: small neighbor distances cause repulsive interactions. In all the cases studied we find small adsorption energies that do not guarantee an efficient adsorption/desorption operation at room temperature and normal pressures. The expectations are better, however, for low temperatures and high pressures.

Adsorption of a single layer of molecules having a coverage of more than one H_2 molecule per graphitic hexagon appears to be unfeasible because the crowding of the nanotube surface leads to strong repulsive interactions between neighbor molecules. The adsorption can be increased by building additional hydrogen ''layers'' around the nanotube, although the molecules of the second (or outer) layer are very weakly bound. Two full layers would correspond to a 14.3 wt% hydrogen adsorbed. This effect may be more relevant for adsorption inside the nanotubes of large enough diameter.

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