Interaction of Molecular and Atomic Hydrogen With Single-Wall Carbon Nanotubes

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***Abstract*—Density functional calculations are performed 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 adsorption state, with the molecule at equilibrium at a distance of 5–6 a.u. from the nanotube wall. The physisorption energies outside the nanotobes are approximately 0.07 eV, and larger inside, reaching a value of 0.17 eV inside the $(5,5)$ nanotube. Although these binding energies appear to be lower than the values required for an efficient adsorption/desorption operation at room temperature and normal pressures, the expectations are better for operation at lower temperatures and higher pressures, as found in many experimental studies. A chemisorption state with the molecule dissociated has also been found, with the H atoms much closer to the nanotube wall. However, this state is separated from the physisorption state by an activation barrier of 2 eV or more. The dissociative chemisorption weakens carbon–carbon bonds, and the concerted effect of many incoming molecules with sufficient kinetic energies can lead to the scission of the nanotube.**

***Index Terms*—Carbon nanotubes, graphite, hydrogen absorption.**

I. Introduction

THE adsorption of hydrogen by graphitic materials, including carbon nanotubes, has been investigated by several groups, but the reports on the adsorption 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 adsorption and storage processes [6]. Computer simulations of hydrogen adsorption 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 (SWNT) has been studied using the density functional theory (DFT), and Gülseren *et al.* [7], [9] and Yildirim *et al.* [8] 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 appears to be the physisorption of molecular hydrogen. Early attempts of studying the adsorption of molecular hydrogen on the nanotube walls failed because the generalized gradient approximations (GGAs) employed to describe exchange and correlation effects between the electrons give a purely repulsive interaction between the closed shell molecule H_2 and the nanotube wall [10]–[12], a prediction that is 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 adsorption of hydrogen that clarifies the relation between the two processes. Under normal conditions, molecular physisorption is preferred. However, if by energetic impact, or under high pressure, the H_2 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 carbon–carbon (C–C) bonds.

II. Computational Method

The calculations of the interaction between the hydrogen atom, or the hydrogen molecule, and carbon nanotubes (or graphite) have been performed with the *ab initio* FHI96MD code [13]. This density functional 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 Bachelet *et al.* [14] and Hamman *et al.* [15]. Below, we present results for static calculations and dynamical simulations of the interaction of H and H_2 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 $(6,6)$ nanotubes. Several tests were performed to control the influence of the cell dimensions and the magnitude of the energy cutoff of the plane-wave basis. The results for nanotubes are complemented with the study of the interaction of H_2 with a planar graphitic layer.

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TABLE I
BINDING ENERGIES (IN ELECTRONVOLTS) OF H_2 TO GRAPHITE AND NANOTUBES

	To graphite	To nanotubes
This work (DFT)	0.09	0.07 outside (5,5)
		0.17 inside (5,5)
		0.07 outside (6,6)
		0.12 inside (6,6)
Okamoto (MP2) [18]	0.09	
Li (DFT) [20]		0.11 inside (7,7)
Mattera (exp) [21]	0.04	
Brown (exp) [24]		0.06 (radius 13 a.u)
Narehood (exp) [25]		0.02

III. PHYSISORPTION OF H_2 ON GRAPHITE AND CARBON NANOTUBES

The interaction between H_2 and a planar graphene layer has been studied in [16]. The equilibrium position is obtained for the molecule in a position above the center of a carbon hexagon, with the molecular axis parallel to the graphene plane. The distance from the center of mass of the molecule to the layer is 5.1 a.u. and the binding energy of the molecule to the graphene layer is 0.086 eV. The electron densities of a pure graphene layer in a plane 5.1 a.u. above the layer are in the range from 6×10^{-5} e/a.u.^{3} to 9×10^{-5} e/a.u.^{3} so the H_2 molecule is in equilibrium in the tail of the graphene electron density. The main contribution to the binding comes from the exchange and correlation effects arising from the weak overlap between the electron densities of the graphene layer and the closed-shell H_2 molecule. Even without any density rearrangement, exchange and correlation effects produce an attractive contribution [17]. In addition, there is a very small density rearrangement [16] that contributes to the weak bonding. All these features indicate a physisorption state. The weakly attractive H_2-graphene interaction potential obtained by the LDA is in remarkable agreement with that calculated using Möller–Plesset perturbation theory (MP2) [18] (a comparison of the binding energies is provided in Table I). The simulation of the diffusion of the molecule from one hollow site to another in a neighbor hexagon, following the shortest path, predicts an activation energy $\Delta E_a = 0.014$ eV (163 K). This is in good agreement with the activation energy for the diffusion of deuterium hydride (HD) adsorbed on exfoliated graphite $\Delta E_a = 152 \pm 20$ K, measured by Bienfait *et al.* [19] using quasi-elastic neutron scattering.

Li *et al.* [20] have performed a simple thermodynamic analysis of the adsorption/desorption process based on a comparison of the free energies of the gas and adsorbed phases of hydrogen. For the absorption/desorption from the surface of graphitic materials to be effective under conditions relevant for the requirements of the automotive industry, that is near room-temperature and normal pressures. Li *et al.* [20] have estimated that a binding energy of 0.15–0.2 eV per H atom is required. However, the calculated binding energies of H_2 to the graphene layer reported above are substantially smaller, and the same occurs with the experimental binding energies [21]. Evidently, the requirements would be less strict under conditions of cryogenic (liquid nitrogen) temperatures and, as discussed by Li *et al.* [20], the calculated H_2-graphene binding energies [16] appear to explain some of the reports of adsorption of hydrogen by graphitic materials.

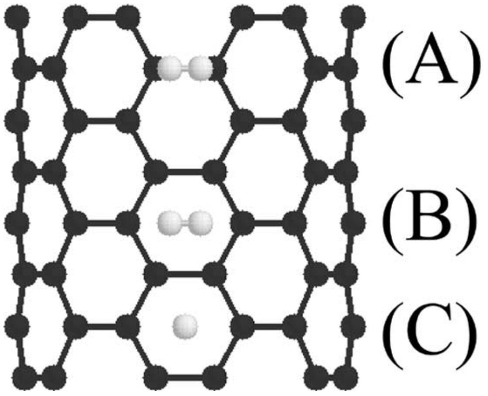

Fig. 1. Configurations of the H_2 molecule above a C–C bond (A), and above an hexagon with the molecular axis parallel (B) and perpendicular (C) to the nanotube wall.

The question then arises if the curvature of the graphene layer, which is characteristic of carbon nanotubes, can increase the binding energy [20], [22], [23]. For this purpose, we have performed calculations of the adsorption of H_2 by $(5,5)$ and $(6,6)$ carbon nanotubes. After 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 Fig. 1, 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 experience with the planar graphene layer [16], we know that these assumptions are valid in the region of the physisorption minimum. Fig. 2 shows that weak physisorption wells are obtained outside and inside the nanotube, and that 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 and 0.17 eV, respectively, and the 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, i.e., 0.086 eV, is, in fact, intermediate between those two values. For the same reason, the short-range repulsion between the molecule and SWNT becomes stronger inside the nanotube. A comparison of the different curves for H_2 outside the nanotube indicates that physisorption on a hollow position is preferred over other sites, which is the same as for graphene.

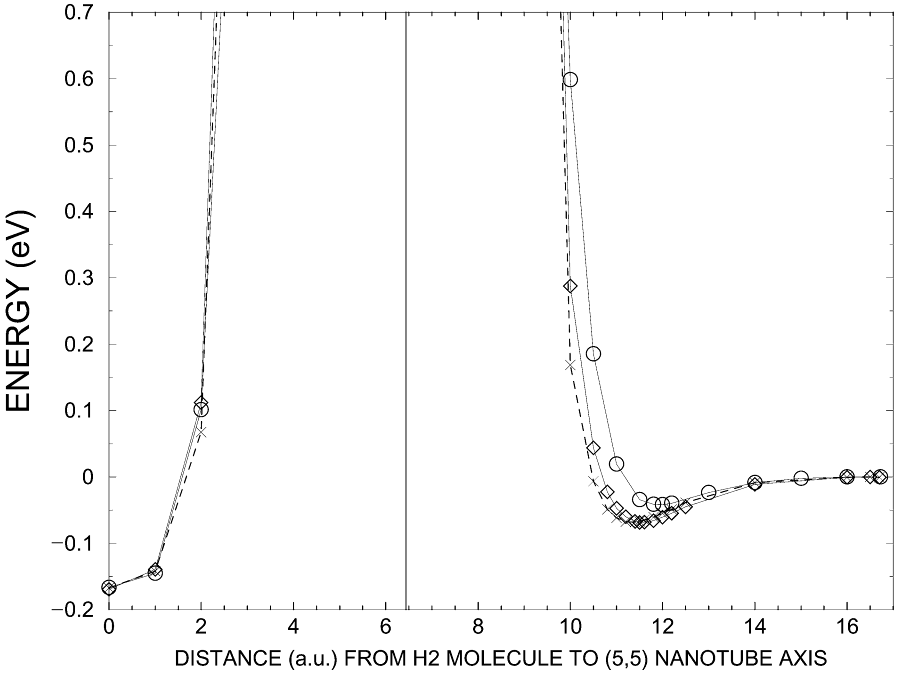

Fig. 2. Potential energy for the physisorption of the hydrogen molecule on a $(5,5)$ carbon nanotube. The vertical line represents the nanotube wall. The curves joining the circles, crosses, and diamonds correspond to the three approaching configurations shown in Fig. 1, from top to bottom, respectively.

We have also studied the interaction of the H_2 molecule with a $(6,6)$ nanotube. The optimized radius of the 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 and 0.12 eV, respectively. The binding energy to the external wall is nearly identical to that for the $(5,5)$ SWNT. An interesting 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 for the $(6,6)$ nanotube, i.e., 0.12 eV, is smaller than the corresponding depth, i.e., 0.17 eV, for the $(5,5)$ nanotube. Our molecular physisorption energies are consistent with those obtained by Li *et al.* [20] for $(7,7)$ nanotubes using a similar DFT method with the LDA. Their calculated value inside the $(7,7)$ nanotube is 0.11 eV/atom. The calculated physisorption energies on the external surfaces of the nanotubes agree with the experimental value of 0.062 eV obtained by Brown *et al.* [24] by thermally activated desorption of H_2 from nanotubes with a radius of approximately 13 a.u. The binding energy deduced by Narehood *et al.* [25] from quasi-elastic neutron scattering is smaller.

From the data collected in Table I, we also notice the good agreement between the DFT and MP2 calculations for adsorption of H_2 on graphene. This is noticeable since the binding energies are very small, less than 0.1 eV. Satisfactory consistency is also found between the theoretical results for graphene and nanotubes, i.e., the binding energy exhibits a dependence on the curvature of the graphitic layer. On the other hand, the theoretical calculations appear to predict higher binding energies than the measured ones. Going back to the original question of the possible enhancement of the physisorption energy due to the nanotube curvature, we notice that the enhancement is substantial for adsorption inside nanotubes, and especially for nanotubes of small radius (a similar enhancement is expected for adsorption in the small channels existing in nanotube bundles). The physisorption energy inside the $(5,5)$ nanotube, i.e., 0.17 eV/molecule, still falls short compared to the value estimated by Li *et al.* [20] to be required for efficient absorption/desorption at ambient pressure and room temperature (0.15–0.2 eV/atom), although the expectations for operation under conditions of lower temperature and higher pressure look better compared to the early estimation based on the calculated physisorption energy on planar graphene.

IV. DISSOCIATIVE CHEMISORPTION

The preferred site for the absorption of a single hydrogen atom on an SWNT is on top of a carbon atom [22], [26]–[29]; in fact, the C–H stretching mode has been observed using Fourier-transform infrared spectroscopy [24]. 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 and 1.3 eV for the $(5,5)$ and $(6,6)$ nanotubes, respectively. The binding energies of an H atom to the nanotube surface calculated previously using DFT show a wide range of values. Gülseren *et al.* [7], [9] and Yildirim *et al.* [8] predicted binding energies higher than 2 eV. Bauschlicher [26] obtained a binding energy $E_b = 0.93$ eV for a $(10,10)$ nanotube. Lee and Lee [28] found $E_b = 1.64$ eV 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

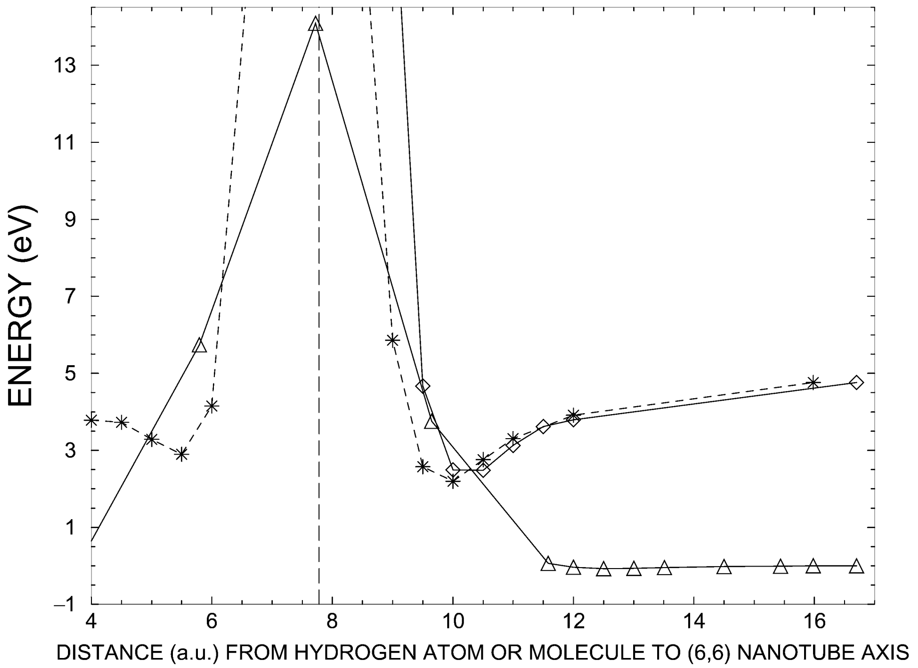

Fig. 3. Interaction energies of molecular (triangles) and atomic (diamonds and stars) hydrogen and a $(6,6)$ SWNT. The atomic curves have been multiplied by two and shifted upwards by 4.76 eV, the dissociation energy of the H_2 molecule. The vertical dashed line represents the nanotube wall.

more drastic on the molecular adsorption: the LDA gives an energy minimum for the interaction between molecular hydrogen and graphene or carbon nanotubes, while the GGA functionals produce a purely repulsive interaction [10], [11], [18].

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 Fig. 3. In the calculations, the C–C bond distances were kept frozen. Another curve, joining the stars, corresponds to the H atom approaching the nanotube over the midpoint of a C–C bond. Molecular adsorption is represented by the curve joining the triangles. In order to compare atomic and molecular adsorption, the two atomic adsorption curves have been multiplied by a factor of two, and have been displaced with respect to the molecular adsorption 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). This 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 this 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, closely approach the nanotube, and the H_2 bond length was also frozen during the approaching of the molecule toward the nanotube.

Several 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 as in configuration A of Fig. 1, i.e., with the molecular axis upon a C–C bond. For distances between the molecule and nanotube wall higher than 3.05 a.u., relaxation of the bond length of the molecule was not observed and the picture drawn from the calculations reported in Section III 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 Fig. 2 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, shown in Fig. 3 for the $(6,6)$ nanotube, remains valid.

V. 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, simulations have been performed 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 toward the physisorption minimum.

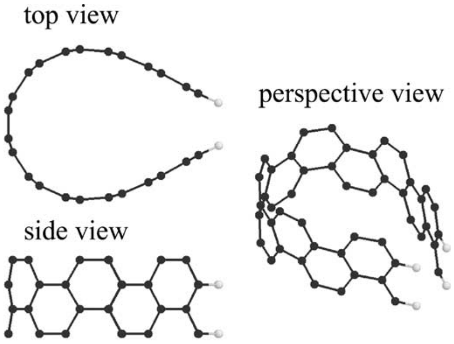

Fig. 4. Broken nanotube for a dynamical simulation starting with the dissociated hydrogen molecule outside a $(6,6)$ nanotube at a distance of 1.2 a.u. from the wall. Three views are shown.

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 III. The simulations also show that the axis of the molecule easily changes its orientation in the physisorption configuration.

Simulations were then 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, although relatively close to each other. This is a configuration of high potential energy, which 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 adsorption of an isolated H atom (see Section IV), and the distance between those two particular carbon atoms increases substantially. A typical snapshot for the $(6,6)$ nanotube is shown in Fig. 4. 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.

Our interpretation is that the scission of the nanotube is due to the sum 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 type of 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 as the starting point of the dynamical simulations. Calculations of atomic chemisorption performed by other authors without the input of that extra potential energy do not lead to nanotube scission [26], [27], thus, we conclude that the extra potential energy has a substantial influence on the breaking of the C–C bonds. As a final effect, it should be stressed that we have performed the simulations for a periodic superlattice geometry, with a relatively small supercell in the direction parallel to the nanotube axis. Due to the periodic repetition of the picture given in Fig. 4, there is a strip of breaking C–C bonds along a line parallel to the nanotube axis. Scission suddenly opens up a new region in the potential energy landscape where the broken nanotube follows a steep path toward 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 complete unfolding of the nanotubes. 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 window allowing foreign atoms or molecules to go inside single-wall nanotubes through their walls, and exploring this possibility may help experimentalists to fill nanotubes with different molecules.

Our simulations have analyzed the effect of an aligned strip of dissociated H–H pairs. Attempts to study more complex configurations than the strip would require an enlarged simulation cell. Calculations performed by Bauschlicher [26] and Bauschlicher and So [27] 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 zigzag pattern related to the configuration of pairs of lines is preferred.

The weakening of C–C bonds could help in explaining the mechanism for the coalescence of SWNTs in ropes and the doubling of SWNT diameters observed by Nikolaev *et al.* [30]. 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 catalyze the coalescence of adjacent nanotubes by the weakening of C–C bonds.

VI. CONCLUSION

First of all, this paper has provided insight into the competition between molecular and atomic adsorption 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 give the following picture: the lowest energy states of those systems are achieved for the H_2 physisorbed outside and inside the nanotubes. Atomic adsorption is possible, but the dissociative chemisorption of the molecule is unfavorable since an energy barrier of approximately 2 eV has to be overcome to dissociate the molecule on the surface of the nanotube. The second conclusion is that the calculated molecular physisorption energies are lower than those required for efficient adsorption/desorption operation at normal pressure and room temperature. The results are then not optimistic for the purposes of hydrogen storage in nanotubes or other porous graphitic materials under normal conditions of temperature and pressure, but the expectations are better for storage at lower temperatures and higher pressures. Finally, when the molecule has enough kinetic energy to closely approach the nanotube wall, the molecule then 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 nanotubes.

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