Theoretical study of the adsorption of H$_2$ on (3,3) carbon nanotubes

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Using density functional theory with the generalized gradient approximation, we have studied the H$_2$ adsorption on (3,3) carbon nanotube with a small diameter of 4 Å. Three adsorption states are found, including one physisorption and two chemisorption states. We find that a chemisorption state similar to that previously reported for larger diameter nanotube will actually evolve into a lower energy state with the underlying C−C bond ripped upon a small perturbation. An energy barrier of 2.7 eV is found for H$_2$ dissociation on the tube. Since the barrier is high, the dissociation of H$_2$ should be a rare event and the interaction of H$_2$ with (3,3) tube is mainly through physisorption. But once chemisorption occurs, the hydrogenated tube is only metastable against ripping.

I. INTRODUCTION

As a renewable and environmentally friendly energy source, hydrogen is believed to be one of the best substitutes for fossil fuels in the future, because of its lightweight, high abundance and its clean oxidation product. However, storage remains problematic till now. Since its discovery,[1] carbon nanotube has attracted much attention with one reason being its suggested suitability as materials for gas storage, and in particular, carbon nanotubes and carbon nanofibers were reported to be promising candidates for H$_2$ uptake. Dillon *et al.*[2] first reported the measurement of its hydrogen storage capacity, and the as-prepared soot containing only about 0.1−0.2 wt % single-wall carbon nanotubes (SWNTs) can absorb H$_2$ molecules of 0.01 wt % at 300 Torr and room temperature, and from this they extrapolated an H$_2$ adsorption for pure SWNTs of 5−10 wt %, assuming that the remainder of the soot is inert. At a cryogenic temperature of 80 K and pressure of 12 MPa, Ye *et al.*[3] found the highly purified SWNTs could adsorb H$_2$ to 8.25 wt %. The amount in another experiment[4] had been found to reach 4.2 wt % at room temperature and about 10 MPa, and 78.3% of the adsorbed H$_2$ could be released under ambient pressure at room temperature. The whole process is revisable. The high H$_2$ uptake of 14−20 wt % was achieved in Chen's experiment[5] by Li- and K-doped multiwalled carbon nanotubes (MWNTs) under ambient pressure at slightly above room temperature, and could be released at higher temperature. The nanotube based H$_2$ storage materials that are safe, practical, and have high enough storage capacity have not been found. There is still much work remaining in this field.

The successful fabrication of ultrathin nanotube[6–9] with diameter of about 4 Å aroused some interest lately in studying its storage ability of hydrogen. Due to its small diameter, its physical properties are found to be somewhat different from tubes of larger diameter[10–13] and a natural question to ask is whether these tubes are good medium for storing hydrogen gas. But before going further into such a study, there are two questions rising: (i) Does H$_2$ like to be physically adsorbed on or to be chemically dissociated adsorbed on such narrow tube? (ii) and if H$_2$ is dissociated adsorbed on tube, does it destroy the tube's structure, given that these ultrasmall tubes are under severe strain? Answering these questions is curial to the study of H$_2$ storage capacity for these ultrathin tubes, either as a standalone entity or embedded inside a template. In the recent years, several first principles calculations have shown that H$_2$ molecule is difficult to dissociate on graphene or nanotube. Miura *et al.*[14] simulated the reaction of H$_2$ on graphene in detail and found that there is a large energy barrier of about 3.9 eV for H$_2$ dissociative chemisorption. As for the (5,5) and (6,6) tube, H$_2$ was also found to be preferably physically adsorbed on the tube's wall. An energy barrier of 3.07 eV was found by Lee *et al.*[15] for H$_2$ dissociated on (5,5) tube. Arellano *et al.*[16] reported that the estimated energy barriers for H$_2$ dissociated on (5,5) and (6,6) tubes are greater than 2.5 eV. However, the ultrathin tube has a diameter of only about 4 Å, and the curvature of the C−C bond on its wall is larger than that on (5,5) and (6,6) tube, and this is expected to contribute to the easier dissociative chemisorption of H$_2$.

There are only three kinds of nanotubes, namely (3,3), (4,2), and (5,0), that have diameters of about 4 Å, and there is strong evidence that tubes of all these chiralities are made simultaneously by the zeolite-templating method.[9,11,12] Among these structures, the tube of (3,3) structure has the largest curvature of C−C bond on tube's wall, which suggests that this tube is most likely to chemically adsorb H$_2$. Hence, in this study, we focus on the (3,3) tube to see if H$_2$ is dissociated when approaching to the wall of tube. In Sec. II of this paper, we present our simulation details and the calculated results of some well known structure parameters. Then we discuss our results in Sec. III. Conclusion is presented in Sec. IV.

II. DETAILS OF CALCULATIONS

Our calculations are performed using a spin-polarized first-principles pseudopotential plane-wave approach within

TABLE I. Structure parameters for graphene, *trans*-polyacetylene $[(HC=CH-)_n]$, diamond and bond lengths for gas molecules acetylene ($HC≡CH$), methane (CH_4); length unit is Å.

System	Hybridization	Experiment[a]	Calculation	Error
$HC≡CH$	sp	$d_{C≡C}=1.203$	$d_{C≡C}=1.201$	$<0.2\%$
		$d_{C-H}=1.060$	$d_{C-H}=1.066$	$<0.6\%$
graphene	sp^2	$a=2.461$[b]	$a=2.463$[b]	$<0.1\%$
$(HC=CH-)_n$	sp^2	$a=2.46$[c]	$a=2.467$[c]	$<0.3\%$
diamond	sp^3	$a=3.567$[d]	$a=3.570$[d]	$<0.1\%$
CH_4	sp^3	$d_{C-H}=1.087$	$d_{C-H}=1.049$	$<0.7\%$

[a]Experimental data cited from Refs. 25–27.
[b]Lattice constant for graphene sheet.
[c]Lattice constant for one dimensional *trans*-polyacetylene chain.
[d]Lattice constant for diamond structure.

the framework of density functional theory (DFT).[18–21] The interaction between the core and valence electrons is described by ultrasoft pseudopotential,[22] and the exchange-correlation energy is calculated using the generalized gradient approximation (GGA).[23] The Perdew-Wang (PW91)[24] parameterization is adopted. The wave functions are expanded in a plane wave base with an energy cutoff of 350 eV. We choose a supercell with a repeat distance of 14.0 Å in X and Y directions, and 8.9 Å in Z direction. Only the Γ point is used in the integration of the Brillouin zone of the simulation cell. Due to the large lattice constants in X and Y direction, the interaction between the tube and its periodic images is negligible. The axis of tube is aligned with the Z direction of surpercell. In order to remove the interaction of H_2 in unit cell with its periodic images, a reasonably large repeat distance of supercell in Z direction is adopted, which is equal to four times of the primitive periodic length of (3,3) tube. The nanotube in unit cell contains 48 C atoms. For each initial configuration, the structure is optimized by the conjugate gradient method,[19] and the relaxation stops when the largest force on all the atoms is smaller than 0.02 eV/Å.

In order to test the accuracy of the method, we have studied the bond lengths of the H_2, C_2, and CH molecules, which are found to be 0.75, 1.26, and 1.13 Å, in good agreement with the experimental results of 0.74, 1.24, and 1.12 Å, respectively.[25] Some well known structure parameters for typical materials with different hybridization of valence orbital are also calculated and presented in Table I. The gas molecules acetylene has sp hybridization character. Two kinds of materials, graphene and *trans*-polyacetylene, have typical sp^2 hybridization character. For the sp^3 hybridization character, diamond, and methane are studied in Table I. The calculated structure parameters presented in Table I are in close agreement with the corresponding experimental results.[25–27]

III. RESULTS AND DISCUSSIONS

In the studies of H_2 on larger diameter carbon nanotube,[15–17] two adsorption states were reported, one is

physisorption and the other one is a chemisorption state. In the chemisorption state, the H_2 molecule dissociates and adheres on two adjacent C atoms on the outer wall of tube. In Fig. 1, we use the (3,3) tube to show the schematic figure of configurations for such adsorption states. The state P stands for the physisorption and the state C for the chemisorption. The two carbon atoms involved directly in the bonding and the H atoms are highlighted. For C1–C2 bond has the largest curvature on tube, it is regarded as the most active area for H_2 dissociated adsorption. Therefore, the previous reported studies adopted the most probable pathway for studying the reaction of H_2 on the wall of tube, by assuming H_2 approaches tube with its molecular bond parallel to the underlying C1–C2 bond, and keeping the center of C1–C2 bond and H–H bond aligned. In our study, we have followed such methodology when pushing H_2 to the outerwall of small diameter (3,3) carbon nanotubes. Arellano *et al.*[16] used the rigid models of (5,5) and (6,6) tubes in their studies, and estimated the energy barrier for H_2 dissociated to be ~2.5 eV. Lee *et al.*[15] fully relaxed both C and H atoms for each position of the center of mass of H_2 along the vertical line on top of the C1–C2, and predicted a 3.07 eV energy barrier for H_2 dissociated adsorption on (5,5) tube. Chan *et al.*[17] pushed the H_2 parallel to the underlying C1–C2 bond toward the outer wall of (5,5) tube and froze the C atoms on the back wall of tube which is in order to simulate the sub-
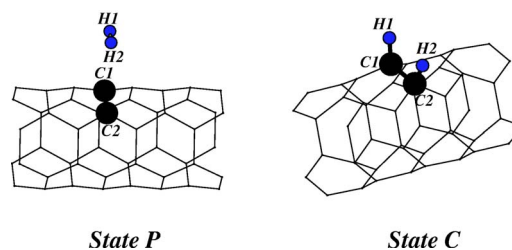

State P   **State C**

FIG. 1. (Color online) Atomic configurations for H_2 adsorbed on (3,3) tube. The left panel is for physisorption with the H1–H2 bond parallel to the underlying C1–C2 bond (state P), and the right one for chemisorption with the underlying C1–C2 bond kept intact (state C).
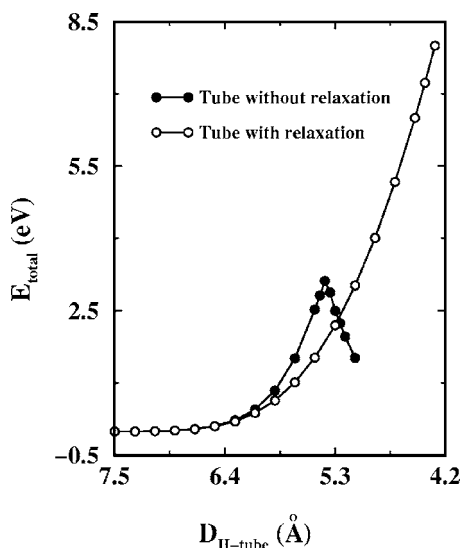
FIG. 2. Total energy vs the distance $D_{H\text{-tube}}$. The solid circle is for the rigid tube, and the open circle is for the tube with relaxation. The H$_2$ is dissociated on the rigid tube with the energy barrier around 3.13 eV, while there is no dissociation even when total energy increases to above $\sim$8.0 eV for tube with relaxation.

strate effect. They first put the H$_2$ far away to the tube, fully relaxed both all the other C atoms and H atoms. Based on the optimized structure, they pushed H$_2$ to the tube by a small distance and then fully relaxed the atoms. By such step by step method, they found that the H$_2$ could not dissociate on tube even when the total energy gained an increase of 8.0 eV.

In the present calculations, we first optimize the configuration of H$_2$ physical adsorption site on the free standing tube. Using the physisorption structure as starting point, we study the reaction mechanism when pushing H$_2$ toward the (3,3) tube (i) by freezing the tube and, (ii) fully relaxing the structure while H$_2$ is approaching the tube. In the latter method by relaxing the structure, we freeze the C atoms on the back wall of the tube when we move H$_2$ toward (3,3) tube as in Ref. 17. In these two methods, the H–H bond is kept parallel to the underlying C–C bond and the H–H bond length is allowed to relax. In order to describe the relative position of H$_2$ to the tube, we define the distance of the center of H–H bond to the frozen back wall of the tube as $D_{H\text{-tube}}$. In Fig. 2, we show the calculated total energy (E_{total}) as a function of the distance $D_{H\text{-tube}}$. The total energy is defined as:

$$E_{total} = E(H_2 + tube) - E(H_2) - E(tube), \qquad (3.1)$$

where $E(H_2+tube)$ is calculated energy of the system containing one H$_2$ and one (3,3) tube, $E(H_2)$ and $E(tube)$ are the energies of free standing H$_2$ molecule and (3,3) tube, respectively. The E_{total} plotted in Fig. 2 shows the basically same results as previously reported. The solid circle is for the method adopting a rigid tube, and the open circle is for the other method adopting a flexible tube. The lines in figure are just for guidance of the eyes. The H$_2$ molecule is difficult to dissociate with two H atoms adsorbed on C1 and C2, respec-

tively, as illustrated in Fig. 2. An energy barrier of $\sim$3.13 eV for H$_2$ dissociation on rigid tube is seen in Fig. 2. However, for the flexible tube which can relax, the open circles in Fig. 2 show that there is no dissociative chemisorption of H$_2$ even when the total energy increases to above 8.0 eV. Our calculation results show that the tube is flexible and it is pressed flat by the approaching H$_2$ when the total energy increases to above 8.0 eV. Within the context of these two methods, the ultrathin tube (3,3) is not particularly chemically active for adsorbing H$_2$ molecule, which is consistent with previous studies for larger radius tube.[15–17]

In fact, finding the minimum energy path (MEP) is a complicated problem. The above discussed methods usually cannot give the correct energy barrier for H$_2$ dissociative chemisorption. It is certainly a rough approximation if we freeze all the atoms of the tube when H$_2$ is approaching, and such study will typically overestimate the barrier. For the particular pathway chosen by the step-by-step method, it seems that the chemical forces to break open the hydrogen molecule is higher than to squash the tube, and thus the H$_2$ molecule never forms chemical bonding with the carbon. The most convincing method for figuring out the MEP is to calculate the potential surface in details. By studying the potential surface in details, Miura et al.[14] studied the H$_2$ dissociated chemisorption on graphene, and found an energy barrier of about 3.9 eV. Considering the curvature of C–C bond compared with its cousin on graphene, it should be more likely for H$_2$ to chemisorb dissociatively on (3,3) tube. However, in the above study for tube with full relaxation, we could not find the dissociation of H$_2$ even when the total energy increases to above 8.0 eV. This suggests that the best pathway on potential surface would probably not be the one with nanotube being pressed too flat, and there is possibility of reaction pathway with lower energy barrier. With the limited computer resource, instead of figuring out the complex potential surface in phase space, we apply the popular nudged elastic band (NEB) method to study the reaction path from state P to state C. The NEB is widely believed to be an efficient and accurate method in finding the MEP.[28,29] We first located the chemisorption state C by optimizing the structure with two H atoms placed close to two adjacent C atoms (the C–C bond is that "wrapping" around the tube). We then choose 16 images along the path from P to C. Figure 3 shows the results related to the MEP calculated based on the electronic structures obtained NEB. In the process of H$_2$ approaching the tube, we note that the H–H bond length ($D_{H–H}$) and the distance $D_{H\text{-tube}}$ change obviously, therefore we choose these two variables to describe the reaction coordinate. In the upper panel of Fig. 3, we present the evolution of these parameters. The lower panel of Fig. 3 shows the total energy as a function of reaction coordinate. Before reaching the saddle point, $D_{H–H}$ sees a very slow increase, and the MEP basically follows a decreasing $D_{H\text{-tube}}$. The repulsion between H$_2$ and tube contributes to the increase of total energy. After reaching the saddle point, the $D_{H–H}$ starts to increase quickly, while $D_{H\text{-tube}}$ remains nearly constant. As the hydrogen molecule breaks up, the bond between C atom and H atom becomes stronger and energy of the whole system decreases to that of state C. An energy barrier of about 2.7 eV could be derived in the lower panel of Fig. 3. Though
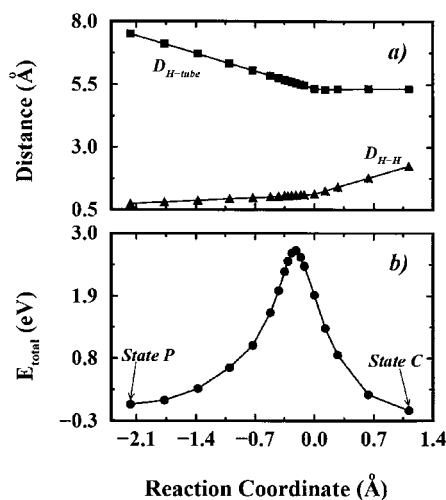
FIG. 3. Results along the minimum energy path from state P to state C. The upper panel presents the evolution of the calculated atomic distances. The squares are for $D_{H\text{-tube}}$, and the up triangles are for D_{H-H}. The lower panel gives the total energy, and the energy barrier for H_2 dissociative chemisorption is found to be ∼2.7 eV. The zero marks the reference reaction coordinate. The left corresponding to the decrease of $D_{H\text{-tube}}$ while the right corresponding to the increase of D_{H-H}.

this barrier of 2.7 eV is smaller than that of larger diameter tubes found previously,[15] it is still high enough that H_2 is hard to be dissociated on (3,3) tube. The total energy of state P is −0.01 eV, while it is 0.1 eV lower for state C. The length of C1–C2 bond in state P is 1.46 Å, while it is weakened in state C. The C1 and C2 atoms are pulled upward in state C with the bond length elongated to 1.61 Å. We note that the GGA formalism is probably not accurate enough to give a quantitative description of physisorption states, and so that value of energy quoted for the P state should be taken to indicate a weak interaction.

Since the diameter of (3,3) tube is only about 4.0 Å, it is under heavy strain and it is interesting to study the stability of state C. In order to check the stability of state C, we have performed first principles molecular dynamics simulation (MD).[20,21] We considered three cases with the initial temperatures of 50, 100, and 300 K, respectively, and a micro-canonical ensemble has been used. The constant energy molecular dynamics run for 1 ps with a time increment of 1 fs. Figure 4 gives the MD results. The distance between C1 and C2 atoms (D_{C-C}) is chosen to measure the stability of state C. In the whole simulation period, the C1–C2 bond is found to stay intact in the first run with a starting temperature of 50 K. There is just some slight fluctuation around its equilibrium bond length of 1.61 Å, which suggests that the state C is stable within that time duration. In the simulations of 100 and 300 K, we note that there are abrupt changes in the interatomic distances between C1 and C2 atoms, which we find to correspond to the ripping open of tube. The abrupt increase happens at a time of 400 fs for 100 K, and it happens at about 110 fs for 300 K. These results indicate that the state C is just a shallow local minimum on the potential surface, and the energy barrier for the transition into a more stable state is very small. In our simulation study, we found
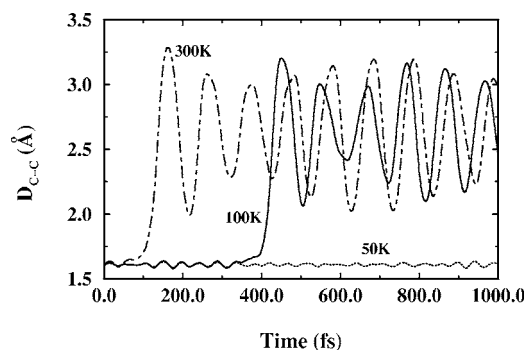

FIG. 4. Molecular dynamics studies of the interatomic distance of the two underlying C atoms. The dotted line is for 50 K, the solid line is for 100 K, and the dot–dashed line is for 300 K. The abrupt increments of the distances for 100 and 300 K suggest the ripping of hydrogenated tube.

that only the underlying C1–C2 bond is broken and all other bonds remain intact in the final state, and for the convenience we label this configuration as state C′. Our results show that the total energy of state C′ is about 1.34 eV lower than state P. For comparison, a larger diameter nanotube (5,5) has also been studied by molecular dynamics. A H_2 molecule is dissociatively adsorbed on its outerwall and the geometry of the chemisorption state is similar to the state C of (3,3) tube. Upon heating to 300 K, we run a molecular dynamics simulation that lasted for 1 ps, found that the geometry remains the intact. This suggests that the hydrogenated (5,5) tube with the underlying C1–C2 bond being intact is a stable configuration, and the curvature indeed plays an important role in the stability of state C of (3,3) tube.

Figure 5 shows the calculated isosurface of the pseudo-charge density of the bare tube, and the tube in state P, state C, and state C′, respectively. The isosurface is plotted here for a charge density value of 1.15 Å^{-3}. The left column of each figure is the top view, and the right column is the side view. The small balls in the figures are used to mark the position of the atoms. Although the C–C bonds on the tube's wall have high curvature, the charge density shows that the characters of bonds for pristine tube are mainly sp^2 hybridization. For state P, we find the physically adsorbed H_2 which is far from the tube has almost no effect on the electronic charge distribution of C–C bonds. However, for state C, the character of hybridization of underlying C1–C2 bond is partially transformed into sp^3 type with two bonds pointing out and terminated by H atoms. This state and the sp^3 character of electronic properties are in good agreement with other theoretical results.[14–16] As discussed above, the state C is not the global minimum, it will evolve to the more stable state C′ under slight thermal agitation. For state C′, there is no charge between C1 and C2 atoms, which suggests that the bond between C1 and C2 is now broken. The C–H bond and two neighboring C–C bonds form the sp^2 hybridization. The special type of bonding configuration as shown in Fig. 5 has not been reported before for larger radius tubes[15,16] and we think that such a configuration is favorable only for ultra-small radius tubes.

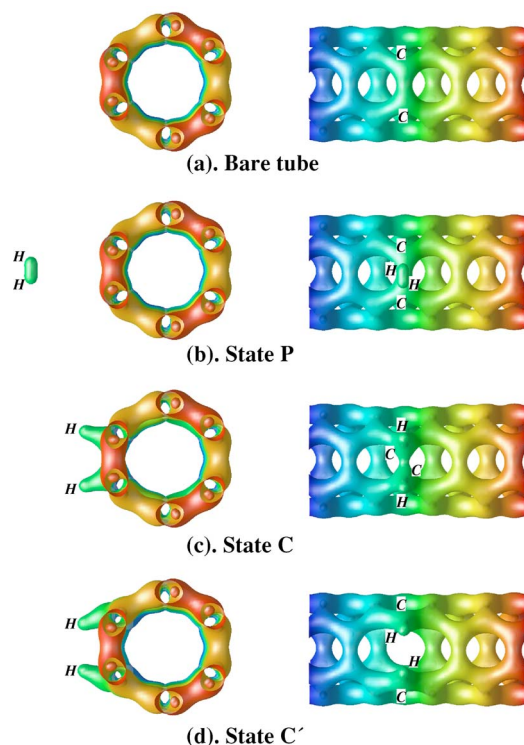Since the state C′ has not been reported before, another implementation of density functional method which is be-

FIG. 5. (Color online) Isosurface of the charge density with the a spacing value of 1.15 Å^{-3} for (a) bare tube; (b) state P; (c) state C; and (d) state C′. Note the splitting open of the C−C bond by the hydrogen in state C′; C′ is the lowest energy state.

lieved to be even more accurate has been used to double check if we get the correct adsorption states. Additional calculations are performed in density functional theory[18–21] using the projector augmented-wave (PAW) method,[30] and the exchange-correlation described by the Perdew, Burke, and Ernzerhof generalized gradient approximation (PBE-GGA).[31] The energy cutoff is 400.0 eV for expanding the wave function using a plane wave basis. The Γ point is used in the optimization of the structures. We found that the structures of state P, state C, and state C′ are almost exactly the same as those found using ultrasoft pseudopotential. The total energies are −0.01, −0.08, and −1.24 eV, respectively, agreeing well with the pseudopotential calculations. The same results have been also obtained by calculations with more k-points along k_z direction in irreducible Brillouin zone.[32]

The MEP discussed above is for the transition from state P to state C, and the energy barrier is found to be 2.7 eV. We employed another method, namely the dimer method developed by Henkelman and Jónsson,[33] to check the results of the barrier from state P to C, and used the dimer method to estimate the energy barrier from state P to state C′. The dimer method is useful in finding the saddle point (although not the entire MEP) by defining a dimer with two neighboring images on potential surface. If the images are away from the saddle point, the dimer will be moved uphill on the potential energy surface. Along the way, the dimer is rotated in order to find the lowest curvature mode of the potential en-

ergy at the point where the dimer is located. This method can give a good estimation of energy barrier. The dimer method gives an energy barrier of 3.95 eV for H_2 dissociated on graphene, which is within 1% of the value reported by Miura.[14] These results show that the dimer method is reliable in estimating the energy barrier on MEP for these carbon systems. For transition from state P to state C, the energy barrier obtained by dimer method is 2.7 eV, and the saddle point is found to be the same one obtained by the NEB method. By the dimer method, we find that the barrier for the transition from state P to state C′ is also 2.7 eV, and the saddle point is the same one for transition from state P to state C. This suggests that the metastable state C may be the intermediate transition state between state P and state C′. More specifically, direct computation of the barrier from P to C′ still gives a value 2.7 eV exactly the same as that between P and C. Since there is a large energy barrier on its MEP, the dissociation of H_2 on the tube is difficult. However, once the system transits to the metastable state C, a small perturbation will drive the system to the final stable state C′, which is shown by our MD simulations results. The tube will be ripped open. The heat released is about 1.3 eV. If there are many H atoms chemically absorbed on tube, there will be much heat to be released and the ripping open of the tube should be irreversible.

IV. CONCLUSIONS

We have performed an extensive theoretical study on the H_2 adsorption on small diameter (3,3) carbon nanotube, the type of ultrasmall radius tube that has been fabricated recently by templating methods. Three adsorption states are found, one is a very weak physical adsorption and the other two are chemisorption states. The weaker state C, with the tube intact, has atomic configurations similar to those previously found for larger tubes, while the ground state C′ corresponds to a locally split-open configuration. The bare tube, the physical adsorption state P, and the chemical adsorption state C′ have sp^2 characters. The chemisorption state C has the sp^2 hybridization character and sp^3 hybridization character as well, and the sp^3 consists of the C−H bond and its three neighboring C−C bonds. The nudged elastic band method is applied to search for the minimum energy path for transition from state P to state C, and the energy barrier is found to be 2.7 eV. The dimer method also finds a barrier of 2.7 eV. The energy barrier from state P to state C′ is calculated to be 2.7 eV by dimer method, and the saddle point is found to be the same as that between state P and state C. The state C may be a transition state for H_2 dissociated chemisorption to a final ground state in which the tube is opened. Because of the large barrier, it is hard for H_2 to dissociate on tube and the preferable adsorption is the physical adsorption. Our MD simulation results show that the state C will be destroyed in the run with starting temperatures being 100 and 300 K, respectively, which indicates that state C is only a metastable state and the barrier is very small for evolution to state C′. The final chemisorption state C′ has two H atoms adsorbed upon two underlying C atoms, and the C−C bond is broken.

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