

## Chemisorption of Hydrogen Molecules on Carbon Nanotubes under High Pressure

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Based on first principles calculations, we propose a mechanism for the dissociative chemisorption of  $H_2$  on carbon nanotubes. The breaking of the H—H bond is concerted with the formation of two C—H bonds on two adjacent carbon nanotubes in solid phase, facilitated by the application of high pressure which shortens the interstitial distance between nanotubes. The process is reversible upon the release of external pressure and could make an important contribution to the observed hydrogen storage capacity of carbon nanotubes. The previously unexplained experimental observations of the direct hydrogenation of fullerenes under high pressure lend further support for such a mechanism.

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Storage of hydrogen by carbon nanotubes has shown great promise and attracted much attention recently [1–3]. Experimentally, this is achieved in the solid phase with carbon nanotubes mixed with hydrogen gas under high pressure and often at low temperature. The mechanism is, for the most part, attributed to physisorption both inside the tubes and in the interstitial regions in several theoretical studies based on classical molecular dynamics [4,5] and density functional theory (DFT) [6]. In contrast, studies on the interaction between hydrogen and fullerenes, the close cousin of carbon nanotubes, have been focused more on the chemical process of hydrogenation, with the products  $C_{60}H_x$  and  $C_{70}H_x$  being of fundamental interest as a model for other fullerene derivatives [7], and also as a potential storage medium for hydrogen. A variety of chemical procedures have been devised to produce hydrogen radicals that could adsorb readily on these carbon atoms, using either reducing reagents [8,9], or catalysts [10].

Of particular interest and very relevant to the study of carbon nanotubes is the direct solid phase hydrogenation, with hydrogen molecules reacting with fullerenes under high pressure (0.5–30 kBar) at elevated temperature (500–600 K) [11]. Potentially, every carbon atom on a fullerene or a carbon nanotube could be a site for chemisorption of one hydrogen atom [7,12], as the  $\pi$  bonding between carbon atoms is saturated. But it takes 4.52 eV to break the H—H bond [13], and the mechanism for a direct reaction between  $H_2$  and  $C_{60}$  or  $C_{70}$  remains unexplained to the best of our knowledge.

The observation of direct hydrogenation of fullerenes invites a question: Could chemical processes also play a role in the hydrogen storage experiments on carbon nanotubes? In fact, reported experiments have already provided some hints. Liu *et al.* noticed that, after treating carbon nanotubes with hydrogen gas under high pressure, there was residual  $H_2$  during the desorption cycle that could be released only upon heating to temperatures above 400 K [2]. They suspected that these residuals may be related to chemical adsorption. A more recent experiment using high

purity single-walled nanotubes found a first order phase transition under high  $H_2$  pressure, similar to the hydride phase observed in metal-hydrogen systems [3]. Very recently, Lee *et al.* considered the carbon nanotubes with a full layer of chemisorbed hydrogen on the exterior wall, and suggested an interesting storage mechanism by flipping H atoms inside [12]. However, they assumed that the chemisorption took place by a hypothetical electrochemical process in solutions, rather different from the conditions for the reported storage experiments [1–3].

In this Letter, we report computational studies on the interaction between a hydrogen molecule with a single carbon nanotube, as in gas phase conditions, and with a solid of carbon nanotube arrays under high pressure. We found that chemical adsorption is unlikely in the gas phase. But in solid, the dissociative chemisorption of hydrogen molecules in the interstitial region on the exterior of carbon nanotubes is made possible by the high pressure environment in the storage experiment. First principles calculations based on DFT with a plane wave basis set [14], Vanderbilt ultrasoft pseudopotentials for the atomic core regions [15], and exchange-correlation functional within general gradient approximation [16] are performed using the Vienna *Ab Initio* Simulation Package (VASP) [17]. The cutoff energy is 287 eV for the plane wave basis set, and two  $k$  points are used in the average sampling.

First, we modeled the interaction between a hydrogen molecule  $H_2$  with one single (6,6) armchair carbon nanotube, in a supercell of the size  $18.5 \text{ \AA} \times 18.5 \text{ \AA} \times 4.996 \text{ \AA}$  with the length of  $c$  adjusted to the periodicity of the (6,6) nanotube. The addition of a hydrogen molecule to two directly bonded carbon atoms on the (6,6) nanotube (the 1,2 addition) results in a small energy loss of 0.45 eV in our calculation.

We first consider the case in which the incoming  $H_2$  has one hydrogen atom pointed directly at a carbon atom with the H—H bond perpendicular to the nanotube wall. The net result is not the formation of a H—C bond and the breaking of a H—H bond. Instead, the nanotube is

deformed and no reaction happens even though the total energy has risen above 6 eV, as shown in Fig. 1. This is hardly surprising. Our calculated binding energy is 4.60 eV for  $H_2$  and 4.78 eV for the  $H-CH_3$  bond. Compared to the corresponding experimental values of 4.52 eV ( $H-H$ ) and 4.54 eV ( $H-C$ ) [13], the calculated energies are in reasonable agreement with experiment. Because of the strain and the disruption to the conjugate  $\pi$  bonding on the surface of a carbon nanotube, the calculated binding energy for a chemisorbed hydrogen atom on the (6,6) nanotube is only 1.57 eV (Table I). Thus, the formation of the  $H-C$  bond is not enough to compensate the breaking of the  $H-H$  bond.

The possibility of a concerted mechanism for the formation of two  $H-C$  bonds and breaking of the  $H-H$  bond is also explored, with the  $H-H$  bond above and parallel to one of the  $C-C$  bonds. Energetically, the formation of the second  $H-C$  bond in the 1,2-addition product is 0.97 eV more favorable than that for the first  $H-C$  bond (Table I), and the simultaneous formation of both would better compensate the energy loss incurred by the  $H_2$  dissociation. Again we observed the deformation of the carbon tube, instead of the  $H_2$  addition. The equilibrium  $H-C$  bond distance is around 1.1 Å. For both trajectories shown in Fig. 1, a steep increase in van der Waals repulsion is encountered around the 2 Å  $H-C$  distance, long before the  $H-C$  bonding interactions could take effect. By the time the  $H-C$  distance decreased to 1.8 Å, the repulsion energy is more than the  $H-H$  binding energy. We have attempted quite a few trajectories with an  $H_2$  molecule approaching the (6,6) nanotube in various orientations. The results are always large deformation of the tube, and, at last, the divergence of our calculation at very high repulsion energy, but never the dissociative chemisorption of  $H_2$ . It indicates that a direct reaction between an  $H_2$  molecule and a single nanotube would indeed be very difficult.

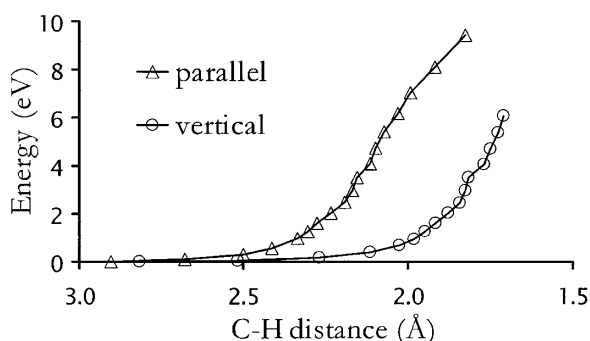


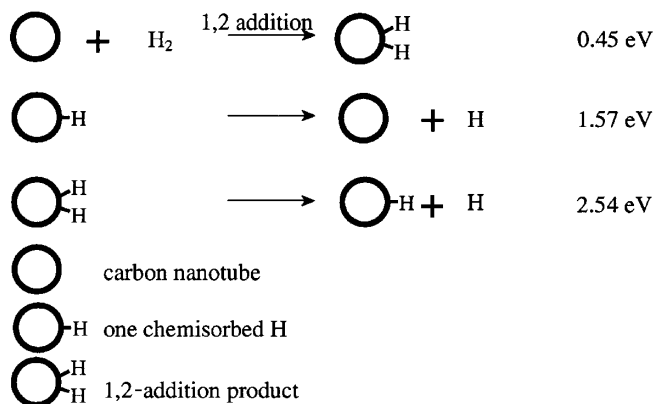
FIG. 1. Relative total energy as a function of  $C-H$  distance when a hydrogen molecule  $H_2$  approaches a single (6,6) armchair carbon nanotube. The total energy at  $C-H$  distance of 2.8 Å is set at zero. In the vertical case, the  $H-H$  bond is perpendicular to the nanotube wall with one  $H$  pointing right at one of the carbon atoms, and the distance between the two atoms is used as the  $C-H$  distance. In the parallel case, the  $H-H$  bond is above and parallel to one of the  $C-C$  bonds, and the two  $C-H$  distances are averaged in the figure. In both cases, there is a sharp increase in energy due to van der Waals repulsion, and no reaction is observed.

In contrast, the solid phase, composed of bundles of carbon nanotubes, provides a unique chemical environment that is dependent on the external pressure and makes it possible for the  $H_2$  dissociative chemisorption on carbon nanotubes. Shown in Fig. 2 is a system with a tightly packed trigonal array of (6,6) tubes and a hydrogen molecule  $H_2$  in the interstitial region. In our calculation, two tubes were used in the unit cell, with the length of  $c$  fixed at 4.996 Å while  $a$  and  $b$  adjusted proportionally to introduce external pressure. The total energy is at a minimum for  $a = 12.0$  Å, and a pressure of  $\sim 50$  kBar is introduced at  $a = 10.5$  Å. Upon heating to 800 K, a reactive trajectory [18], following steps in Fig. 2, is observed. With each  $H$  atom pointing at one nanotube, the  $H_2$  molecule goes through a concerted dissociation, depositing the two hydrogen atoms each on one of the two adjacent nanotubes to form structure *B*. After slight rotations of the nanotubes, one of the hydrogen atoms then further migrates from one tube to another, forming structure *C*, a 1,2-addition product.

The key difference between the solid phase (Fig. 2) and the gas phase (Fig. 1) is the presence of many carbon nanotubes in a tightly packed array in solid. For a concerted dissociative addition process in the gas phase, the  $H_2$  is pushed directly towards the wall of a carbon nanotube and the resulting van der Waals repulsion is too strong to overcome. In solid, the incoming  $H_2$  is pushed towards the interstitial region between two neighboring nanotubes. The van der Waals repulsion is reduced, while the two

TABLE I. Calculated reaction energy for the (6,6) armchair carbon nanotube/hydrogen system. The dissociated state is modeled by moving a hydrogen molecule or a hydrogen atom about 5.5 Å away from the nanotube.

a. Reaction energy for hydrogen addition and subtraction



b. Energy difference between the solid phase structure *A* and *C* (see Fig. 2)

Lattice parameter $a$ (Å)	$E_C - E_A$ (eV)
10.5	-0.52
11.0	0.26
11.5	0.40
12.0	0.41

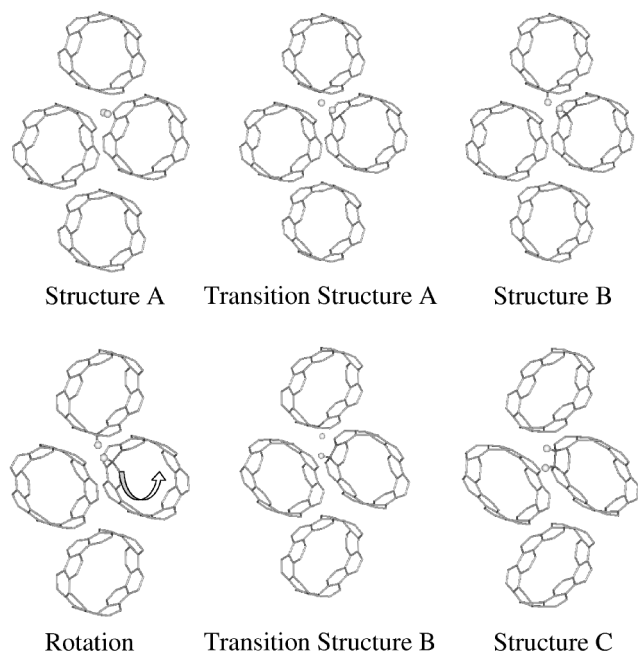


FIG. 2. The structures and transition structures for the dissociative  $H_2$  chemisorption on an array of carbon nanotubes in solid under high pressure. There are three steps involved: first,  $H_2$  dissociation and deposition on two adjacent tubes, from structure A to B, through transition structures (TS) A; second, the rotation of tubes; and finally, hydrogen migration through TS B to structure C, a 1,2-addition product. There is a noticeable deformation of the nanotube as the cylindrical symmetry of the nanotube is broken in structure C.

nanotubes and the  $H_2$  molecule are lined up optimally for converted  $H_2$  dissociation. The external pressure also plays a crucial role in facilitating this process. Suppose the concerted breaking of the H—H bond and formation of the two C—H bonds fall within a straight line, the approximate C—C length, based on simplistic geometry argument, should be around  $2d_{C-H} + d_{H-H} = 2 \times 1.1 + 0.8 = 3.0 \text{ \AA}$  or shorter. Our calculation found that, at  $a = 12.0 \text{ \AA}$ , the shortest carbon-carbon distance between two adjacent tubes is  $3.8 \text{ \AA}$ , which is large enough for  $H_2$  to squeeze through without a reaction, considering the remarkable elasticity of the carbon nanotubes. However, when external pressure is applied by compressing the unit cell to  $a = 10.5 \text{ \AA}$ , the adjacent C—C distance is shortened to  $2.6 \text{ \AA}$ , ideal for capturing  $H_2$  in the concerted dissociative adsorption. The external pressure also decreases the tube elasticity and forces the carbon atoms into bonding interaction with the incoming  $H_2$ . It should be noted none of these considerations depends on any specific alignment between the nanotubes, although perfectly aligned nanotubes are used in our simulation. Whether it is for the bundles or tangles of carbon nanotubes, there are plenty of sites for such chemisorption once external pressure is exerted.

To better understand this process, the transition structures and energy barriers involved (Fig. 2) are obtained by optimization using the nudged elastic band method [19]. For the dissociation step, the calculated energy barrier is

approximately  $1.50 \text{ eV}$ , and the product is an intermediate structure B, as shown in Fig. 3. The subsequent rotation of the tubes has a very low barrier of  $0.06 \text{ eV}$ , while for the final step of hydrogen migration the barrier is  $0.11 \text{ eV}$ . The final structure C, a 1,2-addition product, is  $0.52 \text{ eV}$  lower in energy than structure A and  $1.67 \text{ eV}$  lower than structure B. These last two steps should thus proceed easily and the overall reaction of  $H_2$  addition is exothermic.

Such a mechanism should also explain the observed direct hydrogenation of solid fullerenes under high pressure [11]. In this case, the interstitial region of two adjacent fullerene balls provides the arrangement for the concerted dissociative  $H_2$  chemisorption, as high pressure shortens the interstitial distance between fullerenes and makes fullerenes more rigid. There is nonetheless a significant difference between fullerenes and fullerene tubes regarding hydrogenation. As demonstrated in the Hartree-Fock calculations by Cahill and Rohlfing [7],  $H_2$  addition to  $C_{60}$  results in an energy gain of  $160 \text{ kJ/mol}$  ( $1.7 \text{ eV}$ ), while  $H_2$  addition to the sidewall of a carbon nanotube is nearly thermal neutral. Thus the direct hydrogenation of fullerenes under high pressure can produce hydrofullerite efficiently, which can then be collected for spectroscopic analysis [11].

For carbon nanotubes, the situation is more complicated and interesting. As mentioned earlier, our calculation found a small energy loss of  $43 \text{ kJ/mol}$  for the  $H_2$  addition to the (6,6) nanotube, in agreement with the Cahill-Rohlfing prediction [7]. As a result, structure A is more stable than structure C (hydronanotube) when the unit cell is not compressed ( $a = 12.0 \text{ \AA}$ ). However, this energy difference is dependent on external pressure (Table I), and, when  $a$  is shortened to  $10.5 \text{ \AA}$ , the energy ordering is reversed, with structure C  $0.52 \text{ eV}$  lower in energy than structure A (also see Fig. 3). At  $a = 10.5 \text{ \AA}$ , the distance between the H atoms and the three surrounding nanotube walls is just over  $2.3 \text{ \AA}$ , and the van der Waals repulsion should be very strong (see the energy curve in Fig. 1). Such repulsion can be significantly lowered for the

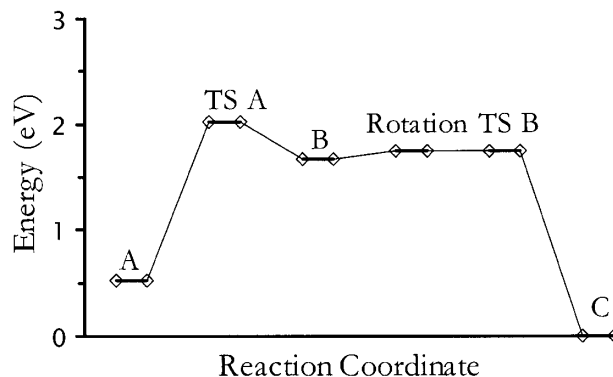


FIG. 3. The relative energies for the structures and transition structures shown in Fig. 2. The initial dissociative chemisorption step (structure A to B) has a barrier of  $1.50 \text{ eV}$ , while the barrier for the subsequent H migration (structure B to C) is much lower at  $0.12 \text{ eV}$ .

1,2-addition product, structure *C*, in which the two hydrogen atoms are bonded on one carbon nanotube. As the H—C distance reduces from 2.3 to  $\sim 1.1$  Å, the van der Waals repulsion is replaced by the attractive H—C bonding interaction. At the same time, the distances between the two hydrogen atoms and the other two tubes are increased, which results in further reduction in the repulsion. On the other hand, the cylindrical symmetry of the tube is broken upon chemisorption of hydrogen atoms, and as a result there is noticeable distortion in the shape of the nanotubes. The reversal of the energy ordering between structures *A* and *C* is thus mainly due to the reduction of van der Waals repulsion.

Overall, there should be a reversible equilibrium between adsorption (structure *C*) and desorption (structure *A*), through the intermediate structure *B*, and its direction is dependent on the external pressure. Similar to the direct hydrogenation of fullerenes [11], elevated temperature may be necessary to facilitate the equilibrium, as the barrier for the first step in the suggested mechanism is 1.5 eV. The well-known rotation of carbon nanotubes could also play a role because it could bring two chemisorbed hydrogens on separate, yet adjacent, nanotubes close to each other, and provide an alternative pathway to the formation of the intermediate structure *B*. Most of the reported studies on hydrogen storage by carbon nanotubes were performed at room and low temperatures, in which physisorption definitely plays an important role. Although there were hints of chemisorption [2], the relative importance of physisorption versus chemisorption has to wait future studies at elevated temperatures, in which the contribution of the chemisorption process could be singled out. It would also be interesting to treat such systems under high hydrogen pressure, first at high temperature and then at low temperature, to explore the possibility of raising hydrogen storage capacity by taking advantage of both chemical and physical adsorption.

In summary, we have found from first principles calculations that direct reaction between an H<sub>2</sub> and two adjacent nanotubes in solid could proceed under high pressure with the dissociative chemisorption of H<sub>2</sub>. Such a mechanism could also be applied to the previously unexplained experimental observation of the direct hydrogenation of solid fullerenes under high hydrogen pressure. In addition, the suggested mechanism also represents an example in which the chemical environment in the interstitial regions of carbon nanotube bundles is dramatically changed by the exertion of external pressure, and, as a result, a previously inaccessible reaction channel is opened. It shall be very interesting to see if similar mechanisms would work for the interaction between other small molecules and carbon nanotubes under pressure.

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- [19] G. Mills, H. Jónsson, and G. K. Schenter, *Surf. Sci.* **324**, 305 (1995); H. Jónsson, *Annu. Rev. Phys. Chem.* **51**, 623 (2000). Briefly, for each reaction step, a series of structures are first generated by linear interpolation combining the structures of the reactant and the product (for example, structures *A* and *B* for the dissociation step), and together they are taken as discrete points of an approximate reaction path. A penalty function, which treats every distance between two adjacent points as a spring (elastic band), is added to the sum over the total energy of every point along the path. This function is then minimized versus the structures of all these points, and at convergence it maps out a minimum energy reaction path and produces the energy barrier and transition structure. In our calculations, we use the scheme implemented within the VASP program, with up to 16 points for a reaction path.