

**Hydrogen on graphene under stress: Molecular dissociation and gap opening**Hayley McKay,<sup>1</sup> David J. Wales,<sup>1</sup> S. J. Jenkins,<sup>1</sup> J. A. Verges,<sup>2</sup> and P. L. de Andres<sup>2</sup><sup>1</sup>*University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW, United Kingdom*<sup>2</sup>*Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, E-28049 Madrid, Spain*

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Density-functional calculations are employed to study the molecular dissociation of hydrogen on graphene, the diffusion of chemisorbed atomic species, and the electronic properties of the resulting hydrogen on graphene system. Our results show that applying stress to the graphene substrate can lower the barrier to dissociation of molecular hydrogen by a factor of 6 and change the process from endothermic to exothermic. These values for the barrier and the heat of reaction, unlike the zero stress values, are compatible with the time scales observed in experiments. Diffusion, on the other hand, is not greatly modified by stress. We analyze the electronic structure for configurations relevant to molecular dissociation and adsorption of atomic hydrogen on a graphene single layer. An absolute band gap of 0.5 eV is found for the equilibrium optimum configuration for a narrow range of coverages ( $\theta \approx 0.25$ ). This value is in good agreement with experiment [D. Elias *et al.*, *Science* **323**, 610 (2009)].

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**I. INTRODUCTION**

The safe and efficient storage of hydrogen is a crucial step toward its use in the future as an energy vector. The U.S. Department of Energy (DOE) has launched an important challenge by funding research to overcome the threshold of 6.5 kg of stored hydrogen per 100 kg of total storage system weight.<sup>1</sup> In the present contribution we focus on the “gas adsorbed on solid” approach, with graphene layers as the supporting material. Adsorption of hydrogen on graphene (G) can take place in different ways: (i) physisorption of molecular hydrogen, (ii) physisorption of atomic hydrogen, (iii) chemisorption of atomic hydrogen, and (iv) chemisorption of small clusters of atomic hydrogen. These scenarios exhibit different adsorption/desorption energies, optimum geometrical configurations, and diffusion barriers. A good understanding of the interplay between molecular physisorption and atomic chemisorption would be useful for addressing the problem of hydrogen storage, as well as for understanding fundamental issues, such as the puzzle of how H<sub>2</sub> is formed in the interstellar medium.<sup>2</sup>

Graphene itself is currently of particular interest due to the recently developed capability for obtaining samples consisting of single or a few layers.<sup>3</sup> Such layers provide an excellent model for advancing the applications of related materials, such as graphite and nanotubes. In particular, graphite is an attractive candidate for hydrogen storage because it is cheap, chemically inert and environmental friendly. However, theoretical and experimental studies have cast doubts about achieving the goal proposed by the DOE, with certain exceptions that have focused on the quantum properties of such a light element as hydrogen.<sup>1</sup>

To investigate the feasibility of loading and releasing hydrogen efficiently in graphite or carbonaceous minerals we have characterized diffusion and dissociation barriers for hydrogen on graphene under stress. External and internal stresses have been reported to induce interesting chemical properties in carbon-based molecules,<sup>4</sup> nanotubes,<sup>5</sup> graphene layers,<sup>6</sup> etc. We find that on applying a moderate amount of

stress the equilibrium state and the barriers for molecular dissociation become much more favorable.

Understanding the hydrogenation of graphene layers is important from several perspectives. Recently, in a series of elegant experiments, Elias *et al.*<sup>7</sup> have demonstrated the reversible transition of graphene layers from a semimetallic to a semiconducting regime upon adsorption of hydrogen. This is an interesting observation, which should help to advance the application of graphene layers in microelectronics. Our results should provide insight into these experiments, particularly the conditions required to create an absolute band gap in the graphene semimetallic band structure, in terms of the adsorbate coverage.

**Methods**

Our calculations are based on density-functional theory (DFT).<sup>8</sup> We calculated the adsorption energies, dissociation pathways, and barriers for atomic and molecular hydrogen on a  $3 \times 3$  periodic supercell with a vacuum gap in the perpendicular direction of 10–20 Å. The wave functions were expanded in a plane-wave basis set up to a cutoff of 350 eV and were sampled on a Monkhorst-Pack  $6 \times 6 \times 1$  mesh inside the Brillouin zone. Electronic bands were obtained using a smearing width of  $\eta = 0.01$  eV. Carbon and hydrogen atoms were described by soft pseudopotentials.<sup>9</sup> The choice of the exchange and correlation (XC) potential is an important aspect of DFT calculations. We considered both the local-density approximation (LDA) (Ref. 10) and a generalized gradient approximation (GGA) functional, Revised Perdew-Burke-Ernzerhof (RPBE),<sup>11</sup> to check the influence of that choice on our results. This formalism is accurate enough to reproduce structural and electronic properties of chemisorbed species, but cannot describe the physisorption regime, because the nonlocal correlation effects needed to address the weak van der Waals interactions are not included. The energy differences of interest here, and their variation with external stress, are relatively insensitive to whether the LDA or RPBE functional is used. Furthermore, the errors associated with

the DFT formalism at large distances are unimportant because the energies involved in making/breaking chemical bonds are much greater than the few millielectron volts associated with van der Waals interactions.

Total energies and gradients were computed with the CASTEP program,<sup>12</sup> interfaced to OPTIM (Ref. 13) for geometry optimization. All the transition states reported below were refined using the gradient-only version of hybrid eigenvector-following<sup>14–16</sup> with a convergence condition of 0.01 eV/Å for the root-mean-square gradient. Approximate steepest-descent paths were calculated by energy minimization for each transition state to characterize the corresponding pathway using the limited-memory Broyden-Fletcher-Goldfarb-Shanno algorithm,<sup>17</sup> following displacements of order 0.01 Å parallel and antiparallel to the Hessian eigenvector corresponding to the unique negative Hessian eigenvalue.

## II. RESULTS AND DISCUSSION

The most favorable configuration for hydrogen on graphene corresponds to molecular physisorption 3.5 Å above the hollow site. The physisorption energy is small,<sup>18</sup> but it is not relevant here, since we are dealing with processes involving much larger changes in energy, such as the formation of a hydrogen-carbon bond or breaking the bond in the hydrogen molecule. In contrast, for atomic hydrogen the most favorable configuration involves chemisorption directly on top of a carbon atom. RPBE calculations show that the C-H bond length is then 1.1 Å, corresponding to an adsorption energy of  $E_{G+H} - E_G - \frac{1}{2}E_{H_2} = +1.68$  eV while the carbon directly below is puckered upward by 0.4 Å. It is important to notice that chemisorption of atomic hydrogen interferes with the strong  $sp^2$  sigma bonds of planar graphene, producing an energetic cost derived from the elastic deformation of the substrate. Hydrogen atoms approaching a graphene surface from the gas phase therefore encounter a barrier in reaching the chemisorbed state. This barrier depends on the position on the surface, varying between 0.28 and 1.27 eV for atop and hollow sites (RPBE functional).

Both atomic and molecular hydrogen are trapped on the graphene surface in a relatively shallow physisorption well at large distances ( $\geq 3.5$  Å for the RPBE functional). The diffusion barriers for physisorption are low and hence the adsorbed species are mobile. However, physisorbed species are subject to a correspondingly high desorption probability; at room-temperature (RT) physisorbed atomic or molecular hydrogen desorb on a time scale of nanoseconds. The only way to keep such a system stable on a reasonable time scale for practical applications is to reach a chemisorbed state. While hydrogen molecules do not chemisorb, atomic hydrogen can form strong bonds on atop sites, provided that (i) the molecule initially dissociates and (ii) atoms can find the favorable region where barriers between physisorbed and chemisorbed minima are small. The values we obtain for the barriers imply that at RT a hydrogen atom would find its way to the chemisorbed well on a time scale of nanoseconds near the atop region while it would take years for chemisorption to occur via a trajectory only involving the local minimum

corresponding to the hollow site. To meet the DOEs challenge we need to consider the formation and dissociation of the hydrogen molecule in the high coverage regime. The reaction  $H_2 \rightarrow 2H$  near a free-standing graphene sheet is associated with a barrier of 3.29 eV and an endothermic heat of reaction of 1.89 eV, making dissociation of molecular hydrogen a rare event (RPBE values quoted here). Furthermore, to load a stack of graphene layers efficiently we need to consider the diffusion barriers for atomic hydrogen. Our calculations show that chemisorbed hydrogen diffuses from top site to top site via bridge sites with an associated barrier of 0.98 eV. External stress increases the diffusion barrier by 9% and 60% for tensile and compressive strains of  $\epsilon=0.1$  and  $-0.05$ , respectively (Fig. 1). These barriers result in diffusion times that are too long for effective loading of chemisorbed hydrogen in graphite at RT ( $\approx 10^4$  s for a single hop), leaving diffusion of molecular hydrogen or physisorbed atomic species as the most practical scenarios. Diffusion through the hollow site is unfavorable, involving a barrier of 4.05 eV, resulting in a practically impenetrable layer in the perpendicular direction at RT, in good agreement with experiment.<sup>7</sup>

### A. $H_2$ dissociation on graphene

We now examine the effect of internal and external stresses on  $H_2$  dissociation/formation. Figure 2 shows how the barriers and reaction energies for the dissociation process are affected by external stress. The deformations considered here are quite realistic for graphene, a material that can accommodate tensile strains up to  $\epsilon=0.25$  Å (corresponding to a stress of  $\sigma \approx 42$  N m<sup>-1</sup>) before breaking up.<sup>19</sup> Compressive strains of up to  $\epsilon=-0.05$  have also been measured from diffraction experiments in hydrogenated samples<sup>7</sup> (our calculations corroborate that these samples tend to buckle on an atomic scale, at least in the region around the adsorbates). Indeed, C-C bonds can accommodate a wide range of values, from 1.37 Å for triple bonds ( $sp$  hybridization) to 1.54 Å for single bonds ( $sp^3$  hybridization), with a typical minimum value in allenes of 1.30 Å and a maximum observed bond length of 1.78 Å.<sup>4</sup> For tensile stresses related to uniform deformations in the two-dimensional (2D) lattice between  $\epsilon=0.10$  and 0.15 the barriers are not strongly affected but the heat of reaction for molecular hydrogen dissociation changes from endothermic ( $\Delta E=1.89$  eV for  $\epsilon=0$ ) to exothermic ( $\Delta E=-0.88$  eV at  $\epsilon=0.15$ ). These results (values quoted for RPBE) show that between RT and 500 K, physisorbed molecular hydrogen would not transform to chemisorbed atomic hydrogen on a reasonable time scale. In contrast, a compressive strain introduces a totally different scenario: for  $\epsilon=-0.05$  the RPBE barrier drops to 2.19 eV, improving the predicted time for dissociation by about a factor of  $10^{11}$ ; for  $\epsilon=-0.1$  the barrier decreases to 0.59 eV, which should allow a single physisorbed  $H_2$  molecule to dissociate on a time scale of milliseconds at RT. These RPBE values are expected to compare well with experiment since good accuracy has been obtained for similar systems, with a slight tendency to overestimate the barriers.<sup>11</sup> To assess the influence of the XC model we compare with LDA to obtain lower bounds for these barriers. The LDA barrier for  $\epsilon=0$  (2.38 eV) drops to

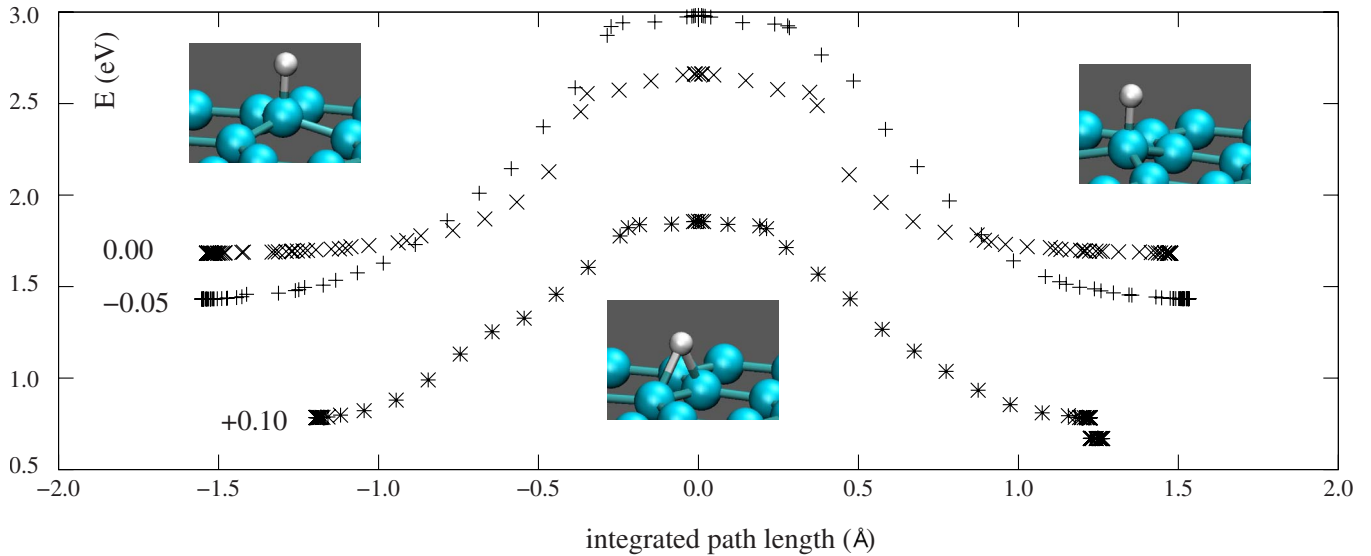


FIG. 1. (Color online) Energy per electron volt [RPBE functional (Ref. 11)] as a function of integrated path length (in Å) for diffusion of chemisorbed atomic hydrogen on graphene under different uniform stresses characterized by the corresponding unit cell strains ( $\epsilon = +0.1$ , tensile and  $\epsilon = -0.05$ , compressive). The structures of the transition state and minima are superimposed.

1.4 eV under a compressive strain of  $\epsilon = -0.05$  and to 0.04 eV under a compressive strain of  $\epsilon = -0.1$ . The rate of change in the barrier with respect to external stress is therefore similar for both functionals (changes of 2.70 and 2.34 eV for  $\Delta\epsilon = -0.1$ ), highlighting the consistency of predicted trends derived from introducing stresses to the system. Different XC models produce slightly different values for the strain threshold necessary for dissociation to occur on a given time scale but our best estimate of  $\epsilon = -0.05$  to  $-0.1$  is narrow enough to be significant. Furthermore, we remark that the reaction would quickly reach equilibrium, due to the more favorable exothermic heat of reaction for compression (Fig. 2, lower curve).

We therefore predict that the pathway for molecular dissociation near stressed graphene enables the reaction to occur

much faster. Elias *et al.*<sup>7</sup> have recently demonstrated that a single graphene layer can be hydrogenated to open a band gap of about 0.5 eV. Transmission electron microscopy provides evidence for a nonuniform distribution of stresses, resulting in measurable variations in the 2D unit-cell parameter ranging from  $-0.05\%$  (compressive) to  $0.03\%$  (tensile). Hydrogenation is performed by exposing graphene to a low-pressure hydrogen-argon mixture (10%  $H_2$ ) at about 600 K. This process is reversible and mass spectrometry has been used to detect molecular hydrogen leaving the substrate after annealing to about the same temperature. From our results we interpret the experimental evidence in the following way. Starting with physisorbed molecular hydrogen, a few molecules dissociate to produce chemisorbed atomic hydrogen on a time scale of  $\tau \approx 1 / (10^{16} \times 10^{12} \times e^{(-B/k_B T)})$ , where

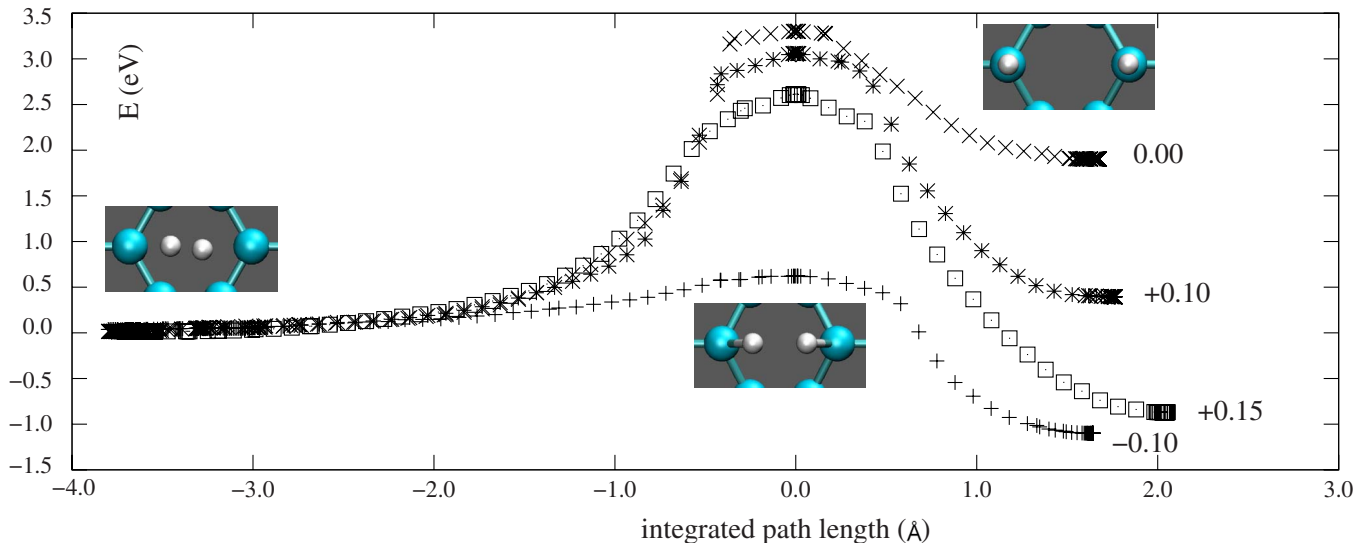


FIG. 2. (Color online) Energy profile per electron volt [RPBE functional (Ref. 11)] as a function of integrated path length (in Å) for  $H_2 \rightarrow 2H$  under different compressive/tensile strains,  $\epsilon$ . The structures of the transition state and minima are superimposed.

$10^{12}$  Hz represents a typical attempt frequency,  $10^{16}$  is the number of molecules in contact with the surface per mole of hydrogen, and the Boltzmann factor defines the dependence on the barrier,  $B$ , for an effective surface temperature,  $T$ . At about  $300^\circ\text{C}$  a few molecules should start to dissociate on a time scale of seconds and the chemisorbed hydrogen induces buckling on the surface, creating a local region where the substrate is under an effective compressive stress. According to our results, this stress lowers the barrier for dissociation (Fig. 2) and helps to dissociate other molecules, the chemisorbed atomic hydrogen cannot diffuse away at a noticeable rate and a cluster of atomic hydrogen is formed around that region. Atomic hydrogen is therefore preferentially adsorbed in strained regions. Strains and stresses derived from the adsorption of hydrogen are well inside the elastic regime and graphene layers can recover their original geometry after annealing to  $300^\circ\text{C}$ , when atomic hydrogen desorbing from the surface recombines to form molecular hydrogen, which is the species detected. This picture is supported by scanning tunneling microscopy experiments, where clustering of hydrogen atoms due to preferential sticking has been observed.<sup>20</sup> In this interpretation, the mechanism responsible for the preferential sticking is the modification of C-C bonds under local stress induced by neighboring chemisorption of hydrogen. The scenario proposed here is physically reasonable and backed up by state-of-the-art calculations that indicate how dissociation can occur on a time scale of days rather than years.

It has been suggested that clustering is related to the elastic energy penalty paid for clustered hydrogen vs maximally dispersed hydrogen at submonolayer coverages. A careful consideration of this point is beyond the scope of this work but nevertheless we can estimate the effect of clustering on the elastic deformation of the substrate by comparing total energies of the carbon atoms alone frozen in their equilibrium positions due to the presence of hydrogen. In particular, in a  $2\times 2$  supercell, chemisorbing a single hydrogen produces an elastic deformation in the substrate that requires 0.88 eV. The corresponding deformation for two hydrogen atoms located in their optimum position [next-to-next-nearest-neighbor (nnNN) site] requires 2.09 eV. Therefore, positioning a second hydrogen in the vicinity of the first one carries a significant energetic penalty and suggests to us that clustering is better explained in terms of our proposed mechanism than by a balance of elastic deformations. However, further work will be required to resolve this question.

### B. Electronic-structure effects

After molecular dissociation and chemisorption of the individual hydrogen atoms the characteristic graphene semimetallic electronic band structure is perturbed and partial gaps open in some directions in the Brillouin zone. However, for the system to acquire semiconducting properties, an absolute gap must appear in the density of states. We find that such an absolute gap is sensitive to the coverage, which allows us to provide an estimate for comparison with experiment. The origin of this gap is related to the periodic potential created by the accumulation of charge around the C-H

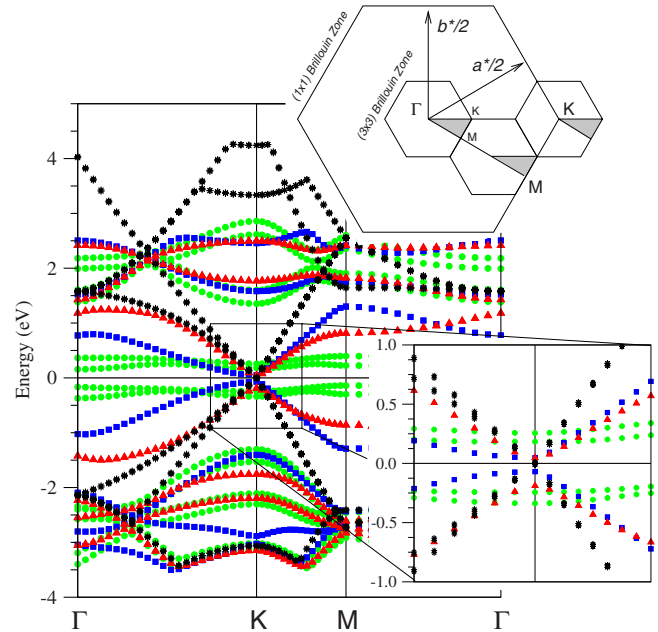


FIG. 3. (Color online) Electronic band structure for clean graphene and hydrogen adsorbed on graphene ( $\theta=1/9$ ): clean graphene (circles, black), H+H (nnNN)/graphene (triangles-up, red), H+H (nNN)/graphene (squares, green), and H+H (NN)/graphene (triangles-down, blue). The central zone around  $\mathbf{K}$  has been magnified on the right. Inset: reciprocal-space path ( $\Gamma$ - $\mathbf{K}$ - $\mathbf{M}$ - $\Gamma$ ) in the  $3\times 3$  irreducible Brillouin zone and its relationship to the  $1\times 1$  zone.

bond and/or by the electronic band shifts originating in the local modifications of the C-H bonding orbital.<sup>21</sup> Figures 3 and 4 show the band structure and density of states corresponding to the different configurations we have considered for two chemisorbed hydrogen atoms in a  $3\times 3$  cell ( $\theta=1/9$ ). Here we describe the LDA results but the GGA calculations are essentially the same.

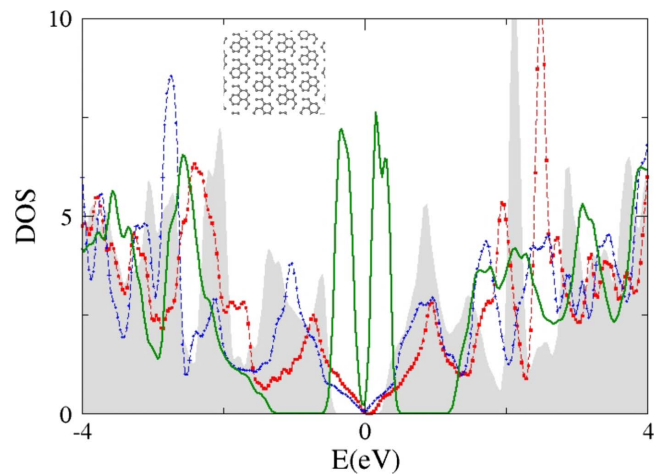


FIG. 4. (Color online) Density of states ( $\text{eV}^{-1}$ , smearing width  $\eta=0.05$  eV) for the following configurations (coverage,  $\theta=1/9$ ): nnNN (red, short-dashed), nNN (green, dotted), and NN (blue, dot-dashed). The shaded curve corresponds to nnNN at  $\theta=2/9$  where an absolute gap of 0.63 eV appears and the inset illustrates the connectivity for this case. The Fermi energy is aligned at the origin.

For clean graphene near the  $\mathbf{K}$  point we observe the distinctive linear crossing of bands at the Fermi energy responsible for semimetal character. Physisorbed atomic and molecular hydrogen do not significantly change this behavior. The next interesting feature is the appearance of a half-filled nondispersing band at the Fermi level upon chemisorption of a single hydrogen atom.<sup>21</sup> Adsorption of a second hydrogen atom after molecular dissociation can occur in three neighboring sites: (i) NN position, (ii) next-to-NN (nNN) position, or (iii) nnNN. According to Lieb's theorem, for a bipartite lattice like graphene the ground state for NN, nNN, and nnNN configurations is attained with  $S=0$ , 2, and  $0\mu_B$ , respectively.<sup>22</sup> Although Lieb's theorem is only strictly valid for the Hubbard Hamiltonian, we have found that it correctly predicts the optimum spin configurations obtained using DFT. The global minimum is related to occupancy of nnNN sites while the next most stable is the NN position. The intermediate site (nNN) is the least stable one; it is a magnetic solution and spontaneously evolves to nnNN under the restriction of  $S=0$ . From an electronic point of view, bands associated with the nNN site appear similar to the ones for only one hydrogen atom, showing that direct interaction between atoms at this distance is weak. However, interaction between adsorbates mediated by the substrate through static elastic distortions can be important and should not be neglected. These distortions produce a departure from a flat geometry and are favorable so long as they promote the  $sp^2$  to  $sp^3$  transformation. For high coverages, chemisorption on nnNN sites opens an absolute gap allowing the system to find a more stable configuration. The absolute band gap evolves from 3.1 eV for  $\theta=1/4$  to 0.6 eV for  $\theta=2/9$ . Below and above these two values for the hydrogen coverage the computed band gap is too small or too large compared with experiment. Therefore, we conclude that the actual coverage in Ref. 7 should be near  $\theta\approx 1/4$  and the geometrical configuration near to the optimum equilibrium one. It is interesting to notice that occupation of the alternative locations (NN and nNN) is not only a nonoptimal configuration but more crucially it does not result in an absolute gap in the density of states even for the larger coverages considered ( $\theta=1/4$ ). A characteristic double peak appears (Fig. 4) similar to that found for chemisorption of a single hydrogen atom, where only a direct gap at the  $\mathbf{K}$  point appears (not an absolute one).<sup>21</sup> These results can be understood in terms of topological connectivity: if we assume that the C-H bond saturates the  $p_z$  electron on that site, occupation of nnNN sites for  $\theta\geq 2/9$  breaks the graphene layer into a set of nearly disconnected hexagons where first-neighbor interactions are too weak and result in a series of narrow peaks and an absolute gap (inset and shaded curve in Fig. 4). For  $\theta=1/4$  the rings become totally disconnected and a larger gap appears. This

kind of reconstruction is reminiscent of a Peierls distortion, where the system minimizes its energy by a rehybridization of the basis in the unit cell under a new balance between kinetic- and potential-energy contributions. While the popular  $2\times 2$  tight-binding Hamiltonian including only  $\pi$  electrons reproduces most of the low energy physics correctly, a proper account of the above effect requires consideration of the in-plane  $sp^2$  sigma bonds responsible for the elastic contribution to the energy.

### III. CONCLUSIONS

In summary, we have studied the effect of external stress on diffusion of atomic chemisorbed hydrogen and on the dissociation of the  $\text{H}_2$  molecule. While external stress has little influence on diffusion barriers we find that compression changes the endothermic dissociation of physisorbed  $\text{H}_2$  to exothermic and lowers the barrier by about 2.5 eV ( $\epsilon=-0.1$ ) for both the LDA and GGA functionals considered. Dissociation of  $\text{H}_2$  is the first step for activated chemisorption of hydrogen atoms and leads to a significant strain in the substrate. This strain lowers the barrier for further chemisorption, favoring the pairing of chemisorbed species over a small region related to the elastic distortion created by the formation of the first C-H bond. The most favorable configuration for a pair of chemisorbed hydrogen atoms is a paramagnetic ground state occupying the next-to-next-nearest-neighbor site, while the second most favorable is the nearest-neighbor site. The intermediate site becomes less favorable in accord with Lieb's theorem, which predicts a ferromagnetic solution of spin  $2\mu_B$ . The electronic structure of these paired chemisorbed hydrogen atoms is such that the graphene-covered layer becomes semiconducting for occupancy of nnNN sites at coverages near  $\theta=2/9$  or greater while it remains semimetallic for NN and nNN sites, even for coverages up to  $\theta=1/4$ . These results should help in the rational design of hydrogen storage systems based on carbon substrates: a graphene layer exposed to molecular hydrogen would form a physisorbed species with low barriers to diffusion. External compressive stress in the range between 5% and 10% helps to dissociate molecules to form atomic chemisorbed hydrogen. These are bound to graphene with a low dissociation probability and diffuse slowly on the surface. Releasing the external stress would induce the reverse reaction, favoring the formation of molecular hydrogen, with a low desorption barrier.

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