

The Location of Adsorbed Hydrogen in Graphite Nanostructures

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Abstract: Recent experiments suggest that the high hydrogen storage capacity in graphite nanostructures might be associated with adsorption on the edges. First-principles calculations are used to study the structure and energetics of H chemisorption on graphite zigzag edges. The properties of both singly and doubly hydrogenated edges are examined. Molecular hydrogen can dissociatively adsorb on the edge directly, with small activation barriers to the formation of either singly or doubly hydrogenated structures. A new model for the location of adsorbed H is proposed.

Introduction

Carbon nanostructures such as carbon nanotubes (CNTs), graphite nanofibers (GNFs), and nanocrystalline graphite have drawn considerable attention as potentially efficient hydrogen storage media.^{1–10} The low specific mass of carbon makes it possible to achieve high gravimetric storage capacities in these carbon-based nanomaterials. Molecular hydrogen can both physisorb and dissociatively chemisorb onto these materials, but the physisorption of molecular hydrogen onto these substances is too weak for them to have a useful storage capacity at room temperature. On the other hand, it is important that the chemisorption energies not be too large. For the equilibrium vapor pressure of H₂ to be 1 bar or more at room temperature, the dissociative chemisorption of H₂ onto the storage material must be exothermic by 0.41 eV (per H₂) or less.¹⁰ As we discuss later in this article, this is probably not the case for most graphitic materials. There has also been considerable interest in the use of metal hydrides, alanates and other light hydrides, metal organic frameworks, and ice clathrates as hydrogen storage materials.¹⁰

The mechanism for incorporation of hydrogen into these carbon nanostructures at room temperature is not well-

understood. Browning et al. measured hydrogen storage capacities in GNFs as large as 6.5 wt %.⁴ They proposed that the mechanism for hydrogen adsorption involved, initially, the dissociation of molecular hydrogen “catalyzed by carbon edge sites”. Orimo et al. reported that after mechanical milling of graphite under a hydrogen atmosphere for 80 h, hydrogen uptake in nanocrystalline graphite reached up to 7.4 wt %.⁵ On the basis of an analysis of the radial distribution functions (RDFs) obtained from neutron diffraction experiments, they proposed two different types of H binding: chemisorption of an H atom to an edge carbon and adsorption of an H atom between the graphite layers.^{5–7} In addition, two distinct thermal desorption peaks for molecular hydrogen were observed for this mechanically milled nanostructured graphite, starting from ~600 and ~950 K, respectively.⁸ More recently, Diño et al. calculated total energies for the chemisorption of hydrogen between graphite layers¹¹ and also suggested that one of the new C–H peaks in the RDFs was due to interlayer H. However, the formation of this interlayer H is energetically unfavorable. For this reason and others discussed in the text, we feel that the formation of interstitial H may not contribute significantly to hydrogen uptake in carbon nanostructures at room temperature.

To better understand hydrogen storage and the hydrogen adsorption/desorption cycle in graphite nanostructures, it is important to understand the interaction between hydrogen atoms and the graphite edges, as well as the energetics of the dissociative adsorption and recombinative desorption of molecular hydrogen on these edge sites. Until now, little theoretical and experimental attention has been paid to this topic. Mehandru et al. studied the hydrogenation of the {10 $\bar{1}$ 0} graphite edge using the atom superposition and electron delocalization (ASED) band technique.¹² Yang et al. recently examined the adsorption of H on the graphite (0001) basal plane, the (1010) zigzag edge,

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and the (1121) armchair edge, using the unrestricted Hartree–Fock (UHF) method.¹³ Unfortunately, these calculations are not sufficiently accurate for our purposes, particularly for finding the transition states involved in the dissociation and recombination of hydrogen. In this article, accurate electronic structure calculations based on spin-polarized and gradient-corrected density functional theory (DFT) have been performed to examine the chemisorption properties of hydrogen atoms on graphite edges. Two different H chemisorption configurations have been found that are consistent with measurements of radial distribution functions of hydrogenated graphite nanostructures. The potential energy surfaces (PESs) for two pathways to the dissociative adsorption of molecular hydrogen on the graphite edge have been mapped out. The activation energies for both mechanisms turned out to be relatively small.

Results and Discussion

Our first-principles total-energy calculations have been performed using the well-established Vienna Ab initio Simulation Package (VASP), developed at the Institut für Materialphysik of the Universität Wien.^{14,15} The approach is based on an iterative matrix diagonalization of the Kohn–Sham equations of the finite-temperature DFT theory in a plane wave basis set. We include nonlocal exchange-correlation effects in the form of a generalized gradient approximation, using the PW91 functional.¹⁶ The interactions between the ionic cores and the electrons are described by fully optimized nonlocal ultrasoft pseudopotentials.¹⁷ To make a proper description of the asymptotic part of the PES, spin-polarized calculations are performed. We have used a $3 \times 6 \times 3$ grid of Monkhorst–Pack special k points to sample the Brillouin zone. A slab supercell approach with periodic boundary conditions is employed to model the graphite step edge structure. The substrate consists of two carbon layers, and a vacuum space of 6.474 Å thick is used to separate the substrate and its repeatable images. The bottom C layer has a (6×2) cell structure and contains 24 atoms, all fixed at their bulklike positions. The other carbons are allowed to relax, unless noted otherwise.

In previous work, we have used VASP to examine H-graphite interactions, and the computed lattice parameters, cohesive energy, elastic constants, and bulk modulus of graphite all show good agreement with experiment.¹⁸ For example, the computed in-plane lattice constant of 2.452 Å compares very well with the experimental value of 2.456 Å. The computed interlayer spacing, 3.24 Å, is a bit less accurate when compared with the 3.35 Å experimental value, but the error is still only 3% and small changes in this spacing do not effect H chemisorption at the edges. The largest error is in the DFT-PW91 H₂ binding energy, which is 4.54 eV, about 0.2 eV less than the experimental value of 4.745 eV. However, this well-known limitation of PW91 does not significantly modify the results of our study. Our computed vibrational frequencies for H and D chemisorbed onto a graphite surface also agree well with HREELS measure-

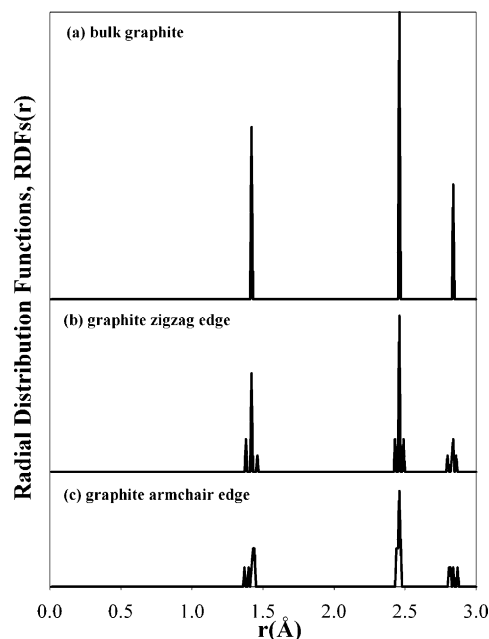


Figure 1. RDFs(r) for the calculated structures of bulk graphite (a), graphite zigzag (b), and armchair (c) edge structures.

ments.¹⁹ The two most widely studied graphite edge types are the $(10\bar{1}0)$ zigzag edge and $(11\bar{2}1)$ armchair edge. For both structures, all the carbon atoms remain in the graphite plane after relaxation. Almost no relaxation can be found for edge C atoms in the zigzag structure, and their second and third in-plane neighbor C atoms relax inward and outward, respectively, compared to the bulk graphite structure. In the armchair structure, the edge C atoms relax inward, while relaxation of the inner C atoms is negligible. All the relaxations here are relatively small, usually ≤ 0.05 Å.

Figure 1 shows our calculated RDFs for bulk graphite (a), and for our graphite zigzag (b) and armchair (c) edge structures. For the edge structures, note that our supercell consists of 24 C atoms in the bottom layer and 12 or 14 C atoms in the top layer, with 4 C atoms along the edge. The relative number of edge, near-edge, and bulk carbons in our supercell is what determines the relative peak heights in Figure 1. The first three RDF peaks of bulk graphite, located at 1.42, 2.46, and 2.84 Å, respectively, correspond to the first, second, and third nearest-neighbor bulk C–C distances. These show excellent agreement with data measured from neutron diffraction experiments, namely, 1.42, 2.46, and 2.84 Å, respectively.⁶ Small RDF peaks appear around the major bulk peaks in both the zigzag and armchair edge structures because of the relaxation of carbon atoms near the graphite edges. Fukunaga et al. used neutron diffraction methods to investigate the structural changes of graphite subjected to mechanical milling. Under an inert gas atmosphere, they reported that the RDF peaks were relatively unchanged except for a little broadening with increasing milling time.⁶ Mechanical milling is expected to create a large number of defects, such as edges and pores, and the defect density will increase with milling time. Both the zigzag and armchair edge structures generate small peaks around the bulk peaks in the RDFs, which would lead to this broadening, especially when thermal effects are taken into account. The coordination number of carbon in bulk

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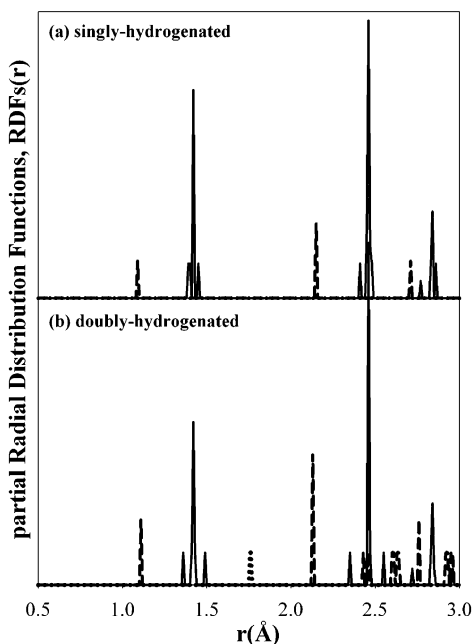


Figure 2. Partial RDFs(r) for the C–C (solid lines), C–H (dashed lines), and H–H (dotted lines) pair correlations, for the calculated singly (a) and doubly hydrogenated (b) graphite zigzag edge structures.

graphite is 3, while each edge C only has two nearest-neighbor atoms, and thus the average coordination number will decrease with increasing defect density. From the area of the first RDF peak, Fukunaga et al. calculated the average coordination number and reported that it decreased from ~ 3.0 to 2.82 after 36 h of milling.⁶ Thus, the average crystal size of nanocrystalline graphite becomes quite small after this much milling. For the edge structures we studied, the coordination numbers are ~ 2.89 for the zigzag case, and ~ 2.88 for the armchair case. Thus, the edge density in our supercell is comparable to that in the experiments, and the RDFs are very similar. In summary, our computed edge relaxation is consistent with the experimentally observed peak broadening, though there is not sufficient resolution to suggest that there is a preponderance of one type of edge structure over another. Since it takes less energy to form the zigzag edge, we will only focus on the chemisorption and dissociation of hydrogen on the graphite zigzag edges.

As the graphite edge carbons are unsaturated, the addition of H atoms to the edges should be strongly exothermic. We find that the binding energy of an H atom to an edge carbon is 5.03 eV at 100% coverage (one H on every edge carbon) and 5.05 eV at 50% coverage (one H on every other edge carbon). This is significantly larger than the binding energy of about 0.7 eV for H chemisorbed on the graphite (0001) plane.^{18,20} The C–H bond is perpendicular to the edge, and after a full relaxation of the structure, all of the C and H atoms remain in one plane, consistent with simple chemical intuition and earlier studies.¹³ Following hydrogenation, the edge carbons and their neighbors can be observed to relax by a small amount, usually less than 0.04 Å. Figure 2a shows the computed partial RDFs for the case of a singly hydrogenated graphite zigzag edge at 50% coverage. The three major C–C peaks (at 1.42, 2.46, and 2.84 Å) are relatively unchanged by the adsorption of H. Three

new peaks corresponding to the C–H pair correlation are found at 1.09, 2.15, and 2.71 Å. No H–H pair correlation exists within 3.0 Å at 50% coverage. In the neutron diffraction study of graphite mechanically milled under a molecular deuterium atmosphere, Fukunaga et al. reported that a new RDF peak at ~ 1.1 Å, a shoulder at ~ 2.2 Å, and a background around $r = 1.8$ Å appeared after 20 h of milling, compared with the same sample milled under an inert atmosphere.⁶ As the mechanical milling increases the edge density, they associated the new peak at ~ 1.1 Å and the shoulder at ~ 2.2 Å with H atoms chemisorbed on the edges. In our calculations, the C–H pair correlations centered at 1.09 and 2.15 Å are in excellent agreement with their measurements. Similar results can be found at 100% coverage.

Fukunaga et al. attributed the RDF peak at $r = 1.8$ Å to deuterium atoms adsorbed between the graphite layers, with a weak bonding (presumably physisorption) to two carbon atoms, each located in a different layer. This is consistent with the fact that the graphite interlayer distance expands slightly to 3.66 Å after milling.⁶ Fortunately, we know a great deal about the interaction of hydrogen with the (0001) graphite surface, and as the interlayer spacing is quite large, the adsorption properties of hydrogen atoms in the interlayer should be similar to that on the surface. The physisorption energies of H and H₂ on graphite are known from experiment to be very small, 0.043²¹ and 0.051 eV,²² respectively. Thus, physisorption should not play a role, except at extremely low temperatures. Because the barriers to the diffusion of physisorbed H atoms are very small,^{18,20} the recombinative desorption of physisorbed interlayer H would take place at very low temperatures and certainly not at the temperatures reported: 600 and 950 K.⁸ In addition, the formation of two physisorbed H atoms from molecular hydrogen is endothermic by 4.7 eV and is not expected to occur under the conditions of the experiment. Using DFT, Jeloica and Sidis²⁰ and Sha and Jackson¹⁸ demonstrated that H can chemisorb on top of a surface C, but only if that C puckers out the (0001) plane by several tenths of an angstrom. Recently, Diño et al. calculated total energies for hydrogen adsorption between graphite layers and found very similar behavior.¹¹ They postulated that these chemisorbed H atoms were responsible for the $r = 1.8$ Å peak in the RDF. Given their chemisorbed C–H bond length of 1.11–1.15 Å, a puckering of 0.26–0.33 Å, and an interlayer spacing of 3.35 Å, they estimated a distance of 1.9–2.0 Å from the chemisorbed H to the nearest C on the other graphite plane. We see several problems with this. First, if one uses the (post-hydrogen exposure) experimental value of 3.66 Å for the interlayer spacing, this C–H distance is more like 2.2–2.3 Å. Second, and more importantly, the binding energy for chemisorption of H on graphite is weak both on the surface and between layers, about 0.6–0.7 eV.^{18–20} Thus, the activation energy for dissociation of H₂ trapped between layers is very large, 1.3–1.7 eV.¹¹ In addition, the overall process of converting gas-phase H₂ into interlayer chemisorbed H atoms is endothermic by over 3 eV. For these reasons, we feel that the formation of interstitial H does not contribute significantly to hydrogen storage in carbon nanostructures at room temperature.

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Perhaps a better explanation for the RDF peak at 1.8 Å, as well as for the emergence of the sp^3 hybridization character of C atoms seen by neutron diffraction in the hydrogenated graphite nanostructures,⁹ are doubly hydrogenated edge carbons. We have used our first-principles total energy methods to compute equilibrium structures for the case where the carbon atoms along the zigzag edge each have two H atoms added. At equilibrium, all the carbon atoms remain in the same plane, with the two H atoms located above and below the plane, symmetrically. Again, this is consistent with chemical intuition and some earlier calculations.¹³ The binding energy is coverage-dependent: 3.92 eV/H atom at 50% coverage (two H atoms on every other edge carbon) and 3.64 eV/H atom at 100% coverage (two H atoms on every edge carbon). Figure 2b shows the partial RDFs for the doubly hydrogenated zigzag edge structure at 50% coverage, for all the C–C, C–H, and H–H pair correlations. The locations of C–C pair correlations are relatively unchanged, but the peaks become “broader”, with many small peaks appearing around the major peaks because of the minor lattice reconstructions associated with hydrogenation. New C–C RDF peaks located at 1.36 and 1.49 Å appear in the vicinity of the bulk 1.42 Å peak. When Itoh et al. measured the structure of hydrogenated nanocrystalline graphite by neutron scattering, they reported that the C–C RDF peak at around 1.45 Å broadened with increasing hydrogen exposure and could be fit by two peaks with positions at 1.42 and 1.54 Å.⁷ They attributed this to the formation of fourfold coordinated C atoms (sp^3 hybridization). We note that the observed peak broadening is consistent with the effects of double hydrogenation as illustrated in Figure 2b. Several small RDF peaks appear, located at 1.11, 2.13, 2.45, 2.62, 2.75, and 2.93 Å, arising from the C–H pair correlations. The C–H RDF peaks at 1.11 and 2.13 Å, attributed to the first and second nearest-neighbor C–H correlations, appear at similar locations as in the singly hydrogenated case. A peak in the RDF, due to the H–H pair correlation, appears at 1.76 Å. This agrees well with the background RDF peak at around $r = 1.8$ Å measured in the neutron diffraction experiments, suggesting that this peak might arise from D–D correlations at doubly hydrogenated edge sites and not interstitial D.^{5–9} The computed RDF at 100% coverage is similar to the 50% case. After double hydrogenation, our equilibrium interlayer distance shows a small increase from 3.18 to 3.21 Å. This is much less than the expansion measured by diffraction, where after several hours of milling under a hydrogen atmosphere the interlayer spacing increases from roughly 3.4 to 3.6 Å.⁵ However, it is well-known that the PW91 functional does not well describe the weak physisorption interactions that control the interlayer spacing. More importantly, there are other factors that contribute to this expansion. For example, milled nanocrystalline graphite might have edge planes, and the repulsion between H atoms adsorbed on adjacent layers would lead to further expansion. Overall, the RDFs for the hydrogenated graphite zigzag edge structures in Figure 2 compare very well with those measured experimentally for graphite milled under a D_2 gas atmosphere,^{5–9} especially when thermal broadening is taken into account.

As the hydrogen uptake in both nanocrystalline graphite and GNPs takes place under an atmosphere of molecular hydrogen, it is important to examine the dissociation and adsorption pathways for H_2 on these structures. We have found that the chemisorption of H on the graphite terrace sites is weak, about

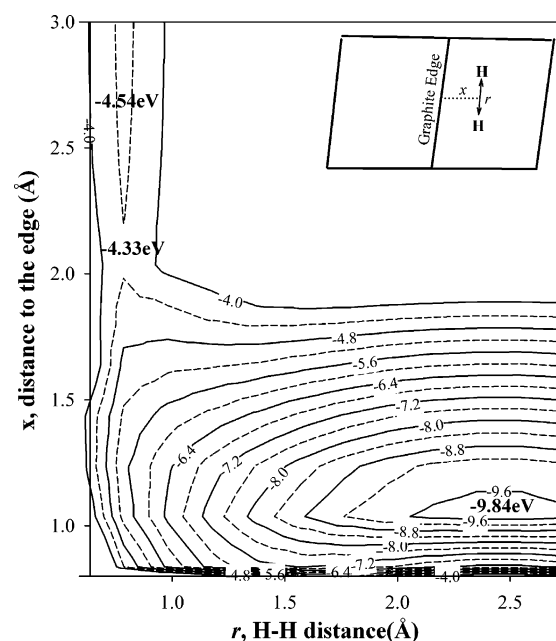


Figure 3. Contour plot of the potential energy surface for molecular hydrogen dissociating to form two singly hydrogenated carbons on a graphite zigzag edge. The hydrogen atoms are located in the same plane as the edge C atoms, and the center-of-mass of the two H atoms remains on a line perpendicular to the edge and centered between the two adjacent edge C atoms. All C atoms are kept fixed at the equilibrium positions for an edge structure with no hydrogen present.

0.7 eV.¹⁸ Thus, there is a prohibitively large barrier to dissociative adsorption of H_2 on the terraces, and the process is endothermic by about 3.4 eV.²³ Similarly, it requires much energy to insert a gas-phase H_2 between the layers of graphite, and once there the barrier to dissociative chemisorption is still very large, estimated in a recent DFT study to be roughly 1.7 eV for a rigid graphite lattice and 1.3 eV for a fully relaxed lattice.¹¹ Because the interlayer H chemisorption is about the same as that on the terraces, the overall process is also endothermic by 3.4 eV.

We now consider the dissociative chemisorption of H_2 at the edge sites, for which no previous theoretical studies exist. Because the binding of H to these unsaturated carbons is so strong, we would expect that the hydrogenation reactions are very exothermic, with relatively small barriers. In Figure 3, we plot the PES for the dissociative chemisorption of molecular hydrogen oriented parallel to a zigzag edge. The H atoms and all of the carbons remain in the same plane, and the C atoms are held fixed at the equilibrium positions for the bare (unhydrogenated) zigzag edge structure. The PES, for a symmetric reaction path, is thus a function of r , the H–H distance, and x , the distance between the edge and the H_2 center-of-mass (see the inset). The initial energy of -4.54 eV corresponds to the DFT-PW91 binding energy of H_2 . The final state corresponds to two neighboring edge carbons, each with a single H. Because the C–H bond is so strong, this process is exothermic by 5.3 eV and the barrier to dissociation is very small, roughly 0.2 eV. Note that if we relaxed the substrate, the product minimum would be lower in energy by about 0.3 eV. Substrate relaxation during the dissociation would also lower the barrier. However, because this entrance channel barrier is over 2 Å from

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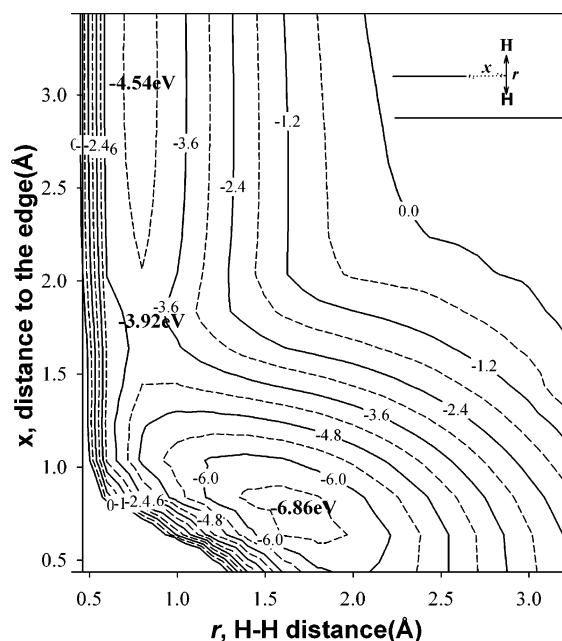


Figure 4. Contour plot of the potential energy surface for molecular hydrogen to dissociate to form a doubly hydrogenated structure on a graphite zigzag edge. The two H atoms are located above and below the graphite sheet, symmetrically. The H atoms and the reacting edge C all remain in a single plane perpendicular to both the graphite sheet and the edge. All C atoms are kept fixed at the equilibrium positions for an edge structure with no hydrogen present.

the edge, this would be a small effect. We conclude that upon exposure to molecular hydrogen, single hydrogenation of the edge carbons as described in Figure 3 takes place very rapidly.

In Figure 4 we consider another edge hydrogenation reaction. In this case, H_2 adds to a single edge carbon, to form one doubly hydrogenated C. For this reaction path the two H atoms are located above and below the graphite sheet, symmetrically. The H atoms and the reacting edge C all remain in a single plane perpendicular to both the graphite sheet and the edge (see the inset). The PES for this symmetric reaction path is a function of r , the H–H distance, and x , the distance between the reacting C and the H_2 center-of-mass. Because the C–H bonds are weaker in the doubly hydrogenated structure than for the singly hydrogenated case, the reaction is less exothermic and the activation barrier is larger. Still, the reaction is exothermic by more than 2.3 eV, and the barrier, again in the entrance channel, is only about 0.6 eV. If we relax the substrate, the product minimum is lower by 0.9 eV. This would increase the reaction exothermicity to 3.2 eV and lower the activation barrier a bit. Overall, this process seems highly probable under the conditions of the experiment.

There are two other edge carbon hydrogenation reactions that we have not explored in as much detail. For example, H_2 could add across two neighboring edge carbons, one with a single H and the other with no H. This process is exothermic by about 2.5 eV, though the barrier to dissociation is probably bigger than for the reactions of Figures 3 and 4. Still, this hydrogenation reaction is far more energetically favorable than any of the mechanisms proposed for the formation of interstitial H. The reaction for H_2 to add across two neighboring singly hydrogenated edge carbons to form two neighboring doubly hydrogenated carbons is actually endothermic by 0.4 eV and not thermodynamically stable. It is possible that H_2 could dissociatively adsorb at the edge sites and that H atoms could migrate along or between the sheets, into the interstitial region. However, this is still a very endothermic process, and the barrier to motion from an edge site to a terrace site would be prohibitively large. Finally, we note that for the three exothermic edge hydrogenation reactions we have examined, the exothermicities are so large that the vapor pressure of H_2 in equilibrium with the sample at room temperature would be much less than 1 bar.¹⁰

Conclusion

In summary, we have performed detailed first-principles total energy calculations to examine the structural and energetic properties of H atoms chemisorbed on a $(10\bar{1}0)$ graphite zigzag edge. One H atom can be chemisorbed directly on an edge carbon, with a binding energy of roughly 5 eV. Two hydrogen atoms can be co-chemisorbed on the same edge carbon atom, with a binding energy of roughly 3.9 eV per C–H bond at 50% coverage. Both of these structures are consistent with the RDFs extracted from X-ray and neutron diffraction studies of graphite milled under a molecular hydrogen atmosphere. Two potential energy surfaces for the dissociative chemisorption of H_2 on the edge carbons have been mapped out. These reactions are very exothermic and have relatively small barriers. Under the conditions of the experiment, it is likely that most edge carbons will be singly or doubly hydrogenated. We also conclude that the formation of interstitial H atoms is unlikely under the conditions of the experiment.

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