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Theoretical investigation of the effect of graphite interlayer spacing on hydrogen absorption

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We investigate the absorption of hydrogen molecules between graphite layers using both first-principles calculations and classical grand-canonical Monte Carlo simulations. While a recent theoretical study showed that graphite layers have high storage capacity at room temperature, previous simulation results on hydrogen-graphite systems showed otherwise. Our first-principles calculations suggest that it is possible to store hydrogen molecules between the graphite layers if the energetically unfavorable initial absorption stage could be overcome. The barrier to the initial absorption originates from the large lattice strain required for H_2 absorption: small amounts of initial absorption cause an interlayer expansion of more than 60%. To determine if significant storage is indeed possible at finite temperature (and pressure), we performed grand-canonical Monte Carlo H_2-absorption simulations with variable graphite interlayer spacing. Using two different potentials for the H_2-C interaction, we found low-H_2-mass uptake at room temperature and moderate pressures (e.g., close to 2 wt % at 298 K and 5 MPa). Our results suggest that a pore width or interlayer spacing around 6 Å in the graphite layers has the optimum absorption capacity.

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I. INTRODUCTION

Hydrogen has been identified as an alternative fuel that could potentially reduce environmental damage and decrease dependence on fossil fuel. One of the outstanding challenges in the practical use of hydrogen fuel technology comes from the difficulty of hydrogen storage. A large density of hydrogen must be stored safely and reversibly, using lightweight materials.

The possibility of storing hydrogen in carbon nanostructures has motivated a number of studies exploring the storage capability of various structures, including carbon nanotubes, graphite sheets, fullerene, and other carbon-based materials.[1–13] Carbon has the advantage of being lightweight and strong, as well as having a number of possible forms that can have different absorption properties. Carbon will covalently bond hydrogen very strongly, but this is not useful for hydrogen storage, as the bonding is essentially irreversible. Experimentally produced solid carbon, including graphite, diamond, nanotubes, and amorphous carbon, has very few dangling bonds, so most hydrogen storage will be physisorbed, with bindings much weaker than the covalent bonding.

The experimental evidence of significant amounts of hydrogen storage has been difficult to reproduce and therefore controversial.[14] Storage is also often found to be irreversible. One experimental issue is that even if a large amount of storage is possible, there may be kinetic barriers to the storage. This may be improved by providing catalysts, such as surface metal particles that help dissociate the H_2 molecule, allowing for individual atoms to penetrate into the material. These metal particles can also serve as adsorption sites for hydrogen. However, the number of molecules adsorbed on the particles does not help the weight percent adsorbed, due to the large atomic weight of metal catalysts. Their roles in attracting and dissociating hydrogen have been topics of much study.[15]

In this work, we address the theoretically possible amount of absorption of H_2 molecules in graphite, under the assumption that kinetics is not an issue. The latter assumption is clearly unrealistic; however, the purpose is to identify possible high-storage systems, then to identify kinetic barriers for these systems. Various calculations, including results presented here, show that the binding of H_2 on graphene sheets is simply too weak to support significant storage. Typically, the binding energy must be on the order of 25 kJ/mol (0.25 eV/molecule) or higher to have significant storage at operating temperatures and pressures, while not irreversibly binding the hydrogen.

In contrast to the weak attractive binding of hydrogen on graphene sheets, hydrogen will not typically absorb into graphite. The typical sheet spacing of ~3.3 Å simply does not leave sufficient room for absorption. While some absorption may take place by expanding the layers, the layers are typically not free to expand significantly and this may limit the total absorption. Recent calculations[6–8] have argued that by artificially spacing the layers, the absorption may be significantly improved. The purpose of our work is to examine both the H_2 absorption in a lattice with artificially spaced layers and the work required to expand the layers. We present results of *ab initio* calculations and grand-canonical Monte Carlo (GCMC) simulations of the hydrogen absorption between graphite layers with variable lattice spacing. The former study indicates a possibility for hydrogen storage, thus motivating the latter study of the hydrogen-absorption properties at finite temperature under applied pressure. A relevant model for the system investigated is that of a slit-pore geometry. In graphite layers, the pore width essentially gives the interlayer spacing. Activated carbon exhibits significant porosity and variable lattice spacing, allowing for a variety of possible absorption environments. Hydrogen absorption for the carbon slit-pore model has been previously reported by Wang and Johnson.[1]

II. FIRST-PRINCIPLES CALCULATIONS

Our first-principles calculations were based on the density functional theory (DFT) and ultrasoft pseudopotential (USPP) method[16,17] within a local density approximation (LDA).[18] We used the Vienna simulation package[19,20] (VASP) to solve the local density-functional equations. Even though the LDA commonly overestimates constituent binding and cohesive energy of solids, theoretical results for the structural properties of hexagonal graphite (*AB* stacking) are in very good agreement with experiments: the DFT result found $a=2.464$ A and $c/a=1.362$, while the experiments found $a=2.46$ A and $c/a=1.35-1.365$. We note that a generalized gradient correction to the local density cannot be used for hexagonal graphite lattice, since it yields a strong reduction in the interlayer binding, resulting in the interlayer expansion to $c/a=1.8$. Obviously, the LDA is a better choice in describing the van der Waals interaction between graphene layers and between H_2 molecules with a graphite surface. The adsorption energy of H_2 on the graphite surface from LDA calculation was found to be 0.08 eV/H_2, which agrees with previously published LDA results.[21,22] As indicated in the Introduction, this binding is too weak to provide significant adsorption. In our calculations we considered supercells consisting of three graphene layers (*ABA* stacking) and three layers of vacuum. The third graphene layer has been added to constrain the relaxations of the top two layers in the presence of H_2 molecules. The energy cutoff was set up to 450 eV.

The H_2 absorption energy is defined as the total energy of H_2 in the relaxed graphite lattice, minus the energies of free H_2 molecules and the equilibrium graphite lattice without H_2 molecules. In Fig. 1 we show our first-principles results on the dependence of H_2 absorption energy and interlayer spacing on the concentration of the H_2 molecules absorbed between the top two graphene layers. Since we found that configurations with different H_2 orientations (with the H_2 molecular axis parallel and perpendicular to the graphene sheets) have comparable absorption energy (to within ~0.02 eV), the results shown in Fig. 1 are only for the configuration with the H_2 molecular axis parallel to the graphene sheets.

The solid curve shown in Fig. 1(a) is the H_2 absorption energies with the energy of the graphite lattice at equilibrium interlayer spacing (i.e., without interlayer expansion) chosen as the reference. In other words, the solid curve line shown in Fig. 1(a) includes the strain energy required to expand the lattice. This expansion is necessary to accommodate the absorption. Figure 1(b) shows this expansion. As H_2 is added, there is a large initial amount of expansion. Once the H/C ratio exceeds 0.1, the expansion changes very little with increasing hydrogen content; i.e., the expansion remains at a constant value of 68% with the H_2 molecular axis parallel to the graphene sheets and increases from 70% (H/C≅0.1) to 75% (H/C=1.0) with the H_2 molecular axis perpendicular to the graphene sheets.

One difficulty in interpreting the absorption curve is that there are two distinct contributions: the energy of the H_2 molecules interacting with the lattice and the lattice strain. In the case where the expansion of the lattice is due to H_2 absorption, both must be accounted for to properly calculate the total absorption energy. However, one can also envision graphitic structures with "preexpanded" lattices, due to intercalated molecules, regions of large "slit" pores, or other structural features (or defects) that provide for a different graphene sheet separation that occurs in graphite. In order to quantify the effect of strain on the H_2 absorption energy, we also show in Fig. 1(a) the H_2 absorption energy without including the strain energy caused by the interlayer expansion (dashed curve line). These calculations were done by using the energy of graphite at the expanded interlayer spacing (at each H/C atom ratio) as the energy reference. As shown, the major cause in prohibiting the H_2 absorption at the initial absorption stage is due to the large penalty paid in the strain energy in order to accommodate the H_2 molecules between the graphene layers. Since the energy reference in calculating the H_2 absorption energy is dependent on the H/C atom ratio (and external charging conditions), the H_2 absorption energy as a function of H/C atom ratio should fall in the area bounded by these two curves shown in Fig. 1(a).

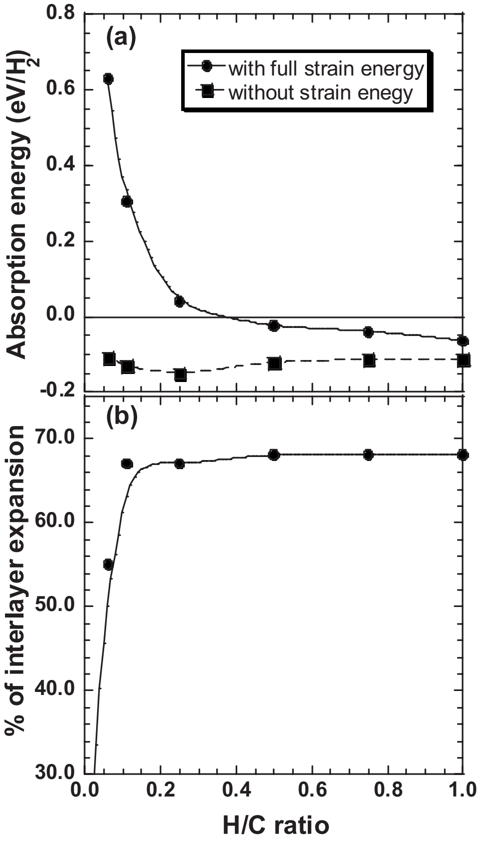

FIG. 1. (a) H_2 absorption energy between two graphene sheets and (b) the percentage of the induced interlayer expansion as a function of the H/C atom ratio for the configuration with the H_2 molecular axis parallel to the graphene sheets.

As shown in Fig. 1, in the dilute limit, H_2 molecules between the graphene sheets are energetically unfavorable; however, a large number of H_2 molecules can have negative absorption energy due to their ability to induce a dramatic expansion of the graphite interlayer spacing. We also found that both the H_2 absorption energy and graphite interlayer spacing show a nonlinear dependence on the hydrogen con-

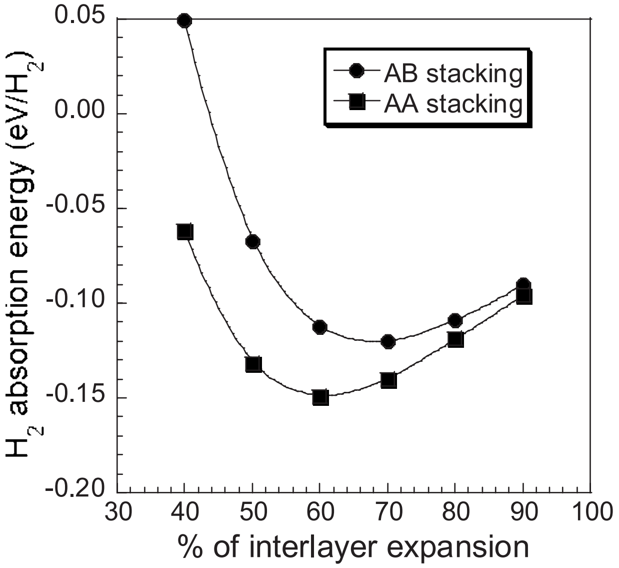

FIG. 2. Absorption energy of a H_2 molecule in preexpanded graphene bilayers with *AA* (squares) and *AB* (circles) layer stacking sequence obtained from first-principles calculations for the configuration with the H_2 molecular axis parallel to the graphene sheets.

centration and a substantial decrease in the H_2 absorption energy together with a significant expansion in the graphite interlayer spacing actually occurs within a very narrow H/C atom ratio. These results suggest that the major cause in limiting the amount of hydrogen storage in the graphite lattice comes from the initial absorption stage. Thus, it might be possible to store hydrogen molecules between graphene layers if the difficulty associated with high H_2 absorption energy at the initial absorption stage can be overcome. Once these "initial" H_2 molecules are absorbed, further lattice expansion is induced [cf., Fig. 1(b)]. An expanded lattice would enable further hydrogen absorption, so that the absorbed H_2 molecules reach a lower-energy state as the concentration of H_2 increases.

Despite the difficulty in the initial absorption stage, the result that H_2 molecules can have negative absorption energies between graphene sheets is significant: the attraction is sufficient to overcome the energy necessary to strain the lattice by 60%. It follows that if the interlayer spacing is preexpanded, the energy penalty due to the initial H_2 absorption would be less and H_2 absorption would increase. The preexpanded interlayer spacing could be due to the effect of intercalated metal particles or other "spacer" molecules. Also, if there are a large number of slit pores with widths corresponding to about 60% expanded spacing, the absorption into the pores may be quite significant (ignoring kinetic effects).

In Fig. 2, we show the dependence of the absorption energy of an isolated H_2 molecule (with the molecular axis parallel to the graphene sheets) between preexpanded graphene layers in a bilayer (with *AA* and *AB* layer stacking) geometry on the amount of interlayer expansion. In these calculations, the lattice remains fixed before and after hydrogen absorption. Here, the reference of the H_2 absorption energy is the energy of preexpanded carbon lattice. The calculated H_2 absorption energy shows a minimum at an expansion at about 70% (for *AB* stacking) and 60% (for *AA* stacking). The absorption energy becomes lower (i.e., more negative) than -0.10 eV/H_2 once the amount of interlayer expansion is greater than 50%–60%. The H_2 in the *AA* stacking geometry has a lower energy than in the *AB* stacking geometry, since H_2 can have a higher carbon coordination number in the *AA* stacking geometry than in the *AB* stacking geometry. Note that for the *AB* stacking geometry, in order to have negative H_2 absorption energy, the amount of preexpansion in the interlayer spacing has to be larger than 40%. These calculations indicate an increased possibility for hydrogen storage if the graphene interlayer spacing is allowed to vary and is preexpanded, thus motivating the study of the hydrogen absorption properties at finite temperature and pressure by using GCMC simulations at various fixed graphite interlayer spacings. The amounts of uptake will be addressed in the next section.

III. GRAND-CANONICAL MONTE CARLO SIMULATIONS

At finite temperature, it is important to account for the change in the entropy of H_2 between the gas phase and absorbed state. It is known that, at room temperature and 1 atm pressure, the entropy per H_2 molecule in the gas phase is about $16k_B$. Thus, in order for room-temperature absorption and desorption to occur in preexpanded spacings, the required change in the entropy has to be smaller than $\sim 4k_B - 6k_B$ (or 0.10–0.15 eV/H_2 at room temperature, corresponding to the adsorption energies shown in Fig. 1). The amount of reduction in the entropy will determine the amount of hydrogen uptake. More precisely, in equilibrium, the chemical potential of the absorbed hydrogen is the same as in the surrounding gas. This is difficult to evaluate directly, with sufficient accuracy. Therefore, in this section, we use empirical potentials combined with GCMC simulations to determine the uptake.

An evaluation of the degree to which fitted potentials agree with first-principles results in the absorption energy is important in validating simulations that make use of the fitted potential energy forms. In particular, the results are sensitive to the H_2-C binding strength; small differences in this make dramatic changes in the absorption, as we will demonstrate. For small to moderate absorptions, the H_2-H_2 interaction may be neglected, as the binding is weak; a small density of H_2 molecules absorbed in the lattice will not cluster significantly at relevant temperatures. At higher absorptions, this is more critical; however, we shall demonstrate that this case is not relevant under normal conditions.

The interaction between graphite layers is described by a Lennard-Jones potential between carbon atoms at different layers. The parameters are given by Wang and co-workers,[23] optimized to reproduce the calculated binding energy between layers. The intermolecular hydrogen interaction is described by the Silvera-Goldman potential.[24] Here, the hydrogen molecule is considered a single particle with no rotational degrees of freedom. (As shown by our first-principles calculations, the configurations with different H_2 orientations have comparable absorption energy and inter-

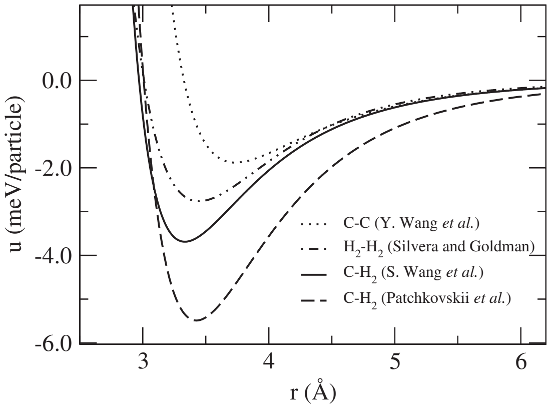

FIG. 3. Interaction potentials used in the classical simulations for carbon-carbon (Ref. 23) (dotted line), hydrogen-hydrogen (Ref. 24) (dash-dotted line), and hydrogen-carbon from Wang *et al.* (Ref. 25) (solid line), and Patchkovskii *et al.* (Ref. 8) (dashed line).

layer expansion, and thus the approximation of the H_2 molecule as a single particle is justified here.)

For the H_2-C interaction, we used two different pairwise interactions currently available in the literature. The absorption capacity may be sensitive to the choice of H_2-C interaction,[8] and comparing results of different interaction potentials allows us to investigate the degree to which H_2-C models affect simulated absorption. One of these was proposed by Wang and co-workers,[25] where parameters were chosen to fit the energy spectra from scattering experiments of H_2 physisorbed on graphite. Considering the H_2 molecule as a single particle, the potential simplifies to a purely 12–6 Lennard-Jones form

$$u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^{6}], \tag{1}$$

where $\varepsilon = 3.69$ meV/molecule (0.356 kJ/mol) and $\sigma = 2.97$ Å. The other H_2-C potential used is an exp-6 Lennard-Jones form proposed by Patchkovskii and co-workers:[8]

$$u(r) = Ae^{-\alpha r} + C_6 r^{-6}, \tag{2}$$

where $A = 1099.52$ eV/molecule (106 073 kJ/mol), $C_6 = -17.3640$ eV Å^6/molecule (-1675.15 kJ Å^6/mol), and $\alpha = 3.5763$/Å.[26] These parameters were chosen to fit *ab initio* results for a H_2 molecule on a coronene system and have been shown to give good agreement with *ab initio* results for H_2/benzene system as well. The above H_2-C potentials are shown in Fig. 3. Also shown are the intermolecular hydrogen[24] and the carbon-carbon[23] interactions.

The potentials of Wang *et al.*[25] and Patchkovskii *et al.*[8] have similar forms, but with significantly different binding energies. The potential of Patchkovskii *et al.*[8] gives a maximum C-H_2 binding 1.8 meV stronger (more negative) than that of the potential of Wang *et al.*[25] Between two graphite sheets, this will lower the energy of a H_2 molecule by an amount on the order of k_BT (or higher) at room temperature, assuming a carbon coordination number ~10. Thus, we expect that this potential will predict significantly higher absorption than the Wang potential of *et al.*[25] We also note that both potentials predict repulsive interactions when the C-H_2 bond is less than ~3 Å. This is consistent with the positive absorption energy calculated for the unexpanded lattice, with graphene layers separated by 3.3 Å. Without expansion, there is no room for the H_2 molecules.

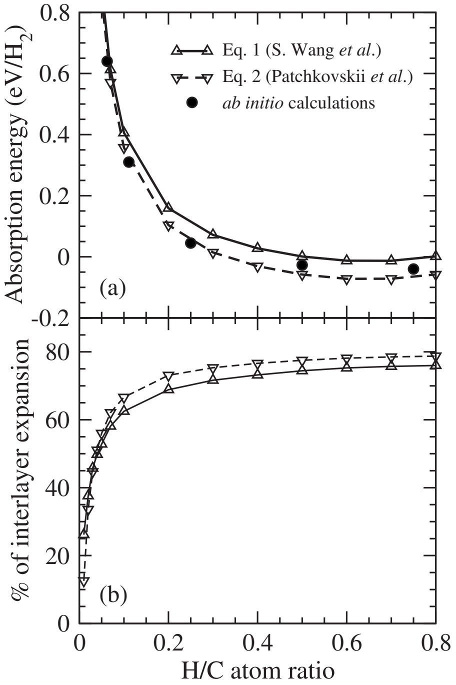

FIG. 4. (a) Hydrogen absorption energy with the equilibrium interlayer spacing as the energy reference employing the empirical potentials (Refs. 8 and 25) for H_2-C in Fig. 3. Also shown are results from *ab initio* calculations (solid circles). (b) Induced interlayer expansion as a function of the H/C atom ratio using empirical potentials.

We determined the absorption energies and interlayer expansions as a function of H/C atom ratio by using these interaction potentials. The calculated hydrogen absorption energies and induced interlayer expansion using these interaction potentials are shown in Figs. 4(a) and 4(b), respectively. As expected from a comparison of the well depths of the H_2-C potentials in Fig. 3, the potential defined in Eq. (2) gives a stronger absorption energy than that in Eq. (1). The difference in the absorption energies remains constant at about 0.06 eV/H_2 molecule starting at an H/C atom ratio of 0.2.

Comparing with the first-principles results shown Fig. 1, the results of Fig. 4 show that these interaction potentials give the same trend as the first-principles calculation. The absorption energy in the region between H/C=0.4 and H/C=0.8 from first-principles calculations lies between the results from these two potentials. In terms of the overall agreement with the first-principles results (in particular, in the low-H/C-ratio range), the potential of Patchkovskii *et al.*[8] is found to be better than the potential of Wang *et al.*[25] Nevertheless, in the following, we will still present two sets of GCMC simulation results corresponding to these two different H_2-C potentials, since comparing results of different interactions allows us to investigate the sensitivity of absorption to the H_2-C models.

Finite-temperature and -pressure hydrogen absorption have been reported previously. Grand-canonical Monte Carlo studies by Wang and Johnson[1] for the carbon slit-pore model showed that at 298 K, hydrogen storage in these structures is very low, attaining only about 1 wt % at 5 MPa. This has led to a conclusion that graphitic nanofibers do not meet the storage capacity for practical applications. In these simulations, the H_2-graphite layer interaction is modeled by the Crowell-Brown potential[27] and the H_2-H_2 interaction is described by the Silvera-Goldman potential.[24] Quantum effects for hydrogen were included by incorporating the path integral Monte Carlo (PIMC) approach into the GCMC simulations. Simulations of hydrogen on graphite planes have also been reported,[7] and the results agree with the low-absorption results of the slit-pore model.[1] However, recent calculations by Patchkovskii and co-workers[8] showed that expanded graphite layers have a high storage capacity. Using an ideal gas approximation for H_2, they predict about 8 wt % storage at 300 K and 5 MPa for a graphite interlayer spacing of 6 Å. Incorporating a nonideality correction, the adsorption is predicted to be reduced to ~3 wt %. For small interlayer spacings ($d \leqslant 9$ Å), however, the authors acknowledge that the absorption capacity may be overestimated and that caution should be taken in interpreting the results. They suggest that the maximum absorption found at interlayer spacings of 6–7.5 Å should be regarded only as a possibility that needs further investigations in order to prove or disprove the obtained high storage capacity. In their calculation, the authors solved the one-particle Schrödinger equation for a H_2 molecule absorbed between graphene layers and the states are used to calculate the partition function and determine the equilibrium constant for H_2 absorption.

In this work, we have performed two sets of GCMC simulations corresponding to the two different H_2-C potentials.[8,25] The same H_2 intermolecular interaction, described by the Silvera-Goldman potential,[24] is used for both sets, and an ideal gas assumption is imposed. The GCMC technique was implemented to calculate the absorption curve for the H_2 molecules between two graphite layers with *AB* stacking, each layer having 1250 carbon atoms. Rhombohedral periodic boundary conditions were imposed in the x and y directions, with z perpendicular to the graphene planes. Carbon atoms were fixed in their lattice sites, where the lattice constant is set to 2.46 Å. The interlayer separation was varied from 4.8 Å to 8 Å, representing a 45%–140% range in the interlayer expansion.

The number of Monte Carlo steps performed for each simulation was chosen to be dependent on the number of expected absorbed molecules, N_{av}. We define one MC cycle as $(N_{av}+1)$ MC steps.[28] For each cycle, N_{av} particle trial moves and one particle exchange with reservoir are performed. The equilibration run consisted of 5×10^5 to 1×10^6 MC cycles. During equilibration, the displacement for trial moves was adjusted to give 30%–40% acceptance probability. Each reported H_2 mass uptake is an average of 100 samples taken every 5000 MC cycles after equilibration. The simulations performed are at room temperature and at pressures of 1 MPa and 5 MPa.

The percentage of hydrogen mass uptake as a function of graphite interlayer spacing from GCMC simulations is shown in Fig. 5. If the H_2-C interaction is modeled by the Lennard-Jones form in Eq. (1) by Wang and co-workers,[25] the maximum hydrogen uptakes at room temperature are 0.24% and 0.90% for 1 MPa and 5 MPa, respectively. If the exp-6 van der Waals form in Eq. (2) by Patchkovskii and co-workers[8] is used, the maximum uptakes are 1.2% and 2.3% for 1 MPa and 5 MPa, respectively. Significantly, for both model potentials, the uptake is highest for a lattice spacing near 6.2–6.4 A, corresponding to an interlayer expansion of ~90%. As the interlayer spacing becomes even larger (e.g., 8 A) the mass uptake decreases and the hydrogen absorption exhibits the properties of the adsorption near an isolated graphene sheet. We note that the two H_2-C potentials show a significant difference of up to a factor of 5 in the mass uptake at room temperature and pressures ranging from 1 MPa to 5 MPa. However, the absorption results are consistently low.

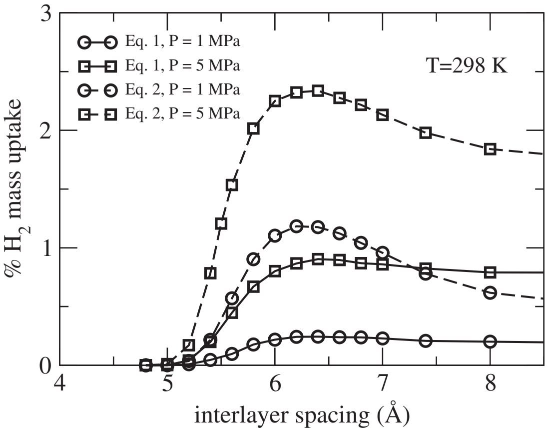

FIG. 5. Hydrogen absorption as a function of graphite interlayer spacing at 298 K for 1 MPa (circles) and 5 MPa (squares) pressures using the H_2-C potential energy functions (Refs. 8 and 25) given in Eqs. (1) and (2).

As noted above, comparing with first-principles results, the potential of Patchkovskii *et al.*[8] gives a better description of the H_2 absorption energy in the low H/C atom ratio range than the potential of Wang *et al.*[25] The same trend is also found in the H_2-absorption energy (U_{abs}) in the fixed bilayer model: although the first-principles U_{abs} values (Fig. 2) lie between those of these two interatomic potentials [Fig. 6(a)], the first-principles U_{abs} values are much closer to those of the potential of Patchkovskii *et al.*[8] than to those of the potential of Wang *et al.*[25] (Note that, however, both interaction potentials seem to predict a larger interlayer separation at the minimum of U_{abs} than the first-principles calculation). While the comparison of the results of different interaction potentials allows us to quantify the upper and lower bounds of the hydrogen uptake, the results from the potential of Patchkovskii *et al.*[8] should be viewed as a better representation of the actual absorption capacity derived from the first-principles calculation.

In an attempt to understand to what extent that the absorbed H_2 molecules approach the ideal gas behavior, we estimate the absorbed density using a simple model. In equilibrium, the chemical potential and temperature in the reser-

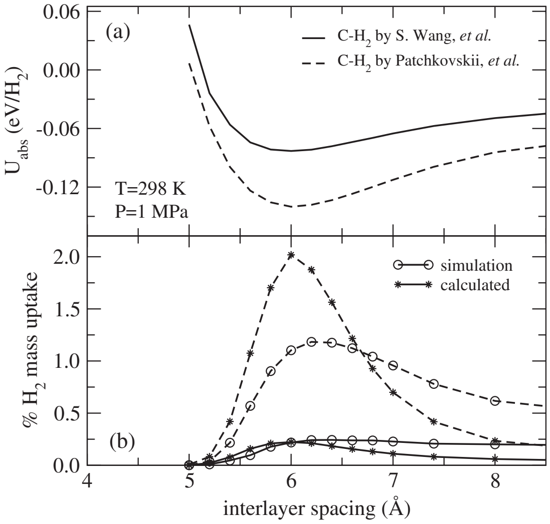

FIG. 6. (a) Absorption energy per hydrogen molecule in graphite with preexpanded interlayer spacing. The spacing at the minimum of U_{abs} (6 Å) corresponds to an interlayer expansion of 80%. (b) Comparison of hydrogen mass uptake obtained from GCMC simulations (circles) and from a model defined in Eq. (3) (stars) at 298 K, 1 MPa. The solid and dashed lines represent the two potentials (Refs. 8 and 25) implemented to describe the H_2-C interaction.

voir gas are equal to those of the absorbed gas.[28,29] We assume that the absorbed hydrogen molecules are confined to have two-dimensional translational degrees of freedom between the graphene sheets and that both the absorbed and reservoir H_2 molecules resemble ideal gas behavior. Setting the chemical potentials of the reservoir and adsorbed systems equal, we obtain

$$U_{abs} + k_B T[\ln(\rho_{xy}\lambda^2)] = k_B T[\ln(\rho\lambda^3)]. \tag{3}$$

Here, the planar density ρ_{xy} is the density (per area) of absorbed H_2 molecules and λ is the thermal de Broglie wavelength. Equation (3) is analogous to that given in Ref. 30, where the adsorption of methane gas on carbon nanotubes is studied. The equation is expected give better predictions in the lower-pressure region, where the behavior of the hydrogen molecules approaches the ideal gas approximation.

A comparison of the calculated absorption density with GCMC simulation results at 1 MPa pressure and room temperature is shown in Fig. 6. By using the calculated U_{abs} values [cf. Fig. 6(a)] from both C-H_2 potentials, the resulting planar densities of H_2 molecules as a function of interlayer spacing are calculated. The calculated mass uptake from Eq. (3) is shown in Fig. 6(b) and is compared with the GCMC simulation results. We find that the calculated absorption capacity is close to the simulation results, but the comparison does not exhibit complete the agreement. This implies that the motion of hydrogen molecules absorbed between graphite layers is close to a two-dimensional ideal gas. As the interlayer spacing is further increased after the optimum spacing is reached, the two-dimensional approximation breaks down. The additional degree of freedom accounted for by the motion perpendicular to the graphene planes starts to contribute significantly to the entropy of the absorbed gas.

IV. DISCUSSION AND CONCLUSION

We have studied the energetics and absorption of hydrogen molecules in a graphite lattice by *ab initio* calculations and found that significant hydrogen absorption is possible at large interlayer expansions. However, the initial stage of hydrogen absorption is energetically unfavorable. The initial absorption has a high energy, due to the close spacing of the graphene layers. Once the layers are expanded, the H_2 molecules have favorable absorption energy, comparable to the amount needed for significant absorption. The interaction is improved if the graphite has an *AA* stacking, as opposed to an *AB* stacking that occurs for pure graphite. This further suggests that artificial connections between the layers that alter the stacking sequence may enhance absorption. The expansion of the layers could be accomplished through the introduction of other "spacer" molecules[6] or clusters of metal atoms, which may also assist in the uptake. Also, this supports the idea that "slit-pore" defects may absorb significant amounts of H_2. In such regions, the H_2 molecules may interact with graphene sheets on either side, with H_2-C distances closer to ideal interaction separations than would occur in the bulk defect-free lattice. However, the number of such pores that can be introduced is limited.

Our room-temperature GCMC simulations with variable graphite interlayer spacing find that external pressures up to 5 MPa are insufficient to enable substantial hydrogen storage capacity of graphite. We have used two separate H_2-C potentials[8,25] to perform these calculations, including the stronger binding potential of Patchkovskii *et al.*[8] The absorption is quite sensitive to the choice of potential. These potentials, combined with relevant C-C and H_2-H_2 potentials, predict absorption curves versus lattice expansion close to those of the first-principles calculations. In the favorable absorption region, these two potentials bound the first-principles calculations, suggesting that the actual absorption would fall between these limits. Making favorable assumptions—namely, using the H_2-C interaction of Patchkovskii *et al.*,[8] we predict an absorption of 2.3 wt % at $T=298$ K and $P=5$ MPa. This is somewhat lower than the predictions of Patchkovskii *et al.*,[8] though in reasonable comparison to their "nonideal" value ($\sim 3\%$). Our calculations suggest a smaller correction from the "ideal" case where the H_2 molecules do not interact: the H_2-H_2 interaction contributes little in all of our calculations and would not indicate a strong difference in adsorption. It should be noted that Ref. 8 predicts large error bars for their results at interlayer spacings less than 9 Å.

As mentioned already, our GCMC simulations use the chemical potential of an ideal gas of H_2 molecules. To estimate how the absorption will be affected if, instead of an ideal H_2 gas, one uses a real gas of hydrogen molecules in the reservoir, we employ a van der Waals equation of state for hydrogen[31] to relate the chemical potential of the real gas with its pressure and temperature. We find that at room temperature and the pressures of interest, the hydrogen molecules have a fugacity coefficient that is slightly greater than

1, by less than a 1% correction. Thus, the use of the van der Waals model will result in a slightly higher absorption capacity at room temperature, but the capacity is not expected to be markedly different from that of the ideal gas simulations.

Thus, our calculations suggest that while absorption in graphite is greatly enhanced by expanding the lattice, the maximum possible uptake is limited, even under optimal conditions. This calculation is limited in its accuracy by the choice of empirical potential; however, first-principles calculations give evidence that the potentials chosen here are reasonable and, in fact, suggest lower absorption than the maximum that we quote in the discussion. We note, however, that the present potentials do not properly predict the H_2 absorption energy differences between an *AB* stacking sequence of graphite layers and an *AA* stacking sequence seen in first-principles calculations. We are currently examining this discrepancy to improve the potentials and to see if an *AA* type of stacking could be used for significant H_2 storage.

Our studies show that the H_2 absorption capacity of graphite layers exhibits strong dependence on the interlayer spacing. First-principles calculations predict the lowest absorption for *AB* stacking to occur at about an interlayer expansion near 70% (5.6 Å) as shown in Fig. 2. Using ideal gas approximation, the grand-canonical Monte Carlo simulations resulted in a maximum mass uptake at an expansion of 90% (6.2–6.4 Å) at room temperature and pressures of 1 MPa and 5 MPa as shown in Fig. 5. This suggests an important consideration that should be taken into account in the design of porous graphitic nanofibers; that is, the optimum pore width or interlayer spacing for maximum H_2 storage capacity is around 6 Å. For smaller pore widths, the repulsive interaction between carbon and the hydrogen molecule is very strong, and for larger pore widths, the binding due to the second graphene layer weakens.

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