

Boron substituted graphene: energy landscape for hydrogen adsorption

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Abstract We have analyzed the modifications of interaction energy between a molecule of hydrogen and graphene layers partially substituted by boron. We show that the presence of boron modifies the symmetry of the energy landscape. It is due to both the larger boron size (with respect to carbon) and its stronger interaction with hydrogen molecules. The changes of energy surface are not confined to the neighborhood of substituted sites but extend over several graphene carbon sites, making the surface more heterogeneous. We show that the average increase of adsorption energy could meet DOE targets for hydrogen storage if a partial charge transfer between boron and hydrogen occurs during adsorption.

Keywords Adsorption · Hydrogen · Boron

1 Introduction

The reversible storage of gases at a priori fixed operating conditions requires a careful choice of a suitable adsorbent. For mobile applications, the DOE target for hydrogen storage to be achieved by the year 2010 is set at 6.5 wt% of stored gas and a volumetric density of 60 kg/m³, increasing to 9 wt% and volumetric density of 90 kg/m³ by 2015.

To reach these values, a variety of materials have been examined. Unfortunately, most of the early promising high-storage materials such as hydrides, zeolites and metal organic framework (MOF) are still economically prohibitive. Therefore, carbons-based adsorbents are amongst the most intensively studied and remain still very attractive candidates, considering their relatively strong adsorption, low weight and low cost.

The highly porous carbons (activated carbon or carbon nanotubes) potentially could store an amount of gas that meets DOE targets. Early euphoric reports of over 60 wt% storage of hydrogen in carbon nanofibers at ambient temperatures and 112 bar pressure (Chambers et al. 1998) and of up to 20 wt% in alkali-doped nanotubes at 1 bar pressure (Chen et al. 1999) have been however scaled down by subsequent studies. Proven storage for carbon nanotubes remains at less than 8 wt% of hydrogen even at cryogenic conditions of 77 K, and a meager 1.5 wt% at ambient temperature (Schlapbach and Züttel 2001; Pfeifer et al. 2008; Poirier et al. 2004). Similar conclusion comes out from numerical simulation (Wang and Johnson 1999; Bathia and Myers 2006; Gigras et al. 2007). The low storage capacity is a consequence of low heat of physisorption of hydrogen on carbon based materials, (about 5 kJ/mol). As it has been discussed (Bathia and Myers 2006) recently, this value is not sufficient to achieve the target storage capacity at room temperature: simple thermodynamic arguments show that for optimal storage/release performance adsorption enthalpy should be approximately three times larger, of the order of 15 kJ/mol.

One way to increase the adsorption energy (and thus the hydrogen uptake) is the modification of graphitic materials by doping or substitution with other atoms. High storage capacities have been reported on alkali doped (Li, K) nanotubes and graphite (Mavrandonakis et al. 2008; Chen et al.

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1999). Although these experimental results remain controversial (Chambers et al. 1998; Panella et al. 2005), some *ab initio* calculations show that Li doping may actually enhance the physisorption energy by the factor of 3 (Cabria et al. 2008). Another group of promising materials are carbon structures partially substituted by boron atoms. *Ab initio* analysis shows that the presence of strongly localized, empty p_z orbital of boron is essential for the enhanced interaction with the occupied σ orbital of H_2 molecules (Kim et al. 2006). This may lead to a partial charge transfer from H_2 to the B-substituted graphitic structure and, as a consequence, much higher adsorption energy. As an example, for hydrogen molecule adsorbed directly above the B atom substituting one carbon atom in the C_{36} fullerene structure, the calculated adsorption energy reaches the value as high as ~ 35 kJ/mol (Kim et al. 2006)

Although the average adsorption energy is the most important parameter defining the strength of adsorption, for practical applications optimum *delivery* (in a complete adsorption-desorption cycle) should also be considered. The same thermodynamic analysis of Bathia and Myers (2006) also shows that a homogeneous surface is preferable when one wants to restore the total amount of the adsorbed gas. Obviously, real surfaces, and, in particular, those that are doped or substituted cannot be homogeneous. In the latter case, surface heterogeneity will be strongly dependent on the percentage and the distribution of the doping/substituting atoms.

In this paper we analyze both adsorption energy and energetic heterogeneity of a variety of graphene surfaces substituted with boron atoms. We show that the difference in atomic size between carbon and boron leads to both local deformation of the initial all-carbon flat structure and a perturbation of hexagonal symmetry of the graphene lattice. We calculate numerically the energy landscape for an H_2 molecule approaching a B-substituted graphene sheet and show how the structural changes introduced by boron substitution affect the energy landscape and its corrugation. To identify the most promising adsorbent, we perform our calculations as a function of the percentage of boron-substituted atoms and we vary the interaction parameters out of the limits determined by standard Lennard-Jones parameters. This procedure is equivalent to the substitution of carbon sites by hypothetical atoms that interact with hydrogen stronger than carbon. Finally we emphasize that a partial charge transfer between boron and hydrogen molecule may enhance the adsorption energy to the value necessary to satisfy DOE requirements.

2 Computational details

The hexagonal structure of the graphene layer is defined by the length of the C–C bond ($d_{C-C} = 1.42$ Å) and is almost

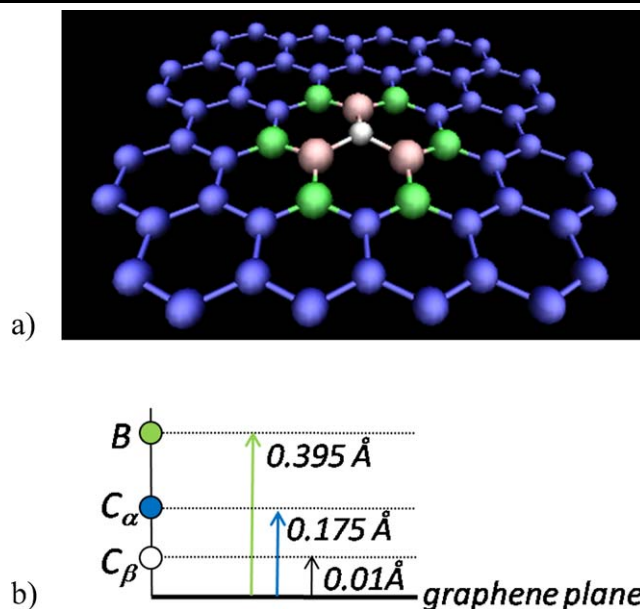


Fig. 1 (Color online) (a) Graphene structure with one carbon atom substituted by boron. White: substituted boron atom, pink: α carbons, green: β carbons. (b) Δz coordinates of the boron atom and its first (C_α) and second (C_β) neighbors, according to Endo et al. (2001)

flat. When substituted with boron, a distortion of the atomic plane occurs. This effect is induced by the fact that the B–C bond is longer than the C–C bond ($d_{B-C} = 1.59$ Å), and in consequence, the substituting boron is located at the slightly higher (lower) position with respect to the non-deformed basal plane of graphite. According to the experimental data (Endo et al. 2001), the deformation is confined to the vicinity of the substituted site (α and β carbons, see Fig. 1). As we will show below, although this out-of-plane displacement of boron and surrounding carbons is relatively small, it causes important changes in the energy landscape for hydrogen adsorption, depending on the way hydrogen molecule approaches the substrate. To account for this geometric effect of substitution, all calculations were done for three substrate geometry when adsorbing H_2 (for definiteness, we will assume the H_2 molecule approaches the adsorbent *from above*): flat surface (in-plane substitution, no deformation), convex surface (a boron-induced protrusion above graphite plane) and concave surface (boron located below graphite plane).

We prepared and analyzed eight BC_n substrates ($n = 3, 5, 7, 8, 11, 17, 23$ and 52) consisting of graphene planes regularly substituted by boron atoms. Among them, BC_3 represents the compound of highest boron concentration (25%) ever prepared experimentally.

The interaction between H_2 molecules and the atoms in the graphene layer were modeled by the Lennard-Jones (6–12) potential. H_2 molecules were considered as structureless superatoms. The interaction parameters for homogeneous contacts are given in Table 1. The heterogeneous

Fig. 2 (Color online) (a) Schematic view of probing graphite surface using hydrogen superatom. (b) The energy landscape of hydrogen above an ideal layer of graphene. The arrows indicate the way of characterizing the landscape heterogeneity (by E_{corr} and E_{saddle} parameters)

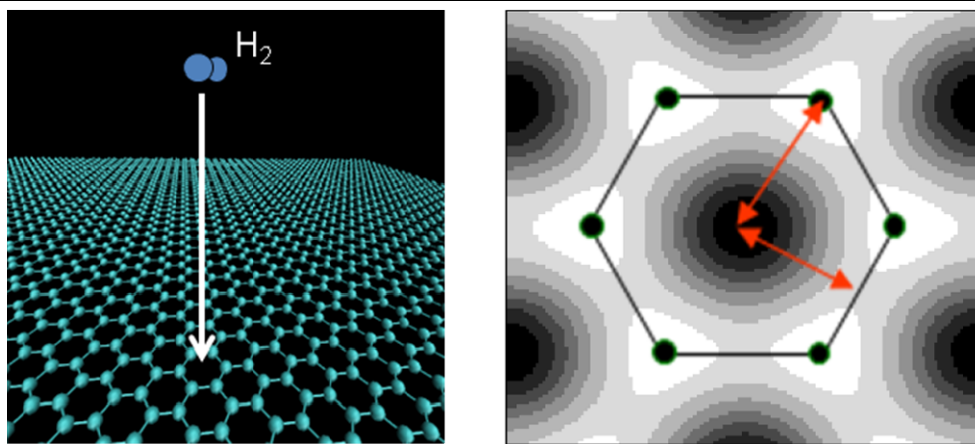


Table 1 Lennard-Jones parameters

	H ₂ (Buch 1994)	C (Steele 1974)	B (Baowan and Hill 2007)
ε [K]	34.0	28.4	47.76
σ [nm]	0.296	0.334	0.3543

interactions were determined using Lorentz-Berthelot mixing rules.

To characterize the heterogeneity of the adsorbing surface we used a probe (H_2 superatom) which interacts with all atoms of the surface within a cut-off distance (for 6–12 interactions) equal 3.0 nm. The interaction energy was calculated as a function of the position above the surface (x, y) and the distance (z) from it (Fig. 2a). For each location (x, y) a minimum of the energy as a function of z was found, at the distance z_{min} from the surface ($E_{\text{min}} = E(z_{\text{min}})$). The energy surface $E_{\text{min}}(x, y)$ obtained in this way represents the energy landscape of the adsorbing surface from the point of view of the probe particle.

Figure 2b shows the energy map for a perfect graphene surface probed by H_2 . The energetic roughness of the surface can be easily characterized by 3 parameters: the value of minimal energy E_{min} , maximal energy E_{max} and the saddle point energy E_{S} that defines the lowest energy between two neighboring minima. In the case of graphene surface, E_{min} is located above the center of the hexagon, E_{max} above carbon atoms and E_{S} -above the middle of the C–C bond. Using these values, the surface heterogeneity can be characterized using two derived parameters: corrugation energy $E_{\text{corr}} = E_{\text{max}} - E_{\text{min}}$ and saddle point corrugation $E_{\text{saddle}} = E_{\text{S}} - E_{\text{min}}$. Both values bring complementary information about the adsorbing surface. A low saddle point corrugation allows easy migration of the gas between the adsorption sites, whereas high corrugation and saddle energies could strongly localize the adsorbate molecules.

3 Results

The results presented in this chapter aim to respond to the following questions: (i) what kind of deformation (of the energy landscape) is introduced by substituting carbon with boron atom, (ii) whether this deformation is localized, (iii) whether it makes the surface energetically more heterogeneous, (iv) how could it affect the adsorption efficiency.

To answer these questions, we show here, as examples, two hypothetical homogeneous structures: BC_3 (25% of carbon atoms substituted with (or by) boron) and BC_8 (11.1%). Figure 3 shows the structures of graphene layers substituted with boron atoms. The inserts indicate the limits of the non-reducible unit cells and, for the reference, the energy landscape of graphene in these limits.

Figure 4 shows the energy landscapes calculated for the systems defined above, assuming different positions of the boron atom with respect to the basal graphene plane: (a) in-plane location ($\Delta z = 0$, the structure of substituted layer remains flat and the only structural heterogeneity of the surface results from difference of atomic radii of carbon and boron, (b) convex location ($\Delta z > 0$, boron) atoms positioned above graphene plane, exactly as defined in Fig. 1), and (c) concave location ($\Delta z < 0$, boron atoms positioned below graphene plane). In all cases the symmetries of the energy landscape have been changed with respect to the initial graphene layer. Here we face an interesting competition: on the one hand boron attracts H_2 more strongly than carbon (higher ε , see Table 1), but at the same time it is a larger atom (larger σ); the consequence is that the boron actually “pushes” the adsorbate farther away compared to a carbon. Since the total adsorption potential results from the addition of the potentials of several individual atoms in the adsorbent, the consequence of a single carbon-boron substitution is hence non-trivial: as a result of this competition, in both in-plane and convex geometries (denoted cases a and b) the minimum of hydrogen- BC_n surface interaction is more distant from the adsorbing surface than in the case of

Fig. 3 (Color online) The graphene layers substituted with (a) 25% (BC_3) and (b) 11.1% (BC_8) of boron atom. The non-reducible unit cells are drawn. The energy landscapes are those of pure graphene in the limits of unit cell. White: boron atoms

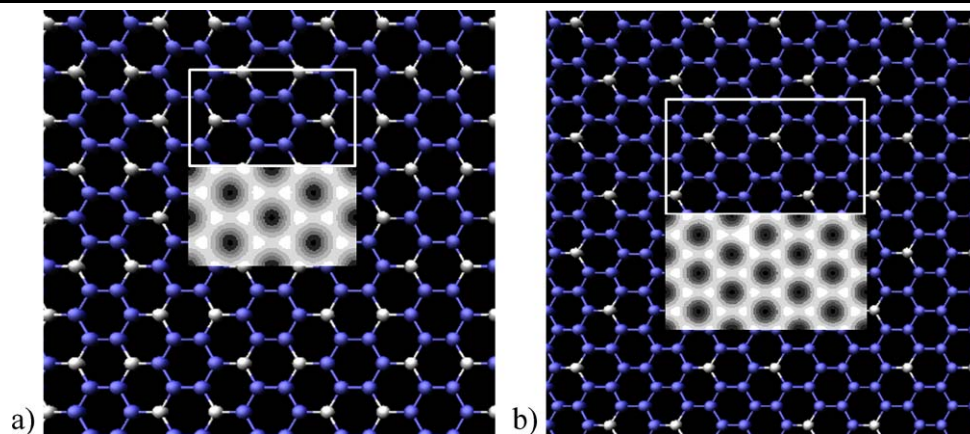
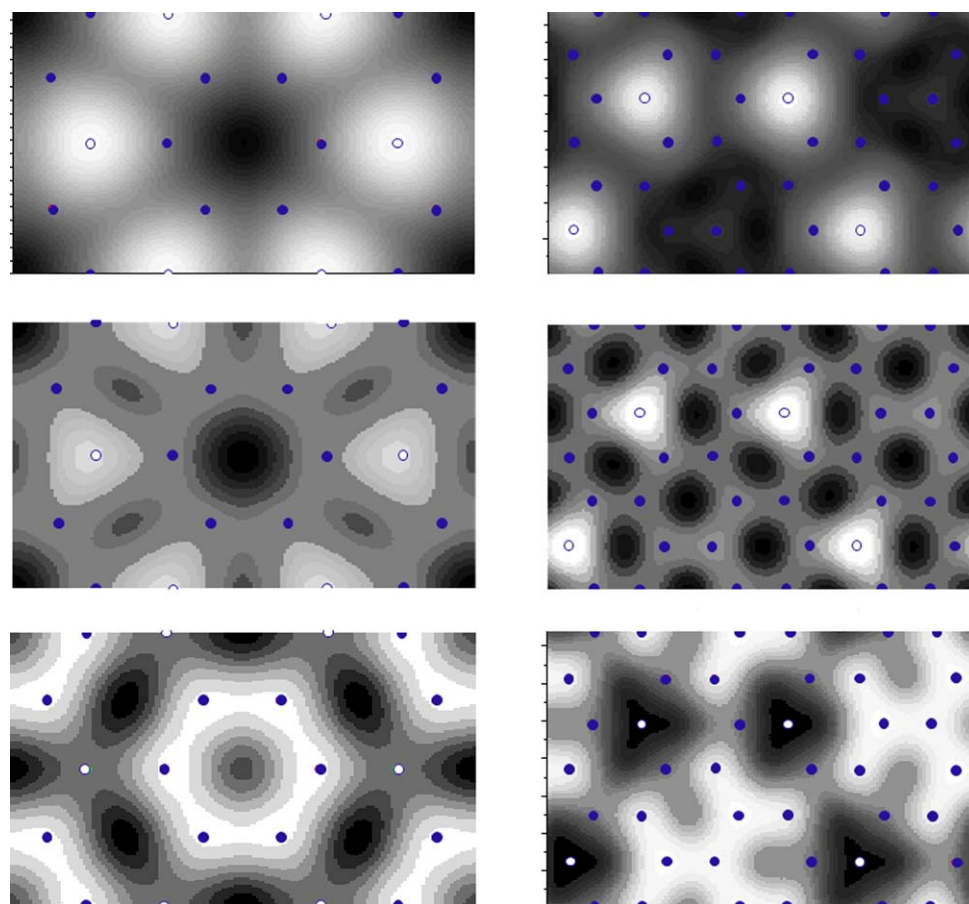


Fig. 4 (Color online) The energy landscapes for graphene layer substituted with 25% (left) and 11.1% of (right) boron for (starting from the top) convex, plane and concave configurations. The minima are black and the maxima are white. The positions of the C (blue, full circles) and B (white, open circles) atoms are shown for the convex and concave maps. For all pictures, the isoenergetic lines are spaced by 5 K



graphite. Therefore, as the distance increases, the value of the energy of interaction decreases and the location of hydrogen above boron becomes less favorable than the neighboring positions. This result rectifies intuitive perception of the role the substituting boron atoms play in the enhancement of the adsorption of graphene structure: in the flat and convex geometries, boron is *not* a site of the strongest adsorption; it enhances the adsorption energy in its vicinity (see Fig. 4, top and center). In the concave configuration

(case c), however, the energy *is* minimal directly above the boron site (see Fig. 4, bottom).

The influence of the substituted atom on the energy landscape is not only limited to local changes of the strength of H_2 interaction with substitution site, but extends over several lattice sites. This observation is important from the point of view of potential applications because it suggests that the modification of energetic heterogeneity of the whole surface can be obtained even at relatively low substitution ratios.

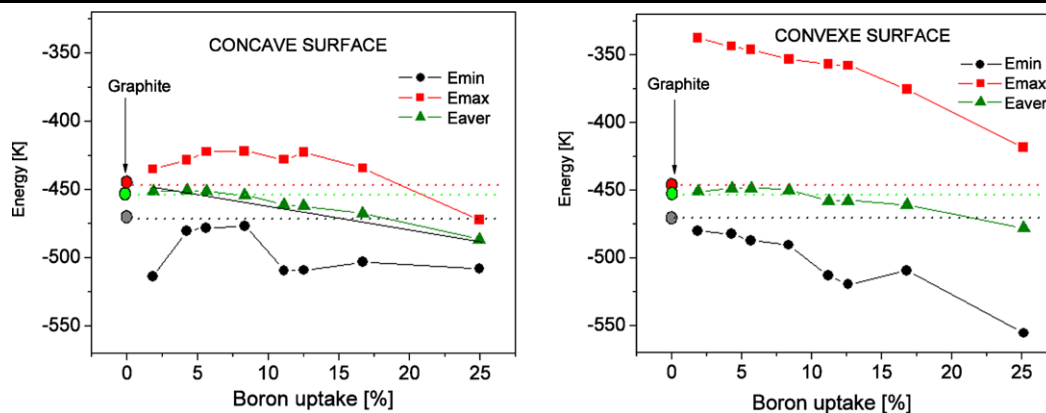


Fig. 5 (Color online) Variations of the average, minimal and maximal energy of H_2 interaction with substituted graphene layer as a function of substitution ratio (in %). The fluctuations of the minimal energy are

To get more insight into this aspect, Fig. 5 shows the variation of energetic heterogeneity as a function of the layer composition. Obviously, the mean value of H_2 interaction with the substrate depends on the layer stoichiometry, but the variation does not exceed 10% of the graphene mean adsorption energy, in the whole range of substitution ratios studied here (from 0% to 25%). In addition, the mean value does not practically depend neither on the boron atoms' distribution nor local geometry of the layer (convex versus concave). High values of the maximal energy (in particular, in convex geometry) do not affect the mean energy, because the statistical weight of high energy points is low.

In general, homogeneous adsorbent is preferable for the maximal *delivery* (Bathia and Myers 2006) of the stored gas but the real materials are always heterogeneous. Therefore, it is important to determine the limits of the heterogeneity which do not decrease the delivery in a critical way. The influence of surface heterogeneity on the adsorption cycle delivery can be estimated using the heterogeneity parameter $s = (E_{\text{corr}})/2kT$ (Bathia and Myers 2006). Small value of s is always preferable and its acceptable limits depend on the mean adsorption energy. If this energy is below 5 kJ/mol (as it is the case for all BC_n structures studied here) the increasing value of the corresponding parameter s is even beneficial for the adsorption cycle. However, if the interaction with the adsorbent surface becomes stronger (e.g., ~ 15 kJ/mol) the value of s should not exceed $s \cong 1$ to avoid decreasing the possible adsorption-desorption delivery (Bathia and Myers 2006). Our simulation of such situation shows that the value of s decreases below 0.2. This value indicates that the influence of the observed heterogeneity on the adsorption mechanism will be negligible if the adsorption-desorption process will be performed at ambient temperature.

The ultimate question is: regarding the results of our calculations, is it possible to conceive such a modification of the graphene layers that the porous material built out of them

related to specific distribution of boron atoms. However, they do not affect the value of the mean energy which decreases with substitution ratio in a continuous way

could store an amount of gas that meets DOE targets? It seems that, as far as we limit our analysis to the graphene layers substituted with boron, storage capacity of such material could be improved only if some additional interactions were induced by boron substitution.

Another option is to change layer's adsorption strength by substitution of different atoms from periodic table. Such a possibility has been thoroughly analyzed for a hypothetical graphene-like structure (Wang and Johnson 1999) where the strength of the solid fluid potential was varied in order to reproduce the experimental excess adsorption. We have calculated the average adsorption energy of a hypothetical XC_8 layer, varying the Lennard-Jones parameter of the hypothetical X atom in the range $48 \text{ K} < \varepsilon < 500 \text{ K}$ and $3 \text{ \AA} < \sigma < 3.7 \text{ \AA}$, respectively. However, the corresponding increase of the interaction strength does not exceed 20% of the initial value, much below the factor of 3 that is necessary for practical applications.

4 Discussion and conclusions

The energy landscape of pure graphene is regularly heterogeneous on the atomic scale. The substitution of carbons by boron atoms makes it heterogeneous on a larger scale. The extent of the modification depends on the percentage of substituted atoms and their random or regular distribution. Our calculations show that even a simple substitution of carbon Lennard-Jones parameters with those of boron (without modifying layer geometry) makes the modification of the energy landscape strongly delocalized. At the same time, the boron atoms positions do not necessarily become the centers of adsorption (that is, local minimal energy sites). Such situation could be observed only if the substitution of boron locally deforms the layer into a concave structure.

In principle, the increase of energetic heterogeneity of the adsorbent may potentially decrease the efficiency of the adsorption-desorption cycle in practical applications. However, as the maximal corrugation (on the convex type surfaces) is estimated to be less than 1 kJ/mol (less than 7% of the optimal adsorption energy, Bathia and Myers 2006), one can suppose that at room temperature the localization of hydrogen in strongly adsorbing sites should not affect significantly the desorption process.

The substitution of carbon atoms by boron increases the adsorption energy because the boron potential model is more attractive than for carbon. However, it is clear that, under the assumptions utilized in the derivations above (B–H₂ interaction with standard Lennard-Jones parameters [8]) even very high percentage of boron atoms (or even all-boron graphene-like surface) cannot increase the average adsorption energy close to required value of 15 kJ/mol. It is evident that only a substantial modification of the interactions (e.g. by a partial charge transfer between the empty p_z orbital of boron and the occupied σ orbital of H₂ molecules, Kim et al. 2006) can lead to a substantial increase in storage capacity.

As the DFT type approaches are not reliable when the dispersion energy plays an important role, more *ab initio* calculations are required to understand theoretical mechanism which can lead to stronger interactions with hydrogen molecules. A possible scenario can be proposed on the base of a formation of dative bond between the σ electron of the H₂ bond and the empty π orbital of boron. In such case, the additional attractive interaction would be due to charge-induced dipole and charge-quadrupole moment between the positively charged B atom and the H₂ molecule. Such a mechanism is under investigations and will be tested both, numerically and experimentally.

Finally, few additional comments concerning possible improvements of the quality of our analysis for future applications are necessary. First, hydrogen is a molecule, so in principle the energy landscape should be discussed as a function of molecular orientations. However, on one hand the hydrogen molecule is nearly spherical (in view of the length of the H–H bond), and on the other, the scale of heterogeneity of the graphite substituted with boron is larger than hydrogen molecular size. Therefore, we do not expect any qualitative modifications of the results presented here whereas the quantitative differences must be small compared to the corrugation amplitudes. It is also important to remember that quantum nature of hydrogen must be also taken into account in modeling of adsorption, even at ambient conditions (Darkrim and Levesque 1998). This effect is being currently studied.

The technical point to be addressed in the future is a development of a tool that could allow one to calculate the interaction with the substrate in a more efficient way than direct atom-atom summation. One of possibilities that we plan

to explore is to define a Steele's type potential expansion for graphite substituted with boron. It is purely technical detail but it could improve the efficacy of future numerical simulations and would allow one to simulate larger systems.

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