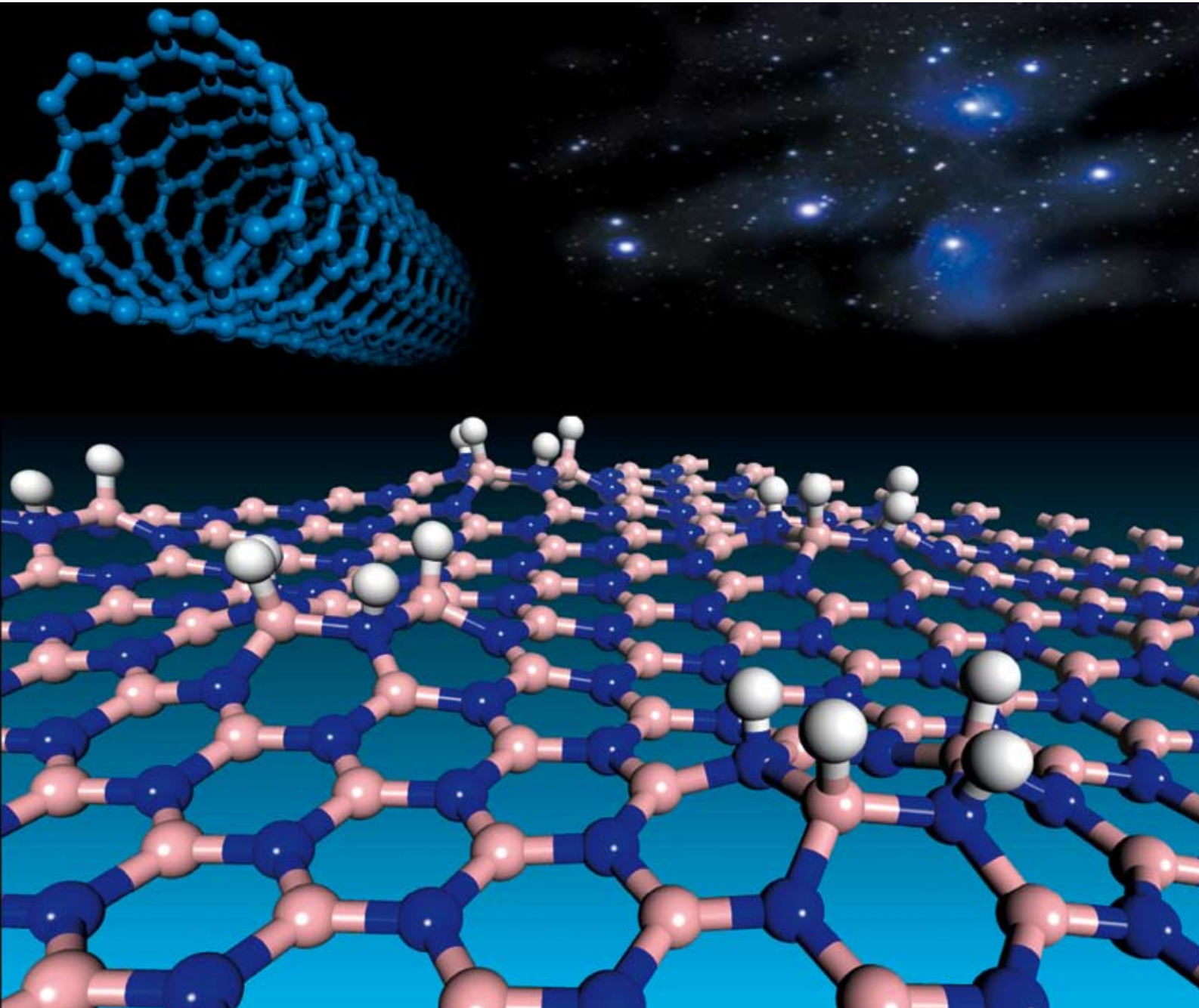


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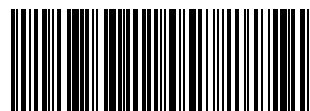
Weck *et al.*

Dimer-induced stabilization of H adsorbate cluster on BN(0001) surface

PERSPECTIVE

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Thin film rupture and polymer flow



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Dimer-induced stabilization of H adsorbate cluster on BN(0001) surface

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Using first-principles calculations, we have studied successive adsorption of hydrogen atoms on a sp^2 -bonded boron nitride graphitic sheet. Our calculations show that clustering proceeds through the creation of contiguous H–H orthodimer structures stabilizing the H adsorbate cluster on the BN(0001) surface, leading eventually to the formation of hydrogen-contiguous boat-shaped quartets.

Hydrogen adsorption on surfaces has received considerable attention owing to its fundamental importance in a broad range of research areas encompassing hydrogen storage,¹ interstellar chemistry,^{2,3} fusion reactor design⁴ and nanotechnology.^{5,6} From previous investigations, graphite (0001) surface and polycyclic aromatic hydrocarbon cluster models have emerged as prototypical systems for studying single H atom adsorption and subsequent H cluster formation on carbonaceous materials.^{3,5,7–11} In particular, recent studies have demonstrated that preferential sticking of H atoms into specific adsorbate structures is responsible for clustering on graphite.^{3,10} From these H adsorbate clusters, molecular hydrogen can form *via* Eley–Rideal abstraction mechanism or recombinative desorption, with important implications for the catalytic role played by carbonaceous dust grains in the formation of H_2 in the interstellar medium.^{2,3} Other authors have also explored the possibility of using selective chemisorption of H atom pairs on graphene to create superlattice strips acting as waveguides and heterostructures for the development of nanoelectronic devices.⁵

Although BN(0001) is isostructural and isoelectronic with graphite, comparatively less attention has been devoted to the study of H adsorption on hexagonal BN surfaces. Using density functional theory (DFT) with a BN(0001) model cluster approach, Mårild *et al.*¹² found that H preferentially adsorbs on boron atoms at low coverage, while adsorption on top of nitrogen atoms is metastable. In both cases, H chemisorption changes the local bonding character of BN(0001) from sp^2 to sp^3 hybridization, accompanied by a pyramidalization of the initial planar surface at the adsorption site.¹³ Several recent computational studies using DFT confirmed these findings and extended the investigation to the case of hydrogen adsorption on BN nanotubes.^{14–16} However, to the best of our knowledge, the possibility of H adsorbate cluster formation on BN(0001) surfaces has not been considered.

In this Communication, we report DFT calculations of the preferential sticking of H atoms into specific adsorbate structures on BN(0001) surfaces, and clustering facilitated by the successive formation of H–H orthodimers. First-principles all-electron calculations of the total energies and optimized geometries were performed using the spin-polarized density functional theory as implemented in the DMol3 software.¹⁷ The exchange correlation energy was calculated using the generalized gradient approximation (GGA) with the parametrization of Perdew and Wang¹⁸ (PW91). Double numerical basis sets including polarization functions on all atoms (DNP) were used in the calculations. The DNP basis set corresponds to a double- ζ quality basis set with a p -type polarization function added to hydrogen and d -type polarization functions added to heavier atoms. The DNP basis set is comparable to 6-31G** Gaussian basis sets¹⁹ with a better accuracy for a similar basis set size.^{17,20} In the generation of the numerical basis sets, a global orbital cutoff of 4.1 Å was used. The energy tolerance in the self-consistent field calculations was set to $10^{-6} E_h$. Optimized geometries were obtained using an energy convergence tolerance of $10^{-5} E_h$ and a gradient convergence of $2 \times 10^{-3} E_h \text{ Å}^{-1}$. A model system consisting of one BN(0001) monolayer was used in our simulations, since H binding to hexagonal BN was found to be very weakly dependent on the layer number.¹⁶ The calculated in-plane lattice parameters of the relaxed hexagonal primitive unit cell are $a = b = 2.51 \text{ Å}$, in excellent agreement with the experimental value of 2.505 Å,²¹ and the corresponding B–N bond length is 1.45 Å. The working cell is a 40-atom $5 \times 4 \times 1$ triclinic supercell, with a vacuum of 10.00 Å along the z direction [*cf.* Fig. 1(a)]. The Brillouin zone was sampled using the Monkhorst–Pack special k -point scheme²² with a $4 \times 4 \times 1$ mesh for structural optimization and total energy calculations.

At each step of the single H atom adsorption sequence, the binding energy was calculated using the formula:

$$E_n^b = E[\text{BN}(\text{H})_n] - E[\text{BN}(\text{H})_{n-1} + \text{H}], \quad (1)$$

where $E[\text{BN}(\text{H})_n]$ is the total energy of the BN system with n H atoms adsorbed and $E[\text{BN}(\text{H})_{n-1} + \text{H}]$ is the energy of the same system with the n th H atom far from the surface.

Consistent with previous studies, the only stable site for single H adsorption is atop the B site [*cf.* Fig. 1(b)], with a binding energy $E_1^b = -0.05 \text{ eV}$, while adsorption of a single H atom on N is metastable and endothermic by 0.57 eV. For adsorption of the first H atom at the B_0 site, the B_0 –H bond length is 1.30 Å, the B_0 –N bond length is 1.50 Å, and the NB_0N and HB_0N angles are 116.1° and 101.6°, respectively. Adsorption of a single H atom at the N_1 site resulted in N_1 –H

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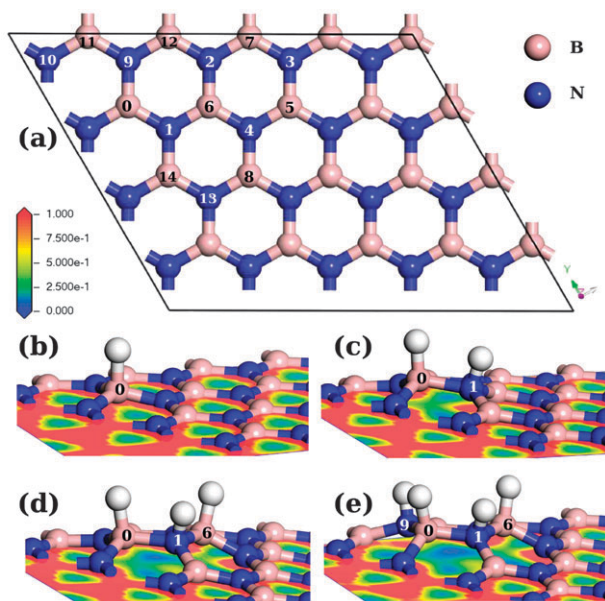


Fig. 1 (a) Boron nitride supercell. (b)–(e) Optimized geometries for the sequential adsorption of H atoms on the hexagonal BN sheet. Cross sections of the electronic charge density in the BN(0001) plane are also plotted (in units of $e \text{ \AA}^{-3}$).

and N_1 –B bond lengths of 1.08 and 1.55 Å, and BN_1B and HN_1B angles of 110.2° and 108.7° , respectively. These values, close to the tetrahedral angle (109.5°), and the strong out-of-plane puckering of N_1 by 0.63 Å (0.45 Å for adsorption on B_0) indicate an almost complete local phase transformation from the sp^2 to the sp^3 hybridized state.

Using the Hirshfeld partitioning of the electron density, we have performed a population analysis to gain insight into the charge transfer occurring when the delocalized π -bond BN system is ruptured locally by the adsorption of a single H atom onto the substrate. For the pristine BN(0001) surface, charges of $-0.195 e$ on the N atom and $+0.195 e$ on the B atom were calculated, characteristic of the strong ionic B–N bonding [cf. Fig. 2(a)]. Upon adsorption of a single H atom at the B_0 site, additional charges of 0.013 e and 0.104 e are transferred to the H and B_0 atoms, respectively, from the electron-donating N atoms surrounding B_0 . For H adsorption on N_1 , H and N_1 donate charges of 0.097 e and 0.081 e , respectively, to the electron-withdrawing B atoms surrounding N_1 . These results contradict the assertion by Zhou *et al.*¹⁵ that H can transfer more electron density to the electron-deficient boron atom, compared to the electron-donating nitrogen atom, in their attempt to explain why the B site is more favorable than the N site for single H atom chemisorption.

With the first H_0 atom adsorbed at the B_0 site, 7 pair arrangements have been considered for the adsorption of the second H atom, as indicated in Fig. 3(a). The H_0 – H_1 orthodimer arrangement [cf. Fig. 1(c) and 2(a)], is found to be the most energetically favorable pair ($E_2^b = -3.24$ eV), lower in energy by 0.50 and 2.34 eV than the possible H_0 – H_2 paradimer and H_0 – H_6 metadimer arrangements, respectively, on the same BN ring. As shown in Fig. 2(b), this can be explained by the presence of pronounced N ($2p$) charge density lobes at

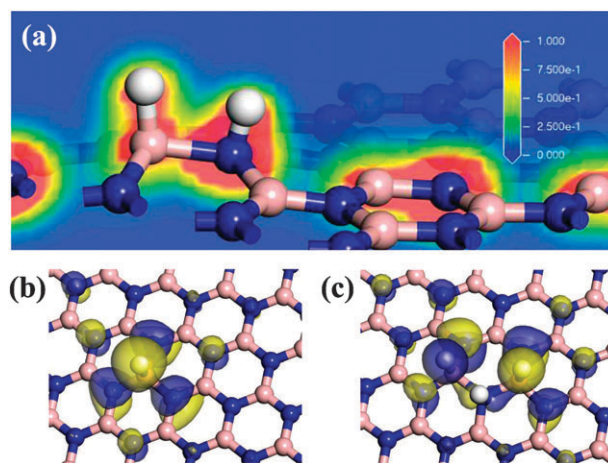


Fig. 2 (a) Electronic charge density cross section of the most stable H–H pair, *i.e.* the orthodimer, adsorbed on BN(0001) (in units of $e \text{ \AA}^{-3}$), plotted in a plane perpendicular to the plane of the BN sheet. Highest occupied molecular orbital (HOMO) of (b) a single H atom and (c) the energetically favorable H triplet adsorbed on the BN sheet.

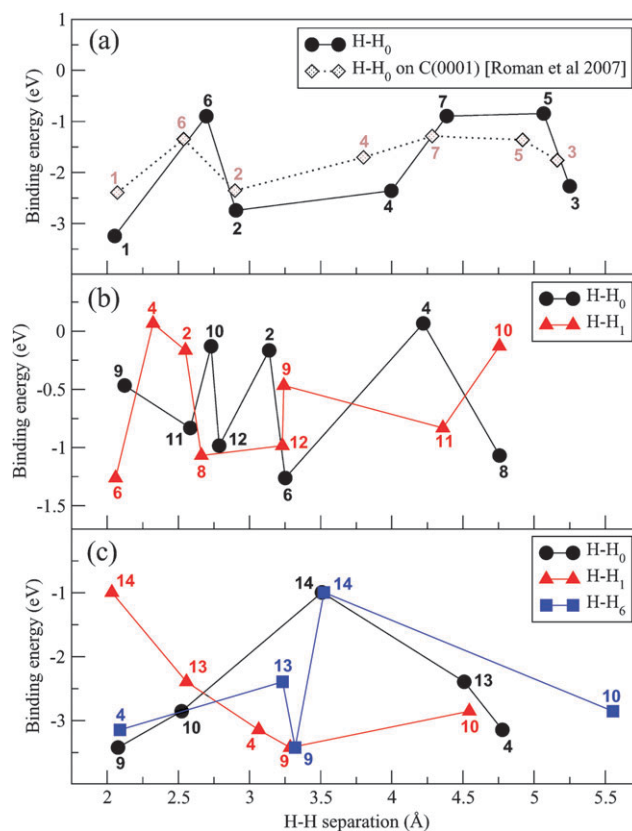


Fig. 3 Binding energy as a function of the pair interatomic separation for the adsorption of (a) the second, (b) third, and (c) fourth H atoms on BN(0001). Indices correspond to the site positions given in Fig. 1(a). For (a), (b) and (c), hydrogen atoms are initially adsorbed at B_0 , B_0 – N_1 , and B_0 – N_1 – B_6 top sites, respectively. The different colored traces refer to the separations between the last adsorbed hydrogen atom, denoted by H, at the stable/metastable site positions investigated and the hydrogen atoms initially adsorbed on the BN sheet.

Table 1 Binding energies (in eV) and H–H and B–N distances (in Å) for the adsorption of the second, third, and fourth H atom corresponding to the energetically most stable hydrogen pair, triplet and quartet adsorbed on the BN sheet

	Binding energy	H ₀ –H ₁	H ₁ –H ₆	H ₀ –H ₉	B ₀ –N ₁	N ₁ –B ₆	B ₀ –N ₉
2nd H	–3.24	2.05			1.65		
3rd H	–1.26	2.06	2.06		1.62	1.62	
4th H	–3.42	2.10	2.05	2.08	1.60	1.65	1.64

ortho positions in the highest occupied molecular orbital (HOMO) of the BN(0001)–H₀ system, thus favoring orbital overlap and electron transfer between N atoms and the second H atom. While N atoms at *para* positions, as well as in adjacent rings, still show smaller charge density lobes in the HOMO, B atoms do not contribute significantly to the HOMO. As a result, the magnitude of the average binding energy of the second H atom at B sites 6, 7, and 5, *i.e.* $\overline{E}_2^b(\text{B}) = -0.87$ eV, is much lower than its corresponding value for adsorption at N sites 1, 2, 4, and 3, *i.e.* $\overline{E}_2^b(\text{N}) = -2.65$ eV. The theoretical results of Roman *et al.*¹¹ for H pair formation on the C(0001) sheet have also been reported in Fig. 3(a) for the sake of comparison. The variation of the binding energy as a function of the pair interatomic separation is found to be similar for BN and C surfaces, although energy variations are stronger between N and B adsorption sites compared to their C counterparts. This stems from the central position occupied by C, relative to B and N, in the periodic table. The average binding energy of the second H atom at the 7 adsorption sites considered is $\overline{E}_2^b = -1.88$ eV for BN(0001), comparable to the value of -1.74 eV for C(0001).¹¹

To determine the preferential adsorption site of the third H atom, 8 positions have been investigated in the vicinity of the H₀–H₁ adsorbed pair [*cf.* Fig. 3(b)]. The H₀–H₁–H₆ contiguous triplet [*cf.* Fig. 1(d)] appears to be the most stable arrangement, corresponding to a H binding energy of $E_3^b = -1.26$ eV, slightly more favorable than the H₀–H₁–H₈ and H₀–H₁–H₁₂ arrangements by 0.19 and 0.28 eV respectively. Relative to the H₁ atom, H₁–H₆ corresponds to a *ortho*-dimer configuration, and H₁–H₈ and H₁–H₁₂ to *para*-dimers, which were found to be energetically favorable pairs. H adsorption on N₄, corresponding to H₁–H₄ *meta*-dimer formation, is metastable. The third H atom binds preferentially at B sites 6, 8, 12, and 11, compared to N stable adsorption sites 2, 9, and 10, resulting in average binding energies of $\overline{E}_3^b(\text{B}) = -1.04$ eV and $\overline{E}_3^b(\text{N}) = -0.25$ eV respectively. The average binding energy of the third H atom at these 7 stable adsorption sites is $\overline{E}_3^b = -0.70$ eV, considerably less than for the formation of the first H pair.

Finally, 9 adsorption sites for the fourth H atom have been considered around the H₀–H₁–H₆ contiguous triplet. The most energetically favorable arrangement is found to be the H₉–H₀–H₁–H₆ contiguous quartet structure [*cf.* Fig. 1(e)], with a H binding energy of $E_4^b = -3.42$ eV [*cf.* Fig. 3(c)]. This arrangement corresponds to the formation of a terminal H–H orthodimer, similarly to the zigzag H₀–H₁–H₆–H₄ contiguous quartet which is only 0.28 eV higher in energy. As shown in Fig. 2(c), the larger N (2*p*) charge density lobes in the HOMO of the BN(0001)–(H)₃ system are at the equivalent N₉ and N₂ sites, thus favoring orbital overlap and electron

transfer between these N atoms and the fourth H atom. Adsorption of the fourth H atom leading to this boat-shape-type structure tends to limit the surface strain by drastically transforming the plane surface structure in an effort to restore the local planarity. A similar trend has been reported for H adsorption on graphene, where the adsorption of four contiguous H atoms resulted in cyclic alkane-like structures of the plane surface.¹⁰ Among the B sites 5, 7, 8, 12, and 14 investigated for adsorption of the fourth H atom, only B₁₄ was found to be a stable adsorption site. The average binding energies of the fourth H atom at the 4 stable N sites and at the 5 stable adsorption sites considered are $\overline{E}_4^b(\text{N}) = -2.95$ eV and $\overline{E}_4^b = -2.56$ eV, respectively.

Binding energies and H–H and B–N distances for the adsorption of the second, third, and fourth H atom corresponding to the energetically most stable hydrogen pair (H₀–H₁), triplet (H₀–H₁–H₆) and quartet (H₉–H₀–H₁–H₆) structures adsorbed on the BN sheet are summarized in Table 1.

In summary, we have performed density functional calculations of the hydrogenation of a *sp*²-bonded boron nitride graphitic sheet by H atoms. Our calculations show that clustering proceeds through the successive creation of H–H orthodimer structures stabilizing the H cluster on the surface, and leading eventually to the formation of hydrogen contiguous quartets. Our findings should have important implications for the development of nanoelectronic devices relying on selective chemisorption of H–H pairs on a graphitic substrate.

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