Nondissociative Adsorption of H$_2$ Molecules in Light-Element-Doped Fullerenes

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First-principles density functional and quantum Monte Carlo calculations of light-element doped fullerenes reveal significantly enhanced molecular H$_2$ binding for substitutional B and Be. A nonclassical three-center binding mechanism between the dopant and H$_2$ is identified, which is maximized when the empty $p_z$ orbital of the dopant is highly localized. The calculated binding energies of 0.2–0.6 eV/H$_2$ is suited for reversible hydrogen storage at near standard conditions. The calculated H$_2$ sorption process is barrierless, which could also significantly simplify the kinetics for the storage.

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Hydrogen is a clean energy source with the potential to replace fossil fuels. However, the practical implementation of H fuel has been impeded by the lack of a safe, economical, and efficient means of storing hydrogen at or near room temperature [1]. Among the various available approaches, carbon-based nanostructures have attracted considerable attention as well as heated debate [2]. On the one hand, carbon is lightweight, which is essential for achieving a high storage weight percentage. On the other hand, studies have so far failed to identify an interaction that would be suitable for room-temperature reversible H storage, namely, an adsorption energy in the 0.2 to 0.6 eV/H$_2$ range. Typically, hydrogen either retains its molecular form and binds only weakly with a carbon surface via a $\sim$0.04 eV/H$_2$ van der Waals (vdW) interaction, or dissociates into atoms and forms strong C-H bonds such as is found in hydrocarbons [3,4]. Recent quantum mechanical molecular dynamics calculations describe an interaction having an intermediate binding energy in which a partial electronic charge is transferred from a hydrogen molecule to a thermally fluctuating single-wall carbon nanotube [5]. However, these results are also quite controversial [6].

In searching for an interaction of intermediate strength between hydrogen and a solid-state storage medium we expect that a nondissociative adsorption of H$_2$ will be more desirable than a dissociative one from the point of view of efficiency and kinetics. As a molecular analogue, we note the existence of the so-called Kubas complexes in which H$_2$ molecules are nondissociatively bound to transition metal (TM) complexes with adsorption energies significantly larger than the typical vdW energy but also significantly smaller than that of a typical metal hydride [7]. Unfortunately, these systems have low reversible hydrogen capacities due to the presence of the heavy TM species. Along these same lines, others [8,9] have calculated that bare metal atoms can bind up to six molecules of hydrogen reversibly as ligands. In practice, however, it will be impossible to use such bare metal atoms as a hydrogen storage medium due to the tendency of the atomic species to agglomerate and form a solid the first time the hydrogen species are removed.

In this Letter, we investigate the possibility of applying the nondissociative H adsorption mechanism to light, non-transition metal doped carbon fullerenes. Extensive first-principles total energy calculations on a prototypical impurity-doped C$_{36}$ system reveal how the adsorption of H$_2$ is modified by the chemistry of various impurities. Among interstitial Li and F and substitutional N, B, and Be, only the latter two show significant adsorption energies: 0.39 and 0.65 eV/H$_2$ for B and Be, respectively. Detailed analysis shows that a strongly localized, empty $p_z$ orbital of B and Be is essential for the enhanced interaction with the occupied $\sigma$ orbital of H$_2$. This leads to a partial charge transfer from H$_2$ to the fullerene. We also studied H$_2$ sorption on more heavily doped fullerenes. A room-temperature reversible storage capacity of 1.7 wt % is predicted for C$_{54}$Be$_6$ with rather similar adsorption energies. This demonstrates that, at least in principle, carbon-based lightweight, room-temperature reversible storage materials can exist.

Our calculations were performed using a combination first-principles, electronic structure methods. Extensive structural searches were carried out using density functional theory calculations within the local density approximation (LDA). The Ceperley-Alder exchange-correlation energy functional was used [10]. We employed the ultra-soft pseudopotentials, as implemented in the VASP package [11]. The electron wave functions were expanded in a plane wave basis with a kinetic energy cutoff of 287 eV. The supercell approximation was used in which the surface atoms of adjacent molecules are separated by at least 7 and 9 Å for C$_{36}$ and C$_{60}$, respectively. We optimized the atomic positions by minimizing the Hellmann-Feynman forces to less than 1 mRy/Å. A nudged elastic band method [12] was used to calculate the energy barrier for separating H$_2$ from C$_{36}$. The adsorption energy is defined as $E_a = E_{\text{far}} - E_{\text{bound}}$, where $E_{\text{far}}$ and $E_{\text{bound}}$ are the energies for the non-bonding and bonding H$_2$ configurations, respectively. In
the nonbonding configuration, the H$_2$ molecule is at least 5.3 Å away from the nearest atom on the fullerene.

We have tested the ultrasoft pseudopotential results against those from all-electron-like projector augmented-wave (PAW) potentials and norm-conserving pseudopotentials provided in the PARTEC package [13]. The results are practically the same. We also carried out calculations using the generalized gradient approximation (GGA) [14]. Strictly speaking, neither LDA nor GGA gives an accurate account of the weak interaction between systems with closed electronic shells such as between H$_2$ and C$_{36}$. It has been suggested that LDA typically overbinds, whereas GGA typically underbinds the H$_2$ to fullerenes, although a recent high-level MP2 study showed that the LDA results are significantly closer to the MP2 results [15].

To enable us to make quantitative predictions of the hydrogen binding energetics we have selectively carried out state-of-the-art fixed node, diffusion quantum Monte Carlo (QMC) calculations using the linear scaling version [16] of the CASINO [17] QMC code. In the QMC calculations, the plane wave orbitals from the LDA and GGA calculations were used to construct the Slater determinant in the trial wave function and norm-conserving LDA and GGA pseudopotentials were used. The plane wave cutoff was increased to 70 Ry to ensure that the nodal surface is converged with respect to cutoff used for the single particle orbitals. This is consistent with the observation in Ref. [16] that a higher cutoff is required to converge the QMC energy than the DFT energy for a given system.

The effect of carbon network curvature.—It has been previously suggested that the curvature of a wrapped sp$^2$ carbon network, e.g., that of a carbon nanotube [5], can significantly affect $E_a$ even in the absence of dopants. Since C$_{36}$ has a rather large curvature and is experimentally available [18], we can use it to test this hypothesis. However, we found that, after full atomic relaxation, the binding between C$_{36}$ and H$_2$ is negligibly small, only 0.07 eV/H$_2$ by LDA. This value of $E_a$ is similar to the one calculated between a carbon nanotube and H$_2$ using the same method [6]. Hence, we conclude that the curvature of either a fullerene or a nanotube has little effect on the physisorption of H$_2$.

The trend in impurity doping.—Next, we studied the effect of doping by lightweight impurities, endohedral Li and F, and substitutional N, B, and Be, as shown in Table I. For Li, although the volume of the cage is slightly increased, which is consistent with electron transfer from Li to the cage, there is no significant increase in the adsorption energy, $E_a = 0.07$ eV/H$_2$. The situation is worse for F where the electron transfer reverses its direction and the adsorption energy decreases to $E_a = 0.04$ eV/H$_2$. A substitutional nitrogen also has no advantage for H$_2$ adsorption. Here, $E_a = 0.06$ eV/H$_2$ and there is no sign that charge transfer between N and H$_2$ has taken place.

In contrast, H$_2$ binds to substitutional B or Be with significantly larger LDA binding energies, 0.39 and 0.65 eV/H$_2$, respectively. The GGA calculation yields $E_a = -0.03$ and 0.37 eV/H$_2$, where the negative value implies a repulsion. Interestingly, however, the differences between the LDA and GGA energies, 0.42 and 0.32 eV/H$_2$, respectively, are nearly a constant to within 0.1 eV. Highly accurate QMC calculations predict 0.2 ± 0.05 eV/H$_2$ adsorption energy for C$_{35}$B-H$_2$ [see Ref. [19]]. While this value is about 0.2 eV/H$_2$ less than that of LDA, it is still significantly larger than the vdW energy of about 0.04 eV/H$_2$. Therefore, other than a systematic correction, the general trends predicted by our LDA calculations should hold.

Figure 1 shows the atomic structure for C$_{35}$B-H$_2$. The distances between B and the two H atoms are approximately 1.40 Å, which is about 23% larger than the sum of the B and H covalent radii, 1.14 Å. However, the B-H distance is significantly shorter than the bond distances found for Li, F, and N atomic impurities, which ranged from 2.5 to 3.3 Å, except for the Be case where the most significant H sorption energy is obtained. The formation of the B-H$_2$ bond causes the H$_2$ bond to be weakened and the bond length in Fig. 1 increases to 0.85 Å, which is about 10% longer than for a noninteracting H$_2$, 0.77 Å.

The energy curve for H$_2$ adsorption and desorption.—To determine the energy barrier, we have considered eight intermediate positions, four of which are shown in Fig. 1(a). Figure 1(b) shows the calculated energy change, as the geometric center of H$_2$ moves away from its adsorption site. It is remarkable that the H$_2$ adsorption is spontaneous without any energy barrier. As a result, H$_2$ desorption can occur in a unimolecular fashion by simply

| Table I. Adsorption energy (in unit of eV) of H$_2$ for doped C$_{36}$. Endo- and sub- stand for endohedral and substitutional doping, respectively. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Stype           | Endo-Li         | Endo-F          | Sub-N           | Sub-B           | Sub-Be          |
| H$_2$ adsorption energy | 0.07 eV       | 0.04 eV         | 0.06 eV         | 0.39 eV         | 0.65 eV         |

In Fig. 1, the binding process of a H$_2$ to substitutional B in a C$_{35}$B. (a) The ball-and-stick model in which only four intermediate (darker) H$_2$ images are shown. (b) Total energy curve as a function of the geometric center of H$_2$ from its minimum-energy position.
overcoming the binding between H$_2$ and B atom in the fullerene. Thus, the reversible storage of H$_2$ in these systems appears promising.

Electronic hybridization.—To understand the enhanced adsorption of H$_2$ in doped fullerenes, we have calculated the site-decomposed local densities of states (LDOS) for B and Be. Figures 2(a) and 2(b) show the LDOS for the initial configurations where the H$_2$ molecules are unbound and Figs. 2(c) and 2(d) show the final configurations where the H$_2$ molecules are bound. For unbound C$_{35}$B-H$_2$ [Fig. 2(a)], the doubly occupied H$_2$ $\sigma$ state shows a single peak about 5 eV below the Fermi level, $\epsilon_F$, whereas the B $p_z$-like state shows two peaks about 1 and 3 eV above $\epsilon_F$. The presence of this doublet is the result of a strong hybridization of B $p_z$ state with carbon $\pi$ states. For bound C$_{35}$B-H$_2$ [Fig. 2(c)], the H$_2$ $\sigma$ state spreads out with two main peaks about 10 eV below $\epsilon_F$, whereas the B $p_z$ states move to higher energies outside the energy range of Fig. 2. These level shifts are consistent with the notion that H$_2$ binds to B through an electronic hybridization. A similar hybridization is also seen for C$_{35}$Be-H$_2$ in Figs. 2(b) and 2(d). Because of a larger separation of the Be $p_z$ state in Fig. 2(b), the magnitude of the shift of the H$_2$ $\sigma$ level (about 3 eV) is smaller than that of B. By comparing Figs. 2(e) and 2(f), we see that the H$_2$-Be coupling perturbs the carbon host states less than the H$_2$-B coupling.

In contrast, we did not find any such hybridization between H$_2$ and other impurities. This is understandable because in endohedral doping with species such as Li and F, there is no localized empty impurity state on the fullerene with which the H$_2$ $\sigma$ state can hybridize. In the case of substitutional nitrogen, the $p_z$-like N lone pair is already doubly occupied. A hybridization with the low-lying H$_2$ $\sigma$ state would increase its energy and is therefore not favored. In other words, the presence of a highly localized empty $p_z$ orbital is essential for the nondissociative adsorption of H$_2$ to doped fullerenes.

Bond formation and charge transfer.—More direct physical insight can be obtained by examining the electron density difference, $\Delta \rho = \rho(C_{35}X-H_2)-\rho(C_{35}X)-\rho(H_2)$, where $\rho(x, y)$ is the planar electron density, integrated over the $z$ direction (out of the plane in Fig. 3) and $X = B$ or Be. Note that when calculating $\rho(C_{35}X)$ and $\rho(H_2)$, we fix the atoms in their respective final, relaxed positions in C$_{35}$X-H$_2$. Figures 3(a) and 3(b) show $\Delta \rho$ for B and Be, respectively. We see that the adsorption of H$_2$ causes significantly larger disturbance to $\rho(C_{35}B)$ than to $\rho(C_{35}Be)$. Noticeably, a new three-center bond forms between H$_2$ and B (Be), at the expense of a weaker H-H bond [20].

Figure 3(c) shows the linear electron density, $\Delta \rho(x,y)$, from which we calculate the total amount of charge transferred from $(x \geq 0)$ region to $(x < 0)$ region where $x = 0$ corresponds to the position of H$_2$. We obtain 0.21 and 0.12 electrons for B and Be, respectively. In the case of B, however, only about 29% = 0.06 electrons are directly involved in the three-center bond. In contrast, in the case of Be, the full 0.12 transferred electrons are involved in the bond formation. Therefore, $E_a$ for Be is significantly larger than that for B. These observations are consistent with the notion that a highly localized $p_z$ orbital is essential for

![FIG. 2](color online). (a)–(d) The calculated local density of states (LDOS) for B (Be) in C$_{35}$B (Be)-H$_2$. The LDOS for B (Be) are solid lined, whereas the LDOS for H$_2$ are open circled. (e) and (f) The squared changes of the carbon states due to H$_2$ sorption, namely, $\sigma^2 = [\delta \text{LDOS(carbon)}]^2$ between the nonbonding and bonding states.

![FIG. 3](color online). (a) and (b) are the differential planar electron density, $\Delta \rho(x,y)$, for B and Be, respectively. Solid and dotted contours indicate electron accumulation and depletion, respectively. The contour interval is 0.003 and the cutoffs are $\pm 0.08$ e/Å$^2$. (c) Linear $\Delta \rho(x)$ for B and Be along the x axis shown in (a) and (b), respectively. The positions of the H$_2$ and B (Be) are indicated.
nondissociative adsorption: it leads to a smaller disturbance to the fullerene as evidenced by the smaller tail in Fig. 3(c) for Be, as well as a smaller disturbance to the H₂ as evidenced by the shorter H₂ bond length of 0.8 Å for Be versus 0.85 Å for B.

**H₂ adsorption on boron-doped C₆₀.**—Boron-doped fullerenes are known to exist experimentally. In a work published in 1991 [21], it was reported that up to six boron atoms could replace carbon to form C₅₄B₆ in the gas phase. Later experiments showed that C₅₀B and C₅₈B₂ could be synthesized even in macroscopic quantity and are stable above room temperature [22–26]. Recently, the existence has also been predicted [27,28]. These findings suggest that one might be able to directly test the nondissociative H₂ binding proposed here. For this purpose, we have calculated multi-H₂ sorption using C₅₄X₆, where X = B or Be [29], as our prototype, although C₅₀B and C₅₈B₂ should also serve the purpose. Figure 4(a) shows Eₐ for each additional H₂ as the number (n) of adsorbed H₂ increases for a specific adsorption pattern where the H₂ molecules occupy the farthest impurity sites possible in a sequence shown in Fig. 4(b). We see that Eₐ increases initially to peak at n = 2. After that, Eₐ decreases with n and reaches the minimum at n = 6. In the case of Be, the number of adsorbed H₂ has little effect on Eₐ. This is consistent with our analysis that Be states involved in the H₂ binding are more localized.

In summary, we have used first-principles calculations to study the general trends in H₂ adsorption on light-element doped fullerenes. For the first time, accurate QMC calculation is used to benchmark the LDA and GGA schemes for such applications. Our calculations reveal a nondissociative chemisorption mechanism for B and Be doped fullerenes. The coupling between a localized empty p_orbital on the dopant and the H₂ σ orbital is essential for the enhanced interaction. The calculated adsorption energies of several tenths of an eV per H₂ are well suited to reversible H storage under standard conditions.

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References

[19] See EPAPS Document No. E-PRLTAO-95-087602 for a comparison of QMC calculation for BH₂-H₂ with high-level QC calculation. This document can be reached via a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).
[29] One issue concerning H₂ adsorption on C₅₄B₆ is whether the H-loaded fullerene would still be stable. To address the issue, we have carried out LDA molecular dynamic (MD) calculations with 1 fs time step. We ramp-up the temperature by 1° in every 10 time steps from 0 to 1000 K. Our MD simulation showed desorption of the H₂ starting at 110 K, but no structural damage to the C₅₄B₆ has been observed. It suggests that C₅₄B₆ in the presence of H₂ is also stable.