Nondissociative Adsorption of H_2 Molecules in Light-Element-Doped Fullerenes

Yong-Hyun Kim,[1] Yufeng Zhao,[1] Andrew Williamson,[2] Michael J. Heben,[1] and S. B. Zhang[1]
[1]National Renewable Energy Laboratory, Golden, Colorado 80401, USA
[2]Lawrence Livermore National Laboratory, Livermore, California 94550, USA

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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 ~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, nontransition 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 σ 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 ultrasoft 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/a.u. 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_{far} and E_{bound} are the energies for the nonbonding 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.

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.

Pristine	Endo-Li	Endo-F	Sub-N	Sub-B	Sub-Be
0.07	0.07	0.04	0.06	0.39	0.65

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

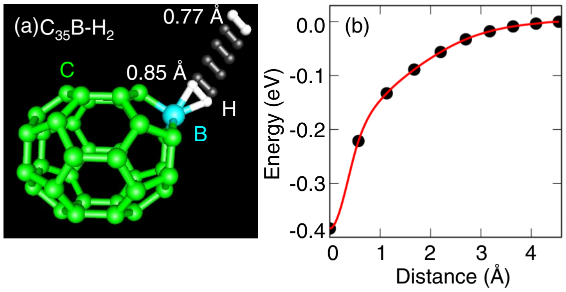

FIG. 1 (color online). The binding process of a H_2 to substitutional B in a $C_{35}B$. (a) The ball-and-stick model in which only four intermediate (darker) H_2 images are shown. (b) Total energy curve as a function of the geometric center of H_2 from its minimum-energy position.

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 σ state shows a single peak about 5 eV below the Fermi level, ϵ_F, whereas the B p_z-like state shows two peaks about 1 and 3 eV above ϵ_F. The presence of this doublet is the result of a strong hybridization of B p_z state with carbon π states. For bound $C_{35}B$-H_2 [Fig. 2(c)], the H_2 σ state spreads out with two main peaks about 10 eV below ϵ_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 σ 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 σ 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 σ 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, $\Delta\rho = \rho(C_{35}X\text{-}H_2)\text{-}\rho(C_{35}X)\text{-}\rho(H_2)$, 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, $\Delta\rho(x)$, 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

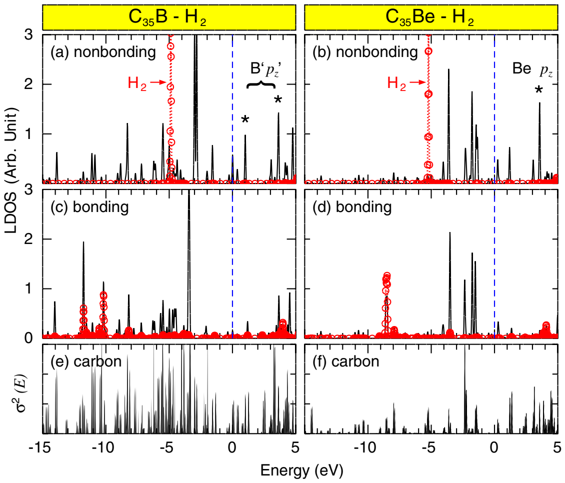

FIG. 2 (color online). (a)–(d) The calculated local density of states (LDOS) for B (Be) in $C_{35}B$ (Be)-H_2. The LDOS for B (Be) are solid lined, whereas the LDOS for H_2 are open circled. (e) and (f) The squared changes of the carbon states due to H_2 sorption, namely, $\sigma^2 = [\delta\text{LDOS(carbon)}]^2$ between the nonbonding and bonding states.

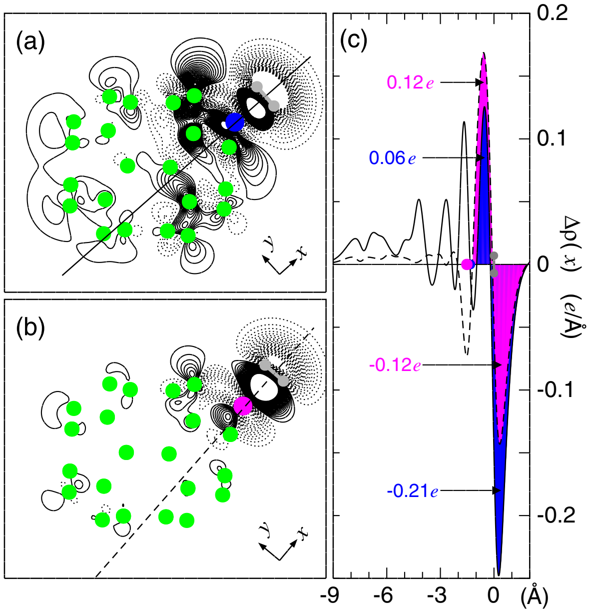

FIG. 3 (color online). (a) and (b) are the differential planar electron density, $\Delta\rho(x, y)$, for B and Be, respectively. Solid and dotted contours indicate electron accumulation and depletion, respectively. The contour interval is 0.003 and the cutoffs are ± 0.08 e/Å^2. (c) Linear $\Delta\rho(x)$ 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.

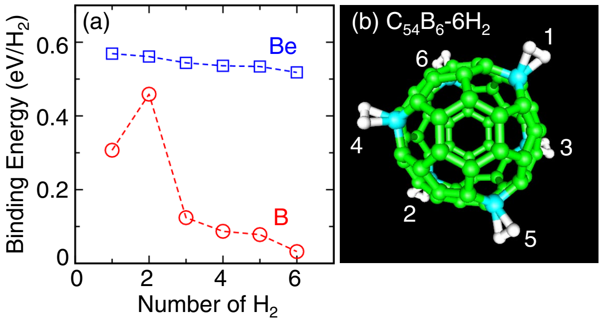

FIG. 4 (color online). (a) Binding energy for each added H_2 as a function of number of adsorbed H_2 molecules and (b) $C_{54}B_6$ with $6H_2$ molecules.

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 H_2 as evidenced by the shorter H_2 bond length of 0.8 Å for Be versus 0.85 Å for B.

H_2 *adsorption on boron-doped* C_{60}.—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 $C_{54}B_6$ in the gas phase. Later experiments showed that $C_{59}B$ and $C_{58}B_2$ could be synthesized even in macroscopic quantity and are stable above room temperature [22–26]. Recently, the existence of $C_{48}B_{12}$ and $C_{48}N_{12}$ has also been predicted [27,28]. These findings suggest that one might be able to directly test the nondissociative H_2 binding proposed here. For this purpose, we have calculated multi-H_2 sorption using $C_{54}X_6$, where $X = $ B or Be [29], as our prototype, although $C_{59}B$ and $C_{58}B_2$ should also serve the purpose. Figure 4(a) shows E_a for each additional H_2 as the number (n) of adsorbed H_2 increases for a specific adsorption pattern where the H_2 molecules occupy the farthest impurity sites possible in a sequence shown in Fig. 4(b). We see that E_a increases initially to peak at $n = 2$. After that, E_a decreases with n and reaches the minimum at $n = 6$. In the case of Be, the number of adsorbed H_2 has little effect on E_a. This is consistent with our analysis that Be states involved in the H_2 binding are more localized.

In summary, we have used first-principles calculations to study the general trends in H_2 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_z orbital on the dopant and the H_2 σ orbital is essential for the enhanced interaction. The calculated adsorption energies of several tenths of an eV per H_2 are well suited to reversible H storage under standard conditions.

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[29] One issue concerning H_2 adsorption on $C_{54}B_6$ 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 H_2 starting at 110 K, but no structural damage to the $C_{54}B_6$ has been observed. It suggests that $C_{54}B_6$, in the presence of H_2, is also stable.