NANO
LETTERS

2008
Vol. 8, No. 1
13−19

Alkali-Metal-Induced Enhancement of Hydrogen Adsorption in C_{60} Fullerene: An *ab Initio* Study

K. R. S. Chandrakumar* and Swapan K. Ghosh

*Theoretical Chemistry Section, Chemistry Group, Bhabha Atomic Research Centre,
Mumbai 400 085, India*

Received June 19, 2007; Revised Manuscript Received November 6, 2007

ABSTRACT

It is demonstrated that the doping of alkali metal atoms on fullerene, C_{60}, remarkably enhances the molecular hydrogen adsorption capacity of fullerenes, which is higher than that of conventionally known other fullerene complexes. This effect is observed to be more pronounced for sodium than lithium atom. The formation of stable complex forms of a sodium-doped fullerene molecule, Na_8C_{60}, and the corresponding hydrogenated species, $[Na(H_2)_6]_8C_{60}$, with 48 hydrogen molecules has been demonstrated to lead to a hydrogen adsorption density of ∼9.5 wt %. One of the main factors favoring the interactions involved is attributed to the pronounced charge transfer from the sodium atom to the C_{60} molecule and electrostatic interaction between the ion and the dihydrogen. The suitability of these complexes for developing fullerene-based hydrogen storage materials is discussed.

In recent years, hydrogen-based fuel systems have been considered to be a highly important topic of research due to the potential applications of hydrogen for future energy schemes as a more efficient fuel in comparison to the existing carbonaceous fossil fuels.[1,2] Despite many recent technological developments in the hydrogen-based fuel systems, it is still a major technical problem to have safe and efficient reversible hydrogen storage systems at ambient conditions.[2] Many methods have been reported for storing hydrogen gas, involving its compression, liquefaction, and adsorption in several metals and metal alloys.[1−2] Although the hydrogen storage capacity of metal hydrides is ∼6 wt % and these systems have been found to be useful, the operational conditions and the recovery process make them less ideal for most of the applications.[3] In recent years, several studies on hydrogen adsorption have been carried out on various materials, such as carbon nanostructures,[4] zeolites,[5] metal−organic frameworks,[6] and clathrate[7] compounds. Although none of these materials has yet been practically or commercially successful, extensive research has been initiated toward the development of promising novel materials—in particular, carbon-based nanomaterials—which are believed to be one of the promising hydrogen storage systems due to their unique structural, mechanical, and electrical properties.

Many experimental and theoretical investigations have been carried out for hydrogen adsorption on carbon nanostructures. Dillon and co-workers have experimentally first reported the adsorption ability of hydrogen by carbon nanotubes (CNT) to be ∼5−10 wt % at ambient conditions.[8] Subsequent experimental studies have refuted their claim and stated that the hydrogen storage capacity of CNT is very poor and is only 2−4 wt %, which is below the 6.5 wt % target of the U.S. Department of Energy.[9,10] There is also a vast inconsistency in most of the experimental reports that is due to the difference in the experimental reproducibility of the carbon nanotubes of suitable length and diameter. Some of the recent studies have also shown that the nanotubes do not satisfy all the criteria to meet the required target.[10−12]

Apart from the CNTs, there have been a few theoretical and experimental studies focusing on hydrogen adsorption on fullerene molecules, (especially C_{60}) and it has been observed that the interaction of hydrogen molecules is very weak and the number of molecules adsorbed is also rather less.[13−18] From these theoretical and experimental observations, it is apparent that neither of these carbon nanostructures is appropriate for storing hydrogen. Since the carbon nanostructures including fullerenes have high surface areas, porosities, and thermal stability along with unique mechanical properties, any improvement of their adsorption capacity by suitable modification would be of immense interest. Thus, the storage of hydrogen molecules by carbon nanostructures is still an important issue and deserves more attention. Here, we have focused our interest on the fullerene molecule as the prototype system for the study of hydrogen adsorption on carbon nanomaterials. One of the advantages of fullerene over nanotubes is the well-established means of producing

---

* Corresponding author. E-mail: krsc@barc.gov.in; skghosh@barc.gov.in.

10.1021/nl071456i CCC: $40.75

the C_{60} fullerene in its pure form in comparison to the nanotubes which is rather difficult to prepare in a pure form with definite dimensions.

Since both metals and carbon nanotubes are known to interact with hydrogen molecules, it may be worthwhile to make an attempt to investigate the adsorption capacity of the novel nanomaterials formed by doping the metal atoms onto the surface of the carbon nanostructures. A few theoretical and experimental studies have already been reported in the literature along these lines of thoughts, and an enhancement of hydrogen adsorption by fullerenes or carbon nanotubes doped with transition metal atoms has been observed.[13−18] Yildirim et al.[14] and Dillon and co-workers[15] have shown that transition metal atom-doped fullerene molecules can adsorb four H_2 molecules per metal atom site. In all cases, it has been noted that the initial adsorption of one H_2 molecule is always accompanied by its dissociation into atoms at the metal site and the additional H_2 molecules are adsorbed as molecules. The charge transfer from filled bonding orbitals of hydrogen to the empty d-orbitals of a transition metal atom/ion has been found to be responsible for the observed stronger binding of the hydrogen molecules, which can be explained by the Dewar−Chatt−Duncanson model.[14,15,19] There are, however, many disadvantages associated with the transition-metal-doped fullerenes, and the suitability of these systems as a basic unit in the hydrogen storage materials has thus been questioned.[4,10,12,20,21] One of the serious drawbacks is that the doped transition metal atoms tend to aggregate and form a cluster around the fullerene due to their high cohesive energy. The recent report also confirms the formation of bulk materials when hydrogen is removed, and hence, the individual metal atoms may not be further accessible for the adsorption of hydrogen molecules.[18,20] Another important problem may also be raised because of the fact that this transition-metal-doped C_{60} is a heavy-weight material, and the number of hydrogen molecules adsorbed at each site is also less.

In view of the above issues, there is a need for the development of new hydrogen storage materials that would satisfy most of the criteria. Accordingly, our strategy in this endeavor is to (i) judiciously select the metal atom as well as the carbon nanomaterials (fullerenes), (ii) study their storage capacity for hydrogen, and (iii) validate as well as satisfy the essential criteria as better storage materials than the existing ones. In the present work, we show that doping of alkali metal atoms into the fullerenes causes a remarkable enhancement in the hydrogen adsorption capacity, which is found to be better than the conventionally known fullerene complexes with transition metal atoms. We first investigate the hydrogen adsorption on pristine C_{60} as well as the alkali metal ions and then study the combined effect of both the fullerene and alkali metal atoms on the hydrogen adsorption. In what follows, we now present the details of our calculated results on the hydrogen adsorption by alkali-metal (Li, Na, and K)-doped fullerenes obtained from an accurate all-electron and Gaussian basis set-based quantum chemical calculations.

Methodological Details. All the geometry optimization (without any symmetry constraint) and the energy calculations have been performed at the level of density functional theory (DFT) with Becke's three-parameter exchange functional[22] and Lee−Yang−Parr correlation functional[23] (B3LYP) using the electronic structure program GAMESS.[24] The standard split valence basis set 6-31G(d,p) along with the diffuse functions has been employed for all the energy calculations of the cation and hydrogen molecular systems. The binding energy of the complexes is calculated from the energy difference between the reactants (metal atom and the relevant number of hydrogen molecules) and the complex product species. Although metal atoms can occupy different sites of a C_{60} molecule, we have considered the cations to be situated at the center of the six-membered rings only. Since the effect of hydrogen adsorption on the geometry of C_{60} is considerably less, we have frozen the coordinates of the C_{60} molecule while studying the hydrogen adsorption process. In the present calculations, a detailed study has also been made for the system containing C_{60} and different numbers of sodium atoms, fixed at the different six-membered rings, with the number of sodium atoms ranging from two to eight . The optimized geometrical parameters of the cation dihydrogen in C_{60} system has been used for studying the interaction of hydrogen molecules with many sodium atoms ($C_{60}Na_8(H_2)_{48}$) located at different positions. All these geometry optimizations and the energy calculations involving the C_{60} molecule and the C_{60} complex with sodium atoms have been performed using the B3LYP/3-21G(d,p) method. However, the electronic property calculations, namely, the polarizability and dipole moment of the alkali-metal-doped fullerenes, were carried out by the B3LYP method using the extensive split valence basis set, 6-31G(d). The initial geometries and all the figures have been generated using the graphical software; namely, Molden[25] and Gabedit.[26] The charge on each atom has been calculated by Mulliken and molecular electostatic potential (MESP) methods. The basis set superposition error (BSSE) has been corrected using the full counterpoise method for all the ion-hydrogen complexes, and the correction has been found to be very small in all cases (of the order of 0.5 kcal/mol).

Adsorption of Hydrogen Molecules on C_{60} and Alkali Metal Cations. Let us first discuss the results on interaction of hydrogen molecules with the isolated C_{60} molecule and alkali metal cations. The optimized structure for all the complexes is shown in Figure 1. It is important to note that molecular hydrogen is found to interact with the alkali metal ion as a dihydrogen molecule, and the ion interacts with both ends of each hydrogen molecule, forming a T-shaped complex and thus retaining their molecular identity. This is an important difference from the transition metal ion and hydrogen interaction. In the case of transition metal atoms/ions, the first hydrogen molecule binds as hydrides (H_2 molecule is dissociated into atoms) with a binding energy in the range of ~ -30 kcal/mol,[14−18] whereas the interaction between the sodium ion and H_2 molecule is rather weak, and the binding energy is -3.8 kcal/mol.

In the case of C_{60}, only one end of the H_2 molecule interacts with the carbon framework with a bond length of 3.22 Å, and the interaction is observed to be extremely weak

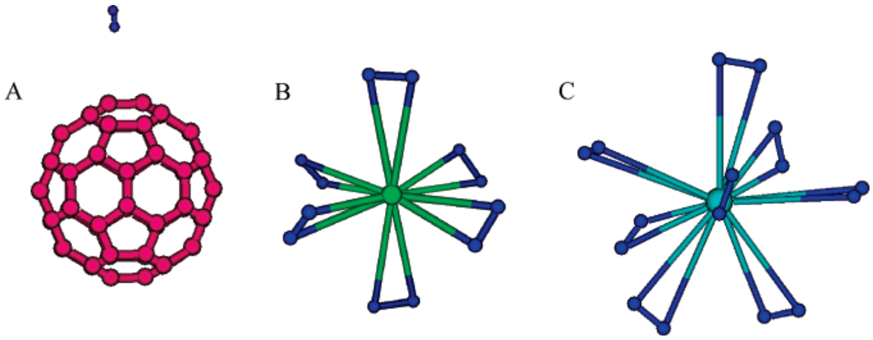

Figure 1. Interaction of hydrogen molecules with fullerene and alkali metal ions: (A) neutral C_{60}, (B) Li^+, (C) Na^+or K^+ ion.

(binding energy <-0.05 kcal/mol). When the second hydrogen molecule is brought closer to interact with C_{60}, we find that there is no binding interaction for the second H_2 molecule at the same six-membered ring where the first H_2 was adsorbed. This is in agreement with one of the experimental results of Ye et al.[13] who have shown that the weak adsorption of H_2 by C_{60} is only 0.7 wt % at 77 K. The Li^+ or Na^+ ion, however, is found to readily interact with the second H_2 molecule with a binding energy of -6.62 and -3.71 kcal/mol, respectively. We continued to add more hydrogen molecules to the alkali metal cation to find out the number of H_2 molecules that can actually be bound with the ion. Our results reveal that the sodium and potassium ion can bind with a maximum of eight H_2 molecules with the binding energy of -16.51 and -9.51 kcal/mol, respectively. In the case of the lithium ion, only six H_2 molecules are adsorbed, and the corresponding total binding energy is -25.73 kcal/mol. Here, the hydrogen molecular axis is always arranged in a manner almost perpendicular to the neighboring hydrogen molecule, thus accommodating a greater number of H_2 molecules by reducing intermolecular repulsion. This has been discussed in the literature, and one of the recent theoretical studies by Gagliardi and Pyykko[27] has shown that the bare transition metals in the neutral and ionic forms (Cr, Mn^+, W, Mo, V^-, Ti^{2-}) can bind with as many as six hydrogen molecules, leading to the formation of MH_{12}.

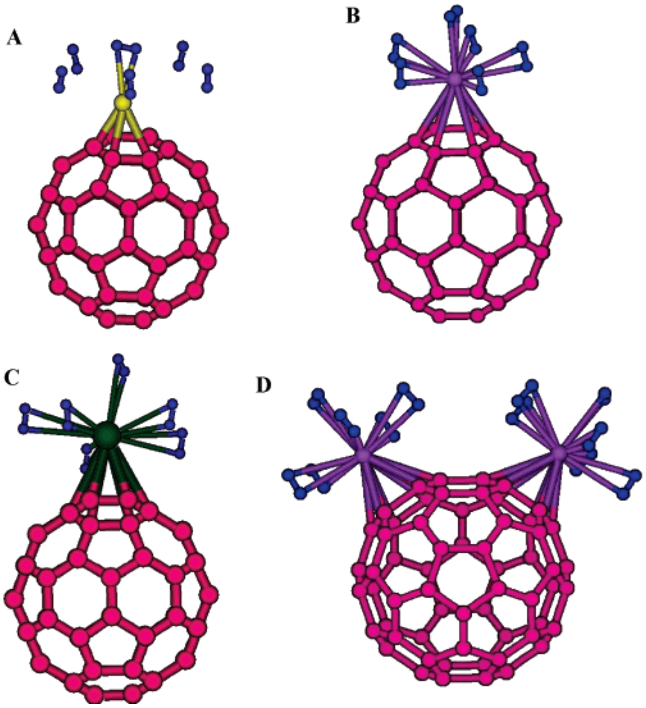

Figure 2. Adsorption of hydrogen molecules on alkali-metal-doped fullerenes. (A) $C_{60}Li(H_2)_2$, (B) $C_{60}Na(H_2)_6$, (C) $C_{60}K(H_2)_6$, (D) $C_{60}Na_2(H_2)_{12}$.

Adsorption of Hydrogen Molecules on Alkali-Metal-Doped C_{60}. The above results demonstrate that the interaction between C_{60} and the hydrogen molecule is very weak, and more than one H_2 molecule is not adsorbed at the same site. Now let us discuss the influence of doping the alkali metals into the C_{60} molecule on hydrogen adsorption. Since the exohedral doping of alkali metals into the C_{60} surface has already been achieved by many experimental methods,[28] the present investigation can give valuable insights into several aspects of the hydrogen adsorption on the alkali-metal-doped fullerene cases. It may also be noted that the bulk solid formed by alkali-metal-doped fullerenes has already been an important material for high-temperature superconductor research. First, we have kept each alkali metal atom individually above the center of the six-membered ring, and then the hydrogen molecules are allowed to interact with the alkali metal atom, as shown in Figure 2. A similar procedure has been followed for a higher number of sodium atoms doped in the C_{60} framework interacting with hydrogen molecules. For illustrative purposes, we have presented the results for the hydrogen adsorption with the two- and eight-sodium-atom-doped fullerene systems. Since the electron affinity of the C_{60} molecule (2.65 eV) is much higher[29] than the alkali metal atoms, partial charge transfer is favored from the alkali metal atoms to the C_{60}, resulting in the formation of fulleride anions due to the lowest triply degenerate unoccupied molecular orbitals of C_{60}. In addition, the alkali metal atoms have very high polarizabilities, which can cause a strong dispersion interaction when these elements are present on the C_{60} surface. These partially ionized alkali metal atoms can polarize the surrounding hydrogen molecules and form a weak bond with the hydrogen molecules. It is also observed that the interaction between the fullerene molecule and the alkali metal atom is quite strong: the binding energies of the lithium and sodium atoms are -35.01 and -32.61 kcal/mol, respectively. Similarly, the binding energy of K in KC_{60} is found to be (-32.75 kcal/mol), a little less than the lithium case, whereas the lithium carbon

Table 1. Geometrical Parameters (Å) and Binding Energy (kcal/mol) Values for the Fullerene−Alkali Metal Atom System, XC_{60} (Where X = Li, Na, and K), Calculated by the DFT-Based B3LYP Method

system	C−X bond length shortest[a]	C−X bond length longest[b]	distance between the metal atoms	metal−C_{60} binding energy[c]	charge on the metal atoms[d]	dipole moment[e]	polarizability[f]
LiC_{60}	2.268	2.329		−35.02	0.42 (0.74)	8.138	511.450
NaC_{60}	2.478	2.530		−32.61	0.55 (0.89)	10.687	513.271
KC_{60}	2.971	3.033		−32.75	0.62 (0.68)	15.345	509.184
Na_2C_{60}	2.430	2.552	6.247	−65.61	0.50 (0.86)	15.917	547.959
Na_8C_{60}	2.460	2.589	6.352	−220.93	0.35 (0.71)	2.367	3890.735

[a,b] Shortest and longest C−X bond length in one of the 6m-rings of C_{60}, respectively. [c] Binding energy = $E(C_{60}X_n) - [E(C_{60}) + nE(X)]$. [d] MESP-derived charges for the X atom in C_{60}. The value in parentheses is obtained by the Mulliken method. [e] Dipole moment in Debye units. [f] Polarizability in atomic units.

Table 2. Geometrical Parameters (Å) and Binding Energy (kcal/mol) Values for the Hydrogen Molecules Adsorbed on Alkali-Metal-Doped Fullerene Systems (XC_{60}, Where X = Li, Na and K) Calculated by DFT-Based B3LYP Method

system	bond length X−H shortest[a]	bond length X−H longest[b]	distance between the metal cations	bond length of H−H in H_2 molecule	binding energy[c] of hydrogen	charge on the metal atoms[d]
$C_{60}Li(H_2)_2$	2.200	2.680		0.752	−5.33 (−2.66)	0.14 (0.53)
$C_{60}Na(H_2)_6$	2.581	2.753		0.751	−10.33 (−1.72)	0.11 (0.59)
$C_{60}K(H_2)_6$	3.080	3.269		0.752	−7.24 (−1.21)	0.62 (0.68)
$C_{60}Na_2(H_2)_{12}$	2.562	2.782	6.612	0.752	−19.25 (1.61)	0.26 (0.57)
$C_{60}Na_8(H_2)_{48}$	2.591	2.750	6.630	0.751	−97.85 (2.04)	0.11 (0.59)

[a,b] Shortest and longest X−H bond length as observed in X-doped C_{60}, respectively. [c] Binding energy = $E(C_{60}X_n(H_2)_n) - [E(C_{60}X_n) + nE(H_2)]$. The value in parentheses is the binding energy per hydrogen molecule. [d] MESP-derived charges for the X atom in C_{60}. The value in parentheses is obtained by the Mulliken method.

distance is less than that of sodium or potassium atoms. These binding energies are obviously much higher than the formation energy of the alkali metal cluster, and hence, one can unquestionably argue that the alkali metal atoms will not form their cluster around C_{60}. This is an important issue for the study of hydrogen adsorption on the metal-doped fullerenes or any carbon nanomaterials. It is, however, interesting to note that in contrast to the alkali metal cations, the transition metal cations doped in fullerenes instantaneously rearranged into an ordered metal cluster due to their high cohesive energy. Jena et al. have recently theoretically studied the stability of titanium-doped C_{60} and shown that titanium prefers to stay as a cluster rather than bind with the C_{60} and concluded that the titanium-doped fullerene is not very effective for hydrogen storage purposes.[20]

As reported in Table 1, the shortest and longest distances between the carbon atoms of the six-membered ring and sodium atom is observed to be of the order of 2.48−2.53 Å in both NaC_{60} and Na_2C_{60} systems. The effect of the alkali metal atom on the structure of C_{60} is seen only on the carbon atoms that are nearest to the alkali metal atom positioned in the C_{60} framework, and the effect is also found to be very marginal. However, the electron population analysis reveals that there is considerable electron transfer from the sodium atom to the C_{60} molecule, which induces a strong permanent electric dipole. In the case of NaC_{60}, the charge on the sodium atom derived from the Mulliken and MESP methods is 0.89 and 0.55, respectively, and for Na_2C_{60}, the corresponding derived charges on each sodium atom are 0.86 and 0.50.

It is very interesting to note that when more than one sodium atom is bonded to the fullerene molecule, the average binding energy of the cations remains almost constant. In addition, the residual charge on each sodium atom also remains unchanged, and the variation is very marginal; that is, less than 5%. This surprising result clearly indicates that each hexagonal ring of the fullerene molecule behaves like disconnected benzenes, and the reactivity is highly localized at the individual ring, as is evident from the values of the binding energy of the cations. Thus, the binding capability of each sodium atom does not depend on the addition of another sodium atom at a different binding site. This can be considered to be one of the unique properties of the C_{60} fullerene molecule, which is in contrast to the general expectation that the affinity of any system toward the electron-donating or -accepting atoms/molecules should decrease linearly (or even exponentially) when a higher number of such groups is added into the system.

We now turn to the discussion on the adsorption of hydrogen molecules with the alkali-metal-doped fullerene framework. The geometrical parameters as well as the binding energies are listed in Table 2, and the optimized geometries are shown in Figures 2 and 3. On the basis of these results, two pertinent comments can be made: First, it can vividly be seen that there is a strong influence of the alkali metal atom on the hydrogen adsorption, particularly in the case of NaC_{60}, which can adsorb six hydrogen molecules at the sodium ion site with a binding energy of −10.33 kcal/mol. This trend is consistent with the results obtained for the bare sodium ion case. The loss of two hydrogen molecules happens at the cost of the interaction of sodium atom with C_{60} framework, which causes the obstruction of the adsorption of two additional hydrogen molecules. The charge on the sodium atom in NaC_{60} is also less than that of the bare cation (+1). Another very

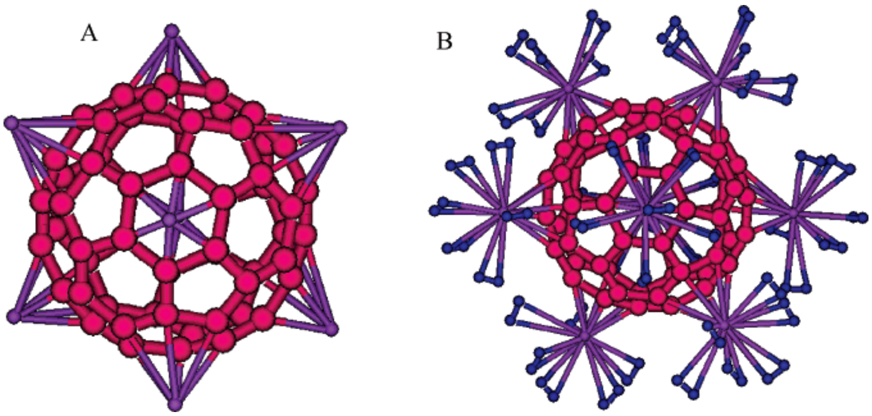

Figure 3. Adsorption of (A) sodium atoms with C_{60} fullerene, Na_8C_{60}, and (B) molecular hydrogen in sodium-doped fullerenes, $C_{60}Na_8(H_2)_{48}$.

interesting and striking feature is that the number of adsorbed hydrogen molecules is only two in the case of the lithium-doped fullerene. In addition, another four hydrogen molecules are stabilized at the carbon atoms of the hexagonal and pentagonal rings of the C_{60} molecule, with a bond distance of more than 3.5 Å, and each of the four H_2 molecules is situated at 4.3 Å from the lithium cation, as shown in Figure 2A. In the case of potassium, although it also interacts with six H_2 molecules, the binding energy is much less (~7 kcal/mol), and the cation−hydrogen bond distance is quite longer than that in the case of other alkali metal atoms.

To analyze the physics of adsorption of hydrogen by these alkali metal atoms in C_{60}, we have calculated the polarizability and dipole moment of all XC_{60}, where, X = Li, Na, and K. It can be seen from Table 1 that there is a significant difference in the values of the dipole moment of alkali-metal-doped fullerenes, and in particular, the dipole moment of LiC_{60} is almost half of KC_{60}. In the case of Na_8C_{60}, since the sodium is placed symmetrically around C_{60}, the net dipole moment is much less due to the symmetric cancellation of the dipoles in each direction. In contrast, the polarizability value of these alkali-metal-doped fullerenes does not vary significantly. However, the polarizability values increase considerably as we increase the number of sodium atoms around the fullerene molecule. The enhanced dipole moment and polarizability of these alkali-metal-doped fullerenes can cause a strong interaction with the surrounding hydrogen molecules. Although these properties explain in part the reactivity of these doped fullerenes toward hydrogen molecules, the geometrical parameters may also play a significant role, which is, however, not directly obvious from the results. Since lithium-doped fullerene adsorbs fewer H_2 molecules and the potassium-doped case is computationally expensive, the subsequent adsorption study was performed only for sodium-doped fullerenes.

In the case of $C_{60}Na_2$, it is interesting to note that the number of hydrogen molecules maintained at each cationic site is six, as observed in the case of NaC_{60}, with a total binding energy of −19.25 kcal/mol, which amounts to approximately −1.60 kcal/mol per hydrogen molecule. Note that all the interaction processes are exothermic in nature. The distance between two Na atoms is increased from 6.25 (as observed in $C_{60}Na_2$) to 6.61 Å in the $C_{60}Na_2(H_2)_{12}$ system so as to allow the hydrogen molecules to accommodate themselves around the cations with reduced repulsive forces. When the bond distance between the cation and hydrogen molecules is compared for the systems, $C_{60}Na_2(H_2)_{12}$ and $Na^+{-}H_2$, the bond length is marginally shortened (of the order of 0.2−0.05 Å) in the fullerene system. A comparison of the binding energy of the hydrogen molecules with sodium cations reveals that the hydrogen adsorption energy in the presence of the C_{60} framework is less than that of the isolated cation which is mostly due to the strong electrostatic field generated by the bare cation. The weakening of the binding interaction with the hydrogen molecules by the surrounding carbon framework atoms in NaC_{60} as compared to bare Na^+ cation is attributed to the screening of the cationic charge of Na^{+1} from +1 to +0.8 au by the carbon framework. Nevertheless, it is gratifying to note that the reduced binding energy is actually ideally matched with the required adsorption energy for the reversible hydrogen storage purposes.

If the sodium atoms are doped at all the available 20 hexagonal sites, it can be expected that 120 H_2 molecules can be adsorbed by the $Na_{20}C_{60}$ system. However, it is important to note that the adsorption of the maximum number of hydrogen molecules at one cationic site is only possible when the cationic sites are separated by more than 5 Å, at which the system can experience minimum electrostatic repulsion and steric hindrance. Accordingly, we have identified only eight such cationic adsorption sites in the fullerene molecule that are separated by more than 5.8 Å from the next nearest cations, and it can adsorb maximum number of six hydrogen molecules per cation with minimum electrostatic repulsion as well as steric interactions. The optimized structure of fullerene with eight sodium atoms at different six-membered rings and its interaction with H_2 molecules is shown in Figure 3. The calculated binding energy shows that there is a strong binding between the metal atom and the fullerene molecule, with the binding energy per sodium atom being in the range of −27 kcal/mol, which is a few kilocalories per mole less than that in NaC_{60}. The other bonding features in Na_8C_{60} are observed to be very similar to the case of NaC_{60} and Na_2C_{60}, and the difference in the binding energy of the systems, NaC_{60} and Na_8C_{60} is only

10% per sodium atom, which clearly signifies the strong affinity of each hexagonal ring of the C_{60} molecule toward the binding of the metal atoms.

The fullerene molecule doped with eight sodium atoms forms a stable nanostructure with 48 hydrogen molecules (Figure 3), corresponding to 9.5 wt % hydrogen adsorption. The calculated total binding energy of the hydrogen molecules is in the range of −98 kcal/mol, and the binding energy per hydrogen molecule remains approximately constant (1.90−2.04 kcal/mol), even in the highly loaded sodium atom cases. The above-mentioned 9.5 wt % of hydrogen is only the minimum number of hydrogens that are adsorbed by the eight sodium atoms doped on the fullerene molecule. It may be noted that a good hydrogen storage material should be able to contain a gravimetric density of about 6 wt % of hydrogen and to adsorb/desorb hydrogen close to ambient conditions (temperature range of 20−50 °C at moderate pressures).[1,2] Although the adsorption capacity of alkali-metal-doped fullerenes (9.5 wt %) is comparable to any other solid-state inorganic materials, the fullerene-based materials have many advantages over other materials. It is possible to achieve a higher weight percent of adsorbed H_2 molecules if we can embed a higher number of alkali metal atoms at all available sites (including five-membered rings) in the fullerene systems. In this context, it may be worthwhile to mention the experimental work carried out by Palpant et al.,[28a] whose results confirm that 12 sodium atoms can be doped around the fullerene molecule, and the formation of cluster aggregation begins at about $N \sim 13$. In addition, they have also observed that other transition metal atoms—in particular, gold atoms—tend to form a cluster on top of the fullerene rather than the direct bonding with the six-/five-membered ring of the fullerene. This experimental report directly suggests the possibility of the formation of sodium-doped fullerenes, Na_nC_{60}, ($n = 1−12$), which is in agreement with the present theoretical results on the formation of Na_8C_{60}.

We now turn to the general discussion on the adsorption mechanism. In the case of the alkali-metal-doped fullerene, the adsorption of hydrogen molecules is essentially driven by the electrostatic interaction between the induced dipole and the quadrupolar interaction of the molecules with the field generated by the cations formed due to charge transfer to the fullerene cage. In contrast, the interaction between the hydrogen molecules and the transition metal ions is mainly driven by the Dewar−Chatt−Duncanson model, and the adsorption usually is first accompanied by chemisorption via atomic dissociation, with subsequent adsorption governed by weak molecular interaction.[14,15,19] Hence, these strongly interacting transition metals ions are more suitable for the activation of the H−H bond rather than for hydrogen storage purposes. In general, to have an efficient storage media along with fast kinetics at ambient conditions, the materials are expected to have a weak nondissociative (molecular) hydrogen adsorption. In addition, Ciraci and co-workers[18] and Jena et al.[20] have shown that Ti prefers to stay as a Ti cluster rather than binding with C_{60}. Due to the heavy mass of these transition metals, the effective gravimetric density will be significantly reduced. In the present case, the interaction of hydrogen is much weaker than the transition metal ions (in the range of a few kilocalories per mole), which suggests that the materials containing the alkali metal ions might be more suitable as candidates for the hydrogen storage purposes than those containing other metal cations. Hence, reversible adsorption may easily be accomplished without destroying the host material; that is, the metal-doped fullerene molecule. One of the advantages of the alkali-metal-doped fullerenes is that being lightweight elements, they can help to achieve a larger gravimetric density (wt %) of hydrogen. It is also very pertinent to note that the number of molecular hydrogens bound to the s-block metal cations in fullerene systems ($n_H = 12$) is more than that of the transition metal cations ($n_H = 6−8$). Finally, on comparing the earlier experimental and theoretical reports with the present study, it can be mentioned that the sodium-metal-doped fullerenes have many advantages and satisfy some of the important requirements for the hydrogen storage materials; namely, (a) weak interaction between the ion and H_2 molecules, (b) remarkably enhanced molecular H_2 adsorption, and (c) light-weight material with higher capacity for the adsorption of H_2 molecules.

Conclusions. In the present work, it has been demonstrated that doping of alkali metal atoms into fullerenes causes a remarkable enhancement in the hydrogen adsorption capacity, which is found to be better than the conventionally known fullerene complexes with transition metal atoms. The effect appears to be more pronounced for the case of the sodium atom as compared to the lithium atom. At high metal coverage on the fullerene, it has been shown that the total number of adsorbed hydrogen molecules over the 8 sodium atoms is 48, with a gravimetric density of ~9.5 wt %. The simple concept of ion−molecule electrostatic interaction explains the observed remarkable hydrogen adsorption capacity of metal-doped fullerenes. Since the important requirements for the hydrogen storage materials—namely, weak interaction between the ion and molecular hydrogen and larger number of hydrogen molecules surrounding the ions—are met with the s-block elements, we hope that the outcome of this particular work may stimulate further research in this area, particularly in designing new materials by exploiting the electrostatics mediated ion−molecular interactions. The alkali-metal-doped fullerene molecule, thus, forms a new class of important nanostructured materials with potential applications for the storage of hydrogen.

Acknowledgment. We thank Dr. T. Mukherjee for his kind support and the computer center for providing the high performance parallel computing facility.

References

(1) (a) For a review, see the special issue, “Towards a Hydrogen Economy”, Coontz, R.; Hanson, B. *Science* **2004**, *305*, 957.
(2) (a) Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353. (b) Züttel, A. *Mater. Today* **2003**, *6*, 24.
(3) Seayad, A. M.; Antonelli, D. M. *Adv. Mater.* **2004**, *16*, 765.
(4) (a) Lochan, R. C.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1357. (b) Dillon, A. C.; Heben, M. *J. Appl. Phys. A* **2001**, *72*, 133.
(5) Arean, C. O.; Nachtigallova, D.; Nachtigall, P.; Garrone, E.; Delgado, M. R. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1421.

(6) Rowsel, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670.

(7) Lee, H.; Lee, J.-W.; Kim, D. Y.; Park, J.; Seo, Y.-T.; Zeng, H.; Moudrakovski, I. L.; Ratcliffe, C. I.; Ripmeester, J. A. *Nature* **2005**, *434*, 743.

(8) Dillon, A. C.; Jones, K. M.; Bekkedahl, T. A.; Kiang, C. H.; Bethyne, D. S.; Heben, M. J. *Nature* **1997**, *386*, 377.

(9) (a) Chen, P.; Wu, X.; Lin, J.; Tan, K. L. *Science* **1999**, *285*, 91. (b) Liu, C.; Fan, Y. Y.; Liu, M.; Cong, H. T.; Cheng, H. M.; Dresselhaus, M. S. *Science* **1999**, *286*, 1127.

(10) (a) Kowalczyk, P.; Holyst, R.; Terrones, M.; Terrones, H. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1786. (b) Meregalli, V.; Parrinello, M. *Appl. Phys. A* **2001**, *72*, 143.

(11) Alonso, F. F.; Bermejo, F. J.; Cabrillo, C.; Loutfy, R. O.; Leon, V.; Saboungi, M. L. *Phys. Rev. Lett.* **2007**, *98*, 215503.

(12) (a) Wang, Q. Y.; Johnson, J. K. *J. Phys. Chem. B* **1999**, *103*, 277. (b) Wang, Q. Y.; Johnson, J. K. *J. Chem. Phys.* **1999**, *110*, 577. (c) Ding, R. G.; Lu, G. Q.; Yan, Z. F.; Wolson, M. A. *J. NanoSci. Nanotechnol.* **2001**, *1*, 7.

(13) Ye, Y.; Ahn, C. C.; Fultz, B.; Vajo, J. J.; Zinck, J. J. *App. Phys. Lett.* **2000**, *77*, 2171.

(14) Yildirim, T.; Íñiguez, J.; Ciraci, S. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *72*, 153403.

(15) Zhao, Y.; Kim, Y.-H.; Dillon, A. C.; Heben, J. M.; Zhang, S. B. *Phys. Rev. Lett.* **2005**, *94*, 155504.

(16) Shin, W. H.; Yang, S. H.; Goddard, W. H., III; Kang, J. K. *Appl. Phys. Lett.* **2006**, *88*, 053111.

(17) (a) Hu, N.; Sun, X.; Hsu, A. *J. Chem. Phys.* **2005**, *123*, 044708. (b) Cheng, H.; Cooper, A. C.; Pez, G. P.; Kostov, M. K.; Piotrowski, P.; Stuart, S. J. *J. Phys. Chem. B* **2005**, *109*, 3780.

(18) Durgun, E.; Ciraci, S.; Zhou, W.; Yildirim, T. *Phys. Rev. Lett.* **2006**, *97*, 226101.

(19) (a) Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes, Structure, Theory and Reactivity*; Kluwer: NewYork, 1999. (b) Kubas, G. J. *J. Organo-metallic Chem.* **2001**, *635*, 37.

(20) (a) Sun, Q.; Jena, P.; Wang, Q.; Marquez, M. *J. Am. Chem. Soc.* **2006**, *128*, 9741. (b) Sun, Q.; Wang, Q.; Jena, P.; Kawazoe, Y. *J. Am. Chem. Soc*. **2005**, *127*, 14582.

(21) Froudakis, G. E. *J. Phys. Condens. Matter* **2002**, *14*, R452−465.

(22) (a) Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 2547. (b) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098.

(23) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785.

(24) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunga, N.; Nguyen, K. A.; Su, S. J.; Dupuis, M., M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(25) Schaftenaar, G. Molden-4.0; 2003; http://www.cmbi.kun.nl/∼schaft/molden/molden.html (accessed January 2006).

(26) Allouche, A. R. Gabedit-2.0.6; 2006; http://lasim.univ-lyonl.fr/perso/allouche/gabedit/download.php (accessed January 2006).

(27) Gagliardi, L.; Pyykko, P. *K. J. Am. Chem. Soc.* **2004**, *126*, 15014.

(28) (a) Palpant, B.; Sanekata, N. M.; Miyajima, K.; Nagao, S.; Judai, K.; Rayner, D. M.; Simard, B.; Hackett, P. A.; Nakajima, A.; Kaya, K. *J. Chem. Phys.* **2001**, *114*, 8459. (b) Dugourd, Ph.; Antoine, R.; Rayane, D.; Compagnon, I.; Broyer, M. *J. Chem. Phys.* **2001**, *114*, 1970. (c) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843.

(29) (a) Cioslowski, J. *Electronic structure calculations on fullerenes and their derivatives*; Oxford University Press: New York, 1995. (b) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: New York, 1996.

NL071456I