

Doping a C₆₀ molecule with potassium atoms: A theoretical study

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We study the doping of a free C₆₀ molecule by potassium atoms. *Ab initio* calculations based on density functional theory indicate that K atoms are fairly strongly bound to the carbon cage. The electrical conduction of the structure is also enhanced after each successive doping of K. We also observe a downward shift of energy levels toward the Fermi energy with the increase of doping. These properties are very consistent with experimental results. The K-doped structure is promising for applications in molecular electronics. © 2005 American Institute of Physics.

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The fullerene C₆₀ is a versatile molecule capable of forming a huge variety of structures that have interesting physical properties as well as potential applications. C₆₀ molecules can form dimers,¹ and can be filled inside carbon nanotubes,^{2,3} which are considered promising building blocks for the emerging nanoelectronics. Radioactive atoms have been inserted inside C₆₀ cages,^{4,5} attracting attention to possible biomedical applications. A single C₆₀ molecule has been placed between gold electrodes and functioned as a transistor,⁶ which is an important step in the development of molecular electronics by utilizing electronic components with the ultimate size.

Doping is a time-honored technique in the semiconductor industry. By introducing impurity atoms into pristine semiconductors in a controlled manner many physical and chemical properties can be manipulated to a desired and sometimes unexpected degree. It is only natural to extend a similar scheme to prospective fullerene-based molecular electronics. Bulk and thin film C₆₀ have long been doped with alkali and alkaline-earth metals, resulting in interesting properties. Potassium and rubidium-doped fullerenes, for example, are known to have relatively high critical temperatures for superconductivity at 18 and 28 K, respectively.⁷⁻⁹ There are also doped fullerenes that display ferromagnetism, antiferromagnetism, and giant magnetoresistance.¹⁰⁻¹²

At the molecular level, a recent experiment by Yamachika *et al.* has shown that a single C₆₀ molecule can be doped with individual potassium atoms.¹³ In the experiment K atoms adsorbed on the Ag (001) surface can be attached to an isolated C₆₀ molecule by moving the molecule over them using a scanning tunneling microscope tip. A total of four K atoms are adsorbed on the C₆₀ molecule one by one in this manner. This procedure demonstrates that it is possible to achieve controlled doping at the atomic level, opening up a wide range of applications for molecular electronic devices. In this Communication we present a theoretical study of a free K-doped C₆₀ molecule. We calculate the electronic structure of the molecule each time a new K atom is attached and see how the extra dopant affects the overall properties of the molecule.

The calculation is based on *ab initio* density functional theory with local density approximation. Plane-wave ultrasoft pseudopotentials as implemented in the VASP code¹⁴⁻¹⁷ are employed for the task by using a cutoff energy of 211 eV. Convergence for self-consistency is set at 0.01%. The C₆₀ molecule and its attached K atoms are placed inside a large supercell to prevent the interaction between adjacent molecules. The size of the supercell is enlarged to accommodate an increased number of adsorbed atoms. All structures are relaxed to find the lowest total energy and thus the optimal configuration. Total density of states (DOS) and local density of states (LDOS) are both calculated with a smearing of 0.025 eV. In the latter part of the calculation, two radii, 1.0 and 2.275 Å, are assigned to the C and K spheres, respectively.

We first produce the electronic structure of a free pristine C₆₀ molecule and show in Fig. 1 the calculated energy levels and degeneracy by vertical lines. The highest occupied molecular orbital (HOMO) is found to be 0.65 eV below the Fermi level and has a fivefold degeneracy. The lowest unoccupied molecular orbital (LUMO) is located at 0.96 eV above the Fermi level with a threefold degeneracy. The LUMO+1, also with threefold degeneracy, is 1.08 eV above

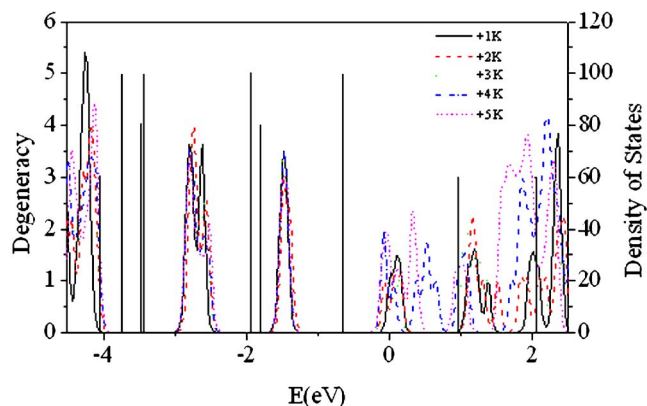


FIG. 1. (Color online) Energy levels for a free C₆₀ molecule are labeled with vertical lines, which also indicate the degeneracy. DOS for the C₆₀ molecule attached with K atoms are shown with curves, each representing the molecule with the number of attached K atoms as indicated in the legend.

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TABLE I. The average binding energy for each adsorbed K atom becomes smaller as the number of K is increased. The five corresponding configurations are those shown from Figs. 2(a)–2(e).

| Number of attached K | 1 | 2 | 3 | 4 | 5 |
|----------------------|------|------|------|------|------|
| Binding energy (eV) | 1.81 | 1.73 | 1.59 | 1.48 | 1.37 |

the LUMO. The gap between the HOMO and LUMO is 1.61 eV. These results are very consistent with experimental and theoretical values.^{18,19}

When calculating the adsorption of potassium atoms, there are usually a few configurations that satisfy the same convergent criterion. These all correspond to the local minima of the binding energy. The average binding energy of an attached K atom, E_b , is defined as $[E(C_{60}+NK) - E(C_{60}) - E(NK)]/N$, where $E(C_{60}+NK)$, $E(C_{60})$, and $E(NK)$ represent, respectively, the total energy of the C_{60} with N attached K atoms, the pristine C_{60} , and the N potassium atoms in the same configuration as those attached on C_{60} . For a fixed number of K dopants, different configurations are tried for the calculation of binding energy. Normally binding energy varies slightly with different adsorption sites. However there is an indisputable trend indicating the decrease of the binding energy with respect to the number of K dopants. Listed in Table I are binding energies taken out of a few such calculations, ranging from 1.81 eV for the first adsorbed K to 1.37 eV for the fifth. The fairly large binding energies (especially for the first and second attached K) indicate that the combined structure is quite stable. The gradual reduction of binding energy with respect to the increase of K dopants is related to the Coulomb repulsion between the electron donated by the newly attached K and those already on the carbon cage. This reduction of binding energy is similar to that in the calculation of solid K_xC_{60} ($x=1-3$) by Saito and Oshiyama,²⁰ in which a reduction of the cohesive energy is reported with respect to the increase of K dopants.

Our calculation also concludes that doping with a sixth K will wreck the carbon cage irreversibly. This is in stark contrast with the crystalline K_6C_{60} ,²¹ which maintains its structural stability under strong interaction between neighboring C_{60} molecules. Figure 2(f) offers a glimpse of the wreckage wrought by the six adsorbed K at one stage of energy minimization. It is clear that each of the K atoms destroys a hexagon by inducing a contraction of distance

between two C atoms and a breaking of the chemical bond. As is pointed out in Ref. 21, the incorporation of K atoms and the concomitant heavy charge transfer weaken some of the bonds in C_{60} . An isolated C_{60} molecule is all the more vulnerable and cannot withstand more than five K atoms.

Shown in Figs. 2(a)–2(e) are the $C_{60}K_x$ molecular structures for $x=1-5$. In Fig. 2(a) a plane passes through the adsorbed K, which is 2.64 Å from the nearest carbon, and the varying charge density on the slice is represented with different colors. Figure 2(b) shows another slice of charge density for two adsorbed K atoms, which are 2.69 Å from the nearest C atoms. Figure 2(c) is an isocharge surface for $C_{60}K_3$, indicating extensive charge delocalization for the adsorbed and host atoms. The average distance between C and K is 2.55 Å. Two more isocharge maps, Figs. 2(d) and 2(e), are shown for $C_{60}K_4$ and $C_{60}K_5$, respectively, both having an average distance of 2.52 Å between C and K atoms.

The electronic structure of the K-doped C_{60} molecule is described by DOS in each of the five curves in Fig. 1, representing the adsorption of K atoms from one to five. One immediately observes that in all five cases of adsorption concentrations of energy levels are found around the Fermi level. These energy levels are hybridized states of the carbon $2p$ and potassium $4s$ orbitals. Since most electronic transport occurs in the vicinity of the Fermi level, the C_{60} molecule with its attached K atoms greatly enhances its electrical conduction. This is certainly one major fulfillment of the purpose of doping.

It is also interesting to note that whereas the DOS corresponding to a different degree of doping are distributed in essentially the same energy ranges below the Fermi level, the DOS above the Fermi level are quite different for that matter. With the increase of doping, energy levels steadily shift down toward those around the Fermi level. As is shown in Fig. 1, the downward shift of energy levels enables the DOS around the Fermi level for $C_{60}K_4$ to connect with a spike of DOS at 0.43 eV, while those for $C_{60}K_5$ merge with another peak just 0.32 eV above the Fermi level. Other structures also have similar but less dramatic displacement of DOS. This downward shift of energy levels is also observed experimentally by Yamachika *et al.*¹³ and is explained by a simple model in which each electron transferred to the LUMO due to one added K shifts the LUMO+1 toward the Fermi level. It is apparent that increased doping also enhances the electron conduction as more energy levels are packed near the Fermi energy.

In Fig. 3(a) LDOS for the pristine C_{60} molecule are presented. As is expected, the LDOS consist mostly of p waves and are distributed on both sides of the Fermi level. Figure 3(b) has five panels from the top to the bottom, representing the LDOS for an attached K atom in the order of increased doping. It is much easier to see the downward shift of energy levels from the top panel for $C_{60}K$ to the bottom panel for $C_{60}K_5$. We also observe that there is almost no distribution of energy levels below the Fermi energy, indicating a nearly complete charge transfer by K to the outside of its atomic sphere. This donation of electrons makes the doping and hence the modification of electronic properties possible.

We conclude that the K-doped C_{60} molecule is a fairly

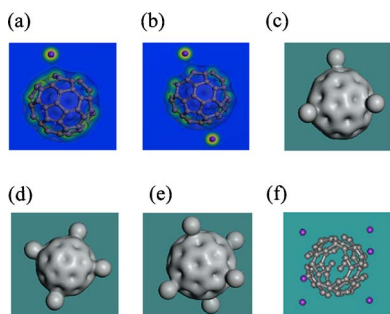


FIG. 2. (Color online) (a) and (b) show charge density on a slice passing through $C_{60}K$ and $C_{60}K_2$, respectively. (c), (d), and (e) are isocharge surfaces for $C_{60}K_3$, $C_{60}K_4$, and $C_{60}K_5$. (f) shows how the carbon cage is destroyed by six K at one stage of energy minimization.

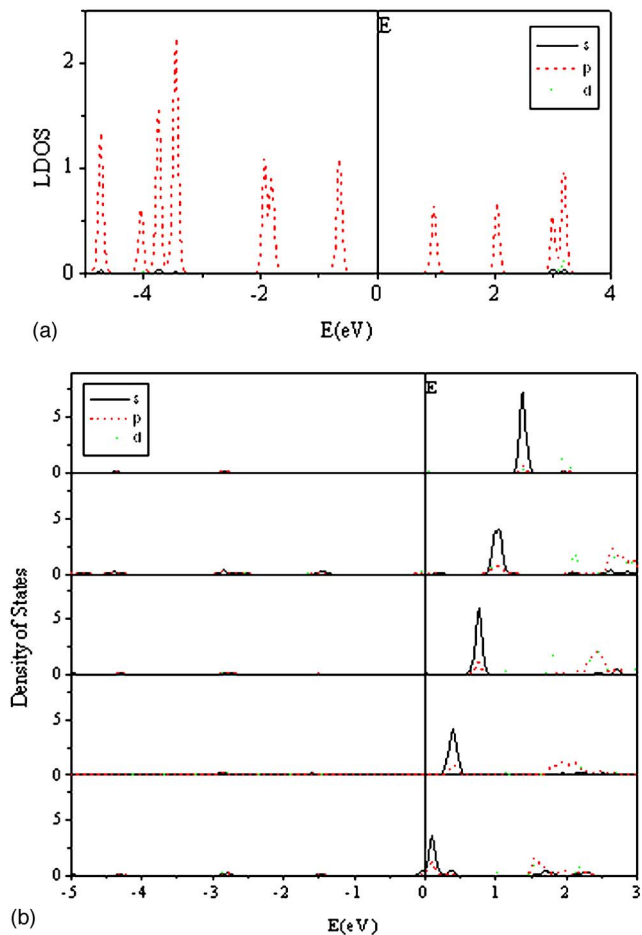


FIG. 3. (Color online) (a) LDOS for a free C_{60} molecule. (b) LDOS for a K atom on $C_{60}K$, $C_{60}K_2$, $C_{60}K_3$, $C_{60}K_4$, and $C_{60}K_5$, from the top panel to the bottom.

stable structure based on the calculation of binding energy. Its electrical conduction is enhanced each time an additional K atom is attached to it and a total of five K atoms are possible for the adsorption without destroying the carbon cage, thus allowing substantial leeway for “tuning” the con-

duction property. It is expected that $C_{60}K_x$ and similar structures should find important applications in the emerging field of molecular electronics.

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