



Electronic structures and large spectrum shifts in hydrogenated fullerenes: Density functional theory study



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ABSTRACT

Electronic structures and band gaps of hydrogenated fullerenes have been investigated by means of density functional theory method. The mechanism of hydrogen addition reaction to the fullerene (C₆₀) surface was also investigated. Addition of one and two hydrogen atoms was examined in the calculations. The binding energies of the second hydrogen atom to C₆₀H were widely distributed in the range 1.5–3.6 eV. It was found that the bonding energy is strongly dependent on the spin density of carbon atom of C₆₀H. The second hydrogen atom preferentially binds to the neighbor site of the first addition site. The electronic states and excitation energies of C₆₀-H were discussed on the basis of theoretical results.

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1. Introduction

The interaction between hydrogen atom (or hydrogen molecule) and carbon materials has attracted considerable interest because the electronic properties of carbon materials are drastically changed by the addition of hydrogen-atom [1–3]. A hydrogen atom behaves mainly as an impurity in the carbon materials such as diamond [4], graphene and fullerene [5]. The atom influences strongly electronic conductivity and the band gap in the semi-conductor. Also, the fullerene and graphene materials have a possibility as a hydrogen storage medium. Especially, hydrogenated fullerenes can be dehydrogenated reversibly [6]. In addition, di-hydrated fullerene, C₆₀H₂ has been shown to be an effective hole transport material with potential applications in organic field-effect transistors and organic light-emitting devices [7–9]. Therefore, the elucidation of an electronic state and the formation mechanism of hydrogenated carbon materials are an important theme to develop the high performance materials.

Recently, Tokunaga et al. have investigated electronic states of mono- and di-hydrated fullerene, C₆₀H and C₆₀H₂, using density functional theory method [10]. They found that energy of C₆₀H radical is smaller than the summation of energy of the fullerene and that of hydrogen atom. They also calculated cationic states of C₆₀H, C₆₀H⁺, and found that dipole moment of C₆₀H becomes significantly larger in cationic state.

In case of graphene–hydrogen atom system, Geim and co-workers showed experimentally that the electronic property of graphene is drastically changed: the highly conductive graphene is converted from

a semimetal into an insulator [11]. The reaction with hydrogen was reversible.

Raman studies reveal that the hydrogenation interrupts the π-bonding system of graphene through the formation of sp³ carbon–hydrogen bonds [12]. Transmission electron microscopy studies indicate that the original hexagonal bonding arrangement is retained, but has a much smaller lattice constant. The hydrogenation is reversible through annealing, thereby restoring the conductivity and structure of graphene. This reversibility also creates the possibility of hydrogen storage.

The electronic states of hydrogen atom added graphene have been investigated by means of density functional theory (DFT) calculation [13–18]. Casolo et al. investigated the adsorption of H atom to a 5 × 5 surface unit cell of graphene using DFT method [13]. The binding energies per one H atom were calculated in the range 0.8–1.9 eV and a barrier to sticking in the range 0–0.15 eV. It was suggested that the change of hybrid orbital from sp² to sp³ is important in the addition of H atom to graphene. Thus, the electronic states of H atom on graphene surface are understood theoretically. However, interaction of hydrogen atoms with C₆₀ is not clearly understood. Especially, the addition process of hydrogen atom to C₆₀ surface and selectivity of second addition of H atom to C₆₀H are scarcely known.

In the present study, the DFT calculations were applied to the hydrogen atom added fullerenes. One and two hydrogenated C₆₀ were examined. The change of electronic states caused by addition of hydrogen atom to C₆₀ was discussed.

2. Method of calculation

All hybrid DFT calculations were carried out using Gaussian 09 program package [19]. The geometries of free C₆₀ and complexes of C₆₀ with mono- and di-hydrogen atoms, expressed by C₆₀H and C₆₀(2H),

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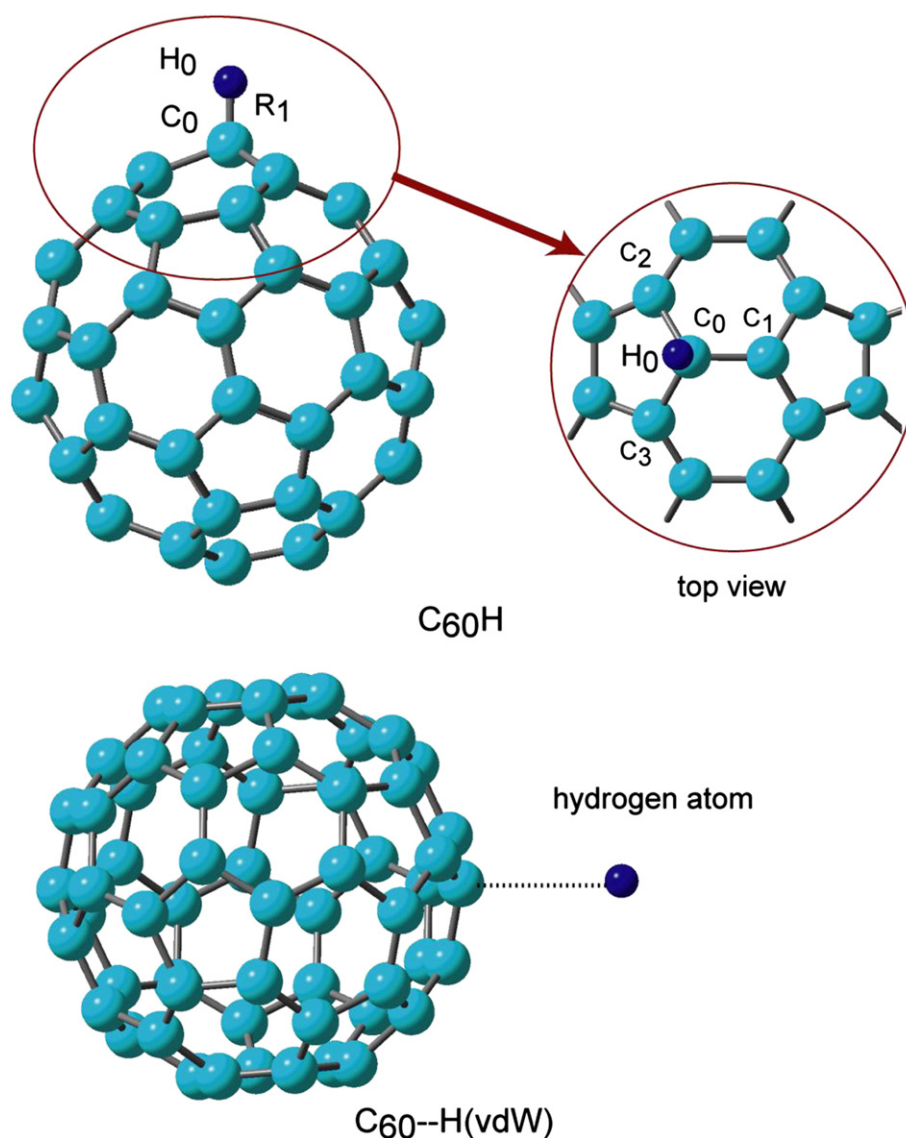


Fig. 1. Optimized structures of hydrogen added to C₆₀ (upper) and van der Waals (vdW) state composed of C₆₀ and H atom (lower).

were fully optimized at the B3LYP/6-31G(d) and B3LYP/6-311G(d,p) levels. Also, CAM-B3LYP and PW91PW91 functionals were used for comparison. These levels of theory gave reasonable electronic structures of graphene systems [20–22]. The harmonic vibrational frequencies of C₆₀H were calculated to elucidate the stabilities of the molecules at the B3LYP/6-31G(d) level. Using the optimized geometries, the excitation energies were calculated by means of time-dependent (TD) DFT calculation at the B3LYP/6-31G(d) level. The electronic states of all

molecules were obtained by natural population analysis and natural bond orbital (NBO) methods at the B3LYP/6-31G(d) level.

3. Results

3.1. A. Structures of mono-hydrogenated C₆₀

Several initial positions of hydrogen atom around C₆₀ surface were examined in the geometry optimization. Two optimized structures were obtained: a hydrogen added fullerene (C₆₀H) and a van der Waals (vdW) state of hydrogen–C₆₀ system, which are expressed by C₆₀H and C₆₀–H(vdW), respectively.

The optimized structures of C₆₀H and C₆₀–H (vdW) are illustrated in Fig. 1. The binding energies are given in Table 1. The bond distance of C₀–H₀ in C₆₀H is calculated to be $R_1 = 1.100 \text{ \AA}$ at the B3LYP/6-311G(d,p) level, where H₀ and C₀ mean additional hydrogen atom and carbon atom in the binding site, respectively. The angles of C₂–C₀–C₃ and C₁–C₀–C₂ are 100.9° and 110.0°, respectively. The position of C₀ atom moved slightly from the original position of normal C₆₀ due to the C₀–H₀ bond formation. The C₀H₀ bond is polarized as C₀ (–0.30)–H₀ (+0.30).

Table 1

Binding energies of hydrogen atom to C₆₀ (in kcal/mol) calculated at the B3LYP/6-31G(d), 6-311G(d,p), and 6-311++G(d,p) levels of theory. Also, PW91PW91 functional was used. The values in kcal/mol are given in parenthesis.

Method	C ₆₀ H (binding state)	C ₆₀ –H (vdW)
B3LYP/6-31G(d)	47.92 (200.3)	0.06 (0.3)
B3LYP/6-311G(d,p)	48.19 (201.4)	0.07 (0.3)
B3LYP/6-311++G(d,p)	48.25 (201.7)	0.10 (0.4)
PW91PW91/6-311G(d,p)	47.90 (200.2)	0.18 (0.8)

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