

Hydrogen Adsorption and Penetration of C_x ($x=58-62$) Fullerenes with Defects

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Abstract. Density functional theory calculations were performed to investigate the endohedral and exohedral adsorption of a H_2 molecule on the classical and nonclassical fullerenes C_x ($x=58, 59, 60, 62$) with seven-, eight-, and nine-membered rings. The amplitude of adsorption energies are within 0.03eV and the molecule-fullerene interaction belongs to van der Waals type. Penetration of a H_2 molecule through different fullerene cages was discussed and the corresponding energy barriers were obtained. We find that the existence of large holes reduces the penetration barrier from 12.6 eV for six-membered ring on perfect C_{60} cage to about 8eV for seven-membered rings and to about 5eV for eight-membered rings.

1 Introduction

Soon after the discovery of carbon fullerenes, it was found that a variety of atoms and molecules can be incorporated into the hollow carbon cages to form endohedral complex structures, which lead to new nanoscale materials with novel physical and chemical properties [1-3]. Endohedral fullerenes are not only of scientific interest but are of technological importance for their potential usage in various fields such as molecular electronics [4], magnetic resonance imaging [5], quantum computer [6-9], and nuclear magnetic resonance (NMR) analysis [10, 11]. On the other hand, tremendous efforts have been devoted to the hydrogen storage in carbon nanostructures like nanotubes [12]. Thus, the study of endohedral fullerene complexes with encapsulation of H_2 molecule is focus of interests from different aspects.

In order to achieve endohedral fullerene complex with hydrogen molecule encapsulated inside, the surface of the fullerene cages must be opened to have a sufficiently large orifice to let the H_2 molecule penetrate. Murata et al. investigated

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the synthesis, structure, and properties of novel open-cage fullerenes with heteroatom on the rim of the orifice [13] as well as the feasibility of inserting small atoms or molecules through the orifice of an open-cage C₆₀ derivative. Hatzimarini et al. reported a novel methodology for the preparation of five-, seven-, and nine-membered fused rings on C₆₀ fullerene [14].

Recently, molecular hydrogen was successfully placed inside open-cage fullerenes [13, 15-21]. Murata et al. [16] reported the first syntheses and X-ray structures of organic and organometallic derivatives of C₆₀ and the usage of the encapsulated molecular hydrogen as a magnetic shielding probe. After the encapsulation of H₂, the endohedral cages were then closed through a “molecularsurgery” method on a gram scale with maximum 100% H₂ incorporation [20]. Stimulated by these experimental progresses, *ab initio* computational studies have been reported for endohedral H₂@C₆₀ complex. Slanina et al. performed theoretical calculations of the encapsulation energy using modified Perdew-Wang and Becke functionals (MPWB1K) [22]. Shigetaa et al. studied dynamic charge fluctuation of endohedral fullerene with H₂ [23].

In addition to the opening and closing of fullerene cages via chemical approaches, it is possible to have the as-prepared defect fullerene cages with large holes [24-26]. For example, Qian et al. detected pronounced peak of C₆₂⁻ on the LD-FTMS mass spectrum and performed DFT calculation of the C₆₂ cage with one 4MR [24]. Deng et al. observed the odd-numbered clusters C₅₉ in laser desorption ionization of C₆₀ oxides [26]. Accordingly, *ab initio* calculations have been carried out for the geometries, energies, and stabilities of these defective fullerene C₆₀ cages [27-29]. Hu et al. computed fullerene cages with large hole. [27, 28]. Lee studied the structure and stability of the defective fullerenes of C₅₉, C₅₈ and C₅₇ [29].

Despite the existing theoretical efforts, within the best of our knowledge, there is no *ab initio* calculation on the hydrogen adsorption and encapsulation in the defect fullerenes. These nonclassical fullerenes with seven-membered ring (7MR), eight-membered ring (8MR), and so on, may serve well as model systems for the open-cage fullerenes obtained from other methods. Thus, it would be interesting to study the relationship between the size of the orifice ring and the barrier for H₂ molecule penetrating from outside to inside of fullerene. In this paper, we address these issues by conducting DFT calculations on the adsorption and penetration of H₂ molecule on C₆₀ and nonclassical fullerenes with 7MR, 8MR, and 9MR.

2 Computational Methods

All-electron DFT calculations were carried out employing the generalized gradient approximation (GGA) with the PW91 functional [30] and the double numerical plus polarization (DNP) basis set that are implemented in the DMol program [31]. Self-consistent field (SCF) calculations were carried out with a convergence criterion of 10⁻⁶ a.u. on the total energy. To ensure high quality results, the real-space global orbital cutoff radius was chosen to be as high as 5.0 Å. It is known that DFT method

within GGA approximation is usually insufficient for describing the weakly van der Waals (vdW) interaction. A recent DFT calculation of the hydrogen adsorption on carbon and boron nitride nanotubes [32] demonstrated that PW91 functional can roughly reproduce the strength of the vdW interaction between a H₂ molecule and a C₆H₆ benzene molecule by highly accurate HF-MP₂ calculations.

3 Results and Discussion

In this work, we considered eight fullerene cages including perfect C₆₀ and those defect fullerenes. The configurations of the defect fullerene cages were taken from Ref. [29] for C₅₈ and C₅₉ with 7MR, 8MR, and 9MR, and from Ref. [24] for C₆₂ with 4MR. On the one side, cages with the vacancy defect (unsaturated atom) were created by removing one atom from C₆₀, such as C₅₉ 4-9 (with one 4MR and one 9MR) and C₅₉_5-8 (with one 5MR and one 8MR). On the other hand, topological defects including larger rings (7MR and 8MR) or smaller 4MR were created on the fullerene cages of C₅₈, C₆₀, and C₆₂. For C₆₀, we considered perfect C₆₀ (I_h) as well as a C₆₀ cage with two 7MR (along with one 4MR), which is denoted as C₆₀ 4-7-7. For C₅₉, the cage with one 4MR and one 9MR is denoted as H₂@C₅₉_4-9, and the cage with one 5MR and one 8MR as H₂@C₅₉_5-8. For C₅₈, the cage with two 5MR and one 7MR is denoted as H₂@C₅₈_5-5-7, the cage with two 4MR, one 8MR, and one 5MR as H₂@C₅₈ 4-4-8(5), and the cage with two 4MR, one 8MR, and one 6MR as H₂@C₅₈ 4-4-8(6).

At the beginning, eight fullerene cages were optimized at level of PW91/DNP. Hydrogen molecule was then placed in the center of each cage as initial configuration of the endohedral complexes. These endohedral H₂@C_x complexes were fully optimized. The optimized structures are shown in Figure 1. Moreover, exohedral adsorption of H₂ molecule on these eight cages was also considered. The adsorption energy of hydrogen molecule is defined as the difference between the total energy of the H₂-cage complex specie and summation of the total energies of the individual H₂ molecule (E_{H_2}) and the fullerene cage (E_{cage}). Hence, the adsorption energies for both endohedral (E_{endo}) and exohedral adsorption (E_{exo}) are computed from

$$E_{endo} = E_{endo-H_2} - E_{cage} - E_{H_2} \quad (1)$$

$$E_{exo} = E_{exo-H_2} - E_{cage} - E_{H_2} \quad (2)$$

To study the penetration behavior of a H₂ molecule from the endohedral site to the exohedral site, we first adjust the orientation of the central H₂ molecule to be perpendicular to the largest hole on the surface of the fullerene cages. Then, single-point energies of the H₂-cage complex (H₂@C₆₀, H₂@C₆₀_4-7-7, H₂@C₅₉_4-9, H₂@C₅₉_5-8, H₂@C₅₈_5-5-7, H₂@C₅₈_4-4-8(5), and H₂@C₅₈_4-4-8(6)) were computed along the penetration path by gradually moving the H₂ molecule from the cage center to the outside of the fullerene cage through the largest hole by a step of 0.3 Å up to

the longest distance of 9 Å from the cage center. The main theoretical results are summarized in Table 1 and Figure 2.

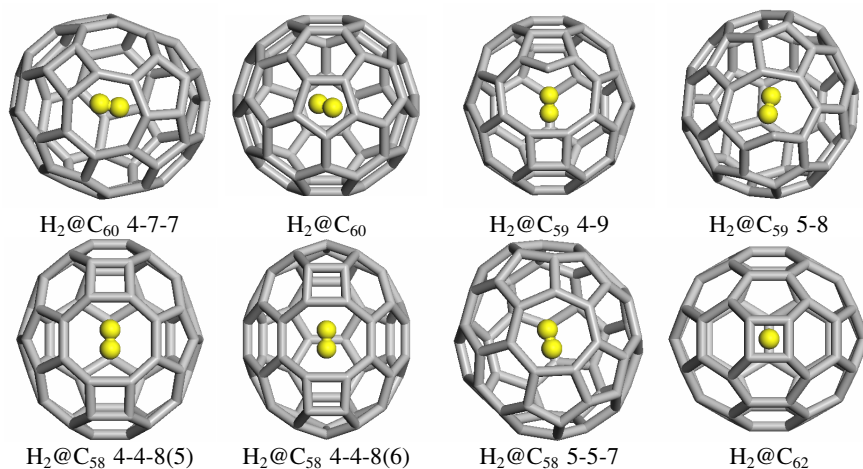


Fig. 1. Optimized configurations of $H_2@C_{62}$, $H_2@C_{60}$, $H_2@C_{60_4-7-7}$, $H_2@C_{59_4-9}$, $H_2@C_{59_5-8}$, $H_2@C_{58_5-5-7}$, $H_2@C_{58_4-4-8(5)}$

Table 1. Total energies of the eight optimized cages of perfect and defect fullerenes C_X ($X=58, 59, 60, 62$) and the corresponding endohedral complex $H_2@C_X$. The total energy of a H_2 molecule from our DFT calculation at the same level is -1.1705707 Hartree. Endohedral adsorption energy (E_{endo}) and exohedral adsorption (E_{exo}) for H_2 on C_X ($X=58, 59, 60$) cage as well as energy barrier for penetration of H_2 through the largest hole on the cage.

	$E_{\text{endo-H}_2}$ (Hartree)	$E_{\text{extro-H}_2}$ (Hartree)	$E(C_X)$ (Hartree)	E_{endo} (meV)	E_{extro} (meV)	Barrier (eV)
C_{62}	-2363.528743	-2363.528763	-2362.357426	-20.3	-20.9	–
C_{60}	-2287.401287	-2287.401230	-2286.216007	-17.7	-16.2	12.6
C_{60_4-7-7}	-2287.273601	-2287.273788	-2286.102568	-12.6	-17.7	7.9
C_{59_4-9}	-2249.062584	-2249.063739	-2247.892223	5.7	-26.3	9.1
C_{59_5-8}	-2249.095940	-2249.097171	-2247.925697	8.9	-24.6	5.2
C_{58_5-5-7}	-2211.063665	-2211.064968	-2209.893787	18.8	-16.6	8.3
$C_{58_4-4-8(5)}$	-2211.012397	-2211.013340	-2209.842018	5.2	-20.5	4.6
$C_{58_4-4-8(6)}$	-2210.892028	-2210.894158	-2209.722625	31.8	-26.2	5.2

The total energy between perfect C_{60} and defect C_{60_4-7-7} is 3.47 eV. In other words, formation of two 7MR and one 4MR on perfect C_{60} requires 3.47 eV, while previous calculation found that formation of two 7MR on a (6,6) carbon nanotube is 2.74 eV [33]. The total energy of C_{59_5-8} is lower than C_{59_4-9} by 0.91 eV, close to the theoretical value of 0.89 eV by Lee et al. at level of B3LYP/6-31G* [29]. For C_{58} , C_{58_5-5-7} is more stable than $C_{58_4-4-8(5)}$ by 1.40 eV and than $C_{58_4-4-8(6)}$ by 4.67 eV, rather close to previous results of 1.34 eV and 4.77 eV by Lee [29].

As shown in Table I, for all the cases studied, the exohedral adsorption of H_2 molecule on the surface of fullerene cage is exothermic, with E_{exo} ranging from -16.6 to -26.3 meV. The exohedral adsorption energy of H_2 molecule is insensitive to the atomic configuration of fullerene cages. Experimentally, the adsorption of a H_2 molecule on the graphite surface is -42 meV. It is known that GGA usually underestimate the surface adsorption energy of vdW type [34]. Therefore, the present GGA calculation might somewhat underestimate the adsorption energy of H_2 molecule.

On the contrary, the endohedral adsorption is either exothermic or endothermic, with E_{endo} ranging from -12.6 to 31.8 meV. The incorporation of a H_2 molecule in C_{60} (perfect or defect) and C_{62} cages is exothermic, while encapsulation of a H_2 molecule in C_{58} and C_{59} cages is endothermic. This finding can be roughly understood by the difference in the interior space of the fullerene cages. In other words, C_{60} and C_{62} cages are larger and have more space for the encapsulation of H_2 molecule. In a previous study [22], the best estimate for the encapsulation energy for $H_2@C_{60}$ was at least 173 meV.

The energy barrier for the penetration of H_2 molecule through the largest hole of the eight different fullerene cages are presented in Table 1 and the corresponding single-point energies for the penetration paths are shown in Figure 2. First of all, in Figure 2 we find all the energy paths for the H_2 penetration are smooth and have clear highest peak on them, which correspond to the energy barriers given in Table 1. Among them, the energy barrier for penetrating the six-membered ring on C_{60} cage is highest, i.e., 12.6 eV, and the energy barrier for penetrating the eight-membered ring on $C_{58_4-4-8(5)}$ cage is lowest, i.e., 4.6 eV. The energy barriers for other cages with 8MR such as C_{59_5-8} and $C_{58_4-4-8(6)}$ are close, both of 5.2 eV. For those defect fullerene cages with 7MR, such as C_{60_4-7-7} and C_{58_5-5-7} , the energy barriers are around 8 eV. In other words, the penetration barrier reduces from 12.6 eV for 6MR on perfect C_{60} cage to about 8eV for 7MR and to about 5eV for 8MR. However, it is interesting to find that the penetration barrier through the largest 9MR on the C_{59_4-9} cage is relatively high, i.e., 9.1 eV.

To summarize, the encapsulation and penetration of H_2 molecule on the perfect and defect C_{60} cages were investigated using density functional theory at level of PW91/DNP. Fullerene cages of C_x with $x=58, 59, 60, 62$ containing 7MR, 8MR, and 9MR were considered. The interaction for H_2 molecule adsorption on fullerene cages is relatively weak and of vdW type. The exohedral adsorption for H_2 molecule on the surface of fullerene cage is exothermic, while the endohedral adsorption is exothermic for C_{60} and C_{62} or endothermic for C_{58} and C_{59} cages. The penetration barrier from endohedral to exohedral site significantly reduces from 12.6 eV for 6MR perfect cage to about 8 eV for 7MR and to about 5 eV for 8MR on defect cages. However, these reduced energy barriers for 7MR and 8MR are still too high for a H_2 molecule to penetrate at ambient conditions. Finally, it is worthy to point out that the present calculations focus on the physisorption and penetration of H_2 molecule while the possible chemisorption of the H_2 molecule and corresponding transition states were not considered.

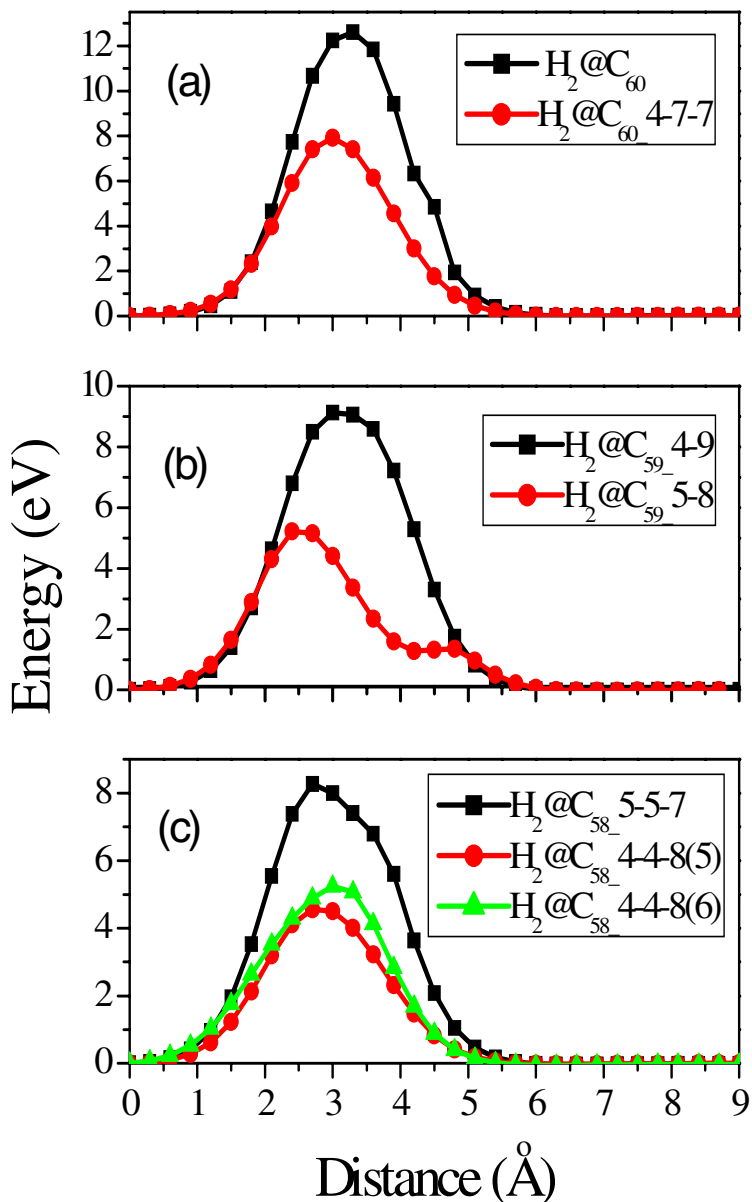


Fig. 2. Relative energy of $H_2@C_x$ complex as function of the distance for H_2 from cage center along the path towards center of the largest ring. The zero energy is set to be the total energy for the H_2 in the center of cage $H_2@C_{62}$, $H_2@C_{60}$, $H_2@C_{60_4-7-7}$, $H_2@C_{59_4-9}$, $H_2@C_{59_5-8}$, $H_2@C_{58_5-5-7}$, $H_2@C_{58_4-4-8(5)}$.

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