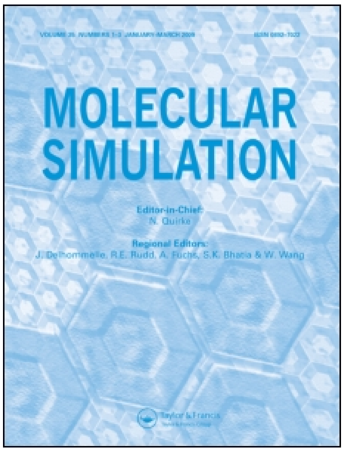

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Density functional based treatment of endohedrally hydrogen-doped fullerene, $nH_2@C_{60}$

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Density functional based treatment of endohedrally hydrogen-doped fullerene, $n\mathrm{H}_2@\mathrm{C}_{60}$

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The possibility of the formation of endohedral complexes between H_2 molecules and C_{60} fullerene is discussed on the basis of general geometric considerations as well as the results of density functional based tight binding (DFTB) calculations. The obtained results reveal that only one hydrogen molecule being incorporated inside the C_{60} cage can form the stable complex in agreement with geometric considerations and recent experimental data. It is also shown that for large numbers of encapsulated hydrogen molecules, some of them become chemisorbed on the inner surface of the cage. We show that for $n_{\mathrm{H}_2} = 21$ the capsule side wall eventually breaks and the mechanism of its breaking is studied by DFTB molecular dynamics simulations thus, this complex seems to be highly improbable.

Keywords: endohedral complexes; hydrogen molecule; DFTB; fullerenes; encapsulation

PACS numbers: 61.46. − w; 61.48. + c

1. Introduction

After the first discovery of C_{60} fullerene by Kroto et al. [1], and carbon nanotube by Iijima [2], various carbon-based nanocage structures, such as fullerene clusters [3–8], single-walled nanotubes [9,10], multi-walled nanotubes [2], nanocapsules [11,12], nanopolyhedra [13], cones [14,15], cubes [16], polyhedra [11] spheres [17] and carbon onions [18] have been studied due to the promising potential for applications in various fields.

The characteristic features of their structural formation, physical and chemical properties are of immense interest to the scientific community. Of all these carbon-based nanocage structures, C_{60} fullerene is most amenable to large-scale synthesis [7].

It is often chosen by scientists as a model variant to conduct studies of its physical and chemical properties for better understanding the compounds from this class of carbon-based nanocage structures. Particular attention has been given to endohedrally doped C_{60} compounds (which can be doped by many atoms including certain gases such as H, He and Ne and solids like La, Sc and U) [19]. The interesting properties of these compounds are extensively studied, such as the superconductivity of alkali-doped C_{60} at reasonably high temperatures, and their applications as magnetic detectors and in magnetic recording technology. The interaction of C_{60} with hydrogen atoms and molecules has also been intensively studied both experimentally [20,21] and theoretically [22–25]. The possibility of the existence of hydrofullerenes associated with C_n cage structures has been discussed [23,26], and investigators have reported that the C_{60} nanocage may accommodate a significant number of hydrogen molecules [23].

There are a few theoretical papers considering endohedral C_{60} fullerene containing more than one hydrogen molecule [27–36]. The results of semiempirical optimisations [27–29,34] (followed by density functional [27,34,36] or Hartree–Fock [28,29] energy calculations) and force field methods [19,20] appear contradictory. The maximum amount of hydrogen to form a stable $H_n@C_{60}$ composite was determined as 23 [27,34], 24 [23], 25 [28,29] or 29 [36] molecules. It was shown [27,29,30] that putting a large amount of hydrogen led to breaking of one or few C—C bonds of the carbon cage, although details of this process were studied only by Yakobson et al. [36] via the *ab initio* DFT molecular dynamics (MD) simulations. From the other side, Dolgonos [30] and Dodziuk [31,33,35] insisted that there was not enough space for more than one hydrogen molecule inside C_{60}. They supported this statement by the calculated highly positive values of stabilisation (formation) energy of the $H_n@C_{60}$ complexes. There is also a disagreement regarding the possibility of hydrogen chemisorption on the inner walls of the fullerene, which was observed in [28,29,36], while in the other studies all encapsulated hydrogen was found in the molecular form [23,27,34]. In addition, some endohedral complexes of C_{60} with only one diatomic molecule like $H_2@C_{60}$ [37,38], $N_2@C_{60}$ [39] and $CO@C_{60}$ [40] were experimentally observed but

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no such complexes with two or more molecules embedded inside the C_{60} cavity were reported up-to-date.

This shows the necessity of more investigations for the structural optimisations of the $H_n@C_{60}$ composites. In this work, we intend to extend our understanding of the stability of endohedrally hydrogen-doped fullerene $n\,H_2@C_{60}$ by means of density functional based tight binding (DFTB) calculations. Since the main factors which influence the stability of such systems are weak but numerous nonbonding van der Waals (vdW) interactions hence, for the first time, the dispersion corrects for the vdW interaction have also been considered. In view of the problems with finding materials for hydrogen storage which satisfy DoE requirements [41], from the one hand, and the relatively easiness of performing computations using standard DFTB program packages, from the other, the results presented in this paper deserve richly some comments.

2. Computational methods

The calculations of the interaction between C_{60} and hydrogen molecules are carried out using the recently developed DFTB+ code [42]. DFTB+ uses DFTB method based on a second-order expansion of the Kohn–Sham total energy in density-functional theory (DFT) with respect to charge density fluctuations. The zeroth order approach is equivalent to a common standard non-self-consistent Tight Binding (TB) scheme, while at second order a transparent, parameter-free and readily calculable expression for generalised Hamiltonian matrix elements can be derived. These are modified by a self-consistent redistribution of Mulliken charges (SCC).

Unlike the typical approximate Hartree–Fock methods, or conventional DFT in tight-binding basis, the DFTB approach uses a tabulated set of integrals derived from *ab initio* DFT calculations [43], leading to a substantial speed-up of the method since explicit integration is not required in the method. Also, unlike conventional tight-binding, due to the DFT basis of the DFTB approach, it is possible to produce parameterisations capable of accuracy close to Local Density Approximation/Generalised Gradient Approximation (LDA/GGA) with minimal adjustable parameters and also transferable between different systems. The DFTB approach is also unusual in that, unlike conventional tight-binding, the basis functions of the method are also available, allowing the reconstruction of actual wave functions from the calculations. The DFTB parameters consist of two parts:

(a) parameters entering the electronic part of the DFTB model;
(b) parameters for the repulsive energy contribution, which is a two-body force field like term.

Electronic part contains atomic and diatomic contributions which are both calculated from an atomic DFT program using either LDA or GGA functionals.

- The atomic parameters are the atomic s, p, d, … Kohn–Sham eigen energies, which enter as diagonal elements the (usually minimal basis) Hamilton matrix. For the SCC–DFTB method additional atomic hardness values (Hubbard parameters) are calculated.
- The non-diagonal matrix (overlap matrix S and Hamilton matrix H) elements are calculated in a two-centre approximation for a neutral atomic reference density. They are distance dependent and are stored as a table for interatomic distances up to about 10 a.u.

Using these parameters the DFTB program does not have to perform any integral evaluation during the program runtime.

The repulsive energy contribution is approximated as a sum of pair potentials, which are represented either by spline functions or polynomials. They are derived by calculating bond stretching energies of selected bonds in a small set of molecules or using data from solid state calculations applying DFT calculations to get the total energy and the DFTB electronic part. In contrast to the diatomic parameters in the electronic part, the repulsive potentials are only needed for elements with a direct covalent bond. Further details of the method have been fully reviewed for instance in [42–45]. In this work, the Slater–Koster (S–K) type parameter set [46] was implemented. Furthermore, since the main factors which influence the stability of such systems are weak but numerous nonbonding vdW interactions hence, the dispersion corrects for the vdW interaction were implemented via the Slater–Kirkwood type model [47].

Geometries of the C_{60} and H_2 are optimised separately prior to the optimisation of the whole system. Structural optimisations were performed using the conjugate gradient algorithm. The DFT-based Tight Binding Molecular Dynamics (TBMD) simulations are done by DFTB+ in the canonical regime; i.e. the thermodynamical system under consideration is described by the number of particles N, volume V and temperature T as variables. The structure under study is in contact with Andersen thermostat [48] having fixed temperature 300 K. The MD time step is 1.0 fs.

The accuracy of our method is tested by comparison of optimised geometries of fullerene C_{60} and hydrogen H_2 molecule against the existing experimental data. In particular, the calculated and experimental [49] values of H—H bond length in hydrogen molecule are 0.743 and 0.741 Å, respectively; the calculated and experimental [50] bond lengths of the single C—C bond of C_{60} molecule (i.e. the bond fusing a pentagon and a hexagon) are 1.455 and 1.458 Å, while for the double bond of the fullerene (fusing two hexagons) values are 1.404 and 1.401 Å, respectively. From the consistency of these results, we conclude that the DFTB is suitable and effective for geometry optimisation of fullerene.

3. Results and discussion

Endohedral doping method is the addition of an atom or an ion into the interior hollow core of the fullerene molecule to form endofullerene [19]. The insertion of 1–3 metal species inside a fullerene cage is common and up to four metal atoms/ions have been already introduced [19]. Endohedrally hydrogen-doped fullerenes are unknown although some theoretical studies on endohedrally metal atom and hydrogen-doped fullerenes have been reported [51,52]. Although, technical accommodation of H_2 molecules in C_{60} cage still remains to be solved, it is interesting to get some idea about the possible structure and stability of $n\,H_2@C_{60}$, where n represents the number of hydrogen molecules encapsulated in C_{60} skeleton. For that purpose, presently DFTB molecular orbital calculations have been performed.

To investigate the stability of the $n\,H_2@C_{60}$ systems we first examined the binding energies (formation energy) of H_2 molecules inserted into C_{60} cage. The binding energy is calculated from

$$E_{\mathrm{B}} = E_{\mathrm{C}_{60}+n\mathrm{H}_2} - E_{\mathrm{C}_{60}} - nE_{\mathrm{H}_2}, \tag{1}$$

where $E_{\mathrm{C}_{60}+n\mathrm{H}_2}$ is the total energy of the C_{60} with n adsorbed hydrogen molecules, n represents the number of hydrogen molecules encapsulated in C_{60} skeleton, $E_{\mathrm{C}_{60}}$ is the total energy of the pure C_{60} and E_{H_2} is the total energy of the isolated hydrogen molecule.

The optimised C_{60} cage structure was used for the molecule interaction. After full structural optimisation of the C_{60} systems, we find that the binding energy value is negative for one encapsulated H_2 molecule and almost zero for two of them. All the structures with larger n have positive formation energies, which are metastable. For the $1H_2@C_{60}$ complex the bond length of H_2 changed to 0.7420 Å, which is basically the same as for an isolated H_2 molecule (0.7432 Å). The small change of the H—H bond is an indication of the weak interaction between the hydrogen molecule and the C_{60} cage. The calculated binding energy E_{B} and average C—H equilibrium distance are about -0.181 eV (-4.172 kcal/mol) and 3.214 Å, respectively, they are comparable with those of gas adsorption on the CNT [53–55]. Table 1 shows binding energies of $n\,H_2@C_{60}$ type (n: 1–4, 9, 10, 12, 15, 19–21) systems.

Figure 1 shows some typical optimised geometries of $n\,H_2@C_{60}$ for $n = 4$, 6, 10, 20 and 21. The fullerene shape deviates from a sphere for a large amount of encapsulated hydrogen, as is clear from Figure 1(d).

For a relatively small number of encapsulated hydrogen molecules, $n < 10$, all the hydrogen inside C_{60} exists only in molecular form, in agreement with Refs. [23,27,34,36]. The bond length in H_2 molecules varies from 0.743 to 2 0.739 Å, which is close to one in a free molecule. Hydrogen molecules are organised into clusters of well-defined shapes, such as a tetrahedron for $n = 4$, as shown in Figure 1(a), trigonal bipyramid for $n = 5$, and octahedron for $n = 6$, as shown in Figure 1(b), similar to the previous optimisation results [27,34,36].

As it can be seen from the figure, when 10 H_2 molecules were encapsulated into the C_{60} cage, a new bond between H_2 and C_{60} was formed. Furthermore, the length of the C=C bond, which was saturated with the H of H_2, changed from 1.44552 to 1.52745 Å, indicating that the C=C (double bond) was transformed into a C—C (single bond). For $21H_2@C_{60}$ system, surprisingly, the C_{60} cage breaks and then, some of the H_2 molecules escape from the cage. Thus this system seems to be highly improbable. Consequently, the $1H_2@C_{60}$ system would be the most stable complex. This fact was corroborated by the recent synthesis of $H_2@C_{60}$ complex [8,9,56] and the theoretical results [30,34,57].

We now investigate the relationship between the number of encapsulated H_2 molecules and the associated repulsive energies in the confined system. In Figure 2, the variation of the energy per H_2 molecule with the number of the confined H_2 molecules is carefully examined. The corresponding average H—H repulsive energies are calculated by [27,58,59]

$$E_{\mathrm{rep}}(\mathrm{H}_2\text{—}\mathrm{H}_2) = (E_{\mathrm{total}}(\mathrm{H}_n) - N_{\mathrm{H}_2}E_{\mathrm{H}_2})/N_{\mathrm{H}_2}, \tag{2}$$

where $E_{\mathrm{total}}(\mathrm{H}_n)$ is the total energy of all the H_2 molecules in the C_{60}, E_{H_2} is the energy of a single H_2 molecule confined in the fullerene and N_{H_2} is the total number of hydrogen molecules in the system. The average H_2—C_{60} repulsive energies are H_2 calculated by [34]

$$E_{\mathrm{rep}}(\mathrm{H}_2\text{—}\mathrm{C}_{60}) = (E_{\mathrm{total}}(\mathrm{H}_2 + \mathrm{C}_{60}) - E_{\mathrm{total}}(\mathrm{H}_n) - N_{\mathrm{H}_2}E_{\mathrm{C}_{60}})/N_{\mathrm{H}_2}, \tag{3}$$

where $E_{\mathrm{total}}(\mathrm{H}_2 + \mathrm{C}_{60})$ and $E_{\mathrm{C}_{60}}$ are the total energy of the system with and without encapsulated hydrogen molecules, respectively.

Table 1. Calculated binding energies E_{B} eV for $n\,H_2@C_{60}$ type (n: 1–4, 9, 10, 12, 15, 19–21) complexes.

Complex $n\,H_2@C_{60}$	$1H_2$	$2H_2$	$3H_2$	$4H_2$	$9H_2$	$10H_2$	$12H_2$	$15H_2$	$19H_2$	$20H_2$	$21H_2$
Binding energy (eV)	−0.18	0.26	0.61	1.92	15.95	19.50	28.31	40.87	49.16	65.84	4.81

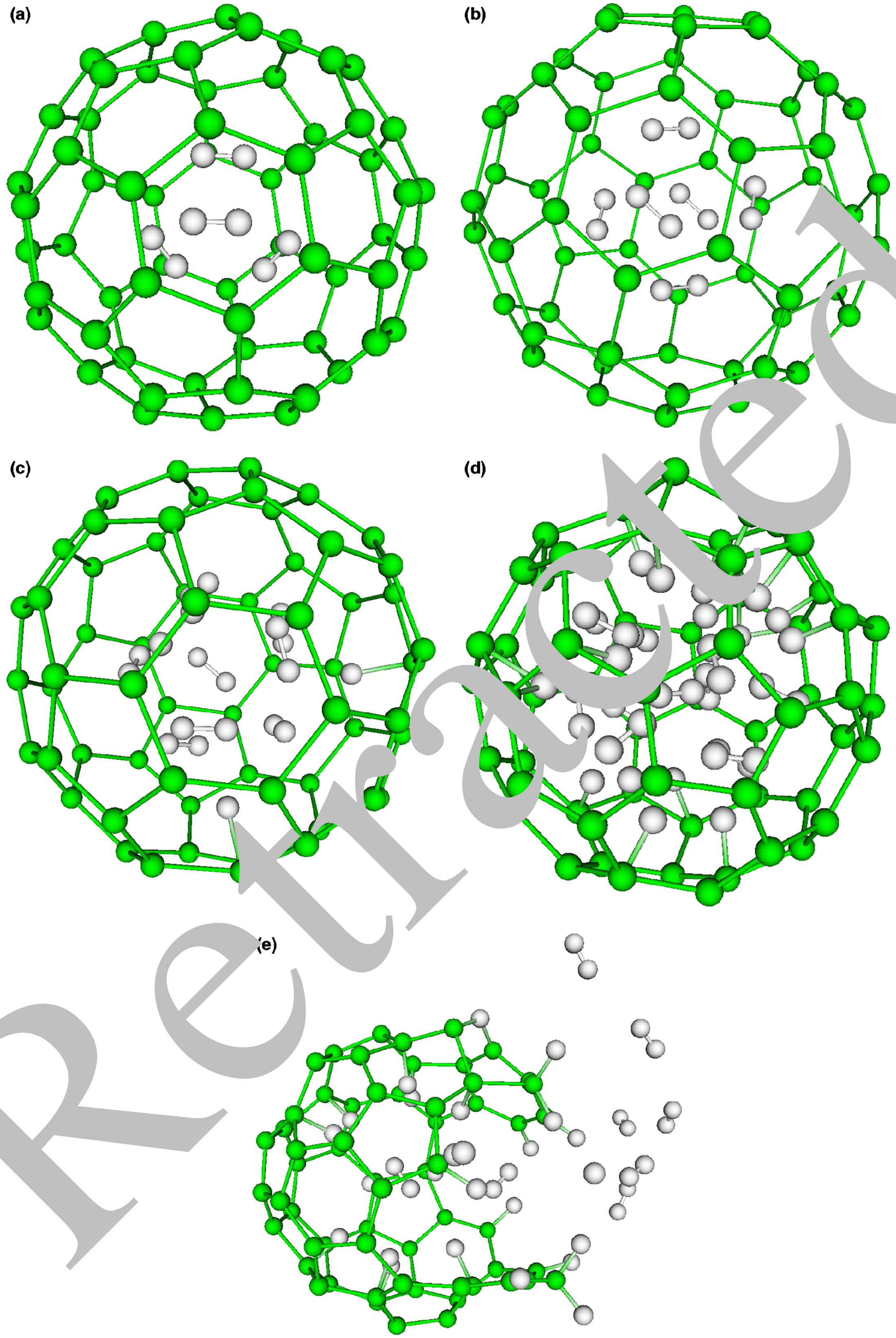

Figure 1. Optimised geometries of $n\mathrm{H}_2@\mathrm{C}_{60}$ structures with (a) $n = 4$, (b) $n = 6$, (c) $n = 10$, (d) $n\mathrm{H}_2 = 20$ and (e) $n\mathrm{H}_2 = 21$. Carbon and hydrogen atoms are shown in green and white colours, respectively.

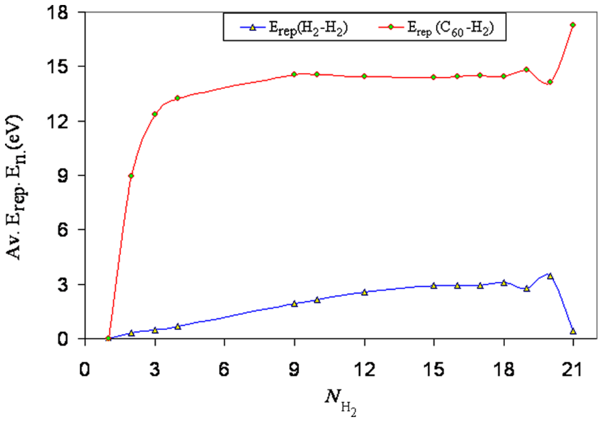

Figure 2. Variation of average H_2—H_2 and H_2—C_{60} repulsive energies with the number of H_2 molecules confined in C_{60} fullerene.

It is noted from Figure 2 that both repulsive energies are positive, and that between the hydrogen molecules and the fullerene wall is generally larger than between the hydrogen molecules. When only one H_2 molecule is confined within the C_{60}, present results show that it behaves as a free molecule and residing at the centre. This phenomenon has also been experimentally observed [59]. The reason is that the distance between the centre of the cage and the carbon cage shell is about 3.7 Å, which is too large for any bonding interaction between hydrogen and carbon. But with more hydrogen molecules being encapsulated, the formation of the various hydrogen molecular clusters within the C_{60} displays a variety of well-defined shapes, and the H_2—H_2 repulsive energy begins to increase.

When the number of H_2 molecules is increased, we observe from Figure 2 that the rate of increase of the H_2—C_{60} repulsive energy becomes progressively higher than that of the H_2—H_2 repulsive energy. It is observed, on the other hand, that with the initial increase in the number of encapsulated H_2 molecules, the average H_2—C_{60} repulsive energy first rises until $N_{H_2} = 9$ but, with subsequent increase in N_{H_2}, it remains constant until $N_{H_2} = 18$. As it can be seen from the figure, when $N > 9$ molecules were encapsulated into the C_{60} cage, the H_2—H_2 repulsive energy rises slightly with H_2 the initial increase in the number of encapsulated H_2 molecules hence a new bond between H_2 molecule(s) and C_{60} was formed thus the H_2—C_{60} repulsive energy remains constant. For $21H_2$ molecules were encapsulated into the C_{60} cage, the H_2—C_{60} repulsive energy was increased while the H_2—H_2 repulsive energy was decreased thus, the wall of the cage break eventually and large amount of H_2 molecules escape from the cage.

From the discussions of these present results, it is evident that the repulsive interactions among the encapsulated H_2 molecules and the fullerene wall, as well as that between the hydrogen molecules themselves, play an important role in determining the structural states of the hydrogenated C_{60}. Since the repulsive energy is a function of the ground state energy, it is thus also of critical importance to the ground-state structure and stability.

In order to investigate the opening of the wall of the C_{60} cage with increase of the H_2 molecules, we have performed TBMD calculations for $21H_2$ molecules encapsulated into the C_{60} cage. The mechanism of cage opening is illustrated in Figure 3. We put the $21H_2@C_{60}$ complex in contact with a thermostat at room temperature. The C–C bonds of the fullerene cage are long, some of them reaching almost 1.67 Å, and thus they are very weak and easy to break. Due to the large amount of hydrogen confined in the fullerene cage, a large number of its carbon atoms are hydrogenised. As it can be seen from the figure, at 70 fs an H atom bridges between two adjacent C atoms via the covalent bonds. Behaviour of these two carbon atoms, shown in red in Figure 3(a), is especially important for the process of fullerene breaking. One of them, which we will henceforth denote as C*, is situated closer to the nearest hydrogen atom in comparison with the other C atom which will denote as C_H (C*—H and C_H—H distances are 1.193 and 1.240 Å, respectively). The length of the C*—C_H bond was extended to 1.685 Å, while the other two bonds involving the C* atom are 1.621 and 1.645 Å and the C_H atom are 1.472 and 1.483 Å. As a result, the bridging of an H atom between C* and C_H atoms and hence, the elongation of the C*—C_H bond causes the bond to breaks after 80 fs (Figure 3(b)).

Atomic movements during MD simulations lead to the full hydrogenation of C_H atom. The partial p-bond between C* and H atom breaks and C* becomes a radical. As one can see from Figure 3(c), this bond is already broken after 155 fs. Then the hydrogen bound to C_H quickly changes its position such that this carbon atom restores sp hybridisation. Internal pressure pushes hydrogen toward the opened hole in the fullerene surface. This results in the further hydrogenation of C_H (among other carbon atoms), leading to a CH_2-group formation, as shown in Figure 3(f). This makes the process of fullerene breaking irreversible. The escape of H_2 molecules from the cage and hydrogenation of the remaining carbons are shown in Figure 3(g) (1000 fs). We can conclude that the cage opening is promoted by the breaking of one of the weak C—C bonds formed by two carbon atoms, all of whose nearest neighbours are fully or partially hydrogenised. Thus, we found that C_{60} nanocage cannot accommodate 21 hydrogen molecules. Our observation is, however, in contrast with the results of Yakobson et al. [36] indicated that maximum of 29 hydrogen molecules inside a C_{60} cage remains a metastable structure. Although they used the high level *ab initio* DFT-MD calculations but, however, the main factors which influence the stability

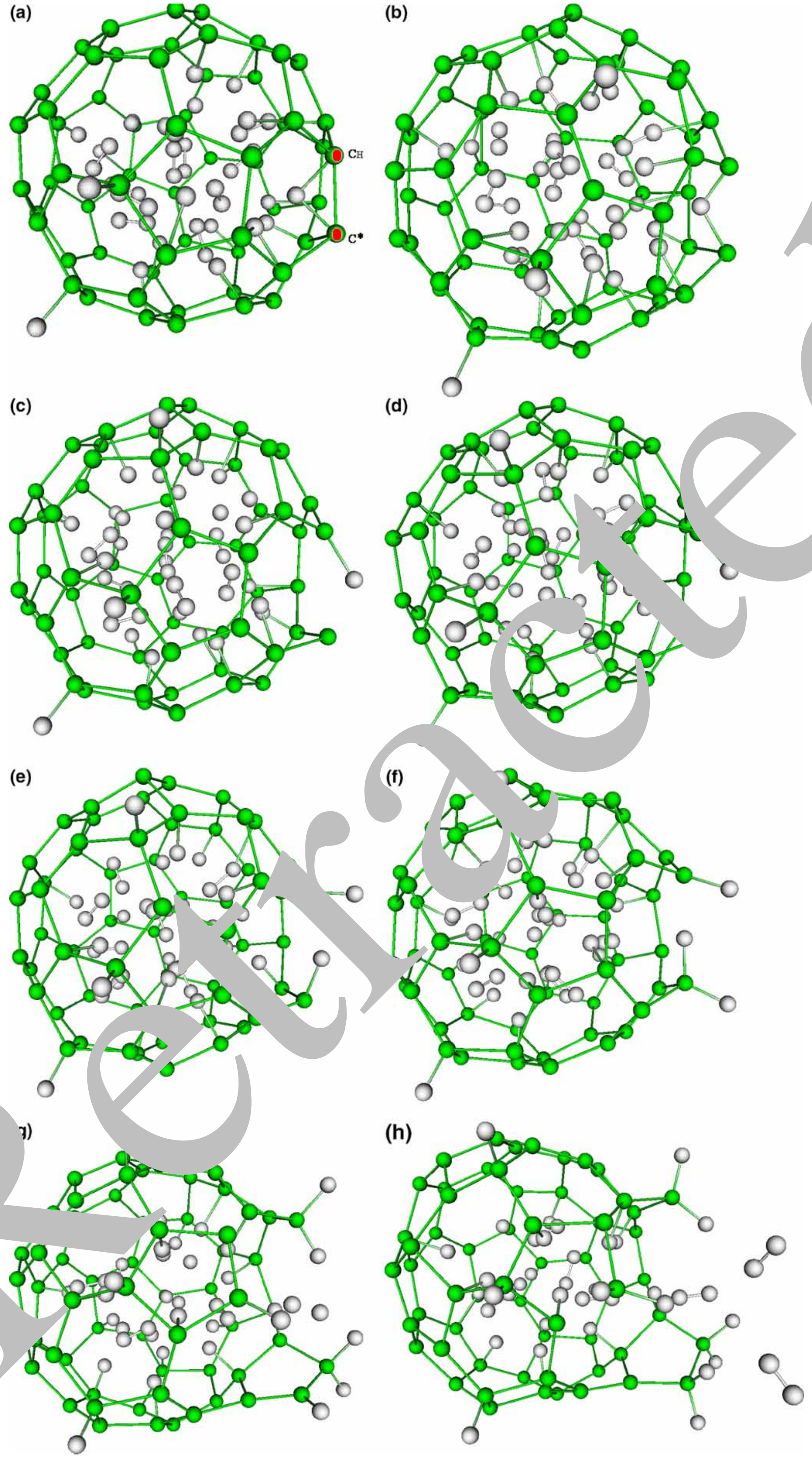

Figure 3. Snapshots of DFT-based tight binding MD simulations of $21H_2@C_{60}$ structure at 300 K: (a) 70 fs, (b) 80 fs, (c) 155 fs, (d) 170 fs, (e) 200 fs, (f) 300 fs, (g) 1000 fs and (h) 2000 fs.

of such systems that are weak but numerous nonbonding vdW interactions have not considered in their calculation.

4. Conclusions

Endohedrally hydrogen-doped C_{60} systems, $n\,H_2@C_{60}$ (n: 1–4, 9, 10, 12, 15, 19–21) have been theoretically investigated at the level of DFTB type treatment. Their binding energy (formation energy) and the H_2—H_2 and H_2–wall repulsive energies are calculated as functions of the number of encapsulated hydrogen molecules N_{H_2}.

The presently performed calculations revealed that C_{60} cage may accommodate quite a number of hydrogen molecules. Although structures with a large amount of encapsulated hydrogen are highly endothermic, they have metastable structures. It is found that for large n, some hydrogen atoms can be chemisorbed on the inner surface of the carbon cage; i.e. they can form covalent C—H bonds. The maximum number of hydrogen molecules inside C_{60}, which can form a metastable structure is determined to be $N_{H_2} = 20$. The mechanism of $21H_2@C_{60}$ breaking is studied by DFTB MD simulations at room temperature. It is shown that the hydrogen chemisorption, which weakens the fullerene C—C bonds, plays the key role in the opening of the nanocage.

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