Carbon 114 (2017) 635–641

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Quantum mechanical simulation reveals the role of cold helium atoms and the coexistence of bottom-up and top-down formation mechanisms of buckminsterfullerene from carbon vapor

Hu-Jun Qian [a, *], Ying Wang [b, **], Keiji Morokuma [c, d]

[a] State Key Laboratory of Supramolecular Structure and Materials, Institute of Theoretical Chemistry, Jilin University, Changchun, 130021, China
[b] State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China
[c] Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto, 606-8103, Japan
[d] Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, GA, 30322, USA

ARTICLE INFO

Article history:
Received 21 September 2016
Received in revised form
22 December 2016
Accepted 22 December 2016
Available online 24 December 2016

ABSTRACT

After the discovery of the highly symmetric Buckminsterfullerene (BF), a major goal of the fullerene community has been to understand its formation mechanism. In the various mechanisms proposed in literature, BF forms by either a bottom-up only or a top-down only process. Here we present a comprehensive quantum mechanical molecular dynamics simulation study, that reports for the first time the observations of multiple icosahedral symmetric I_h-C60 cages formations at the atomic level. Our simulation results demonstrate that helium atoms can not only reduce the temperature of the carbon species, but more importantly they can dramatically influence the reaction dynamics and eventually the fullerene yield through thermal collisions with carbon species. The direct evidence for coexistence of both bottom-up and top-down mechanisms are shown. Interestingly, rather than ceasing magically at C60, a similar process also applies to the formation of larger or smaller fullerenes. Prolonged vacuum annealing simulations show a typical top-down process where shrinking and surface healing of defective cages can enhance the I_h-C60 yield. Our results shed new light on the fundamental BF formation process in graphite laser ablation, in carbon arc-discharge experiments, as well as in the interstellar space.

1. Introduction

Discovery of the highly symmetric buckminsterfullerene (BF) [1], C_{60}, has led to an explosion in modern nanotechnology, especially in innovational advances related to its analogs, i.e., graphenes, carbon nanotubes and metallofullerenes. Despite their expanding applications, how these novel ordered structures, especially the *Ih*-C_{60} cage, self-assemble from carbon vapor remains a major mystery. In the past decades, many C_{60} formation mechanisms [2–12] were proposed based on available experimental [13–18] or interstellar [11,19] observations. Among these models, "party line" model [2], "pentagon road" model [3], "fullerene road" model [4], and "ring coalescence and annealing" [5] model were representatives in early 1990s'. Recently, a new "closed network growth" [12] (CNG) mechanism is advanced by Kroto and coworkers. Other than these, Irle and Morokuma proposed a "shrink hot giant road" (SHG) model based on extensive quantum mechanical molecular dynamics (QM/MD) simulations [20–25]. However due to complex chemical reaction environments and limitations in experimental techniques, most of these models were either partially hypothetical or postulated based on limited information during a particular stage of the C_{60} formation process. For instance, "ring coalescence and annealing" [5] model was proposed based on the observations of linear chains and ring structures in the initial stage [26–29]. The CNG model was evidenced by a further growth of C_{60} cage in carbon vapor [12]. While SHG simulations was initially performed with a high local carbon density. A major debate among these mechanisms is, whether C_{60} cage is formed via a bottom-up self-assembly or a top-down shrinking process. On the other hand, all of these models overlooked the effect of carrier helium gas atmosphere, which is known as an important factor leading to the high yield of BF, as has

* Corresponding author.
** Corresponding author.
E-mail addresses: hjqian@jlu.edu.cn (H.-J. Qian), ywang_2012@ciac.ac.cn (Y. Wang).

http://dx.doi.org/10.1016/j.carbon.2016.12.062
0008-6223/

been reported by Kroto, Smalley and their coworkers [1] in original BF discovery paper. In addition, they also reported that the post annealing process introduced by an 'integration cup' can enhance the yield of C_{60}. Specifically, (i) low content of helium was reported to generate a roughly Gaussian distribution of large cages, as can be found in Fig. 2c in Ref. [1]; (ii) A maximum helium density presented in the vaporization zone before the firing of the laser can lead to an obvious enhancement in the yield of C_{60} (Fig. 2b in Ref. [1]); (iii) Finally a presence of an 'integration cup' which can maximize the thermalization before expansion to cold vacuum led to an extremely high yield of C_{60} (Fig. 2C in Ref. [1]). Note that a recent simulation work [30] by Deng and coworkers has demonstrated that the inclusion of cold helium atoms has a crucial effect on both empty fullerene and metallofullerene formations. However, detailed formation mechanisms of empty fullerenes were not well discussed. Moreover, formations of I_h-C_{60} were not reported. Therefore, a fully disclosure of the formation mechanism of C_{60} under the influence of helium carrier gas is both fundamentally and practically important. It directly relates to a precisely controllable synthesis of C_{60} and its allotropies, which is a prerequisite for exploiting unique properties of these nanostructured carbon materials.

In this article the process of fullerene self-assembly from high temperature carbon vapor under the influence of cold carrier helium atoms is simulated via extensive QM/MD simulations based on density functional tight-binding (DFTB) potentials [31,32]. Encouragingly a high yield of fullerene cages with different sizes is achieved. We find that a proper content of helium can shift the cage size distribution from giant (>C_{80}) to the ones close to C_{60}/C_{70}. More importantly, we observe *for the first time* the multiple formations of C_{60}/C_{70} cages. In post annealing simulations mimicking "integration cup" effect reported in original discovery paper [1], we excitingly find two I_h-C_{60} formations. Our simulation results challenge the traditional view of the existing fullerene formation mechanisms in literature where fullerene cages form exclusively via either a bottom-up or a top-down mechanism. Instead, we demonstrate that C_{60} cage can form from both mechanisms. Our results provide new insights for understanding of the formation mechanism of fullerenes in laser ablation, in carbon arc-discharge, as well as in interstellar environments.

2. Simulation method and details

2.1. Density functional tight-binding method (DFTB)

DFTB is an approximate density functional theory method based on the tight binding approach and utilizes an optimized minimal LCAO Slater-type all valence basis set in combination with two-center approximation for Hamiltonian matrix elements [31,32]. The molecular orbitals obey the following generalized eigenvalue equation,

$$\sum_{\nu} c_{\nu i}\left(H_{\mu\nu} - \varepsilon_i S_{\mu\nu}\right) = 0, \tag{1}$$

the total energy is described as follows,

$$E_{tot} = 2\sum_{i} f_i \varepsilon_i + E_{rep}, \tag{2}$$

where $H_{\mu\nu}$ and $S_{\mu\nu}$ are Hamiltonian matrix and overlap matrix, respectively. f_i and ε_i represent fractional occupation and orbital energy of the ith Kohn-Sham (KS) molecular orbital. E_{rep} denotes the distance-dependent diatomic repulsive potential.

2.2. Molecular dynamics (MD) simulation

The MD simulations are performed using the DFTB + program. The non-charge-consistent (NCC) approximation of DFTB potential in combination with a finite electronic temperature approach [33,34] with electronic temperature of Te = 5000 K is adopted for the evaluation of energies and nuclear gradients for carbon species on the fly. C/He and He/He interactions are described by the classical UFF force field [35]. Initially, 120 C_2 units and 120 Helium atoms are generated homogeneously in a simulation box of $80 \times 80 \times 80$ Å^3 at a carbon density of 4.69×10^{20} cm^{-3}, which is at the experimental scale of 10^{20}~10^{21} cm^{-3}. 20 parallel simulations are performed with different initial positions and different initial velocities of carbon/helium atoms. Initial velocities of atoms are set according to Boltzmann distributions at corresponding temperatures. Each bottom-up trajectory is simulated for 200 ps Simulation time for the vacuum annealing simulations of preformed fullerene cages are all on nanoseconds scale. To accelerate the annealing simulation, the temperature is set at a relatively high value, T = 3000 K.

3. Results

3.1. Simulated cage size distribution

Simulations are performed in a periodic cubic box with a size of $80 \times 80 \times 80$ Å^3, which contains 120 homogeneously distributed C_2 units with a high temperature of T_C = 2500 K. The system has a carbon density of 4.69×10^{20} cm^{-3}, which is exactly on the experimental [3] scale. In order to simulate the helium effect, three systems containing 0, 40, 120 room temperature (T_{He} = 298 K) helium atoms are simulated. They are labeled as 'He-X-Y', where X indicates the number of helium atoms, Y is the ensemble temperature averaged from T_C and T_{He} according to equipartition theorem. The last system has a helium pressure of ~10 atm according to the idea gas equation, which is exactly the same as the helium source pressure used in Ref. [1]. Resulted cage size distributions from 20 parallel trajectories for three systems are shown in Fig. 1a, 1b and 1c respectively. Resulted cage/cluster sizes and the corresponding record time from each trajectory are listed in Tables S1-S3, all of the formed cages are visually shown in Figs. S1-S3, respectively. Clearly, in the pure carbon system with no helium, cages are almost equally distributed from C_{66} to C_{178}. With an increase of the helium content, resulted cages are obviously smaller. Especially cages in system 'He-120-1766K' are found much concentrated around C_{60} (Fig. 1c). The smallest cage has a size of C_{43}, which is in accord with the prediction of the "fullerene road" [4]. More importantly, we find two formations of C_{60} cages via a bottom-up self-assembly process in system 'He-120-1766K'. Although they have either fused pentagons or a linear chain attached on cage surface (see structures 'C60-0@trj1' and 'C60-11@trj10' in Fig. S3), it is the first time to directly observe C_{60} cage formations in QM/MD simulations. In order to simulate the annealing effect caused by an "integration cup" reported in Ref. [1], two additional sets of simulations are performed for the cages formed in system 'He-120-1766K'. Cages larger than C_{60} are casted to prolonged annealing simulations performed in vacuum. For all vacuum simulations, periodic boundary conditions are switched off. These simulations are referred to as 'post vacuum annealing (PVA) simulations' in the following text. The resulted cage/cluster sizes and record time are listed in Table S4. On the other hand, in order to simulate a possible further growth of small cages, cages smaller than C_{80} are annealed in a smaller box of $40 \times 40 \times 40$ Å^3 with a low-density atmosphere of 10 C_2 units and 10 helium atoms. They are referred to as 'post growth (PG) simulations'. To accelerate the annealing process in both PVA and PG