Formation of N-doped C$_{60}$ Studied by \textit{Ab Initio} Molecular Dynamics Simulations

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A large-scale \textit{ab initio} molecular dynamics simulation of the insertion of nitrogen atom into C$_{60}$ is carried out by using the all-electron mixed-basis approach. In this approach, a one-electron wave function is expressed by superposing truncated numerical atomic orbitals and plane waves. The LDA (local density approximation) is used to calculate electronic states. 4169 plane waves having a cut-off energy of 7\textit{Ry} (1\textit{Ry}=13.6\textit{eV}), and 1s, 2s and 2p atomic orbitals for carbon and nitrogen atoms are used in this calculation. Consequently, we found that with proper incident kinetic energy around 80\textit{eV} (1\textit{eV} = 1.602 \times 10^{-19} \text{J}) the nitrogen-encapsulated C$_{60}$, N@C$_{60}$ is finally realized by a collision of a nitrogen atom against C$_{60}$.

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1. Introduction

Since the discovery of fullerenes$^1$ and the synthesis of large amount of C$_{60}$, numerous experimental studies for endohedrally doped or exohedrally doped fullerenes with foreign atoms have been undertaken by resorting to arc-desorption or laser vaporization techniques.$^3$ Most of the studies have been directed toward the encapsulation of a metal atom into a fullerene with charge transfer of one or more electrons. Another approach is the encapsulation of a noble gas atom. For example, Saunders \textit{et al.}$^4$ discussed the possibility of the process of encapsulation of a noble gas into fullerene under a high pressure and high temperature condition. On the other hand, the possibility of encapsulation of a covalent atom such as nitrogen was studied by Murphy \textit{et al.}$^5$ In their experiment, nitrogen ions released from ion source collide with C$_{60}$ molecules in the C$_{60}$ thin film. They reported that the nitrogen-encapsulated fullerene, N@C$_{60}$, is created.

In the present paper, we will perform \textit{ab initio} molecular dynamics simulations of a collision between nitrogen atom and C$_{60}$ and show that N@C$_{60}$ can be created under certain conditions of the collision.

2. Methodology

\textit{Ab initio} molecular dynamics simulations, which are now widely performed in the field of condensed matter physics, are based on the adiabatic approximation and the density functional theory (DFT). In the present work, we use the local density approximation (LDA) in the DFT. Once a density functional has been given by this approximation, the remaining work is to solve for the electronic states under the effective one electron Hamiltonian. Determining the electronic states enables us to calculate the force acting between nuclei. Then, the atomic position is updated. Following this, the electronic states are solved again for the new atomic positions. For the calculation of electronic states, our all-electron mixed-basis approach$^6-8$ is used.

The all-electron mixed-basis approach uses the linear combination of plane waves and atomic orbitals to describe the one-electron wave function in a unit cell. Here, 4169 plane waves are used, as well as five (1s, 2s, 2p$_x$, 2p$_y$, 2p$_z$) atomic orbitals for both carbon and nitrogen atoms. For plane waves, a unit cell (a super cell) is divided into 64 \times 64 \times 64 mesh for ease of using the fast Fourier transformation. (One mesh equals 0.0196\text{nm}.) In handling atomic orbitals, we use nonoverlapping atomic spheres in which the radial direction is divided by a logarithmic mesh. In carrying out the \textit{ab initio} molecular dynamics method, we renew the electronic states by applying the steepest descent method five times during the atomic position renewal operation to get the convergence of the electronic states. The time step is set at $\Delta t = 0.1\text{fs}$. In the calculation, we use Newton’s equation of motion for nuclei.

3. Simulations and Results

We first investigate the possibility of the penetration of nitrogen atom through the cage of C$_{60}$ (\textit{i.e.}, the creation of N@C$_{60}$), when the nitrogen atom hits the center of a six-membered ring of C$_{60}$ with a certain initial kinetic energy. In particular, we are interested in the threshold energy above which the nitrogen atom can be encapsulated. For this purpose, we assume two initial kinetic energies for the nitrogen atom: 40\text{eV} and 80\text{eV}. Next, in order to investigate the possibility that NC$_{59}$ is created instead of N@C$_{60}$ by emitting one carbon atom after collision, we put one nitrogen atom inside the cage and one carbon atom outside the cage of C$_{59}$, along the line connecting the missing carbon position and the center of C$_{59}$, and start the simulation with zero initial velocity. Therefore, we perform altogether three simulations.

The results of these three simulations are as follows:

1. When a nitrogen atom is launched vertically toward the center of the six-membered ring of C$_{60}$ at 40\text{eV}, the nitrogen atom collides with the surface of C$_{60}$ and is rebounded (Fig. 1).

2. When a nitrogen atom is launched vertically toward the center of the six-membered ring of C$_{60}$ at 80\text{eV}, the nitrogen atom penetrates through the six-membered ring and is
encapsulated to generate N@C₆₀ (Fig. 2).

3. When one of carbons on C₆₀ shifts outward (a radius of 0.49 nm) and a nitrogen atom shifts inward by 0.13 nm (a radius of 0.22 nm), we perform a simulation at zero initial speed. We confirm that the carbon atom is pulled inward by a strong force, resulting in the formation of N@C₆₀ (Fig. 3).

From the first two results, it is found that the threshold energy needed for the penetration of nitrogen atom through a six-membered ring of C₆₀ is between 40 eV and 80 eV. Since the simulations require huge amount of CPU time, we could not perform another simulation with kinetic energy between 40 eV and 80 eV. To determine more precise threshold is left for the future study. On the other hand, from the third simulation, the possibility that NC₉₉ is created by emitting one carbon atom from the C₆₀ cage after collision is found to be small.

4. Concluding Remarks

We have investigated theoretically the possibility of creating nitrogen-encapsulated fullerene by using the all-electron mixed-basis approach which has been originally developed by ourselves. Our results are summarized as follows:

When a N atom is launched at 40 eV, the encapsulation does not take place. However, when a N atom is launched at 80 eV, the encapsulation takes place. On the other hand, for the simulation starting from the initial condition that a carbon atom in C₆₀ is shifted outward and an N atom is put inward from the original carbon site, the carbon atom is pulled toward C₉₉, resulting in the formation of N@C₆₀. The present simulation reveals that there is a strong possibility of N@C₆₀ being formed. This conclusion itself agrees with the experimental evidence by Murphy et al.⁵ However, in the paper by Grupp et al.,⁹ they argued that the nitrogen atom is trapped
right at the center of C_{60}, although, in our precise analysis, we find that it is trapped at 0.13 nm away from the center due to the covalent bonding between N and C_{60}. Our results agree also with the experimental results by Oku et al.,\textsuperscript{[10]} who showed that encapsulation takes place at 100 eV. However, because there is a possibility of heterofullerene such as C_{59}N being generated by changing the nitrogen atom launching conditions, further study is required. For the other study of inserting atoms of different kind into fullerenes, refer to the Refs. 11)–13). These references report both experimental and theoretical works, and, for the theoretical part, they employ the same simulation technique of the all-electron mixed-basis approach as the present paper.

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