Ab Initio Molecular Dynamics Simulations for Collision between C60 - and Alkali-Metal Ions: A Possibility of Li@C60

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Ab Initio Molecular Dynamics Simulations for Collision between C_{60}^- and Alkali-Metal Ions: A Possibility of Li@C_{60}

Kaoru Ohno, Yutaka Maruyama, Keivan Esfarjani, and Yoshiyuki Kawazoe
Institute for Materials Research, Tohoku University, Sendai 980-77, Japan

Noriyoshi Sato, Rikizo Hatakeyama, and Takamichi Hirata
Department of Electronic Engineering, Tohoku University, Sendai 980-77, Japan

Michio Niwano
Institute of Electrical Communication, Tohoku University, Sendai 980-77, Japan
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Collisions between C_{60}^- and alkali-metal ion are investigated by an *ab initio* molecular dynamics simulation at 1000 K. When Li^+ with kinetic energy ~5 eV hits the center of a six-membered ring of C_{60}^-, Li@C_{60} is created. If either the kinetic energy is lower or the collision occurs off center, the Li^+ ion stays outside, and C_{60} is deformed by the shock. In some cases, several bonds of C_{60} break after the bombardment; this may make the insertion of alkali-metal ion easier. [S0031-9007(96)00138-X]

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Endohedral fullerenes have recently attracted considerable interest. Experimentally, it has been confirmed that at least more than one lanthanum [1,2], yttrium [3,4], and scandium [5] atoms can be encapsulated inside C_{82} or C_{84} in fullerene-formation processes using arc-discharge vaporization of composite rods made of graphite and metal oxide. Also, laser vaporization techniques have revealed the production of endohedral C_{60}, in which an alkali-metal atom such as potassium or cesium is trapped [1,6]. On the other hand, it has been reported than endohedral $[Li@C_{60}]^+$ and $[Na@C_{60}]^+$ species are formed during collisions of alkali-metal ions with C_{60} vapor molecules [7]. (Here, the notation Li@C_{60}, for example, means a LiC_{60} molecule with one Li atom encapsulated inside a C_{60} cage.) Recently, in a plasma state consisting of fullerene and alkali-metal ions, endohedral complexes such as K@C_{60}, K@C_{58}, ..., have been created [8]. Because of the abundance of C_{60} in the usual fullerene production, endohedral C_{60} should have more practical importance in the future.

Ab initio calculations concerning the electronic states have been done so far for endohedral fullerenes such as Na@C_{60} [9,10], La@C_{60} [11,12], and La@C_{82} [13]. References [9] and [10] investigated the optimal position of the encapsulated atom as a function of distance from the center of C_{60} and concluded that Na is trapped just below the cage surface. According to those results, the energy gain does not change much with the angle. Nagase and Kobayashi [13] suggested that La is located just below the center of a six-membered ring of C_{82}. On the other hand, several simple analytic calculations concerning the radial vibration of the encapsulated atoms [14], the potential function inside the cage [15,16], and the deformation of the cage structure [17] have been performed for Li@C_{60}, Na@C_{60}, and other complexes. However, no theoretical work has been done so far concerning the formation process of the endohedral C_{60}, even, for example, in the simplest case of a plasma state. Needless to say, since it is essentially dynamic, only an *ab initio* molecular dynamics simulation can offer the desirable information about the process of encapsulation.

In this Letter, we confine ourselves to the collision between Li^+ and C_{60}^- in a plasma state, where collisions may proceed more effectively due to the electrostatic interaction, and report, for the first time, the result of a constant temperature *ab initio* molecular dynamics simulation yielding an ideal Li@C_{60}. Also, we present briefly our result in the collision between Na^+ and C_{60}^-, and discuss generally the possibility and mechanism of the encapsulation of alkali-metal elements in C_{60}.

The electronic states are treated in an all-electron mixed-basis approach within the framework of the local density approximation (LDA), with Fermi-Dirac (FD) distribution [18,19] of the excited levels. The method of simulation employed here is the same as our previous work concerning the stability and reactivity of C_{60} [20]. In the present simulation, we put one C_{60} molecule and one alkali-metal atom in a supercell with given initial velocities. Once the electronic states are well converged by the steepest descent (SD) method, a charge transfer from the alkali-metal atom to the C_{60} molecule automatically takes place. In the calculation, we used 60×5 $(1s, 2s, 2p_x, 2p_y, 2p_z)$ Slater-type atomic orbitals (STO's) and 2969 plane waves. For the damping factors of the 1*s* and other STO's, we used, respectively, $1/0.18$ a.u.$^{-1}$ and $1/0.24$ a.u.$^{-1}$. We divided the supercell into $64 \times 64 \times 64$ meshes and set 1 a.u. = 0.52918 Å = 2.7 meshes. We set $\Delta t = 4$ a.u. ~ 0.1 fs and perform six SD iterations between two adjacent updations of atomic positions in order to converge the electronic states.

We performed several different simulations by changing the initial kinetic energy (KE) of the alkali-metal element and the position of collision. All the simulations

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have been performed at $T = 1000$ K (similar to the experimental condition [8]) by a velocity rescaling and a FD distribution. In the following, we show just the conditions assumed in the simulations and the main results. To choose the value of the KE, we also referred to experiments [7,8].

(A) Li^+ ion with KE = 5 eV hits the center of a six-membered ring of C_{60}^- perpendicularly. In this case, the Li^+ ion penetrates into the cage through the center of the six-membered ring without difficulty, since the ionic radius of Li^+ is ~ 0.6–0.9 Å, and the hole of a six-membered ring is of the same size or slightly smaller. That is, a direct penetration of a Li ion through the center of a six-membered ring occurs with suitably high kinetic energy of the Li^+ ion. The Li^+ ion passes deeply into C_{60} (at a distance of 1.6 Å from the six-membered ring) and comes back to be trapped at a distance of 1.0 Å from the center of the same six-membered ring (see Fig. 1). (Because of a velocity rescaling to make the temperature of the whole $Li^+ + C_{60}^-$ system constant, the KE of the Li^+ ion is still considerably reduced after going through the cage. But, this is not a realistic feature of the present simulation.) The final position of the Li^+ ion near the center of a six-membered ring is more favorable because of the initial condition of insertion (vertically, toward the center of a six-membered ring) and because of the symmetry. The stable position of Li^+ very close to the cage surface is in reasonable agreement with the recent x-ray image of $Y@C_{82}$ [21], although the encapsulated ion is different. According to our estimate from the calculated forces, the potential energy for the Li^+ ion at the cage center is about 4 eV higher than the potential minimum at the stable position near the cage surface. There are at least two local energy minima inside the cage; one is along the six-hold axis, as was realized in this simulation, and the other along the five-hold axis. From our simulation, we found that, when a Li^+ ion with KE = 5 eV hits the center of a five-membered ring of C_{60}^- perpendicularly, the Li ion cannot penetrate into the cage and stays outside on the center of the five-membered ring. This is because the hole in the five-membered ring, which also has a transferred charge, is too small even for Li^+ to go through.

(B) Li^+ ion with KE = 1 eV hits the center of one six-membered ring of C_{60}^- perpendicularly. In this case, the Li^+ ion bounces several times on the cage of C_{60} and ends up at the center of a six-membered ring outside the cage. By the shock of the initial hit and successive collisions, the cage deforms considerably (see Fig. 2).

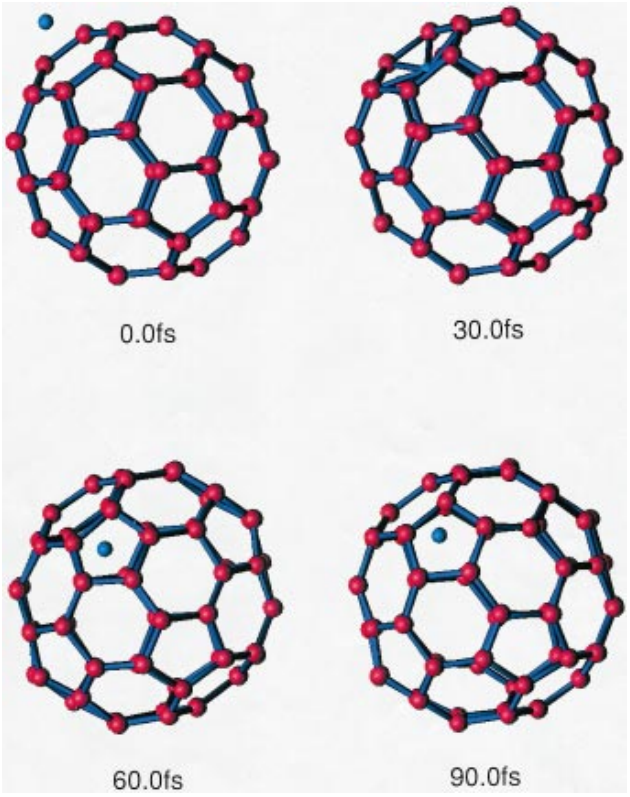

FIG. 1 (color). Snapshots of the simulation (A), where Li^+ hits with 5 eV kinetic energy the center of a six-membered ring of C_{60}^-. The figures show only the positions of the carbon atoms in C_{60} (red circle) and Li atom (blue circle). In this case, after 60 fs, $Li@C_{60}$ is created.

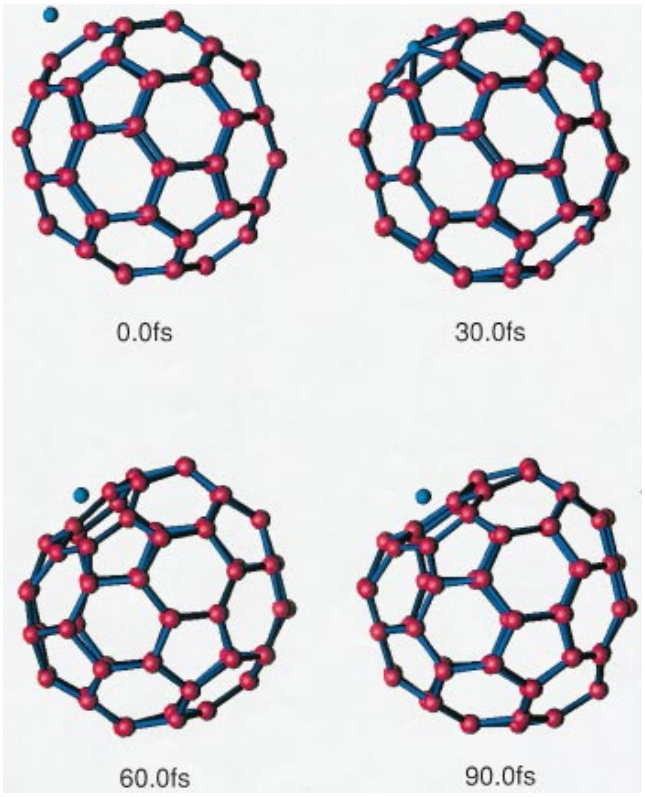

FIG. 2 (color). Snapshots of the simulation (B), where Li^+ hits with 1 eV kinetic energy the center of a six-membered ring of C_{60}^-. The figures show only the positions of the carbon atoms in C_{60} (red circle) and Li atoms (blue circle). In this case, Li stays outside the cage.

(C) Li^+ ion with KE = 5 eV hits the C_{60}^- near a double bond (off center of a six-membered ring) perpendicularly. In this case, the Li^+ ion bounces several times on the cage of C_{60} and ends up bound to the outside of the cage, similar to (B). By the shock of the initial and successive collisions of the Li^+ ion, the cage deforms extremely near the position of the collision (see Fig. 3). All these simulations have been carried out for 75–90 fs, thus further annealing is presumably possible.

In the real experimental situation, the mean time interval for alkali-metal positive ions with average KE of 5 eV to hit the center of a six-membered ring of C_{60}^- molecules in a direction nearly perpendicular to the cage sphere would be $\sim 10^{-10}$ sec if 10^{11} lithium ions and the same number of C_{60} ions exist in a 100 cm^3 box. Therefore, it is reasonable to consider that the direct insertion process, as in the simulation (A), is the mechanism of the Li@C_{60} formation. However, the situation might be somewhat different in the case of alkali metals heavier than Li. The ionic radius of Na^+ is ~0.95–1.16 Å, slightly larger than the radius of the hole of a six-membered ring, while the radius of K^+ is ~1.33–1.52 Å much too large to enter through the six-membered ring. Therefore, the direct insertion process is rather unlikely because of the strong overlap between the electronic clouds of the cage surface and the alkali-metal ion. Nevertheless, there is experimental evidence [7] that Na^+ is encapsulated in C_{60}, if Na^+ obtains somewhat higher kinetic energy (~20 eV). In addition, K@C_{60} was detected in a recent experiment using a plasma state of C_{60}^- and K^+ (≤10 eV) [8].

In order to find out the mechanism of the insertion of Na^+ ion, we performed a simulation of a direct hit of Na^+ to the center of a six-membered ring of C_{60}^-. For this purpose, we used 128 × 128 × 128 meshes and set 1 a.u. = 5.4 meshes in order to represent the sharp 1*s* core orbital of Na precisely enough. In this case, we did not succeed in obtaining the encapsulation even at the kinetic energy up to 50 eV of Na^+, in contrast to the case (A) yielding Li@C_{60}. What we obtained instead is a deformed C_{60} with Na adsorbed outside, as shown in Fig. 4. Here, a remark should be made on the resulting structure of the complex: A relatively large hole is created on the cage sphere which has a radius of ~1.7 Å. This result suggests a new mechanism of the alkali-metal encapsulation which is different in part from the direct insertion process (A): The encapsulation may proceed as a result of the insertion through a hole which was created in the cage of C_{60} due to the bombardment

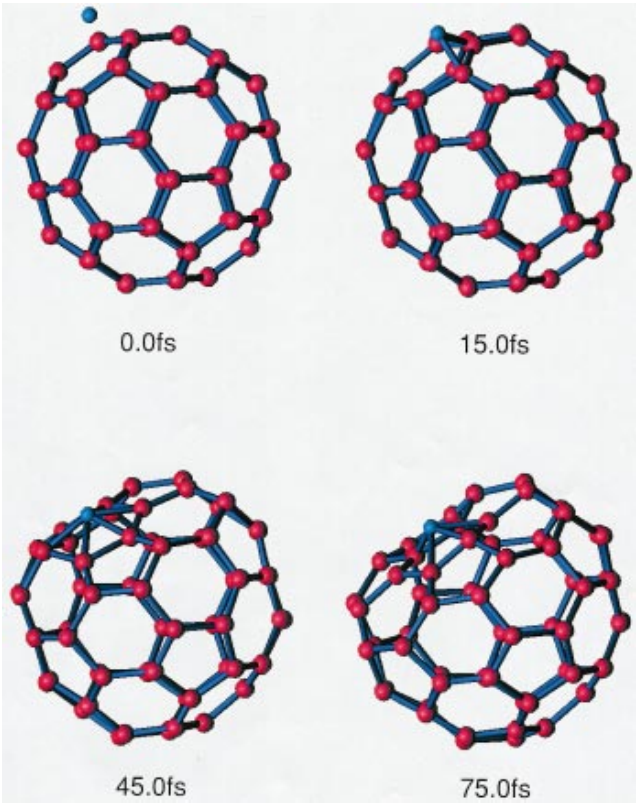

FIG. 3 (color). Snapshots of the simulation (C), where Li atom hits with 5 eV kinetic energy near the center of a C-C bond of C_{60}. The figures show only the positions of the carbon atoms in C_{60} (red circle) and Li atom (blue circle). In this case, a large deformation of C_{60} due to the bombardment occurs.

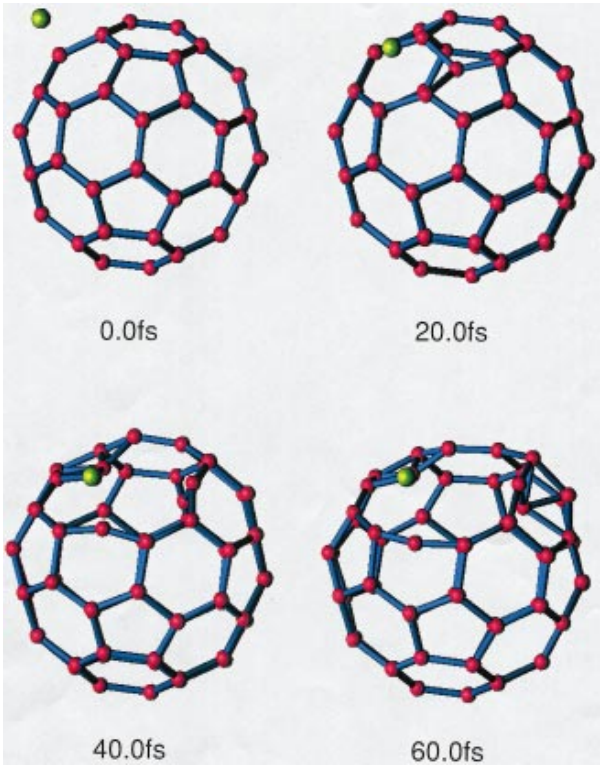

FIG. 4 (color). Snapshots of the atomic positions of C_{60} and Na in the case where a Na atom hits with 50 eV kinetic energy the center of a six-membered ring of C_{60}. In contrast to the case (A) of Li, Na@C_{60} is not created by this direct insertion process.

of other alkali-metal ions. In other words, the bond breaking after the bombardment may make the insertion of alkali-metal ion easier than the simulation (C). After the insertion of Na^+ ion through the largely open hole, the original C_{60} cage is reconstructed after annealing. This procedure is expected to take a fundamentally longer time than the direct insertion, and it is not possible to simulate the process even if the fastest supercomputer would be dedicatedly used for one year. Similarly, in order to realize the C_2 loss, which has been observed experimentally [7,8], much longer time simulations, as well as the simulations involving multiple collisions, are required, although we could realize the C_2 loss of C_{60} at higher temperatures (>4500 K) even at short times [20]. Such heavier calculations are left for future studies. In conclusion, we can say that there is a strong possibility to create alkali-metal encapsulated C_{60} by a plasma processing technique with direct and multiple-step insertion processes.

Finally, we briefly comment on the related experimental works now in progress. The plasma experiment of the Li^+ and C_{60}^- system is highly desirable, and our group is planning to do it. T. Ohtsuki [22] at the Laboratory of Nuclear Science of Tohoku University is revealing that a first row isotope element such as ^{7}Be can penetrate into the C_{60} cage to reproduce $^7Be@C_{60}$ by the recoil of the nuclear reactions. ($^7Be@C_{60}$ later becomes $^7Li@C_{60}$ by the EC decay.) We are also collaborating with him and found from a similar simulation that Be can be inserted from the outside with KE = 5 eV. This is also the experiment supporting the present simulation.

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