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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	41
number	2
page range	183-186
year	1996-03-22
URL	<a href="http://hdl.handle.net/10097/28572">http://hdl.handle.net/10097/28572</a>

# Ab-initio Molecular Dynamics Simulation of Li Insertion in C<sub>60</sub>\*

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(Received November 30, 1995)

Complexes composed of fullerenes and metal elements offer important examples as new nanomaterials in the field of materials design. In the collisions between C<sub>60</sub><sup>-</sup> and Li<sup>+</sup> in plasma state, there is a possibility that the endohedral fullerene, Li@C<sub>60</sub> is created as well as Li@C<sub>58</sub> and so on. To study this phenomenon theoretically, we perform an all-electron mixed basis *ab initio* molecular dynamics simulation at 1,000K which was developed by ourselves. When Li<sup>+</sup> with the kinetic energy  $\sim 5eV$  hits the center of a six-membered ring of C<sub>60</sub><sup>-</sup>, an endohedral complex, Li@C<sub>60</sub> is created. This direct insertion process is possible because the ionic radius of Li<sup>+</sup> is shorter than the radius of a six-membered ring. However, if either the kinetic energy is lower or the collision occurs off-center, the Li<sup>+</sup> ion stays outside and C<sub>60</sub> is deformed by the shock.

KEYWORDS: C<sub>60</sub>, Li, endohedral fullerene, ab-initio molecular dynamics

## 1. Introduction

Interactions between fullerenes and metal elements have been studied with much current interest in the field of physics and chemistry, and especially in the field of materials design. One of the most dramatic phenomena is an encapsulation of metal elements inside the cage structure of fullerenes or nanotubes. That has also an industrial importance as a candidate of a new catalyst. Also, the endohedral complexes have a basic importance as a candidate of pseudoatoms.

The experimental evidences of the creation of endohedral fullerenes have rather been concentrated to those composed by higher fullerenes and heavy metal elements, such as La@C<sub>82</sub>, [1,2] Y@C<sub>82</sub>, [3,4] and Sc@C<sub>84</sub>. [5] Those endohedral complexes are created by using arc-discharge vaporization of composite rods made of graphite and metal-oxide. However, since the natural abundance of C<sub>82</sub> and C<sub>84</sub> are very small compared to C<sub>60</sub>, there is a question in the future possibility of their mass production.

On the other hand, the production of endohedral C<sub>60</sub>, in which an alkali-metal atom like potassium or cesium is trapped, [1,6] has been reported by using a laser vaporization technique. Or, more clearly it has been pointed out that endohedral [LiC<sub>60</sub>]<sup>+</sup> and [NaC<sub>60</sub>]<sup>+</sup> species are formed during collisions of alkali-metal ions with C<sub>60</sub> vapor molecules. [7] Quite recently, in a plasma state consisting of fullerene and alkali-metal ions, endohedral complexes such as K@C<sub>60</sub>, K@C<sub>58</sub>, ... have been created. [8] Another possibility of creating Li@C<sub>60</sub>, Be@C<sub>60</sub>, O@C<sub>60</sub>, and so on (endohedral C<sub>60</sub> with the first low elements) is to use the nuclear reaction ( $\beta$  decay) by inserting slow neutrons in a C<sub>60</sub> crystals. [9] Because of the abundance of C<sub>60</sub> in the usual fullerene production, endohedral C<sub>60</sub> should have more practical importance in the future.

So far, a lot of *ab-initio* calculations have been performed for endohedral fullerenes like Na@C<sub>60</sub>, [10,11] La@C<sub>60</sub>, [12,13] and La@C<sub>82</sub>. [14] References 10 and 11 investigated the optimal position of the encapsulated

atom as a function of distance from the center of C<sub>60</sub>, and concluded that Na is trapped just below the cage surface. On the other hand, several simple analytic calculations concerning the radial vibration of the encapsulated atoms, [15] the potential function inside the cage, [16,17] and the deformation of the cage structure [18] have been performed for Li@C<sub>60</sub>, Na@C<sub>60</sub> and other complexes.

However, no theoretical work has so far been done concerning the formation process of the endohedral C<sub>60</sub> even in the simplest case of a plasma state, for example. 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 the present paper, we confine ourselves to the collision between Li<sup>+</sup> and C<sub>60</sub><sup>-</sup> in a plasma state, and report the result of a constant temperature *ab-initio* molecular dynamics simulation yielding an ideal Li@C<sub>60</sub>. [19]

## 2. Methodology

The method of simulation employed here is the same as our previous work concerning the stability and reactivity of C<sub>60</sub>. [20] We assume the Born-Oppenheimer (BO) adiabatic approximation, and consider the grand canonical ensemble for the electronic states, where both the temperature and the chemical potential are fixed. For usual system, it is natural for the electronic states to maintain the same temperature as assumed for the atomic dynamics. In the present study, a finite temperature effect of the electron system is first taken into account by the assumption of the Fermi distribution. We adopt the density functional formalism extended to the grand canonical ensemble by Mermin. [21] We then use the corresponding local density approximation (LDA) due to Gunnarsson and Lundqvist. [22] For the exchange-correlation functional,  $F^{xc}[\rho]$ , however, we utilize the X $\alpha$  method with  $\alpha = 0.7$ . Within this formalism, the charge density is given by

$$\rho(\mathbf{r}) = 2 \sum_i \frac{\psi_i^*(\mathbf{r})\psi_i(\mathbf{r})}{e^{(\epsilon_i - \mu)/k_B T} + 1}, \quad (1)$$

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where the spin duplicity at each level gives the prefactor 2. The chemical potential  $\mu$  is determined by

$$2 \sum_i \frac{1}{e^{(\epsilon_i - \mu)/k_B T} + 1} = N \quad (2)$$

with  $N$  as the total number of electrons in the system.  $\epsilon_i$  and  $\psi_i(\mathbf{r})$  are the eigenvalue and eigenfunction of a one-particle Hamiltonian  $H$

$$H = -\frac{\hbar^2}{2m} \nabla^2 + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \sum_n \frac{Z_n e^2}{|\mathbf{r} - \mathbf{R}_n|} + v^{xc}(\mathbf{r}), \quad (3)$$

where  $R_n$  denotes the position of the  $n$ -th atom,  $Z_n$  the nucleous charge of the  $n$ -th atom, and  $v^{xc}(\mathbf{r}) = \delta F^{xc}[\rho]/\delta \rho(\mathbf{r})$ .

In the all-electron mixed-basis approach, wave functions are expanded by not only plane waves, but also Slater-type atomic orbitals (STO's).[23,24] This method has following several advantages;

1. Reduction of the number of plane waves.
2. Account of core electrons.
3. No usage of pseudopotential.
4. Analytic evaluation of forces to some extent.
5. Reduction of both memory and CPU time.

Note that the pseudopotential approach requires a large number of plane waves, typically 100,000!, [25] even for a single  $C_{60}$ . (Our method can reproduce fairly well the result of Ref.[25] in the fcc  $C_{60}$  crystal with much smaller number of plane waves.[23])

To achieve convergence of electronic states and orthogonalize different electronic levels, we adopt Gram-Schmidt orthogonalization and Payne algorithm,[26] which are commonly used as a usual steepest descent (SD) algorithm. Moreover, since basis functions are not mutually diagonal in mixed-basis approach, we start from the modified equation which guarantees the orthogonality;

$$\mu S \dot{\Psi}_i = -(H - \Psi_i^\dagger H \Psi_i S) \Psi_i, \quad (4)$$

where  $\mu$  denotes the friction constant for updating electron wave functions  $\Psi_i$ ,  $H (= \langle k|H|l \rangle)$  the Hamiltonian of the electrons, and  $E$  the total energy of the system.

The distinction of the present equations of the mixed-basis approach from those of the original PW approach[26-30] is the presence of the overlap matrix  $S (= \langle k|l \rangle)$  in Eq.(2), which is due to the fact that the bases are not mutually orthogonal. Introducing the lower half triangular matrix  $U$  which satisfies  $S = UU^\dagger$ , and writing  $U^\dagger \Psi_i = \Phi_i$  and  $H' = U^{-1} H U^{-1}$ , we have

$$\mu \dot{\Phi}_i = -(H' - \Phi_i^\dagger H' \Phi_i) \Phi_i. \quad (5)$$

Once we adopt this representation, the main algorithm of updating the wave function  $\Phi_i$  is the same as the original PW approach.

In the present simulations, we put one  $C_{60}$  molecule and one alkali-metal atom in a supercell with given initial velocities. Five STO's (1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub>) being located at each atomic site, and 2,969 plane waves are adopted as a basis set. For the exponential damping factors of the 1s and other STO's, we used 1/0.18a.u.<sup>-1</sup>

and 1/0.24a.u.<sup>-1</sup>, respectively. Especially, 2s and 2p STO's are chosen to be rather narrow, in order to avoid overlaps between neighboring atoms. We expect that the extended part of the wave function is described mainly by PW's. We divided the supercell into 64 × 64 × 64 meshes and set 1a.u.=0.52918Å=2.7meshes. We set  $\Delta t = 4a.u. \sim 0.1fs$  and perform six SD iterations between two adjacent updations of atomic positions in order to converge the electronic states. Matrix elements and forces associated with STO's are evaluated analytically as far as possible. For the computation, we used HITAC S-3800/380 supercomputer(24GFLOPS) at our Institute with parallel coding. Each SD iteration step took about 20 seconds, and the present code requires 370MB in main memory. We adopt 4a.u.=0.1fs as the basic time step  $\Delta t$  for all simulations.

For each simulation, we first fix atomic positions until the electronic states well converge to the BO surface. We used conventional matrix-diagonalization to achieve good convergence. Once the electronic states are well converged by the subsequent steepest descent (SD) method, a charge transfer from the alkali-metal atom to the  $C_{60}$  molecule automatically takes place. Then, starting from these converged electronic states, all the constraints on atomic positions are released. Atomic dynamics are governed by classical mechanics with the Hellmann-Feynman force at constant temperature by usual velocity rescaling technique. We perform typically 6 SD iterations of electronic states before each updation of atomic positions, and one velocity rescaling in every 10 atomic movements. At each SD step, we make new electronic charge density by mixing 50% with the density at the last step in order to stabilize the convergence.

### 3. Results and discussions

We performed several different simulations by changing the initial kinetic energy(K.E.) of the alkali-metal element and the position of collision. All the simulations have been performed at  $T = 1,000K$  by a velocity rescaling and a FD distribution. In the following, we show just the conditions assumed in the simulations and the main results.

(A)  $Li^+$  ion with K.E.=5eV hits the center of a six-membered ring of  $C_{60}^-$  perpendicularly. In this case,  $Li^+$  ion penetrates into the cage through the center of the six-membered ring without difficulty, since the ionic radius of  $Li^+$  is 0.6 ~ 0.9Å, and the hole of a six-membered ring is of the same size or slightly smaller. That is, a direct penetration of 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  $C_{60}$  and comes back to be trapped 1.0Å below the center of the same six-membered ring(see Fig.1).

The final position of  $Li^+$  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. There are at least two local energy minima inside the cage; one is along the six-fold axis and the other along

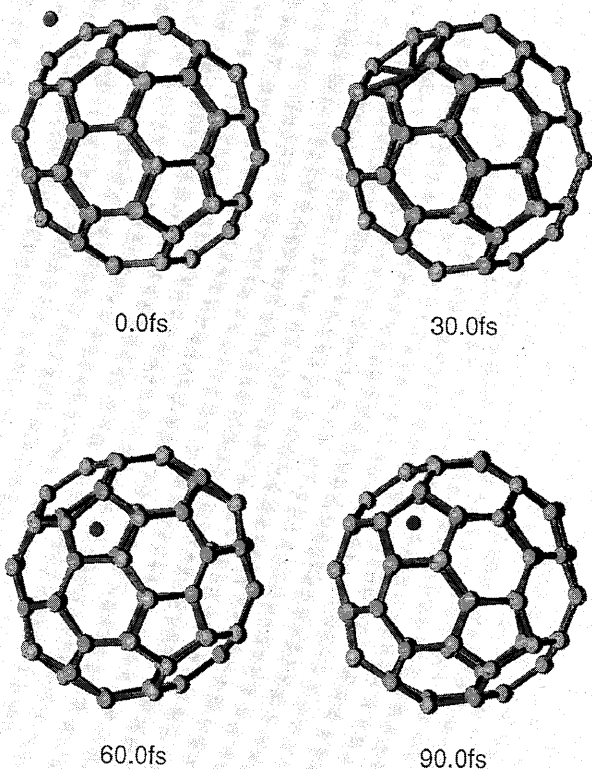


Figure 1. Snapshots of the simulation (A), where  $\text{Li}^+$  hits with K.E.= 5 eV the center of a hexagon of  $\text{C}_{60}^-$ .

the five-fold axis. From our simulation we found that, when  $\text{Li}^+$  ion with K.E.=5eV hits the center of a five-membered ring of  $\text{C}_{60}^-$  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  $\text{Li}^+$  to go through.

(B)  $\text{Li}^+$  ion with K.E.=1eV hits the center of one six-membered ring of  $\text{C}_{60}^-$  perpendicularly. In this case,  $\text{Li}^+$  ion bounces several times on the cage of  $\text{C}_{60}$  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).

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

In the real experimental situation, the mean time interval for alkali-metal positive ions with average K.E. of 5eV to hit the center of a six-membered ring of  $\text{C}_{60}^-$  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  $\text{C}_{60}$  ions exist in a  $100\text{cm}^3$  box. Therefore, it is reasonable to consider that the direct insertion process as in the simulation (A) is the mechanism of the  $\text{Li}@\text{C}_{60}$  formation. However, the situation might be somewhat different in the case of alkali-metals heavier

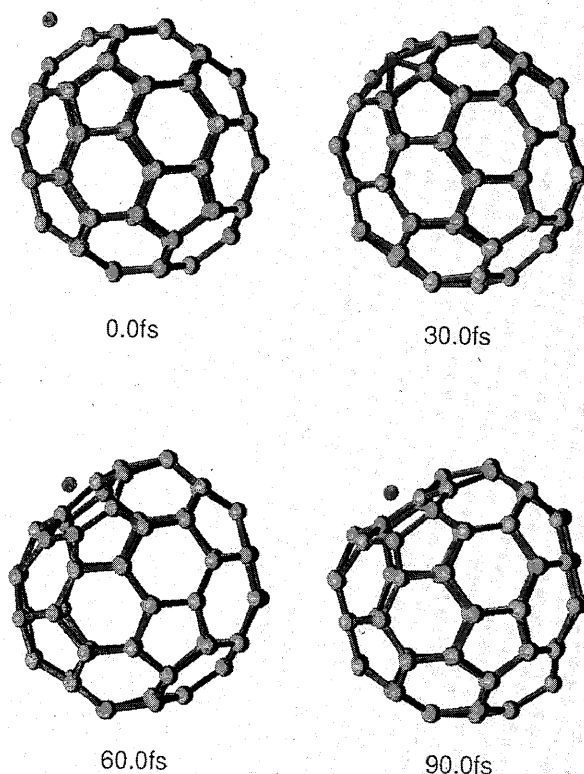


Figure 2. Snapshots of the simulation (B), where  $\text{Li}^+$  hits with K.E.= 1 eV the center of a hexagon of  $\text{C}_{60}^-$ .

than Li. The ionic radius of  $\text{Na}^+$  is  $0.95 \sim 1.16\text{\AA}$  slightly larger than the radius of the hole of a six-membered ring, while the radius of  $\text{K}^+$  is  $1.33 \sim 1.52\text{\AA}$  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 an experimental evidence[7] that  $\text{Na}^+$  is encapsulated in  $\text{C}_{60}$ , if  $\text{Na}^+$  obtains somewhat higher kinetic energy ( $\sim 20\text{eV}$ ). In addition,  $\text{K}@\text{C}_{60}$  was detected in a recent experiment using a plasma state of  $\text{C}_{60}^-$  and  $\text{K}^+$  ( $\leq 10\text{eV}$ ).[8]

In order to find out the mechanism of the insertion of  $\text{Na}^+$  ion, we performed a simulation of direct hit of  $\text{Na}^+$  to the center of a six-membered ring of  $\text{C}_{60}^-$ . For this purpose, we used  $128 \times 128 \times 128$  meshes and set  $1\text{a.u.} = 5.4\text{meshes}$  in order to represent the sharp  $1s$  core orbital of Na precisely enough. In this case, we did not succeed in obtaining the encapsulation even at the kinetic energy up to  $50\text{eV}$  of  $\text{Na}^+$ , in contrast to the case (A) yielding  $\text{Li}@\text{C}_{60}$ . What we obtained instead is a deformed  $\text{C}_{60}$  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  $\sim 1.7\text{\AA}$ . 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  $\text{C}_{60}$  due to the bombardment of other alkali-metal ions. In other words, the bond breaking after the bombardment may make the insertion of alkali-metal ion

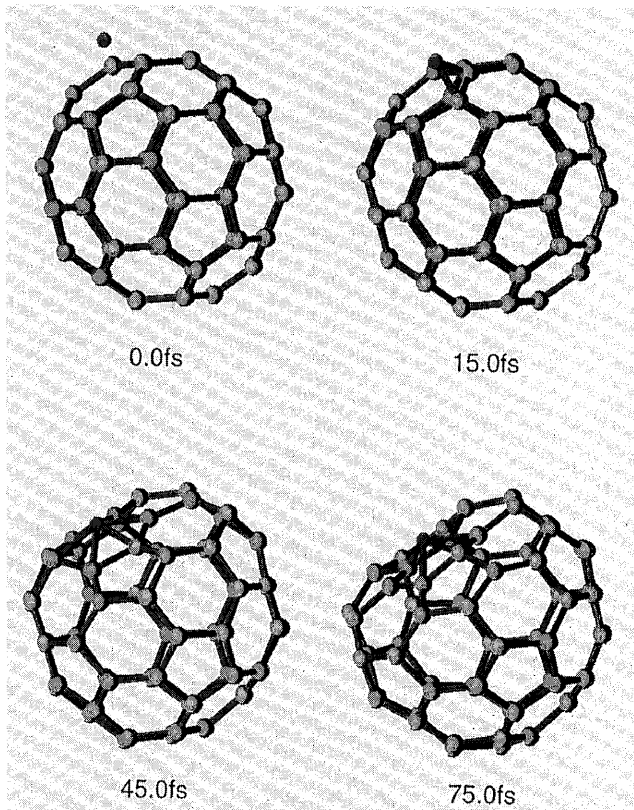


Figure 3. Snapshots of the simulation (C), where  $\text{Li}^+$  hits with  $\text{K.E.} = 5 \text{ eV}$  near the center of a C-C bond of  $\text{C}_{60}^-$ .

easier than the simulation (C). After the insertion of  $\text{Na}^+$  ion through the largely open hole, the original  $\text{C}_{60}$  cage is reconstructed after annealing. This procedure is expected to take 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. Therefore, in conclusion, we can say that there is a strong possibility to create alkali-metal encapsulated  $\text{C}_{60}$  by plasma processing technique with direct and multiple-step insertion processes.

#### Acknowledgments

We are grateful to Prof. N. Sato, Prof. R. Hatakeyama, and Dr. T. Hirata at Department of Electrical Engineering, and to Prof. N. Niwano at Institute of Electrical Communication, Tohoku University, for informing us this interesting topics and their recent result suggesting  $\text{K@C}_{60}$ . [8] We are also grateful to the Materials Information Science Group of the Institute for Materials Research, Tohoku University, for continuous support of the supercomputing facilities. This work has been supported in part by a grant-in-aid program of the respected area "carbon clusters" by the Ministry of Education, Science and Culture.

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