Incorporation of Sb Atom and Fullerene by Using Nuclear Recoil and Their MD Simulation

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The formation of an Sb atom incorporated fullerenes has been investigated by using radionuclides produced by nuclear reactions. From the trace of radioactivities of ^{120}Sb or ^{122}Sb after High Performance Liquid Chromatography (HPLC), it was found that the formation of endohedral fullerenes or heterofullerenes in atoms of Sb is possible by a recoil process following the nuclear reactions. To confirm the produced materials, *ab initio* molecular-dynamics(MD) simulations based on an all-electron mixed-basis approach were carried out. We present possibility of the formation of endohedral fullerenes or substitutional heterofullerenes incorporated with an Sb atom.
Key words: Endohedral fullerene, Heterofullerene, Nuclear recoil, MD simulation.

1. INTRODUCTION.

Since the discovery of fullerene[1] and the successful production of a large amount of fullerene[2], many experimental data have been reported on various kind of physical and chemical quantities associated with endohedrally doped[3,4,5], exohedrally doped[6,7] fullerenes and heterofullerenes[8,9,10]. However, the knowledge of atom incorporated fullerene is still partial, especially, on the insertion of foreign-atom for already created C_{60} or C_{70}. Here, chemical interaction between C_{60} (C_{70}) and a variety of atoms seems to be very important for the formation of such complexes.

In our previous studies, we reported that not only the endohedral doping of ^{7}Be, ^{79}Kr and ^{127}Xe[11,12] but also the substitutional doping of ^{11}C[13], ^{13}N[14], ^{69}Ge and ^{72}As[15] were successful by a recoil-implantation process following nuclear reactions. However, only partial facts for the formation process and the produced materials have been unveiled on the nature of the chemical interaction between a foreign atom and a fullerene cage. Therefore, it is important and intriguing to synthesize new complexes, such as several foreign-atom incorporated fullerenes, and their properties should be investigated due to acquirement of the knowledge for producing a large amount of the complexes.

In this paper, we show evidence of an Sb atom incorporated fullerenes on the collision between a C_{60} cage and an Sb atom, which was generated from a recoil process following nuclear reactions. We performed *ab initio* molecular-dynamics(MD) simulations: whether the Sb atom can be incorporated in the fullerene with the endohedral doping (Sb@C_{60}) or the substitutional doping (SbC$_{59}$). Furthermore, the doping process of an Sb atom in a fullerene is compared with that of an As atom.

2. EXPERIMENTAL PROCEDURE

To produce Sb atom incorporated fullerenes, natural antimony was used in experiment. Two radioisotopes of ^{120}Sb and ^{122}Sb can be produced by photonuclear reaction, (γ,n) reactions, by a bombardment on natural Sb, as shown in Table I. About 10 mg of C_{60} fullerene powder was mixed homogeneously with 10 mg of Sb$_2$O$_3$. The samples were irradiated with bremsstrahlung of E_{max}=50 MeV which originated from the bombardment of a Pt plate of 2 mm in thickness with an electron beam which was provided by a 300 MeV electron linac, Laboratory of Nuclear Science, Tohoku University. Irradiation time was set to about 8 hours and the average beam current was typically 120 µA. The sample was

Table I. Nuclear data and experimental condition for the radioactive fullerenes.

Nuclide produced	γ-ray	Half-life($T_{1/2}$)	Reaction	Material abundance*
^{120}Sb	197 keV	5.76d	^{121}Sb$(\gamma,n)^{120}$Sb	^{121}Sb, 57.4
^{122}Sb	564 keV	2.70d	^{123}Sb$(\gamma,n)^{122}$Sb	^{123}Sb, 42.6

*, Irradiated material as a target: Sb$_2$O$_3$

cooled with water bath during the irradiation.

After the irradiation, the samples were left for one day to cool down the several kinds of short-lived radioactivities of byproducts, such as [11]C ($T_{1/2}$=20 min, which is produced by a [12]C(γ,n)[11]C reaction). The radioactivities of [120]Sb or [122]Sb with its characteristic γ-ray and the half-life (see Table I).

The fullerene samples were dissolved in *o*-dichlorobenzene after being filtrated to remove insoluble materials through a membrane filter (pore size=0.45 and/or 0.20 μm). The soluble fraction was injected into a high-performance liquid chromatograph (HPLC) equipped with a 5PBB (silica-bonded with the pentabromobenzyl group) column of 10 mm (inner diameter)×250 mm (length), at a flow rate of 3 ml/min. The eluted solution was passed through a UV detector, the wavelength of which was adjusted to 290 nm in order to measure the amount of fullerenes and their derivatives.

The fraction was collected at 30 sec intervals, and the γ-ray activity of each fraction was measured with a Ge-detector coupled to the 4096-channel pulse-height analyzer whose conversion gain was set to 0.5 keV per channel. Therefore, the existence of [120]Sb or [122]Sb could be confirmed by their characteristic γ-rays[16].

3. RESULTS AND DISCUSSION

Fig. 1 shows three elution curves of the C_{60} sample irradiated by bremsstrahlung of E_{max}=50 MeV, solid circles for [120]Sb and open circles for [122]Sb radioactivities, respectively, and by a UV detector (solid line). The horizontal axis indicates the retention time after injection into the HPLC and the vertical one the counting rate of the [120]Sb or [122]Sb radioactivities.

A strong absorption peak was observed at the retention time of 6.5-7 min in the elution curve (solid line) which was measured by the UV detector. This peak position corresponds to the retention time of C_{60}, which was confirmed by the calibration run using the C_{60} sample before the irradiation. Following the first peak, two peaks at around 9-9.5 min and 13-16 min were consecutively observed in the UV chromatogram. This fact indicates that the second and small third peaks can be assigned to C_{60} dimers and C_{60} trimers, respectively. These materials can be produced by the interaction between C_{60}'s in coalescence reactions after ionization by incident γ-rays[17]. Three peaks appeared in the curve of the radioactivities [120]Sb ([122]Sb) in the radiochromatogram. Aside from a slight delay, the first peak (7 min) corresponds to the C_{60} UV absorption peak. The second as well as the relatively broad third peaks were observed at the retention time of 9-11 min, and of 14-20 min, respectively. Though there is a delay in the elution peaks of the radioactivities against that of the UV absorption peaks, it seems that the elution behavior is similar. This result indicates that the radioactive fullerene monomers and their polymers (dimers and tetramers) labeled with [120]Sb ([122]Sb) possibly exist in the final fractions. A similar trend was observed in the elution curves of As and Xe cases[12,15].

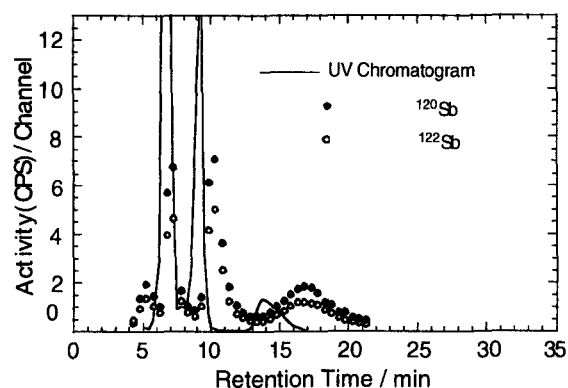Here, it should be noted that no evidence of exohedral

Fig. 1 HPLC elution curves of the soluble portion of the crude extracted in the γ-ray irradiated sample of C_{60} mixed with Sb_2O_3. The horizontal axis indicates retention time, and the vertical axis represents the counting rate of the radioactivities of [120]Sb or [122]Sb measured with Ge-detector.

molecules with a covalent nature has been presented so far by an extraction in the soluble portion. Such molecules can be removed out during the solvation process if they are exohedral. Therefore, two possibilities should be considered in the present results; (a) endohedrally Sb atom doped fullerenes, Sb@C_{60}, (b) substitutionally Sb atom doped heterofullerenes as a part of the cage, SbC$_{59}$.

In order to understand the present experimental results, *ab initio* molecular-dynamics(MD) simulations were carried out. The method, which is used here, is based on the all-electron mixed-basis approach[18,19] using both plane waves (PW's) and atomic orbitals (AO's) as a basis set within the framework of the local density approximation (LDA). In the present study, all the core atomic orbitals are determined numerically by a standard atomic calculation based on Herman-Skillman's framework with logarithmic radial meshes[20,21]. For the present system, we use 313 numerical AO's and 4,169 PW's corresponding to a 7 Ry cutoff energy. For dynamics, we assume the adiabatic approximation where the electronic structure is always in the ground state. We utilize a supercell composed of 64×64×64 meshes, where one mesh corresponds to 0.196 Å. We set the basic time step as δt = 0.1 fs and perform five steepest descent(SD) iterations after each updation of atomic positions. We do not impose any velocity control, so that the system is almost microcanonical with a little energy dissipation from the SD algorithm.

Here, we describe the main results of the present simulations. (a) First, we shift one of the C atoms of C_{60} outward by 1.3 Å and put additionally one Sb atom on the same radial axis by 1.3 Å inward from the original C position (see Fig.2). Then, starting the simulation with zero initial velocity, we found that there is force acting on the Sb atom to move innerward to encapsulate. On the other hand, the C atom of C_{60} placed outward by 1.3 Å is induced a force acting to move innerward as if it would create one of membering u-C_6, and finally u-C_6 recovers its original configuration of C_{60}. This
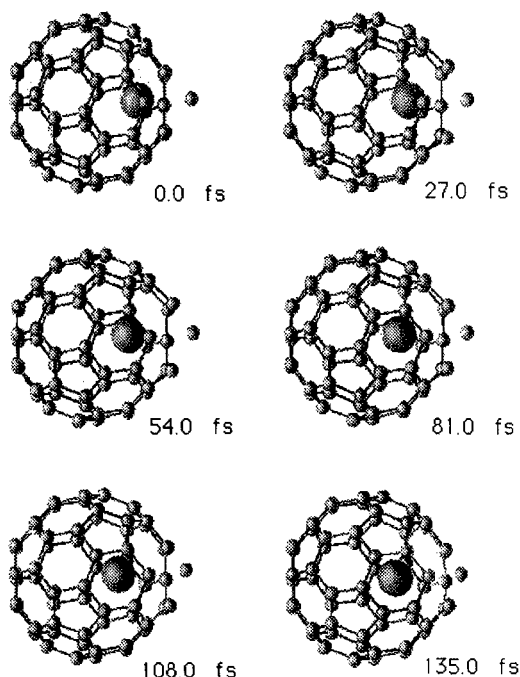
Fig. 2. Simulation of the structural stability of $Sb@C_{60}$ or SbC_{59}: Change from an unstable innerside(Sb atom) and outer side(C atom) with an initial kinetic energy of 0 eV to a final stabilized configuration.
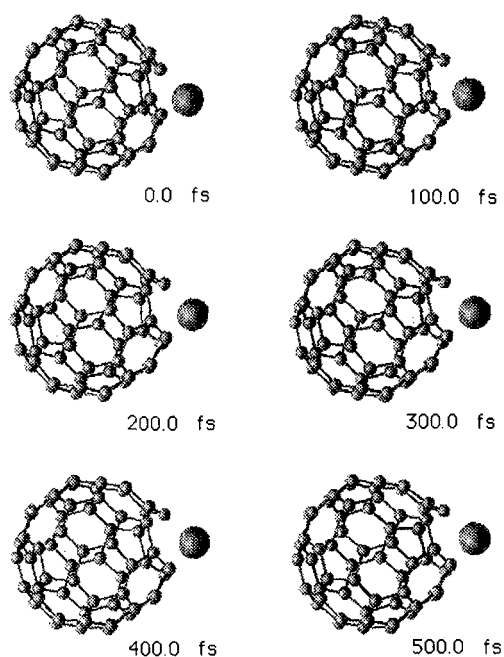

Fig. 3. Simulation of structural stability of SbC_{59}: Change from an unstable outer-side (0.13 Å outward from the cage sphere) with a initial K.E. of 0 eV to a final stabilized configuration in SbC_{59}.

result may indicate the formation of $Sb@C_{60}$. (b) Second, one Sb atom was put at 1.3 Å outward from the cage sphere instead of one C atom of $u-C_6$. Then, starting the simulation with zero initial velocity, we found that there is a slight moving force acting on the Sb atom againt the cage. But the Sb atom is still staying near by the initial position even after full relaxation (t =500 fs) with some rotational inertia in the system of SbC_{59} (see Fig.3). Therefore, it seems that the Sb atom, when put outside the cage, can be stable to create a heterofullerene such as SbC_{59}.

In our previous study, we also performed similar simulations in the case of an As atom[15]. From the simulations, the As atom put inside the cage is quite unstable and has a strong tendency to repel the closest C atom of C_{60} and stabilized slightly outside the cage sphere to create AsC_{59} (even if the As atom puts outside the cage). Therefore, we confirmed that a heterofullerene(AsC_{59}) exist stably under realistic conditions. In the present results, however, it seems that formation of $Sb@C_{60}$ is rather likely for the interaction between Sb atom and C_{60} cage, but it may remain the local stable point at around the cage sphere to create heterofullerene (SbC_{59}). The difference can be due mainly to a magnitude of the covalent bonding between C atom and Sb (or As) atom; it seems that the magnitude of the covalent bonding in Sb case is weaker than that in As case. The results of analyses of the present work have to be further supported by some other experimental data such as   direct mass measurements by a Time-Of-

Flight MAss Spectrometry(TOFMAS). We briefly comment on the experimental works now in progress for the cases of As and Sb.

Finally, schematic view of a partial periodic table is shown in Fig. 4. In the figure, elements which is experimentally and theoretically confirmed as an incorporation in the fullerene cage are shown by under-

Fig. 4. Schematic view of a partial periodic table. In the figure, the formation of atom-doped C_{60} or C_{70} , which has been confirmed by using several techniques, is indicated by under-bars. Elements shown by the gray area are investigated by the present method.

bar(endohedrally doping, or substitutionally doping). Elements shown by the gray area are investigated by the present method. It is interesting to note that the group elements such as 4B~6B, even in heavier elements like an Sb and Te atoms, can be possible for a formation of complex materials.

4. CONCLUSION

In this study, the formation of an Sb atom incorporated fullerenes has been investigated by the traces of radioactivity of ^{120}Sb (or ^{122}Sb) produced by nuclear reactions. It was found that 5B element, like Sb, remained in the final C_{60} portion after a HPLC process. This fact suggests that the formation of endohedral fullerenes, Sb@C_{60} and their polymers, (or substituted heterofullerenes, SbC$_{59}$ and their polymers), can be possible by a recoil process following nuclear reactions. Carrying out *ab initio* molecular-dynamics(MD) simulations on the basis of the all-electron mixed basis approach, we confirmed that endohedral fullerene and heterofullerene with an Sb atom can be possible.

5. ACKNOWLEDGEMENTS

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