

Formation of New Materials in Fullerenes by Using Nuclear Recoil

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The formation of Sb or Te atom-incorporated fullerenes has been investigated by using radionuclides produced by nuclear reactions. From the trace of radioactivities of ¹²⁰Sb (¹²²Sb) or ¹²¹Te after High Pressure Liquid Chromatography (HPLC), it was found that the formation of endohedral fullerenes or heterofullerenes in atoms of Sb or Te is possible by a recoil process following the nuclear reactions. To confirm the produced materials, *ab initio* molecular-dynamics simulations based on an all-electron mixed-basis approach was carried out. We present possibility of the formation of endohedral fullerenes or substitutional heterofullerenes incorporated with Sb or Te atoms.

§ 1. Introduction

Chemical interaction between C₆₀ and a variety of atoms is becoming a very new field of cluster research. So far, numerous experimental studies for endohedrally doped [1-10] or exohedrally doped [11-13] fullerenes with foreign atoms have been undertaken by resorting to are-desorption or laser-vaporization techniques. On the other hand, it has become possible to synthesize the heterofullerenes, where the foreign atom is incorporated into the carbon cage. Experimentally, heterofullerenes doped with foreign atoms, such as boron(B) [14,15], nitrogen(N) [16,17], silicon(Si) [22,23] have been reported. In our previous studies, we have studied not only the endohedral doping of Kr and Xe [26] but also the substitutional doping of ¹¹C [18,19], ¹³N [20], ⁶⁹Ge and ⁷²As [21] by a recoil-implantation process following nuclear reactions. In spite of the intense research, 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 very important and intriguing to synthesize new plastic materials, such as several atom-incorporated fullerenes, and their properties should be investigated for getting in quantities and opening up a new application in the future.

In this paper, we show evidence of Sb (or Te) atom-incorporated fullerenes on the collision between a C₆₀ cage and an Sb (Te) atom, which was generated from a recoil process following nuclear reactions. We performed *ab initio* molecular-dynamics (MD) simulations: whether the Sb (Te) atom can be incorporated in the fullerene with the endohedral doping; Sb@C₆₀ (Te@C₆₀), or the substitutional

doping ; SbC_{59} (TeC_{59}). Furthermore, the doping process of the Sb (Te) atom in a fullerene is compared with that of an As atom or a noble-gas atom.

§ 2. Experimental Procedure

According to the source nuclide used, high-energy bremsstrahlung or charged particle irradiation was used. In Table I, nuclide produced, characteristic γ -ray, half-life and reaction are listed for each material used here. About 10 mg of C_{60} fullerene powder was mixed homogeneously with 10 mg of Sb_2O_3 , and used to the target material. (1) For production of ^{120}Sb (^{122}Sb)-doping fullerene, 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. Two radioisotopes of ^{120}Sb and ^{122}Sb can be produced by photonuclear reaction, (γ, n) reactions, by an irradiation on a natural Sb. Irradiation time was set to about 8 hour and the average beam current was typically $120 \mu\text{A}$. The sample was cooled with water bath during the irradiation. (2) For production of ^{121}Te -doping fullerene, deuteron irradiation with beam energy of 16 MeV was performed at the Cyclotron Radio-Isotope Center (CYRIC), Tohoku University. Radioisotopes of ^{121}Te can be produced by (d, 2n) reaction by an irradiation on a natural Sb. The beam current was typically $5 \mu\text{A}$ and the irradiation time was about 1 hour. The sample was cooled with He-gas during irradiation.

After the irradiation, the samples were left for one day to cool down the several kinds of short-lived radioactivities of byproducts. After the one-day cooling, radioactivities, such as ^{11}C or ^{13}N (e.g., ^{11}C decays to ^{11}B with $T_{1/2} = 20$ min), the radioactivities of ^{120}Sb (^{122}Sb) or ^{121}Te could be measured with its characteristic γ -rays (see Table I).

The fullerene samples were dissolved in *o*-dichlorobenzene after being filtrated to remove insoluble materials through a membrane filter (pore size = $0.45 \mu\text{m}$). The soluble fraction was injected into a high-pressure liquid chromatograph (HPLC) equipped with a 5PBB (silica-bonded with the pentabromobenzyl group) column of 10 mm (inner diameter) \times 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 activities of each fraction were 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 (^{122}Sb) or ^{121}Te could be confirmed by

Table 1. Nuclear data and experimental condition for the radioactive fullerenes

Nuclide produced	γ -ray*	Half-life	Reaction	Material** and abundance (%)
^{120}Sb	197 keV	5.76 d	$^{121}\text{Sb}(\gamma, n)^{120}\text{Sb}$	^{121}Sb , 57.4
^{122}Sb	564 keV	2.70 d	$^{123}\text{Sb}(\gamma, n)^{122}\text{Sb}$	^{123}Sb , 42.6
^{121}Te	573 keV	16.80 d	$^{121}\text{Sb}(\text{d}, 2\text{n})^{121}\text{Te}$	^{121}Sb , 57.4

* : γ -ray used for the analysis [27].

** : Irradiated material as a target (both for the case of Sb and Te) : Sb_2O_3 .

their characteristic γ -rays [27].

§ 3. Results and Discussion

Figure 1 shows three elution curves of the C_{60} sample irradiated by bremsstrahlung of $E_{max} = 50$ MeV, open circles for ^{120}Sb and solid 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. For characterization of the components, the fraction corresponding to the second peak in the sample of C_{60} irradiated was collected and examined with MALDI TOF (matrix-assisted laser-desorption ionization time-of-flight) mass spectrometry in a separate run. The mass spectrum of the fraction exhibited a series of peaks at m/z $1440 - 24n$ ($n = 1-4$) corresponding to the molecular ion peak of $C_{120-n}C_2$ in addition to the peak for C_{60} as a base peak [24]. This fact indicates that the second and smaller 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 or produced charged particles [26,28].

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

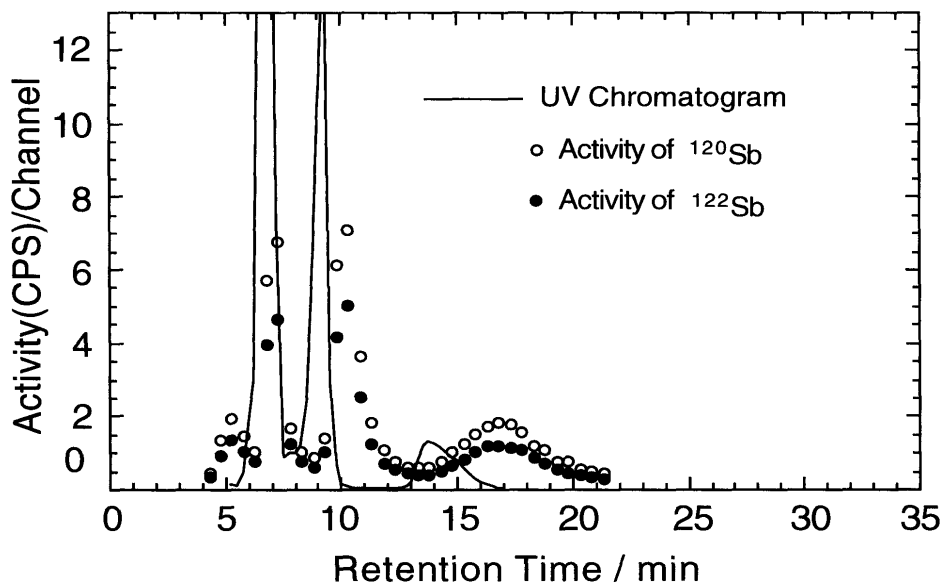


Fig.1. HPLC elution curves of the soluble portion of the crude extracted in the γ -ray-irradiated sample of C_{60} mixed with Sb_2O_3 . The horizontal axis indicates retention time, and the vertical axis represents the counting rate of the radioactivities of ^{120}Sb or ^{122}Sb measured with a Ge-detector.

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. In our previous study, a similar trend was also observed in the elution curve of Kr or Xe case [26]. The amount of the Sb-incorporated radioactive fullerenes produced here is estimated to be about $10^{10}\sim 10^{11}$ molecules.

The elution curves shown by solid line and solid circles in Fig.2 indicate the absorbance monitored continuously by a UV detector and γ -counting rate of ^{121}Te measured by a Ge-detector, respectively. The horizontal and the vertical axes are also same as Fig.1. From the mass measurements, three components in the UV chromatogram can be also attributed to C_{60} monomers, their dimers and trimers, respectively. Three populations of ^{121}Te are appeared at retention times of 7 min, 10 min and 14 - 18 min in Fig.2. The amount of the radioactive fullerenes seems to be the same order of magnitude of that of the Sb case.

Here, it should be noted that no evidence of exohedral 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; (1) endohedrally Sb (Te) atom-doped fullerenes, Sb@C_{60} (Te@C_{60}), (2) substitutionally Sb (Te) atom-doped heterofullerenes as a part of the cage, SbC_{59} (TeC_{59}).

In order to understand the present experimental results, *ab initio* molecular-dynamics simulations were carried out. The method, which is used here, is based on the all-electron mixed-basis approach [25,26,28-31] 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 [25]. For the present system, we use 313 numerical AO's and 4,169

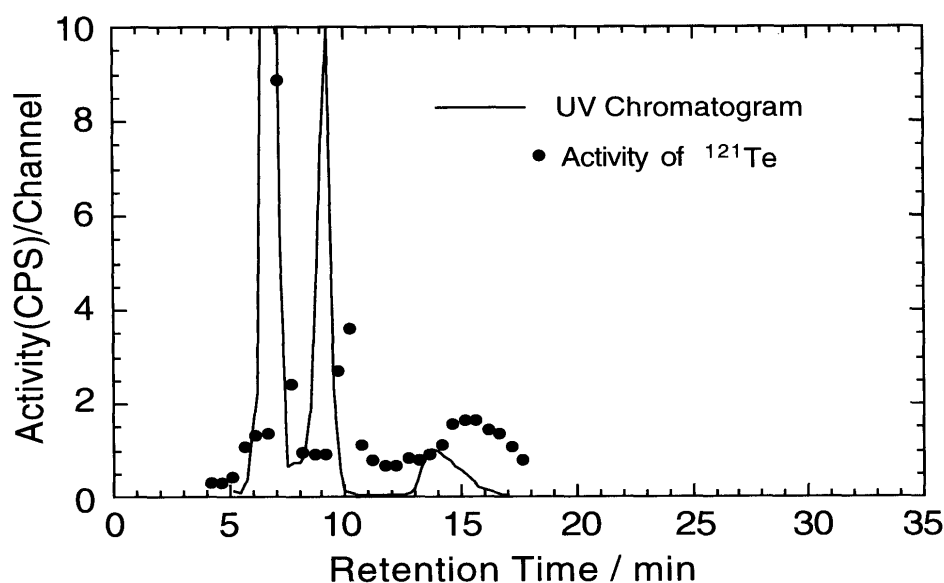


Fig.2. HPLC elution curves of the soluble portion of the crude extracted in the deuterium-irradiated sample of C_{60} mixed with Sb_2O_3 . The horizontal axis indicates retention time, and the vertical axis represents the counting rate of the radioactivities of ^{121}Te measured with a Ge-detector.

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 $64 \times 64 \times 64$ meshes, where one mesh corresponds to 0.196 \AA . We set the basic time step as $\Delta t = 0.1 \text{ fs}$ 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.

We performed the following three types of simulations for As or Te case; (A) insertion between one Sb atom and one C atom in C_{60} cage, and (B) structural stability of SbC_{59} . (C) insertion of Te atom through a six-membered ring of C_{60} ($u-C_6$).

Here, we describe the results of the present simulations. (A) First, we shift one of the C atoms of C_{60} outward by 1.3 \AA and put additionally one Sb atom on the same radial axis by 1.3 \AA inward from the original C position (see Fig.3). Then, starting the simulation with zero initial velocity, we found that there is a force acting on the Sb atom to move innerward to encapsulate ($\sim 135 \text{ fs}$). On the other hand, the C atom of C_{60} placed outward by 1.3 \AA induced a force acting to move innerward as if it would create one of the membering $u-C_6$, and finally $u-C_6$ recovered its original configuration of C_{60} . This results may indicate the formation of $Sb@C_{60}$. (B) Second, one Sb atom was put at 1.3 \AA outward from

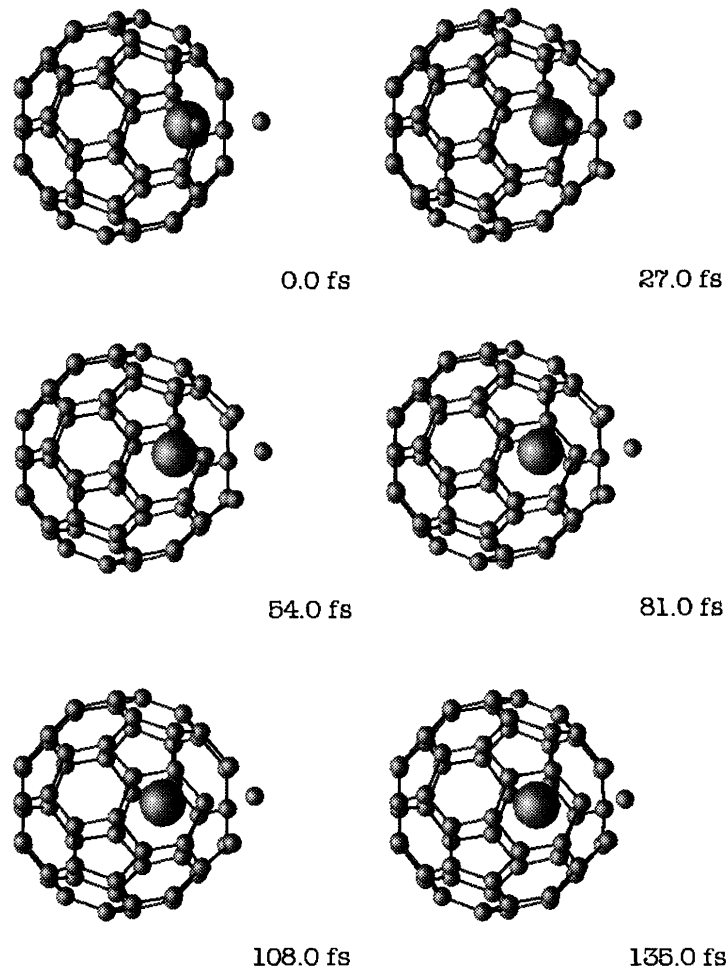


Fig.3. Simulation of the structural stability of $Sb@C_{60}$ or SbC_{59} : Change from an unstable innerside (Sb atom) and outer side (C atom) with an initial kinetic energy of 0 eV to a final stabilized configuration.

the cage sphere, instead of one C atom of u -C₆. Then, starting the simulation with zero initial velocity, we found that there is a slight moving force acting on the Sb atom against the cage, but still staying near by the initial position even after full relaxation ($t = 500$ fs) with some rotational inertia in the system of SbC₅₉. Therefore, it seems that the Sb atom, when put outside the cage, can be stable to create a heterofullerene such as SbC₅₉. (C) Third, in the case of Te, Te atom with the initial kinetic energy (K.E.) of 40 eV can penetrate into the cage of C₆₀ through the center of u -C₆ without difficulty, Figure 4 shows several snapshots (~ 150 fs) of the Te atom insertion with 40 eV (K.E.). In the figure, after the Te atom first touches u -C₆, carbon atoms are pushed to open u -C₆ and goes through. But the u -C₆ recovers soon its initial configuration. Finally the Te atom bounced at the other side and come back towards the center of the cage. The result of simulations changes, of course, according to the impact energy, impact point and angle. For relatively low initial K.E., C₆₀ shows a tendency to recover its original shape within the simulation period. For higher initial kinetic energies six C₂ losses occur simultaneously from the upper side of C₆₀. If an atom is inserted toward off-center positions of a six-or five-membered ring, the damage suffered on C₆₀ increases significantly.

It is interesting to note that the nature of the doping process of the Sb atom in the C₆₀ cage can be compared with that of As atom, because the As and Sb atoms are the same 5B group element. In our

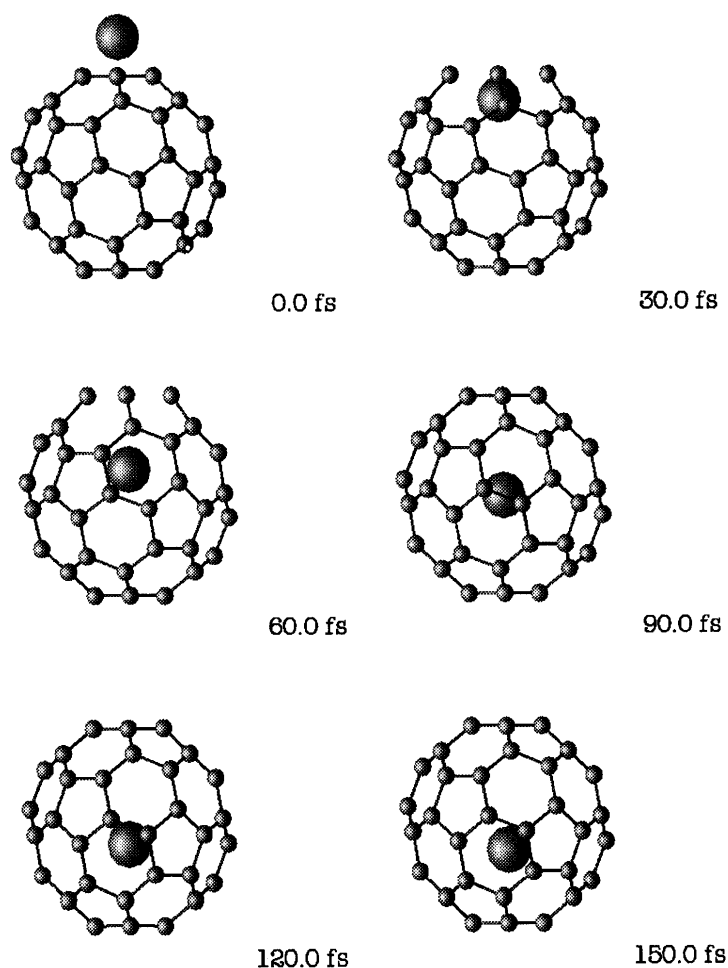


Fig.4. Simulation of Te hitting the center of a six-membered ring of C₆₀ with a kinetic energy of 40 eV. Here, local skeleton disappears from the figure when the bond-length is elongated more than by 1.5Å.

§ 4. Conclusion

In this study, the formation of atom-incorporated fullerenes has been investigated by the traces of radioactivity of ^{120}Sb (or ^{122}Sb , ^{121}Te) produced by nuclear reactions. It was found that 5B~6B elements, like Sb or Te, remained in the final C_{60} portion after a HPLC process. This fact suggests that the formation of endohedral fullerenes, Sb@C_{60} (Te@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 fullerenes of Sb (Te) atoms inside the C_{60} cage can be possible. From the difference between the case of Sb (Te) and the case of As, the chemical nature of a doping atom seems to play an important role in the process of endohedrally doping or substitutionally doping in fullerenes.

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