Radiochemical approaches for formation of endohedral fullerenes and MD simulation

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Abstract

The formation of atom-doped fullerenes has been investigated by using several types of radionuclides produced by nuclear reactions. From the trace of the radioactivities after a high performance liquid chromatography, it was found that formation of endohedral fullerenes (or heterofullerenes) of small atoms (Be, Li), noble-gas atoms (Kr, Xe) and 3B–6B elements (Ge, As, Se, Sb, Te, etc.) is possible by a recoil process following the nuclear reaction. In order to show the possibility of creating endohedral fullerenes with a suitably high kinetic energy of foreign atoms, we have carried out large-scale ab initio molecular dynamics simulations on the basis of the all-electron mixed-basis approach with atomic orbitals and plane waves for several atoms.

Keywords: Endohedral fullerenes; Radioactivities; MD simulations

1. Introduction

After the discovery of the C₆₀ and the subsequent successful production of large amounts of fullerene [1,2], endohedral complexes can be created simultaneously with ordinary fullerenes by using arc-discharge vaporization of composite rods made of graphite and the metal compounds [3,4]. Those are important pseudo-atom candidates and the materials processed can be expected to have a high possibility for functional materials such as superconductors, stable molecular devices, nano-molecular containers, etc. However, the production rate of atom endohedral C₆₀ is quite low compared to ordinary C₆₀.

An alternative way of producing endohedral C₆₀ is to insert foreign atoms into the cages of the preexisting C₆₀ afterwards, and it has been presented several techniques for insertion of foreign atoms into the C₆₀ [5–7]. However, the nature of the chemical interaction between foreign atoms and fullerene cages, the formation process and the possible materials produced cannot be fully understood even at present. Therefore, it is important and intriguing to synthesize new complexes, such as several foreign atoms incorporated fullerenes, and their properties should be investigated due to acquirement of the knowledge for producing a large amount of the complexes.

In the present study, we have examined the production of endohedral C₆₀ derivatives created when radioactive nuclides (in alkali and alkali-earth, transition metals, 3B–6B elements and noble-gas elements) were produced by nuclear reactions. In order to check the possibility of creating endohedral C₆₀ by inserting foreign atom with a suitably high kinetic energy (K.E.) into C₆₀, large-scale ab initio molecular dynamics simulations are performed for several foreign atoms.

2. Experimental

In order to produce the source of radioactive nuclides, several materials (for example, Li₂CO₃, Ga₂O₃, etc. as listed in Table 1), were used in powder form. The grain size of the materials was smaller than 50 μm. Purified C₆₀ were elaborately mixed with each material (weight ratio = 1:1)
in an agate mortar, adding a few milliliter of carbon disulfide (CS₂). After drying up, about 30 mg of the mixture sample was wrapped in a pure aluminum foil of 10 mm in thickness for irradiation. According to the source nuclide, either charged-particle or high-energy bremsstrahlung irradiation was used. In Table 1, the radionuclide produced, its characteristic γ-ray, its half-life, and the nuclear reaction are listed for each target material. (1) Proton and deuteron irradiation with a beam energy of 16 MeV was performed for production of a doping nuclide such as ⁷Be, ⁷⁵Se, ¹²⁷Xe, etc. at the Cyclotron Radio-Isotope Center, Tohoku University. The beam current was typically 5 μA and the irradiation time was about 2–3 h. (2) For production of a doping nuclide such as ¹¹C and ¹²⁰Sb, a sample was set in a quartz tube and irradiated with bremsstrahlung of \( E_{\text{max}} = 50 \text{ MeV} \) which originated from the bombardment of a Pt plate of 2 mm in thickness with an electron beam provided by a 300 MeV electron linac at the Laboratory of Nuclear Science, Tohoku University. The beam current was typically 120 μA and the irradiation time was about 6–8 h.

The irradiated sample was dissolved in o-dichlorobenzene and filtered through a millipore filter (pore size = 0.2 and/or 0.45 μm) to remove insoluble materials. The soluble portion was injected into a high performance liquid chromatography (HPLC) device equipped with a 5PBB (Cosmosil) (silica-bonded with a pentabromobenzyl group) column of 10 mm (in inner diameter) and 250 mm (in length) at a flow rate of 3 or 4 ml/min in each run. For the confirmation of fullerenes and their derivatives, a UV detector was installed with a wavelength of 290 nm. Downstream of the UV detector, two γ-ray detectors consisting of a bismuth-germanate scintillator and of a photomultiplier (BGO-PM) were used to count the 511-keV annihilation γ-rays emanating from ¹¹C, ¹³N, ⁶⁹Ge and ⁷²As in coincidence. Data from the radio-chromatogram were accumulated by means of a multichannel scaler system (MCS), using a personal computer. In order to measure the γ-rays emanating from other radionuclides such as ⁷Be, ⁷⁵Se, ⁷⁹Kr, ¹²⁰Sb, ¹²¹Te, ¹²⁷Xe, eluent fractions were collected for 30 s intervals (0–30, 30–60, 60–90, … seconds), and the γ-ray activities of each fraction were measured with a Ge detector coupled to a 4096-channel pulse-height analyzer. Therefore, each nuclide listed in Table 1 could be uniquely detected by means of its characteristic γ-rays, and any other sources were ruled out.

### 3. Results and discussion

Panels (a)–(d) of Fig. 1 show the radiochromatogram for several materials mixed with C₆₀ samples, respectively, measured with the UV- and the γ-ray detector. The horizontal and vertical axes, respectively, indicate the retention time after their injection into the HPLC and the absorption intensity of the UV as well as the γ counting rate of the radionuclide being produced. From the correlation of the elution behavior between the UV chromatogram and the radioactivities of radionuclides, we found that several atom-doped fullerenes, namely ⁷⁹KrC₆₀ [8], ⁷⁵SeC₆₀ [9], ¹²¹TeC₆₀ [10], ⁷²As [11], etc. can be produced by nuclear recoil implantation. Similar results were observed in the elution behavior between the UV and the population of radioactivities for ⁷Be [12], ¹¹C [13], ¹³N [14,15], ¹²⁰Sb, ⁶⁹Ge, ¹²⁷Xe. For characterization of the UV components in Fig. 1 (a)–(d), the fraction corresponding to the first and second peaks in the irradiated sample of C₆₀ was collected and examined with a matrix-assisted laser-desorption ionization time-of-flight (MALDI TOF) mass spectrometry. The mass spectrum of the fractions exhibited the base peak of C₆₀ and the molecular ion peaks of C₁₂₀n⁻nC₂. Therefore, the observation of the first and second peaks in Fig. 1 (a)–(d), respectively, corroborates the formation of fullerene trimers. It seems that the collisions induced by the irradiation produces fullerene dimers and trimers by interacting with neighboring fullerene cages. A correlation of the elution behavior between the C₆₀ populations (UV) and the radionuclide populations (radioactivities) indicates that the radioactive atoms (⁷⁹Kr, ⁷⁵Se, ¹²¹Te, ⁷²As as shown in Fig. 1 (a)–(d)) may encapsulate inside the C₆₀ cages (i.e. the fractions for the first and second peaks of the UV may contain the endohedral fullerenes encapsulated radionuclide). Therefore, the first peak of each radiochromatogram in

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

| Nuclide produced | γ-Ray (keV) | Half-life (T₁/₂) | Reaction | Target material |
|-----------------|------------|-----------------|----------|----------------|
| ⁷Be             | 478        | 53 d            | ⁷Li(p,n)⁸Be | C₆₀+Li₂CO₃     |
| ¹¹C             | 511        | 20 m            | ¹¹C(γ,n)¹⁴C | C₆₀            |
| ¹³N             | 511        | 10 m            | ¹³C(d,n)¹⁴N | C₆₀            |
| ⁶⁹Ge            | 511        | 39.6 h          | ⁶⁹Ga(d,n)²⁰⁹Ge | C₆₀Ga₂O₃     |
| ⁷²As            | 511        | 26 h            | ⁷²Ge(d,n)¹²²As | C₆₀+GeO       |
| ⁷⁵Se            | 136        | 120 d           | ⁷⁵As(d,n)²⁰⁹Se | C₆₀As₂S₁     |
| ⁷⁹Kr            | 261        | 34.9 h          | ⁷⁹Br(d,n)²⁰⁹Kr | C₆₀+KBr        |
| ¹²⁰Sb           | 197        | 5.76 d          | ¹²⁰Sb(γ,n)²³⁵⁰Sb | C₆₀+Sb₂O₃     |
| ¹²¹Te           | 573        | 16.8 d          | ¹²¹Sb(d,n)¹²¹Te | C₆₀+Sb₂O₃     |
| ¹²⁷Xe           | 203        | 34.6 h          | ¹²⁷I(d,n)²⁰⁹Xe | C₆₀+KI         |

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Fig. 1 (a)–(d) can be, respectively, assigned to $^{79}\text{Kr}@\text{C}_{60}$, $^{75}\text{Se}@\text{C}_{60}$, $^{121}\text{Te}@\text{C}_{60}$, $^{72}\text{As}@\text{C}_{60}$.

In order to understand the present experimental results, we use an ab initio molecular dynamics method based on the all-electron mixed basis approach which uses both atomic orbitals (AO) and plane waves (PW) as a basis set within the framework of the local density approximation (LDA). So far, we have carried out simulations of Li- and Be-insertions into C$_{60}$ [12,16] by using analytic Slater-type atomic orbitals. Our recent calculations involving the insertion of Kr, Xe [8], K, Cu, As [11,17], Se [9], Sb, Te [10] have used atomic orbitals determined numerically by a standard atomic code based on Herman–Skillman’s framework with logarithmic radial meshes [18,19]. For example, we adopt 318 numerical atomic orbitals for the C$_{60}$ + Se system as well as 4169 plane waves corresponding 7 Ry cutoff energy. For dynamics, we assume adiabatic approximation where the electronic structure being always in the ground state. In a supercell composed of $64 \times 64 \times 64$ meshes, in which 1 a.u. = 0.52918 Å corresponds 2.7 meshes, we put one C$_{60}$ molecule which is stationary at $t = 0$ and one atom moving with a given initial velocity toward the center of a six-membered ring ($u$-C$_6$) of C$_{60}$ vertically. The initial distance from the center of $u$-C$_6$ is 1.5 Å. The basic time step is typically set to $\Delta t = 4$ a.u. $\approx 0.1$ fs and perform five to six steepest descent (SD) iterations after each update of atomic positions in order to converge the electronic states.

Snapshots obtained by the simulations for Kr, Se, Te and As with several initial K.E. are inserted in Fig. 1(a)–(d). Here, we show results of the simulations. (a) Kr, Xe: Kr with the initial K.E. greater than 80 eV or Xe with the initial K.E. greater than 120 eV penetrates into the cage of C$_{60}$ through the center of $u$-C$_6$ without difficulty. For the kinetic energies higher than 150 eV for Kr or 200 eV for Xe, the foreign atom passes through the center of the six-membered ring at the opposite side of the cage. The result of simulations changes of course according to the impact energy, impact point and angle. For higher initial kinetic energies (300 eV for Xe and Kr), six C$_2$ losses occur simultaneously from the upper side of C$_{60}$. If a noble-gas atom is inserted toward off-center positions of a six- or five-membered ring, the damage suffered on C$_{60}$ increases significantly. (b) Se, Te: Se@C$_{60}$, Te@C$_{60}$ are created with a 40 eV initial K.E. However, for higher energies such as 80 eV, both atoms pass through the other side of C$_{60}$. (c) As, Sb: Heterofullerenes such as C$_{59}$As and C$_{59}$Sb are possible as well as As@C$_{60}$ and Sb@C$_{60}$ [10,11]. The penetration into the C$_{60}$ cage is possible with 40 and 80 eV, respectively, for As and Sb. A possibility of heterofullerenes (C$_{59}$As) created stably is shown in Fig. 1(d).
In the present study, several elements in a periodic table have been investigated by a recoil implantation following nuclear reactions. A schematic view of a periodic table is shown in Fig. 2. Elements shown by the symbol ($) are investigated by the present method. In the figure elements which are experimentally confirmed to combine with fullerene cages are shown in dark area. It is interesting to note that the group elements of small ion-radius (like Be), 4B–6B and noble-gas might possibly form complex materials such as the atom-doped fullerenes. Most of the other elements, such as alkali, alkali-earth and transitional metals, could not be detected in the C\textsubscript{60} portion. This fact indicates that elements (Na, Ca, Sc, etc.) may destroy the fullerene cages due to strong chemical reactivity between atoms and fullerenes. It is also interesting to noted that a simultaneous creation of large endohedral fullerenes (e.g. for C\textsubscript{82} by using an arc-discharge vaporization method) can be successful for atoms such as alkali, alkali-earth elements (shown by diagonal lines in Fig. 2) [20]. The production mechanism of atom endohedral fullerenes can be quite different between the simultaneous creation for C\textsubscript{82} and the atom insertion for C\textsubscript{60} afterwards.

4. Conclusion

In this study, the formation of atom-doped fullerenes has been investigated by using several types of radioactivity which are produced by nuclear reactions. It was found that small ion-radius elements (like Be), noble-gas elements (like Kr and Xe), as well as 3B–6B group elements (like C, N, Ge, As, Se, Sb, Te) remained in the C\textsubscript{60} portion after a HPLC process. By carrying out ab initio molecular-dynamics (MD) simulations on the basis of the all-electron mixed-basis approach, we confirmed that the insertion of several atoms into C\textsubscript{60} through six-membered rings. These facts suggest that the formation of endohedral fullerenes (or heterofullerenes) is possible in small, 3B–6B group and noble-gas elements by a recoil process following nuclear reactions.

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