

Insertion of Xe and Kr Atoms into C₆₀ and C₇₀ Fullerenes and the Formation of Dimers

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The radioactive endohedral fullerenes $^{127}\text{Xe}@C_{60}$, $^{127}\text{Xe}@C_{70}$, $^{79}\text{Kr}@C_{60}$, and $^{79}\text{Kr}@C_{70}$, and their dimers, are detected using radiochemical and radiochromatographic techniques in the final solution of samples in which Xe or Kr has penetrated into C₆₀ or C₇₀ by a nuclear reaction recoil process. Carrying out *ab initio* molecular dynamics simulations based on an all-electron mixed basis approach, we confirmed that the insertion of Xe and Kr atoms into C₆₀ through six-membered rings is possible in a certain range of the kinetic energy: 130–200 eV for Xe and 80–150 eV for Kr. [S0031-9007(98)06734-9]

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Endohedral fullerenes are important pseudoatom candidates and are expected to have future possibilities in the areas of magnetism and superconductivity. Experimentally, metallofullerenes such as La [1,2], Y [3,4], Sc [5,6] atoms encapsulated in C₈₂ or C₈₄ have been confirmed using arc-desorption or laser vaporization techniques. Here, encapsulation occurs when fullerenes are created in a vapor phase. On the other hand, insertion of atoms *a posteriori* into already created fullerenes has been challenged. However, successful production of endohedral fullerenes has been reported for small ion-radius atoms [7,8], which can pass through the tight six- or five-membered rings. Recently, endohedral noble-gas fullerene compounds have also been investigated by some workers [9–11]. Gadd *et al.* have tried to produce noble-gas endohedral fullerenes from interstitial fullerene by the prompt gamma recoil method using neutron irradiation. They believed to have observed endohedral compounds of RN@C₆₀ (where RN is radionuclide such as ^{125g}Xe , ^{133g}Xe , ^{135g}Xe , ^{41}Ar , or ^{85m}Kr) [11]. Saunders *et al.* also demonstrates the possibility of the incorporation of noble-gas atoms in fullerenes at high-pressure and high-temperature conditions, and they proposed an open-window mechanism for restoration of the broken carbon-carbon bonds [10]. In spite of the intense search, to the best of our knowledge, the existence of endohedral noble-gas fullerenes has not been confirmed after removal of damaged or incomplete fusion products.

In this Letter, we present evidence that a noble-gas element like Xe or Kr can penetrate into the C₆₀ cage to produce endohedral fullerenes, i.e., $^{127}\text{Xe}@C_{60}$ and $^{79}\text{Kr}@C_{60}$ and their dimers, in a nuclear recoil reaction. We proved the presence of endohedral fullerenes in the final product

by use of radiochemical and radiochromatographic techniques. This suggests that radioactive ^{127}Xe is inserted directly into the C₆₀ or C₇₀ cages by the recoil implantation process following nuclear reactions. In order to check the possibility of the direct insertion, we carried out *ab initio* molecular dynamics (MD) simulations using our all-electron mixed-basis code. We confirmed that such an insertion process may occur in realistic conditions.

To produce endohedral noble-gas (Xe, Kr) fullerene compounds, deuteron-induced reactions for iodine (^{127}I) and bromine (^{79}Br), namely $^{127}\text{I} (d, 2n) ^{127}\text{Xe}$ and $^{79}\text{Br} (d, 2n) ^{79}\text{Kr}$, are used. (Note that ^{127}Xe decays again to ^{127}I with a half-life of 36.4 days and emits 203, 172, and 375 keV γ rays, while ^{79}Kr decays again to ^{79}Br with a half-life of 34.9 h and emits 261, 398, and 606 keV γ rays [12].) At first, four samples were prepared by homogeneously mixing 10 mg of C₆₀ (C₇₀) with 10 mg of potassium-iodide, KI (potassium-bromide, KBr), and one sample was also prepared by mixing 10 mg of C₆₀ + C₇₀ with 10 mg of KI. The samples were irradiated with deuterons, at the Cyclotron Radioisotope Center of Tohoku University, using a beam energy of 16 MeV. Irradiation time was set to about 1 h and the average beam current was typically 5 μA . The sample was cooled with water and low-temperature He gas during the irradiation. After the irradiation, the sample was dissolved in *o*-dichlorobenzene. The solution was then filtered to remove insoluble materials through a membrane filter with pore size of 0.45 μm . The solution was injected into a high pressure liquid chromatography (HPLC) equipped with a 5PBB (silica bonded with pentabromobenzyl-group) column of 10 mm (inner diameter) \times 250 mm (length), at the

flow rate of 3 ml/min. The eluted solution was passed through a UV detector whose wavelength was adjusted to 290 nm in order to measure the amount of fullerenes and their derivatives. Eluent fractions were then collected in 30 sec intervals (0–30, 30–60, 60–90, . . . sec), 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. The energy resolution of the Ge detector is 1.8 keV in FWHM at the 1332 keV photopeak of ^{60}Co source. Therefore, the existence of ^{127}Xe or ^{79}Kr can be identified by its characteristic γ ray during its decay into ^{127}I or ^{79}Br , and any other sources can be ruled out.

The elution curves shown by solid lines in Figs. 1(a) and 1(b) indicate the absorbances monitored continuously by a UV detector for the irradiated samples of C_{60} mixed with KI and of C_{70} mixed with KI, respectively. The horizontal axis indicates the retention time after injection into the HPLC and the vertical axis indicates the absorption intensity monitored by the UV detector. Strong UV absorption exists at 7.75 min (8.5 min) in Fig. 1(a) [Fig. 1(b)].

The peak positions correspond to the retention time of C_{60} (C_{70}), which were determined by the calibration run using the C_{60} (C_{70}) samples before the irradiation. Second and small third peaks of Fig. 1(a) can be assigned to C_{60} dimers and C_{60} trimers, respectively. The second peak of a retention time 14–18 min in Fig. 1(b) can also be attributed to C_{70} dimers. These materials can be produced by the interaction between C_{60} 's or between C_{70} 's in coalescence reactions after ionization by incident deuterons or produced charged particles [13]. To confirm the existence of dimers, a $\text{C}_{60} + \text{C}_{70}$ mixed sample was prepared with weight ratio, $\text{C}_{60}:\text{C}_{70}:\text{KI} = 1:1:2$, and irradiated. The result of the UV chromatogram for the mixed sample is shown in Fig. 1(c) by a solid line. A new peak appears in a retention time of 11–14 min in the UV chromatogram, while no corresponding peak exists in the same retention time range in Figs. 1(a) and 1(b). This peak can be attributed to fullerene dimers, each being made of one C_{60} and one C_{70} by coalescence reactions. The same trend has been observed in our previous study of radioactive fullerenes labeled with ^{11}C [14,15].

The solid circles in Figs. 1(a)–1(c) indicate the radioactive counting rate of ^{127}Xe of each eluent fraction measured with the Ge detector. There are three peaks of ^{127}Xe radioactivity at retention times, 8 min, around 11 min, and 16.5 min, in Fig. 1(a) for the sample of C_{60} mixed with KI, while two peaks of ^{127}Xe radioactivity exit at retention times, 9.0 min and around 16.5 min, in Fig. 1(b) for the sample of C_{70} mixed with KI. Figures 1(a) and 1(b) show a clear correlation between the elution behaviors of the UV chromatogram (which measures fullerene populations) and the ^{127}Xe radioactivity (which measures ^{127}Xe populations). There is a slight shift in the eluent peaks in the UV chromatogram and the ^{127}Xe radioactivity. That is, the peaks in the ^{127}Xe radioac-

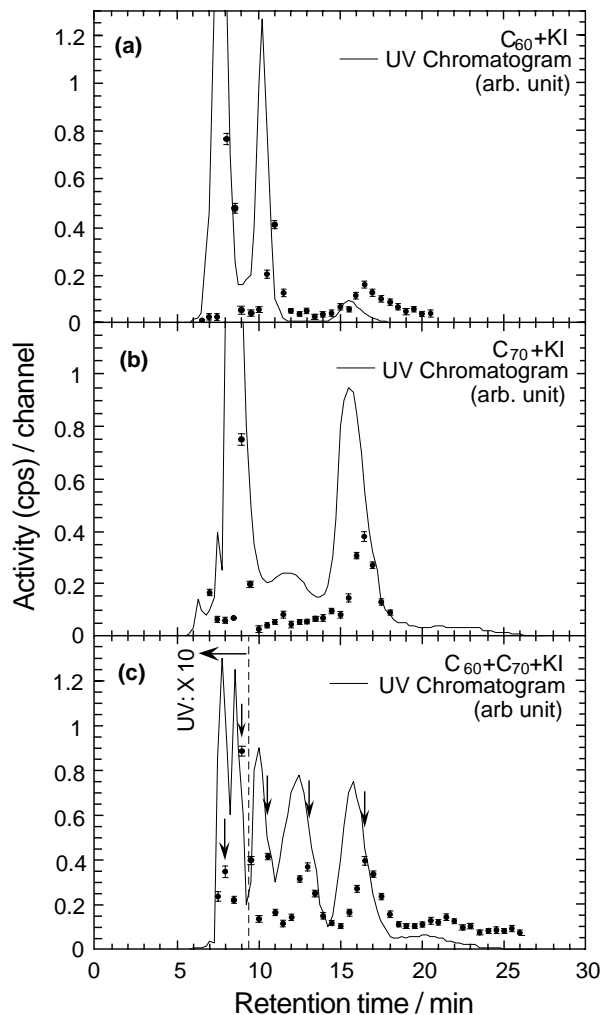


FIG. 1. (a) HPLC elution curves of the soluble portion of the crude extracted in the deuteron irradiated sample of C_{60} mixed with KI. The horizontal axis indicates retention time, and the vertical axis represents the counting rate of the radioactivities of ^{127}Xe in each fraction (solid circle), and the absorbance of UV chromatogram of C_{60} (solid line). Error bars indicate the statistical error of the γ counting rate. (b) HPLC elution curves as the same as (a), but for the sample of C_{70} mixed with KI. (c) HPLC elution curves as the same as (a) and (b), but for the sample of $\text{C}_{60}:\text{C}_{70}:\text{KI} = 1:1:2$. Vertical arrows indicate the position of ^{127}Xe radioactivity in retention time.

tivity (^{127}Xe populations) are shifted to later times from the peaks in the UV chromatogram (fullerene populations). The same trend was observed in the elution behavior of the metallofullerene extraction such as $^7\text{Be}@\text{C}_{60}$ [8] and $^{159}\text{Gd}@\text{C}_{82}$ [16]. Therefore, the first peak in Fig. 1(a) and that in Fig. 1(b) can be assigned, respectively, to $^{127}\text{Xe}@\text{C}_{60}$ and $^{127}\text{Xe}@\text{C}_{70}$, since noble-gas atoms are neutral and cannot make a bond with fullerene cages. Furthermore, the $\text{C}_{60}\text{-C}_{70}$ -dimer peak of ^{127}Xe radioactivity is also clearly observed in a retention time 12–14 min when the mixed sample made from three materials (C_{60} , C_{70} , and KI) is examined, as is seen in Fig. 1(c). Again, in this figure, it is noted that all of the eluent peaks

of ^{127}Xe radioactivity are slightly delayed from the absorption peaks of the UV chromatogram. This observation also corroborates the formation of endohedral fullerenes with encapsulated ^{127}Xe and their dimers (and trimers), namely $^{127}\text{Xe}@C_{60}$, $^{127}\text{Xe}@C_{60}\text{-}C_{60}$, and $^{127}\text{Xe}@C_{60}\text{-}C_{60}\text{-}C_{60}$ for the sample of C_{60} mixed with KI irradiated [Fig. 1(a)], $^{127}\text{Xe}@C_{70}$, and $^{127}\text{Xe}@C_{70}\text{-}C_{70}$ for the sample of C_{70} mixed with KI [Fig. 1(b)], $^{127}\text{Xe}@C_{60}$, $^{127}\text{Xe}@C_{70}$, $^{127}\text{Xe}@C_{60}\text{-}C_{60}$, $^{127}\text{Xe}@C_{60}\text{-}C_{70}$, or $^{127}\text{Xe}@C_{70}\text{-}C_{60}$, $^{127}\text{Xe}@C_{70}\text{-}C_{70}$ (here, contain small amount of $^{127}\text{Xe}@C_{60}$ trimers) for the $C_{60} + C_{70}$ sample mixed with KI [Fig. 1(c)]. Activities of ^{127}Xe on the eluent fractions were corrected and integrated for the decay of ^{127}Xe . Total activities of ^{127}Xe incorporated within fullerenes was estimated to be of the magnitude of $\sim 20\text{--}30$ Bq/mg.

Similar results for C_{60} and C_{70} fullerenes were obtained also in the elution behavior of ^{79}Kr radioactivity for the samples of C_{60} (C_{70}) mixed with KBr. Total activities of ^{79}Kr incorporated within fullerenes are also estimated to be of the magnitude of $\sim 200\text{--}300$ Bq/mg. The amount of endohedral fullerenes of ^{127}Xe and ^{79}Kr produced here is then estimated to be about 10^{10} molecules.

All the experimental results presented here support the following scenario: The ^{127}Xe or ^{79}Kr atoms are produced by nuclear reaction and removed from their own material with kinetic energies of about a few hundred keV [8,14]. Then, the kinetic energy decreases in the sample to a magnitude which is appropriate for the encapsulation. Finally, ^{127}Xe or ^{79}Kr penetrate into the C_{60} or C_{70} cages and stop inside. Further, the shock induces the cages to coalesce with neighboring cages with high probability. The purified endohedral noble-gas fullerenes produced in the present experiment seem to be rather more stable than diverse wide mixture of cluster fragments that are detected by mass spectrometry.

Now we turn our attention to *ab initio* molecular dynamics simulations. The method used here is based on an all-electron mixed basis approach [7,17] using both plane waves and atomic orbitals as a basis set within the framework of the local density approximation (LDA). So far, we have carried out similar simulations of Li and Be insertions into C_{60} [7,8] or into C_{70} [18]. In the present study, all the core atomic orbitals are determined numerically by a standard atomic calculation based on Herman-Skillmann's framework with logarithmic radial meshes. (Most of our previous studies have used analytic Slater-type atomic orbitals [7,8,17,18].) For the present system, we use 323 (for Xe systems) or 314 (for Kr systems) numerical atomic orbitals and 4169 plane waves corresponding 7 Ry cut-off energy. For dynamics, we assume the adiabatic approximation where the electronic structure is always in the ground state. In a supercell composed of $64 \times 64 \times 64$ meshes, where one mesh corresponds 0.196 Å, we put one C_{60} molecule which is stationary at $t = 0$ and one Xe (or Kr) atom moving with a given initial velocity toward the center of one six-membered ring [hereafter, we will call

this (uppermost) six-membered ring, $u\text{-}C_6$] of C_{60} vertically. The initial distance from the center of $u\text{-}C_6$ is 1.50 Å. We set the basic time step to be $\Delta t = 1/80 \sim 0.1$ fs and perform five steepest descent (SD) iterations after each updation of atomic positions in order to converge the electronic states. Here, we do not impose any velocity control, so that the system is almost microcanonical with little energy dissipation from the SD algorithm. All the calculations were performed on the supercomputer, HITAC S3800/380 (8 Gflops peak speed per CPU) at IMR, Tohoku University.

Let us briefly summarize the result of the simulation. First of all, Xe with initial kinetic energy greater than 130 eV and Kr with initial kinetic energy greater than 80 eV penetrate into the cage of C_{60} through the center of $u\text{-}C_6$ without difficulty, similar to our previous simulations of Li [7] and Be [8] insertions into C_{60} . Kinetic energies higher than 200 eV for Xe and 150 eV for Kr allow the atom to leave the fullerene again from the opposite side of the cage. Figure 2 shows several snapshots of the Xe insertion with 160 eV initial kinetic energy. Here we note that, in the case of Na [7], the simple insertion through the six-membered ring does not occur even with 50 eV initial velocity. Why can atoms much larger and heavier than Na pass through the six-membered ring so easily? The reason is mainly due to the chemical inactivity of noble-gas atoms. We estimated roughly from the monitored total energy during simulation that the energy barrier at the center of $u\text{-}C_6$ is about 8 Ry for Xe and 4 Ry for Kr. In Fig. 2, after the noble-gas atom first touches $u\text{-}C_6$, $u\text{-}C_6$ is significantly enlarged and pushed upward. On the other hand, the next six carbon atoms which are all adjacent to $u\text{-}C_6$ are first pushed downward due to the shock of collision, but, after propagating the shock to the carbon atoms at one row below, they start going up to maintain bonds with the carbon atoms constituting $u\text{-}C_6$. For relatively low initial kinetic energies (typically ≤ 300 eV for Xe and Kr), we observe the tendency to recover the original shape of $u\text{-}C_6$ within the simulation period. Of course, the simulation depends on 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 top of C_{60} after 50 fs or less from the insertion. If a noble-gas atom is inserted away from the center of $u\text{-}C_6$, the damage suffered on C_{60} increases significantly.

The result of the present simulations may tell us a story which is somewhat different from the open-window mechanism discussed in Ref. [10]. According to the open-window mechanism, one of the bonds of C_{60} should break off to create a widely opened hole in the cage, before atomic insertion. This may occur either by heating up C_{60} as was discussed in Ref. [10] or by a collision of another atom, as was discussed independently in Ref. [7] for the Na^+ collision against C_{60}^- . The possibility of realizing stable endohedral fullerenes by this open-window mechanism is much smaller compared to the present direct

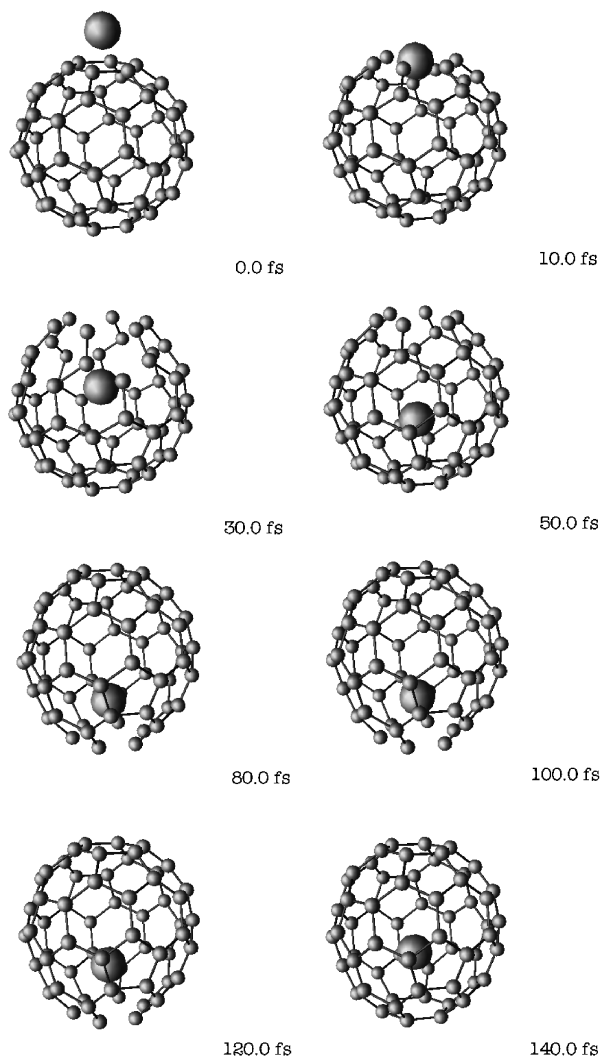


FIG. 2. Simulation of Xe hitting the center of a six-membered ring of C_{60} with a kinetic energy of 160 eV. Here, local skeleton disappear from the figure when the bond length is elongated more than 1.5 Å.

insertion process. That is, the creation rate of stable $Xe@C_{60}$ and $Kr@C_{60}$ can be much higher than that of stable $Na@C_{60}$. This is certainly consistent with the experimental evidence reported recently by us [18] using the same technique accompanied by the solvation process.

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