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Fourier transform infrared and mass spectrometry studies of a photoirradiated K_xC_{60} film

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Abstract. A photoirradiated potassium-doped C_{60} film has been studied by Fourier transform mass spectrometry (FT-MS) and by *in situ* high-resolution Fourier transform infrared spectroscopy (FT-IR) in combination with tight-binding IR calculations. The results of FT-MS and FT-IR strongly suggest that C_{120} bucky peanuts, which have been theoretically predicted to be stable, were formed in the photoirradiated film.

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1 Introduction

Since the first report on C_{60} photopolymerization by Rao *et al.* [1], many reports on C_{60} polymers formed by various methods such as photoirradiation, high pressure and high temperature, and alkali-metal doping have been published [2]. The cross-linking between adjacent C_{60} molecules has been found to be (i) a $[2+2]$ cycloadditional four-membered ring with photoirradiation [3, 4] and high pressure at high temperature [5–9], and (ii) a C–C single bond with alkali-metal doping [10–12].

Strout *et al.* [13] predicted theoretically that not only dumbbell-shaped C_{120} dimers but also C_{120} bucky peanuts are present and that the latter are energetically more stable than the former. Osawa *et al.* [14, 15] have recently proposed that C_{120} bucky peanuts can be formed from the dumbbell-shaped dimers through a series of the generalized Stone–Wales rearrangement (GSW), as shown in Fig. 1. However, no experimental evidence for the presence of C_{120} bucky peanuts has been reported so far. In this paper, we present the spectral evidence for the formation of C_{120} bucky peanuts in a potassium-doped C_{60} film under UV-visible light irradiation, using Fourier transform mass spectrometry (FT-MS) and *in situ* Fourier transform infrared spectroscopy (FT-IR) in combination with theoretical IR calculations based on a tight-binding method.

2 Experiments

About 1000 mg of C_{60} powder ($> 99.98\%$ pure) was placed into a quartz crucible. Thin films of C_{60} were formed on CsI substrates by sublimation at 400 °C for 90 min in a stainless steel vacuum chamber (a base pressure of 2×10^{-9} Torr) at a substrate temperature of 100 °C for achievement of good crystallinity (fcc structure) in the C_{60} film. The C_{60} films thus formed were estimated to be about 100 nm thick. Thereafter, potassium (K) was doped into the C_{60} films by means of a K dispenser from which potassium atoms were desorbed by joule heating. After the formation of the K_xC_{60} film on the CsI substrate, the sample holder was rotated by 90° for the measurement, at a high resolution of $0.25\ \text{cm}^{-1}$ before and after photoirradiation, of *in situ* FT-IR absorption spectra of the IR-active modes of the K_xC_{60} film. The details of this *in situ* high-resolution FT-IR apparatus have already been described in [16].

The composition of the K_xC_{60} films was determined by X-ray photoelectron spectroscopy [VG ESCALAB MkII], and the value x was estimated to be 2.0. The $[\alpha+3]$ phase is well known to be the most stable phase in the range $x = 0 - 3$ at a temperature of -13–150 °C for K_xC_{60} [17]. Therefore, the present films obtained under the conditions of $x = 0.5 - 2.0$ and 100 °C have the $[\alpha+3]$ phase, and C_{60}^{3-} anions were present in the K_xC_{60} films. In fact, we measured *in situ* FT-IR absorption spectra of the K_xC_{60} films and found that a new IR peak appeared at about $1370\ \text{cm}^{-1}$. Martin *et al.* has reported the dependence of the four fundamental IR mode frequencies on dopant concentration x for K_xC_{60} films [18]. Comparison of our IR

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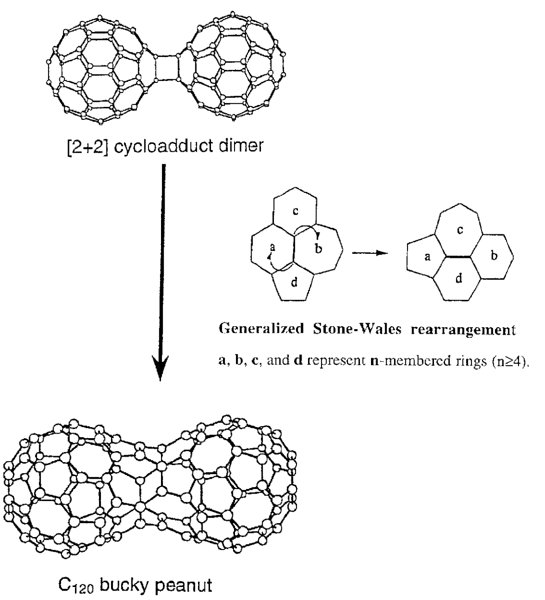


Fig. 1. A possible reaction scheme for formation of C_{120} bucky peanuts from dumbbell-shaped C_{120} dimers via a series of GSW.

result with theirs shows that the mode at $1370\,\mathrm{cm}^{-1}$ corresponds well to the $F_{1u}(\omega_4)$ mode for C_{60}^{3-}.

In order to determine the structure of the product in the photoirradiated K_xC_{60} film from experimental IR spectra, we have performed IR calculations using a tight-binding (TB) method that is useful for determining which structure is suitable to explain the whole trend of the experimental IR spectra of C_{120} formed in a photopolymerized C_{60} film [4]. The details of this calculation method have been described in [4]. *Ab initio* (first-principle) calculations of full geometry optimization, vibrational frequency, and IR intensity are more accurate than the TB calculations, but are now indeed out of the reach of many powerful supercomputers for the present molecular system containing 120 carbon atoms.

A 500-W mercury (Hg) lamp (Ushio) was used as a light source for photopolymerization of the K_xC_{60} films. Because the infrared light from the lamp causes an undesirable rise in substrate temperature, the IR light was cut off by a colored glass filter (Toshiba, IR-25S). Thus only UV-visible light (emission lines in the range 2–4 eV) from the Hg lamp was used for photopolymerization. The intensity of this UV-visible light over an area 50 mm in diameter was 3–4 W.

For FT-MS measurement of the K_xC_{60} films after irradiation, the films were taken out of the vacuum chamber equipped with FT-IR and subsequently mechanically removed from the CsI substrates. The films were then deposited onto an electroconducting carbon sheet glued to a stainless steel sample holder. The sample holder was thereafter introduced into the vacuum chamber of an FT-MS system (Extrel, FT-MS 2001). The sample was measured by N_2 laser ($\lambda = 337\,\mathrm{nm}$; intensity, $< 10\,\mathrm{mJ/cm^2}$) desorption FT-MS. When a pristine C_{60} film was examined as a reference, only a mass peak due to C_{60} monomers was observed, and no peak corresponding to C_2 fragments or polymers formed from those species was detected under the present FT-MS measurement conditions.

3 Results and discussion

3.1 FT-MS

Figure 2 shows the negative ion FT-MS spectra of the K_xC_{60} films after 20 h of UV-visible light irradiation in the

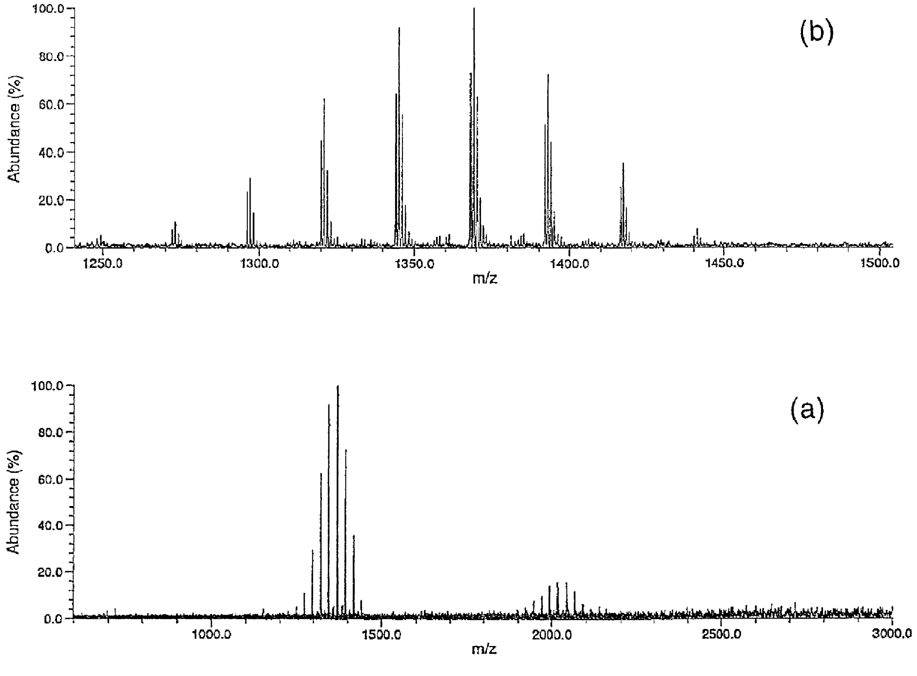
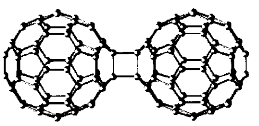


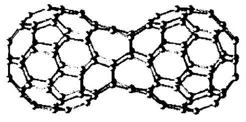
Fig. 2. FT-MS spectra of the K_xC_{60} film after 20 h irradiation with UV-visible light at a substrate temperature of 100 °C in the ranges of (a) 600–3000 m/z and (b) 1240–1500 m/z.

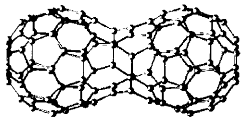
range of (a) 600–3000 m/z and (b) 1240–1500 m/z. It was found from the mass spectrum of Fig. 2a that mass peaks of C_{120} and its fragments were observed as major contributions and that mass peaks corresponding to fragments from C_{180} trimers by C_2 loss were also observed as minor contributions, while the parent peak of the C_{180} trimers was not detected. We next focused our attention on the dimers observed as a main product. Because no peak corresponding to C_2 fragments or polymers of C_{60} was observed under measurement conditions identical to that for the pristine C_{60} film, the dimer formation is not attributed to collision between C_{60} and its fragments in the gas phase upon laser desorption, but to UV-visible light irradiation of the K_xC_{60} film. This indicates that the FT-MS peaks with a mass smaller than 1440 m/z originate from fragmentation of the C_{120} dimers with an increment in C_2 loss. In addition, because the abundance of each mass peak observed in Fig. 2b corresponds well to the calculated natural abundance of C_{120} (1.11% ^{13}C isotope), we find that the mass peaks in Fig. 2b consist of only carbon and are due to the C_{120} and its fragments by C_2 loss. Furthermore, it is interesting to note that no peak corresponding to C_{60} monomers is observed in Fig. 2a. In C_{60} photopolymerization, the cross-linking of C_{60} dimers is well known to form a [2 + 2] cycloadditional four-membered ring [3, 4]. Very recently, Wang *et al.* synthesized the [2 + 2] cycloadduct C_{60} dimers and obtained FT-MS results in which C_{60} monomers were observed as the main contribution, along with C_2 loss from the dimer, and the parent peak and its C_2-loss fragments due to the dumbbell-shaped C_{120} dimers were quite small for both positive [19] and negative [20] ion measurements. On the other hand, Fig. 2a shows a mass spectrum different from that of the dumbbell-shaped C_{120} dimer reported by Wang *et al.*: C_2-loss fragmentation occurred for the C_{120} dimers, while no peak of C_{60} monomers resulting from decomposition of the dimers appeared.

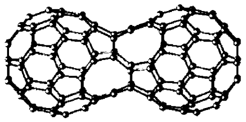
3.2 FT-IR

As described in the previous section, the present FT-MS results cannot be explained by the assumption that the product in photoirradiated K_xC_{60} film is the dumbbell-shaped C_{120} dimer. The question then remains: What structure of the C_{120} dimer is suitable to explain our present FT-MS results? In spite of the fact that substantial C_2 loss from the dimers occurred, the dimers were not decomposed to C_{60} monomers. This suggests that the dimers formed in the K_xC_{60} film have a more coalesced structure so as to maintain the cage of the dimer structure against C_2-loss fragmentation. In order to determine the geometric structure of the coalesced dimer, we have performed *in situ* FT-IR spectroscopy (the measurement region of this FT-IR apparatus was 400–4000 cm^{-1}) of the phototransformed K_xC_{60} film and compared this with theoretical IR spectra of several C_{120} candidate isomers. For the candidates, we examined the dumbbell-shaped C_{120}, three C_{120} bucky peanuts isomers [P55, P56, P66], and a C_{120} bucky tube, as shown in Fig. 3, and calculated the IR spectrum of the individual negatively charged C_{120}^{6-} isomers whose geometries were energetically optimized.


(a) Dumb-bell


(b) Peanuts P55


(c) Peanuts P56


(d) Peanuts P66

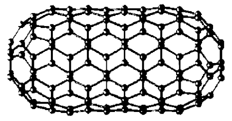

(e) Tube

Fig. 3. Geometric structures of several kinds of C_{120} isomers examined in the present paper. Individual isomers have 6 negative charges; these structures were optimized energetically by tight-binding calculations.

Figure 4 shows the FT-IR absorption spectrum of (a) the K_xC_{60} film after 20 h photoirradiation at a substrate temperature of 100 °C and compares this with theoretical IR spectra (b)–(f) of the negatively charged C_{120}^{6-} isomers. No peak was observed in the range 1600–4000 cm^{-1}; therefore, only the IR spectrum (a) in the range 400–1600 cm^{-1} is shown. In Fig. 4a, photopolymerization between C_{60} molecules in the $\alpha{-}C_{60}$ phase did not proceed at a substrate temperature of more than 100 °C even after 20 h of photoirradiation [3]; thus the arrowed peaks are attributed to the four fundamental modes of C_{60} molecules in the $\alpha{-}C_{60}$ phase. In addition, because the FT-MS results showed that no mass peak corresponding to C_{60} monomers was observed, photopolymerization in the K_3C_{60} phase occurred completely. This means no presence of C_{60}^{3-} in the K_3C_{60} phase after 20 h irradiation. Consequently, all the IR peaks except the four arrowed peaks shown in Fig. 4a were due to the negatively charged C_{120}^{6-} dimers formed in the K_3C_{60} phase.

Comparison of the experimental IR spectrum (a) with the theoretical spectra (b)–(f) in Fig. 4 clearly shows that the calculated IR spectra of the C_{120} bucky peanuts P66 (e) and the C_{120} bucky tube (f) were quite different from the experimental spectrum (a). For the IR spectrum (b) of the dumbbell-shaped C_{120}, although the frequencies of individual IR modes seem to coincide roughly with the experimental result (a), their relative IR intensities are

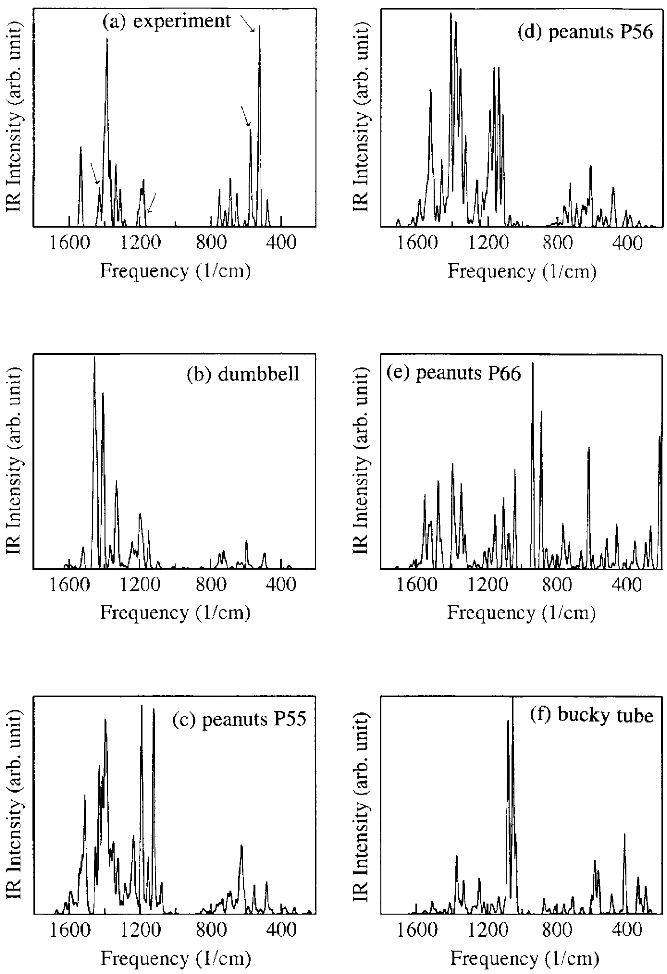


Fig. 4. FT-IR spectrum of (a) the K_xC_{60} film after 20 h irradiation with UV-visible light at a substrate temperature of 100 °C, together with theoretical IR spectra of (b) a C_{120} dumbbell, (c) C_{120} bucky peanuts P55, (d) C_{120} bucky peanuts P56, (e) C_{120} bucky peanuts P66, and (f) a C_{120} bucky tube with 6 negative charges. Theoretical IR spectra were obtained using tight-binding calculations. Four arrows in Fig. 2a indicate the four fundamental IR modes of C_{60}.

quite distinct from those of the spectrum (a), in particular for the relative intensities of the peaks appearing around 700, 1400, 1430, and 1550 cm^{-1}. This indicates that the dimers formed in the photoirradiated K_xC_{60} film were not the dumbbell-shaped C_{120} dimers; this conclusion is consistent with the FT-MS results described in the previous section. We next compare the experimental results with the calculated IR spectra of the bucky peanuts P55 and P56. For the bucky peanuts P55 (c), the frequencies seem to agree reasonably with those of the experimental spectrum (a); however, the relative intensities of the peaks around 1200 cm^{-1} were more intense than those around 1400 cm^{-1}. This is opposite to the experimental result (a). In addition, in the range 600–800 cm^{-1}, only one peak appearing around 650 cm^{-1} was intense for the P55, while three intense peaks appeared in the range for the experimental result. On the other hand, for the bucky peanuts P56 (d), both the frequencies and relative intensities of the individual IR modes agree roughly with those for the experimental spectrum (a), except that the intensities of the peaks around 1200 cm^{-1} are somewhat intense in comparison with those for the experimental result. Furthermore, when the dimers have 6 negative charges, their geometric symmetry was reduced, except for the P56 isomer: $D_{2h} \rightarrow C_{2v}$ for the [2 + 2] dumbbell, $D_{3d} \rightarrow C_{1h}$ for the P55, $C_{3v} \rightarrow C_{3v}$ for the P56, $D_{3d} \rightarrow C_{2h}$ for P66, and $D_{5d} \rightarrow C_{1h}$ for the bucky tube. This indicates that only the P56 isomer has a stable structure following the addition of 6 negative charges. Consequently, the FT-IR results strongly suggest that the C_{120} dimers formed in the photoirradiated K_xC_{60} film were assigned to the C_{120} bucky peanuts with the structure P56 shown in Fig. 3c.

3.3 The effect of potassium on C_{60} photopolymerization

According to previous reports by Osawa *et al.* [14,15], the activation energy of the GSW rearrangement has a very high value, 6 eV, so that the GSW rarely occurs in a pristine C_{60} film under the experimental conditions of photoirradiation [1,3,4]. In the present case, C_{60}^{3-} anions were present in the K_xC_{60} film, as has been described in Sect. 2. The electron transfer from K atoms to the LUMO π^* molecular orbital (t_{1u}) of C_{60} reduces the molecular symmetry of the neutral C_{60} [21]. The C_{60}^{3-} anion was proposed to have a C_{2v} distortion symmetry, which completely removes the degeneracy of the t_{1u} (LUMO) and t_{1g} (LUMO+1) levels, i.e., $t_{1u} \rightarrow a_1 + b_2 + b_1$ and $t_{1g} \rightarrow b_2 + b_1 + a_2$ [21]. This leads to the increase in optical allowed transitions as compared with those for the neutral C_{60}, and the photoabsorption efficiency of the anion is larger than that of the neutral C_{60}. In addition, the reactivity of the C_{60}^{3-} anion with the distorted structure is assumed to be greater than that of the neutral C_{60}. Consequently, the effect of potassium on C_{60} photopolymerization enhances both the photoabsorption efficiency and reactivity of C_{60} molecules, playing the role of reduction of the activation energy of the GSW. This predicts that the GSW would readily take place under the present conditions. The formation mechanism of the C_{120} bucky peanuts is reasonably explained in terms of a series of the GSW rearrangement from the [2 + 2] dumbbell-shaped C_{120} as an initial product (see Fig. 1).

4 Summary

In this paper, we have shown spectral evidence for the formation of C_{120} bucky peanuts (P56) in a photoirradiated potassium-doped C_{60} film, using FT-MS and *in situ* FT-IR in combination with theoretical calculations based on the TB method. In order to determine the structure of the bucky peanuts more satisfactorily, it is necessary to purify the bucky peanuts and to thereafter measure the crystal structure of the molecules with X-ray diffraction at the next stage.

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