In situ high-resolution infrared spectroscopy of a photopolymerized C_{60} film

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Photopolymerized C_{60} film has been studied under a water-vapor-free condition by means of *in situ* high-resolution (0.25 cm^{-1}) Fourier-transform infrared (FT-IR) spectroscopy. It was found that the IR spectrum of a pristine C_{60} film changed markedly after 10-h irradiation with a 500 W mercury lamp at a CsI substrate temperature of 27 °C, whereas no change in the IR spectrum of the C_{60} film was observed after 20-h irradiation with the lamp at a substrate temperature of 100 °C. Compared with the previous FT-IR result reported by Rao *et al.* [Science **259**, 955 (1993)], the present IR spectra for the photopolymerized film had many new peaks and the peaks corresponding to the four intrinsic intensive IR-active modes were split. A C_{60} dimer structure is postulated after comparison between the present results and the theoretical IR calculations reported by Adams *et al.* [Phys. Rev. B **50**, 17 471 (1994)] and Pederson and Quong [Phys. Rev. Lett. **74**, 2319 (1995)]. [S0163-1829(96)04333-0]

I. INTRODUCTION

Since Rao *et al.*[1] reported that C_{60} molecules are polymerized by Ar-ion laser or UV visible lamp irradiation of a pristine C_{60} film at room temperature, there have been many reports on C_{60} dimers or polymers formed by various methods, such as photo irradiation,[2–7] under high pressure and temperature conditions,[8,9] alkaline-metal doping,[10–14] and electron impact.[15] For compounds formed by all of these methods, many researchers have strongly suggested that C_{60} dimers form a [2+2] cycloadditional four-membered ring shown in Fig. 1.[16–23]

The dimer structure in Fig. 1 gives rise to a reduction in C_{60} molecular symmetry (I_h). Since IR-active modes are sensitive to changes in molecular symmetry, IR spectroscopy is a powerful tool for the study of the dimer structure in phototransformed C_{60}. Rao *et al.* reported the IR spectrum of a photopolymerized C_{60} film.[1] Although they proposed the dimer drawn in Fig. 1 as a possible structure, they did not determine the structure on the basis of the IR spectra. This is probably because the influence of water vapor or oxygen on the photopolymerization was not fully avoided, since they obtained the IR spectra of the photopolymerized C_{60} film in a glove box filled with argon gas in order to minimize the effect of the contaminants in air. In fact, some peaks corresponding to water vapor were observed in the 3200 cm^{-1} region in the Fourier-transform infrared (FT-IR) spectrum for the C_{60} film in a similar experiment carried out by Narasimhan *et al.*,[24] where the exposure of the C_{60} film to air
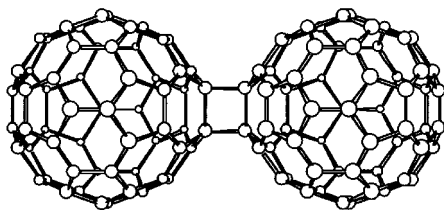
was minimized by keeping it in a dry box filled with argon gas.

In a recent study,[25] we developed an apparatus for *in situ* high-resolution (0.25 cm^{-1}) FT-IR spectroscopy of C_{60} film, which enables us to prevent the exposure of the film to air. No peak due to water vapor was observed in the FT-IR spectrum of the C_{60} film (see Fig. 2 in Ref. 25). In the present work, we examine the photopolymerized C_{60} film by *in situ* measurement of FT-IR spectra and compare the results with those of theoretical IR calculations.

II. EXPERIMENT

Figure 2 shows a schematic representation of the apparatus for *in situ* high-resolution FT-IR spectroscopy of phototransformed C_{60} film. The details of this system were described in Ref. 25.

About 1 g of C_{60} powder (Matsubo, $>99.98\%$ pure) was placed into a quartz crucible (15 mm in diameter and 50 mm long). Then the crucible was held at 200 °C *in vacuo* for more than 10 h in order to remove the residual organic solvents from the C_{60} powder. Thin films of C_{60} were formed onto a CsI substrate (Pureoptics, 20 mm in diameter and 2

FIG. 1. C_{60} dimer structure consisting of a [2+2] cycloadditional four-membered ring.
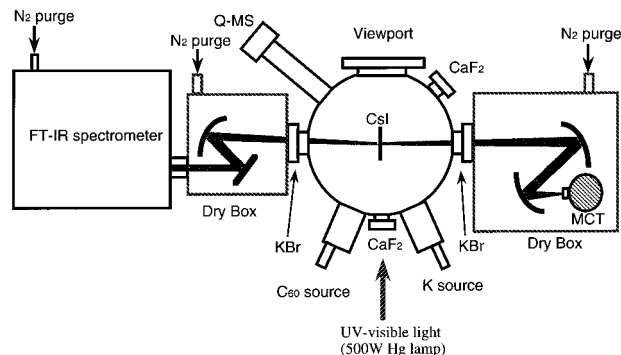

FIG. 2. Schematic representation of an *in situ* high-resolution FT-IR apparatus for the study of photopolymerized C_{60} film.

mm thick) by sublimation of 400 °C for 90 min in a vacuum chamber (base pressure: 3×10^{-8} Torr) under a pressure of about 10^{-7} Torr. During the deposition of C_{60}, the substrate was heated to and maintained at 100 °C in order to obtain good crystallinity (fcc structure) in the C_{60} film.[26] The thickness of the C_{60} film thus formed was estimated to be about 1000 Å using the Lambert-Beer equation, $A = \kappa d$, where A, κ, and d denote absorbance, absorption coefficient, and thickness, respectively. The value of A for each IR-active mode was obtained experimentally and the value of κ for each mode used in the calculations was taken from a previous experimental report.[27]

After the formation of the C_{60} film on the CsI substrate, the sample holder was rotated by 90° in order to measure FT-IR absorption spectra of the IR-active modes of the phototransformed C_{60} film with a high resolution of 0.25 cm^{-1}. As shown in Fig. 2, a FT-IR spectrometer (Mattson Research series) was connected to the vacuum chamber via an external optical system mounted in a plastic box with N_2 purge. The IR beam that passed through the CsI substrate was incident on a mercury-cadmium-tellurium (MCT) detector which was placed in a similar N_2-purge box connected to the opposite side of the chamber. An S/N ratio of about 300 was obtained for 500 scans at 0.25 cm^{-1} resolution (a system with this S/N ratio can be used to detect one monolayer of C_{60} on the CsI substrate). Two KBr single crystals (50 mm in diameter and 12 mm thick) were installed in the vacuum chamber as an IR beam window. Dry N_2 gas was introduced at a rate of 50 L/min into the FT-IR spectrometer and the two attached external boxes in order to eliminate water vapor from the IR-beam optical path. In this system, it was found that no diffuse absorption peak appeared in the 3200 cm^{-1} region corresponding to water vapor and thus a water-free condition for the FT-IR measurement of C_{60} film was achieved.

The partial pressures of residual gases were very low during FT-IR measurement. For example, the partial pressure of H_2O vapor was typically less than 10^{-8} Torr. The partial pressures of H_2, He, CH_4, N_2, O_2, CO, CO_2, Ar, and other hydrocarbons were in the range 10^{-9}–10^{-10} Torr.

A 500 W mercury (Hg) lamp (Ushio Electric. Co.: Model HB-50110AA) was used as a light source for photopolymerization. Since infrared light from the lamp causes an undesirable rise in substrate temperature, the IR light was absorbed by a colored glass filter (Toshiba: IR-25S). Thus only UV visible light from the Hg lamp (emission lines in the range 2–4 eV) was used for photopolymerization. The intensity of this UV visible light over a 50-mm-diam area was 3–4 W. The C_{60} film was irradiated with the focused UV visible light beam through a CaF_2 optical window (40 mm in diameter and 4 mm thick). A quartz lens (50 mm in diameter and $f = 500$ mm) was used to focus the light on the C_{60} film for photopolymerization. The substrate temperature increased to about 50 °C during irradiation. After the substrate temperature returned to 27 °C, FT-IR spectra were measured for the phototransformed C_{60} film.

III. RESULTS AND DISCUSSION

When the C_{60} film was irradiated with the Hg lamp at a substrate temperature of 100 °C, the spectrum of the photoir-
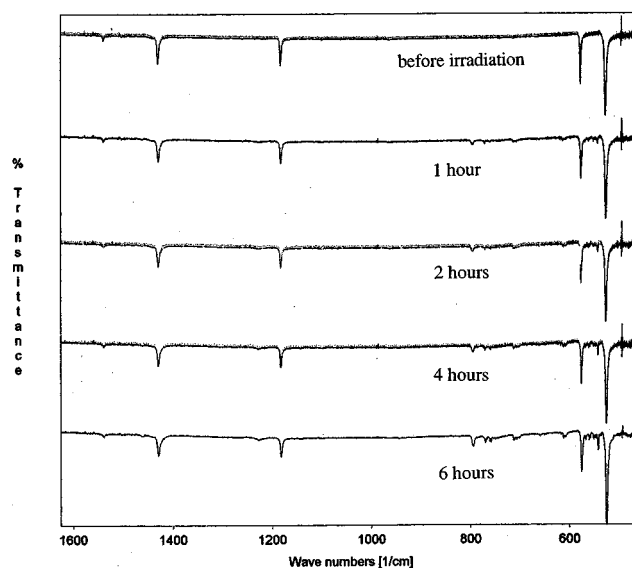

FIG. 3. The irradiation-time evolution of FT-IR spectra for the C_{60} film at a substrate temperature of 27 °C.

radiated C_{60} film changed little in comparison with that of the pristine C_{60} film. This indicates that photopolymerization in C_{60} film does not proceed at a substrate temperature of 100 °C, which is consistent with the previous result reported by Eklund et al.[5] that the photopolymerization is reversible at temperatures higher than 100 °C.

When the substrate temperature was reduced to 27 °C, however, photopolymerization occurred. Figure 3 shows time-evolution IR spectra for the C_{60} film irradiated with the Hg lamp. After 1 h of irradiation, many new weak IR peaks appeared. The new IR peaks became stronger after 6-h irradiation, as shown in the bottom spectrum in Fig. 3. Figure 4 shows the IR spectrum for the phototransformed C_{60} film after 26-h irradiation. There are not only many new weak IR peaks but there is also peak splitting of the four intrinsic IR-active modes, which indicates that the molecular symmetry of C_{60} was lowered. Table I summarizes the intensities and frequencies (cm^{-1}) of the IR modes seen in Fig. 4, together with those reported in the previous works.[1,8,11] Compared with the result obtained by Rao et al.,[1] more detailed information on IR spectra of photopolymerized C_{60} film was obtained in the present work.

Martin et al.[28] have recently reported experimental vibrational modes and their group-theoretical assignments for pristine C_{60} film. Compared with the present IR results in Table I, it is found that the IR spectrum in Fig. 4 is quite different from that of the pristine C_{60} film, except for the four intrinsic IR modes. This fact indicates that the new peaks in the spectrum for the phototransformed C_{60} film are not attributable to the IR silent or intramolecular coupling modes of the pristine C_{60} but to the modes originating from C_{60} photopolymerization.

Theoretical calculations[16–23] have suggested that C_{60} dimers form a [2+2] cycloadditional four-membered ring structure (Fig. 1) under photopolymerization, high pressure and temperature, and alkaline metal doping. Table I shows that a compressed C_{60} film gives an IR spectrum similar to that for the phototransformed C_{60} film, while a Rb-doped
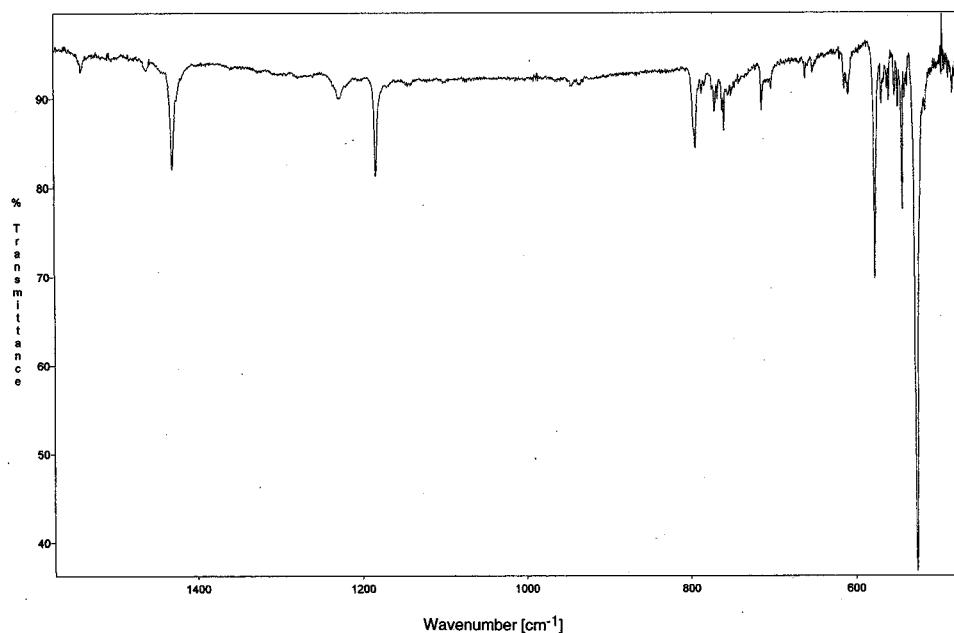
FIG. 4. FT-IR spectrum for the phototransformed C_{60} film after 26-h irradiation using the 500 W Hg lamp at 27 °C.

C_{60} film has a distinct spectrum. This discrepancy may be due to the charge on a C_{60} dimer. A C_{60} dimer formed by photo- or pressure-induced polymerization is neutral, while the dimer formed by Rb doping has approximately two negative charges, $[C_{60}\text{-}C_{60}]^{2-}$. This implies that a change in molecular potential affects the vibrational modes. It is unclear whether or not the [2+2] cycloadditional four-membered ring structure with two negative charges is still stable. It is also necessary to determine the C_{60} dimer structure formed in alkaline-metal doped C_{60} film.

We first compare the present IR results with the results of theoretical IR calculations reported by Adams *et al.*[19] for the C_{60} dimer based on the structure in Fig. 1. They performed first-principles molecular-dynamical relaxations for seven different configurations of a C_{60} dimer. The relaxed C_{60} dimer configuration with D_{2h} point symmetry shown in Fig. 1 in Ref. 19 was found to have the lowest energy among the seven configurations. Based on this relaxed structure, they calculated the frequencies of the IR-active modes of C_{60}, the C_{60} dimer, and an infinite chain polymer (see Fig. 3 in Ref. 19). Figure 5 shows a comparison of the present results and the theoretical frequencies for the IR modes of the relaxed C_{60} dimer, along with previous experimental IR results.[1,8] It is found that the theoretical IR calculations based on the relaxed C_{60} dimer reproduce the present results roughly except at frequencies higher than 1400 cm^{-1}. This suggests that relaxed C_{60} dimers with D_{2h} symmetry are formed in phototransformed C_{60} film. The disagreement at frequencies higher than 1400 cm^{-1} may be because the calculation error becomes larger at higher frequencies when the four intrinsic IR-active modes are compared (see Fig. 4 in Ref. 19). The theoretical IR frequencies of $F_{1u}(1)$ and $F_{1u}(2)$ were in good agreement with the experimental values, while those of $F_{1u}(3)$ and $F_{1u}(4)$ were higher by about 40 and 100 cm^{-1} than the experimental values of 1183 and 1430 cm^{-1}, respectively. In order to identify the dimer structure more satisfactorily, it is necessary to compare the intensities of IR

modes in the present and the theoretical results quantitatively. Unfortunately, Adams *et al.* did not calculate the IR strength in their report.

Next we compare our results with those of the IR calculations obtained by Pederson and Quong.[20] They performed 120-atom dimer calculations using a complete all-electron, full potential self-consistent local-density approximation. They obtained a slightly different structure from that reported by Adams *et al.*, although the crosslink between C_{60} molecules is basically a [2+2] cycloadditional four-membered ring for both calculations. For IR calculations of F_{1u} modes, they employed the $R8$ and Th models. The
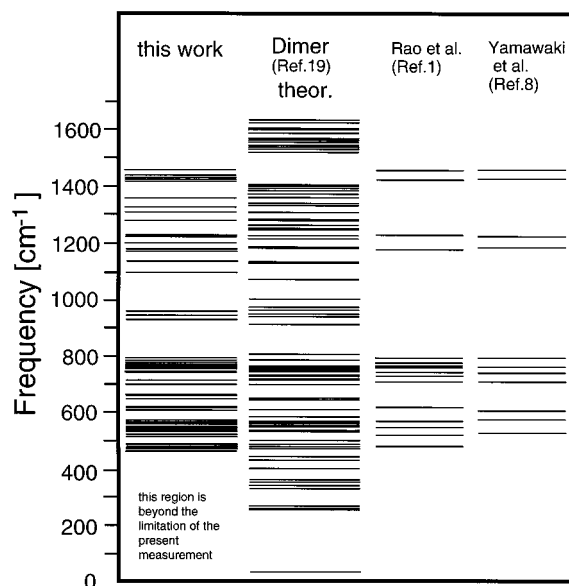

FIG. 5. Comparison of IR frequencies obtained experimentally and calculated theoretically, together with previous experimental IR results for photopolymerized and compressed C_{60} films.

TABLE I. Comparison of IR modes (cm^{-1}) of photopolymerized C_{60} obtained in this experiment and those reported in the previous studies. The intensities are given in parentheses: w, m, and s denote weak, medium, and strong, respectively.

This work	Previous works			This work	Previous works		
	Rao et al.[a]	Yamawaki et al.[b]	Martin et al.[c]		Rao et al.[a]	Yamawaki et al.[b]	Martin et al.[c]
C_{60}	C_{60}	Compressed C_{60}	RbC_{60}	C_{60}	C_{60}	Compressed C_{60}	RbC_{60}
1460(m)	1460(w)	1460(w)	1451(m)	745(w)			480(w)
1442(w)	1424(m)	1426(w)	1430(m)	712(m)			
1430(s)	1229(w)	1223(w)	1412(w)	701(m)			
1424(w)	1183(w)	1185(w)	1406(s)	667(w)			
1418(w)	796(m)	797(w)	1368(m)	660(w)			
1359(w)	779(w)	765(w)	1341(s)	650(w)			
1326(w)	769(w)	744(w)	1313(m)	618(w)			
1308(w)	761(w)	710(w)	1244(m)	612(m)			
1277(w)	743(w)	611(w)	1192(w)	607(m)			
1228(m)	727(w)	575(w)	1183(s)	576(s)			
1219(w)	709(w)	527(m)	1145(m)	568(m)			
1202(w)	616(w)		1093(w)	564(w)			
1183(s)	569(m)		1082(m)	561(m)			
1170(w)	550(m)		960(w)	558(m)			
1139(w)	526(m)		838(m)	552(m)			
1100(w)	484(m)		816(m)	547(m)			
962(w)			761(w)	542(s)			
944(w)			742(w)	540(m)			
925(w)			724(m)	537(w)			
793(s)			705(w)	526(s)			
785(w)			689(m)	515(w)			
782(w)			682(w)	491(w)			
773(w)			665(w)	489(w)			
769(m)			576(s)	487(w)			
766(w)			565(m)	482(m)			
760(w)			558(w)	479(w)			
758(m)			542(w)	475(w)			
753(w)			526(s)	473(w)			
750(w)			517(w)	468(m)			
748(w)			503(m)				

[a]Reference 1.
[b]Reference 8.
[c]Reference 11.

former is a one-ball model for the vibrational modes of polymerized C_{60}, while the latter is a one-ball model for those due to an fcc lattice of C_{60}. According to the results obtained using the Th symmetry model, coupling between the $F_{1u}(4)$ and $G_u(6)$ vibrational modes gives rise to the appearance of strong and weak IR-active peaks that are 10 and 105 cm^{-1} below the original $F_{1u}(4)$ peak (1430 cm^{-1}), respectively. That is, a strong IR peak at 1420 cm^{-1} and a weak one at 1325 cm^{-1} are predicted to appear when a [2+2] cycloadditional dimer is formed. Compared with the present results in Table I and Fig. 4, it is found that one of the two peaks at 1420 cm^{-1} corresponds to the observed peak at 1418 cm^{-1} and the other at 1325 cm^{-1} corresponds to that at 1326 cm^{-1}. However, the observed peak at 1418 cm^{-1} is weak against the above prediction. On the contrary, the $R8$ model cannot be used to explain the appearance of these two peaks. Using both models, it was predicted that the

$F_{1u}(4)$ mode is split into two peaks that are separated by about 10 cm^{-1}. The splitting of $F_{1u}(4)$ is determined as about 6 cm^{-1} in the present work. The theoretical predictions are in qualitative agreement with our results for this peak splitting.

Pederson and Quong briefly discussed the change in the $F_{1u}(3)$ mode for the C_{60} dimer in terms of the two models. Using the Th model, it was predicted that there is a nearly pure $F_{1u}(3)$ peak plus two very small peaks, as shown in Fig. 3 in Ref. 20. In this model, the $H_u(5)$ and $F_{2u}(4)$ retain much of their icosahedral identity with less than 4% of F_{1u} admixture. In contrast, using the $R8$ model, it was predicted that there are at least three distinct peaks, spread out over about 20 cm^{-1} that have $F_{1u}(3)$ admixtures ranging between 17 and 100%. The present IR spectrum of the phototransformed C_{60} film shown in Fig. 4 corresponds more closely to the Th model than to the $R8$ one.

Comparison of the two models suggests that the *Th* model can be used to explain the present IR results for the change in F_{1u} modes upon C_{60} polymerization.

IV. SUMMARY

In situ high-resolution FT-IR measurements for the study of phototransformation in a C_{60} film have been carried out under water-vapor-free conditions. The IR spectra of the phototransformed C_{60} film have many more peaks than the previous IR spectra of photopolymerized and compressed C_{60} films. Compared with theoretical IR calculations, the present work strongly suggests that a C_{60} dimer has a relaxed configuration (D_{2h} symmetry) with a [2+2] cycloadditional four-membered ring structure, and that the *Th* model based on a fcc lattice of C_{60} can be used to explain the change in F_{1u} IR-active modes for C_{60} dimers.

IR spectroscopy is a powerful tool for determining molecular structure accurately when it is used in connection with theoretical calculations. Unfortunately, the C_{60} dimer structure in photopolymerized C_{60} film has not been identified satisfactorily at this stage. In order to explain the present IR results quantitatively, it is necessary to calculate the intensities of IR modes by performing more accurate first-principles vibrational calculations for the C_{60} dimer.

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