

Article

# Pressure-Induced Dimerization of C<sub>60</sub> at Room Temperature as Revealed by an *In Situ* Spectroscopy Study Using an Infrared Laser

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**Abstract:** Using *in situ* high-pressure Raman spectroscopy and X-ray diffraction, the polymerization and structure evaluation of C<sub>60</sub> were studied up to 16 GPa at room temperature. The use of an 830 nm laser successfully eliminated the photo-polymerization of C<sub>60</sub>, which has interfered with the pressure effect in previous studies when a laser with a shorter wavelength was used as excitation. It was found that face-centered cubic (fcc) structured C<sub>60</sub> transformed into simple cubic (sc) C<sub>60</sub> due to the hint of free rotation for the C<sub>60</sub> at 0.3 GPa. The pressure-induced dimerization of C<sub>60</sub> was found to occur at about 3.2 GPa at room temperature. Our results suggest the benefit and importance of the choice of the infrared laser as the excitation laser.

**Keywords:** fullerenes; polymerization; pressure-induced; Raman; infrared laser

## 1. Introduction

C<sub>120</sub>, which is formed with two C<sub>60</sub> cages via a 2 + 2 cyclo-addition reaction, has attracted considerable interest due to its unique geometry and interesting physical and chemical properties [1–4]. The formation of C<sub>120</sub> can be induced by the mechanochemical reaction of C<sub>60</sub> with KCN [1], the high-pressure reaction of C<sub>60</sub> at a certain temperature range [2], and the light irradiation of C<sub>60</sub> crystals if the energy of the photon is higher than the band gap (1.7 eV, ~730 nm) of the sample [5]. Compared to all the aforementioned methods, high pressure is much more effective and has been widely studied [4,6–9]. Because the formation of bonds between neighboring C<sub>60</sub> molecules is a thermally activated process, the polymerization reaction is very slow at room temperature [4,9]. The majority of high-pressure studies have shown that the dimerization of C<sub>60</sub> can only form under the conditions of high temperature (373–473K) and high pressure (1.5 GPa) [4,9,10]. However, few studies have provided evidence, suggesting that C<sub>60</sub> polymerizes at room temperature [2]. Therefore, whether C<sub>60</sub> can polymerize at room temperature is still an open question.

Raman spectroscopy is a very important diagnostic technique in the study of polymerization of  $C_{60}$  [4–13]. In-situ Raman studies on  $C_{60}$  at high pressure using a visible laser have been carried out for pressures over 15 GPa [12,13]. An abrupt change in the slope of the Raman modes of  $C_{60}$  was found at around 2.5 GPa. It was claimed that the change was due to the phase transition from the partially ordered simple cubic (sc) phase to the rotation free orientationally ordered sc phase of  $C_{60}$ , which occurred at 2.5 GPa at room temperature [12]. No signs of the pressure-induced polymerization of  $C_{60}$  were found, even though the pressure was up to 15 GPa [12]. However, it should be noted that the selection of an excitation laser for Raman studies on  $C_{60}$  is important because it is known that a laser with a wavelength shorter than 730 nm will introduce photo-induced polymerization of  $C_{60}$  [4,11]. Therefore, to successfully eliminate the effect of light irradiation, an excitation laser with a much lower energy (or a longer wavelength) should be used. Unfortunately, almost all in-situ Raman studies of  $C_{60}$  under high pressure, which were carried out at room temperature, employed visible lasers (400–700 nm) as the excitation. The use of these high-frequency lasers will induce photo-polymerization and interfere with pressure effect, as also found in the polymerization process of butadiene and 2-(hydroxyethyl)methacrylate under high pressure [14,15]. Therefore, it was necessary to carry out an in-situ study to investigate the pressure-induced dimerization using a laser with much lower energy as the excitation.

It is also noted that the band gap of  $C_{60}$  decreases as the pressure increases. It has been well determined that the gap closing rate under high pressure is about  $-0.05$  eV/GPa [16,17]. In this study, an infrared laser with an 830 nm ( $\sim 1.49$  eV) wavelength, which would not induce polymerization as a pressure lower than about 4 GPa, was selected as a probe in order to study the behavior of  $C_{60}$  under cool compression (at room temperature) by carrying out in-situ Raman experiments. Our obtained results showed unambiguous evidence, indicating the dimerization of  $C_{60}$  at a pressure of about 3.2 GPa at room temperature. This result was different to that obtained using visible lasers as excitations, showing the pressure effect.

## 2. Experiments

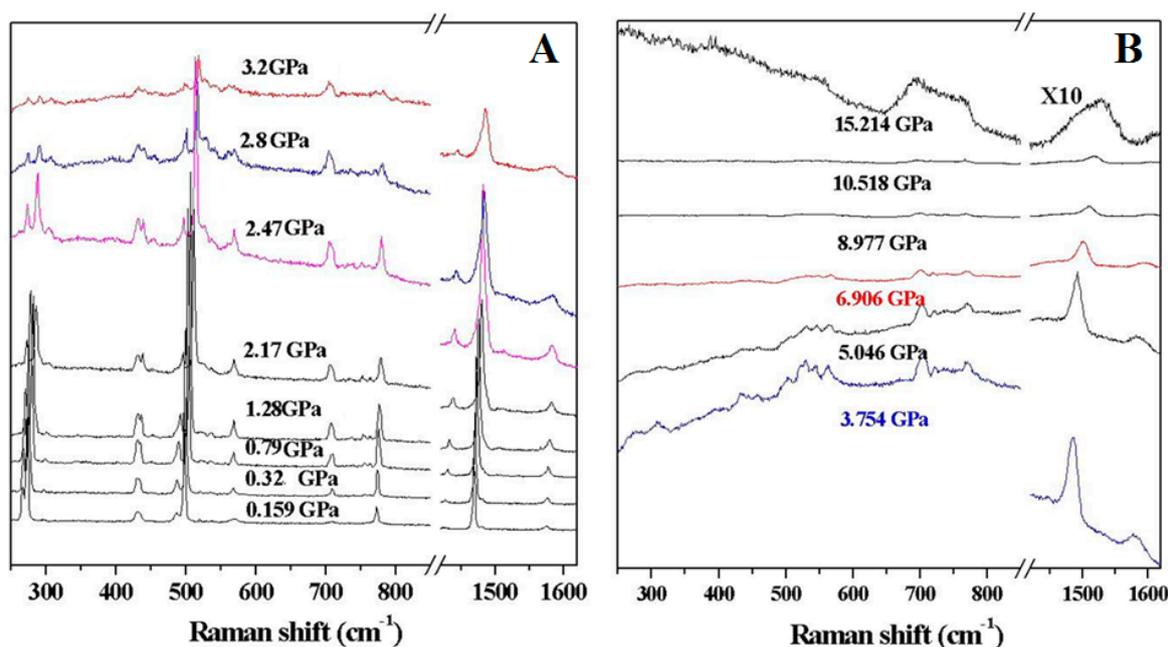
$C_{60}$  with purity higher than 99.9% was purchased from the Wuda Sanwei Carbon Cluster Corporation, China. It was used without any further treatment. A Mao-type diamond-anvil cell was used to generate high pressure for the samples [18,19]. The  $C_{60}$  crystals were loaded into a hole with a diameter of 120  $\mu\text{m}$  that was drilled in a T301 stainless steel gasket, preindented to a thickness of 50  $\mu\text{m}$ . A methanol-ethanol-water mixture in the volume ratio of 16:3:1 was used as pressure-transmitting medium [20]. The pressure at the sample chamber was determined using the shift of the ruby fluorescence [21]. The Raman spectra were recorded by a Raman spectrometer (Renishaw inVia, UK) with an 830 nm laser as the excitation. The system was well calibrated using a strain-free Si wafer. Two different locations of the sample were studied at each pressure point, and the obtained results were consistent. To avoid the heating effect of the laser, a power of  $<1$  mW was used for the Raman measurements. The collection time of each spectrum was 60 s.

In-situ high-pressure angle-dispersive x-ray diffraction (ADXRD) experiments were carried out with the high-pressure collaborative access team (HPCAT), 16ID-B station at the Advanced Photon Source facility, in Argonne National Laboratory. The focused monochromatic beam with dimensions of approximately  $5 \mu\text{m} \times 5 \mu\text{m}$  in full width at half maximum (FWHM) was utilized for the ADXRD measurements. The wavelength of the X-ray was 0.34531 Å. The diffraction patterns were collected with a MAR345 image plate with a pixel size of 100  $\mu\text{m}$ , and they were processed using standard techniques. The pressures were obtained from the equation of state of Au, which was loaded along with the sample.

## 3. Results and Discussions

The Raman spectra of different pressures are shown in Figure 1A and B. Based on the spectrum of the ambient conditions, 10 peaks with positions at  $270.0 \text{ cm}^{-1}$ ,  $430 \text{ cm}^{-1}$ ,  $493.0 \text{ cm}^{-1}$ ,  $708.0 \text{ cm}^{-1}$ ,

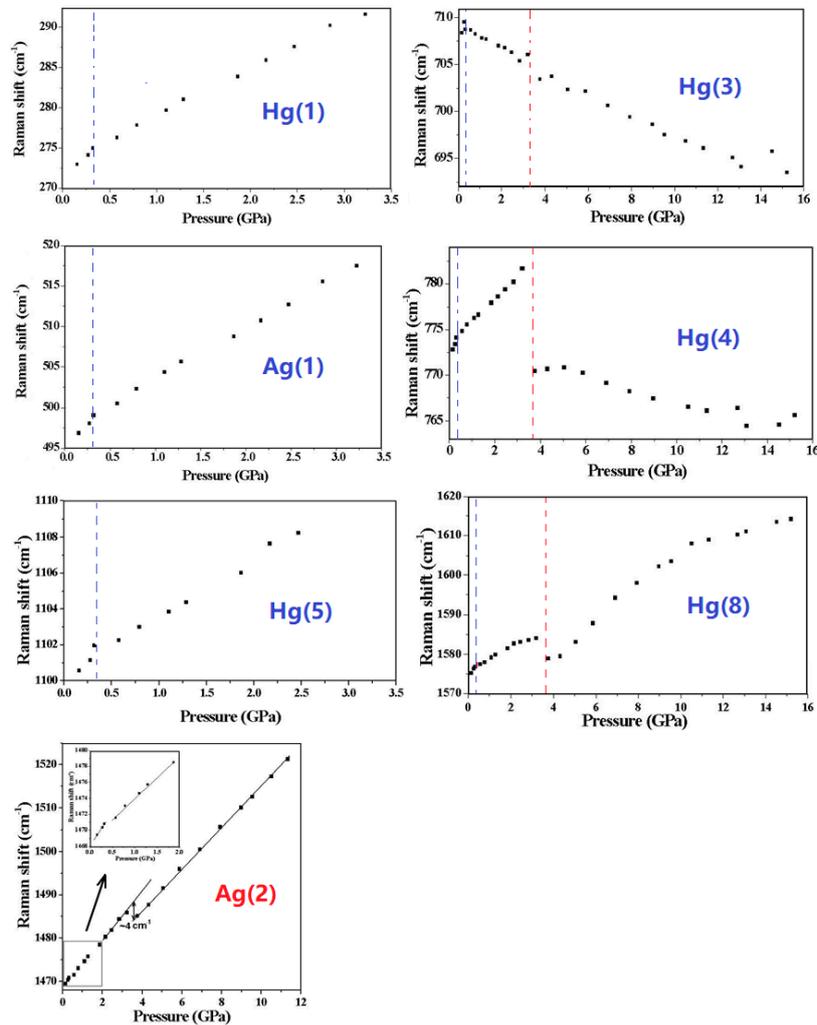
772.0  $\text{cm}^{-1}$ , 1099.0  $\text{cm}^{-1}$ , 1248.0  $\text{cm}^{-1}$ , 1426.0  $\text{cm}^{-1}$ , 1469.0  $\text{cm}^{-1}$ , and 1573.0  $\text{cm}^{-1}$  were found. They were indexed as eight  $H_g$  and two  $A_g$  modes of  $C_{60}$  [7,11]. It is necessary to point out that the Raman spectrum measured at ambient pressure showed that the  $A_g(2)$  pentagonal pinch mode was at 1469.0  $\text{cm}^{-1}$ , which is the characteristic frequency for pristine  $C_{60}$ . It is known that this vibration mode will shift to a lower frequency in polymerized  $C_{60}$  [4,7]. Therefore, this indicated that the starting sample was monomeric  $C_{60}$ . As the pressure increased at a relatively low-pressure range, the peaks shifted gradually, as shown in the pressure dependences of the peak positions. It was also found that the peaks became broad and the intensities decreased as the pressure increased further. As marked in Figure 1A, some peaks split and some new peaks appeared, indicating that the symmetry of the  $C_{60}$  was reduced at high pressure. As the pressure reached up to about 3.75 GPa, the peaks with frequencies of less than 600  $\text{cm}^{-1}$  became too broad and weak to be recognized. The peaks of  $H_g(3)$ ,  $H_g(4)$ ,  $A_g(2)$ , and  $H_g(8)$  persisted up to 15 GPa.



**Figure 1.** Raman spectra of  $C_{60}$  under different pressures: low pressure range (A) and higher pressures (B).

The pressure dependencies of the Raman shifts were analyzed, as shown in Figure 2 and Table 1. Because  $A_g(2)$  is the characteristic pinch mode of the pentagon rings in  $C_{60}$ , its pressure dependence will be discussed first. As seen from the figure, two obvious changes in the entire range of pressure were found. One took place at around 0.3 GPa, and another occurred at about 3.2 GPa. As shown in Table 1, the pressure dependence of  $A_g(2)$  was 8.2  $\text{cm}^{-1}/\text{GPa}$  below 0.3 GPa. It was reduced to 5.4  $\text{cm}^{-1}/\text{GPa}$  as the pressure increased. As the pressure rose up to about 3.2 GPa, an obvious softening was observed for the  $A_g(2)$ . Based on the pressure dependences of all the other peaks shown by the dash lines in Figure 2 and the table, it could be found that all the changes of the peaks took place at the same pressure. Taking  $H_g(3)$  as an example, it shifted to a higher frequency at < 0.3 GPa, and it turned to red shifts as the pressure increased further. These changes suggested that some transitions must have taken place in the sample at 0.3 GPa and 3.2 GPa. Based on the previous studies, the  $C_{60}$  cages rotated freely at each site in the fcc structure at ambient pressure. The free rotation was hinted at as the pressure reached about 0.4 GPa, causing the structural transition from fcc to sc [4,22]. This happened at a similar pressure to that of our result. Therefore, we suggest that the change at 0.3 GPa was induced by the phase transition of  $C_{60}$  from the fcc structure to the sc structure. This was verified by our in-situ X-ray diffraction and the refinements, as shown in Figure 3. The crystal structure at 0.2 GPa could be indexed as an fcc structure. As the pressure increased, several new peaks appeared, indicating a phase

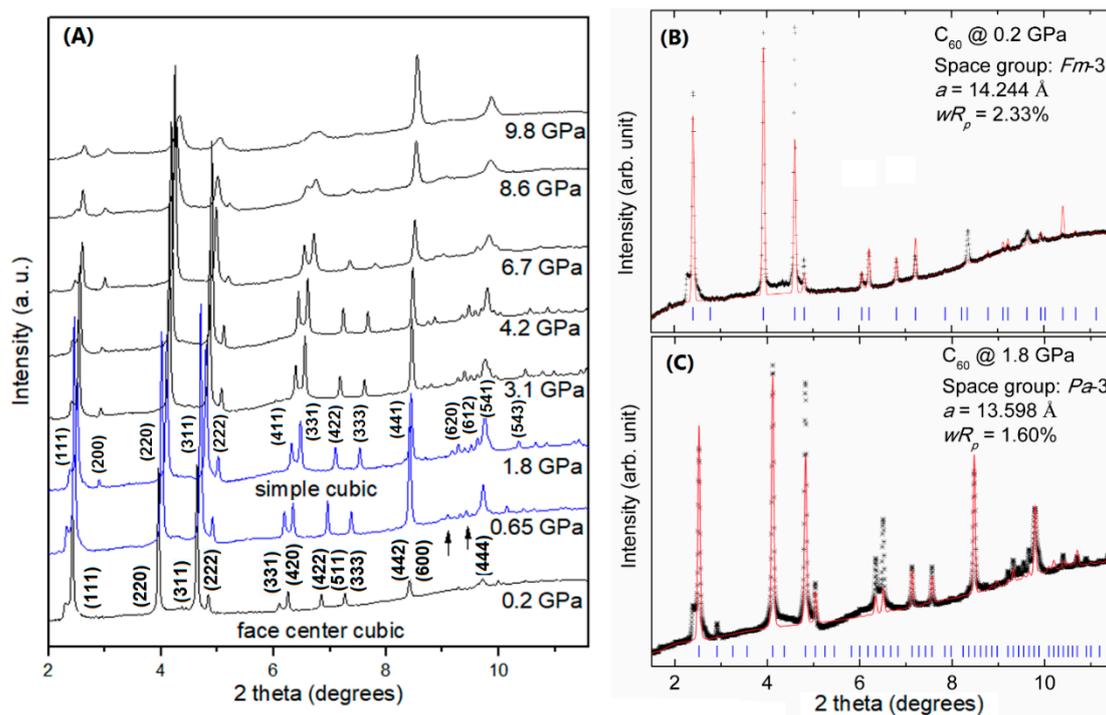
transition. As shown in Figure 3C, the new phase could be indexed as sc, consistent with the previous report and our findings for the Raman study.



**Figure 2.** The pressure dependence of the Raman shifts: H<sub>g</sub>(1), H<sub>g</sub>(3), A<sub>g</sub>(1), H<sub>g</sub>(4), H<sub>g</sub>(5), H<sub>g</sub>(8), and A<sub>g</sub>(2).

**Table 1.** The slopes of Raman shifts of C<sub>60</sub> versus pressure at room temperature.

Modes	Pressure Dependences of Raman Shift (cm <sup>-1</sup> /GPa)				
	0–0.3 GPa	0.3–3.2 GPa			>3.2 GPa
H <sub>g</sub> (1)	11.9 (2.2)	5.8 (0.1)			—
H <sub>g</sub> (2)	—	0.34 (0.05)			—
A <sub>g</sub> (1)	13.2 (2.7)	6.3 (0.1)			—
H <sub>g</sub> (3)	9.6		−1.09 (0.04)		
H <sub>g</sub> (4)	7.7 (2.4)	2.4 (0.1)		0.29 (0.06)	−0.59 (0.07)
H <sub>g</sub> (5)	8.1 (2.9)	3.2 (0.1)			—
H <sub>g</sub> (6)	6.2 (4.1)	2.9 (0.2)			—
H <sub>g</sub> (7)	12.4 (5.5)	6.3 (0.1)			—
A <sub>g</sub> (2)	8.2 (0.5)	5.4 (0.1)			4.73 (0.04)
H <sub>g</sub> (8)	9.7 (0.2)	3.3 (0.1)	1.4 (0.04)	1.2	4.6 (0.2)

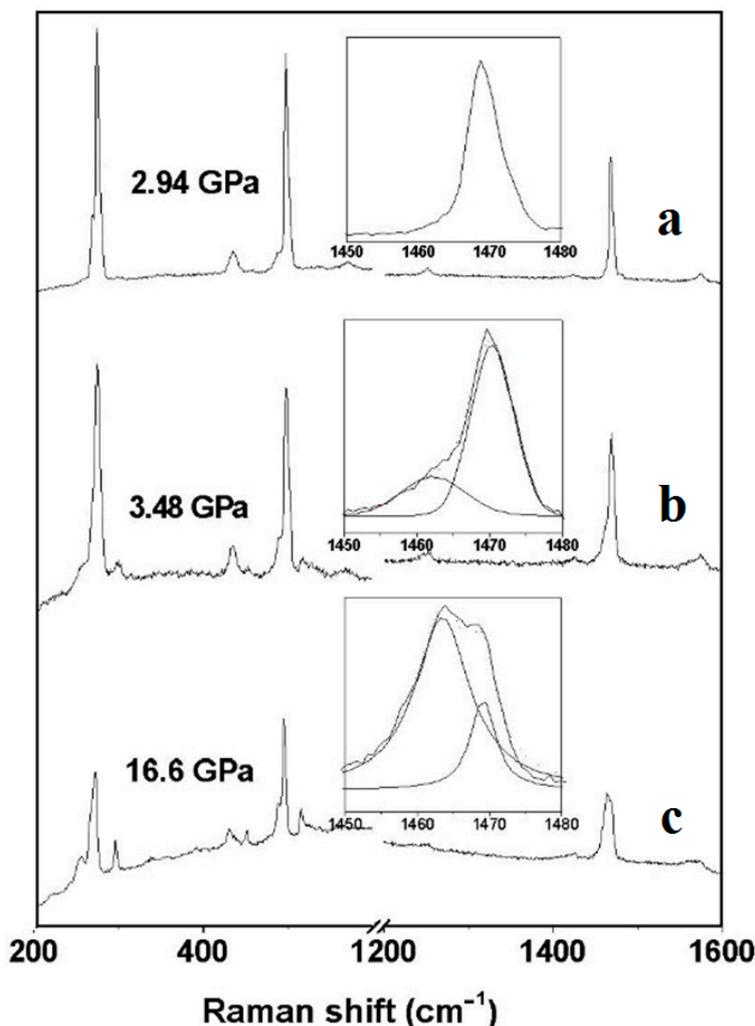


**Figure 3.** X-ray diffraction of C<sub>60</sub> at high pressures (A), and refinements of the diffraction spectra at 0.2 GPa (B) and 1.8 GPa (C), respectively.

As mentioned previously, similar significant softening at 3.2 GPa could also be found in the H<sub>g</sub>(4) and H<sub>g</sub>(8). These results confirmed that the transition occurred in the sample at high pressure. Through careful analysis, a softening of about 4 cm<sup>-1</sup> was found with A<sub>g</sub>(2). Based on our knowledge, the A<sub>g</sub>(2) of C<sub>60</sub> shifts to a lower frequency as polymerization occurs [4,6,7,9]. The shift is about 4 cm<sup>-1</sup> for the dimerization of C<sub>60</sub>. This suggests that the pristine C<sub>60</sub> underwent a pressure-induced dimerization as the pressure increased to 3.2 GPa. To confirm the dimerization of C<sub>60</sub> at about 3.2 GPa, we further studied the samples decompressed from different maximum pressures by Raman spectroscopy using 830 nm laser that could not induce photo-dimerization of the C<sub>60</sub> at room temperature. The Raman spectra measured after the decompression from different pressures of 2.94 GPa, 3.48 GPa, and 16.6 GPa for the samples are shown in Figure 4(a)–(c), respectively. Based on the comparison with the Raman spectrum of pristine C<sub>60</sub>, no obvious change was found in the Raman spectrum of the C<sub>60</sub> recovered from 2.94 GPa. It was noted that the position of the A<sub>g</sub>(2) mode was still at 1469 cm<sup>-1</sup>, which indicated that the C<sub>60</sub> quenched from 2.94 GPa was monomeric C<sub>60</sub>. However, it was remarkable that the A<sub>g</sub>(2) peak split into two peaks as the pressure went over about 3.2 GPa. The split was able to be fitted into two peaks, with their positions at 1464 cm<sup>-1</sup> and 1469 cm<sup>-1</sup>. Additionally, the intensity of the peak at 1464 cm<sup>-1</sup> grew as the pressure increased over this pressure. As mentioned above, the peak at 1464 cm<sup>-1</sup> was from C<sub>60</sub> dimers and the peak at 1469 cm<sup>-1</sup> was of monomeric C<sub>60</sub> [4,6,7,9]. Furthermore, as marked in Figure 4, some new peaks that were observed in the spectra of the sample recovered from 3.48 GPa and 16.6 GPa also proved the existence of the dimerization of C<sub>60</sub> in the samples. Since the use of the 830 nm laser could not induce the photo-polymerization of C<sub>60</sub> even at the pressure of 4 GPa and room temperature, these results indicated that the pressure did induce the dimerization of C<sub>60</sub> as the pressure went up to around 3.2 GPa at ambient temperature.

Compared with the results that were obtained using a 514.5 nm laser as the excitation, the results obtained in this study were very different. As shown, both the Raman spectra of the sample under high pressure and the quenched samples with different pressures proved that the pressure-induced dimerization of C<sub>60</sub> occurred at a pressure of about 3.2 GPa. However, this phenomenon was not found in the previous investigations, even for the pressures of up to 15 GPa. Based on the comparison of the

two experiments, the major difference was the wavelength of the excitation. Therefore, the selection of the wavelength of a laser is crucial for spectroscopic studies of the behavior of  $C_{60}$  under high pressure.



**Figure 4.** The Raman spectra of the samples recovered from different pressures of 2.94 GPa (a), 3.48 GPa (b), and 16.6 GPa (c).

In summary, we carried out in situ Raman studies of  $C_{60}$  under high pressure using an infrared laser as the excitation, which could not induce photo-polymerization even for a pressure of up to 5 GPa at room temperature. Our result showed that the  $C_{60}$  underwent a phase transition from an fcc structure to an sc structure at around 0.3 GPa. This result agreed with the previous neutron diffraction data very well. The high-pressure-induced dimerization of  $C_{60}$  at room temperature was first observed by an in-situ experiment using the infrared laser as the excitation. The pressure of the dimerization of  $C_{60}$  at room temperature was about 3.2 GPa. Our results were very different from those of the previous ones obtained using a visible laser as the excitation, indicating the benefit and importance of the choice of the infrared laser as the excitation laser.

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**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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