

# Infrared Study of Vibrational Property and Polymerization of C<sub>60</sub> and C<sub>70</sub> under Pressure

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Infrared spectra were measured for solid C<sub>60</sub> and C<sub>70</sub> to 7 GPa under hydrostatic or quasi-hydrostatic pressure at room temperature. Some vibrational modes showed negative or insensitive dependence of frequency on pressure, suggesting destabilization of C<sub>60</sub> and C<sub>70</sub> molecules by compression. In solid C<sub>60</sub> new absorption bands gradually grew with increasing pressure in association with an intensity decrease of the original bands. These spectral changes were interpreted in terms of polymerization of C<sub>60</sub> molecules. Polymerized molecules recovered at ambient pressure were converted back to the monomer by thermal annealing at 473 K.

## Introduction

The structural stability and reaction activity of C<sub>60</sub> (solid) have been intensively studied. High-pressure experiments are capable of tuning intermolecular distances and provide an effective method for study of the molecular structure and bonding nature of C<sub>60</sub>. It has been shown from X-ray diffraction measurement that the spherical C<sub>60</sub> molecule is stable to at least 20 GPa under hydrostatic pressure, whereas uniaxial stress deforms the molecular shape or crystal structure even below 10 GPa.<sup>1</sup> Conversion to diamond was reported for a recovered specimen which blew out during pressure release from 20 GPa.<sup>2</sup> Transformation to amorphous carbon was also indicated by Raman measurement above 14 GPa.<sup>3</sup>

The vibrational modes of C<sub>60</sub> have been studied under pressure by infrared absorption<sup>4–6</sup> and Raman spectroscopy.<sup>3</sup> An interesting result was the "softening" in some of the intramolecular modes. One of the four IR active modes, which is characterized as a radial vibrational motion, showed a negative dependence of the frequency on pressure.<sup>4–6</sup> Recent Raman measurements also showed that several bands shifted to lower frequency with pressure.<sup>3</sup> This softening probably reflects a change in the chemical bonding within, and between, C<sub>60</sub> molecules under pressure.

We have measured the infrared spectra of C<sub>60</sub> under hydrostatic or quasi-hydrostatic condition. The purpose was to investigate the high-pressure behavior of the molecular vibrations and to explore the possibility of pressure-induced chemical reaction in the solid state. The spectra of C<sub>70</sub> were also measured. The high-pressure data on C<sub>70</sub> are of great help for understanding the characteristic bonding nature of the fullerene molecules.

## Experimental Section

High-pressure infrared spectra were measured with a gasketed diamond anvil cell.<sup>7</sup> The sample chamber was a small hole 0.3 mm in diameter drilled in a metal gasket of Inconel X-750 approximately 0.1 mm thick. Infrared transmission spectra were recorded on a Microscope FT-IR instrument (HORIBA FT-530) with a wide-band MCT (mercury-cadmium-tellurium) detector sensitive down to 450 cm<sup>-1</sup>. Four hundred repeated measurements were accumulated to obtain a spectrum of good quality with a spectral resolution of 0.5 cm<sup>-1</sup> for a masked measuring area of 100 × 100 μm<sup>2</sup>. Powders of pure C<sub>60</sub>, and of pure C<sub>70</sub>, were prepared by standard techniques previously

reported in the literature.<sup>8</sup> All measurements were made at room temperature, and the pressure was determined by using the ruby fluorescence method.<sup>9</sup>

Two kinds of infrared measurement were undertaken. First, infrared frequencies were measured for solid C<sub>60</sub> and C<sub>70</sub> so as to investigate vibrational properties of these fullerenes under high pressure. A flake approximately 20 μm thick was made by compressing one grain of the fullerite, and its small fragment was packed into the gasket hole. Subsequently, a pressure medium (Xe or Kr) was charged in the hole. Both media are capable of generating a quasi-hydrostatic environment in the relatively low pressure region. In addition to the measurements on solid C<sub>60</sub> and C<sub>70</sub>, infrared spectra of a CS<sub>2</sub> solution of C<sub>60</sub> (about 3 × 10<sup>-3</sup> mol/dm<sup>3</sup>) were measured. A thicker gasket (~0.3 mm) was used in order to obtain sufficient absorption intensity for the solubilized C<sub>60</sub>.

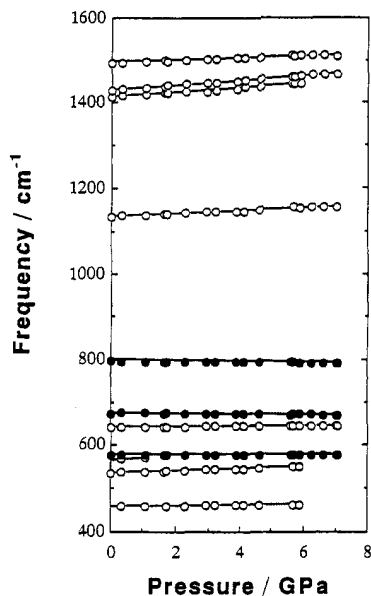
Second, the dependence of infrared absorption intensity on applied pressure was measured for solid C<sub>60</sub>. Before compression, a reference spectrum was taken for the solid C<sub>60</sub> placed in the gasket hole of the opened diamond cell. The specimen was then packed with a methanol-ethanol (4:1) mixture and compressed in the closed cell to the desired pressure. After holding the pressure for 1 day, the cell pressure was reduced to ambient. The opened cell was heated in a vacuum oven at 340 K in order to evaporate the pressure medium. An infrared spectrum was again measured for the recovered specimen and compared with the reference spectrum.

## Results and Discussion

**Frequency Shift in Solid C<sub>60</sub> and C<sub>70</sub>.** The pressure dependence of the infrared frequencies was obtained for the four infrared active modes of C<sub>60</sub> (1F<sub>1u</sub>, 2F<sub>1u</sub>, 3F<sub>1u</sub>, and 4F<sub>1u</sub> modes<sup>10</sup>) in a quasi-hydrostatic condition up to 6 GPa. The present results agree with the previous infrared data measured to 19.5 GPa by direct compression of powdered C<sub>60</sub>.<sup>6</sup> All absorption bands broadened and weakened substantially as the pressure was increased, so that further measurement beyond 6 GPa was prevented. No indication of a phase transition was observed. New bands, however, appeared in the frequency region from 600 to 800 cm<sup>-1</sup>, suggesting molecular deformation or chemical reaction. This remarkable spectral change will be described in detail in the following sections.

In the CS<sub>2</sub> solution of C<sub>60</sub>, three of the four bands were observed up to 1 GPa. The 4F<sub>1u</sub> band expected to appear around 1500 cm<sup>-1</sup> overlapped with the strong band of the stretching mode of CS<sub>2</sub>. The 2F<sub>1u</sub> and 3F<sub>1u</sub> bands shifted to higher frequency, giving

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**Figure 1.** Pressure shifts of the infrared frequencies for solid  $C_{70}$ . Three bands (●) slightly shift to lower frequency with pressure.

derived pressure coefficients,  $d\omega/dp = 3.9$  and  $3.7 \text{ cm}^{-1}/\text{GPa}$ , respectively, whereas the  $1F_{1u}$  band shifted to lower frequency with a pressure coefficient of  $-1.0 \text{ cm}^{-1}/\text{GPa}$ . Although the frequencies of  $1F_{1u}$  and  $2F_{1u}$  modes in solution state were about  $2 \text{ cm}^{-1}$  higher than those in solid state in the pressure range measured, no significant difference was observed in the pressure dependence. The  $3F_{1u}$  mode showed the same peak position and pressure dependence as those of the solid state. It was observed by visual inspection with a microscope that  $C_{60}$  crystals separated out from  $CS_2$  solution at 1 GPa. This prevented us from proceeding with further measurement. In the measured pressure region, solidification was not observed in  $CS_2$  which is known to crystallize at 1.3 GPa and room temperature.

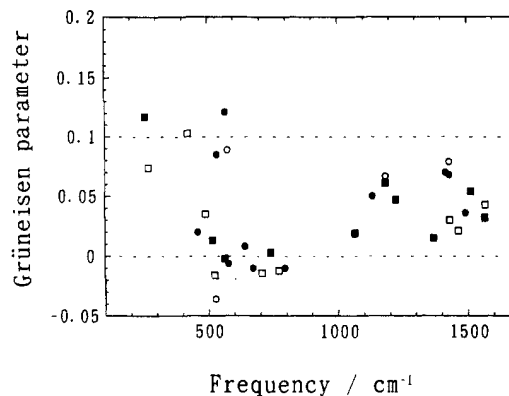
For solid  $C_{70}$ , only 11 bands of the 31 modes ( $10A_2'' + 21E'$ ) predicted as infrared active<sup>11</sup> were observed. The observed band frequencies of  $C_{70}$  are plotted as a function of pressure in Figure 1. The frequencies, whose ambient-pressure values agree well with those reported previously,<sup>12,13</sup> change linearly with pressure. It is notable that three bands originally located at 578, 673, and  $795 \text{ cm}^{-1}$  (filled circles in Figure 1) shift to lower frequency, as was the case for the lowest frequency  $1F_{1u}$  mode of  $C_{60}$ . In solid  $C_{70}$ , however, the lowest frequency band at  $458 \text{ cm}^{-1}$  shifts to slightly higher frequency. Besides the shift of the band positions, no significant change was observed in the spectra. This was in contrast to  $C_{60}$ , which showed appearance of the new absorption bands growing with increasing pressure. An order-disorder transition associated with the molecular reorientation has been observed in solid  $C_{70}$  below 1.2 GPa by powder X-ray diffraction experiment.<sup>14</sup> In our infrared measurement no discontinuous change in frequency was found at the corresponding pressure region. Pressure coefficients  $d\omega/dp$  obtained by fitting the  $\omega$ - $p$  relation with a linear equation and mode Grüneisen parameters  $\gamma_G = K_0 \ln d\omega/dp$  calculated by using the bulk modulus  $K_0 = 18.1 \text{ GPa}$  of solid  $C_{60}$ ,<sup>1</sup> are summarized in Table I.

The mode Grüneisen parameters  $\gamma_G$  are plotted in Figure 2 against ambient-pressure frequency ( $\omega_0$ ) on the basis of the infrared and Raman data of  $C_{60}$  and  $C_{70}$ . They are scattered in the range from  $-0.04$  to  $0.12$ . A characteristic behavior in the  $\gamma_G$ - $\omega_0$  relation is found in the frequency region of  $500$ – $800 \text{ cm}^{-1}$ , where the  $\gamma_G$  falls on the zero line. Several modes of  $C_{60}$  and  $C_{70}$  apparently have negative values. According to the normal mode vibration analysis for  $C_{60}$ ,<sup>10</sup> the vibrational modes are roughly divided into two classes: the modes with frequencies above  $1100 \text{ cm}^{-1}$  are associated with atomic motions tangential to the

**TABLE I: Infrared Frequencies ( $\omega_0$ ) at Ambient Pressure, Pressure Coefficients ( $d\omega/dp$ ), and Grüneisen Mode Parameters ( $\gamma_G$ ) for Solid  $C_{70}$**

$\omega_0$ ( $\text{cm}^{-1}$ )	$d\omega/dp$ ( $\text{cm}^{-1}/\text{GPa}$ )		$\gamma_G^b$
	present work	Huang et al. <sup>a</sup>	
458	0.54	2.8	0.020
534	2.50	2.7	0.085
566	3.80	3.4	0.121
578	-0.20	-0.4	-0.006
642	0.28	0.3	0.008
673	-0.39	-0.5	-0.010
795	-0.44	-0.6	-0.010
1133	3.10	0.7	0.050
1414	5.44	-7.6	0.070
1430	5.38	1.3	0.068
1493	3.01		0.036

<sup>a</sup> Reference 5. <sup>b</sup>  $\gamma_G$  for  $C_{70}$  were evaluated by using a bulk modulus of  $K_0 = 18.1 \text{ GPa}$  in solid  $C_{60}$  (ref 1).



**Figure 2.**  $\gamma_G$ - $\omega_0$  relation in solid  $C_{60}$  and  $C_{70}$  (○, IR for  $C_{60}$ ; □, Raman for  $C_{60}$ ; ●, IR for  $C_{70}$ ; ■, Raman for  $C_{70}$ ). The  $\gamma_G$  for Raman bands were evaluated by using the previous Raman data.<sup>3</sup>

molecular surface, and the modes below  $1100 \text{ cm}^{-1}$  are mixed modes of radial and tangential motions. In particular, the  $1F_{1u}$  mode of  $C_{60}$  was analyzed to be a purely radial motion. There has been no literature available for characterization of the normal vibrational modes of  $C_{70}$  on the basis of the atomic motions. However it seems reasonable to consider the softening modes to be the mixed modes of radial tangential motions, since their frequencies are in the region of usual benzene-ring bending vibrations. The  $\gamma_G$ - $\omega_0$  plot (Figure 2) suggests that the normal vibrations involving radial motions tend to have a negative value of  $\gamma_G$ .

The mechanism of the softening of the radial mode in  $C_{60}$  remains unclear. Evidently the interaction of the  $C_{60}$  molecule with its nearest neighbors change as a function of pressure in such a way that the radial normal mode frequency is lowered. However this is not an interaction which is specific to a  $C_{60}$ - $C_{60}$  nearest neighbor force field, because the frequency of the purely tangential  $1F_{1u}$  mode also decreases in the dilute  $CS_2$  solution. The observed pressure coefficients  $d\omega/dp$  of  $C_{60}$  in  $CS_2$  corresponded well with those for the pure  $C_{60}$  solid. The  $C_{60}$  molecules in the dilute  $CS_2$  solution should be surrounded almost entirely by  $CS_2$  solvent molecules, on average. Apparently the influence of nearest neighbor molecules on  $C_{60}$  vibrational frequency shift is quite similar whether the nearest neighbor molecules are  $CS_2$  or  $C_{60}$ . This presents, we feel, a clue for future theoretical treatments, which are needed for a deeper understanding of the experimental data.

We speculate that the stress tensor which are individual  $C_{60}$  molecule experiences as a function of pressure must be quite similar for  $C_{60}$  in  $CS_2$ , and for  $C_{60}$  solid, in the pressure range studied. The face-centered cubic (fcc)  $C_{60}$  is an isotropic solid, and the stress tensor for hydrostatic loading is also isotropic. At very low applied pressure the  $CS_2$  solution remains a liquid, and

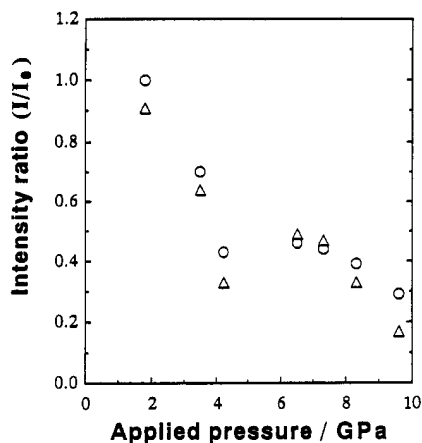


Figure 3. Relative intensity of the infrared 2F<sub>1u</sub> (O) and 3F<sub>1u</sub> (Δ) bands of solid C<sub>60</sub> plotted against applied pressure.

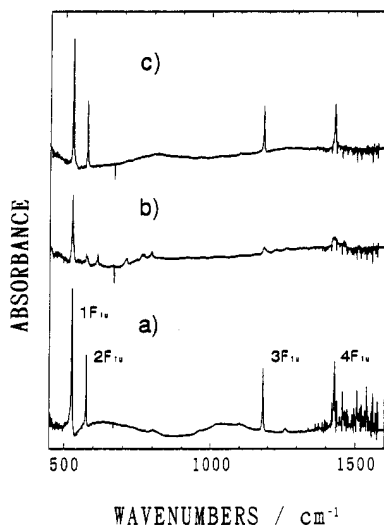


Figure 4. Infrared spectra for solid C<sub>60</sub> at ambient pressure: (a) before compression; (b) after reduction of pressure from 6 GPa; (c) after thermal annealing at 473 K in a vacuum oven.

the stress tensor in a liquid is always isotropic. We suggest that the magnitudes of the tensor elements are comparable for the two different media in the pressure range used here. What remains unexplained is why the radial mode frequency decreases.

**Intensity Change in Solid C<sub>60</sub>.** Change in the absorption intensity in solid C<sub>60</sub> is plotted as a function of applied pressure in Figure 3. The 2F<sub>1u</sub> and 3F<sub>1u</sub> bands were fitted with Lorentzian functions<sup>15</sup> to obtain integrated intensities. The other two bands, 1F<sub>1u</sub> and 4F<sub>1u</sub>, were not available since the 1F<sub>1u</sub> band was saturated in intensity and the fitting of the 4F<sub>1u</sub> band was distributed by the infrared absorptions from atmospheric water vapor, as seen in Figure 4a. The intensities strongly decreased as the applied pressure increased. For the specimen recovered from 10 GPa, the intensity was decreased to less than one-third of the initial intensity. In addition to this large intensity reduction, the compression caused the appearance of new absorption bands in the frequency region from 600 to 800 cm<sup>-1</sup> (Figure 4b). These bands disappeared by annealing at 473 K for 16 h with recovery of the reduced intensities of the C<sub>60</sub> bands (Figure 4c).

Intensity decrease of the original bands and appearance of the new bands in pressurized solid C<sub>60</sub> are probably attributable to polymerization of C<sub>60</sub>. The spectral features newly appearing in the 600–800-cm<sup>-1</sup> region are quite similar to those of a C<sub>60</sub> film irradiated with a Hg lamp;<sup>16</sup> the correspondence in the frequencies

TABLE II: Comparison of Infrared Frequencies (cm<sup>-1</sup>) between Compressed and Phototransformed C<sub>60</sub><sup>a</sup>

compressed C <sub>60</sub> <sup>b</sup>	phototransformed C <sub>60</sub> <sup>c</sup>	compressed C <sub>60</sub> <sup>b</sup>	phototransformed C <sub>60</sub> <sup>c</sup>
	484 (w)		761 (w)
527 (m)*	526 (m)	765 (w)	769 (w)
	550 (w)		779 (w)
	569 (w)		796 (w)
575 (w)*		797 (w)	
611 (w)	616 (w)	1185 (w)*	1183 (w)
710 (w)	709 (w)	1223 (w)	1229 (w)
	727 (w)	1426 (w)*	1424 (w)
744 (w)	743 (w)	1460 (w)	1460 (w)

<sup>a</sup> Intensities are given in parentheses. w, m = weak, medium. <sup>b</sup> Original bands of C<sub>60</sub> are marked with asterisks. <sup>c</sup> Reference 16.

between the compressed and phototransformed specimens is fairly good, as shown in Table II. A mass spectrum of the phototransformed C<sub>60</sub> showed formation of a series of cross-linked fullerenes (C<sub>60</sub>)<sub>n</sub>.<sup>16</sup> A similar polymerization likely occurs in compressed solid C<sub>60</sub>, where the adjacent molecules get sufficiently close to form cross-linking bonds. Our observations of recovery of C<sub>60</sub> band intensities and removal of the new bands by thermal annealing at 473 K are indicative of destruction of cross-linking bonds and reproduction of the C<sub>60</sub> monomer. The measured large reduction in intensity of the characteristic C<sub>60</sub> monomer bands shows that the polymerization is significantly accelerated at high pressures. Further study in the degree of polymerization and its pressure dependence is needed to clarify the reaction mechanism.

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