

# High Pressure Vibrational Study of C<sub>70</sub> Using Diamond Anvil Cell

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High pressure FTIR and Raman spectra of solid C<sub>70</sub> were measured at pressure up to 11 GPa and room temperature. The slope(dv/dp) of the frequency-pressure plots for several IR and Raman mode changed around 1.5 GPa, where a solid-solid transition might occur. In IR study, we can observe new mode appeared around 777 cm<sup>-1</sup> above 5.5 GPa which might indicate another solid-solid transition. Our study showed that this transition might be irreversible

**Key words :** Diamond anvil cell(DAC), Raman, FTIR, High pressure, C<sub>70</sub>

## I. Introduction

Fullerene has many fascinating chemical and physical properties. There has been much study in many science fields since the discovery of a method to produce macroscopic amounts of the material in the solid form.<sup>1)</sup> Among these properties, there has been a considerable interest in their structural transformations as a function of temperature and pressure.<sup>2)</sup>

The structure and solid state properties of C<sub>70</sub> which is a member of a fulleren family, are much less understood than C<sub>60</sub>. Early X-ray diffraction and electron microscopy studies revealed that cubic closed packed(ccp) phase and hexagonal closed packed (hcp) phase coexist in room temperature and atmospheric pressure.<sup>3,4)</sup> Van Tendeloo *et al.* reported that the freshly prepared C<sub>70</sub> in the hcp phase can transform into fcc phase at room temperature and atmospheric pressure over a period of a few days.<sup>5)</sup> It has been known that C<sub>70</sub> has very large hysteresis effects. Christides *et al.* reported that the fcc phase transforms to the rhombohedral (rh) phase around 280 K, which undergoes another phase transition to a phase of lower symmetry below 200 K in cooling cycle. They also reported that on heating, the rh phase transforms to the fcc phase around 270 K but the rh phase persists until 340 K.<sup>6)</sup> McGhie *et al.* reported that in their DSC experiment, C<sub>70</sub> shows four first order transitions, two strong ones and two weak ones which were associated with the two different molecular rotational degree of freedom in the majority and the minority phase.<sup>6)</sup> And they also reported that transition temperature depends on C<sub>60</sub> impurity concentration.<sup>6)</sup> There have been some high pressure studies on the structure of C<sub>70</sub>. Christides *et al.* reported in their XRD experiment that C<sub>70</sub> shows fcc→rh transition at 0.35 GPa, with the fcc phase coexisting until 1 GPa and transforms irreversibly to an amorphous phase beyond 18 GPa.<sup>6)</sup> However Chandrabhas *et al.* re-

ported in their high pressure Raman spectroscopy that C<sub>70</sub> molecules are stable up to 31.1 GPa and the high pressure amorphous carbon phase is reversible.<sup>17)</sup> Lundin *et al.* reported that the compressibility of C<sub>70</sub> shows a very rapid change below 0.15 GPa and they interpreted this as transformation from mixture of fcc and rh phase to mainly pure rh phase.<sup>7)</sup>

In this work, we measured IR and Raman spectra of solid C<sub>70</sub> under high pressure in order to investigate the high pressure phase of solid C<sub>70</sub> and its vibrational and bonding property.

## II. Experiment

Our fullerene sample was prepared by the well-known contact arc method.<sup>1,8)</sup> Pure C<sub>70</sub> was isolated from the C<sub>60</sub>-C<sub>70</sub> mixture by chromatographic separation. Raman and IR spectrum obtained with C<sub>70</sub> was identical with that previously reported<sup>9)</sup> and vibrational bands corresponding to C<sub>60</sub> was not discovered in both spectrum. <sup>13</sup>C NMR, mass spectrum and UV-visible spectrum were also employed to identify C<sub>70</sub>. There was no impurity within the detection limits of applied techniques.

The high pressure Raman spectra were recorded in diamond anvil cell(DAC) equipped with type I diamond. And the high pressure IR spectra were obtained in DAC equipped with type II diamond. The sample of C<sub>70</sub> was loaded in a 300 μm hole drilled in a stainless-steel gasket of average thickness 250 μm. All measurements were carried out at room temperature. We employed fresh KBr as a pressure medium. The pressure was determined by the ruby fluorescence method.<sup>10)</sup> Over the pressure range studied, our high pressure sample could be regarded as hydrostatic or at least quasi-hydrostatic because the ruby fluorescence difference of R<sub>1</sub>-R<sub>2</sub> line remained constant about 29 cm<sup>-1</sup> and they are well resolved. The Raman spectra were excited using 514.5 nm ra-

diation from an argon ion laser. Using back scattering geometry, scattered light was detected with single photon counting system. The spectra were analysed in a Jovin-Yvon U-1000 1.0  $\mu\text{m}$  double monochromator. IR transmission spectra were recorded on Bomem MB 103-C15 FTIR instrument equipped with the spectra-bench beam condenser. One thousand repeated measurement were accumulated to obtain each spectrum. FTIR spectrum were recorded over the frequency region from 400  $\text{cm}^{-1}$  to 1400  $\text{cm}^{-1}$  with a resolution of 1  $\text{cm}^{-1}$ .

### III. Results and Discussion

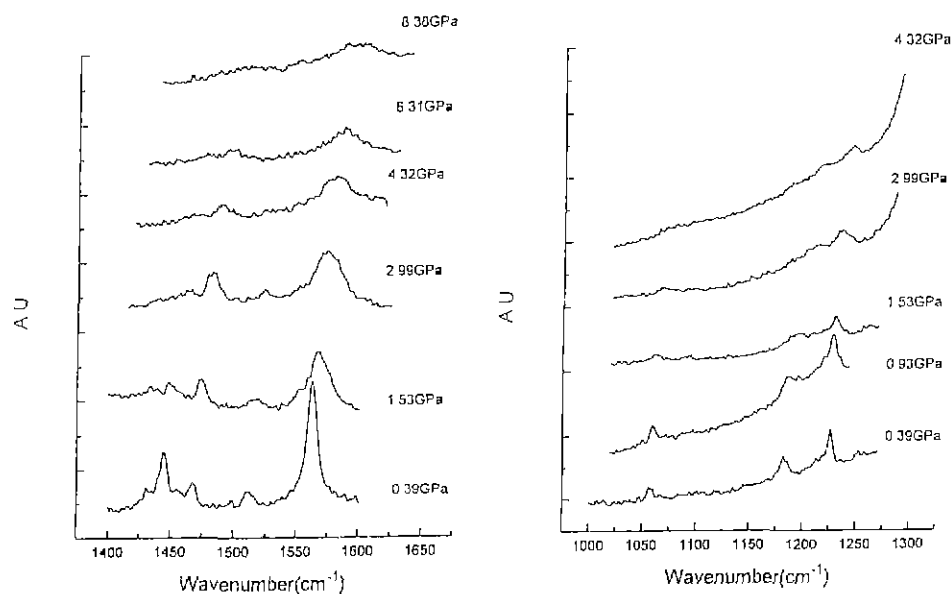
Molecular C<sub>70</sub> has D<sub>5h</sub> symmetry and a point group consideration shows that the vibrational modes give 122 fundamentals which are the following representation:

**Table 1.** Ratio of Radial Character and Belt atom Contribution of C<sub>70</sub> Normal mode

Frequency ( $\text{cm}^{-1}$ )	Symmetry	Activity	P <sub>r</sub> (%)	P <sub>b</sub> (%)
457	E <sub>1</sub> '	IR	93.7	21.9
535	A <sub>2</sub> '	IR	95.8	0.3
564	E <sub>1</sub> '	IR	95.7	44.5
577	E <sub>1</sub> '	IR	68.7	22.3
641.5	E <sub>1</sub> '	IR	96.7	27.4
673	A <sub>2</sub> '	IR	64.3	7.3
794	E <sub>1</sub> '	IR	65.2	13.1
1134	E <sub>1</sub> '	IR	3.0	33.7
255	E <sub>2</sub> '	Raman	73.1	24.7
1056	E <sub>2</sub> '	Raman	11.3	27.4
1183	E <sub>2</sub> '	Raman	3.7	3.3
1442	E <sub>2</sub> '	Raman	1.0	17.5
1465	A <sub>1</sub> '	Raman	0.4	2.4
1562	E <sub>2</sub> '	Raman	0.7	1.4

$$\Gamma = 12A'_1 + 9A'_2 + 21E'_1 + 22E'_2 + 9A''_2 + 10A''_3 + 19E''_1 + 20E''_2$$

Among these, A<sub>2</sub>' and E<sub>1</sub>' modes are IR active, A<sub>1</sub>', E<sub>2</sub>' and E<sub>1</sub>' modes are Raman active. During recent years, there have been a couple of works that assigned each normal modes to the symmetry notation.<sup>11,12)</sup> However there is some inconsistency between these works. In this work, we adapted the symmetry notation for the normal mode given in the reference (12). The symmetry notation, their ratio of radial character and belt atom contribution is summarized in Table 1. Fig. 1 shows Raman spectrum in the range from 20  $\text{cm}^{-1}$  to 1700  $\text{cm}^{-1}$  at various pressure. Because of very strong first order Raman line of diamond, the range between 1270  $\text{cm}^{-1}$  and 1400  $\text{cm}^{-1}$  was not investigated in the Raman spectrum. Fig. 2 shows IR spectrum of C<sub>70</sub> in the range from 400  $\text{cm}^{-1}$  to 1290  $\text{cm}^{-1}$  at various pressure. In both spectrum, the peak intensity of most modes keeps decreasing as the pressure increase. Even the most intense 1565  $\text{cm}^{-1}$ (E<sub>1</sub>') mode could be investigated up to 11 GPa in the Raman spectrum. After 11 GPa, this merges with background. The vibrational peak position and full width at half maximum (FWHM) of IR and Raman spectrum were determined by least-squares fitting of data with Lorentzian line shape. The pressure dependence of the Raman frequency is shown in Fig. 3. The frequency of Raman modes except the modes at 1567  $\text{cm}^{-1}$ (E<sub>1</sub>') and 1465  $\text{cm}^{-1}$ (A<sub>1</sub>') could be determined up to only 5 GPa. The pressure dependence of Raman band width of 1567  $\text{cm}^{-1}$ (E<sub>1</sub>') mode is shown in Fig. 4. The FWHM of other Raman mode could not be determined, due to their weak intensities. In Fig. 3, it is clearly shown that the pressure dependence of frequency (dv/dp) for each mode change around 1.5 GPa. Also the pressure dependence of FWHM of Raman 1565  $\text{cm}^{-1}$  mode change around this pressure as shown in Fig. 4. The change of slope in the fre-



**Fig. 1.** The Raman spectra of C<sub>70</sub> at various pressure.

quency-pressure plot and the FWHM-pressure plot around 1.5 GPa might be connected with the f.c.c.→rhombohedral phase transition which was previously reported in high pressure X-ray diffraction experiment.<sup>6</sup> Maksimov *et al.* reported that the change of  $dv/dp$  occurred around  $2 \pm 0.2$  GPa,<sup>13</sup> and A.K. Sood *et al.* showed that the change of slope occurs around 1.0 GPa in their data taken at closer pressure intervals than the intervals of data in the work of Maksimov *et al.*<sup>14</sup>

The pressure dependence of IR frequency is shown in Fig. 5 and the pressure dependence of FWHM of several selected IR mode is shown in Fig. 6. In the previous

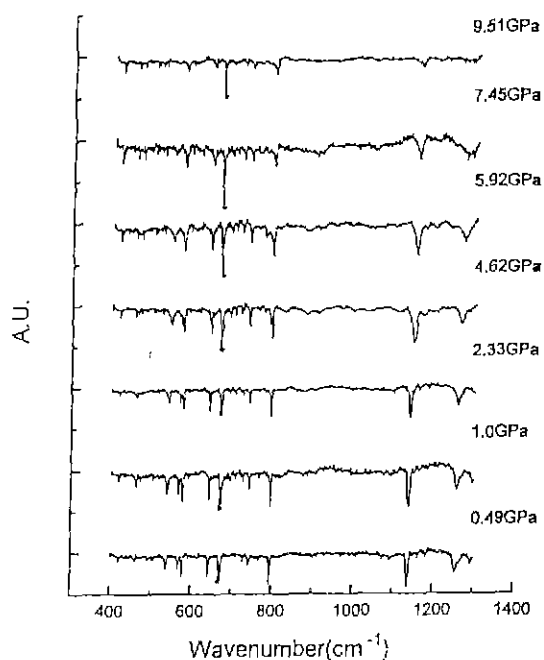


Fig. 2. The IR spectra of  $C_{70}$  at various pressure Diamond mode is marked by asterisk (\*).

high pressure IR studies<sup>15,16</sup>, Yamawaki *et al.* and Huang *et al.* reported that they did not see any change of  $dv/dp$  in the pressure range up to 3 GPa. However we studied the pressure dependence of frequency shift in this pressure range with smaller pressure interval. It could be observed that the pressure dependence of the frequency and FWHM of several modes also change around 1.5 GPa. This might be indicative of f.c.c.→rh phase transition, which is similar result as Raman study. The pressure dependence of Raman and IR frequency for each mode which was determined by fitting with linear equation, is summarized in Table 2.

$C_{60}$  molecule has the electron-excess double bond (hexagonal face) and the electron-deficient single bond (pentagonal face). In the orientationally ordered phase of  $C_{60}$ , the electron deficient single bond faces the electron excess double bond of neighbouring molecule. Because there might be coulomb interaction between these two faces, it was suggested that coulomb attraction might cause the softening of radial mode under high pressure. The  $C_{70}$  molec-

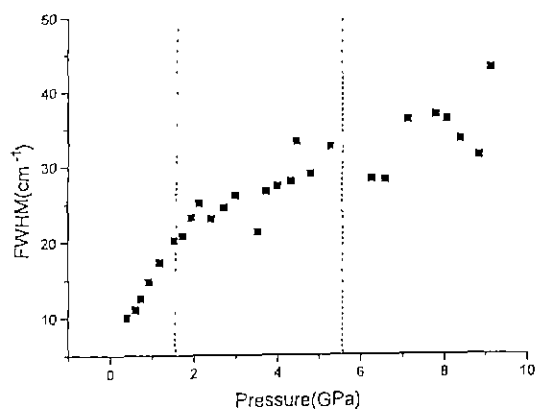


Fig. 4. The pressure dependence of FWHM of Raman mode at  $1565 \text{ cm}^{-1}$ .

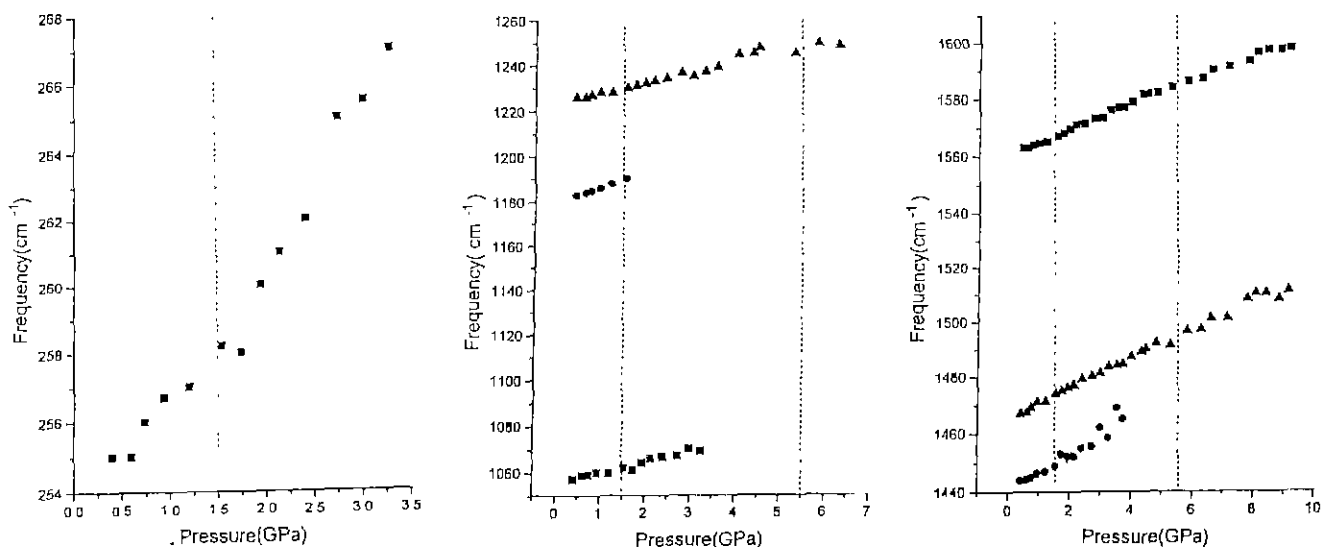


Fig. 3. The pressure dependence of frequencies of Raman modes

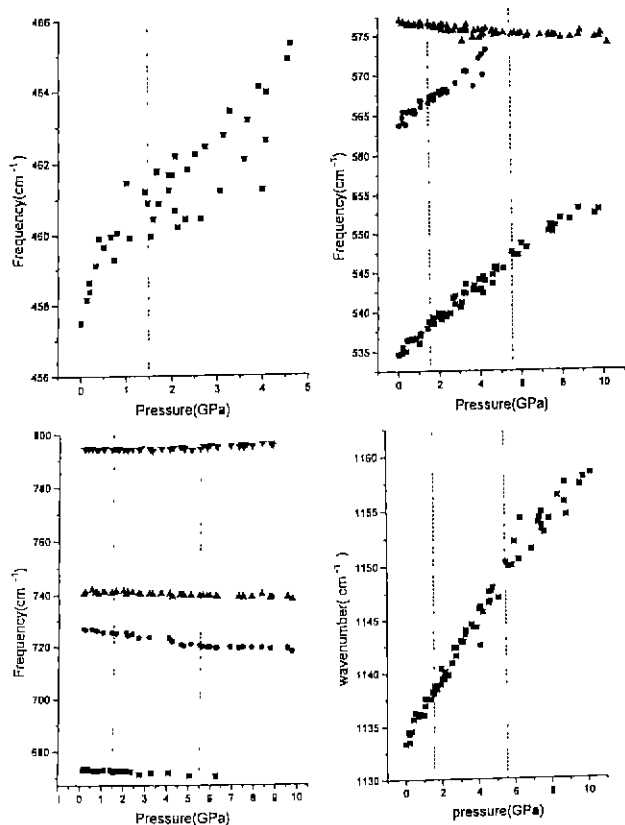


Fig. 5. The pressure dependence of frequencies of IR modes.

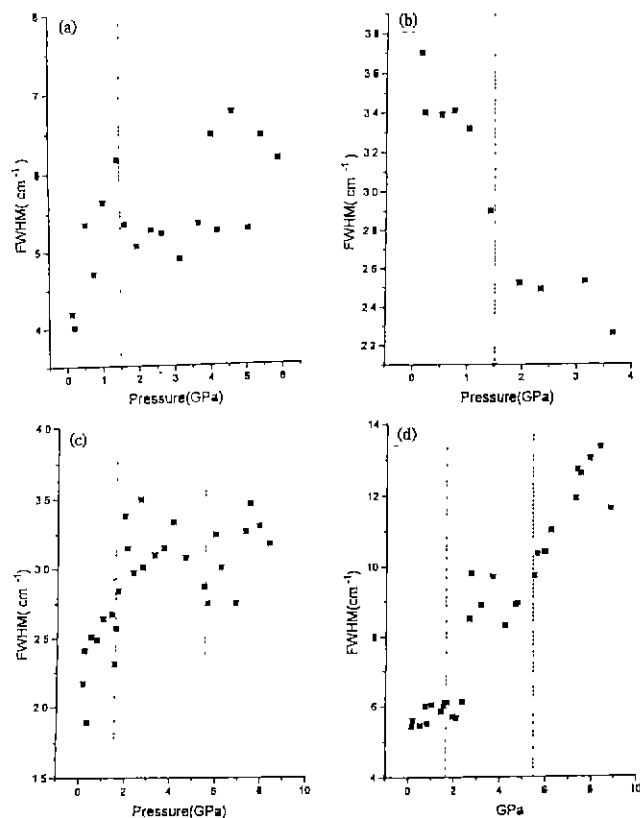


Fig. 6. The pressure dependence of FWHM of IR modes. (a)

Table 2. Pressure Dependence of the Frequencies in the IR and Raman Mode

Mode	Activity	dv/dp (cm <sup>-1</sup> /GPa)		
		0~1.5 GPa	1.5~5.5 GPa	5.5-10.0 GPa
255 cm <sup>-1</sup>	Raman	2.93	5.72	
418 cm <sup>-1</sup>	IR	0.011	-0.081	
458 cm <sup>-1</sup>	IR	2.63	1.06	
535 cm <sup>-1</sup>	IR	2.44	2.13	1.42
564 cm <sup>-1</sup>	IR	1.97	1.92	
577 cm <sup>-1</sup>	IR	-0.312	-0.292	-0.120
641 cm <sup>-1</sup>	IR	0.162	0.281	0.072
673 cm <sup>-1</sup>	IR	-0.574	-0.476	
726 cm <sup>-1</sup>	IR	-1.246	-1.378	-0.271
741 cm <sup>-1</sup>	IR	-0.021	-0.081	
794 cm <sup>-1</sup>	IR	-0.183	0.229	0.195
1056 cm <sup>-1</sup>	Raman	3.80	4.94	
1134 cm <sup>-1</sup>	IR	2.94	2.85	1.73
1183 cm <sup>-1</sup>	Raman	6.44		
1226 cm <sup>-1</sup>	Raman	3.53	4.76	
1442 cm <sup>-1</sup>	Raman	4.47	7.63	
1465 cm <sup>-1</sup>	Raman	6.13	5.19	5.05
1562 cm <sup>-1</sup>	Raman	3.84	4.38	3.75

ule has two  $C_{60}$ -like polar regions of 20 atoms and belt region of 30 atoms. The polar region consists of a top pentagon and five hexagons which share long bonds (electron deficient) with top pentagon and short bonds (electron excess) with each other. The five hexagonal faces around belt region comprise essentially two types of bonds. Among these bonds, 30 bonds have slightly larger lengths than bonds of the polar region and the other bonds have a length similar to long bonds in  $C_{60}$ . The radial modes of polar region in  $C_{70}$  were expected that it might be softened under the high pressure like the case of  $C_{60}$ . Following reference (12), IR active 577 cm<sup>-1</sup>(E<sub>1</sub>) mode has 68.7% radial character and 22.3% belt character. IR active 673 cm<sup>-1</sup>(A<sub>2</sub>) mode has 64.3% radial character and 7.3% belt character. These two modes show negative pressure dependence as might be expected like the case of  $C_{60}$ . IR active 564 cm<sup>-1</sup>(E<sub>1</sub>) has 95.7% radial character but it is a belt mode so this mode showed positive pressure dependence. IR active 457 cm<sup>-1</sup>(E<sub>1</sub>) mode has 93.7% radial character, 21.9% belt character. IR active 535 cm<sup>-1</sup>(A<sub>2</sub>) mode has 95.8% radial character and 0.3% belt character. So these two modes might be expected negative pressure dependence, however these two modes show positive pressure dependence. Raman active 1442, 1465, 1562 cm<sup>-1</sup> modes have almost pure tangential character and polar character. These three modes show strong positive pressure dependence as might be expected.

In Fig. 7. we show the change of IR spectrum in the range from 750 cm<sup>-1</sup> to 800 cm<sup>-1</sup> at various pressures. It is noteworthy that a new mode appeared at pressure higher than about 5.5 GPa. In Fig. 3, it is shown that the pressure dependence of the Raman 1565 cm<sup>-1</sup> mode

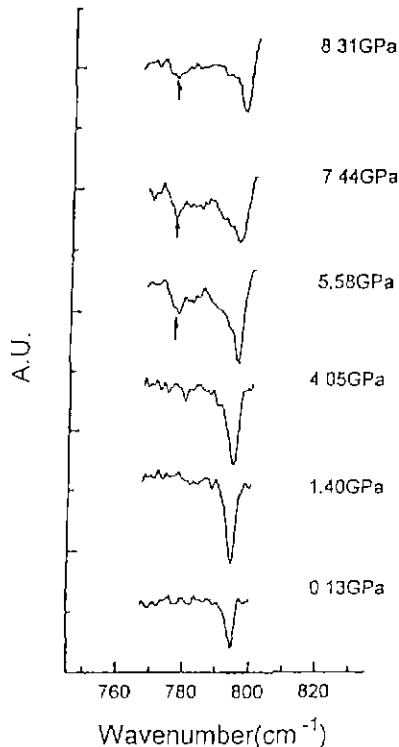


Fig. 7. The change of IR spectrum in the range from 750  $\text{cm}^{-1}$  to 800  $\text{cm}^{-1}$ .

slightly change around that pressure. This phenomena might be connected with the results of the previous high pressure XRD study of Christides *et al.*,<sup>9</sup> in which they reported that a progressive reduction of the intensities of the 311, 31 $\bar{1}$ , 11 $\bar{3}$  peaks and 22 $\bar{2}$  reflection was observed and  $\text{C}_{70}$  appears to become more compressible at the pressure higher than about 6.5 Pa. In that report, they considered this observation associated with a distortion of the rhombohedral unit cell, possible driven by a reduced shear strength from the anisotropic structure of the molecule. In order to study radiation effects, we irradiated  $\text{C}_{70}$  sample in the DAC with 514.5 nm laser light (200 mW) for different irradiation time at 7.5 GPa. The IR spectra of the irradiated  $\text{C}_{70}$  with different irradiation time at 7.5 GPa were shown in Fig. 8. In the figure, we show that intensity of new mode does not depend on the irradiation time, which means that the appearance of the possible new phase is independent of irradiation.

In Fig. 9, we show two IR spectra at 0.1 GPa, the upper spectrum is a spectrum of  $\text{C}_{70}$  before pressure applied and the lower spectrum is a spectrum of  $\text{C}_{70}$  recovered after pressurized. In this two spectra, we can see several differences. First, the new mode that appears above 5.5 GPa still exists and their intensity is strong. Second, 725, 741, 1253  $\text{cm}^{-1}$  modes are not observed in the recovered spectrum, which might mean that the recovered  $\text{C}_{70}$  has different phase compared to the phase before pressure applied. However, we could not investigate this phenomena in the Raman study, which is same as the results of Mak-

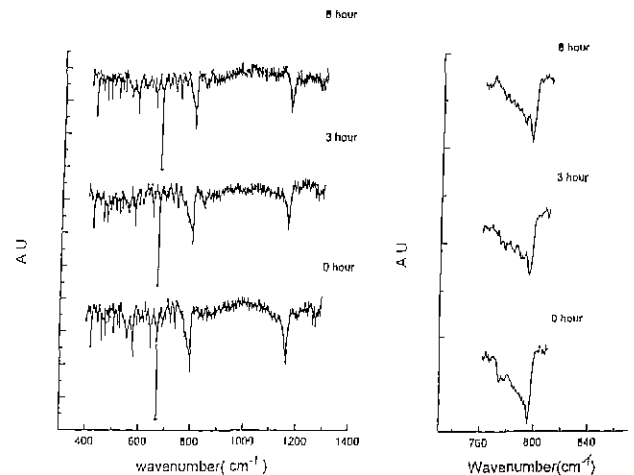


Fig. 8. The IR spectra of irradiated  $\text{C}_{70}$  with different time. The right figure is spectra in the range from 750  $\text{cm}^{-1}$  to 850  $\text{cm}^{-1}$ . Diamond mode is marked by asterisk (\*).

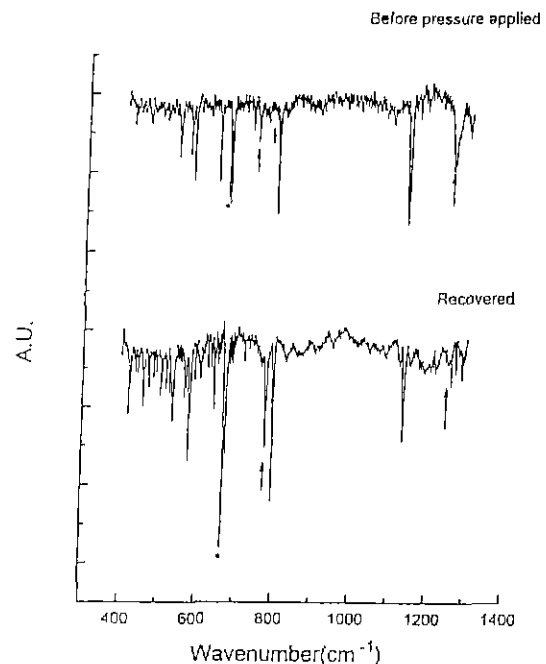


Fig. 9. The IR spectrum of  $\text{C}_{70}$  in the pressure loading cycle and after pressure released. Diamond mode is marked by asterisk (\*).

simove *et al.*<sup>13</sup> and A. K. Sood *et al.*<sup>14</sup>

In summary, we observed the slope of frequency-pressure plot for several Raman and IR mode changed around 1.5 GPa, which might be connected with solid-solid phase transition. We observed that new IR mode appeared above 5.5 GPa which might be indicative of another transition, and this new mode was not disappeared after pressure released to 0.1 GPa, which might indicate the possible new phase appeared above 5.5 GPa still exists around ambient pressure. We investigated the radiation effect. In this study, we could conclude that the possible new phase above 5.5 GPa is independent of irradiation.

### Acknowledgement

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