

## PRESSURE INDUCED DIMERISATION OF C<sub>70</sub>

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Solid C<sub>70</sub> has been subjected simultaneously to high pressures and temperatures (HPHT), with pressures upto 7.5 GPa and temperatures upto 750°C. X-ray diffraction measurements on the recovered samples indicate that the initial h.c.p. solid C<sub>70</sub> transforms to a rhombohedral structure which recovers to an f.c.c. structure on annealing. The associated changes in the intra molecular vibrational modes have been probed through infrared (IR) and Raman measurements. The IR measurements on these HPHT samples show splitting of some of the pristine modes and occurrence of several new modes. These sharp IR modes in the HPHT treated samples, which are seen to be different from that reported for photopolymerised C<sub>70</sub>, have been attributed to the formation of C<sub>70</sub> dimers. © 1997 Published by Elsevier Science Ltd

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### 1. INTRODUCTION

The synthesis of polymeric fullerenes from solid state precursors and an investigation of their properties has been a topic of considerable interest [1], since the first report of polymerisation of C<sub>60</sub> film under laser irradiation [2]. Polymerisation of C<sub>60</sub> has been observed [3] in Rb<sub>1</sub>C<sub>60</sub> and K<sub>1</sub>C<sub>60</sub>, as also in pristine C<sub>60</sub> when subjected to high pressure (~5 GPa) and high temperature (-800°C) treatment [4-7]. Polymeric fullerenes consist of covalently bonded cages which are arranged in linear chains or two-dimensional sheets. The chains can be as short as dimers, but can also extend to many units. Polymerisation in C<sub>60</sub> is associated with the (2+2) cycloaddition reaction [2], wherein the parallel double bonds of the neighbouring molecules react to form polymerised structure, linked through a four-membered cyclobutane ring. Under different conditions of pressure and temperature, f.c.c. C<sub>60</sub> is seen to transform to various polymerised structures, such as an orthorhombic structure consisting of one-dimensional polymeric chain or rhombohedral and tetragonal structures consisting of two-dimensional polymeric layers [6].

In contrast to extensive investigations on the polymerisation of C<sub>60</sub>, there have been fewer studies on C<sub>70</sub>. It has been shown that C<sub>70</sub> can be photopolymerised [8, 9], albeit with a much lower efficiency compared to C<sub>60</sub> and more recently there has been evidence [10] for cross linking of C<sub>70</sub> molecules in Ar plasma. The difficulty in the polymerisation of C<sub>70</sub> has been attributed to the topochemical constraints specific to the C<sub>70</sub> molecule [8] in that only the double bonds on the polar caps of the molecule are reactive, whereas the cyclic double bonds on the equatorial belt are ineffective in undergoing (2+2) cycloaddition reaction. For the polymerisation reaction to occur in C<sub>70</sub> under HPHT conditions, as in the case of C<sub>60</sub>, it is necessary that the parallel configurations of C=C double bonds of the neighbouring molecules be brought close together under compression. In the case of solid C<sub>70</sub>, it is known [11] that there are two orientational ordering transitions, one corresponding to the free rotor phase going to a long axis oriented rhombohedral phase and the second corresponding to a completely oriented C<sub>70</sub> in the monoclinic phase. Both these transitions are influenced by pressure [12, 13]; the rhombohedral to f.c.c. transition temperature increases at the rate of 300 K GPa<sup>-1</sup>, whereas the monoclinic to rhombohedral transition temperature increases at a much slower rate of 50 K GPa<sup>-1</sup>.

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Thus, depending on the high pressure and temperature conditions employed, solid  $C_{70}$  could be in different orientationally ordered states, which would influence the possibility of polymerisation. This together with the topochemical features of the  $C_{70}$  molecule was used to rationalise the non-observance of polymerisation in our earlier investigations [7] on HPHT treated  $C_{70}$ , which had been carried out over a limited range of pressure and temperature.

In the present study, which is a continuation of our earlier work [7], we have spanned a wider range of pressure–temperature regimes, viz.,  $P = 1\text{--}7.5\text{ GPa}$  and  $T = \text{RT}\text{--}750^\circ\text{C}$ , to look for conditions that would favour polymerisation. In particular, we have investigated the influence of keeping the system at high pressure (7.5 GPa) and low temperature (RT), and low pressure (1 GPa) and high temperature ( $750^\circ\text{C}$ ), wherein solid  $C_{70}$  is expected to be in monoclinic and rhombohedral structures respectively. The structural information on the HPHT treated samples has been obtained through X-ray diffraction measurements and the intramolecular vibrational modes have been probed by Raman and IR measurements. The significant result of the present investigations is the dramatic splitting of IR modes in the HPHT treated samples [14], which is seen to recover to pristine modes on annealing. In order to find out if this splitting of IR modes is associated with the formation of orientationally ordered  $C_{70}$ , *in situ* IR measurements across the low temperature orientational ordering transitions [11] in pristine  $C_{70}$  have also been carried out. With support from these experiments and Raman measurements, the observed splitting of IR modes in the HPHT treated samples has been attributed to the formation of  $C_{70}$  dimers [15].

## 2. EXPERIMENTAL DETAILS

Chromatographically purified polycrystalline  $C_{70}$  powder was synthesised using the procedure described in [16] and this was heat treated in vacuum at  $250^\circ\text{C}$  for over 24 h to get rid of the trapped organic solvents. A pellet of 3 mm diameter and 2 mm thickness, wrapped in a  $7.5\ \mu\text{m}$  stainless steel foil, was mounted along with steatite disks inside a pyrophyllite gasket containing a small annular graphite ring heater and this assembly was loaded into an opposed anvil high pressure apparatus [17]. This whole procedure, which was carried out under ambient conditions, entailed an exposure of the samples to atmospheric oxygen for a period of  $\sim 30$  min, before being sealed between the gaskets. After raising the pressure upto 7.5 GPa maximum, over a period of 10 min, the temperature was increased upto a maximum of  $750^\circ\text{C}$ . The sample was allowed to *soak* under high pressure and temperature for  $\sim 6$  h, following which the

temperature was lowered gradually and the pressure was subsequently released slowly. X-ray diffraction measurements on finely chopped pellets were carried out using Siemens D-500 diffractometer operating in the Bragg–Brentano arrangement. Raman measurements were carried out, under ambient conditions, using DILOR X-Y spectrometer with liquid nitrogen cooled CCD detector. Infrared absorption spectra were recorded using a Bomem (Model MB 100) FTIR spectrometer, on samples pelletized with KBr. Thin films of  $C_{70}$ , vacuum deposited on single crystal KBr substrates, were used for low temperature FTIR measurements, the temperatures being achieved using a Leybold Heraeus closed cycle helium refrigerator.

## 3. RESULTS AND DISCUSSION

Figure 1(a) shows X-ray diffraction (XRD) patterns of the pristine  $C_{70}$  and those treated at various pressures

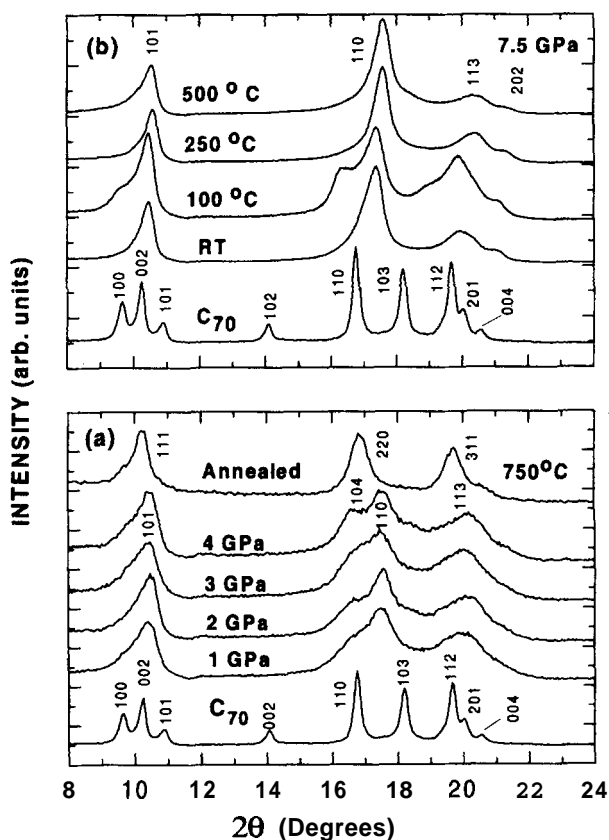


Fig. 1. (a) X-ray diffractograms of the starting  $C_{70}$  powder, indexed to h.c.p. structure and those of samples treated at various pressures at  $750^\circ\text{C}$ , indexed to rhombohedral structure. The XRD pattern of HPHT treated samples subsequently annealed in vacuum at  $250^\circ\text{C}$  is indexed to f.c.c. structure. (b) XRD pattern of  $C_{70}$  treated at various temperatures at 7.5 GPa. Note the shift of the RT and  $100^\circ\text{C}$  treated spectra towards smaller  $2\theta$  values, which are indexable to rhombohedral structure.

at 750°C. The XRD pattern of the starting C<sub>70</sub> powder can be indexed to h.c.p. structure with lattice parameter  $a = 10.60 \text{ \AA}$  and  $c = 17.26 \text{ \AA}$ , consistent with earlier studies [18]. In the case of the HPHT treated samples, broad diffraction lines corresponding to a new crystalline phase is observed. As reported earlier [7] these could be indexed to a rhombohedral structure (space group  $R\bar{3}m$ ) with the hexagonal lattice parameters,  $a = 10.10 \text{ \AA}$  and  $c = 26.88 \text{ \AA}$ . In the course of our studies on various HPHT treated C<sub>70</sub>, we observed that in case of samples treated at higher pressure (7.5 GPa) and low temperature, viz., RT and 100°C, the diffraction pattern was shifted towards smaller angles, as shown in Fig. 1(b). Correspondingly these could be fitted to a rhombohedral structure with a marginally expanded lattice parameters ( $a = 10.23 \text{ \AA}$  and  $c = 27.56 \text{ \AA}$ ) as compared to the rest of the samples. The rhombohedral structure obtained after HPHT treatments were seen to transform to f.c.c. structure ( $Fm\bar{3}m$ ) with  $a = 14.94 \text{ \AA}$  on annealing at 250°C for 24 h, as shown in the top panel of Fig. 1(a).

The broad diffraction patterns of the HPHT treated C<sub>70</sub> were not amenable to a detailed structural analysis, in particular to obtain information on the formation of intra molecular bonds. In order to find out if the rhombohedral structure corresponds to a polymeric phase, we have estimated the inter-fullerene distance. It must be remarked that in the case of polymeric C<sub>60</sub> obtained by HPHT treatment, there is a distinct reduction [6, 7] in the interfullerene distance to 2.2 Å, from 3 Å in the f.c.c. phase, providing a strong evidence for the formation of intra-molecular bonds. With the known [18] molecular dimensions of C<sub>70</sub> and assuming that the C<sub>70</sub> molecules are aligned along the long axis, the smallest distance between the double bonds on polar caps of neighbouring C<sub>70</sub> molecules at (0, 0, 0) and (2/3, 1/3, 1/3) can be estimated [7] to be 2.61 Å, while the distance between the equatorial double bonds is 3.01 Å. These inter-fullerene distances in the rhombohedral phase are not significantly different from that in the starting h.c.p. phase or the annealed f.c.c. phase [18]. Thus, our X-ray diffraction measurements do not provide any direct evidence for the polymerisation of C<sub>70</sub>. We may also point out that qualitatively different diffraction patterns have been obtained for polymerised C<sub>70</sub> obtained by other methods: For example, an amorphous XRD pattern has been obtained [10] in the study of plasma polymerised C<sub>70</sub> and Rao *et al.* [9] have observed an increase in lattice parameter on UV polymerisation of f.c.c. C<sub>70</sub> film. While these differences need to be investigated in more detail, they point out to a greater variety in structures possible in the linking of C<sub>70</sub> molecules.

Figure 2 shows the results of IR studies on pristine C<sub>70</sub> and those treated at 750°C at various pressures. In

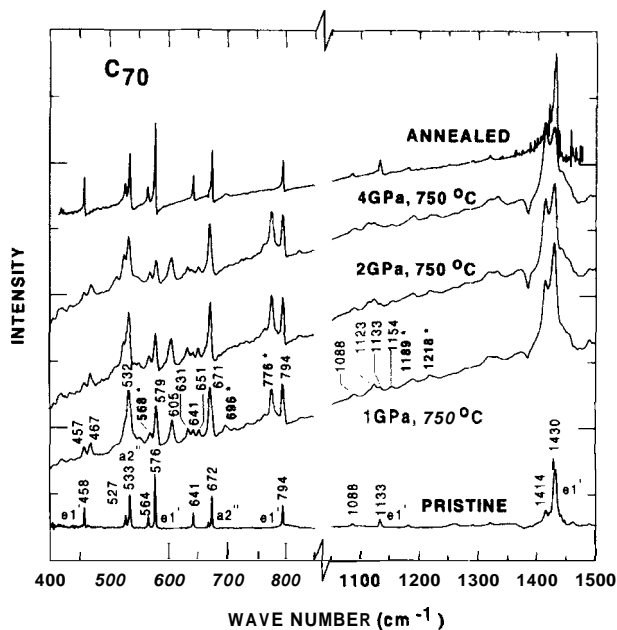
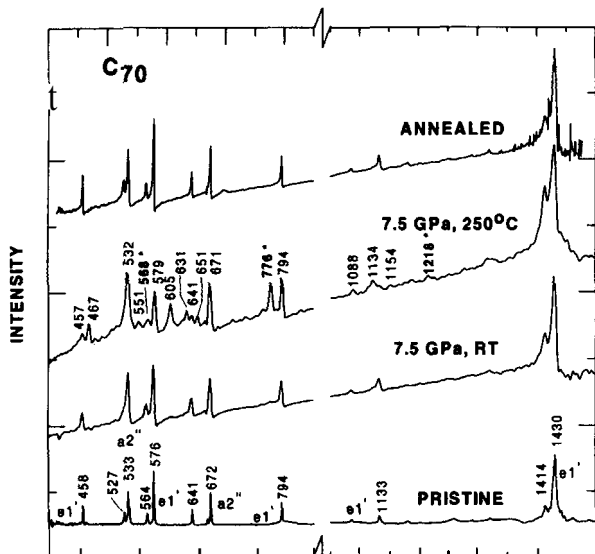


Fig. 2. IR spectra of pristine and C<sub>70</sub> treated at various pressures at 750°C. The split IR pattern are seen to recover to pristine modes on annealing at 250°C. The IR modes marked with \* correspond to Raman modes measured at  $T = 23 \text{ K}$  [23].

comparison with the IR spectrum of pristine C<sub>70</sub>, which is in conformity with earlier results [19, 20], in the HPHT treated samples the IR spectrum has developed fine structure and several new modes have appeared. This is particularly striking in the low wave number region: For example, the pristine modes at 641 cm<sup>-1</sup> develops new features on either sides, the pristine mode at 458 cm<sup>-1</sup> is seen to develop a feature on the high wave number side at 467 cm<sup>-1</sup> while the mode at 794 cm<sup>-1</sup> is associated with an additional mode on the lower wave number side at 776 cm<sup>-1</sup>. In addition, new modes are seen to emerge in the spectra of the HPHT treated samples, for example the mode at 605 cm<sup>-1</sup>. It is noted that similar features are seen in all the pressure treated samples. Since some of the modes in the HPHT treated sample are coincident with those of pristine C<sub>70</sub>, it is possible that there is some untransformed material. While, we have not carried out quantitative studies on the solubility of HPHT treated samples in toluene, which provides an indicator of the residual C<sub>70</sub>, it was generally observed that the solubility of the pressure treated samples were much lower compared to pristine C<sub>70</sub>. The sharp split IR spectrum of HPHT treated samples are seen to recover to the modes of pristine C<sub>70</sub> on annealing at 250°C as shown in the top panel of Fig. 2.

It was noted earlier that treatment at 7.5 GPa at low temperatures (RT and 100°C) resulted in a rhombohedral structure with marginally larger lattice parameters



as compared to that obtained on treatment at high temperatures, beyond 250°C [cf. Fig. 1(b)]. Select results of IR measurements on the samples treated at 7.5 GPa are shown in Fig. 3. It is noted that whereas in the case of sample treated at 250°C a split IR spectrum similar to that in Fig. 2 is obtained, in the case of sample treated at RT, the IR spectrum is unsplit and is similar to pristine C<sub>70</sub>. This difference is striking and as we shall see below, has a bearing on the interpretation of the origin of the split IR spectra.

The changes in the vibrational modes on HPHT treatment of C<sub>70</sub> have also been probed using Raman spectroscopy. Figure 4(a) and (b) shows the results of Raman measurements. In the case of HPHT treated samples, the Raman spectra are not very different from that of pristine C<sub>70</sub> [19], except for a shoulder at 1426 cm<sup>-1</sup>, to the left of the 1444 cm<sup>-1</sup> peak and a weak new feature at 278 cm<sup>-1</sup> to the right of the Raman mode at 255 cm<sup>-1</sup>. These subtle changes in Raman spectra are to be contrasted with the dramatic splitting of IR spectra in HPHT treated C<sub>70</sub>. It may be noted [4, 7, 21] that even in the case of pressure polymerised C<sub>60</sub> the changes in the Raman spectra are minimal when compared to the changes in IR spectra.

In the following, we analyse the origin of the sharp-split IR spectrum in C<sub>70</sub> treated at 1 GPa, 750°C. At the outset, we may attribute the splitting of IR modes to a change in the site symmetry associated with the

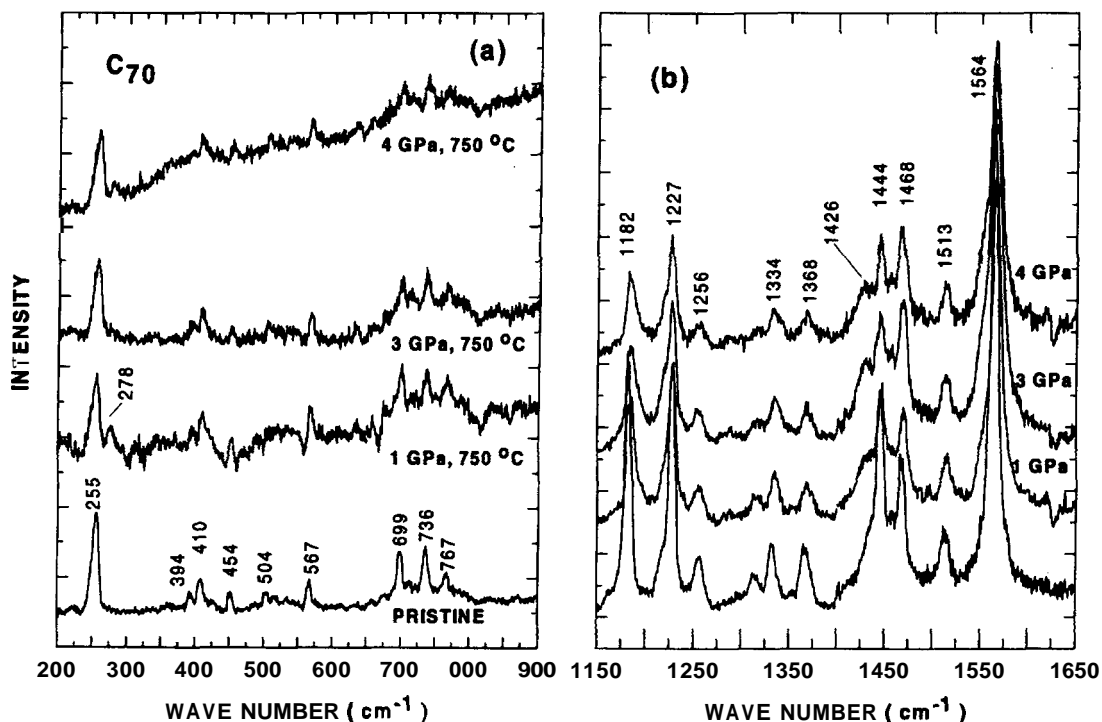


Fig. 4. Raman spectra of pristine and C<sub>70</sub> treated at various pressures at 750°C, in the range (a) 200–900 cm<sup>-1</sup> and (b) 1150–1650 cm<sup>-1</sup>. Note the development of new mode at 1426 cm<sup>-1</sup> and 278 cm<sup>-1</sup>.

structural transformation from the initial h.c.p. to the rhombohedral structure. However, in this assignment we encounter a difficulty in that splitting is not seen in the case of sample treated at 7.5 GPa, RT (cf. Fig. 3), in which case also the sample has a rhombohedral structure [cf. Fig. 1(b)]. In order to explore further if the splitting of IR pattern is in any way related to the structural transition [11] associated with the orientational ordering of  $C_{70}$  molecules, we have also carried out IR measurements on pristine  $C_{70}$  films on KBr substrates at low temperatures upto 12 K. These results are shown in Fig. 5. It is seen that with the decrease of temperature, while there is a systematic decrease in the line widths of most of the IR modes, the modes at 458 and 565  $cm^{-1}$  show indications of broadening and splitting and these results are in conformity with earlier studies [22]. These small changes in the IR spectra at low temperatures are to be contrasted with the large splitting and occurrence of several new modes in the IR spectra (cf. Fig. 2) in the case of HPHT treated  $C_{70}$ . This clearly indicates that the features seen in the IR spectra of HPHT treated samples is not related to the structural transition involving orientationally ordered  $C_{70}$  monomers.

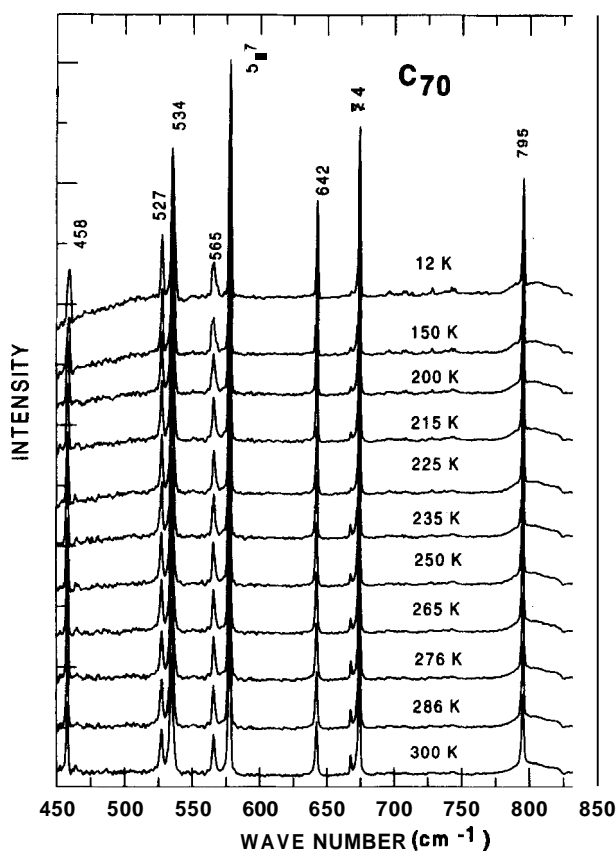


Fig. 5. IR spectra of pristine  $C_{70}$  at various temperatures. The modes at 458 and 565  $cm^{-1}$  broaden at low temperatures, whereas the other modes are seen to sharpen.

In trying to find out if the split IR modes are associated with the formation of polymeric phase, we were led to compare with the earlier IR measurements [8] on photopolymerised  $C_{70}$ . The only distinctive feature in the IR spectrum of photopolymerised  $C_{70}$ , is a broad band centered at 1086  $cm^{-1}$ , which incidentally is also seen in photopolymerised  $C_{60}$  and has been attributed to disorder [9]. Our IR spectra of HPHT treated  $C_{70}$ , shown in Figs 2 and 3, are very different from that reported [8] for photopolymerised  $C_{70}$ .

Given that the IR spectrum of HPHT treated  $C_{70}$  is distinct from that of photopolymerised  $C_{70}$  and monomeric  $C_{70}$  in orientationally ordered state, it is tempting to speculate that the splitting of IR modes arises due to the formation of  $C_{70}$  dimers. In support of this speculation, we may point out that some of the new modes, marked with asterisks in Fig. 2 can be identified with the Raman modes of  $C_{70}$  measured at low temperature [23]. Further, the mode at 1426  $cm^{-1}$  seen in Raman spectra [cf. Fig. 4(b)] can be associated with the dominant IR mode at 1430  $cm^{-1}$ . It is well known [24] that Raman modes and IR modes are no longer strictly complimentary once the inversion symmetry is broken, i.e. Raman modes are also observed in the infrared spectrum and vice versa. In fact such an argument has been used to identify  $C_{60}$  dimer in  $Rb_1C_{60}$  [25]. To obtain more definitive confirmation on the formation of  $C_{70}$  dimers under HPHT treatment, detailed theoretical analysis of the vibrational spectrum of  $C_{70}$  dimers are called for, as has been done recently [21] for dimers of  $C_{60}$ .

To summarise, our present studies on solid  $C_{70}$  treated at high pressure and temperatures ( $>250^\circ C$ ), indicate transformation to a rhombohedral structure and this is associated with sharp split IR spectra. These IR spectra, which are different from that seen in photopolymerised  $C_{70}$  and in orientationally ordered monomeric  $C_{70}$  have been attributed to the formation of  $C_{70}$  dimers. In the case of  $C_{70}$  treated at high pressure (7.5 GPa) and low temperatures (RT and  $100^\circ C$ ), the IR spectra are similar to that in pristine  $C_{70}$ . This is consistent with our initial premise that under these treatment conditions, solid  $C_{70}$  can be expected to be in monoclinic structure, whose orientational order is not conducive to the formation of covalent linkages between molecules. In our earlier studies [7], we had inferred that  $C_{70}$  does not polymerise, based on a limited scan of pressure and temperature range. Further, in these studies, the vibrational modes were mainly monitored through Raman measurements, which as we have seen presently is far less sensitive to the formation of intra molecular bonds. Our present conclusion on the dimerisation of  $C_{70}$  on HPHT treatment is principally based on dramatic changes seen in the IR spectra.

The formation of only the dimers in the case of HPHT treated  $C_{70}$  is to be contrasted with the Occurrence of polymeric chains and sheets in the case of similarly treated  $C_{60}$  [6, 7]. This may be due to the stereochemical constraints, specific to  $C_{70}$  molecule, which prohibit the formation of long range ordered chains. Alternatively, it is possible that  $C_{70}$  polymers have limited metastability in that they break up during the slow cooling and release of pressure after HPHT treatment. Further investigations on pressure quenched  $C_{70}$ , instead of slow cooling as in the present series of experiments, will be of interest.

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