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Polymeric Fullerenes: Optical High-Pressure Investigations

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High hydrostatic pressure ~~has~~ a number of effects in partially polymerized fullerenes, the most interesting of them being further pressure-induced polymerization and subsequent structural phase transitions. The behavior ~~of~~ the phonon modes of the polymeric one-dimensional orthorhombic [1D(O)] phase and the two-dimensional tetragonal [2D(T)] and rhombohedral [2D(R)] phases of C₆₀ are studied as a function of pressure, up to ~30 GPa, at room temperature. The two-dimensional polymeric phases undergo irreversible structural transformations at different pressures. The phonon spectra of the high-pressure phases reveal that the fullerene molecular cage is preserved in the recovered phases. These observations suggest that these phases are related to a three-dimensional network of C₆₀ cages.

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1. Introduction

Polymerization involving C₆₀ molecules is a very complicated process because carbon atoms are found in both *sp*² and *sp*³ hybridized states and therefore many possibilities exist for the formation of bonds. Polymerized C₆₀ was found to exist in a variety of crystal structures with interesting optical and mechanical properties,⁽¹⁾ and this, in turn, has stimulated further research of these materials. It was established that the polymerization process can be initiated by photons of visible or ultraviolet light,⁽²⁾ alkali metal doping^(3,4) and high-pressure high-temperature (HPHT) treatment of C₆₀.⁽⁵⁾ The polymerization of pristine C₆₀, under HPHT conditions, results in the formation of fullerene cage networks of various dimensionalities.^(5,1,6) The covalent polymeric bonds are usually formed by the so-called [2+2] cyclo-addition mechanism via the formation of four-membered rings between adjacent fullerene molecules.⁽²⁾ The structure of the HPHT polymers of C₆₀ strongly depends

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on the treatment conditions - the pressure and temperature. Thus, linear chains and/or dimers and higher oligomers at $P \leq 1$ GPa, 2D polymeric layers at intermediate pressure, and structures based on three-dimensionally (3D) cross-linked molecular cages at higher pressure and temperature can be formed.^(1,6,7,8) The 2D polymers of C_{60} have either a rhombohedral, 2D(R), or a tetragonal, 2D(T), crystal structure. Although it has been proposed^(1,8,9) that the polymeric tetragonal phase is a growth fault of the orthorhombic (1D polymer) or the rhombohedral phase, this polymeric phase was proven to be a stable one.⁽¹⁰⁻¹²⁾ A stable 3D polymerized structure was predicted, in a theoretical study based on density functional methods, by applying uniaxial pressure of about 20 GPa to the tetragonal 2D polymeric phase of C_{60} ⁽¹³⁾ with new inter-plane bonds formed by additional fourfold coordinated sp^3 -like hybridized carbon atoms. Another study,⁽¹⁴⁾ based on semi-empirical potentials and *ab initio* density functional methods, predicted the formation of three related 3D polymerized phases having 52, 56, and 60 tetra-coordinated atoms per molecule by pressurizing the 1D or the 2D polymeric phases.

Our interest, over several years, has been focused on the experimental study of the pressure-induced transformations in various polymeric phases of C_{60} and the structural stability of the new high-pressure-induced polymeric phases by means of *in situ* Raman spectroscopy using the diamond anvil cell (DAC) technique. The perturbations in the structure of the C_{60} cages, caused by external disturbances such as pressure, temperature, chemical bond formation, etc., are manifested in the phonon spectrum. Therefore, Raman spectroscopy, which probes inter- and intra-molecular vibrations, is a suitable tool for the studies of structure evolution and possible phase transformations in fullerene materials under pressure.⁽¹⁵⁾

2. Raman Spectra of Polymeric Phases and their Pressure Dependence

The Raman spectra of the 1D(O), 2D(T) and 2D(R) phases in the frequency region of $100\text{--}2000\text{ cm}^{-1}$ measured under normal conditions, are illustrated, in Fig. 1, along with that of the pristine C_{60} . The phonon frequencies, obtained by fitting the Raman data with Voigtian lines, are listed in Table 1. Polymerization results in the lowering of the molecular symmetry and therefore the Raman active fivefold degenerated H_g modes are split and, in addition, new peaks may appear, originating from the initially inactive modes of the C_{60} molecule. The assignment, given in Table 1, is based on the icosahedral modes of the C_{60} molecule,^(10,12,16) in which, for simplicity, the irreducible representations of the C_{60} molecule are used to characterize the corresponding modes in the polymeric phases.

The most important probe for the investigation of the polymerization processes is the behavior of the $A_g(2)$ pentagonal pinch (PP) mode of the C_{60} molecule. This mode is related to the in-phase stretching vibration of the five C=C bonds, which involves tangential displacements with a contraction of the pentagonal rings and an expansion of the hexagonal rings. Its frequency is very sensitive to any perturbation on the molecular cage and particularly to the breakdown of some of the C=C bonds involved in the polymerization processes. The PP mode is downshifted in all polymeric forms of C_{60} , as the formation of intermolecular covalent bonds leads to a lower intramolecular average bond stiffness.⁽¹⁾ In the case of fullerite, the $A_g(2)$ mode is observed at 1468 cm^{-1} . In the 1D(O) polymer, two

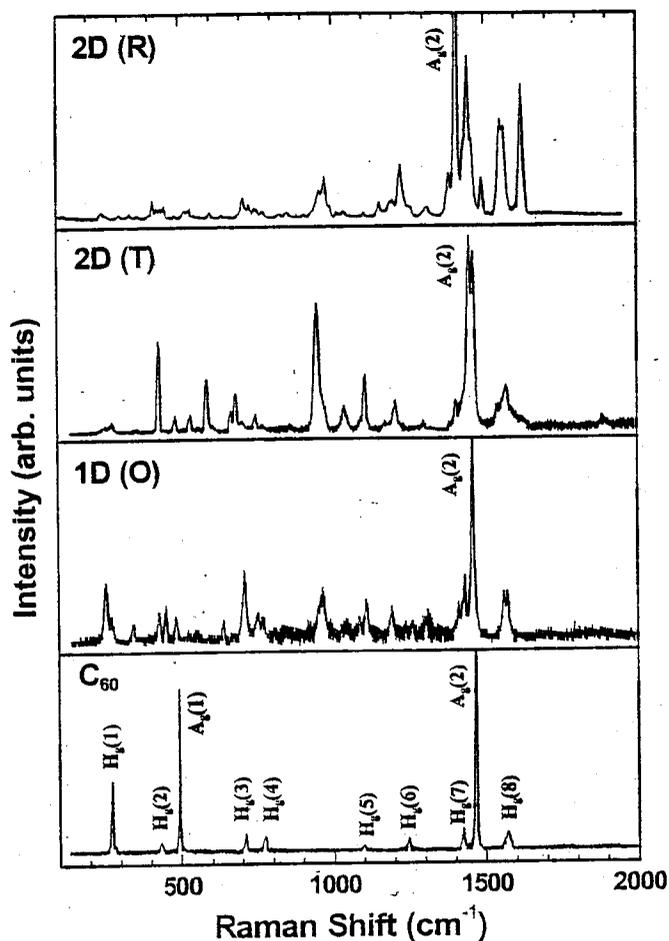


Fig. 1. Raman spectra of polymeric phases along with that of monomeric C_{60} recorded under normal conditions. The assignment given for C_{60} refers to its molecular modes.

peaks are observed at 1458 and 1464 cm^{-1} , which are in excellent agreement with those observed by Persson *et al.*⁽¹⁷⁾ On the basis of Porezag *et al.*'s calculations,⁽¹⁸⁾ it was suggested⁽¹⁾ that the component at 1464 cm^{-1} may be due to the presence of C_{60} dimers, while that at 1458 cm^{-1} is the frequency of the PP mode in the case of C_{60} linear chains. In the 2D(T) polymer, the downshift of the PP mode is expected to be even larger than that in the 1D(O) polymer as additional inter-molecular bonds are formed. We indeed observed two peaks at 1446 and 1464 cm^{-1} , in good agreement with a recent report.⁽¹⁰⁾ The lower energy peak was proposed to be the PP mode in the case of a 2D(T) polymer,⁽¹⁾ while the 1464 cm^{-1} peak can be attributed to the PP mode of C_{60} dimers. However, from complementary analysis of the Raman and infrared spectra of the 2D(T) phase, it was concluded that the presence of an

Table 1

Phonon frequencies of various polymeric phases of C_{60} and their assignment based on C_{60} molecular modes.

Mode	1D(O) ω (cm ⁻¹)	2D(T) ω (cm ⁻¹)	2D(R) ω (cm ⁻¹)	Mode	1D(O) ω (cm ⁻¹)	2D(T) ω (cm ⁻¹)	2D(R) ω (cm ⁻¹)
H _g (1)	—	—	245	F _{1g} (2)	967	972	977
H _g (1)	255	257	267	F _{2u} (4)	—	—	1016
H _g (1)	273	279	308	F _{2u} (4)	1044	1039	1037
H _u (1)	345	—	342	H _g (5)	—	—	1042
F _{2u} (1)	—	—	366	H _g (5)	1087	1090	1078
G _u (1)	—	—	406	H _g (5)	1110	1108	1109
H _g (2)	429	432	415	G _g (3)	—	1176	1158
H _g (2)	—	—	438	G _g (3)	1193	—	1195
H _g (2)	453	—	451	F _{2g} (3)	—	1208	1204
A _g (1)	488	487	492	H _g (6)	1239	—	1224
F _{1u} (1)	528	—	520	H _g (6)	—	—	1230
F _{2g} (1)	—	537	532	H _g (6)	1260	—	1260
F _{1g} (1)	555	562	558	G _g (4)	1307	1299	1314
F _{1g} (1)	—	589	—	H _g (7)	1398	—	1385
H _u (2)	—	—	579	H _g (7)	1411	1405	—
H _u (2)	—	610	596	H _g (7)	1426	1428	—
H _u (3)	639	—	640	H _g (7)	1433	—	—
H _g (3)	—	666	—	H _g (7)	1448	—	—
H _g (3)	—	684	695	A _g (2)	1458	1446	1410
F _{2u} (2)	—	—	709	F _{1g} (3)	1464	1464	1461
H _g (3)	710	706	712	F _{1g} (3)	—	—	1495
H _g (3)	—	—	731	F _{2g} (4)	—	1543	—
H _g (4)	748	753	749	H _g (8)	1562	—	1554
F _{2g} (2)	—	—	767	H _g (8)	1575	1571	1563
H _g (4)	771	772	776	H _g (8)	—	—	1569
F _{2u} (3)	—	—	827	G _g (6)	—	1599	1621
H _u (4)	843	863	856	G _g (6)	—	1624	1627
H _u (4)	917	—	868	2×G _g (2)	—	1888	—
G _g (2)	955	950	958				

appreciable amount of dimers in the system is unlikely.⁽¹⁹⁾ Therefore, this peak is of another origin; one possibility may be the activation of an initially inactive mode in I_h symmetry {F_{1g}(3)}, which becomes active in the D_{2h} symmetry of the 1D(O) and 2D(T) phases. Finally, in the case of the 2D(R) phase, the A_g(2) mode exhibits a pronounced softening and is observed at 1410 cm⁻¹. *molecular in*

The Raman spectra of the 2D(T) and 2D(R) phases of C_{60} , in the frequency region of 200–2000 cm⁻¹ and for several pressures up to 30 GPa, are shown in Fig. 2. The spectra were recorded upon pressure increase, while the spectral region around the significantly strong triply degenerate T_{2g} mode of diamond appearing at 1332 cm⁻¹ was excluded. As the pressure increases, the majority of the Raman peaks shift to higher energies and their bandwidths

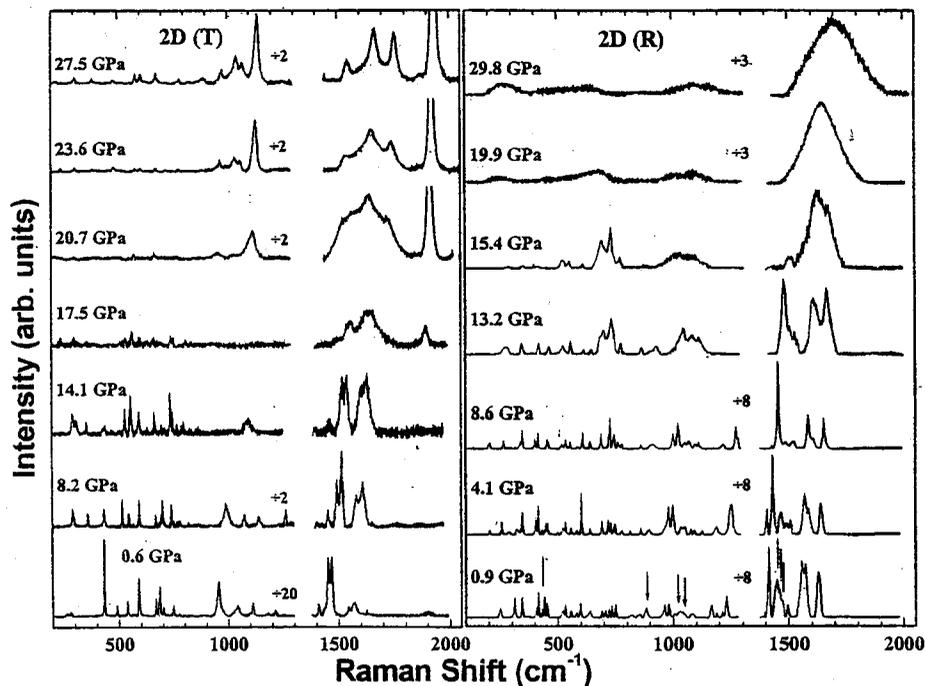


Fig. 2. Raman spectra of ^{13}C polymeric phases of C_{60} in the frequency region of 200–2000 cm^{-1} at various pressures at room temperature, recorded upon pressure increase. The vertical lines, in the 2D(R) spectra, indicate some peaks related to the presence of oligomers in the material, while arrows indicate three methanol-ethanol mixture peaks.

gradually increase. Dramatic changes in the Raman spectrum are observed in the pressure region around 20 GPa for the 2D(T) phase. New features appear that rapidly grow in intensity and the new Raman spectrum differs significantly from the initial one with respect to the number of peaks and their intensities and positions. The new peaks are located primarily in the frequency region above 1000 cm^{-1} , with the most intense of them found at $\sim 1920 \text{ cm}^{-1}$. A number of less intense peaks are located in the frequency region below 1000 cm^{-1} . The majority of the peaks can be traced back to the peaks observed in the 2D(T) polymeric phase and may be related to the fullerene molecular cage. Nevertheless, some of the peaks, located in the high-energy region, do not have any obvious relationship with the molecular cage modes and therefore should be of a different origin.

Significant changes are also observed in the Raman spectrum of the 2D(R) phase at pressures higher than ~ 15 GPa when the Raman spectrum becomes very diffuse and loses its fine structure. This transformation is preceded by a rapid decrease in the intensity of the $A_g(2)$ PP-mode and a relative increase in the intensities of the split $H_g(8)$ and $G_g(6)$ modes.⁽²⁰⁾ Comparing the Raman spectra of the high-pressure phases of the 2D compounds,^(20–22) we observe that the 2D(R) spectrum does not contain any peak in the high-energy region, like

the 1920 cm^{-1} peak in the 2D(T) phase. In addition, the high-pressure phase of the 2D(R) shows a spatially uniform Raman response over the entire surface of the sample,⁽²⁰⁾ as was evidenced by probing various places in the sample, and this behavior differs drastically from that of the 2D(T) phase of C_{60} .⁽²²⁾ The Raman spectra of both 2D phases, upon pressure release, are shown in Fig. 3. These downstroke cycles in pressure lasted a long time (more than one month). The high-pressure phases in both materials remained stable even in ambient conditions.

The pressure dependence of the intramolecular Raman modes of the 2D(T) polymer in the frequency region of $250\text{--}1300\text{ cm}^{-1}$ is shown in Fig. 4. The $A_g(1)$ (breathing) mode in the 2D(T) polymer is located at 487 cm^{-1} , which is downshifted by $\sim 8\text{ cm}^{-1}$ with respect to the pristine C_{60} .⁽¹⁷⁾ The number of Raman active modes has been increased considerably with respect to the pristine C_{60} . This is attributed mainly to the splitting of the $H_g(1)$, $H_g(3)$ and $H_g(4)$ modes, implying that in the 2D(T) polymer, a $\sim 5\%$ deviation from the quasi-spherical shape of the pristine C_{60} molecule⁽²³⁾ can have a considerable effect on the intramolecular modes. The most important feature of this pressure dependence is related to the drastic changes observed in the pressure region of $\sim 20\text{ GPa}$. These changes point to a structural transformation of the material and the new phase remains stable at ambient pressure.

The pressure dependence of the phonon modes in the high-frequency region ($1400\text{--}1950\text{ cm}^{-1}$) of both 2D compounds is shown in Fig. 5. Several important differences are clearly

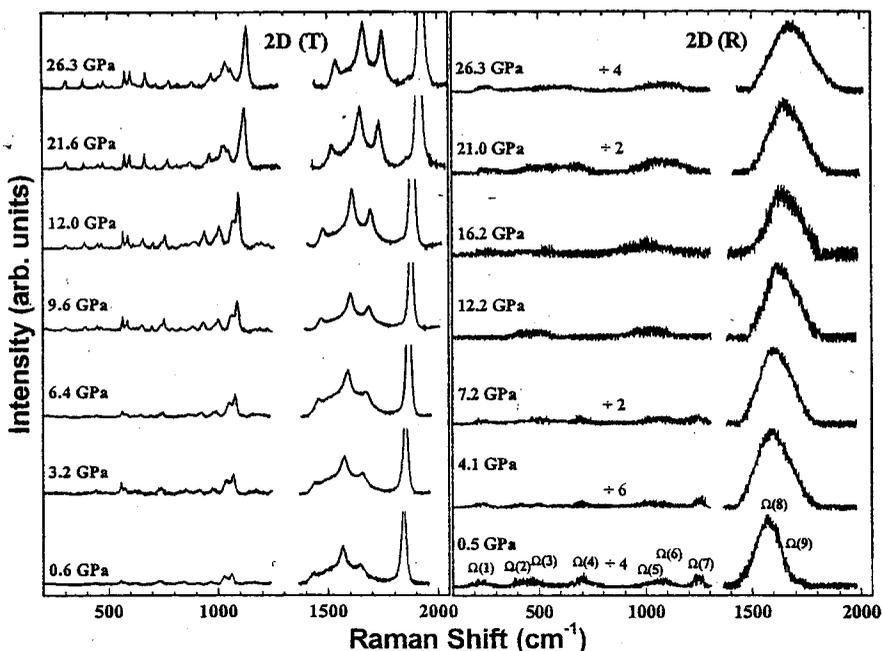


Fig. 3. Raman spectra of 2D polymeric phases of C_{60} in the frequency region of $200\text{--}2000\text{ cm}^{-1}$ at various pressures at room temperature, recorded upon pressure decrease.

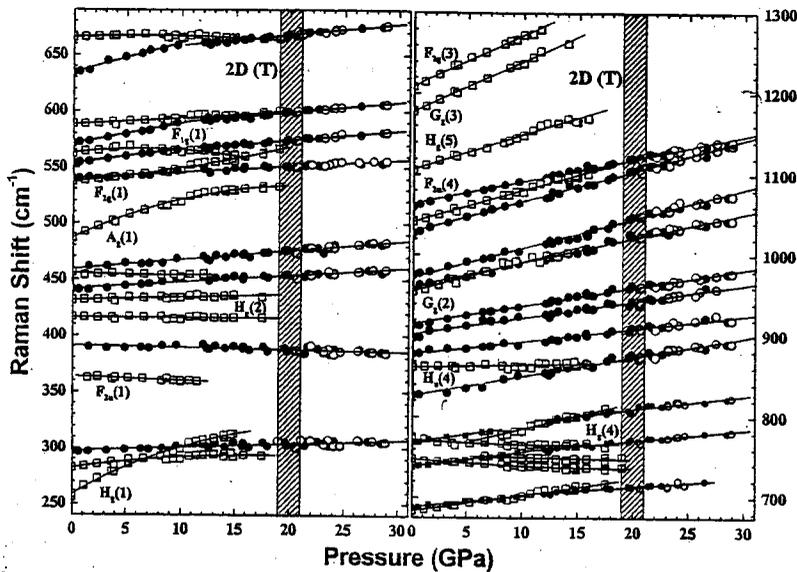


Fig. 4. Pressure dependence of Raman active modes of the 2D(T) polymeric phase of C_{60} in the frequency region of 250–1300 cm^{-1} . Open (solid) symbols represent data taken at the increasing (decreasing) pressure cycle.

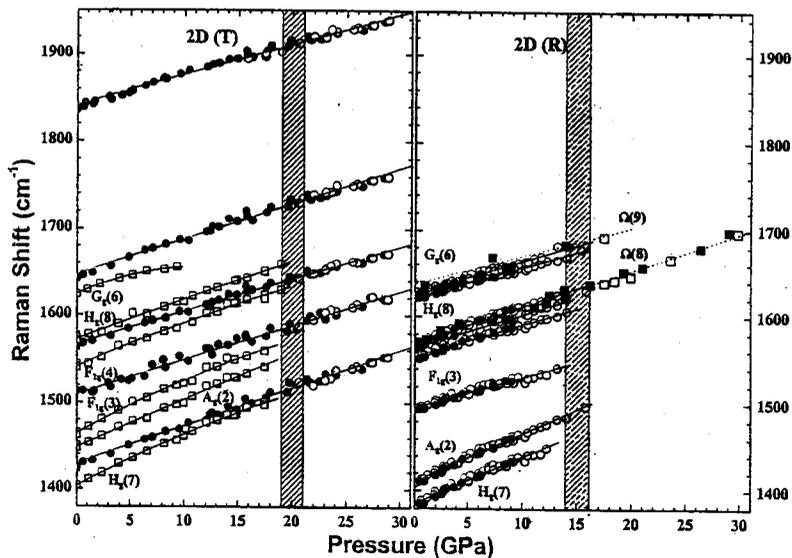


Fig. 5. Pressure dependence of Raman active modes of 2D polymeric phases (T and R) of C_{60} in the frequency region of 1400–1950 cm^{-1} . Open (solid) symbols represent data taken at the increasing (decreasing) pressure cycle.

seen in the phonon frequencies and their pressure response between these two polymeric forms of C_{60} . In the 2D(T) compound and in the frequency region of the $A_g(2)$ mode, two peaks appear at 1446 and 1463 cm^{-1} . The lower energy component was proposed to be the PP mode of the 2D polymer⁽¹⁾ while the second component, at 1463 cm^{-1} , may be associated with a vibration [$F_{1g}(3)$], which is silent in the pristine C_{60} and becomes Raman-active in the 2D(T) polymer. The $A_g(2)$ mode, in the 2D(R) polymer, is further downshifted, appearing at ~ 1410 cm^{-1} . Another important difference is the significantly different number of Raman-active modes in the high-pressure phases of these materials as well as the pressure range of the phase transition. In the high-frequency region of the 2D(T) polymer, there appear five distinct Raman peaks with frequencies as high as 1920 cm^{-1} , whereas in the 2D(R) polymer, only two diffuse bands below 1700 cm^{-1} are observed. These differences may be related to the phase transition as well as to the nature of the high-pressure phases, a matter that will be addressed in the next section.

3. Phase Transition and Stability of High-Pressure Phases

The pressure dependence of the Raman modes strongly suggests that both materials undergo phase transitions. In the 2D(T), above 20 GPa, the initial Raman spectrum transforms to a new well-resolved one via an intermediate rather than a diffuse Raman spectrum, which characterizes a disordered pre-transitional state. There are three important observations indicating that this transformation is related to the 3D polymerization, better characterized as a solid-state chemical reaction rather than a structural phase transition. i) The phonon modes of the C_{60} cage seem to be present in the new phase. ii) The rapid quenching of the PP mode observed in the pre-transitional pressure range and the simultaneous changes in the modes related to the stretching vibrations of the double C=C bonds. iii) The Raman peak at 1042 cm^{-1} , which is associated with covalent intermolecular bonds in tetragonal 2D(T) polymer,⁽²²⁾ is split into two components with frequencies of 1026 cm^{-1} and 1060 cm^{-1} in the high-pressure phase. This may be explained by assuming that the high-pressure phase possesses at least two types of sp^3 -like hybridized carbon atoms that form in-plane (2D) and out-of-plane (3D) intermolecular bonds with different bond lengths (1.64 and 1.60 Å,⁽¹³⁾ respectively). The frequency of this band was observed to differ significantly in different polymeric phases, namely, in the orthorhombic and tetragonal phases of C_{60} ,⁽¹⁹⁾ while a double-peak structure was often observed in spectra from mixed phases.

Concerning the most intense Raman peak of the high-pressure phase at ~ 1920 cm^{-1} , it should be noted that this cannot be related to any mode in the fullerene molecular cage. Its appearance may be associated with a considerable distortion of the PP mode of the pristine C_{60} due to the breakdown of a large number of double C=C bonds and the sp^3 -like hybridization of the carbon atoms involved in the intermolecular bonding in the high-pressure phase. The strong Raman peaks with frequencies as high as 2000 cm^{-1} in some chemical compounds of carbon are related to the stretching vibrations of the isolated double C=C bond.⁽²⁴⁾ The existence of this mode in the high-pressure phase is not compatible with the model for 3D polymerization proposed by Burgos *et al.*,⁽¹⁴⁾ as they did not predict any phonon modes above 1600 cm^{-1} . Our experimental results on the transition pressure (~ 20 GPa) agree well with the theoretical prediction of Okada *et al.*⁽¹³⁾

The experimental data strongly indicate that the 2D(R) phase of C_{60} undergoes an irreversible transformation at $P > 15$ GPa. The initial well-resolved Raman spectrum is transformed into a diffuse one that is typical of a disordered phase. The rapid decrease of the $A_g(2)$ mode intensity and the enhancement of the neighboring $H_g(8)$ and $G_g(6)$ modes in the pre-transitional pressure range are reminiscent of the analogous behavior exhibited by these modes in the 2D(T) phase before further polymerization under high pressure.^(21,22) Taking into account the nature of the PP-mode, the decrease of its intensity may be related to the destruction of some of the double C=C bonds and the subsequent creation of covalent bonds between molecules belonging to adjacent planes. Even though pressure preferentially decreases the inter-plane distance in the polymer, C_{60} molecular cages belonging to adjacent polymeric planes of the 2D(R) structure do not have relative orientations that are optimal for the formation of inter-plane covalent bonds. Therefore, we may assume that the new bonds are formed in a random way due to some distortion in the molecular orientation. As a result, the new high-pressure phase exhibits a degree of disorder characterized by a random out-of-plane polymerization.⁽²⁰⁾ Note that this behavior differs significantly from that of the 2D(T), in which the pressure-induced shortening of the intermolecular distances, accompanied by the optimal orientation of molecules, leads to a high degree of regularity in the formation of the out-of-plane covalent bonds. This regularity in the inter-plane bonding is manifested in the Raman spectra of the high-pressure phase of the 2D(T) phase, giving well-resolved and rich Raman spectra.^(21,22)

The recovered samples were examined by means of micro-Raman probing at various sites in order to check their uniformity. The 2D(T) recovered sample was in fact in a metastable phase and after a period of ~3 days was violently broken up (“detonated”) into pieces upon laser irradiation at an intensity of ~0.4 mW at 514.5 nm. The results of the micro-Raman probing of the recovered sample at ambient conditions before and after detonation are presented in Fig. 6, along with the spectrum of the initial 2D phase (a), which is included for comparison. The spectrum in (b) was taken before the sample detonation and is that of the high-pressure phase. The two lower spectra, (c) and (d), taken by micro-probing from several pieces resulting from the detonated sample, are related to a “diamond-like” carbon phase and to a mixture of pristine (monomeric) and dimerized C_{60} phases. The main part of the detonated sample is related to the pristine or partially dimerized C_{60} phase, as seen from its Raman spectrum (d). We note that the existence of this phase in the detonated sample gives definite proof that the C_{60} molecular cages are retained in the high-pressure phase. The “diamond-like” carbon, which is only a small part of the detonated sample, has a strong Raman peak at 1342 cm^{-1} (spectrum c) resembling the “D” (“diamond”) peak of microcrystalline graphite. The second Raman peak of this phase at 1591 cm^{-1} is the “G” (“graphite”) peak of graphite. This “diamond-like” carbon phase was not present in the starting material.

The results of the micro-Raman probing of the recovered 2D(R) sample at ambient conditions are shown in Fig. 7, along with the spectrum of the initial 2D(R) phase (a). The spectra in Fig. 7 are shown for the region of $1350\text{--}1800\text{ cm}^{-1}$, which contains the most intense Raman peaks. Our observations from several pressure runs showed that the recovered sample is in a highly uniform and rather stable phase (b), which does not change at ambient conditions, at least for a period of more than one week. To reveal the possible contribution of the pressure-induced imperfections and the structural defects to the broadening of the

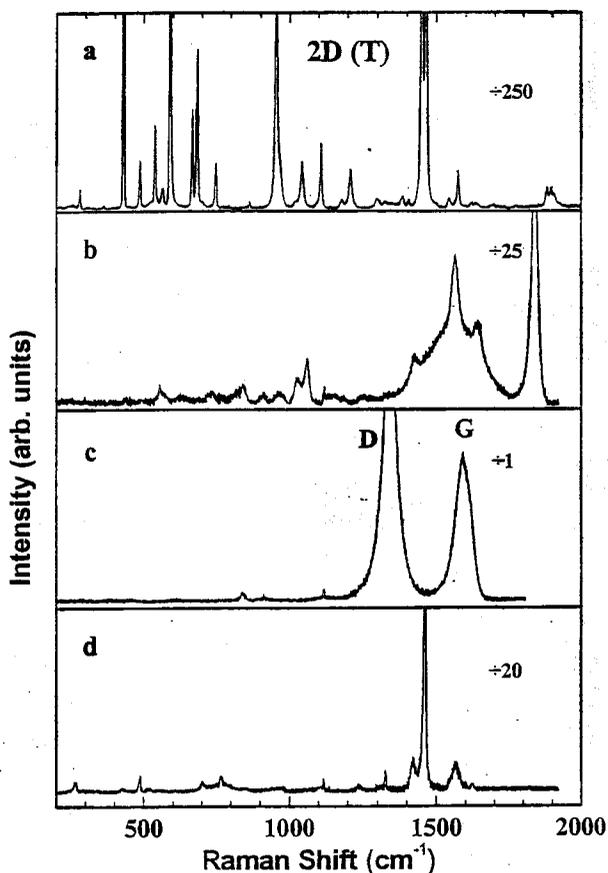


Fig. 6. Raman spectra of the initial 2D(T) polymeric phase of C_{60} and of the recovered sample recorded at ambient conditions by means of micro-Raman probing. (a) The initial 2D(T) polymeric phase. (b) The high-pressure phase of the 2D(T) C_{60} polymer after the pressure cycle. (c) The "diamond-like" carbon phase identified among the pieces of detonated sample. (d) The pristine/dimerized C_{60} phase identified as the main component among the pieces of detonated sample.

Raman bands, we annealed the recovered samples under various temperature conditions. The Raman spectra of the annealed samples showed that the material undergoes some transformation when subjected to a temperature higher than 300°C . The Raman spectrum of the annealed material (c) contains a relatively narrow and intense Raman band near 1464 cm^{-1} , which is related to the PP-mode in the case of a mixture containing monomers and dimers of C_{60} , and is similar to the spectra of various annealed polymeric phases of C_{60} .^(1,21) This means that the fullerene molecular cage is retained in the high-pressure phase of the 2D(R) polymer. Thus, the diffuse Raman spectrum of the high-pressure phase may be related to a disordered polymeric phase of C_{60} characterized by random covalent bonding between molecules belonging to adjacent planes of the initial 2D(R) phase. This conclusion

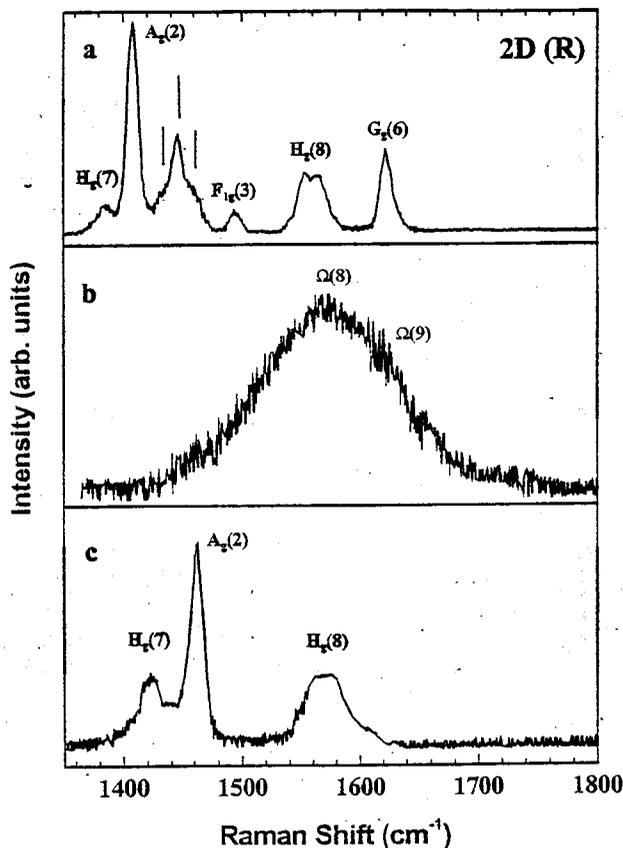


Fig. 7. Raman spectra of the initial 2D(R) polymeric phase of C_{60} and of the recovered sample after pressure release in the frequency region of $1350\text{--}1800\text{ cm}^{-1}$, recorded under ambient conditions. (a) The initial 2D(R) polymeric phase. The vertical lines indicate peaks related to the presence of oligomers in the material. (b) The "high-pressure" phase of the polymer. (c) The Raman spectrum of the "high-pressure" phase after annealing at -600 K and at ambient pressure. The spectrum contains mainly C_{60} monomer and dimer peaks.

is supported by the retention of the C_{60} molecular cage in the high-pressure phase as well as by the similarity of the pre-transitional behavior to that of the 2D(T) phase.

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