

Raman modes of the two-dimensional tetragonal polymeric phase of C₆₀ under high pressure

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The effect of high hydrostatic pressure, up to 12 GPa, on the phonon spectrum and the material stability of the two-dimensional (2D) tetragonal C₆₀ polymer have been studied by means of Raman spectroscopy in the frequency range 100–2000 cm⁻¹. A number of Raman modes appear in the spectrum for pressures above ~1.4 GPa, whose intensities increase with pressure. The pressure coefficients of the majority of the phonon modes change gradually to lower values for pressures around 4.0 GPa. The deformation of the C₆₀ molecular cage along with the change of the material to a more isotropic state (as far as its elastic properties are concerned) resulting from the application of high pressure may be causing the observed effects in the Raman spectra. These effects are reversible upon pressure release and therefore the material is stable in the pressure region investigated. © 2001 American Institute of Physics. [DOI: 10.1063/1.1367388]

I. INTRODUCTION

C₆₀ has been found to polymerize either under illumination with visible or ultraviolet light¹ or upon alkali metal doping.^{2,3} Furthermore, high pressure treatment of C₆₀ at high temperatures also leads to polymerization of the pristine material.⁴ The polymeric forms of C₆₀ consist of molecular units linked by bridging C–C covalent bonds.⁵ The polymerization process involves either [2+2] cycloadditions between double bonds of neighboring C₆₀ molecules or the formation of single C–C bond linkages. The polymeric forms of C₆₀ have attracted considerable attention because of the variety of their crystal structures and optical and mechanical properties.⁶

The structure of the high pressure-high temperature (HPHT) C₆₀ polymers strongly depends on the treatment conditions, i.e., the pressure (*P*) and temperature (*T*). Thus the C₆₀ molecular units form linear chains and/or dimers and higher oligomers at *P* ≤ 1 GPa, two-dimensional polymeric layers at intermediate *P*, and structures based on three-dimensionally (3D) cross-linked molecular cages at higher *P*

and *T*.^{6–8} The two-dimensional (2D) C₆₀ polymers have either a rhombohedral or a tetragonal crystal structure. Although it has been proposed^{6,9,10} that the polymeric tetragonal phase is rather a growth fault of the orthorhombic [one-dimensional (1D) polymer] or the rhombohedral phase, experimental evidence supports the fact that the tetragonal polymeric phase is a stable one.^{11–13} Also, theoretical calculations showed that the tetragonal polymeric phase of C₆₀ is as stable as the rhombohedral one.¹⁴

The perturbations in the structure of the C₆₀ cages, caused by external disturbances like 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 the fullerene materials under pressure.¹⁵ In this work we present a detailed Raman study of the 2D tetragonal polymer of C₆₀ at pressures up to 12 GPa and address the problem of stability of this material and the role of the anisotropic intermolecular interactions in its pressure response.

II. EXPERIMENTAL DETAILS

The samples were prepared from sublimed 99.99% pure C₆₀ powder pressurized in a piston and cylinder device. The

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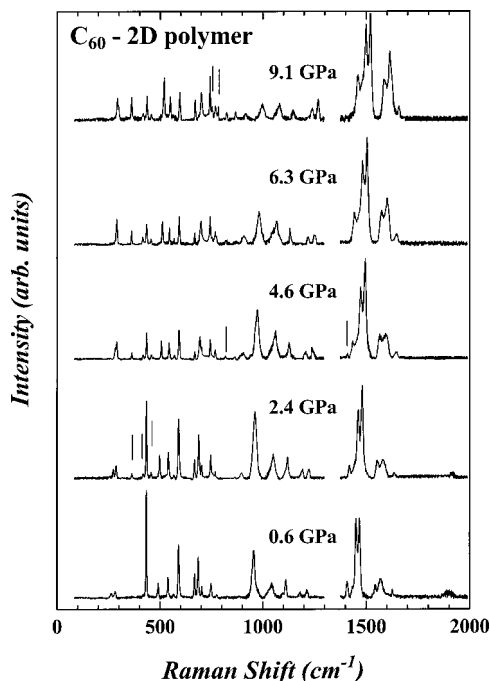


FIG. 1. Raman spectra of the 2D polymeric tetragonal phase of C_{60} at room temperature and various pressures. The vertical lines indicate the new modes appearing at higher pressure.

pristine material was subjected to pressures in the range 2.3–2.5 GPa at a temperature of about 820 K to obtain 2D polymerized C_{60} .^{16,17} X-ray analysis of the samples from the same batch after the high pressure-high temperature treatment confirmed that the crystal structure of the polymer is tetragonal ($a=b=9.082$ Å and $c=14.990$ Å)¹⁷ and is described better in a space group $P4_2mmc$ rather than $Immm$ due to a possible high degree of stacking disorder in the direction perpendicular to the polymeric layers.

Raman spectra were recorded using a triple monochromator (DILOR XY-500) equipped with a charge coupled device liquid-nitrogen cooled detector system. The spectral width of the system was ~ 4 cm^{-1} . The 514.5 nm line of an Ar^+ laser was used for excitation. The laser power was kept lower than 4 mW, measured directly before the cell, in order to avoid depolymerization caused by laser heating effects and related changes in the phonon spectrum and the crystal structure.^{5,18,19} Measurements of the Raman spectra at high pressures were carried out using the diamond anvil cell (DAC) of Mao–Bell type.²⁰ The 4:1 methanol-ethanol mixture as well as pure glycerol were used as pressure transmitting media, giving both equivalent experimental results. The well-known ruby fluorescence technique was used for pressure calibration.²¹ The phonon frequencies were obtained by fitting Voigt peak functions to the experimental peaks after background subtraction.

III. RESULTS AND DISCUSSION

The Raman spectra at various pressures and room temperature of the tetragonal phase of the 2D pressure polymerized C_{60} , in the frequency region 100–2000 cm^{-1} , are illustrated in Fig. 1. At first glance the Raman spectrum of the

TABLE I. Correlation table of the symmetry groups I_h (molecular symmetry in the monomeric C_{60}) and D_{2h} (molecular symmetry in the 2D tetragonal polymeric C_{60}) (Ref. 13).

I_h	D_{2h}	Splitting ($I_h \rightarrow D_{2h}$) (active modes)
A_g	A_g	1 \rightarrow 1
F_{1g}	$B_{1g} + B_{2g} + B_{3g}$	0 \rightarrow 3
F_{2g}	$B_{1g} + B_{2g} + B_{3g}$	0 \rightarrow 3
G_g	$A_g + B_{1g} + B_{2g} + B_{3g}$	0 \rightarrow 4
H_g	$2A_g + B_{1g} + B_{2g} + B_{3g}$	1 \rightarrow 5
A_u	A_u	0 \rightarrow 0
F_{1u}	$B_{1u} + B_{2u} + B_{3u}$	1 \rightarrow 3
F_{2u}	$B_{1u} + B_{2u} + B_{3u}$	0 \rightarrow 3
G_u	$A_u + B_{1u} + B_{2u} + B_{3u}$	0 \rightarrow 3
H_u	$2A_u + B_{1u} + B_{2u} + B_{3u}$	0 \rightarrow 3

polymer appears richer in structure compared to that of pristine C_{60} . This is mainly due to the lowering of the molecular symmetry, from I_h in pristine C_{60} to D_{2h} in the 2D tetragonal polymeric phase, which results in the splitting of the modes according to the compatibility scheme shown in Table I. In addition to the splitting, the lowering of symmetry may also activate modes in the polymer that in pristine C_{60} are inactive. As the 2D polymeric phase retains the inversion center of the monomeric C_{60} , the mutual exclusion rule of Raman and IR modes is still valid, so gerade (*g*) modes will be Raman active while ungerade (*u*) modes IR (infrared) active. Nevertheless, we cannot discard the possibility that imperfections and stresses in the crystal structure of the polymer, as well as natural isotopic ^{13}C substitution, may facilitate the appearance of some *u* modes in the Raman spectrum of the 2D polymer.

The phonon spectrum of the 2D polymer at normal conditions has been already reported²² and compared to that of the 1D polymeric phase. Furthermore, the Raman and IR spectra of the various polymeric phases of C_{60} have been studied extensively by Davydov *et al.*,¹³ where a complete assignment of the observed modes is given. In the present paper, the various modes in the 2D polymer have been assigned in analogy to their counterparts in the parent C_{60} molecule, following in general the same designation as in Davydov *et al.*¹³ We point out that the Raman peaks of the 2D polymer are very narrow (see Fig. 1), a feature which is quite different from other fullerenes. This fact is due, in our opinion, to the homogeneity and high quality of the samples used in the present study. It is also important to emphasize that the Raman peaks remain narrow for pressures up to 12 GPa implying an increased hardness of the 2D polymer, in comparison to that of the pristine C_{60} , where a considerable broadening is observed.²³

As the pressure increases a number of new Raman peaks appear in the spectrum of the 2D polymer (see Fig. 1). Specifically, in the pressure region 1 to 2 GPa three additional modes are observed with frequencies 363, 418, and 455 cm^{-1} and their intensities are increasing gradually with pressure. The 363 and 455 cm^{-1} modes and a mode at ~ 413 cm^{-1} have already been observed in the 2D tetragonal polymeric phase even at ambient pressure.^{10,13,17} In our case we cannot discard the possibility that these peaks might be too

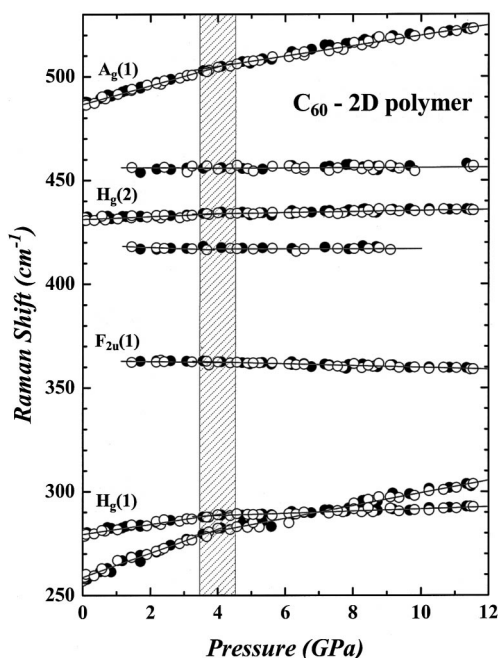


FIG. 2. The pressure dependence of the intramolecular Raman modes of the 2D polymeric tetragonal phase of C_{60} in the frequency region 250–530 cm^{-1} . The open (closed) symbols denote data taken for increasing (decreasing) pressure runs. The shaded area at $P=4.0\pm 0.5$ GPa denotes the change in the slope of the pressure dependence.

weak to be observed at normal pressure. We believe that the appearance of these modes in the Raman spectrum of the 2D polymer and their continuous increase of intensity with pressure can be understood by assuming possible pressure-induced molecular cage deformations. Such an assumption has been already used to explain the Raman spectra of the 1D and the 2D polymers under high pressure.²² This deformation of the C_{60} molecules, starting at relatively low pressures, can be explained by taking into account the high anisotropy in the molecular bonding (covalent bonds along the polymerized planes and van der Waals interactions perpendicular to the planes) of the 2D polymer. Even at ambient pressure this bonding anisotropy leads to the deformation of the C_{60} molecular cages; namely, they are contracted by $\sim 5\%$ with respect to their dimension in pristine C_{60} along the perpendicular to the polymeric planes.²⁴ In the pressure range 4–6 GPa, four additional modes appear in the Raman spectrum of the 2D polymer with frequencies 755, 773, 817, and 1406 cm^{-1} . It is difficult to say if the appearance of these modes is due to higher molecular deformation or to an enhancement in the splitting of the corresponding modes at normal pressure. The appearance of the above mentioned modes, as well as the changes in their intensity, is fully reversible with pressure decrease. This suggests that the intermolecular bonds are stable, at least for pressures up to 12 GPa, and the modes appearing in the spectrum cannot be related to new polymeric bond formation or breaking of the existing ones. This result is also substantiated by the fact that the Raman peaks remain narrow up to 12 GPa.

In Figs. 2–5, the pressure dependence of the intramolecular Raman modes of the 2D tetragonal polymer in the

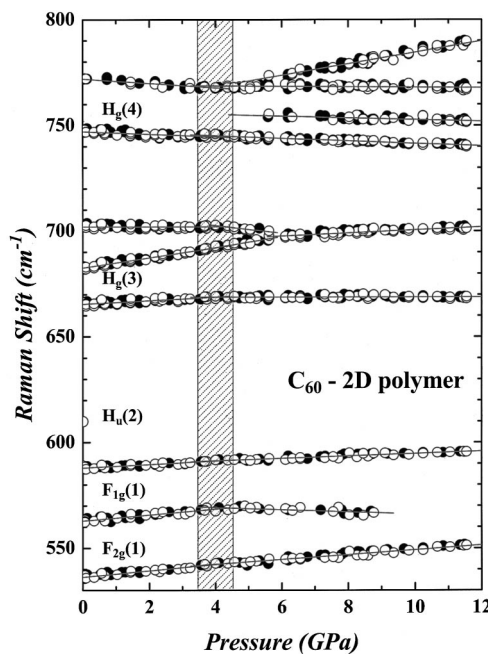


FIG. 3. The pressure dependence of the intramolecular Raman modes of the 2D polymeric tetragonal phase of C_{60} in the frequency region 530–800 cm^{-1} . The open (closed) symbols denote data taken for increasing (decreasing) pressure runs. The shaded area at $P=4.0\pm 0.5$ GPa denotes the change in the slope of the pressure dependence.

frequency region 250–1650 cm^{-1} is shown. In Table II a compilation of the mode assignment, their frequencies, and the corresponding pressure coefficients for the 2D polymer is presented. The mode assignment refers to the irreducible representations of the parent C_{60} molecule in accordance to that

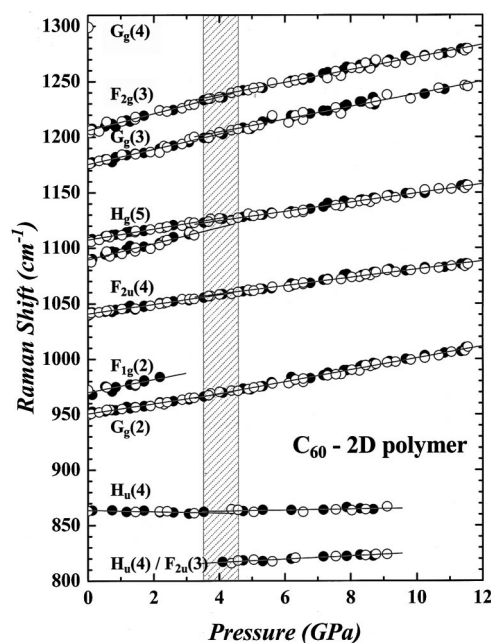


FIG. 4. The pressure dependence of the intramolecular Raman modes of the 2D polymeric tetragonal phase of C_{60} in the frequency region 800–1300 cm^{-1} . The open (closed) symbols denote data taken for increasing (decreasing) pressure runs. The shaded area at $P=4.0\pm 0.5$ GPa denotes the change in the slope of the pressure dependence.

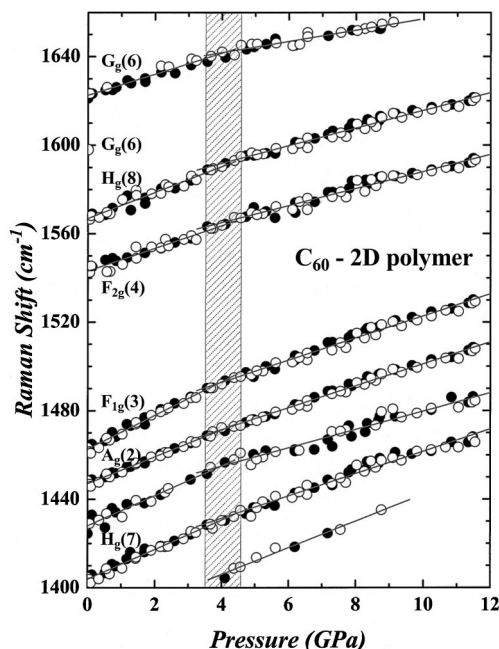


FIG. 5. The pressure dependence of the intramolecular Raman modes of the 2D polymeric tetragonal phase of C_{60} in the frequency region 1400–1660 cm^{-1} . The open (closed) symbols denote data taken for increasing (decreasing) pressure runs. The shaded area at $P=4.0\pm 0.5$ GPa denotes the change in the slope of the pressure dependence.

of Davydov *et al.*¹³ The pressure coefficients, obtained by linear least-squares fit to the experimental data, are given in Table II along with the corresponding values for the pristine C_{60} (Refs. 25 and 26) for comparison.

In the frequency region 250–530 cm^{-1} all the observed modes show positive pressure slopes in analogy to the pristine C_{60} (Ref. 25), except those at 363 and 418 cm^{-1} which show a small negative slope. The pressure response of the two lower energy modes (at 259 and 280 cm^{-1}), possibly originating from the splitting of the $H_g(1)$ mode of the pristine C_{60} , is quite remarkable. The two components show a continuous intensity enhancement and a crossing behavior at $P\approx 7.0$ GPa, indicating that these modes belong to different irreducible representations in the 2D polymer. The $A_g(1)$ (breathing) mode in the 2D polymer is located at 487 cm^{-1} , downshifted by ~ 8 cm^{-1} from the corresponding mode in the pristine C_{60} .²⁵ This downshift of the breathing mode agrees well with the fact that the formation of the intermolecular covalent bonds leads to a lower intramolecular average bond stiffness.⁶ Finally, we note that the modes at 365, 418, and 455 cm^{-1} that appear in the spectrum above 1.4 GPa have pressure slopes close to zero.

The pressure dependence of the observed phonon mode frequencies in the range 530–800 cm^{-1} is shown in Fig. 3. Their parameters are tabulated in Table II. The modes at 666, 683, and 703 cm^{-1} may originate from the splitting of the $H_g(3)$ mode of the C_{60} parent molecule at 710 cm^{-1} . Moreover, the modes at 747 and 772 cm^{-1} may originate from the splitting of the $H_g(4)$ mode of the C_{60} molecule. The two modes at 755 and 773 cm^{-1} , which appear in the spectrum above 5.6 GPa, may originate from further splitting of the close lying $H_g(4)$ mode. Nevertheless, the possibility that

they are connected to the appearance of some stress and/or imperfections activated u modes cannot be excluded as, in this frequency region, a great number of silent IR modes of C_{60} appear. The Raman peaks at 588, 666, and 683 cm^{-1} , which are characteristic of the 2D polymer,²² as well as those at 536 and 563 cm^{-1} , exhibit positive pressure slopes. The $H_g(3)$ at 710 cm^{-1} and the $H_g(4)$ at 772 cm^{-1} intramolecular modes as well as the split component of $H_g(4)$ at 755 cm^{-1} in the pristine C_{60} have negative slopes.²⁵ For the 2D tetragonal polymer the split components of the $H_g(3)$ and $H_g(4)$ modes show similar pressure behavior except those at 666 and 683 cm^{-1} [split components of the $H_g(3)$ mode] and the mode at 773 cm^{-1} [split component of the $H_g(4)$ mode], which appear in the spectrum above 5.6 GPa. Such a difference in their pressure behavior may be explained by assuming that the corresponding components belong to different actual irreducible representations in the 2D tetragonal polymer (see Table I). Finally, the two components of the $H_g(3)$ mode with frequencies 683 and 703 cm^{-1} exhibit a crossing behavior at $P\approx 6.0$ GPa, similar to that observed for the two components originating from the $H_g(1)$ mode (Fig. 2). The above observations concerning the pressure behavior of the modes originating from the splitting of the $H_g(1)$, $H_g(3)$, and $H_g(4)$ modes implies that a $\sim 5\%$ deviation from the quasispherical shape of the pristine C_{60} molecule in the 2D polymer can affect considerably the intramolecular modes.

In the case of the pristine C_{60} (Ref. 23) as well as in the cases of the one-dimensional polymeric CsC_{60} (Ref. 27) and the dimeric $(\text{C}_{59}\text{N})_2$ (azafullerene)²⁸ the modes in the intermediate frequency region 800–1300 cm^{-1} (having a mixed radial and tangential character) were very weak. Therefore it was not easy in the previous studies to follow their pressure evolution. In the 2D tetragonal polymer, because of the considerable initial strength of the Raman active modes in this frequency region, we have been able to follow their pressure dependence up to 12 GPa (Fig. 4) although their intensities decrease quickly with increasing pressure (Fig. 1). All the observed modes in the intermediate frequency region, except the rather weak one at 864 cm^{-1} , exhibit positive pressure slopes. The two components at 1090 and 1107 cm^{-1} , attributed to the splitting of the $H_g(5)$ mode, are merged into one for pressures higher than 4 GPa.

In Fig. 5 we present the pressure dependence of the high frequency region Raman peaks, where the tangential modes of the 2D tetragonal polymer are located. In the frequency region of the $A_g(2)$ [pentagonal pinch (PP)] mode, two peaks appear with frequencies 1447 and 1463 cm^{-1} . The lower energy component has been proposed to be the PP mode in the case of a 2D tetragonal polymer.⁶ This component is ~ 20 cm^{-1} downshifted from that in fullerite C_{60} (Ref. 25) for the same reason as in the case of the $A_g(1)$ mode. The Raman spectrum of the 1D polymer also contains two peaks in the frequency region of the PP mode, one at 1458 cm^{-1} and a second at 1464 cm^{-1} (shoulder-like).²² Sundqvist⁶ has attributed the first component to the PP mode in the case of the 1D polymer, and the second one to the presence of C_{60} dimers by comparing the experimental results to the calculations of Porezag *et al.*²⁹ On the other hand, in the case of the 2D

TABLE II. The phonon frequencies and their pressure coefficients for the 2D tetragonal polymeric phase of C₆₀. The corresponding values for monomeric C₆₀ are also included.

Mode ^a	2D polymer			Monomeric C ₆₀ ^e	
	ω_i cm ⁻¹	$\partial\omega_i/\partial P$ cm ⁻¹ /GPa		ω_i cm ⁻¹	$\partial\omega_i/\partial P$ cm ⁻¹ /GPa
		$P < 4$ GPa	$P > 4$ GPa	$0.4 < P < 2.4$ GPa	
$H_g(1)$	259	5.8	3.1	272	3.2
$H_g(1)$	280	2.3	0.6	294	2.5
$F_{2u}(1)$	363 ^b	-0.2	-0.4	345	2.9
				389	-0.2
$H_g(2)$	418 ^b	-0.1	0.0		
$H_g(2)$	431	0.6	0.3	435	2.4
$H_g(2)$	455 ^b	0.3	0.1	454	1.4
$A_g(1)$	487	4.5	2.5	495	4.2
$F_{2g}(1)$	536	1.4	1.2	522	1.0
$F_{1g}(1)$	563	1.4	-0.5	563	0.8
$F_{1g}(1)$	588	0.8	0.6		
$H_u(2)$	610 ^g			624	1.5
$H_g(3)$	666	0.7	0.0	710	-0.8
$H_g(4)$	747	-0.7	-0.6	729	-2.9
$H_g(4)$	755 ^c		-0.4	755	-4.1
$H_g(4)$	772	-1.2	-0.1	772	-2.7
$H_g(4)$	773 ^c		2.7		
$H_u(4)/F_{2u}(3)$	817 ^d		1.5		
$H_u(4)$	864	-0.6	0.4		
$G_g(2)$	951	4.5	5.4		
$F_{1g}(2)$	970	5.8			
$F_{2u}(4)$	1041	4.2	3.7		
$H_g(5)$	1090	7.2			
$H_g(5)$	1107	4.8	4.2	1100 ^f	
$G_g(3)$	1176	6.7	5.7		
$F_{2g}(3)$	1206	7.6	5.7		
$H_g(6)$				1243 ^f	
$G_g(4)$	1299 ^g				
$H_g(7)$	1406 ^d		6.0		
$H_g(7)$	1404	6.6	5.0		
$H_g(7)$	1428	6.8	4.1	1422	9.8
$A_g(2)$	1447	6.1	4.9	1467	5.5
$F_{1g}(3)$	1463	7.6	5.0		
$F_{2g}(4)$	1543	5.1	3.9		
$H_g(8)$	1567	5.9	4.0	1570	4.8
$G_g(6)$	1598 ^g				
$G_g(6)$	1623	4.7	2.6	1623	5.0
$2G_g(2)$	1888	9.7			
		$P < 4$ GPa	$4 < P < 6$ GPa	$P > 6$ GPa	$0.4 < P < 2.4$ GPa
$H_g(3)$	683	2.3	2.3		
$H_g(3)$	703	-0.2	-1.2	0.7	710
					-0.8

^aThe mode assignment follows that in Ref. 13.^bFrequency value at $P = 1.4$ GPa.^cFrequency value at $P = 5.6$ GPa.^dFrequency value at $P = 4.0$ GPa.^eData taken from Ref. 25.^fData taken from Ref. 26.^gSeen only at normal pressure.

tetragonal polymer a complementary analysis of its Raman and IR spectra shows¹⁷ that the presence of an appreciable amount of dimers in the material is unlikely. This implies that the second component at 1463 cm⁻¹ in the 2D polymer may be associated with a vibration [$F_{1g}(3)$], which is silent in the monomeric C₆₀, and becomes Raman active in the 2D polymer.¹³ All the Raman modes in the high frequency region exhibit positive pressure slopes in analogy to those in the pristine C₆₀.²⁵

In the 2D tetragonal polymer a very high frequency mode at 1888 cm⁻¹ appears in the Raman spectrum (Fig. 1,

its pressure dependence is not shown in Fig. 5). The intensity of this mode decreases very rapidly with pressure and therefore it is difficult to follow its frequency shift for pressures higher than 2.5 GPa. This Raman peak has been attributed²² to a second order Raman scattering from the mode at 951 cm⁻¹, whose intensity also decreases drastically. Besides, the initial pressure slope of the peak at 1888 cm⁻¹ is almost double the slope of the mode at 951 cm⁻¹ (Table II), supporting the previous assumption.

As it can be inferred from Figs. 2–5 and Table II, the majority of the Raman modes show fully reversible changes

of the pressure coefficients to lower values at 4.0 ± 0.5 GPa. In the absence of any experimental or theoretical investigation of the 2D polymeric phase of C_{60} under pressure, the observed changes in the pressure coefficients of the Raman peaks could be understood by considering the existence of two types of bonds in the two-dimensional polymeric C_{60} , the in-plane covalent bonds, and the out-of-plane van der Waals interactions. In the low-pressure regime the out-of-plane intermolecular distances will decrease faster than the in-plane ones, which remain essentially unchanged. This implies that the anisotropic compressibility for low pressure of the 2D polymer becomes more isotropic at higher pressure. Similar reversible changes in the pressure coefficients to lower values have been observed earlier also for the dimeric azafullerene at $P = 6.0 \pm 0.5$ GPa.²⁸ X-ray diffraction measurements under high pressure in $(C_{59}N)_2$ showed that above 6.5 GPa the interdimer distance should be approximately identical to the intradimer one (more isotropic phase).³⁰ In analogy to the case of azafullerene, the observed for several phonon modes in the 2D tetragonal C_{60} polymer reversible changes in the pressure coefficients about 4.0 GPa may be also associated with the change of the material to a more isotropic phase.

IV. CONCLUSION

The anisotropy in the intermolecular bonding in the 2D tetragonal phase of the C_{60} polymer is mainly responsible for the pressure-induced effects observed in its Raman spectrum: (i) Appearance of new peaks and changes of their intensities, probably caused by molecular cage deformations. (ii) Changes of the pressure coefficients of several modes above 4 GPa, attributed to the modification of the material to a more isotropic phase as far as its elastic properties are concerned. As all the above changes observed in the Raman spectra of the material are reversible and the Raman peaks remain narrow in the pressure region investigated (up to 12 GPa), we conclude that the 2D tetragonal polymer is stable in this pressure region.

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