

HIGH PRESSURE STUDY OF THE 2D POLYMERIC PHASE OF C₆₀ BY MEANS OF RAMAN SPECTROSCOPY

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The effect of high hydrostatic pressure, up to 12 GPa, on the intramolecular phonon frequencies and the material stability of the two-dimensional tetragonal C₆₀ polymer has been studied by means of Raman spectroscopy in the spectral range of the radial intramolecular modes (200–800 cm⁻¹). A number of new Raman modes appear in the spectrum for pressures ~ 1.4 and ~ 5.0 GPa. The pressure coefficients for the majority of the phonon modes exhibit changes to lower values at $P=4.0$ GPa, which may be related to a structural modification of the 2D polymer to a more isotropic phase. The peculiarities observed in the Raman spectra are reversible and the material is stable in the pressure region investigated.

Keywords: Fullerenes; 2D tetragonal polymer; Raman spectroscopy; high pressure

1. INTRODUCTION

The polymerized C₆₀ materials have attracted considerable attention during the last few years due to the variety of their structures and their

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interesting optical and mechanical properties [1]. C_{60} has been found to polymerize under light illumination [2] and upon alkali metal doping [3,4]. In addition, high-pressure treatment of C_{60} at high temperatures leads to polymerization of the pristine material [5]. The polymerized forms of C_{60} comprise of molecular units linked by C—C covalent bonds [6]. The polymerization process involves either [2 + 2] cycloadditions between double bonds of neighboring C_{60} molecules or the formation of single C—C bond links.

The Raman studies of fullerenes under external perturbations, like temperature and pressure, or doping have yielded a wealth of information on phase transitions and irreversible chemical transformations induced by them [7–9]. In this work we present a high pressure Raman study of the two-dimensional (2D) tetragonal C_{60} polymer in the frequency range 200–800 cm^{-1} . The pressure response of the phonon spectrum allows us to investigate the stability of the material and the role of the anisotropic intermolecular interactions upon pressure application.

2. EXPERIMENTS

The samples were prepared from sublimed 99.99% pure C_{60} powder pressurized in a piston and cylinder device. The 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} . According to X-ray analysis of the samples after the high-pressure treatment the crystal structure of the polymer is tetragonal [10].

Raman spectra were recorded using a triple monochromator (DILOR XY-500) equipped with a CCD liquid-nitrogen cooled detector system. The spectral width of the system was $\sim 5 \text{ cm}^{-1}$. The 514.5 nm line of an Ar^+ laser was used for excitation. The laser power kept lower than 4 mW, measured directly before the cell, in order to avoid de-polymerization caused by laser heating effects and related changes in the phonon spectrum and the crystal structure [6,11]. Measurements of the Raman spectra at high pressures were carried out using the diamond anvil cell (DAC) of Mao-Bell type [12]. The 4:1 methanol–ethanol mixture as well as pure glycerol were used as pressure transmitting media and the well-known ruby fluorescence technique was used for pressure calibration [13].

3. RESULTS AND DISCUSSION

The spectrum of the polymer at normal conditions is more complicated than that of the pristine C₆₀ because of the splitting of the Raman active fivefold degenerate H_g modes. In addition, the lowering of the molecular symmetry may result in the appearance of new peaks in the spectra of the polymer which are not Raman active in pristine C₆₀. The phonon frequencies of the 2D polymer, at normal conditions, obtained by using the same experimental setup, were reported earlier [14]. In this work, we follow the assignment given in Ref. [14], in which for simplicity the irreducible representations H_g and A_g of the C₆₀ molecular vibrations are used for characterization of the appropriate modes of the polymer. It must be emphasized that the Raman peaks of the 2D polymer under study are very narrow, a feature which is quite different from other polymeric fullerenes. This fact is related, in our opinion, to the higher homogeneity of the 2D polymerization along with the high quality of the samples used. It is also important to note that the Raman peaks remain narrow for pressures up to 12 GPa showing the high hardness of the 2D polymer, in comparison with the pristine C₆₀ [7].

The pressure dependence of the observed phonon mode frequencies is shown in Figures 1 and 2. The open (solid) symbols denote data taken for increasing (decreasing) pressure cycles. The peak positions were determined by fitting of Voigtian line shapes to the experimental data. A number of new modes appear in the spectrum under high pressure. Three of them at frequencies 363, 418 and 455 cm⁻¹ appear for pressures higher than 1.4 GPa and their intensities continuously increase with pressure. It is important to note that even at ambient pressure the first peak, and possibly the others, have been observed by Davydov *et al.* [15]. The mode at 363 cm⁻¹ may be related to that at 344 cm⁻¹ observed in the 1D polymer, which has been proposed to be the Raman signature of the linear chains constructed from covalently bonded C₆₀ molecules [16]. The appearance of the new modes in the 2D polymer and the enhancement of their intensities under pressure may be associated with deformations in the C₆₀ molecular cages [14]. Another reason for appearance of new modes is the pressure-induced enhancement of the initially small mode splitting, resulting from symmetry lowering. For pressures higher than 5 GPa two additional modes appear at frequencies 755 and 768 cm⁻¹. It is difficult to say if

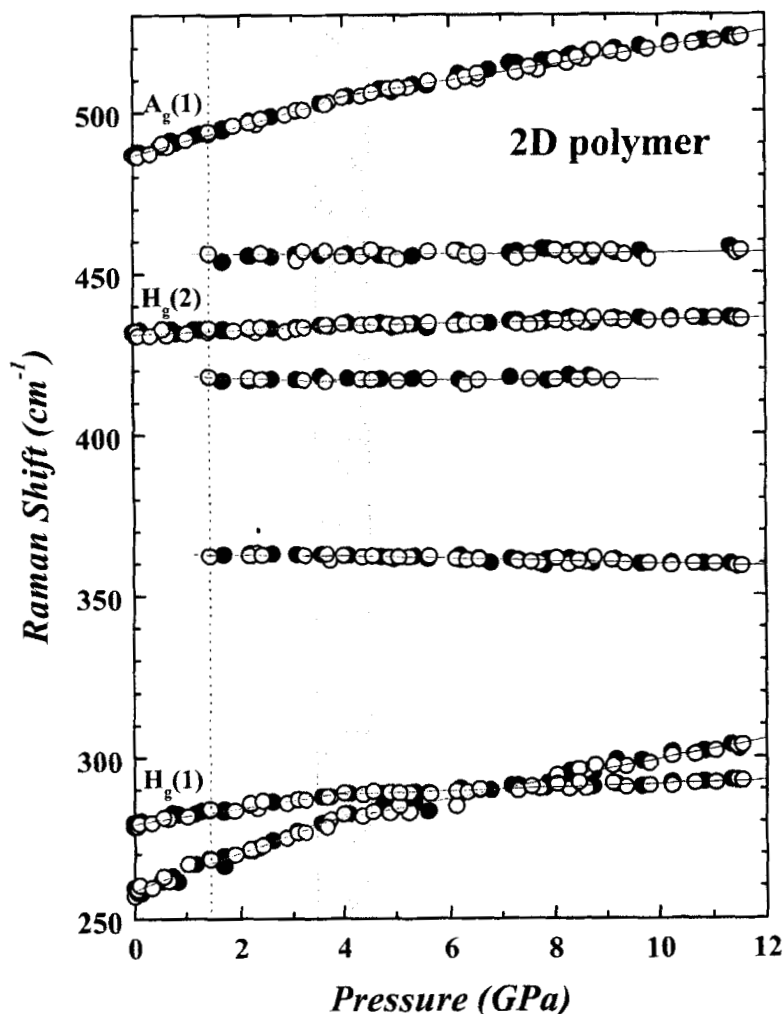


FIGURE 1 The pressure dependence of the intramolecular Raman modes of the 2D polymer in the frequency region $250-530\text{ cm}^{-1}$. The open (solid) symbols denote data taken for increasing (decreasing) pressure runs. The dashed line denotes the pressure where new peaks appear while the shaded area at $P=4.0 \pm 0.5\text{ GPa}$ denotes the change in the slope of the pressure dependence.

this further splitting is due to molecular cage deformation or to an enhancement in the splitting of the $H_g(4)$ mode. All the above changes in the Raman spectrum of the 2D polymer under high pressure are

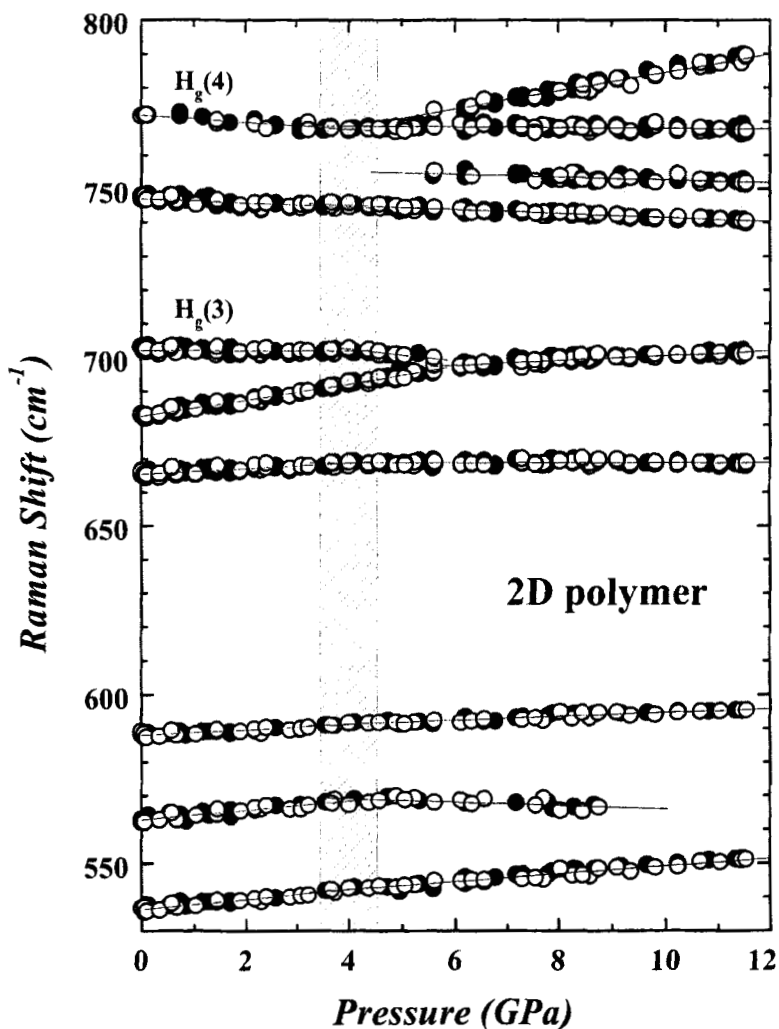


FIGURE 2 The pressure dependence of the intramolecular Raman modes of the 2D polymer in the frequency region 530–800 cm⁻¹. The open (solid) symbols denote data taken for increasing (decreasing) pressure runs. Shaded area at $P = 4.0 \pm 0.5$ GPa denotes the change in the slope of the pressure dependence.

reversible upon pressure release. This means that the intermolecular bonds are stable, at least for pressures up to 12 GPa, and the appearance of new modes cannot be related to polymeric bond breaking.

The modes $A_g(1)$ and $H_g(1) - H_g(4)$, according to Refs. [14] and [16], are related to the intramolecular modes of pristine C_{60} whereas other modes are associated with molecular symmetry lowering and splitting of degenerate modes. We have been able to follow the pressure evolution of all the individual components because they exhibit very narrow line-shapes. With increasing pressure, most of them exhibit positive pressure slopes except those in the frequency region $700 - 800 \text{ cm}^{-1}$, which soften as in the case of the pristine C_{60} [7].

The pressure response of the two components belonging to the $H_g(1)$ mode is very impressive. These components show continuous intensity enhancement and their crossing at $P \approx 7.0 \text{ GPa}$, is an indication that they belong to different symmetry species in the polymer. In addition, the modes at 666 , 683 and 703 cm^{-1} , which possibly result from the splitting of the $H_g(3)$ mode of the pristine C_{60} , show different sign in their pressure response compared to their parent mode. It is known from X-ray diffraction measurements that in the 2D polymer the molecular dimensions decrease by $\sim 5\%$ in the direction perpendicular to the polymerization planes [17]. The above observations concerning the different pressure behavior of the split components show that this 5% deviation from the initially quasi-spherical shape of the pristine C_{60} molecule can affect considerably the intramolecular modes.

As can be seen from Figures 1 and 2, the majority of the Raman modes show, at 4.0 GPa , reversible changes in the pressure coefficients to lower values. The two-dimensional polymerization of C_{60} results in different nature of the in-plane (covalent) and out-of-plane (van der Waals) intermolecular bonds. In the low-pressure limit the out-of-plane intermolecular distances will decrease faster than the in-plane ones, which remain essentially unchanged. This implies that the compressibility of the 2D polymer is rather anisotropic up to some pressure range, above this range, where the out of plane and the in plane intermolecular distances become comparable, the material becomes more isotropic. Similar behavior was observed earlier in the case of the linear polymerized CsC_{60} [18]. The reversible changes in the pressure coefficients of the phonon modes in the vicinity of 4.0 GPa may be attributed to the fact the material is approaching a more isotropic phase as far as its compressibility is concerned.

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