

# Phase transitions in hydrofullerene C<sub>60</sub>H<sub>36</sub> studied by luminescence and Raman spectroscopy at pressure up to 12 GPa

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The effect of hydrostatic pressure on the photoluminescence and Raman spectra of hydrofullerene C<sub>60</sub>H<sub>36</sub> has been investigated for pressure up to 12 GPa at room temperature. The samples were synthesized by means of high-pressure hydrogenation. The pressure coefficients of the phonon modes are positive and demonstrate singularities at  $\sim 0.7$  and  $\sim 6$  GPa. The pressure shift of the luminescence spectrum is unusually small and increases somehow at  $P \geq 6$  GPa. All observed features are reversible with pressure and C<sub>60</sub>H<sub>36</sub> is stable in the pressure region investigated. This work was supported, in part, by the Russian Foundation for Fundamental Research (grants N 99-02-17555 and 99-02-17299), and the Russian Research and Development Program "Fullerenes and Atomic Clusters" (grant N 98079). The support by the General Secretariat for Research and Technology, Greece (grant N ПЕНΕΔ99, 99ΕΔ/62) is acknowledged.

Hydrofullerenes have been predicted theoretically [1] and synthesized by the use of various methods [2,3]. The stable hydrofullerene C<sub>60</sub>H<sub>36</sub> has been studied extensively to identify its molecular structure and properties [4,5]. It was found that the C<sub>60</sub>H<sub>36</sub> molecule has a great number of isomers, and the most stable of them have  $T_h$ ,  $D_{3d}$ ,  $S_6$  and  $T$  symmetry. The presence of various isomers in C<sub>60</sub>H<sub>36</sub> samples depends mostly on the preparation method [4,6,7]. The condensed phase of C<sub>60</sub>H<sub>36</sub> has the body-centered cubic (*bcc*) structure (cell constant 11.78(5) Å), which is expected to transform to a body-centred tetragonal (*bct*) one at low temperatures [5]. In the present paper, we report the results of the pressure behavior of Raman and photoluminescence spectra of C<sub>60</sub>H<sub>36</sub> prepared by high-pressure hydrogenation. Our motivation was to study the effect of pressure on the energy spectrum, phase transitions and stability of the C<sub>60</sub>H<sub>36</sub> molecule at high pressure.

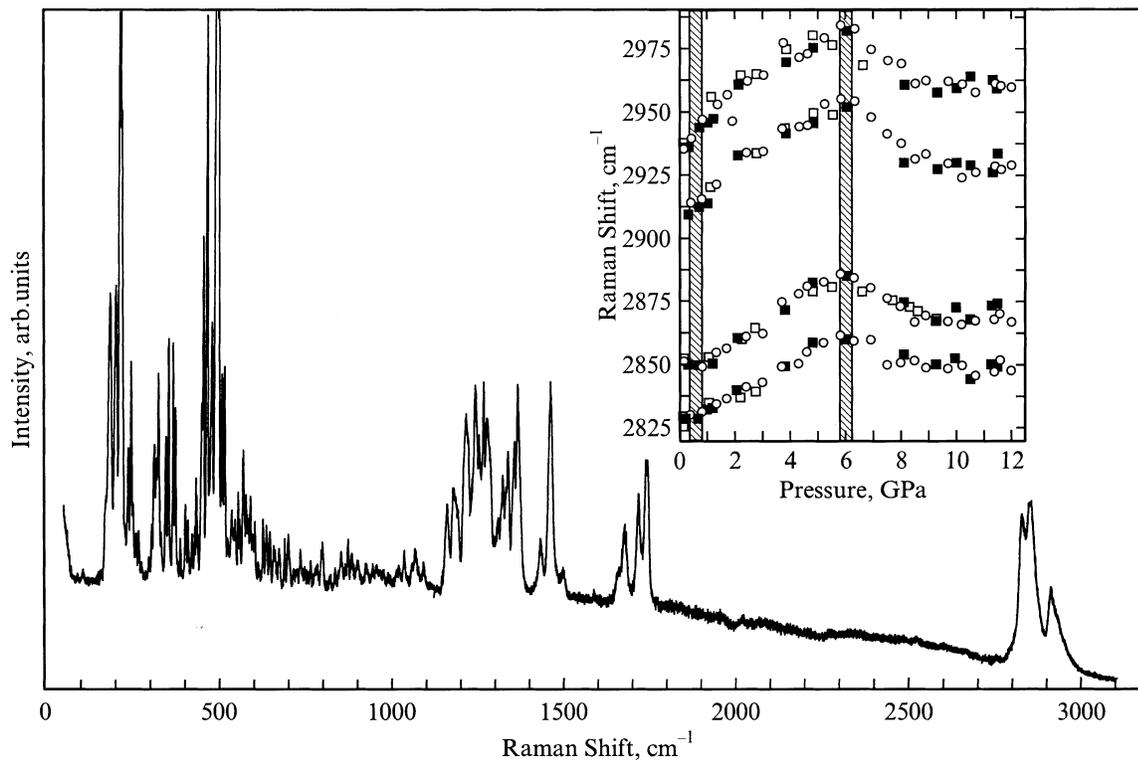
## 1. Experimental

For the preparation of hydrofullerene, pellets of C<sub>60</sub> (99.99% purity) were placed into a copper capsule, covered with a disc of 0.01-mm thick Pd foil, and then annealed in vacuum at 620 K. The remaining space was filled with AlH<sub>3</sub> and the capsule was tightly plugged with a copper lid using gallium as solder. Since Cu and Ga are highly impermeable to hydrogen, the encapsulation described prevents effectively hydrogen losses during the treatment. The assembled capsule was pressurized to 3 GPa in a torroid-type cell and maintained at 700 K for a time up to 48 hours. AlH<sub>3</sub> decomposes above 400 K and the evolved hydrogen reacts with C<sub>60</sub>. The mass-spectroscopy data show that at least 95% of final material is related to C<sub>60</sub>H<sub>36</sub>, while the X-ray study shows that the material is in the *bcc* structure with lattice parameter 11.83 Å. For the optical study at high pressure, colorless transparent specimens of C<sub>60</sub>H<sub>36</sub> were

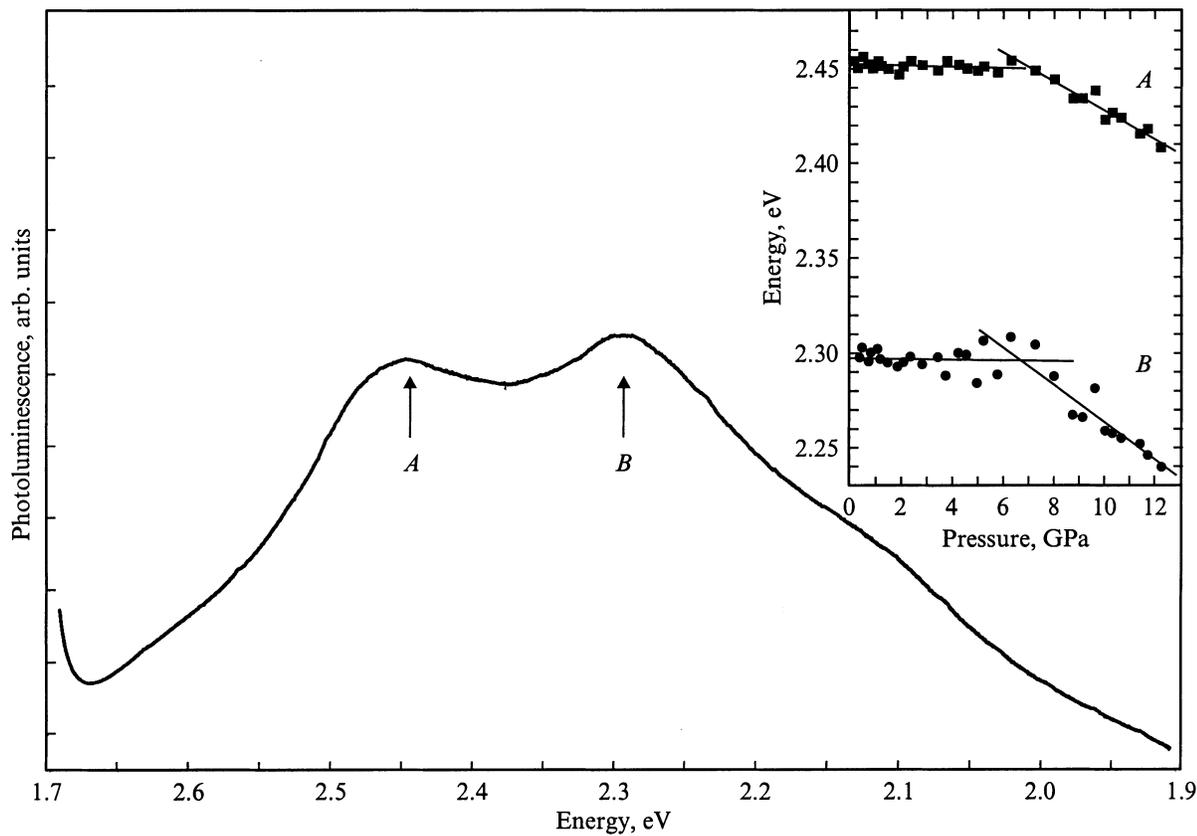
placed into the diamond anvil cell. Photoluminescence and Raman spectra were recorded using single and triple monochromators, JOBIN YVON THR-1000 and DILOR XY-500, respectively, both equipped with a CCD liquid-nitrogen cooled detector system. The 676.4 and 457.9 nm lines of Kr<sup>+</sup> and Ar<sup>+</sup> lasers were used for excitation of Raman and luminescence spectra. The laser power was varied from 2 to 10 mW measured directly in front of the cell. The 4:1 methanol-ethanol mixture was used as pressure transmitting medium and the ruby fluorescence technique was used for pressure calibration.

## 2. Results and discussion

The Raman spectrum of C<sub>60</sub>H<sub>36</sub> at normal conditions is shown in Fig. 1. The spectrum is considerably richer than that of the pristine C<sub>60</sub> and contains very sharp and intense peaks in the low frequency region, while in the high frequency region becomes rather broad and weak. This rich spectrum is related to the hydrogenation of the C<sub>60</sub> molecule, which results in the lowering of the molecular symmetry and the formation of new C–H-bonds. Except for the C–H stretching modes near  $\sim 2800$  cm<sup>-1</sup>, there appear also new modes related to the C–H bending vibrations in the region 1150–1350 cm<sup>-1</sup> [7]. The expected number of Raman active modes of the C<sub>60</sub>H<sub>36</sub> molecule depends on the symmetry and is equal to 118, 60, 73 and 95 for the  $T$ ,  $T_h$ ,  $D_{3d}$ , and  $S_6$  isomers, respectively. The recorded number of peaks in the Raman spectrum of C<sub>60</sub>H<sub>36</sub> is at least 126, which means that the samples under investigation are a mixture of at least two major isomers. A detailed study of the recorded Raman frequencies and comparison with molecular dynamics calculations [4], indicate that the samples contain all five stable isomers with most abundant those with symmetry  $D_{3d}$  and  $S_6$  [7]. The application of pressure strongly affects the Raman spectrum resulting



**Figure 1.** Raman spectra of  $C_{60}H_{36}$  recorded at normal conditions. Insert: the pressure behavior of the C–H stretching modes. The shadowed areas near 0.7 and 6 GPa indicate possible phase transitions. Open and closed symbols are related to the increase and decrease of pressure, respectively.



**Figure 2.** Photoluminescence spectrum of  $C_{60}H_{36}$  recorded at normal conditions. Insert: the pressure dependence of the positions of the main luminescence peaks.

in a positive shift of the Raman peaks and a relative increase in their widths. The pressure behavior of almost all Raman modes shows two singularities near  $\sim 0.7$  and  $\sim 6$  GPa related to the change in the slope of the pressure dependence. However, the situation is essentially different for the C–H stretching vibrations, whose behavior is shown in the insert of Fig. 1. These modes exhibit positive shift up to  $\sim 6$  GPa, which is changed to negative at higher pressure. The softening of the C–H stretching modes at high pressure may be associated with hydrogen bonding interaction between the hydrogen and carbon atoms of the adjacent molecules resulting in the pressure-induced enlargement of the C–H bond length [8].

The photoluminescence spectrum of C<sub>60</sub>H<sub>36</sub>, at normal conditions, is depicted in Fig. 2. The intensity of the luminescence and the onset of the spectrum are higher than that of the pristine C<sub>60</sub> [9]. The pressure behavior of the luminescence spectrum of C<sub>60</sub>H<sub>36</sub> is shown in the insert of Fig. 2. The pressure coefficients for the main luminescence peaks, *A* and *B*, are negative and close to zero at pressure up to  $\sim 6.5$  GPa, but they increase, in absolute value, at higher pressure to  $-7.5$  and  $-9$  meV/GPa, respectively. The pressure behavior of C<sub>60</sub>H<sub>36</sub> is not typical for molecular crystals whose electronic states have usually a large negative pressure shift, which rapidly decreases with pressure [10]. It is known also that the pressure-induced shift of electronic states in molecular crystals may be positive for molecules, which do not have the centre of symmetry [11]. Taking into account that the samples contain *T* isomer in abundance, which does not have the centre of symmetry, the pressure behavior up to 6.5 GPa may be associated with mutual compensation of the opposite shifts of the luminescence spectra, originating from electronic states of various isomers. At higher pressure, however, luminescence related to other isomers which have center of symmetry dominates, their electronic states are downshifted in energies and therefore we have an overall negative pressure shift.

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