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Phase Transitions in Hydrofullerene $C_{60}H_{36}$ Studied by Luminescence and Raman Spectroscopy at Pressures up to 12 GPa¹

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Abstract—The effect of hydrostatic pressure on the photoluminescence and Raman spectra of hydrofullerene $C_{60}H_{36}$ was investigated for pressures up to 12 GPa at room temperature. The samples were synthesized by means of high-pressure hydrogenation. The pressure coefficients of the phonon modes were found to be positive and demonstrate singularities at ~ 0.7 and ~ 6 GPa. The pressure shift of the luminescence spectrum is unusually small and increases slightly at $P \geq 6$ GPa. All observed features are reversible with pressure, and $C_{60}H_{36}$ is stable in the pressure region investigated. © 2002 MAIK “Nauka/Interperiodica”.

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

1. EXPERIMENTAL

For the preparation of hydrofullerene, pellets of C_{60} (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_3 , and the capsule was tightly plugged with a copper lid using gallium as a soldering agent. Since Cu and Ga are highly impermeable to hydrogen, the encapsulation described prevents hydrogen losses effectively during treatment. The assembled capsule

was pressurized to 3 GPa in a toroid-shaped cell and maintained at 700 K for a time of up to 48 h. Above 400 K, AlH_3 decomposes and the evolved hydrogen reacts with C_{60} . The mass-spectroscopy data show that at least 95% of the final material is related to $C_{60}H_{36}$, while the x-ray study shows that the material has a bcc structure with a lattice parameter of 11.83 Å. For optical study at high pressure, colorless transparent specimens of $C_{60}H_{36}$ were placed into a diamond anvil cell. Photoluminescence and Raman spectra were recorded using a single (JOBIN YVON THR-1000) and a triple (DILOR XY-500) monochromator, both equipped with a CCD liquid-nitrogen cooled detector system. The 676.4 and 457.9 nm lines of Kr^+ and Ar^+ laser radiation, respectively, were used for excitation of the Raman and luminescence spectra. The laser power was varied from 2 to 10 mW when measured directly in front of the cell. A 4 : 1 methanol-ethanol mixture was used as the pressure-transmitting medium, and the ruby fluorescence technique was used for pressure calibration.

2. RESULTS AND DISCUSSION

The Raman spectrum of $C_{60}H_{36}$ under normal conditions is shown in Fig. 1. The spectrum is considerably richer than that of the pristine C_{60} and contains very sharp and intense peaks in the low-frequency region, while in the high-frequency region, its features are rather broad and faint. This rich spectrum is related to the hydrogenation of the C_{60} molecule, which results in the lowering of the molecular symmetry and the formation of new C–H bonds. In addition to the C–H stretch-

¹ This article was submitted by the authors in English.

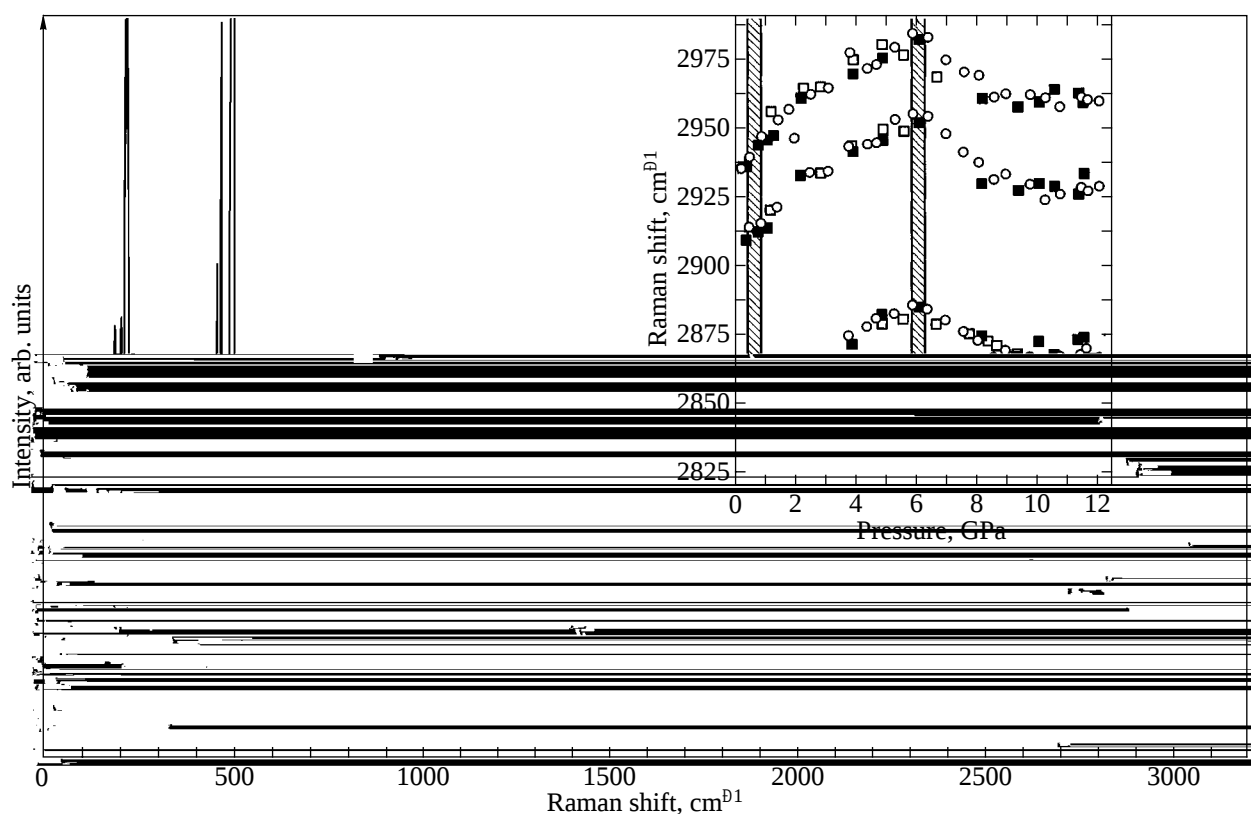


Fig. 1. Raman spectra of $C_{60}H_{36}$ recorded under normal conditions. Insert: the pressure behavior of the C–H stretching modes. The shaded areas near 0.7 and 6 GPa indicate possible phase transitions. Open and shaded symbols are related to an increase and decrease in pressure, respectively.

ing modes near $\sim 2800\text{ cm}^{-1}$, new modes related to C–H bending vibrations appear in the region $1150\text{--}1350\text{ cm}^{-1}$ [7]. The expected number of Raman active modes of the $C_{60}H_{36}$ 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 number of recorded peaks in the Raman spectrum of $C_{60}H_{36}$ is at least 126, which means that the samples under investigation are a mixture of at least two basic isomers. A detailed study of the recorded Raman frequencies and a comparison with molecular dynamics calculations [4] indicate that the samples contain all five stable isomers, the most abundant among them being those with D_{3d} and S_6 symmetry [7]. The application of pressure strongly affects the Raman spectrum, resulting in a positive shift of the Raman peaks and a relative increase in their widths. The pressure dependence of almost all Raman modes shows two features (changes in the slope) near 0.7 and 6 GPa. However, the situation is essentially different for the C–H stretching vibration modes, whose behavior is shown in the inset to Fig. 1. These modes exhibit a positive shift up to ~ 6 GPa that changes into a negative one at higher pressures. The softening of the C–H stretching modes at high pressures may be associated with hydrogen bonding interaction between the hydrogen and car-

bon atoms of the adjacent molecules, resulting in a pressure-induced enlargement of the C–H bond length [8].

The photoluminescence spectrum of $C_{60}H_{36}$ under normal conditions is depicted in Fig. 2. The intensity of the luminescence and the threshold for the onset of the spectrum are higher than those for the pristine C_{60} [9]. The pressure behavior of the luminescence spectrum of $C_{60}H_{36}$ is shown in the inset to Fig. 2. The pressure coefficients for the main luminescence peaks, A and B, are negative and close to zero at pressures up to ~ 6.5 GPa; at higher pressures, they increase in absolute value to -7.5 and -9 meV/GPa , respectively. The pressure behavior of $C_{60}H_{36}$ is not typical of molecular crystals, whose electronic states usually exhibit a large negative pressure shift which rapidly decreases with pressure [10]. It is also known that the pressure-induced shift of electronic states in molecular crystals may be positive for molecules that have no center of symmetry [11]. Taking into account that our samples contain the (noncentrosymmetric) T isomer in abundance, the pressure behavior up to 6.5 GPa may be associated with mutual compensation of the opposite shifts of the luminescence spectra, originating from the electronic states of various isomers. At higher pressures, however, lumi-

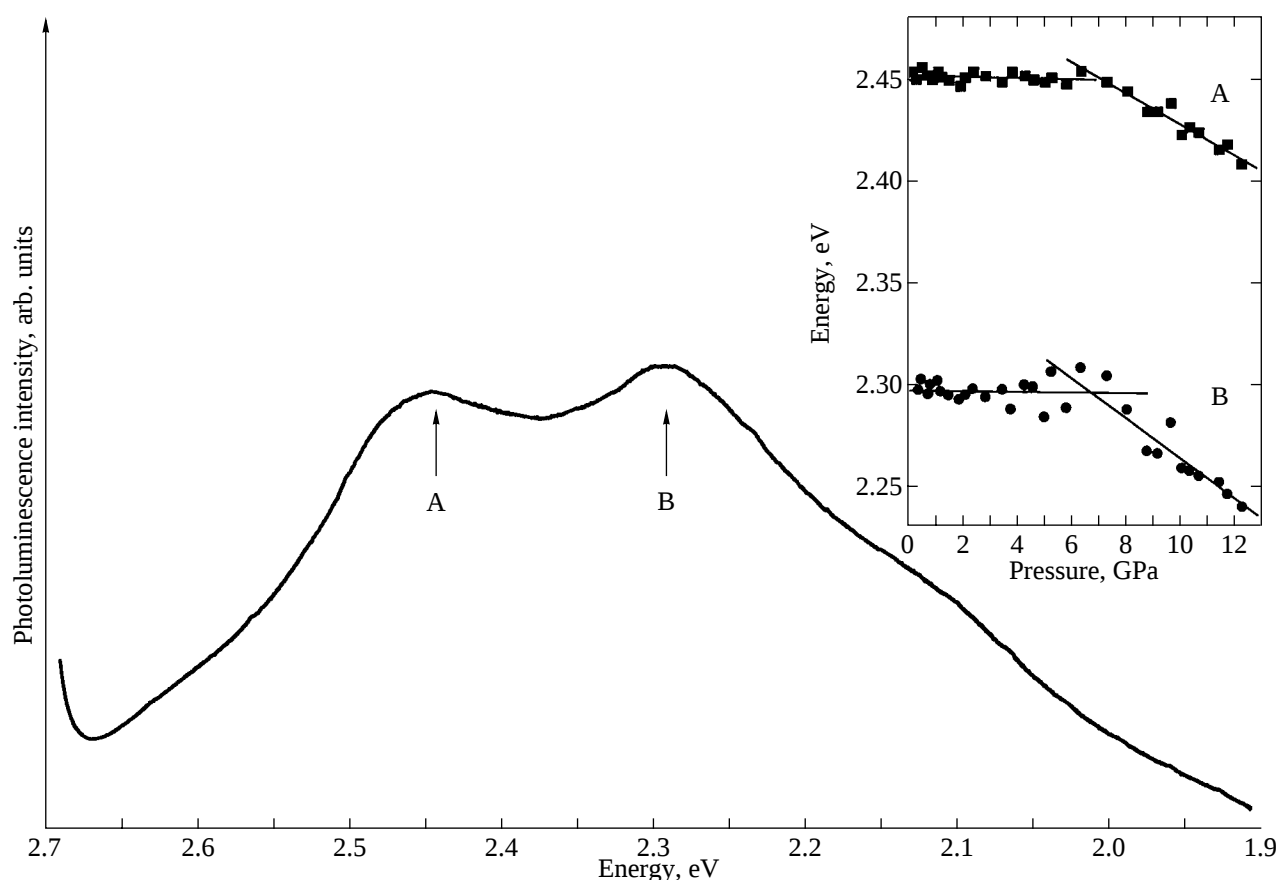


Fig. 2. Photoluminescence spectrum of $C_{60}H_{36}$ recorded under normal conditions. Insert: the pressure dependence of the positions of the main luminescence peaks.

nescence from other isomers (which have a center of symmetry) dominates; their electronic states are downshifted in energy, and, therefore, we have an overall negative pressure shift.

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