

Pressure studies on fullerene peapods

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We carried out pressure-dependent transmission measurements on single-walled carbon nanotubes (SWCNTs) filled with C₆₀ molecules, so-called C₆₀ peapods, in the near-infrared and visible frequency range, where the optical transitions between the Van Hove singularities of the carbon nanotubes are excited.

The pressure-induced shifts of the optical transitions exhibit an anomaly associated with the deformation of the carbon nanotubes. The results are compared with those for empty SWCNTs. Furthermore, the importance of the pressure transmitting medium used in the measurements is discussed.

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1 Introduction A large number of recent studies demonstrated that the structural properties of single-walled carbon nanotubes (SWCNTs) can be tuned by applying external pressure [1–12]: they undergo severe structural deformation above a critical pressure p_c , namely a reversible change from the circular cross-section to an oval or elliptical shape [1–4, 6, 7]. The value of p_c decreases with increasing carbon nanotube diameter and follows the relation $p_c \propto 1/d^3$ for both individual SWCNTs [1, 5, 6, 8] and bundled SWCNTs [1, 5–7]. The pressure-induced effects on the electronic band structure of carbon nanotubes were predicted theoretically. For moderate pressures a significant $\sigma^*-\pi^*$ hybridization and symmetry-breaking effects are induced, which lower the conduction band and hence cause a shift of the optical transitions between the Van Hove singularities in the density of states to lower energies [13, 14].

The optical transitions between the Van Hove singularities in the density of states of carbon nanotubes can be probed by transmission measurements in the infrared and visible frequency range. Recent detailed transmission studies on SWCNTs under pressure indeed revealed the predicted phenomena, namely the pressure-induced shift of the optical transitions to lower energies and an anomaly in the redshift at the critical pressure p_c for the deformation of the nanotubes [15], and furthermore elucidate the role of the pressure transmitting medium for the results [16–18].

There are only a few pressure studies on C₆₀ peapods by X-ray diffraction or Raman spectroscopy, and they mainly focus on the polymerization of the fullerene molecules inside the nanotubes [19–22]. Naively, one would expect an

alteration of the pressure-induced effects due to the filling of the carbon nanotubes with molecules. A recent Raman spectroscopy study on C₇₀ peapods found an anomaly in the linewidth of the radial breathing mode of the nanotubes at 2–2.5 GPa, in agreement with the predicted value of p_c for unfilled SWCNTs for the same diameter range [23]. The data furthermore suggest the onset of the interaction between the fullerenes and the tube walls at ~ 3.5 GPa and a second phase transitions at pressures between 10 and 30 GPa [23].

In order to further clarify the influence of the molecular filling on the pressure-induced effects on the carbon nanotube cage, we carried out transmission studies on C₆₀ peapods as a function of external pressure. Here, we focus on the near-infrared and visible energy range, where the electronic excitations between the Van Hove singularities are probed, thus giving insight into the effects of pressure on the nanotubes' band structure.

2 Experimental Peapods were prepared from arc discharge SWCNTs type P2 with an average diameter of 1.4 nm, purchased from Carbon Solutions Inc. [24]. For the filling, C₆₀ 99.5+% purity from NANOS Research was used. The SWCNTs were opened by annealing in air at 570 °C for 20 min. The filling was performed by annealing the opened SWCNTs with C₆₀ in vacuum in a quartz tube. The excess of C₆₀ from the outer surface of the tubes was removed by sonication in toluene in an ultrasonic bath [24].

Transmission measurements in the near-infrared and visible frequency range (3500–20 000 cm⁻¹) were carried out with a Bruker IFS 66 v/S Fourier transform

infrared spectrometer coupled with a Bruker IR Scope II infrared microscope. Pressures up to ~ 8 GPa were generated by using a diamond anvil cell (Cryo DAC Mega from Diacell) equipped with type IIA diamonds. Argon, CsI, and 4:1 methanol–ethanol alcohol mixture served as quasi-hydrostatic pressure transmitting media. The ruby luminescence method was used for pressure determination. The intensity $I_{\text{sample}}(\omega)$ of the radiation transmitted through the sample placed in the DAC and the intensity $I_{\text{ref}}(\omega)$ of the radiation transmitted through the pressure transmitting medium in the DAC were measured. From $I_{\text{sample}}(\omega)$ and $I_{\text{ref}}(\omega)$ the transmittance and absorbance spectra were calculated according to $T(\omega) = I_{\text{sample}}(\omega)/I_{\text{ref}}(\omega)$ and $A(\omega) = -\log_{10} T(\omega)$, respectively. A linear background due to $\pi-\pi^*$ absorption has been subtracted prior to the analysis of the data, as described in Ref. [15].

3 Results and discussion The absorbance spectrum of a free-standing film of SWCNTs and that of SWCNTs from the same batch but filled with C_{60} molecules are shown in Fig. 1. In both cases the absorbance spectrum consists of pronounced absorption bands due to optical transitions between pairs of Van Hove singularities in semiconducting and metallic SWCNTs, labeled S_{ii} and M_{ii} , respectively, where the indices ii indicate the energy sequence of the involved Van Hove singularities. For a quantitative analysis the absorption bands were fitted with several Lorentz functions, and the so-obtained energies of the terms are listed in Table 1. At ambient conditions we consistently find for both the SWCNTs and the C_{60} peapods two and four strong contributions to the S_{11} and S_{22} absorption bands,

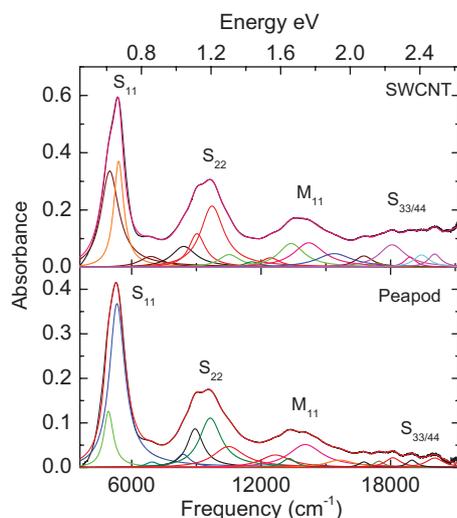


Figure 1 (online color at: www.pss-b.com) Background-subtracted absorbance spectra of free-standing films of SWCNTs and C_{60} peapods. The fit with Lorentz oscillators shows the various contributions to the absorption bands. The labels S_{ii} and M_{ii} denote the optical transitions between pairs of Van Hove singularities in semiconducting and metallic SWCNTs, respectively, where the indices ii indicate the energy sequence of the involved Van Hove singularities.

Table 1 Energy (in eV) of the Lorentz contributions to the S_{11} and S_{22} absorption bands.

| | SWCNTs | C_{60} peapods |
|-------------|--------|------------------|
| $S_{11}(1)$ | 0.62 | 0.60 |
| $S_{11}(2)$ | 0.67 | 0.66 |
| $S_{22}(1)$ | 1.04 | 1.04 |
| $S_{22}(2)$ | 1.11 | 1.11 |
| $S_{22}(3)$ | 1.20 | 1.20 |
| $S_{22}(4)$ | 1.30 | 1.30 |

respectively. According to these results, the band structure of the SWCNTs is not significantly altered by the fullerene molecules inside the tubes.

In Fig. 2 we present the absorbance spectra of C_{60} peapods as a function of pressure, for (a) alcohol mixture, (b) argon, and (c) CsI used as pressure transmitting medium. Under the application of pressure the absorption bands are broadened, and thus one can resolve only one Lorentzian contribution for the S_{11} and M_{11} absorption bands (except for the alcohol mixture as pressure transmitting medium, where one finds two contributions for the M_{11} band) and two Lorentzian terms for the S_{22} absorption band. The absorption bands are observed up to the highest applied pressure

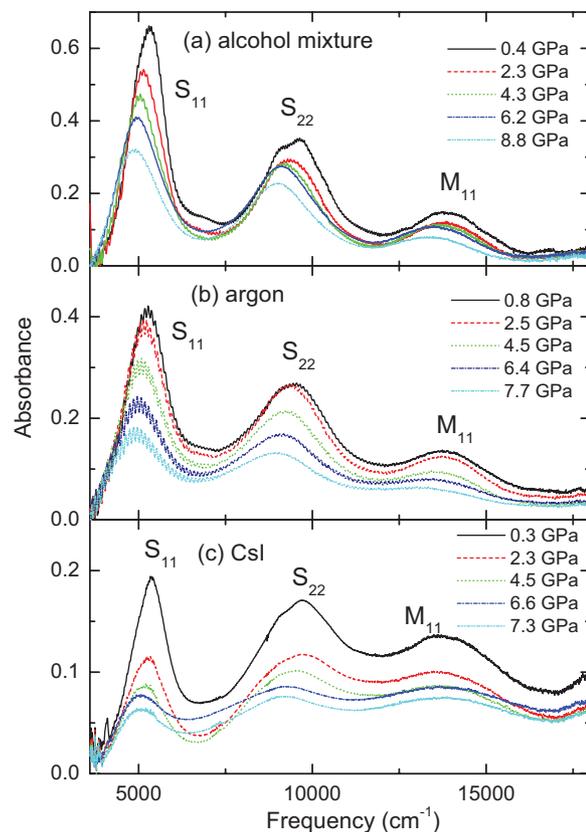


Figure 2 (online color at: www.pss-b.com) Background-subtracted absorbance spectra of free-standing films of C_{60} peapods as a function of pressure, for (a) alcohol mixture, (b) argon, and (c) CsI as pressure transmitting medium.

(~8 GPa). Generally, the broadening of the absorption bands is lower for the alcohol mixture and thus the various contributions to the bands can be resolved up to 8 GPa, in contrast to argon or CsI as pressure medium. The most obvious changes on the absorption bands with increasing pressure are (i) a shift to lower energies and (ii) a broadening and damping.

The frequencies of the optical transitions in C₆₀ peapods as a function of pressure are presented in Fig. 3. Like for empty SWCNTs the pressure-induced redshift of the contributions can be attributed to the $\sigma^*-\pi^*$ hybridization and symmetry-breaking effects in deformed tubes, which lower the conduction band and hence cause a shift of the optical transitions between the Van Hove singularities in the density of states to lower energies [13, 14]. The absolute values of the frequency shifts are similar to those found for empty SWCNTs; hence a stabilization of the SWCNTs by the filling with fullerene molecules is not obvious based on our results. This is in agreement with the interpretation of recent Raman measurements on C₇₀ peapods under pressure, pointing out the weak character of the fullerene–tube interaction below ~2 GPa [23]. However, we cannot rule out that the observed anomaly is related to the pressure effects in partially empty nanotubes.

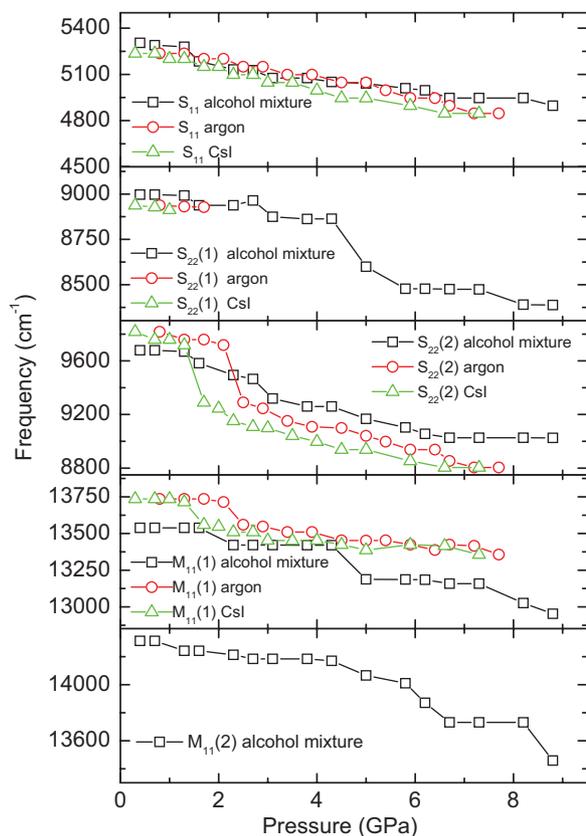


Figure 3 (online color at: www.pss-b.com) Absolute frequency shifts of the optical transitions in C₆₀ peapods as a function of pressure, for alcohol mixture, argon and CsI as pressure transmitting medium.

The pressure-induced shifts exhibit an anomaly at a critical pressure p_c , which is attributed to a structural deformation of the SWCNTs, where the circular cross-section is deformed to an oval or ellipse-like shape. The S₁₁ optical transitions seem to be the least sensitive ones regarding the pressure-induced effects, in agreement with earlier reports [15–18].

The absolute value of p_c depends on the pressure transmitting medium: For CsI, with the lowest hydrostaticity level, the anomaly occurs at ~1.5 GPa, while for argon and alcohol mixture it is observed at ~2 and 3 GPa, respectively. A higher critical pressure for better hydrostatic conditions is consistent with earlier results [16, 25]. The dependence of the critical pressure on the pressure transmitting medium is illustrated by the relative frequency shifts of the various contributions, shown in Fig. 4. For argon and CsI the anomaly is most obvious, while for the alcohol mixture the changes are more subtle. In the latter case the pressure-induced frequency shifts exhibit a second anomaly at around 4–5 GPa (see Fig. 4). This second anomaly might be due to the onset of the interaction between the carbon nanotubes and the fullerene molecules, as suggested in

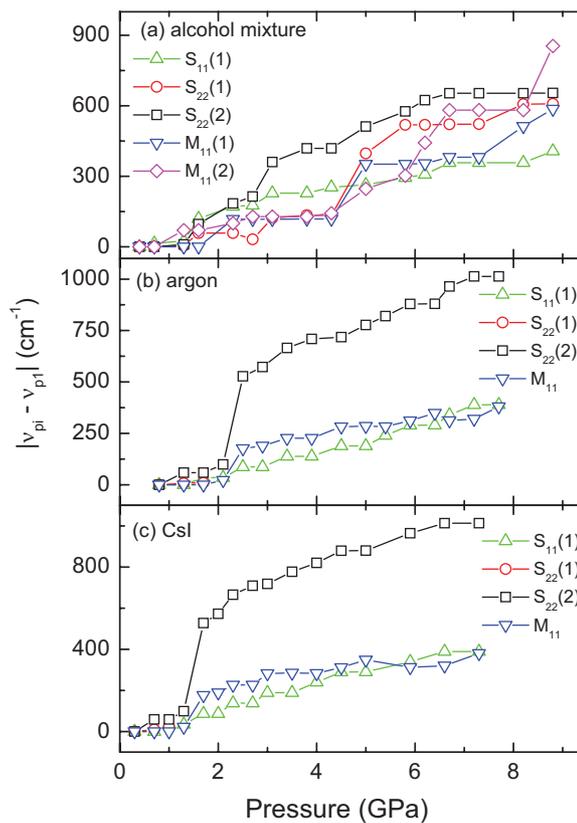


Figure 4 (online color at: www.pss-b.com) Relative frequency shifts of the optical transitions in C₆₀ peapods as a function of pressure for (a) alcohol mixture, (b) argon, or (c) CsI as pressure transmitting medium. The relative shifts are given with respect to the lowest applied pressure, calculated as the difference between the frequency of the contribution ν_{p_i} at a certain pressure p_i , and the corresponding frequency ν_{p_1} at the lowest pressure p_1 .

Ref. [23]. For the other pressure transmitting media (argon, CsI) the anomaly is blurred by the broadening of the absorption bands.

4 Conclusions The effects of pressure on the electronic properties of C_{60} peapods are very similar to those of the empty SWCNTs: the application of pressure causes a shift of the optical transitions to lower energies, with an anomaly at a critical pressure due to the nanotubes' deformation. A low filling ratio of the peapods cannot be excluded as the reason for this observed similarity in the pressure effects. The second anomaly at around 4–5 GPa in the pressure-induced shifts of the absorption bands suggests that the tube–fullerene interaction affects the electronic band structure of the nanotubes above \sim 4–5 GPa.

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