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Filling factors, structural, and electronic properties of C₆₀ molecules in single-wall carbon nanotubes

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We report recent measurements of the electronic and structural properties of bulk samples of C₆₀ molecules encapsulated in single-wall carbon nanotubes (so-called peapods) using electron-energy-loss spectroscopy in transmission. We demonstrate that C₆₀ peapods with a single-wall carbon nanotube (SWNT) diameter distribution of 1.37 ± 0.08 nm have an average fullerene filling of 60%. Regarding the electronic and optical properties, the overall shape of the response of the SWNT and the peapods is very similar, but with distinct differences in the fine structure. The interband transitions of the SWNT are slightly downshifted in the peapods, which can be explained by either a small increase of the SWNT diameter or by a change of the intertube interaction. The electronic and optical properties of the encapsulated C₆₀ peas closely resemble those of solid fcc C₆₀ showing small changes in the relative intensities, peak positions, and peak width, which point to a weak van der Waals interaction between the tubes and the encapsulated fullerenes.

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I. INTRODUCTION

Since their discovery approximately ten years ago,¹ carbon nanotubes have generated much enthusiasm and scientific curiosity due to their unique properties and potential applications.²⁻⁴ The high aspect ratio for both single-walled and multiwalled varieties, in combination with their one-dimensional electronic properties that can be either conducting or semiconducting, make these materials ideal for a number of nanoscale electronic applications. The unique structure of carbon nanotubes provides an ideal template for obtaining a number of nanoscale materials.⁵

Individual single-wall carbon nanotubes (SWNT's) enclose a cylindrical empty space, and thus it is a natural idea to try to introduce atoms or molecules into this one-dimensional cavity. Many of the future applications of SWNT's are dependent upon the ability to utilize or controllably modify their intrinsic properties by manipulating or selecting their microstructure. Endoheadral doping of SWNT's offers a unique method to alter their electronic, transport, and mechanical properties, and thus to endow them with functionality. Filling of SWNT's with C₆₀ molecules was first observed in material prepared by laser ablation using high-resolution transmission electron microscopy (TEM).⁶ Later on, fullerene-filled SWNT's, so-called peapods, were produced in a two-step process. The SWNT's are purified and opened; then they are filled by exposure to a fullerene vapor at high temperature.⁷ In this way, peapods filled with fullerenes and metallofullerenes have been produced (C₆₀, C₇₀, Gd@C₈₂, La₂@C₈₀, etc.) in macroscopic quantities.⁸ The exact degree of filling is still under intense discussion and ranges from a few percent to almost 100% filling.

In this paper we report on electron-energy-loss spectroscopy (EELS) experiments on C₆₀ peapods performed in transmission with high energy and momentum resolution but with no spatial resolution. From a comparison with empty SWNT's, we obtain an accurate measure of the filling factor in bulk samples of peapods. In addition, our results on the changes of the structural and electronic properties of the SWNT's and of encapsulated C₆₀ peas are reported.

II. EXPERIMENT

The production of the C₆₀ peapods was reported in detail elsewhere.⁷ The diameter distribution of the C₆₀ peapods was evaluated as 1.37 ± 0.08 nm.⁹ A typical high-resolution TEM image of the peapod material is shown in Fig. 1. It is obvious that a very high filling ratio is seen on a nanometer scale. However, as high-resolution TEM is a very local probe, it is dangerous to estimate the filling factor from this type of measurement alone. Here we use a truly macroscopic bulk sensitive probe (EELS) to analyze both the filling factor, as

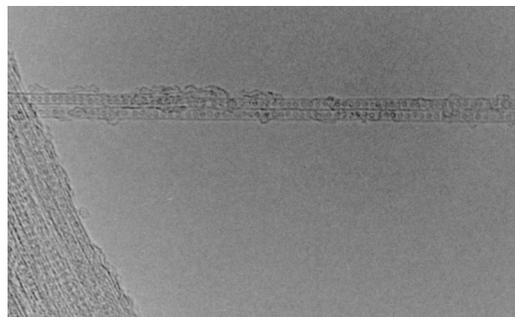


FIG. 1. High resolution TEM micrograph of C₆₀ peapods.

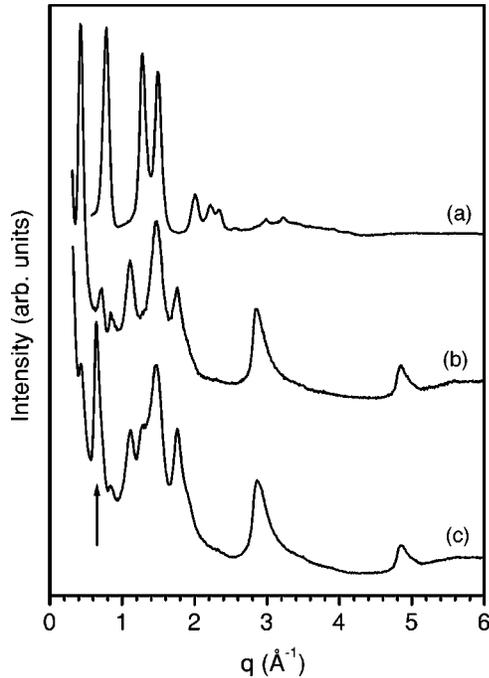


FIG. 2. Electron-diffraction data of (a) solid C_{60} (b) empty SWNT's and (c) C_{60} peapods. The arrow indicates the Bragg peak at a momentum transfer of $q=0.65 \text{ \AA}^{-1}$, which corresponds to the interfullerene separation of 0.97 nm of the C_{60} peas.

well as the structural and electronic properties of these types of fullerene hybrid nanostructures. Thin films of peapods and the SWNT reference sample (from the same SWNT batch) without C_{60} with an effective thickness about 1000 Å were prepared by drop coating of an acetone suspension onto KBr single crystals. The KBr was then dissolved in distilled water, and the films were transferred onto a standard 200 mesh platinum electron microscopy grid. The films were heated for 6 h in ultrahigh vacuum up to 350 °C, which has been shown to remove organic contaminations from the SWNT, but does not damage the peapods. The EELS measurements were carried out using a dedicated 170-keV spectrometer described in detail elsewhere.¹⁰ The energy and momentum resolution were chosen to be 180 meV and 0.03 \AA^{-1} for the electron diffraction experiments and for the measurements of the low-energy-loss function in the region of the valence band excitations. For the measurement of C 1s core-level excitations, a slightly reduced energy resolution of 0.33 eV and a momentum resolution of 0.1 \AA^{-1} were chosen. The loss function $\text{Im}[-1/\epsilon(\mathbf{q}, \omega)]$, which is proportional to the dynamic structure factor $S(\mathbf{q}, \omega)$, was measured for various momentum transfers q . All experiments were performed at room temperature in ultrahigh-vacuum conditions.

III. RESULTS AND DISCUSSION

A first characterization of the samples was performed by measuring the electron-diffraction profiles. Figure 2 shows the electron diffraction of the C_{60} peapods in comparison with the corresponding spectrum of the empty SWNT reference sample, together with that of solid fcc C_{60} . The most

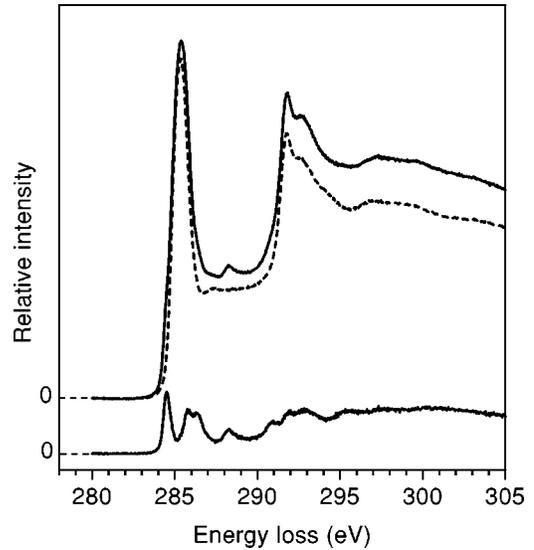


FIG. 3. C 1s core-level excitation spectra of peapods (solid line) and reference empty SWNT's (dashed line). The difference spectrum below is the resulting response of the C_{60} peas.

obvious difference is that additional diffraction peaks appear for the peapods as compared to the SWNT reference. Most pronounced is the Bragg peak at 0.65 \AA^{-1} , which corresponds to the nearest-neighbor distance of two encapsulated C_{60} molecules of about 0.97 nm. This value is in good agreement with the previously reported peapod interball separation of 0.95 nm obtained from TEM electron-diffraction data.⁷ A simple estimate shows that this separation is in between the nearest-neighbor distance in fcc C_{60} (1 nm) and the one-dimensional (1D) C_{60} pressure polymer phase which has a separation of the interlinked fullerenes of about 0.92 nm. Therefore, from the position of the Bragg peak at 0.65 \AA^{-1} , we can conclude that it is very unlikely that the C_{60} molecules inside the SWNT are polymerized, but that they could be dimerized.

Information about the electronic structure can be extracted from an analysis of the core-level excitations at the C 1s edge. The core-level excitations in peapods and empty SWNT's are presented in Fig. 3, whereby the spectral features correspond to transitions into C 2p-related (unoccupied) π^* and σ^* electronic states. The former are found at 285.4 eV and the latter at 292 eV, which are similar energies as observed for the analogous excitations in graphite.¹¹ Compared to C_{60} , no pronounced fine structure related to transitions into narrow molecular states is observed in the SWNT spectrum. In graphite, the features at the π^* (Ref. 12) and σ^* (Ref. 13) onsets are both strongly excitonic in nature, and it is reasonable to assume that the same holds for the SWNT's and peapods. However, there is a significant difference in the fine structure between the SWNT's and the peapods. In particular, there are shoulders at 284.5 and 286.3 eV and an obvious peak at 288.3 eV in the peapod spectrum, which are not present in the SWNT reference and therefore are assigned to the C_{60} peas. It is tempting to perform an appropriate normalization and to analyze the difference spectrum which would then be related to the energy distribution of the

unoccupied C $2p$ -related electronic states of the C_{60} peas. In a core-level excitation experiment, the intensity difference between energy locations well before and well after the spectral fine structure is often referred to as the edge jump, and gives a direct measure of the number of atoms in the sample volume probe. Consequently, the edge jump in different C_{60} compounds (e.g., fcc C_{60} or C_{60} polymers, etc.) is found to be essentially independent of the details of the electronic structure and bonding in each case.¹⁴ Based upon this idea, one can scale the empty SWNT spectrum with respect to that of the peapods prior to subtraction with the condition that the edge jump of the resulting “pea” spectrum must be the same as that of C_{60} . To fulfill this condition, the reference (empty) nanotube spectrum must be scaled by a factor of 0.82 before subtraction. The uncertainty of the fit corresponds to the signal-to-noise ratio in the measurements. For the observed spectra, this leads to an overall error of about 1%. The resulting difference spectrum of the C_{60} peas after subtraction of the scaled spectra of the SWNT reference and the peapods are depicted in the lower part of Fig. 3. Similar to C_{60} below the σ^* onset at about 290 eV several structures are seen in the spectrum of the C_{60} peas, which can be assigned to excitations into the unoccupied π^* -derived molecular states.¹⁴ The width of these shape resonances is strongly depending on the distortion of the C_{60} cage due to polymerization and dimerization.¹⁵ The first π^* resonance at 284.5 eV corresponds to excitations into the lowest unoccupied molecular orbital (LUMO) of C_{60} of t_{1u} symmetry. The charge transfer to the C_{60} is followed by filling of the LUMO, which leads to a suppression of the intensity of the LUMO peak and is directly related to the number of transferred electrons.¹⁴ The next peaks at 285.8 and 286.3 eV are derived from the LUMO+1 and LUMO+2 molecular orbitals of t_{1g} and $t_{2u} + h_g$ symmetry. The relative intensity of these features is strongly dependent on the local bonding environment and coordination of the C_{60} molecules.^{16,17} Consequently, for a C_{60} monolayer on graphite the relative intensity of the LUMO+1 peak was strongly enhanced compared to the LUMO+2 resonance. The additional van der Waals bonding to the graphite substrate was found to have a negligible impact on the shape of the spectra of the C_{60} molecules.¹⁷

In order to clarify the role of the local bonding environment and charge transfer the C $1s$ excitation spectra of the encapsulated C_{60} peas are shown in Fig. 4 in comparison with fcc C_{60} and the 1D C_{60} polymer. In the pea spectrum, there is a clear upshift of the LUMO peak of about 0.1 eV compared to both fcc C_{60} and the 1D C_{60} polymer; meanwhile, the LUMO peak in the encapsulated 1D C_{60} becomes asymmetric. As regards the spectral form of the π^* resonances in the peas, the relative intensity of the LUMO+1 feature at 285.8 eV with respect to the LUMO+2 peak at 286.3 eV is enhanced. This spectral shape is very similar to the absorption spectra of a C_{60} monolayer on graphite.¹⁷ In this case the change was assigned to a reduced coordination number of nearest C_{60} neighbors in the monolayer. Consequently, the intensity change in the case of the encapsulated C_{60} can be attributed to a change of the nearest-neighbor coordination from 12 in fcc C_{60} to only 2 for the C_{60} peas.

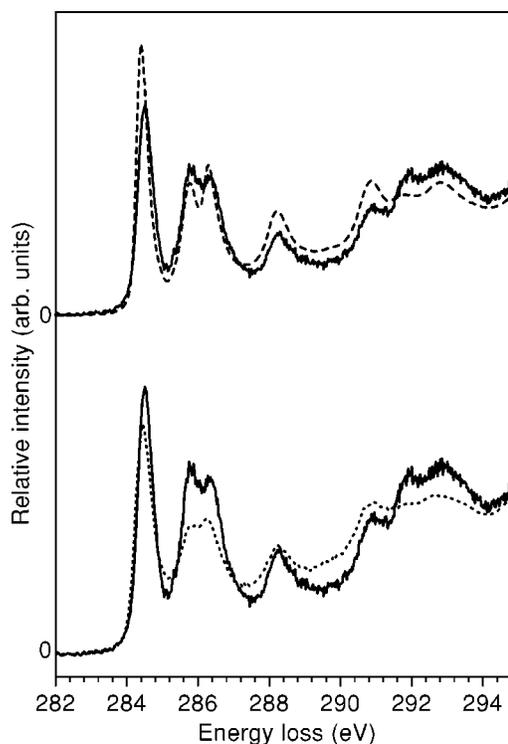


FIG. 4. Upper panel: C $1s$ core-level excitation spectra of the encapsulated C_{60} peas (solid line) compared with that of fcc C_{60} (dashed line). Lower panel: C $1s$ core-level excitation spectra of the encapsulated C_{60} peas (solid line) compared with 1D polymerized C_{60} (dashed line). All spectra are normalized at the edge jump.

Similar to the above-mentioned van der Waals interaction between C_{60} and graphite, the interaction to the inner wall of the SWNT's has only a weak impact on the overall shape of the spectra of the C_{60} peas. The changes in the interaction between C_{60} and graphite and C_{60} and the SWNT's, which are related to the curvature of the SWNT's, therefore have only a minor effect on the unoccupied electronic structure. This is in good agreement with recent calculations showing that the interaction to the inner wall of the SWNT is similar as in fcc C_{60} and as the interaction between C_{60} and graphite.¹⁸

Furthermore, the width of the LUMO peak is increased from about 0.4 eV in C_{60} to about 0.55 eV in the peas and to about 0.65 eV in the 1D C_{60} polymer. From the comparison of the area of the LUMO resonance, one can conclude that the charge transfer from the SWNT to the C_{60} molecules is very small. The LUMO peak area of the C_{60} peas between 283 and 285.2 eV is reduced by only about 1% compared to fcc C_{60} , showing that the charge transfer from the SWNT to the C_{60} molecule is less than $0.1e^-$. This is in good agreement with recent theoretical calculations of C_{60} peapods which show that for (10,10) SWNT's a low charge density is observed between the C_{60} and the SWNT's.¹⁸

As a last point we deal with the question of polymerization of the C_{60} peas. The overall broadening of the C_{60} resonances can be attributed to a distortion of the C_{60} ball due to dimerization or polymerization.¹⁵ Since the width of the transitions for the peas is in between those for fcc C_{60} and the 1D

polymer (and much lower than for the 2D polymer¹⁵), this is further evidence against polymerization of the C_{60} molecules within the SWNT, in keeping with the electron diffraction data presented above. The small overall broadening of the resonances is also in good agreement with the above-mentioned fact, that there is only a weak van der Waals interaction between the C_{60} peas and the inner wall of the SWNT. Consequently, covalent bonding between the C_{60} and the nanotube cage can be excluded for the measured peapods.

In addition to the analysis of the unoccupied local electronic structure, another key characteristic of the peapods—the filling factor of the peas—can also be accurately determined from high-spectral-resolution EELS in transmission data. Though up to 100% filling would be the natural conclusion from the consideration of TEM images such as that shown in Fig. 1, we do point out that these figures are only strictly applicable on the nanoscale. EELS carried out, as here, *without* spatial resolution probes a bulk sample of several mm^2 , which then can give a more representative evaluation of the overall filling of the peapods. From the edge jump scaling factor mentioned above, we can derive the relative contribution of the encapsulated C_{60} to the overall C 1s edge per C atom to be about $22\% \pm 1.5\%$. From straightforward geometrical considerations, one can show that, taking SWNT's with a mean diameter of 1.37 nm and 100% filling with C_{60} at an interfullerene distance of 0.97 nm, the C_{60} carbon atoms can be estimated to be $\sim 38\%$ of the total carbon atoms present. Thus, for our C_{60} peapods, we arrive at an overall, bulk C_{60} filling factor of $61\% \pm 5\%$. Furthermore, we have to consider the SWNT diameter distribution, together with the condition that there is a minimal SWNT diameter which is able to be filled. Using the approximation, that only nanotubes bigger than the hard sphere C_{60} diameter plus four times the C van der Waals radius (1.35 nm) are able to be filled we estimate that only 72% of the total number of nanotubes are filled with C_{60} . Thus the nanotubes which are able to contain C_{60} are filled on an average value of 85%, which is fully consistent with the nanoscale TEM observation of 100% filling shown in Fig. 1. These considerations highlight the importance of a precise control of the SWNT diameter distribution in this context. We also point out that, in recent calculations for armchair nanotubes, the minimal diameter for a filling with C_{60} was about 1.3 nm in good agreement with our estimations.¹⁸

We now focus on the valence-band excitations in the peapods. The low-energy-loss function provides further information about the momentum-dependent optical properties of our samples. Regarding the overall shape of the loss function in the peapods the collective excitation of the π -electron system, the so-called π plasmon, at about 6 eV, and the collective excitation of all valence electrons, the $\pi + \sigma$ plasmon, at about 22 eV, closely resemble those of pristine SWNT's.¹⁹ Moreover, the plasmon dispersion of the π and $\pi + \sigma$ plasmons are unaffected by the incorporation of C_{60} inside the SWNT. However, there are small differences regarding the position of the interband transitions of the SWNT. In Fig. 5 we compare the first three interband transitions in SWNT's and in the peapods as measured by optical

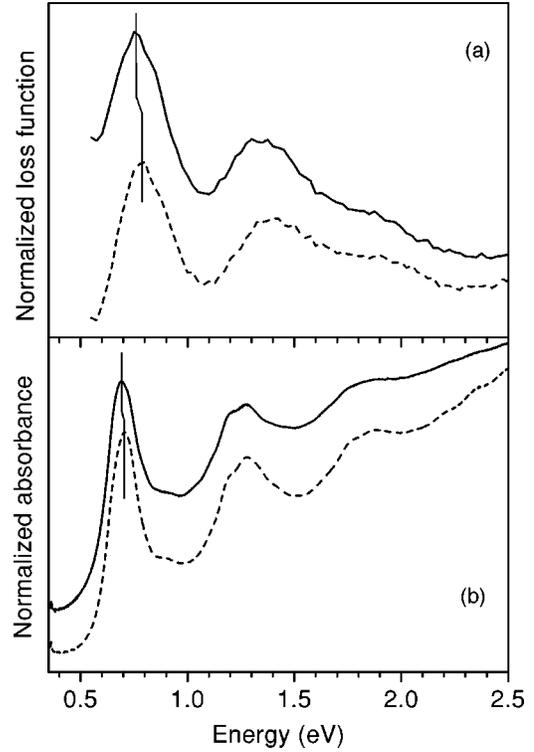


FIG. 5. (a) Loss function ($q=0.1 \text{ \AA}^{-1}$) in the energy range of the interband transitions for the C_{60} peapods (solid line) and empty SWNT's (dashed line). The spectra are offset after normalization at the $\pi + \sigma$ plasmon (not shown). (b) Optical absorption spectra of the same energy region: C_{60} peapods (solid line), empty SWNT's (dashed line). The spectra are offset after normalization to the minimum at 1 eV. The guidelines indicate the downshift of the first allowed optical transition upon C_{60} encapsulation.

absorption and by EELS at a momentum transfer $q = 0.1 \text{ \AA}^{-1}$. Clearly a downshift of the optical transition of the SWNT is observed after filling with C_{60} . The guideline emphasizes the downshift of the first allowed optical transition of 0.014 and 0.025 eV for the absorbance and for the loss function, respectively. There are three possible contributions to this effect. First, the SWNT diameter can be slightly changed due to the filling. From the inverse proportionality of the optical transitions to the SWNT diameter we can roughly estimate an increase of the diameter of about 0.03 nm. This diameter change is also consistent with the observed downshift of the radial breathing mode frequency in Raman studies.⁹ Although such a change should also be observed in the electron diffraction, it corresponds to only a shift of 0.008 \AA^{-1} of the bundle peak, which is well below the resolution limit of our spectrometer. Second, for both the Raman response²⁰ and the optical absorption²¹ the intertube interaction between the individual SWNT inside a SWNT bundle plays an important role and a small change of it could lead to a similar downshift. Third, the dielectric screening (ϵ_∞) is different in the two systems. For the peapods the screening effect, due to the enhancement of ϵ_∞ , will downshift the peak in EELS as can be estimated from a Drude-Lorentz model. However, the downshift of the optical absorption peaks in the Drude-Lorentz model should be much

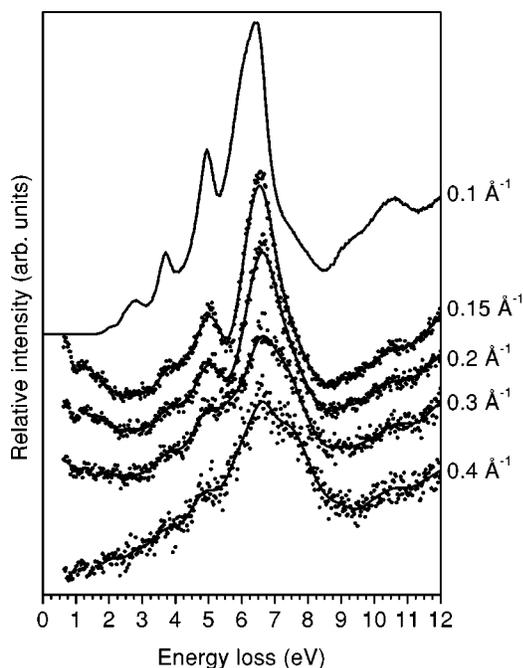


FIG. 6. Loss function of C_{60} (solid line) measured at a momentum transfer of $q=0.1 \text{ \AA}^{-1}$, compared to data from encapsulated C_{60} peapods measured with momentum transfers of $q=0.15, 0.2, 0.3,$ and 0.4 \AA^{-1} , respectively. For details, see the text.

smaller than observed. Consequently, the change in the background dielectric screening has only a small contribution to this effect. Therefore the change of the intertube interaction is the most likely explanation for the downshift of the valence-band excitations.

We finally discuss the valence-band excitations of the C_{60} peapods. In order to extract the signal of the encapsulated C_{60} we have employed the same scaling factor as used above for the edge jumps in the $C1s$ excitation edges to the $\pi+\sigma$ plasmon. The resulting difference spectrum at low momentum transfer is in very good agreement with the loss function of fcc C_{60} above 2 eV, as can be seen in Fig. 6. Below 2 eV the difference spectrum is complicated by the above-mentioned shift between the interband transitions of the SWNT's and the peapods. For fcc C_{60} optically allowed $\pi\rightarrow\pi^*$ transitions are observed at 2.7, 3.6, and 4.9 eV. The normally dipole-forbidden gap transition of $h_u\rightarrow t_{1u}$ symmetry is observed at 2.2 eV, the π plasmon is seen at 6.45 eV.¹⁴

With increasing momentum transfer no dispersion of the transitions is observed, but transitions with monopolar and quadrupolar character gain intensity. This can be seen by the increase of the intensity of the dipole forbidden gap transition and of the quadrupole transition at about 8 eV.^{22,23} For the C_{60} peapods we observe an upshift of the π plasmon to 6.6 eV, whereas the low-lying interband transitions are only slightly upshifted similar to optical absorption. Similar to C_{60} , at high momentum transfer the intensities of the dipole-forbidden transitions at 2.2 and 7.5 eV are increased. The width of the interband transitions in the C_{60} peapods is increased by about a factor of 2, but still much smaller than in the 1D pressure polymer.¹⁵ For the 1D C_{60} polymer, the broadening—which is accompanied by a downshift of the transitions—was explained by an increase of the intermolecular overlap and by a lowering of the fullerene symmetry. Since we observe an upshift of the transitions for the peapods, the broadening in this case is most likely to be due to mainly a lowering of the symmetry.

To summarize, we have demonstrated that the C_{60} peapods are filled up to 60% for a SWNT diameter distribution of 1.37 ± 0.08 nm. Regarding the electronic and optical properties the overall shape of the response of the SWNT's and the peapods is very similar, with distinct differences in the fine structure. The interband transitions of the SWNT's are slightly downshifted in the peapods which is consistent with a small increase of the SWNT diameter or a change of the intertube interaction. The electronic and optical properties of the encapsulated C_{60} peapods are very similar to fcc C_{60} , but show small changes in the relative intensities of the π^* -derived molecular orbitals and regarding the peak positions and peak width. We conclude that there is only a weak van der Waals interaction between the SWNT's and the C_{60} peapods similar to the interaction between C_{60} and graphite.

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