Interaction between Inner and Outer Tubes in DWCNTs

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Abstract. By annealing fullerene peapods at high temperatures in a dynamic vacuum it is possible to produce double-wall carbon nanotubes. A Raman investigation revealed that the inner single-wall carbon nanotubes are remarkably defect free showing very strong and very narrow radial breathing modes (RBMs). The number of observed RBMs is larger than the number of geometrically allowed inner tubes. This splitting is caused by the interaction of one type of inner tube with several types of outer tubes the inner tube may grow in.

INTRODUCTION

Single-wall carbon nanotubes (SWCNTs) [1, 2, 3] have attracted a lot of scientific interest over the last decade due to their unique structural and electronic properties. A few years ago, it was discovered that fullerenes can be encapsulated in SWCNTs, forming so-called peapods [4]. By annealing such peapods at high temperatures in a dynamic vacuum it became possible to transform the enclosed C60 peas into SWCNTs within the outer tubes, producing double-wall carbon nanotubes (DWCNTs) [5, 6]. The growth process of the inner tubes is a new route for the formation of SWCNTs in the absence of any additional catalyst.

A detailed Raman study of the radial breathing modes (RBMs) of the inner tubes revealed that these modes have intrinsic linewidths of about 0.4 cm⁻¹ [7]. This is about a factor 10 smaller than reported for isolated tubes so far. This small linewidths indicate long phonon lifetimes and therefore highly defect free inner tubes, which is a proof for a nano clean room reactor on the inside of SWCNTs.

A closer inspection of the RBM response of the inner tubes revealed that there are more Raman lines than geometrically allowed inner tubes. In this contribution we will explain this splitting by the interaction of one type of inner tube with several types of outer tubes.

EXPERIMENTAL

As starting material for our DWCNTs we used C60 peapods (in the form of buckypaper) produced with a previously described method [8]. The outer tubes had a mean diameter of about 1.39 nm as determined from the RBM Raman response [9]. The filling of the tubes large enough for C60 to enter was close to 100% as evaluated from a Raman
FIGURE 1. High resolution Raman response of the inner tube RBMs for several excitation wavelengths at 20 K. Selected chiralities after Kramberger et al. [13] and splitting widths are indicated.

[10, 11] and EELS analysis [12]. These peapods were slowly heated up to 1300°C in a dynamic vacuum for 12 hours and were then slowly cooled down to room temperature. The Raman spectra were measured with a Dilor xy triple spectrometer using various lines of an Ar/Kr laser, a He/Ne laser and a Ti:sapphire laser. The spectra were recorded at 20 K in high resolution mode ($\Delta \bar{\nu}_{HR} = 0.4 \text{ cm}^{-1}$ in the red). In these measurements the samples were glued on a copper cold finger with silver paste.

RESULTS AND DISCUSSION

Fig. 1 depicts selected high resolution Raman spectra of the RBMs of the inner tubes. Using the frequency–diameter relation from [13], one should find the RBMs of 28 distinct inner tubes between 270 and 400 cm$^{-1}$. However, the observed number of lines in this region is about three times larger. This means, that the RBMs of the inner tubes are split into several components.

In order to determine the number of the split components and the width of the splitting we fitted six selected high resolution spectra with a number of Voigtian lines. Using our chirality assignment [13], each individual inner tube was assigned a number of RBM frequencies. For each tube we subtracted from these frequencies the mean value and plotted the split components vs. inner tube diameter in Fig. 2. It shows that the number of split components ranges between two and five and the width of the splitting is about
In the following, we will show that the splitting is caused by two reasons: due to the interaction with the outer tube the RBM frequency of the inner tube depends on the diameter of the outer tube and one type of inner tube may form in several types of outer tubes. To calculate the RBM frequency of the inner tube of a DWCNT, we used a continuum model with two elastic concentric cylinders of the appropriate diameters. The interaction of these two cylinders was modeled with a Lennard-Jones potential [14]. The possible diameter differences between inner and outer tubes were assumed to be in the range $0.66 - 0.70$ nm. This range was centered around $0.68$ nm which is about twice the layer distance in graphite.

Fig. 3 demonstrates the dependence of the calculated RBM frequency of a $(6,4)$ inner tube on the diameter of the outer tube. The isolated $(6,4)$ tube has a diameter of $d_{\text{inner}} = 0.691$ nm and a frequency of $\nu^{\text{isolated}}_{\text{inner RBM}} = 337.4$ cm$^{-1}$ (excluding $C_2$) [13]. This RBM frequency increases with decreasing outer tube diameter.

In a first step, we assumed that in all outer tubes in our sample (Gaussian distribution with $\bar{d} = 1.39$ nm and $\sigma = 0.1$ nm) only the best fitting inner tubes are formed. The splitting calculated with this assumption is depicted in Fig. 4 (left). The number of split

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1 Dobardžić et al. [15] performed similar calculations of the inner tube RBM frequencies using a harmonic interaction between the inner and outer cylinder.

2 “Best fitting” means $(d_{\text{outer}} - d_{\text{inner}} - 0.68 \text{ nm})^2 \rightarrow \text{min}$.
FIGURE 3. RBM frequency of a (6,4) inner tube depending on the diameter $d_{\text{outer}}$ of the encapsulating tube. The diameters were calculated from the interpolation formula from Kramberger et al. [13].

FIGURE 4. Number of split components and width of splitting for individual inner tubes from the theory after subtracting the mean value of the calculated RBM frequencies. Left: Only the best fitting inner tubes are formed. Right: The best and second best fitting inner tubes are formed.

components and the width of the splitting are smaller than the experimentally observed values. Therefore, in a second step, we assumed that also the second best fitting inner tubes may be formed. As Fig. 4 (right) shows, this assumption results in a larger splitting than observed. This suggests that also second best fitting inner tubes are formed but not in all cases.

In summary, we have shown that the RBMs of the inner tubes of DWCNTs are split
into several components. This is attributed to the interaction between inner and outer tubes that causes a change of the inner tube RBM frequency. Since it is possible that one type of inner tube forms in several types of outer tubes (with slightly different diameters) every inner tube gives rise to more than one RBM in the Raman spectrum.

ACKNOWLEDGMENTS

The authors acknowledge financial support from the FWF in Austria, project P14893, and from the EU, project PATONN Marie-Curie MEIF-CT-2003-501099. VNP was partly supported by a fellowship from the Federal Science Policy Office for promoting the S&T cooperation with Central and Eastern Europe and by a NATO CLG. We thank Prof. H. Kataura for providing the peapod samples used for the production of the DWCNTs.

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