High pressure Raman studies of carbon nanotube materials

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Abstract. Raman spectroscopy is employed to study the pressure response of single-wall (SWCNTs), double-wall (DWCNTs) and multi-wall (MWCNTs) carbon nanotube materials. In DWCNTs, the outer tubes exhibit a similar pressure response to SWCNTs, where the tube sensitivity to pressure application is diameter dependent (higher for larger diameter tubes). On the other hand, the inner tubes in DWCNTs and the innermost tubes in MWCNTs appear to be much less sensitive to pressure application, indicating the pressure screening inside the outer tubes. The pressure screening effect is strongly enhanced in MWCNTs.

1. Introduction
The mechanical and transport properties of carbon nanotube materials, crucial for technological applications, are determined by the structural characteristics of the individual tubes and their mutual interaction, either in a nanotube bundle (intertube interaction) and/or within a double- or multi-shell system (intratube interaction). High pressure application on these systems is a valuable tool for the investigation of their mechanical and structural stability, while resonance Raman spectroscopy allows the selective probing of different tubes [1,2]. This is possible due to the size-dependent peculiar electronic structure of carbon nanotubes, originating from the quasi one-dimensional electron confinement [3,4], in combination with the inversely proportional relation between the radial breathing
mode (RBM) frequency and the tube diameter [5]. In this work, we study the effect of high-pressure on SWCNT, DWCNT and MWCNT materials by means of Raman spectroscopy, in order to compare the structural stability of the coaxial tubes in the various carbon nanotube systems.

2. Experimental

The bundled SWCNT sample (Carbon Nanotechnologies Incorporated, BuckyPearls™), with tube diameters 0.8-1.2 nm, has been prepared by the high pressure catalytic decomposition of carbon monoxide (HiPCO). The bundled DWCNT material has been synthesized by means of the C_{60}-peapod conversion process, following Bandow’s procedure [6]. The inner tubes diameters are 0.6-0.9 nm while those of the outer tubes 1.3-1.6 nm. The infrared irradiation purified MWCNTs were prepared by DC arc discharge evaporation of graphite rods in pure hydrogen gas. They consist of 10-15 concentric tubes with outermost and innermost tube diameters of ~10 and ~1 nm, respectively [7].

Raman spectra were recorded in the back-scattering geometry using a micro-Raman, triple grating system (DILOR XY) equipped with a cryogenic CCD detector. High pressure Raman measurements were carried out using a Mao-Bell type diamond anvil cell (DAC) with the 4:1 methanol-ethanol mixture as the pressure transmitting medium, while the ruby fluorescence technique was used for pressure calibration. The 676.4 nm line of a Kr⁺ laser was focused on the sample by means of a 20x objective, while the laser power was kept below 4 mW, measured directly before the DAC.

3. Results and discussion

The Raman spectra in the RBM frequency region of the studied carbon nanotube materials at lower (0.1-0.2 GPa, bottom panels) and higher pressures (2.4-2.7 GPa, top panels) are illustrated in figure 1.

![Figure 1. Raman spectra of SWCNTs, DWCNTs and MWCNTs at different pressures.](image)

The various RBM peaks appearing in the spectra correspond to different tubes that are in resonance with the excitation wavelength. In the DWCNT spectra, the low frequency, relatively broad, RBM band corresponds to the outer tubes, while the numerous narrow peaks at higher frequencies to the smaller diameter inner tubes. The narrow lineshape of the latter reflects the structural perfection of the inner tubes, well protected by the outer ones. The large number of the inner tube RBMs originates from their splitting due to their intratube interaction-dependent frequency upshift [8]. A similar situation is also anticipated for the MWCNT innermost tubes. Usually, the observation of their RBMs...
is not possible due to the large number of encapsulating tubes. In our case, the smaller number of coaxial tubes allows their appearance in the Raman spectrum, though with low signal to noise ratio. From the RBM frequencies ($\omega$) and the relation $\omega = \frac{223}{d_t}+10$ [9], we can make a rough estimation for the diameters $d_t$ of the resonantly probed carbon tubes in the investigated samples. The calculated diameters are 0.8-1.2 nm for SWCNTs, 0.6-0.9 nm ($\sim$ 1.3 nm) for the inner (outer) tubes of DWCNTs and 0.6-1.3 nm for the innermost tubes of MWCNTs.

The pressure dependence of the frequencies of some characteristic RBMs in the Raman spectrum of the studied nanotube materials is plotted in figure 2. With increasing pressure, all the presented RBMs shift towards higher frequencies at different rates. Their pressure slopes are 5.2-7.2 cm$^{-1}$/GPa for SWCNTs, 6.7 cm$^{-1}$/GPa (9.3 cm$^{-1}$/GPa at low pressures) for the DWCNT outer tubes, 1.0-1.1 cm$^{-1}$/GPa for the DWCNT inner tubes and 0.1-0.3 cm$^{-1}$/GPa for the MWCNT innermost tubes. The pressure-induced frequency shift of the SWCNT RBMs is larger for the lower frequency Raman peaks (larger tube diameters) and is accompanied by their gradual broadening and intensity attenuation (figure 1). These observations are in line with earlier experimental studies [10] and theoretical predictions for bundled SWCNTs [11], which suggest that the tubes suffer significant pressure induced cross-section deformations with carbon nanotubes of smaller diameter exhibiting higher structural stability. We emphasize that if a shift of the resonance conditions was the only pressure effect, it would have led to the decrease of the RBM signal of some tubes but it should have enhanced the signal originating from other tubes, initially out of resonance, which is not the present case. Therefore the observed behavior should be attributed to the pressure-induced increase of the intertube interactions and the theoretically expected cross-section deformation of the tubes.

![Figure 2](image_url)

Figure 2. Pressure dependence of the RBM frequencies in SWCNTs, DWCNTs and MWCNTs. Open (solid) symbols denote data acquired for increasing (decreasing) pressure.

The RBM band attributed to the outer tubes of DWCNTs exhibits also an intensity decrease and broadening at elevated pressures, while its pressure slope is comparable to that of SWCNTs with similar size. Nevertheless, it persists to higher pressures than the corresponding in SWCNTs, possibly due to the presence of the inner tube in the former material that structurally supports the outer tube against pressure-induced cross-section deformations. The presence of the inner tubes in DWCNTs could also explain the sublinear pressure response of the outer tube RBM frequency by assuming that with increasing pressure the intratube interaction becomes progressively stronger further supporting...
the outer tubes (reduced slope at elevated pressures). On the other hand, the inner tube RBM peaks remain narrow and intense up to the highest pressure attained in our experiments (~9 GPa). This behavior reflects the protection of the encapsulated inner tubes from external perturbations, in contrast to the pressure-induced structural distortions encountered for SWCNTs and the outer tubes in DWCNTs. As the inner tubes suffer an effective pressure smaller than that exerted on the outer ones, the observed changes in the profile of the relative intensities can be mainly attributed to pressure-induced changes of their resonance conditions as any other cross-section-related changes should be minimal inside the outer tubes. The substantially smaller pressure slopes of the inner tube RBM frequencies as compared to those of the outer tubes in DWCNTs and the SWCNTs of similar diameters, further supports the scheme of pressure screening inside carbon nanotubes. Our detailed high pressure Raman studies, by means of several excitation wavelengths, combined with theoretical calculations suggest that the pressure screening in DWCNTs depends strongly on the intratube interaction and consequently on the inner-outer tube separation [12]. Finally, the experimental data presented in figure 2 clearly reveal that the addition of more graphene shells in the case of MWCNTs results in an even stronger reduction of the pressure slopes of the RBM frequencies. Thus, the pressure screening becomes much more efficient in this case, where the innermost tubes are well protected against external perturbations in the interior of several coaxial tubes. Then, differences in the pressure slopes of the RBM frequencies should also be related to the different number of shells comprising the MWCNTs. Note that, in accordance to the pressure screening scheme, the relative intensities among the different RBM peaks in the spectrum do not change significantly as compared with the changes observed for the DWCNTs and SWCNTs.

Upon pressure release, the frequency shifts of all the observed Raman peaks are fully reversible and the original frequency positions are restored after total pressure release (figure 2). However, the RBM intensities corresponding to the larger SWCNTs and the DWCNT outer tubes are attenuated and the peaks remain broader after release of the pressure (not shown). These divergences suggest the existence of residual pressure-induced deformations in these tubes.

4. Conclusions
The pressure response of carbon nanotube materials consisting of one or more coaxial rolled graphene sheets is deduced from the evolution of the RBM frequencies and their lineshape modifications upon pressure application. The larger tubes in SWCNTs are more vulnerable to pressure application than the smaller ones, while the outer tubes in DWCNTs exhibit similar pressure response to the SWCNTs of the same size. On the contrary, the inner tubes in DWCNTs appear to be less sensitive to pressure application, reflecting the pressure screening in the interior of carbon nanotubes. This interpretation is further supported by our results on MWCNTs for which no Raman data on the high pressure RBM response of the innermost tubes existed until now. The significant reduction of the RBM pressure slopes (almost two orders of magnitude with respect to those of SWCNTs of similar size) and the milder changes of the RBM intensity profile constitute clear evidences of the protection-enhancement provided by increasing the number of coaxial nanotubes.

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