High pressure Raman study of the second-order vibrational modes of single- and double-walled carbon nanotubes


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The pressure response of the second-order Raman G’ band of bundled double- (DWCNTs) and single-wall carbon nanotubes (SWCNTs) has been investigated by means of Raman spectroscopy using the 632.8 nm excitation. The different pressure responses of the G’ peak in SWCNTs and its corresponding components associated with the inner and the outer tubes in DWCNTs can be attributed to the different diameters of the resonantly probed tubes and the strength of the inner-outer tube interaction.

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1 Introduction

The Raman spectrum of carbon nanotube (CNT) materials can provide us with a wealth of information about their structure, phonon and electronic properties as well as sample imperfections. The one-dimensional confinement of the phonon and electronic states and the subsequent singularities in the joint density of states for optical transitions in CNTs, result to an easily detectable second-order double resonance Raman signal (either two-phonon or defect-induced). This allows the experimental observation of overtones and combination modes which are, in principle, very weak in condensed matter [1]. Their study provides a means to shed new light on novel aspects of nanotube physics and to enrich the fundamental knowledge in resonance Raman spectroscopy [2].

The dominant feature in the second-order Raman spectrum of CNTs is the energy dispersive G’ band, which is the second harmonic of the disorder-induced D-band. Unlike the D-band, G’ involves a scattering process with the participation of two intervalley phonons having almost opposite wavevectors and allows its observation even in defect-free samples [1]. In this work, we investigate the effect of high

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hydrostatic pressure, up to 10 GPa, on the G’ bands of high quality bundled peapod-derived DWCNTs and the parent SWCNT sample.

2 Experimental

The starting SWCNT material was produced by the pulsed laser vaporization of a carbon rod, while the DWCNT sample was synthesized by the peapod conversion route, following Bandow’s procedure [3]. Details for the synthesis of both DWCNTs and the parent SWCNTs can be found elsewhere [4–7]. Raman spectra were recorded using a microscope equipped single monochromator (Jobin Yvon, THR1000) combined with a liquid-nitrogen cooled CCD detector system. High pressure Raman measurements were carried out using a diamond anvil cell of the Mao and Bell type. The 4:1 methanol–ethanol mixture was used as pressure transmitting medium, while the pressure was monitored using the luminescence of a ruby chip placed inside the cell. The spectra were acquired in the back-scattering geometry with a spectral width of ∼2.5 cm⁻¹, while the 632.8 nm line of a He–Ne laser was used for excitation at a power of 1.2 mW, measured directly before the cell. The phonon frequencies were obtained by fitting Voigtian lineshapes to the experimental peaks.

3 Results and discussion

Figure 1a depicts Raman spectra of the parent SWCNTs in the G’ band frequency region for various pressures. At ambient conditions the G’ peak is located at 2633 cm⁻¹ and exhibits a blue shift and linewidth broadening as the pressure increases.

The corresponding Raman spectra of DWCNTs at various pressures are presented in Fig. 1b. A two peak feature is apparent in the spectrum, with the most intense peak being located at the same frequency as that of the G’ band in SWCNTs and the weaker one appearing at its low frequency side. It is reason-
able to attribute the additional $G'$ component at 2588 cm$^{-1}$ to the smaller diameter inner tubes ($G_{\text{in}}'$) and the $G'$ component at 2633 cm$^{-1}$ to the larger diameter outer tubes ($G_{\text{out}}'$), in accordance with the $G'$ frequency-tube diameter correlation [1]. The pressure dependence of the $G'$ peaks for both SWCNTs and DWCNTs is quasi-linear (Fig. 2), exhibiting small second order coefficients in the parabolic fitting. The linear and quadratic pressure coefficients for SWCNTs and DWCNTs obtained after fitting the experimental data are given in Table 1.

Regarding the pressure response of the DWCNTs, the peak assigned to the $G_{\text{out}}'$ band exhibits much larger linear pressure coefficient than that attributed to the inner tubes ($G_{\text{in}}'$), leading to a clear separation of the two peaks at elevated pressures (Fig. 1b). Additionally, the relative intensity of the $G_{\text{out}}'$ to the $G_{\text{in}}'$ component decreases with increasing pressure. Similar behavior has been also observed in the studied DWCNT sample, excited by the 514.5 nm wavelength [8]. This trend is analogous to that encountered for the pressure coefficients and the relative intensities concerning the radial breathing (RBM) and tangential modes ($G$) of the outer with respect to those of the inner tubes [9, 10]. The different pressure coefficients of the inner and outer tubes, as reflected in the evolution of their first order Raman peaks, have been attributed to the reduction of the effective pressure exerted to the inner tube (pressure screening effect) owing to its encapsulation [9, 10]. On the other hand, the strong intensity attenuation and broadening of the Raman peaks originating from the outer tubes have been attributed to the pressure induced deformation of these tubes [9], in accordance to what has been observed earlier for SWCNTs [11]. The physical origin of the $G'$ mode complicates the interpretation of its pressure dependence as this

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
 & $\omega_0$ (cm$^{-1}$) & $\partial \omega_0 / \partial P$ (cm$^{-1}$/GPa) & $\partial^2 \omega_0 / \partial P^2$ (cm$^{-1}$/GPa$^2$) \\
\hline
SWCNT & 2634 & 17.6 & -0.25 \\
DWCNT & $G_{\text{in}}'$ & 2588 & 5.3 & 0.37 \\
 & $G_{\text{out}}'$ & & 2633 & 23.0 & -0.50 \\
\hline
\end{tabular}
\caption{$G'$ peak frequencies and their pressure coefficients for the studied SWCNTs and DWCNTs.}
\end{table}
can be the sum of two effects. More specifically, pressure application not only causes the tube stiffening but also modifies the resonance conditions, which in turn define the wavevector of the participating phonons in the double resonance process [12]. This picture is even more complicated in DWCNTs due to the inner-outter tube interaction. Despite the anticipated complexity, the pressure screening effect and the larger vulnerability of the outer tubes should be also reflected in the pressure response of the $G'$ components. Consequently, the much smaller pressure coefficient of the $G'_\text{in}$ component and the intensity reduction and broadening of the $G'_\text{out}$ component could be attributed to these effects.

As revealed from Fig. 2 and demonstrated in the results summarized in Table 1, the $G'_\text{out}$ peak exhibits a sublinear pressure dependence with a quadratic coefficient that is two times larger than the corresponding one in SWCNTs. On the contrary, the $G'_\text{in}$ peak shows a superlinear response. These findings are also similar to those observed for the first order $G$ modes attributed to inner and outer tubes and can be explained if we consider that as the pressure increases the inner-outter tube interaction becomes progressively stronger, supporting the outer tubes (reduced slope), while at the same time the inner tubes are increasingly affected by the pressure (increased slope).

It is interesting to compare the results of the present work, where the DWCNT sample is excited by the 632.8 nm wavelength, with our previous results obtained from the same sample excited by the 514.5 nm wavelength [8]. In the latter case, both the $G'_\text{out}$ and the $G'_\text{in}$ bands exhibited almost linear frequency dependencies with pressure coefficients 16.7 cm$^{-1}$/GPa and 7.3 cm$^{-1}$/GPa, respectively. Interestingly, the pressure coefficient for the outer tubes is smaller than that obtained from the present study, while the respective one for the inner tubes is larger. If we focus only on the mechanical response of the DWCNT system, this observation could reflect that the 632.8 nm excitation probes selectively larger inner-outter tube spacings (weaker support of the inner to the outer tubes and larger pressure screening) than those probed by the 514.5 nm line. This consideration agrees well with our recent findings concerning the RBMs of the inner tubes in DWCNTs, where the red excitation probes mainly inner tubes having larger inner-outter tube spacings than those probed by the green excitation [13]. Within this context, the absence of parabolic behaviour in the pressure dependence of the $G'$ component frequencies excited by the green excitation could be ascribed to the stronger inner-outter tube interaction even at ambient or low pressure values. Thus, the simplified picture, where only the tube stiffening and the inner-outter tube interaction are considered, could describe qualitatively the pressure response of the $G'$ bands in DWCNTs. However, a more complete interpretation of the experimental data needs also to take into account the encapsulation- and the pressure-induced changes of the electronic transition energies.

Finally, it is interesting to note the larger linear pressure coefficient of the $G'$ peak for the outer tubes in DWCNTs compared to that for SWCNTs, which is in contrast to what we expect if we consider the support effect for the outer tubes due to the inner-outter tube interaction. Upon nanotube encapsulation, the inner-outter tube interaction causes the shift of the resonance conditions [14]. This results to the probing of different points in the phonon dispersion curves of the outer tubes or even to the probing of different outer tubes than those probed in SWCNTs and could account for the observed behavior.

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