Similarities of the RBM and D Raman bands in double wall carbon nanotubes

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Abstract

We have examined several sets of heterogeneous double wall carbon nanotubes and analysed the frequency in a wide range of values. We have found that a statistical correlation exists between the D band intensity and the RBMs intensity. All the sample sets show a correlation of the RBM and D Raman intensity which is monotonic and non-linear using the 514nm laser excitation. Our results suggest that a similar mechanism is at the origin of the RBM and D bands. These results are corroborated by observations on carbon nanotubes embedded in a polymer matrix. We derive the phonon potential deformation for the D band and extend the excitation wavelength dependence of the D band to the UV. The intensity of the D band decreases with increasing hydrostatic pressure and fanishes at a pressure comparable to what has been observed earlier for the RBM and D* band.

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I. INTRODUCTION

Carbon nanotubes (CNT) have been studied in great detail due their fascinating optical, electronic and mechanical propepties [1]. Many potential applications of CNTs are currently considered and some applications have found their way into products. While the structure of CNTs has been examined using electron microscopy, complementary techniques such as Raman spectroscopy have been found useful in characterizing the structural propertis from mascroscopic amounts to single isolated CNTs. The technique is efficient in evaluating the structure of CNTs. Several bands are typically observed (1) in the low frequency range the radial breathing mode (RBM, 100-500 cm^{-1}), a narrow peak which gives the diameter of the tube and sometimes the chirality if the tube diameter in case of small diameter tubes, (2) the D band which varies with the wavelength at a rate of $50cm^{-1}/eV$ [2] attributed to disorder induced double resonant processes of metallic tubes, (3) the optical phonon band of graphene (G-band) and the overtone bands (D*=2D band 2600 cm^{-1}, 2D+G band at 4200 cm^{-1})[3]. Apart of the RBM all these bands are also observed for graphite [4].

Thomsen and Reich explaind the D-mode frequency shift with excitation wavelength in graphite by considering disorder induced double resonance scattering processes [5]. It is not quite clear whether disorder induced double resonant scattering processes might not also be active in other Raman bands. By analysing the large and the small signal in the CNT spectrum, which includes overtones, Saito et al [3] have been able to derive the phonon dispersion relations of a single CNT. Kurti et al suggest that van Hove singularities in CNTs enhance the double resonance Raman process [6] and related this to the D band shape [7]. CNTs under hydrostatic pressure have shown that certain Raman bands and notably the RBM modes but also the D* band disappear below 2.5 GPa [8–10]. This has been attributed to reversable tube facetting [11]. Tube flattening is proposed to occur at higher pressure (¿10 GPa) [11]. New phases have been observed at large pressure (26 GPa) [12]. The intensity of the RBM is particularly sensitive to the spectroscopic location of the van-Hove singularities. Typical resonance windows of 20-60 meV are observed for isolated tubes.[13, 14] Other low frequency vibrational modes of CNTs are not experimentally observed. The G band intensity is found to be less sensitive to the excitation wavelength. Jorio et al [15] showed that the G band is mainly caused by single resonance scattering processes. We explore here the relative correlations of the Raman band intensities to see whether the double resonance scattering

process is compatible with the experimental observation for other bands than the D band.

II.   EXPERIMENTAL DETAILS

The double wall CNT (DWCNT) were prepared by the catalytic chemical vapour deposition method (CCVD) [15]. High-resolution electron microscopy (HRTEM) images showed DWCNTs with radius ranging from 0.5 to 2.5 nm. The tubes are arranged in small bundles with very few other graphitic forms of carbon. The tubes are single, double (80 %) or triple walled.[16, 17]. One set of tubes were filled at $450°C$ by capillarity filling by PbI_2 [18]. From the HRTEM observations, the filling yield was between 60 % and 70 %. Pressure studies (25GPa) have been carried out using a diamond anvil cell with a methanol-ethanol mixture (4:1 by volume mixture) as pressure-transmitting medium. The pressure was monitored using the luminescence of a ruby chip inside the cell. The agglomerated DWCNTs were first dispersed by sonication before loading into the pressure cell. CNT composites were prepared as follows. A dispersion of CNTs in water was first sonicated for 1 h before addition of epoxy resin which was then dried in a vacuum at $100°C$. Palmitic acid was added and the suspension was again sonicated for 1 h at room temperature. After the addition of the hardener, the final mixture was cured at $120°C$ for 20 min and $145°C$ for 4 h [19, 20]. The polymer composite contained 0.4 wt % of palmitic acid and 0.4 wt % of CNT. The CNTs used for the preparation of the composite contained 50 % single, 35 % double and 15 % three or four walls [21] CNTs (average radius of 1.5 nm). The composite samples were successively polished with alumina powder of 10, 1, and 0.01 mum in size in order to have a flat surface for Raman mapping. We assume that the CNTs concentration is sufficiently low and the sampled volume sufficiently large so that the polishing process does not influence the Raman measurement. Raman spectra were recorded at room temperature using a Renishaw Raman microprobe instrument (microscope objective: ×100, excitation wavelength: 514.5nm). The output laser power was kept below 1 mW to reduce laser heating.

III.   EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 1 compares the intensity of the radial breathing mode and the defect induced D-band by recording Raman spectra of tubes. All RBM and D bands were normalized with

4

the G-band intensity of the same spectra. To reduce the error we only consider spectra with a G band intensity larger than 200cps/mW. We show the result of three sets of samples. First we observe that the D band is less than half the intensity of the G band and the RBM bands less than 1/6 of the G-band. Secondly, we observe that the RBM intensity is correlated to the D-band intensity. The correlation is close to linear for DWCNTs, but is non-linear for PbI_2@DWCNTs. The intensity of the RBM band is increased and D band is reduced for PbI_2@DWCNTs in the case of pressure cycled PbI_2@DWCNT.
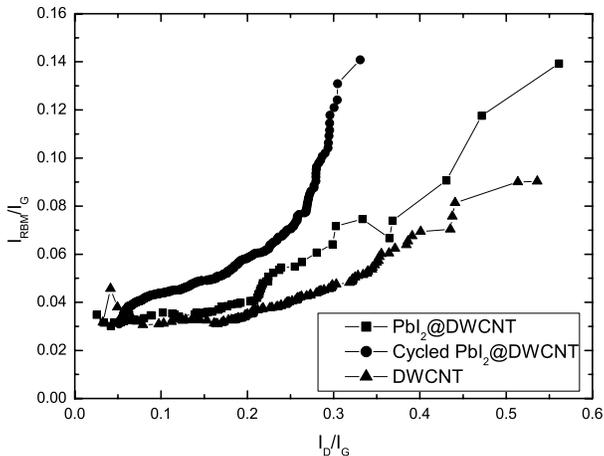

FIG. 1: Intensity of the RBM band as a function of the intensity of the D band.

Fig. 2 shows a series of spectra recorded for PbI_2 filled DWCNTs after they have been exposed to a pressure of 25GPa using the 514.5nm laser excitation. The spectra have been sorted according to the function of the D band intensity. We observe RMB modes between $180cm^{-1}$ and $350cm^{-1}$. Using the Kataura plot [14, 22] we expect to probe with the 514.5nm excitation preferentially semiconducting tubes at the E_{33} energy gap for tubes diameters falling in the 0.9-1.1nm range which corresponds to tubes with 24 different chiralities (helicities). The E_{11} energy gap falls also in the same range for small diameter metallic tubes (0.7nm). 190 cm^{-1} and 205 cm^{-1} can be associated to 1.24 nm and 1.13 nm tube diameter and can correspond to the (11,7) and (14,1) chirality respectively. In the range of 250 cm^{-1}, we found two main peaks, one located at 245 and the other at 265 cm^{-1}. These peaks correspond to tube diameter of 0.94 and 0.88 nm respectively. With the 515 nm wavelength, metallic tubes on the E_{11m}transition are excited. The tube chirality could

be (7,7) and (8,5) respectively. The highest energetic peak is located at 310 cm^{-1} and could be associated to the (6,5) semi-conducting tube (d=0.74 nm) but the E_{22s} transition is far from the exciting wavelength (about 0.3 eV). This peak is stronger with filled tubes.

We find again a clear correlation of the intensity of the RBM peaks with the intensity of the D band. The D* band however is not correlated, the intensity stays much the same with some change in the line shape and compares well with what is observed for HOPG. We find only little differences between the DWCNT and the DWCNT filled with PbI$_2$ in agreement with similar work [23] and we find only little modification of the G band after a pressure cycle (25 GPa) of the filled DWCNTs. The asymmetry on the lower energy side of the G-band becomes larger after the pressure cycle. The shape of the G band is found to be unchanged for all the recorded spectra whereas the shape of the D* band varies. We find that the normalized G+D overtone band intensity is correlated to D band intensity. But no correlation between the D* and D band is observed.
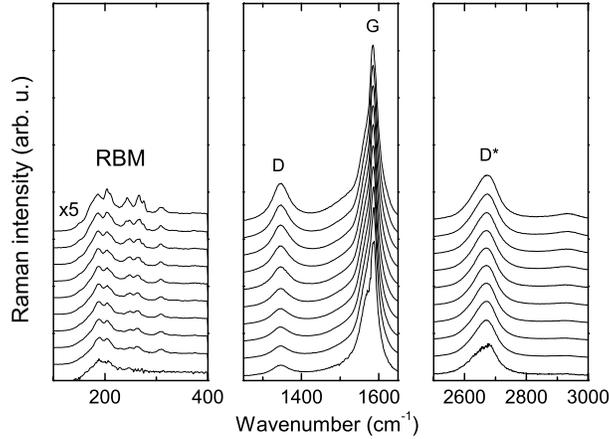

FIG. 2: Transformed DWCNT filled by PbI2 after a pressure of 25 GPa acquired in the hole gasket. The spectra are sorted by D band intensity.

We examined the D-mode shift of DWCNTs as a function of excitation energy. In the visible range we observe the same results as found in the literature for graphite and SWCNTs [24].We have extended the energy to the UV range and we find that the D band shift is constant up to 4.5 eV. For the value at 4.5 eV we used the energy band position of D* band to deduce the position of the D band. At 4.5 eV the D band intensity is much reduced in Fig. 3. The D-band shifts for DWCNT's at a rate of $50cm^{-1}/eV$ for an exciting energy

ranging from 1.7 to 4.5 eV. This energy shift as a function of excitation energy has been explained by Thomsen et al. by defect induced double resonance processes [5]. The D band is also observed for ion implanted HOPG [4] and other forms of disordered forms of graphite related structures and is not related to the particular form of the electronic structure of the tubes. The fact that the D band disappears (reduced by two orders of magnitude) at 4.5eV but the G band is not affected, clearly suggests that the scattering processes are different for the two bands and that double resonance effect is less important for the G band [15].
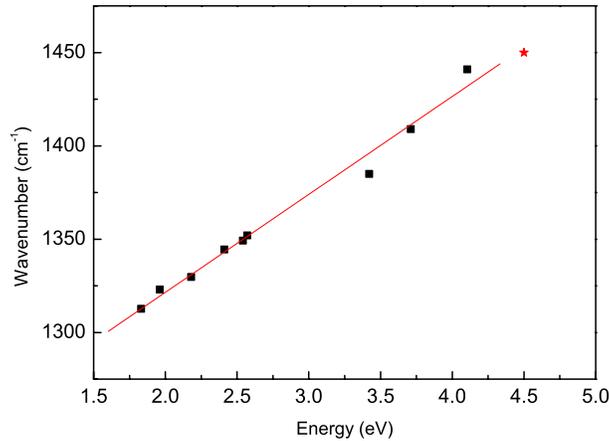

FIG. 3: Frequency of the D band in air as a function of the exciting wavelength. The star corresponds to the value deduced from overtones.

As reported by Wood et al, the D* band position is particularly sensitive to the external pressure and is suppressed for pressures larger than 2.2 GPa.[10] Similarly we can observe a decrease of the D and D* band intensities associated with CNT composites. The tube surrounding in the composite appears to play the same role as the external pressure.[10] Consequently, the spectra recorded at various places in the heterogeneous composite can present a strong G-band shift as reported in Fig. 4.

We now correlate the energy band position (Fig. 5) and intensity (Fig. 6) of the D band with respect to the G band position. The D and G band positions are clearly correlated. While the G band shift ranges within $20cm^{-1}$, D band shift ranges within $10cm^{-1}$. Fig. 6 shows that the D band intensity is anticorrelated with the G band position. Low G band positions results in a more intense D band. The statistical effect described in the first part is averaged here and leads to some fluctuations in Figs. 5 and . 6.
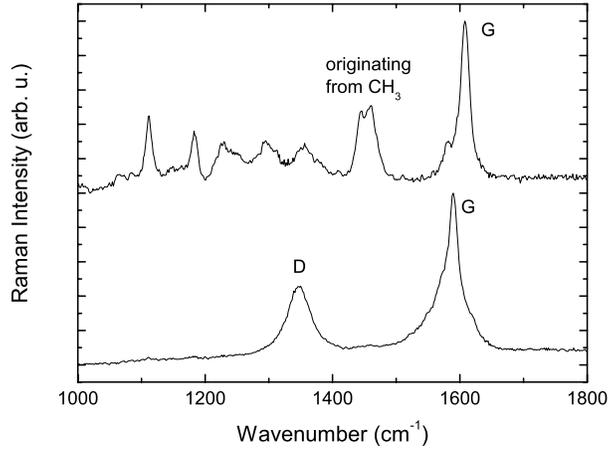
FIG. 4: Two typical spectra obtained on an heterogeneous composite (0.4 % in weight of CNT and 0.4 % in weight of palmitic acid).

We find for the hydrostatic pressure coefficient of the D band, which is in part masked by the diamond signal of the anvil cell at 1355 cm^{-1} in hydrostatic experiment :

$$\frac{\Delta\omega_D}{\Delta\omega_G} = 0.51 \text{ and } \frac{\Delta\omega_{D^*}}{\Delta\omega_G} = 1.0$$

The disappearance of the D band corresponds to the same estimated pressure than for the D* band, in the range of 2-3 GPa. We note that D* band shift is twice the D band shift.

The RBM intensity decrease can be associated to pressure induced electronic band structure changes. The resonance profile window shows a line-width of 60 meV for isolated tube.[13, 14] Nevertheless, even if the pressure shifts the van-Hove singularities, the disappearance of the RBMs is unlikely to be due to this effect.

It has been proposed that the pressure leads to structural distortion [25] but recent ab-initio calculations suggest that distortions are not energetically stable [26]. Other authors have been able to follow the RBM to higher pressure and a significant change in the pressure coefficient is observed before the RBMs disappear [27]. Provided the double resonant scattering process plays a role, the disappearance could be related to the change of the conditions for disorder induced resonant scattering processes when a pressure is applied.

The RBM, D and D* bands are clearly related when considering the pressure dependence of the band positions. While the G band has a little smaller intensity with increasing
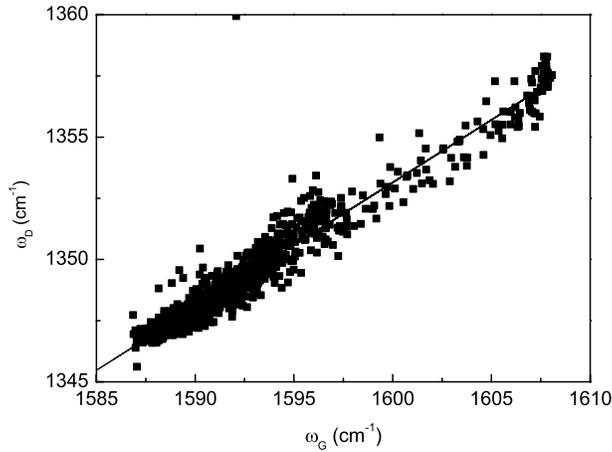
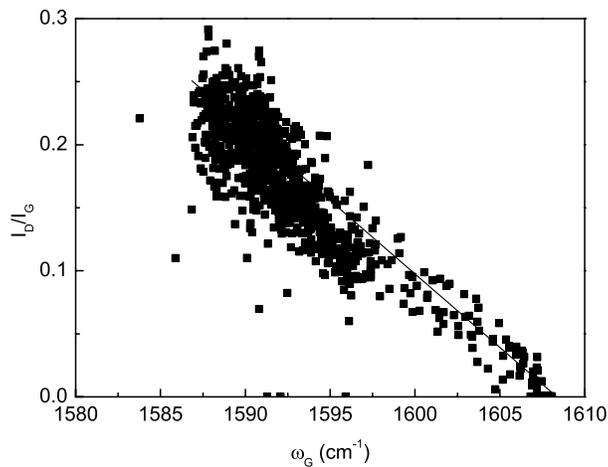FIG. 5: Frequency of the D band versus the frequency of the G band.

FIG. 6: Intensity of the D band versus the frequency of the G band.

pressure, it still persists and does not disappear as observed for the D, D* and RBM bands. Its has been shown that the D band can disappear completely when annealing the tubes [28] even if disordered forms of carbon could sometimes be observed on the surface of the CNTs. It is important to point out that in some cases no D band is observed at all even if RBM bands can be observed. This is in contrast with the fact that there is no report so far known to us where no D* band have been observed.

Thomsen [24] has suggested that the entire Raman spectrum might be dominated by

double resonance scattering processes. For the G-band, it seems that single resonance effects are stronger[15]. Whatever the resonance effect, strong one dimensional singularities in the electronic density of states are expected to enhance the scattering cross-section [6] and complicate the analysis.

The correlation of RBM intensity with the D band intensity suggests that some similar resonant mechanism acts in both cases. The fact that RBM modes can be seen in some cases where no D band is observed indicates that the RBM intensity is not entirely caused by the same scattering process as for the D band. Thomsen has indicated that if RBM is due to double resonant process, the Raman peak frequency does not necessarily correspond to the Γ-point frequency of this mode[29]. Unfortunately, no significant effect on the frequency is expected by varying the wavelength as the phonon dispersion of the RBM is nearly flat close to the Γ-point and the resonant window is limited to 60meV due to van-Hove singularities. While the correlation of the RBM and D bands suggests that the RBM modes are caused by double resonant processes, the small spectral window limits to verify the spectral dispersion as observed for the D band.

IV. CONCLUSION

We have shown for different sets of DWCNT samples with a large size distribution, that the intensity of the D band is correlated with the intensity of the RBM band. The correlation coefficient between both bands depends on filling and the history of the sample as well as its composition. In polymer composite, we observe a clear correlation in the D and G band positions which we use to derive the phonon potential deformation for the D band. The pressure medium affects the RBM and D band intensities, leading to a disappearance of both at low pressure. These observations suggest that both are caused by a similar resonant process.

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11

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