Surrounding effects in single-walled and multi-walled carbon nanotubes

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ABSTRACT

The low frequency RBM observed in SWNTs has been proved to probe efficiently their diameter distribution. We have built a model to estimate the interactions between individual nanotubes when arranged in bundles which leads to a RBM upshift of 10 to 20 cm⁻¹. In a PMMA-SWNTs composite, our model shows that an upshift can be also predicted as due to the stress applied by the polymer on the bundles upon breathing. Finally, the interaction between concentric layers in MWNTs can lead to low frequency modes originating from the RBM of individual tubes as observed experimentally.

INTRODUCTION

Carbon nanotubes are fascinating materials which are extensively studied nowadays, both from the fundamental point of view or for their potential applications [1]. Several techniques are used to characterized them. Indeed, electron or near field microscopies are well adapted to the study of these objects at the nanometric scale. On the other hand, one frequently needs to characterize the materials at a macroscopic scale. Raman spectroscopy is very powerful for this purpose[2]. First order Raman spectra of carbon nanotubes can be divided into three parts. The high frequency region (1500-1600 cm⁻¹) reveals the intense tangential modes of nanotubes. The 1200-1400 cm⁻¹ part of the spectra shows the so-called D-band of graphitic materials which is sensitive to the degree of disorder. In this paper, we will focus on the low frequency region (100-250 cm⁻¹) of the spectrum which reveals the radial breathing mode (RBM) of single walled nanotubes (SWNTs). The RBM are especially interesting since they seem to be a unique signature of SWNTs. Furthermore their eigenfrequencies scale inversely with the nanotube diameters. The experimental low frequency Raman spectra give thus a picture of the nanotube diameter's distribution in macroscopic samples.

Actually, the situation may be more complex. It was suggested recently that the breathing vibrations of SWNTs are affected when they are arranged in bundles [3-4]. Furthermore, low frequency modes have also been observed in multiwalled nanotubes (MWNTs) samples [5]. In this paper, we present theoretical considerations supported by experimental results which show that the RBM is affected by the surrounding of the individual tube. First we propose a simple model to reveal the bundle effect. We show how this effect is affected when embedding the SWNTs in a polymer matrix. It gives an indirect experimental proof of the bundle effect. Then we use the same model to explain why low frequency modes are also observed on MWNTs.
EXPERIMENTAL

SWNTs and MWNTs were produced by the arc discharge technique in GDPC Montpellier and TCD Dublin respectively. The SWNTs sample were purified according to the Liu’s procedure [6]. Raman spectra were obtained using a Jobin Yvon T64000 Spectrometer with 514.5 nm and 676 nm excitations for SWNTs and MWNTs samples respectively. SWNTs/PMMA composites were elaborated by dispersing SWNTs and PMMA in toluene. The solution was ultrasonically homogeneized. Homogeneous and transparent composite thin films with SWNTs/PMMA mass fractions less than 1% were deposited by spin coating.

RESULTS AND DISCUSSION

Bundle effect:

The 100-250 cm\(^{-1}\) part of the Raman spectrum of purified SWNTs is shown in Figure 1a. Several peaks with frequency ranging from 144 to 178 cm\(^{-1}\) are observed. Indeed these peaks are due to RBM of nanotubes. However when arranged in bundles, the Van der Waals interaction between nanotubes influences the breathing vibrations of individual nanotubes. Actually, it hinders the breathing vibration upshifting the mode. We propose the following model to discuss this effect.

Finite bundles are described as 2D hexagonal packing of nanotubes with an hexagonal shape (D\(_{6h}\) symmetry): bundles of 7, 19, 37 ... nanotubes are thus generated. All the (infinite) tubes of a bundle are supposed to be identical (same diameter, same chirality, same polarisability tensor). The carbon-carbon long range interaction is described within a Lennard-Jones potential. The adjacent tube-tube interaction is deduced from the mutual integration of this potential when assuming a continuous mass density over the tubes. The tube-tube force constants are obtained from the second derivatives of the interaction. These force constants \(C\) depend on the two adjacent graphene interplane force constant \(C_g\) and scale with the reciprocal square root of the tube diameter \(d_0\) [8].

Figure 1: Low frequency part of the Raman spectrum of (a) purified SWNTs (b) PMMA/(0.5%SWNTs) composite (c) PMMA/(0.75%SWNTs) composite (d) restored SWNTs after PMMA dissolution

Figure 2: Low frequency part of the Raman spectrum of a high quality MWNTs sample.
\[
\frac{C}{m_c} = \frac{\tau}{\sqrt{d_0}} \quad \text{with} \quad \tau \propto \frac{C_g}{m_c}
\]  

(1)

Let us start with a bundle of seven tubes (an inner tube and one adjacent layer of neighbouring tubes) for which the breathing mode frequency when isolated is \(\omega_0\). In the bundle, the seven individual breathing modes will be coupled to give seven new modes. Within the D\(_{6h}\) symmetry, only two of them are Raman active with \(A_{1g}\) symmetry. In our model, the most intense is the one for which all the tubes vibrate in phase. Its frequency \(\omega_1\) is obtained through the numerical diagonalization of the dynamical matrix. It gives:

\[
\omega_1^2 = \omega_0^2 + n \frac{C}{m_c}
\]

(2)

with \(n=8\) for the seven tubes bundle. Increasing the bundle size will increase \(n\) from \(n=8\) to \(n=12\) in the case of the infinite bundle. The convergence is quite fast. As mentioned earlier, \(C\) depends on the interplane force constant \(C_g\). We extract this force constant from the \(B_{1g}\) graphite mode at 127 cm\(^{-1}\) [8]. \(C_g = 2.3\) N/m is used.

In Table 1, we report the results of our calculation for \((n,n)\) armchair nanotubes. The RBM of isolated \((n,n)\) tubes is derived using a valence force field model [9] which gives \(\omega_0(\text{cm}^{-1}) = 2230/d_0(\text{Å})\) in agreement with other works. \(\Delta \omega\) is the upshift of the frequency when taking into account the bundle effect. The two extreme cases are given: the seven tubes bundle (smallest effect) and the infinite bundle. The expected bundle effect is of the order of magnitude of 10-20 cm\(^{-1}\). It depends on the size of the bundle and it increases with the nanotube diameter. The bundle effect was also discussed by Henrard et al. [3] and Khan et al. [4]. They found an upshift for the \((10,10)\) armchair tube RBM of 6 cm\(^{-1}\) and 15 cm\(^{-1}\) respectively to be compared with our results 11-16 cm\(^{-1}\).

Of course, an experimental confirmation of the effect should be appreciated. While it is out of the state of the art for the moment, an indirect confirmation can be obtained when inserting SWNTs in a polymer matrix.

### Table 1: Upshift of the RBM due to Bundle effect for a \((n,n)\) armchair tube of diameter \(d_0\). \(\omega_0\) is the RBM frequency when isolated. \(\Delta \omega\) gives the minimum and maximum upshift (see text).

<table>
<thead>
<tr>
<th>(n)</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d_0) (Å)</td>
<td>10.8</td>
<td>12.2</td>
<td>13.6</td>
<td>15.0</td>
<td>16.3</td>
<td>17.6</td>
<td>19.0</td>
<td>20.3</td>
</tr>
<tr>
<td>(\omega_0) (cm(^{-1}))</td>
<td>205.6</td>
<td>182.7</td>
<td>164.5</td>
<td>149.5</td>
<td>137</td>
<td>126.5</td>
<td>117.5</td>
<td>109.6</td>
</tr>
<tr>
<td>(\Delta \omega) (cm(^{-1}))</td>
<td>10.0-14.8</td>
<td>10.1-15.6</td>
<td>11.0-16.3</td>
<td>11.5-17.0</td>
<td>12.0-17.6</td>
<td>12.4-18.2</td>
<td>12.8-18.8</td>
<td>13.2-19.3</td>
</tr>
</tbody>
</table>

**Matrix effect:**

As can be seen in Figures 1b and 1c, the low frequency Raman spectrum is significantly affected when SWNTs are embedded in the PMMA matrix. The overall feature is upshifted by \(~10-20\) cm\(^{-1}\), the maximum peaks now at 180 cm\(^{-1}\) instead of 160 cm\(^{-1}\). This effect is reversible. As shown in Figure 1d, the pure SWNTs spectrum is restored when the PMMA matrix is destroyed by thermal annealing under vacuum at 400 °C. Embedding SWNTs in a matrix results thus in a hardening of the RBM. We suggest that the physical origin of this matrix effect is...
equivalent to the classical modification of the eigenfrequency of a vibrating cord when immersed in water. In a composite, the breathing motion of the tube imposes a dynamic stress to the PMMA which in turn hinders the vibration. Knowing the elastic constants (Young modulus $E$ and Poisson ratio $\nu$) of PMMA [10], we can give a quantitative estimate of this effect using classical dynamics. Two situations can be envisioned.

In the first one, we assume that the polymer intercalates the tubes within a bundle. The breathing vibration of amplitude $\Delta r$ for a tube with radius $r$ induces internal stresses on PMMA. The polymer responds with a radial force given in the hydrostatic elastic regime by:

$$ F = \frac{E}{1 - 2\nu} \left( \frac{\Delta r}{r} \right) S $$

per surface area $S$ of tube. We write the equation of motion in the radial direction by relating the $\Delta r$ amplitude of the breathing motion to the CC bond length elongation. The breathing frequency in this model is given by:

$$ \omega^2 = \frac{C_1 a^2}{m_c r^2} \left( 1 + \frac{3\sqrt{3}}{4} \frac{E}{1 - 2\nu} \frac{r}{C_1} \right) $$

where $C_1$ is the CC force constant, $a$ is the CC bond length. In the absence of polymer effect, we recover the usual relationship between the breathing frequency and the nanotube radius $\omega_0$ (cm$^{-1}$) = 1116/r (Å) in agreement with more sophisticated treatments. When the tube is surrounded by the polymer, the RBM is upshifted. However the effect is of the order of 3% for a (10,10) tube i.e. of 5 cm$^{-1}$. It seems too small to explain our observation. Furthermore, HRTEM observations after the destruction of the polymer matrix do not show any significative modification of the morphology of our sample. It suggests that the polymer does not intercalate the bundle.

In the second situation we assume that the polymer just surrounds the bundle. In this case, the stress induced force will apply on the whole bundle upon breathing. If we neglect the single tube effect described above, it is equivalent to a reinforcement of the tube-tube interaction when in-phase breathing occurs. We can introduce an effective force constant which replaces the interplane force constant discussed previously and which is meaningful only for dynamic motion:

$$ C_{eff} = C_g + \frac{E}{1 - 2\nu} d_{VdW} $$

where $d_{VdW}$ is the Van der Waals distance ($d_{VdW} \sim 3.4$ Å) and $C_g \sim 2.3$ N/m is the interplane constant. Using this effective constant within the previous model leads to a polymer effect in the range of 11-16 cm$^{-1}$ for (10,10) tubes. Indeed this effect is additive to the bundle effect. It is in agreement with our observations. It gives also an indirect proof that the bundle effect is really effective in carbon nanotubes.

**Radial breathing mode in multiwalled nanotubes:**

Surprisingly, low frequency modes from 120 to 200 cm$^{-1}$ are also observed in MWNTs as shown in Figure 2. The growth conditions as well as HRTEM observations exclude the presence of SWNT's in the sample. Observations of low frequency modes in MWNTs samples have
already been reported by other groups[5]. We are thus pretty confident that these modes originate from MWNTs. HRTEM shows that the investigated MWNTs are highly graphitized with typically 3-10 perfect and concentric graphene layers. We do not observe low frequency modes in poorer graphitized samples.

Calculations of vibrational modes in MWNTs face the difficult problem of the registry of the different graphene layers in a MWNT. To our knowledge, such a registry does not occur. We propose thus to investigate these modes starting from the SWNTs and adding the Van der Waals interaction. Regarding the low frequency modes, we will thus couple in a classical way the breathing modes of individual shells through the shell-shell interaction. We start from a MWNT with an inner radius \( r_1 \), an outer radius \( r_N \) and \( N \) shells. The isolated shells of radius \( r_i \) are SWNTs with breathing mode frequency \( \omega_{0i} \propto 1/r_i \). We need to estimate the shell-shell interaction. We use the same procedure as discussed above. The concentric tube-tube interactions are derived from the Lennard-Jones potential by mutual integration. We limit our calculation to first neighbouring shells. Within this limitation, the tube-tube interactions are found essentially diameter independent with force constants close to \( C_g \approx 2.3 \text{ N/m} \). This difference with respect to adjacent tubes (formula (1)) is indeed due to the geometry. Starting from the \( N \) isolated breathing modes, the \( N \) new modes of the MWNTs are obtained by diagonalizing the dynamical matrix. In Table 2 we present the results of the calculation for a typical 6-walls tube, inner and outer diameters 13.6 Å and 47.6 Å respectively. \( \omega_{0i} \) is the frequency of the RBM of the isolated shell number \( i \), \( \omega_i \) is the frequency from our calculation. One can note that all the modes appear at higher frequency than in the isolated case. As expected, the most important upshift (~40 cm\(^{-1}\)) is obtained for the middle shells. It has also to be noticed that starting from a situation where four RBM have frequencies below 100 cm\(^{-1}\), we find now four modes in the 110-190 cm\(^{-1}\) region.

This simple model may explain why low frequency modes are observed in highly graphitized MWNTs. We suggest that they arise from the shell-shell coupling of the RBM of neighbouring shells. Still this model needs to be improved to take into account the intensities of the resulting modes. The assumption that all the shells have the same polarisability tensor is obviously not valid here. It leads to the fact that the most intense mode corresponds to the lower frequency, which is not observed. Preliminary calculations indicate that the polarisability is higher for the inner shells than for the outer ones which makes the higher frequency modes more intense.

### Table 2: Low frequency modes of a 6-shells MWNTs. \( d_i \) is the diameter of the shell number \( i \), \( \omega_{0i} \) is the RBM frequency of this shell when isolated, \( \omega_i \) is the frequency of the corresponding mode in the MWNTs.

<table>
<thead>
<tr>
<th>( d_i ) (Å)</th>
<th>13.6</th>
<th>20.4</th>
<th>27.2</th>
<th>34.0</th>
<th>40.8</th>
<th>47.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega_{0i} ) (cm(^{-1}))</td>
<td>163.9</td>
<td>109.3</td>
<td>82.0</td>
<td>65.6</td>
<td>54.6</td>
<td>46.8</td>
</tr>
<tr>
<td>( \omega_i ) (cm(^{-1}))</td>
<td>178.0</td>
<td>139.8</td>
<td>122.4</td>
<td>106.6</td>
<td>85.0</td>
<td>55.0</td>
</tr>
</tbody>
</table>

### CONCLUSION
In summary, we propose here both theoretical and experimental considerations which show that the low frequency modes in carbon nanotube materials are extremely sensitive to the surrounding of the individual single walled tubes. Three cases have been investigated. The Van der Waals interaction between adjacent SWNTs in a bundle leads to an upshift of the RBM which is found in the range of 10-20 cm$^{-1}$. This shift depends on the tube diameter and on the bundle size. When the bundles are surrounded by a polymer matrix in a composite, an additional shift of $\sim$10 cm$^{-1}$ appears due to the stress induced force applying on the bundle upon breathing. This effect gives an indirect proof of the bundle effect. The Van der Waals interaction is also able to couple the breathing modes of the individual shell of a MWNT leading to low frequency modes in highly graphitized MWNTs, in agreement with experimental observations. Further works are needed to clarify this effect in more details.

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REFERENCES:

[7] This scaling reflects the number of interacting carbon atom pairs
[10] for PMMA: Young modulus E=3.3 GPa, Poisson ratio $\nu$=0.3

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