Wall thickness effects on the infrared spectra of multi-walled carbon nanotubes

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Abstract. In this theoretical work, we investigate the infrared vibrational features of multi-walled carbon nanotubes (MCNTs). We calculate the polarized infrared spectra of multi-walled carbon nanotubes using the spectral moment’s method. This original approach allows us to consider MCNTs with a large number of walls. We discuss the evolution of the low, intermediate and high wavenumber regions of these spectra as a function of the inner diameter and the size of MCNTs. Both the XX and ZZ polarisations are considered. Our results provide benchmark theoretical data for understanding the experimental infrared spectra of MCNTs.

1. Introduction
Since the time of their discovery [1,2], many efforts were taking to study Carbon nanotubes (CNTs). They became more and more popular to the scientists due to their various remarkable chemical, physical and mechanical properties [3,4]. These characteristics open the way for their use in many applications [3-5]. Initially, the electronic and optical properties give them the great interest. The ability to engineer them offers exciting possibilities for photovoltaic with hydrogen storage applications [6,7]. Many forms exist of CNTs, namely single-walled carbon nanotubes (SCNTs), double-walled carbon nanotubes (DCNTs) and multi-walled carbon nanotubes (MCNTs) [8].

The MCNTs forms like a concentric graphene layer rolled in a cylindrical form, the diameters are around tens of nanometers [9]. There are many developed synthesis methods to fabricate both SCNTs and MCNTs. The most promising method for producing CNTs is the catalytic vapor chemical deposition (CVD) [10]. Either SCNTs or MCNTs can be produced for many applications [11-15]. It depends on the operating conditions and the catalyst system used.

Raman spectroscopy has provided a powerful technique for studying the CNTs. It is used to investigate the vibrational properties of CNTs in relation to their structural and electronic properties [16,20]. Various kind of carbon nanotube forms can be analysed by the Raman spectroscopy including SCNTs, DCNTs and MCNTs. Since the Infrared activity is related to a dynamic dipole moment that is weak, the Infrared spectroscopy of CNTs has been neglected. Nevertheless, a surprising number of phonon mode bands are IR-active through transient dipole.
Various optical spectroscopy tools cannot be applied directly to MCNTs because of multiple absorptions and emissions between concentric cylindrical structures. We note that, in the literature, there are very few infrared investigations on SCNTs and on MCNTs. We observed two regions, where vibrational structure is apparent: around 1200 and 1584 cm\(^{-1}\)\[22\]. The first band at 1200 cm\(^{-1}\) arises from the translational symmetry of the diamond lattice \[23\]. The second one has been appeared in the range of the E\(_{1u}\) infrared active-modes of graphite at 1590 cm\(^{-1}\) \[24\].

Many works on the phonons in MCNTs using the Raman spectroscopy have been devoted \[25-27\]. In this context, the Raman spectra of infinite MCNTs have been calculated in a previous works \[26, 27\]. To have a deeper insight on the vibrational properties of MCNT, the aim of this study is to identify the IR active-modes in MCNT.

In this paper, the IR calculated spectra of MCNTs in the breathing-like Mode (BLM), intermediate-like mode (ILM) and tangential-like mode (TLM) ranges were investigated. We report the dependence of wavenumber on walls number in MCNT and on the innermost tube diameter. The main aim of the present paper is to use our results in the interpretation of experimental IR features of MCNTs.

2. Models and Computational Methods
A MCNT consists of concentric single-walled carbon nanotubes (SCNTs) greatly spaced by intermolecular distance \(d=0.34\) nm close to the interlayer distance in graphite. In MCNTs, the relation between the diameters, \(D_1\) and \(D_N\), of the inner and outer tubes is \(D_N = D_1 + 2(N-1)d\), where \(N\) is the number of walls tube forming the MCNT. The C-C interactions between the carbon atoms of each layer are described using the force constants model published by Saito \[28\] and previously employed to simulate the IR and Raman spectra of SCNTs \[9,11,26\]. The inter-tube interactions are described by the Lennard-Jones potential, given by the following expression:

\[
U_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
\]  

(1)

The parameters values of the Lennard-Jones were chosen as \(\epsilon = 2.964\) meV and \(\sigma = 0.3407\) nm. The IR absorption intensity of the spectrum is given by \[29\]:

\[
I_\alpha(\omega) = \frac{\omega}{n c} \sum_j \frac{|a_j|}{2\omega_j} \left( \delta(\omega - \omega_j) - \delta(\omega - \omega_j) \right)
\]  

(2)

With

\[
a_{j\alpha} = \sum_k \frac{q_k}{\sqrt{M_k}} e_j(k\alpha)
\]  

(3)

c and \(n\) are respectively the speed of light and the refractive index of the material. \(q_k\) is the effective charge tensor and \(M_k\) the mass of the \(k^{th}\) atom. \(e_j(k\alpha)\) and \(\omega_j\) are the \((k\alpha)\) component of the displacement amplitude and the wave number for the \(k^{th}\) atom \((\alpha\) is Cartesian coordinate) in the \(j^{th}\) mode. A usual method to simulate the IR spectra consists of injecting in the previous expressions the values of \(\omega_j\) and \(e_j(k\alpha)\) obtained by direct diagonalization of the dynamical matrix \(\tilde{D}\) of the system by resolving the equation

\[
\tilde{D} |j\rangle = \omega_j^2 |j\rangle
\]  

(4)
To enhance the IR response of the systems, dynamical effective charges on tied carbon atoms were fixed at $q_A = +1$ and $q_B = -1$ for a given A-B bond.

### 3. Results and Discussion

In this section, we focus on the calculated IR lines for infinite MCNTs, which are obtained by applying periodic conditions. In order to identify all IR active modes and their symmetries, we present in Figure 1 the ZZ (dashed lines) and XX (solid lines) calculated IR spectra for typical zigzag MCNTs, as a function of the number of the single tube in individual MCNT $N=3, 4, 5,$ and $6$. The spectra are displayed in the Breathing-like Modes (BLM) (right), intermediate modes (middle) and tangential-like modes regions (TLM) (left).

![Figure 1](image_url)

**Figure 1.** The ZZ (dashed lines) and XX (solid lines) calculated Infrared spectra for typical zigzag (9,0) MCNTs (Din=0.7nm), as a function of the number of walls in individual MCNT $N=3, 4, 5,$ and $6$. The left panel is the BLM region, the middle is the intermediate region and the right panel is the TLM one.

The results for a typical zigzag MCNTs show that, in TLM region, spectra present many peaks, located between 1580 and 1595 cm\(^{-1}\), corresponding to active modes for each individual tube of MCNTs. When the number of tubes increases, this region is dominated by a strong peak around 1589 cm\(^{-1}\) for both polarizations. As a consequence, a strong band located in the TLM region is expected to be experimentally observed. More generally, since the sample is a multilayer tubes of different sizes, formed of tubes for different diameters and chirality, a broadening of the TLM band is expected in the IR spectra measured for MCNTs macroscopic samples.

In the intermediate wavenumber (ILM) range, for a given number of tubes $N$ of MCNTs, we found that the infrared spectra present $N$ modes for XX polarization, located between 865 and 890 cm\(^{-1}\). Independently of the number of layers, no infrared-active mode appears in the ZZ polarization. A dominant mode located at 870 cm\(^{-1}\) is predicted, independently of the number of layers. In a real sample, the number of tubes in a multilayer tube varies from a few tubes to ten of tubes. As a consequence, a broad band located in the intermediate range is expected in the experimental infrared spectrum of a MCNTs macroscopic sample.

In the BLM region, we note the same behaviour of active modes in the intermediate one. The spectrum presents $N$ modes for both polarizations, for each individual tube forming the system. In this region, also we can note that the vibration of the most internal and external layers are the intense modes. However, when the number of tubes increases, their intensities decrease.
To illustrate the in-phase and the counter-phase collective motions of inner and outer tubes, we plot in Figure 2 the eigenvector displacements of the E₁ BLM

![Image of eigenvector displacements](image)

**Figure 2.** BLM and ILM atomic displacements for selected E₁ modes in the (5,5)@(10,10)@(15,15) 3-CNT. The arrows indicate the magnitude and direction of C atom displacements and ILM for (5,5)@(10,10)@(15,15) triple-walled nanotubes (3-CNT). These vectors allow us to identify the mixing of tangential and radial character of these optical modes: (165,895), (251,878) and (470,870) cm⁻¹ for in phase, mixed-phase and counter-phase modes, respectively. From these results, we conclude that the inner tube diameter and the number of layers in the MCNTs are two parameters of primary importance. In comparison with SCNTs Raman spectra, we note that the BLM region of MCNTs is characterized by an upshift of the frequency modes. The ILM and TLM modes regions of SCNTs are slightly affected by MCNTs.

We report in Figure 3 (right), the XX polarized calculated infrared spectra for the zigzag MCNTs in the BLM region for three innermost diameter tubes D_{in} = 0.7, 1.22, and 2.5 nm. The number of layers were fixed to N=15 tubes. In the left of Figure 3 spectra are displayed for four values of N=5, 10, 15, and 18 with innermost diameter fixed to D_{in} = 0.7 nm. We note at highest wavenumbers (Figure 3 on the right) that the modes originate from the inner tube and the intensity of these modes decreases when the inner diameter wall increases. As we can see these modes are too weak to be easily observed for MCNTs with large inner diameter wall. Concerning the MCNTs spectra dependence with N walls (Figure 3 on the left), with fixed inner diameter, the two modes at highest wavenumbers are strongly sensitive to the number of walls. The intensity of all modes decreases when the number of tubes increases.

To illustrate the intermediate wavenumber dependence on the number of walls in MCNTs and on the innermost tube diameter, we have presented the XX polarized infrared spectra for a typical zigzag MCNTs for four numbers of tubes N=5, 10, 15, and 18 with innermost diameter fixed to D_{in} = 0.7 nm (Figure 4: left). In the left of Figure 4, IR spectra are displayed for three innermost diameter tubes D_{in} = 0.7, 1.22, and 2.5 nm, with a number of layers fixed to N=15 tubes.
Figure 3. The ZZ (dash dot lines) and XX (solid lines) calculated Infrared spectra for typical zigzag MCNTs in the BLM region, upon the number of walls in individual MCNTs N=5, 10, 15, and 18. The left panel indicates the effect of the number of walls on MCNTs of inner diameter $D_{in} = 0.7 \text{nm}$, whose number of walls varies between 5 and 18. The right panel shows the effect of the inner diameter $D_{in}$ on 15 wall tubes.

We found that for large innermost diameters and when the number of walls increases, one can observe that the intermediate infrared peaks progressively change in intensity and overlap leading to a single band centred at 870 cm$^{-1}$ close to the out-of-plane radial buckling mode in graphite.

Figure 4. The ZZ calculated Infrared spectra for typical zigzag MCNTs in the ILM region, upon the number of walls in individual MCNTs N=5, 10, 15, and 18. The left panel indicates the effect of the number of walls on MCNTs of diameter $D_{in} = 0.7 \text{nm}$, whose number of walls varies between 5 and 18. The right panel shows the effect of the inner diameter $D_{in}$ on 15 wall tubes.
Now, we focus on the dependence of the polarized infrared spectrum as a function of the number of walls. Figure 5 shows the evolution of the position of the wavenumber of the intermediate modes in zigzag MCNTs as a function of the number of walls. As expected we note that the number of infrared modes increases with increasing the size of the MCNTs. For a given inner diameter $D_{in} = 0.7$ nm, the wavenumber of the lowest mode decreases monotonically to $800$ cm$^{-1}$, as the number of layers increased, while the wavenumber of the higher mode tends to a constant value of about $894$ cm$^{-1}$.

![Figure 5](image-url)

**Figure 5.** Dependence of the wavenumbers of the intermediate wavenumber modes of multilayer tubes of zigzag MCNTs, calculated for a fixed diameter $D_{in} = 0.7$nm of the innermost layer and different numbers of layers $N$.

4. Conclusion
In this article, the infrared spectra of MCNTs in large diameters are reported taking advantage of the spectral moment's method. The dependence of the positions of the infrared-active modes in the low and intermediate-wavenumber ranges as a function of the number of walls in MCNTS is discussed. We find that for large number of walls, the position and intensity of all intermediate modes overlap to give a large band located at $870$ cm$^{-1}$ close to the out-of-plane radial buckling mode in graphite. Our method is well adapted to understand the experimental infrared spectra of MCNTs.

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