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Modeling and simulation of vibrational breathing-like modes in individual multiwalled carbon nanotubes

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HIGHLIGHTS

- We study the Raman-active modes of multiwalled carbon nanotubes.
- Different diameter and number of layers have been considered.
- The breathing modes are strongly coupled through the concentric tube–tube van der Waals.
- The calculated results are compared with the experimental Raman data.

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ABSTRACT

We study the collective vibrational breathing modes in the Raman spectrum of multiwalled carbon nanotubes (MCNTs). First, a bond polarization theory and the spectral moment's method (SMM) are used to calculate the non-resonant Raman frequencies of the breathing-like modes (BLMs) and the tangential-like ones (TLMs). Second, the Raman active modes of MCNTs are computed for different diameters and numbers of layers. The obtained low frequency modes in MCNTs can be identified to each single-walled carbon nanotubes. These modes that originate from the radial breathing ones of the individual walls are strongly coupled through the concentric tube–tube van der Waals interaction. The calculated BLMs in the low-frequency region are compared with the experimental Raman data obtained from other studies. Finally, special attention is given to the comparison with Raman data on MCNTs composed of six layers.

1. Introduction

Since the time of the discovery of carbon nanotubes by Iijima [1], many researchers have devoted their efforts to studying carbon nanotubes (CNTs) due to their various remarkable chemical, physical and mechanical properties [2,3]. These characteristic properties allow great potential applications [1,4] of CNTs in many fields, such as photocatalysis [5], medicine [6], nanoscale electronics [7], optoelectronic devices [8], hydrogen storage [9,10], mechanical systems [11], electrochemical devices [12], composites [13], SEM probes [14] and field emission devices [15,16]. Many studies have shown the capability of CNTs in the adsorption and removal of different pollutants [17–19]. They exist in a wide variety of forms, namely single-walled carbon nanotubes (SCNTs), double-walled carbon nanotubes (DCNTs) and MCNTs [20]. The MCNTs are made of concentric graphene sheets rolled in a cylindrical form with diameters of tens of nanometers [20]. In addition, MCNTs offer remarkable electrical, mechanical and chemical properties similar to SCNTs with less cost and comparatively lesser carbonaceous and metallic impurities.

There are some developed synthesis methods for the fabrication of both SCNTs and MCNTs. The popular processes include electric arc discharge, laser ablation, chemical vapor deposition (CVD), electrochemical synthesis and ball milling–annealing methods [21]. New synthesis methods are developed to give a broad range of new nanotubular materials, such as carbon nanotubes filled with metals [22], encapsulated with oxides [22], doped with *B* or *N* atoms [23], or even layered materials other than carbon [24,25] were synthesized over the past years.

CNTs have proven to be a unique system for the study of Raman spectra in one-dimensional systems [26], and at the same time, Raman spectroscopy has provided an exceedingly powerful tool useful in the study of the vibrational properties and electronic structures of CNTs [27], particularly for their characterization with respect to their diameters and quality of the sample properties [28]. Using Raman spectroscopy, different carbon materials can be analyzed including SCNTs, DCNTs and MCNTs.

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A DCNTs can be considered to be a kind of MCNTs, for which the interlayer interaction is generally considered to be turbostratic between the inner and outer nanotubes. For armchair–armchair DCNTs, some commensurate structure can be expected. In spite of numerous applications demonstrated using MCNTs, no protocol exists for characterizing and quantifying these materials. Protocol [29] and various experimental methods [30] of the characterization of SCNTs have been well studied. The diameter-dependent optical properties of SCNTs have been extensively studied [31]. Raman spectroscopy has evolved as a tool to probe the properties of CNTs, such as diameter distribution, chirality, doping, nature-like semiconducting or metallic. [26]. Detailed analysis of mean diameter and diameter distribution of SCNTs has been done from their optical response [32]. The diameter grouping of bulk samples of SCNTs from optical absorption spectroscopy has been illustrated [33]. Raman scattering intensity is known to depend on the diameter for SCNTs [34]. But most of the optical spectroscopy techniques cannot be directly applied to MCNTs due to multiple absorptions and emission between concentric cylindrical structures. We note that, in the literature, only few studies are dedicated to Raman spectroscopic analysis of MCNTs. Radial breathing mode (RBM) like feature in MCNTs is reported to originate from the innermost wall of MCNTs, and it is found to be inversely proportional to the diameter of the innermost tube [35]. It has been proposed that the inner tubes of MCNTs contribute to the SCNTs-like feature in the spectra, while the other tubes resembled graphite, more closely [36]. Splitting of graphitic mode G-band has been observed in MCNTs case [35]. High resolution transmission electron microscopy (HRTEM) has been utilized to find the interlayer *d*-spacing, which increases with the decreasing diameter of MCNTs (diameter less than 10 nm) [37]. However, large diameter MCNTs (diameter in the range of 10–100 nm) have not been systematically studied. A recent study has shown influence of diameter of MCNTs on the Raman shift [38]. However, no detailed analysis was made on the diameter-dependence of line width, intensity and splitting of G-band in Raman spectra [35].

In a previous paper, using SMM [39,40], in the framework of the bond-polarization theory, one has calculated the polarized Raman spectra for different achiral–achiral, chiral–chiral, achiral–chiral, and chiral–achiral DCNTs of different sizes, upon their diameter and length. The dependence of the Raman spectrum, upon diameter tube and chirality, was clearly observed. In this work, we study the Raman spectra of individual MCNTs from polarizability theory. Their dependence on the diameters and the number of tubes in the MCNTs are investigated. It is obvious that the Raman intensity calculated by this non-resonant method cannot match the experimental spectra. In fact, one would expect that for a given laser energy one of the tubes in the multiwalled nanotube happens to be in resonance with the laser and the corresponding BLM should thus be strongly enhanced. Thus it is not only the absolute scaling of the Raman spectra that cannot be compared with experimental data, but it is also the relative peak-height of the different BLMs that is not properly reproduced. Also, to reproduce Raman spectrum intensities of thick multiwalled nanotubes requires multiple-light scattering process. One would expect that the highest frequency BLM should be considerably damped for a large number of layers. Nevertheless, SMM predictions concerning the number and frequencies of Raman-active lines, as a function of diameter, length and number of layers, do not depend on the resonant process of Raman scattering. As a consequence, SMM predictions can help to interpret the frequencies of the Raman active modes. In addition, results of the calculation of BLMs and TLMs of MCNTs, with different numbers of layers and different diameters obtained within the model, are given in detail and discussed in comparison with available experimental Raman data. In this way, unambiguously, we are able to attribute the vibrational modes obtained from the experimental measurements to the diameter of the nanotube shells. This paper is organized as follows. In Section 2, we present the used model and the method. Results and discussion are the aim of Section 3. Finally, some summary is drawn in the last section.

2. Model and method

Individual MCNTs are considered to be formed by coaxial cylindrical carbon layers, one inside the other. Each layer can be obtained from a graphene sheet by rolling it up along the straight line connecting two lattice points into a seamless cylinder, in such a way that the two points coincide [41]. Following the usual terminology [42], the tube can be specified by two integers (n, m), with $n \geq m \geq 0$, which define the translation vector between the two points. Alternatively, the tube can be described by its diameter, D, and the chiral angle, θ, which is the angle between the tube circumference and the nearest zigzag of carbon–carbon bonds. The tube is called achiral, for $\theta = 0^\circ$ (zigzag type), of armchair type, for $\theta = 30^\circ$, and chiral, for

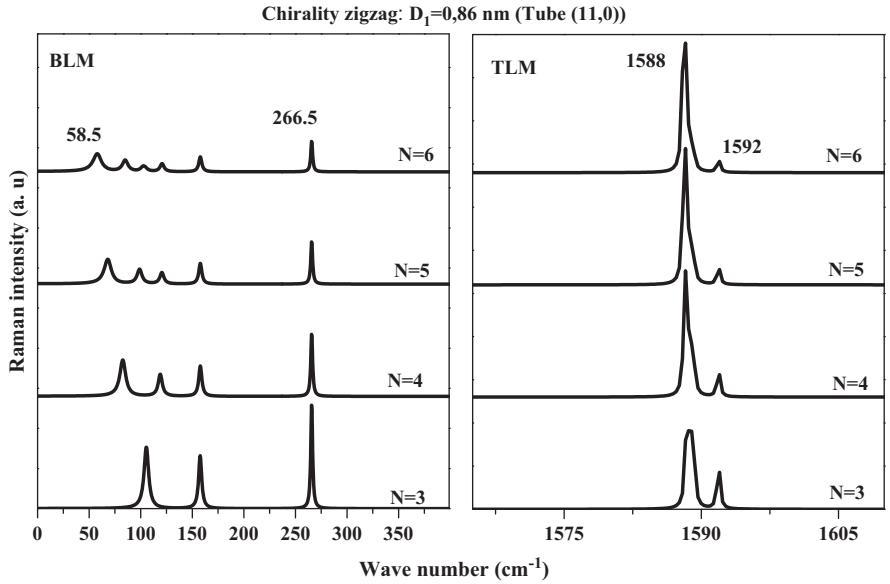

Fig. 1. The *ZZ* calculated Raman spectra for typical zigzag MCNTs, as a function of the number of walls in individual MCNTs $N = 3$, 4, 5, and 6. Here, the left panel is the BLM region, and the right panel is the TLM one.