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Mechanical coupled vibrations in an individual double-walled carbon nanotube*

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Abstract. In this paper we calculate the Raman spectra of different double-walled carbon nanotubes (DWCNTs) by using the spectral moments method. Using a convenient Lennard-Jones expression of the van der Waals intermolecular interaction between the inner and outer tubes, the optimized structures of DWCNT are derived. We found that the C-C bond length in DWCNT is depending on the metallic (M) or semiconducting (Sc) character of the inner and outer nanotubes. We show that the radial breathing-like modes (RBLM) of DWCNT are characterized by concerted inner and outer wall motions. Comparison with Raman spectra measurements is given.

1 Introduction

Carbon nanotubes (CNTs) [1] can be classified into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Double-walled carbon nanotubes (DWCNTs) are a limiting case between the SWCNTs and MWCNTs, and are very important from both theoretical and experimental viewpoints [2]. DWCNTs provide the simplest systems for studying the interactions between layers. The structure of DWCNT can be considered as consisting of two coaxial SWCNTs, and fully defined by chiral indices $(n_o, m_o)@(n_i, m_i)$ of the coaxial outer-/inner-wall [3–5]. Compared to single-walled carbon nanotubes, DWCNTs have higher mechanical strength and thermal stability and they also possess interesting electronic and optical properties [6].

In the low frequency range of the Raman spectrum of DWCNT, the RBLMs are dominant [7]. The mechanical coupling depends on the interlayer distance and the tube diameters. Recently, it was experimentally found that for an interlayer distance larger than 0.4 nm, interaction between layers is weak independently of tube diameter [7]. Theoretically, two coupling regimes are predicted as a function of the tube diameter [7]: (i) for outer tube diameters smaller than 2 nm, the vibrations of the inner and the outer tubes are independent. In this weak coupling regime, an upshift of the in-phase and the counterphase RBLMs with respect to the radial breathing-mode (RBM) of the corresponding SWCNT was calculated, (ii) for outer tube diameter larger than 2 nm, the RBLMs are collective breathing vibrations of both layers.

In a previous papers, using the spectra moment's method (SMM) [8,9], in the framework of the bond-polarization theory, one has calculated the polarized Raman spectra for different DWCNTs of different sizes upon their diameter, chirality and length. The dependence of the Raman spectrum, upon these parameters, was clearly observed [8]. In other works using the combination of high resolution transmission microscopy (HRTEM), electron diffraction (ED) and resonant Raman spectroscopy (RRS) on DWCNTs, the effect of coupling between semiconducting (Sc) and/or metallic (M) nanotubes on the phonons was investigated [10].

In this work, we focus our study on the Sc@Sc and M@Sc configurations. We investigate quantum coupled RBM oscillation in chirality-defined on Sc@Sc and M@Sc DWCNTs by simultaneously determining structural, electronic and vibrational properties. We consider here the low-frequency range of the Raman spectrum, where the breathing modes are detected, and the calculations have been performed in the framework of the bond-polarization theory using the spectral moment's method (SMM) [11,12].

2 Models and computational method

In the DWCNTs, the inner and outer tubes are assumed to be at a distance d close to 0.34 ± 0.01 nm, and the relation

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between diameters of the inner (D_{inner}) and outer (D_{outer}) tubes is:

$$D_{\text{outer}} = D_{\text{inner}} + 2d. \quad (1)$$

The diameter of a (n, m) SWCNT is given by:

$$D = a_0[3(m^2 + mn + n^2)]^{1/2}/\pi, \quad (2)$$

with $a_0 = 0.142$ nm (C-C length).

Among all the models used to describe the phonon bands, the force constants model (FCM) has the lowest computation time requirements. In this model, the dynamic of the systems is described by a few force springs connecting an atom to its surroundings up to given numbers of neighbors. Despite its simplicity, this model can provide accurate and robust method to investigate dynamics and thermal properties of crystals and in particular carbon nanotubes [13].

In the present study, the intratube interactions are restricted only to the first-, second-, third- and fourth-nearest neighbors and the C-C interactions in SWCNT are described by the force constants model introduced by Saito et al. [13]. The values of the force constants used in this model are given in Table 1.

A Lennard-Jones potential:

$$U_{\text{LJ}}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \quad (3)$$

is used to describe the van der Waals intertube interactions between the inner and outer tubes, with parameters $\epsilon = 2.964$ meV and $\sigma = 0.3407$ nm.

In our calculations, inner and outer super-cells of more than 10 000 atoms are considered and the electronic exchange effects between relaxed tubes are represented by van der Waals mechanical interactions. We suppose that inter-tube electronic coupling is negligible between the incommensurate inner- and outer-wall carbon nanotubes because coupling at different carbon atom sites oscillate with random phases and could cancel each other [15].

We calculated the Raman spectra of DWCNTs using the SMM (for more detail see Ref. [11]). Raman intensity of each vibrational mode is calculated in the framework of non-resonant bond-polarizability model [14]. The frequencies of Raman-active modes are derived from the position of the peaks in the calculated Raman spectra. The Raman intensity is normalized with respect to the number of carbon in the sample under consideration. In our calculations, the common axis of the two tubes is along the Z axis.

Table 1. Force constant parameters for SWCNT in units of N/m. Here the subscripts ϕ_r, ϕ_i, and ϕ_o refer to radial, transverse in plane, and transverse out of plane, respectively [13].

N	ϕ_r	ϕ_{ti}	ϕ_{to}
1	365.0	245.0	98.2
2	88.0	−32.3	−4.0
3	30.0	−52.5	1.5
4	−19.2	22.9	−5.8

3 Results and discussion

First, to compare our calculations to DWNT samples synthetized by Wang et al. [16], we have generated DWNT structures by considering bond length C-C variations under van der Waals interactions. The optimized structures are obtained for interatomic bond length between 0.139 and 0.1420 nm for the outer (resp. inner) tubes and between 0.1422 and 0.1424 nm for inner (resp. outer) tubes in the Sc@Sc (resp. M@Sc) configuration. A contraction (dilatation) of the outer tube and a dilatation (contraction) of the inner tube are obtained for the Sc@Sc (M@Sc) DWCNT configuration.

In order to reproduce the experimental positions of the RBLM measured by Wang et al. [16], the first-nearest-neighbor radial force constant (ϕ_r) of the Saito et al. model is slightly modified (±10%). To compare our results with respect to the experimental data, we present in the Table 2 the RBLMs of relaxed (expansion or contraction of the tubes) and un-relaxed DWCNTs. One can see that the frequency values of the RBLMs obtained for relaxed structures are in agreement with the experimental values [16]. We found that the structure and the RBLMs positions are controlled by the electronic properties of DWCNTs.

We present in Figure 1, the Raman spectra of two Sc@Sc DWCNTs ((16,14)@(12,8) and (27,5)@(18,5)) with diameters close to those of Wang et al. synthesized samples. One observes two strong components at 128 cm^{-1} and 192 cm^{-1} (resp. 108 cm^{-1} and 158 cm^{-1}) for (16,14)@(12,8) (resp. (27,5)@(18,5)) DWCNT. The frequency of the counterphase RBLM calculated for the (16,14)@(12,8) DWCNT, located at 192 cm^{-1}, can be compared to that of the RBM calculated at 164 cm^{-1} for the (12,8) SWCNT. The RBM frequency of the (12,8) SWCNT upshifted by about 28 cm^{-1} with respect to the counterphase RBLM of the DWCNT. The in-phase RBLM calculated at 128 cm^{-1} downshifted of about 18 cm^{-1} with respect to the RBM frequency 110 cm^{-1} of the (16,14) SWCNT. The calculated upshifts are in agreement with the experimental values for these systems.

Next, we consider the second configuration where the outer nanotube is metallic and the inner one is semiconductor. In Figure 2, we present the Raman spectra of (31,4)@(15,13) and (40,1)@(22,14) M@Sc DWCNTs. For example, for (31,4)@(15,13) DWCNT, two strong components are observed at 97 cm^{-1} and 142 cm^{-1}. We found an upshift by 28 cm^{-1} (18 cm^{-1}) of couterphase (in phase) with respect to the RBM frequency of the isolated SWCNTs.

Raman spectra of DWCNTs, for Sc@Sc and M@Sc configurations, show many coupling modes originate from interactions between inner and outer nanotubes. The profiles of the RBLM bands associated to inner and outer tubes are depending on their metallic or semiconducting character.

Table 2. Comparison the radial-breathing modes for double-walled carbon nanotubes calculated in this paper with those obtained with $a_0 = 0.142$ nm (any change in the structure of the tubes).

	Our work		Experimental results [16]		Results with $a_0 = 0.142$ nm	
Systems	ω_{LF} (cm^{-1})	ω_{HF} (cm^{-1})	ω_{LF} (cm^{-1})	ω_{HF} (cm^{-1})	ω_{LF} (cm^{-1})	ω_{HF} (cm^{-1})
(27,5)@(18,5)	108	158	108	154	107	160
(23,13)@(14,12)	103	144	103	143	100	147
(19,15)@(19,3)	110	158	110	156	108	162
(20,19)@(24,1)	93	129	93	129	92	132
(24,7)@(13,9)	116	168	123	169	112	166
(16,14)@(12,8)	128	192	133	186	116	194
(27,6)@(15,10)	105	163	105	155	103	165
(27,12)@(20,9)	93	138	93	133	91	145
(26,17)@(27,2)	83	114	84	114	85	118
(32,11)@(23,10)	82	113	83	112	80	116
(31,4)@(15,13)	97	142	98	137	96	143
(40,1)@(22,14)	79	117	79	115	78	118

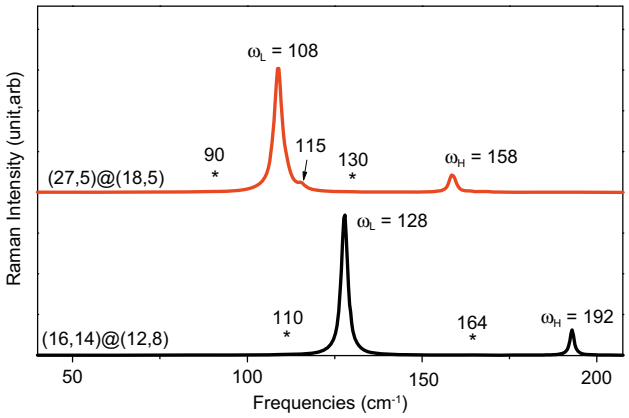

Fig. 1. Low frequency range of the Raman spectra of Sc@Sc DWCNTs (stars present the RBM of SWNCTs).

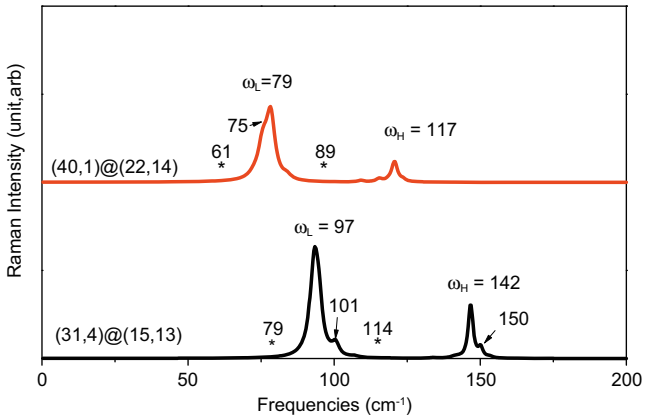

Fig. 2. Low frequency range of the Raman spectra of M@Sc DWCNTs (stars present the RBM of SWNCTs).

4 Conclusion

We have calculated Raman spectra of infinite DWCNTs. We found that the structure of the inner and the outer tubes are controlled by the electronic properties of the tubes. A contraction (expansion) of the outer tube and an expansion (contraction) of the inner tube are obtained for the Sc@Sc DWCNT (M@Sc DWCNT) configuration. Our results are compared to the experimental data.

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