

# Raman spectra of carbon nanowires made of single walled carbon nanotubes encasing polyynes

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**Abstract:** In this work, the Raman spectra of LCCs encapsulated single-walled carbon nanotubes (SWCNTs) are calculated using the spectral moment's method. To derive the optimum configurations of the linear carbon chains inside nanotubes, the minimum energy calculations using a convenient Lennard-Jones expression of the van der Waals intermolecular potential is devoted. The optimized structures show that the minima correspond to nanotubes configurations with diameter close to 0.68nm. The influence of the nanotube diameter and chirality are investigated. We also address the important question of the effect of filling degree using the frequency of Raman active modes. These predictions are useful to interpret the experimental data.

## 1 Introduction

Since their first observation in 1991 by Iijima, carbon nanotubes (CNTs) have drawn in enormous attention of both experimentalists and theoreticians. Several studies have been carried out on CNTs for their potential technical applications, including field emission displays, hydrogen storage media, sensors, nano-sized semiconductor devices, etc., and their rich physical phenomena, such as superconductivity and possible Peierls distortion. A linear carbon chain with pure sp hybridization is expected to be promising for atomic scale field emission devices and other electronic devices, thus further enriching the characteristics and functions of CNTs. High-resolution transmission electron microscopy and resonance Raman spectra confirm that finite linear chains can be truly stable in CNTs.<sup>[1]</sup>

Raman spectroscopy has been shown to be a valuable tool for investigating both vibrational and electronic properties of carbon nanostructured materials.<sup>[2,3]</sup> Therefore, an accurate calculation of their vibrational properties is useful for a better comprehension of this class of nanostructures using Raman spectroscopy

Hydrogen-capped polyynes are one of the simplest series of linear carbon molecules that provide a basic appreciation of the molecular physics of hybrid sp. The electronic properties of these molecules are very

special that their  $\pi$ -electron conjugated systems are doubly degenerate due to their almost perfect linearity.

In this paper, the Raman spectra of LCCs (Polyynes:  $C_{2n}H_2$   $n=2-30$ ) encapsulated in single-walled carbon nanotubes (SWCNTs) are calculated by the spectral moment method.<sup>[4,5]</sup> using a different size of the polyynes molecules and the diameter distribution of the SWCNTs.

## 2 Model, Method & Approach

The structure of the LCCs inside SWCNTs (LCC@SWCNT) are first optimized. In this study, we consider in our computation SWCNTs with diameters ranging from 0.62 nm to 0.78 nm. The energy minimization of the different hybrid systems is performed and the configuration of encased polyynes molecules inside SWCNTs is obtained to adopt a linear structure along tube's long axis. These results are consistent with those from Chang *et al.*<sup>[6]</sup> who showed using DFT that LCCs molecules form a linear chain along the (5,5) and (8,0) SWCNTs axis.

Using the spectral moments methods (SMM), we calculate the Raman spectrum for carbon linear chain inside single-wall carbon nanotubes (SWCNT). We consider that intratube interaction is represented by the force constants<sup>[7]</sup>. A Lennard-Jones potential:

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

is used to describe the LCC-tube interactions with parameters:  $\sigma=3.407\text{\AA}$  and  $\epsilon=0.002964\text{ eV}$ .

### 3 Results and discussions

#### 3.1 Raman spectra of SWNTs and free C<sub>12</sub>H<sub>2</sub> molecule

The polarized Raman spectrum of SWCNT is significantly dominated by Tangential Mode (TM) situated between 1400 and 1600 cm<sup>-1</sup> and by the RBM lower than 400 cm<sup>-1</sup>. A lot of experimental and theoretical Raman studies have shown that the TM region is mainly sensitive to the tube chirality, while the wavenumber of the RBM downshifts as the tube diameter increases according to the relation  $\omega = \frac{A}{D}$ , where D and  $\omega$  are respectively the diameter and the RBM wavenumber. This relation have been also reproduced by the empirical force field of the Saito.<sup>[8,9]</sup>

**Table 1:** Calculated and measured vibrational wavenumbers (in cm<sup>-1</sup>) for the Raman active modes in C<sub>12</sub>H<sub>2</sub> with their assignments:

Calculation		Experiment		Assignment
This Work	Ref [10]	Ref [10]	Ref [11]	
2241	2292	2183	2012	$\sigma_g$
2107	2176	2097	1930	$\sigma_g$
2072	2144	2053	1890	$\sigma_g$
1509	1483			$\sigma_g$
966	690			$\sigma_g$
589	646			$\pi_g$
491	596			$\pi_g$
477	517			$\pi_g$
400	438			$\pi_g$
337	332			$\sigma_g$
220	239			$\pi_g$
83	81			$\pi_g$

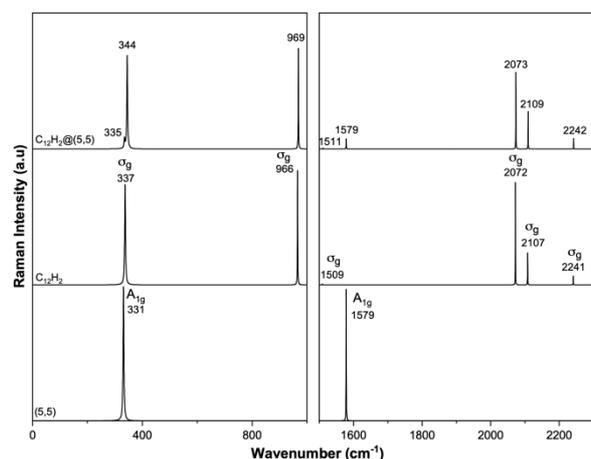
The calculated Raman mode wavenumbers of the C<sub>12</sub>H<sub>2</sub> are listed in Table 1 and are in good agreement with the previous DFT calculations. Raman spectra of free polyynes molecules (Din point group) such as C<sub>2n</sub>H<sub>2</sub> (n = 2, 4, 6 and 8) have been studied intensively in the literature and their Raman-active modes have been reported. For C<sub>12</sub>H<sub>2</sub>, our wavenumbers, calculated using DFT combined with the bond polarizability model, are listed in Table 1 and they are close to that obtained by Wakabayashi. From first principles-based methods. The two sets of theoretical data are also in good agreement with the experimental data. Our first calculations validate that the dynamical matrices of the considered LCCs and SWCNTs are predicted to be well founded and can be utilised to compute the bi-diagonal part of

the dynamical matrix of LCCs enclosed inside SWCNTs hybrids.

#### 3.2 Polarized Raman spectra of C<sub>12</sub>H<sub>2</sub> inside infinite (5,5) SWCNT

We have calculated the Raman ZZ polarized spectra of an infinite armchair (5,5) filled with C<sub>12</sub>H<sub>2</sub> polyynes molecules. Infinite tube has been obtained by applying periodic conditions along the generatrice of the tube. A typical ZZ Raman spectra calculated for C<sub>12</sub>H<sub>2</sub> and C<sub>12</sub>H<sub>2</sub>@(5,5) are reported in Figure 1 and compared with the ZZ Raman spectrum of infield (5,5) SWCNT. The Raman bands can be divided into three wavenumber ranges: (i) below 400 cm<sup>-1</sup> where the breathing-like modes (BLMs) dominate, (ii) an intermediate wavenumber range between 400 and 1000 cm<sup>-1</sup> where the intermediate-like modes (ILMs) are located, and (iii) above 1000 cm<sup>-1</sup> where the tangential-like modes (TLMs) dominate. The atomic motions (eigen displacement vectors) of the main Raman modes in the C<sub>12</sub>H<sub>2</sub>@(5, 5) are displayed in Figure 2. We used here the direct diagonalization of the dynamical matrix instead of the spectral moment's method to have access to the eigen displacement vectors. For (5,5) SWCNT, a single A<sub>1g</sub> mode is calculated in the BLM and TLM regions, whereas three modes with the  $\sigma_g$  symmetry (with a weak intensity for the lowest line) are systematically calculated in the case of a C<sub>12</sub>H<sub>2</sub> polyynes molecules.

**Figure 1:** ZZ polarized Raman spectra of oriented samples of infinite (5,5) (lower), C<sub>12</sub>H<sub>2</sub> (middle), and C<sub>12</sub>H<sub>2</sub>@(5,5) (upper). wavenumber regions are divided into three ranges: BLMs (left), ILMs (middle), and TLMs (right).



For C<sub>12</sub>H<sub>2</sub>@(5, 5), the insertion of C<sub>12</sub>H<sub>2</sub> inside tube seems to have small effects on the TLM modes as weak wavenumber up-shifts (1 cm<sup>-1</sup>) are observed. In this range, Raman spectrum of C<sub>12</sub>H<sub>2</sub>@(5, 5) is dominated by the G-band at 1579 and three lines at 2073, 2109 and 2242 cm<sup>-1</sup>. Experimentally, these Raman bands are observed in the same domains<sup>[12]</sup>. For instance, the bands for the polyynes inside SWCNTs were observed at 2048 cm<sup>-1</sup> and 2130 cm<sup>-1</sup> and associated to the different length of LCCs inside the SWCNTs with different diameters.

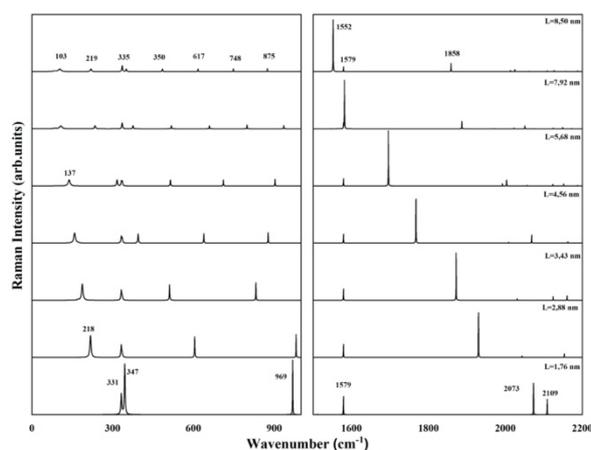
With respect to the tube axis and for  $C_{12}H_2@(5,5)$ , the G-band located at  $1579\text{ cm}^{-1}$  is a transverse optical mode. The lower (upper) wavenumber mode shifts from  $2072\text{ cm}^{-1}$  ( $2107\text{ cm}^{-1}$ ) in free  $C_{12}H_2$  molecule to  $2073\text{ cm}^{-1}$  ( $2109\text{ cm}^{-1}$ ) in  $C_{12}H_2@(5,5)$  (Fig. 1).

Our calculations state a systematic wavenumber upshift of the breathing like modes in  $C_{12}H_2@(5,5)$  with respect to unfilled SWCNTs due to the van der Waals interactions between  $C_{12}H_2$  and (5,5) tube. For instance, they are located at 335, 347 and  $969\text{ cm}^{-1}$ . The line centred at  $966\text{ cm}^{-1}$  and assigned as the symmetric  $\sigma_g$  mode of  $C_{12}H_2$  shifts to  $969\text{ cm}^{-1}$  in  $C_{12}H_2@(5,5)$ . The calculated upshifts can be explained by the van der Waal intermolecular interactions acting between the molecules and the SWCNTs.

### 3.3 Chain length effect

In real SWCNTs encapsulating linear carbon chains samples, it is reasonable to consider that all the nanotubes are not filled with a defined chain length. To avoid finite size effects, we applied periodic conditions to the tube. We investigate the Raman spectra of  $C_{2n}H_2@SWCNT$ s as a function of the encapsulated chain length  $L$ . For this aim, the dependence of the ZZ polarized Raman spectrum with the chain length has been calculated for the  $C_{2n}H_2$  chain inside (5,5) nanotube (figure 2). The spectra were calculated for 8 values of the chain length  $L = 1.76, 2.88, 3.43, 4.56, 5.68, 7.92$  and  $8.50\text{ nm}$  corresponding to  $n = 6, 10, 12, 16, 20, 28$  and  $30\text{ }C_{2n}H_2$  molecules, respectively, inside (5,5) SWCNTs.

**Figure 2:** Dependence of the ZZ-polarized Raman spectra of  $C_{2n}H_2@(5,5)$  as a function of the encapsulated  $C_{2n}H_2$  length  $L$  in the range of BLMs (left) and TLMs (right).



Because the Raman spectra of  $C_{2n}H_2@SWCNT$ s show qualitatively the same behavior as a function of the nanotube chiralities, only the case of  $C_{2n}H_2@(5,5)$  reported in Figure 2 will be discussed. We found that the linear chain length inside the SWCNT has significant effect on the Raman spectrum and a number of lines are calculated, especially in the BLM and TLM ranges. The position of the lowest wavenumber mode of these lines rapidly decreases as the length of the chain increases.

We found also that the position of the Raman lines associated to the LCCs decreases with an increasing number of carbon atoms composing a LCC and the peak wavenumbers about  $1800\text{ cm}^{-1}$  are lower than that of polyene possessing the length of about  $5\text{ nm}$ . In consequence, the effect of the chain length on the Raman spectrum could be experimentally observed on finite chain length. These results highlight the peaks observed experimentally between  $1800$  and  $2100\text{ cm}^{-1}$ .<sup>[13]</sup> Therefore, these lines could be assigned to the presence of different finite length LCC structures confined inside nanotubes. Our calculations for the finite polyene length inside carbon nanotubes can be used to interpret the Raman experiments. Indeed, our calculation that predicts the G-band ( $1579\text{ cm}^{-1}$ ) is always weaker than the LCC band in agreement with the measured Raman spectra<sup>[14,15,16]</sup>

### 4 Conclusions

In this paper, the structure and nonresonant Raman spectra of carbon nanotubes encapsulating linear carbon chains are calculated using the spectral moments method combined with the bond polarizability model. The modifications of the Raman spectra of the carbon nanotubes are correlated with the intermolecular interactions. A general good agreement is found between calculations and measurements.

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