Raman spectroscopy analysis of single wall carbon nanotubes with penta- and hexa-vacancies defects

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Abstract. In this paper the effect of penta- and hexa-vacancies defects on a vibrational properties of single wall carbon nanotube (SWNT) was investigated. The bond-polarizability model combined with the spectral moments method are carried out to calculate the non-resonant Raman spectra. The changes of Raman spectra as a function of the nanotube chirality and the vacancies defects concentration on the wall of the nanotube are identified. The intensity ratio of D-band to G-band ($I_D/I_G$ ratio) reflects the purity of SWNTs. Our study offers a means to distinguish between pristine and defective SWNTs even at low defect concentrations.

1. Introduction
Since the discovery of carbon nanotubes (CNT) [1], due to their various and remarkable properties [2, 3, 4, 5], several efforts have been made regarding their potentials applications [6, 7, 8, 9], and much attention has been devoted to the investigation of their properties [10, 11, 12, 13]. While a relatively simple description of the nanotube properties can be achieved by using the perfect CNT structure. However, in real CNTs, defects are unavoidable in non-equilibrium conditions, e.g., during the nanotube growth [14, 15, 16]. Various kinds of defects, such as impurities [18, 17], Stone-Wales (SW) defects [20, 19] and vacancies; like the mono-vacancy (MV) [21, 22, 23], di-vacancy (DV) [24, 25, 26] and its derivative point defect can be contained in the CNTs samples.

The mechanical, optical and electrical properties of carbon nanotubes (CNTs) and related materials have been an active research fields [1, 27, 28, 29]. In contrast to theoretical considerations the experimental verifications of the CNTs strength or Young’s modulus demonstrate evidently discrepancies that may reach even up to 30% [30]. Structural defects in nanotubes have been identified by STM and HRTEM imaging [31, 32]. Possible single or multiple defects in CNTs provide an explanation for the extant theoretical experimental differences. While such defects in single-wall carbon nanotubes (CNTs) have a great influence on their physical properties [33, 34]. Then, the evaluation of effects of defects and impurities on properties of these nano-structures would be crucial because of the inevitable creation of defects during the synthesis and purification processes [35, 36] and under mechanical strains [37]. Among structural defects, vacancy and Stone-Wales defects [38] are more prevalent and their numbers and locations would be unclear and it is necessary to investigate their influences from different points of view.
CNTs characterizations relies extensively on Raman spectroscopy [34], it’s one of the most powerful tools to the analysis of CNTs of varying diameter and chirality [39]. In the Raman spectra of defective CNTs and all sp² hybridized disordered carbon materials, the defect-induced phonon mode so-called D band is observed [40, 41] at around 1350 cm⁻¹ [42, 43, 44]. It’s a signature of the presence of defects or disorder in the graphene lattice [45], and is often used to characterize defective CNTs. The D band intensity can be enhanced as function of the number of defects is increased in CNTs. The D band has been used for the assessment of imperfection of SWNTs and the understanding of the properties of their defects. However, it is possible that D band is derived from a many defective CNTs in the sample, while the radial breathing mode (RBM) or graphitic G-band are due to the presence of the other CNTs in the same sample, then it may be the interpretation of the D-band feature might be ambiguous. Further, identifying Raman modes associated with points defects can lead the Raman spectroscopy to a more effective tool for the characterization of defects signatures.

The purpose of the current study is to reveal the dependence on the polarized ZZ Raman spectra of penta- and hexa-vacancy defect in the single wall carbon nanotube as a function of defect concentration and chirality of nanotube. Also we calculate the ratio of D- to the G-band intensity (I_D/I_G) which provides a parameter that can be used to quantifying the defects. The non-resonant Raman spectra are calculated in the framework of spectral moments method [10], together with a bond polarizability model.

2. Model and method
The key element of this study is Raman spectroscopy, such as a perfect tool to get important information and characterization of both perfect and defective carbon nanotube and peapod. In this work, we focus on vibrational properties of penta- and hexa-vacancies defect in SWNT (Figure 1). For this purpose we described the C-C intratube interactions at the surface of SWNT by using the force constant model introduced by Wirtz and Rubio [46], but for the interaction of carbon atoms sited in the vacancy defect border are calculated by using Density Functional Theory (DFT) as implemented inside the SIESTA package [47].

Figure 1. Molecular models of (A) penta-vacancy and (B) hexa-vacancy defect.

The Raman intensity is calculated according to the bond polarizability model [48, 49]. In this approach, the polarization is only modulated by the nearest-neighbor bonds and the components of the induced polarizability tensor \( \tilde{\pi} \) are given by the empiric equation:

\[
\pi_{\alpha\beta}(r) = \frac{1}{3}(\alpha_l + 2\alpha_p)\delta_{\alpha\beta} + (\alpha_l - \alpha_p) \left( r_{\alpha} r_{\beta} - \frac{1}{3} \delta_{\alpha\beta} \right)
\]

where \( \alpha \) and \( \beta \) relate to the Cartesian components (x,y,z) and \( \hat{r} \) is the unit vector along the vector \( \vec{r} \) connecting atom \( n \) and atom \( m \) which are covalently bonded. The parameters \( \alpha_l \) and
\( \alpha_p \) correspond to the longitudinal and perpendicular bond polarizability respectively. Within this approach, one can assume that the bond polarizability parameters are functions of the bond lengths \( r \) only. The derivatives \( \pi^n_{\alpha\beta,\gamma} \) are given by:

\[
\pi^n_{\alpha\beta,\gamma} = \sum_m \frac{1}{3} (\alpha'_l + 2\alpha'_p) \delta_{\alpha\beta} \hat{r}_\gamma + (\alpha'_l - \alpha'_p) \left( \hat{r}_\alpha \hat{r}_\beta - \frac{1}{3} \delta_{\alpha\beta} \right) \hat{r}_\gamma + \frac{\alpha_l - \alpha_p}{r} \left( \delta_{\alpha\gamma} \hat{r}_\beta + \delta_{\beta\gamma} \hat{r}_\alpha - 2 \hat{r}_\alpha \hat{r}_\beta \hat{r}_\gamma \right)
\]

where \( \alpha' = \left( \frac{\partial \alpha}{\partial r} \right) \bigg|_{r=r_0} \) and \( r_0 \) is the equilibrium bond distance. The bond polarizability parameters are:

\[
\alpha = 2\alpha'_p + \alpha'_l, \quad \beta = \alpha'_l + \alpha'_p, \quad \text{and} \quad \gamma = \frac{\alpha_l - \alpha_p}{r}
\]

The values of these parameters are fitted to reproduce the experimental Raman spectrum.

3. Results and discussion

In this section a complete investigation between perfect and penta- (hexa-) vacancies defects sited in the wall of SWNT is conducted. In this study, the concentration of defects is defined by the number of the removed atoms divided by the total number of atoms in the perfect tube. Our systems are large nanotubes composed by 80000 carbon atoms, whose the maximum number of penta- (Hexa-) vacancies defects can reach 640 (533) respectively. In all our Raman spectra calculations, the nanotube axis is along the Z-axis and a carbon atom is along the X-axis of the nanotube reference frame. The laser beam is kept along the Y-axis of the reference frame. We consider that both incident and scattered polarizations are along the Z-axis to calculate the polarized ZZ spectra.

3.1. Raman Spectra of carbon nanotubes with penta-vacancies defects

We study the Raman spectra of defective SWNT as a function of defect concentration and chirality. For this purpose, three chiralities of SWNTs have been considered with a diameter of 1.356 nm [(10,10) armchair], 1.335 nm [(14,5) chiral], and 1.330 nm [(17,0) zigzag] at a penta-vacancies concentration varied from 2% to 4%. The calculated ZZ-polarized Raman spectra of penta-vacancy nanotube are shown in the panels of Figure 2 along with their corresponding pure nanotubes. The spectra are displayed in the RBM range (left), in intermediate range (middle), and in the range of tangential modes (right).

It is found from Figure 2 that compared with that in the perfect SWNTs, although the penta-vacancies leads to a redshift of the tube’s RBM frequency. When the concentration of penta-vacancies increases, RBM downshift from 164 cm\(^{-1}\) [166 and 167 cm\(^{-1}\)] in pristine tube to 161 cm\(^{-1}\) [164 and 165 cm\(^{-1}\)], 158 cm\(^{-1}\) [161 and 162 cm\(^{-1}\)], and 156 cm\(^{-1}\) [158 and 159 cm\(^{-1}\)] for 2%, 3%, and 4% penta-vacancies concentrations in (10,10) [(14,5) and (17,0)] SWNT, respectively. A second-lowest Raman-active peak is observed in the case of defect tube only and located at 340 cm\(^{-1}\) [330 and 336 cm\(^{-1}\)], 338 cm\(^{-1}\) [328 and 334 cm\(^{-1}\)], 334 cm\(^{-1}\) [325 and 330 cm\(^{-1}\)] for 2%, 3%, and 4% penta-vacancy concentrations for (10,10) [(14,5) and (17,0)] nanotube, respectively.

In the intermediate range, the spectrum is dominated by a strong bands at around 1342 cm\(^{-1}\) in three chiralities of SWNT, while no Raman line is expected for perfect SWNT. This mode arises from penta-vacancy defect and its position slightly dependent on the tube chirality and on defect concentration. Similarly to the previous calculations for SWNTs, the G-band
Figure 2. ZZ-polarized Raman spectra of different SWNT chirality as a function of penta-vacancies defects concentration.

located in the TM range depends on the tube chirality, is weakly downshift as a function of defect concentration. For instance, the G mode downshifts from 1586 cm\(^{-1}\) in the perfect (10,10) nanotube to 1582 cm\(^{-1}\) in the 4% defective nanotube. When the concentration of penta-vacancies increases this mode weakly downshifts for the three chiralities.

The eigenvector displacements of the modes located around 338 cm\(^{-1}\) and 1342 cm\(^{-1}\) in (10,10) SWNT with penta-vacancy defect, are given in Figure (3-A). These vectors allow us to identify the radial displacements of atoms belonging to the penta-membered ring: all atoms in the penta-vacancy move in phase in the radial direction and the mode is fully symmetric. This mode could be used to estimate penta-vacancy defect of nanotubes.

Figure 3. A : Raman active mode atomic displacements for 338 cm\(^{-1}\) and 1342 cm\(^{-1}\) (resp. 305 cm\(^{-1}\) and 1330 cm\(^{-1}\)) normal modes in the (10,10) nanotube with penta-vacancy defects (resp. B : hexa-vacancy defects).

In the present study, a systematic investigation of the relationship between the Raman spectroscopic response and microstructural changes of CNTs were performed. In practice, the use of Raman spectroscopy to study the structural quality of pristine and defective SWNT is
limited to the evaluation of the $I_D/I_G$ ratio, where $I_D$ is the intensity of the D band, activated by the presence of defect in carbon systems, and $I_G$ is the intensity of the G band. In fact, the decrease of the intensity of the G mode upon defect creation increases the $I_D/I_G$ intensity ratio, which could lead to an estimation of the amount of defects.

Figure 4. The evolution of the intensity ratio $I_D/I_G$ as a function of the penta-vacancies defects concentration in armchair (triangle), zigzag (square), and chiral (circle) nanotubes.

Figure 4 shows the normalized $I_D/I_G$ intensity ratio as a function of defect concentration (DC) for three chiralities of SWNT (armchair (10,10), zigzag (17,0) and chiral (14,5)). From 0 to 5.5% concentration, the $I_D/I_G$ ratio increased linearly until it peaked at 0.0325 [0.0196] for (14,5) [(17,0)] penta-vacancy tube. After this value of DC, the $I_D/I_G$ intensity ratio is considerably stable, it is clear that the main discrepancy between both behavior of (14,5) and (17,0) defect tube is caused by the difference chirality between them. Contrariwise, the armchair defect tube behavior increased without reaching its stable state.

3.2. Raman Spectra of carbon nanotubes with hexa-vacancies defects

The figure 5 shows the calculated ZZ polarized Raman spectra of perfect SWNT and hexa-vacancy defect SWNT. Three concentration of hexa-vacancy defect are considered (2%, 3%, 4%), and the results are compared with perfect one: (top) armchair ((10,10) tube diameter close of 1.356 nm), (middle) chiral ((14,5) tube diameter close of 1.335 nm), and (bottom) zigzag nanotubes ((17,0) tube diameter close of 1.330 nm). The ZZ Raman spectra can be divided into three selected frequency regions: the RBM range (left), the region of the defect modes (middle), and tangential range: G-modes of the tubes (right).

By examining the Raman active modes calculated for defective nanotube compared with the perfect one, as shown in figure 5, a notable effect in the defective SWNTs is the reduction of the intensity of active modes independently of the nanotube chirality compared to the pristine SWNT. This result can be understood due to the loss of symmetry induced by the defects. Additionally, in the high-frequency region, the G-mode red-shifted when the concentration of defect increase independent of chirality of nanotube. For instance the G-mode frequency passed from 1586 cm$^{-1}$ in perfect nanotube to 1582 cm$^{-1}$ in the highest concentration of hexa-vacancy defect in (10,10) SWNT. As for intermediate range between 600 and 1400 cm$^{-1}$, a new mode is showed around of 1330 cm$^{-1}$. This mode located in the D-band of SWNTs Raman spectra arises from hexa-vacancy defect, whose is not sensitive to the defect concentrations and not to SWNT chirality. Within the 0-600 cm$^{-1}$ range, we observe a downshift of $A_{1g}$ mode for different chirality
of SWNT, and a new mode appears near 305 cm$^{-1}$ and keeps the same value independently of the SWNT chirality. The eigenvector displacements of the modes located around 305 cm$^{-1}$ and 1330 cm$^{-1}$ in (10,10) SWNT with hexa-vacancy defect, are given in Figure (3-B). These vectors allow us to identify the radial displacements of atoms belonging to the hexadeca-membered ring: all atoms in the hexa-vacancy move in phase in the radial direction and the mode is fully symmetric. This mode could be used to estimate hexa-vacancy defect of nanotubes.

Figure 5. ZZ-polarized Raman spectra of different SWNT chirality as a function of hexa-vacancies defects concentration.

Raman spectroscopy is a very effective method to characterize the detailed bonding structure of carbon nanomaterials. The intensity ratio of the tangential mode of SWNTs (G-band) to the disorder-induced D-band centered at around 1330 cm$^{-1}$ ($I_D/I_G$) provides a parameter that can be used for quantifying disorder in SWNT. The G band is a result of in-plane vibrations of $sp^2$ bonded carbon atoms whereas the D band is due to out of plane vibrations attributed to the presence of structural defects. Figure 6 shows a plot of ($I_D/I_G$ ) versus hexa-vacancy

Figure 6. The evolution of the intensity ratio $I_D/I_G$ as a function of the hexa-vacancies defects concentration in armchair (triangle), zigzag (square), and chiral (circle) nanotubes.
defect concentration for different chirality of nanotube (armchair (10,10), zigzag (17,0) and chiral (14,5)).

4. Conclusion
The nonresonant Raman spectra of SWNT with penta- and hexa-vacancies defects have been calculated using bond-polarizability model combined with the spectral moments method. For the hexa-vacancy defect in SWNT, we found that (i) The RBMs and G-mode of SWNTs are strongly dependent on the concentration of defects on the wall of nanotube. (ii) Two new modes are appeared due to hexa-vacancy defect on the D-band. The $I_D/I_G$ ratio can be used to investigate the correlations between the Raman spectra and the defect structure of SWNT. We found that the low-energy Raman profiles showed more variations with the introduction of the defects in the wall of nanotube, whereas the high-energy profiles did not change appreciably depending on the defect concentration. The result of Raman spectra didn’t significantly depend on the tube chirality. Our work provides benchmark theoretical results to understand the experimental Raman spectra of SWNTs with defect.

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