Infrared active modes in double walled CBN nanotube: theoretical study

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Abstract. This work focuses on a hybrid system consist of single-wall carbon nanotube inside single-wall boron nitride nanotube (CBN nanotube). The intertube interactions between the outer boron–nitride nanotube and inner carbon nanotube are described using a van der Waals interaction. The infrared spectra of CBN nanotubes are calculated in the framework of spectral moments method. The evolution of the infrared spectra of CBN nanotube as a function of their diameters and lengths are discussed. The obtained results are useful for the interpretation of the experimental infrared spectra of CBN nanotube.

1. Introduction
Boron nitride nanotubes (BNNTs) is a similarly structured to that of carbon nanotubes (CNTs) \cite{1, 2} in which carbon atoms are replaced entirely by equal numbers of nitrogen and boron atoms, arranging in a hexagonal lattice. The BNNTs and CNTs share some similar chemical and physical properties \cite{3,4,5}, but the electronic properties of CNTs are different from those of BNNTs, when CNTs can be semiconducting or metallic depending on the rolling direction \cite{6} and BNNTs are an excellent insulator \cite{7} with a wide bandgap (5–6 eV) irrespective of the number of walls, diameters and chiralities \cite{6, 8}. In addition, the mechanical properties of CNTs and BNNTs are different because the B-N bond is ionic \cite{1}. These numerous excellent properties of BNNTs and CNTs make them widely studied by experimental and theoretical workers and a candidate for many innovative applications in nanotechnology.

Figure 1. Structure CNT@BNNT.

Similar to carbon nanotube, BNNT can be confined different molecules \cite{9,10}. In addition, under appropriate conditions C60@BNNT provide an effective material for preparing a coaxial structure.
composed of an inner CNT and an outer BNNT. Experimentally, hybrid nanostructure CNT@BNNT was observed by high resolution bright-field transmission electron microscopy imaging [11]. This hybrid system can offer an exciting opportunity to form a conducting nanowire inside an insulating BNNT. The infrared spectrum of the synthesized BNNTs and CNTs are dominated by two strong characteristic bonds located around 800 - 820 cm$^{-1}$ and 1360-1400 cm$^{-1}$ for BNNTs [12,13,14,15,16] and around 840-900 cm$^{-1}$ and 1560-1600 cm$^{-1}$ for CNTs [6,17].

The Raman scattering and infrared absorption are the most powerful tools for investigating the vibrational properties of carbon and BN nanomaterials in relation to their structural and electronic properties [18, 16]. In a previous theoretical work [19], we studied the Raman spectra of C70 and C60 fullerenes inside BNNTs where these molecules adopt a linear arrangement for BNNT diameter lower than 1.45 nm. The calculation of Raman spectra shows that the behaviour of the breathing-like modes (BLM) with the pod diameter was clearly modified in peapod. To obtain a complete assignment of the CBN nanotube, we follow the same methodology but in the case of the infrared spectroscopy in the framework of spectral moments method, where the inner molecule is the carbone nanotube and the outer is BBNT. Our work supports the infrared spectra of (armchair@armchair) CBN nanotubes as a function of their lengths and diameters. The results are useful to understand the experimental infrared data of CBN nanotube.

This paper is organized in the following way. In section 2 we present the used model and method. Results of calculations are the aim of section 3, the final section is conclusion.

2. Computational method
A CBN nanotube consists of the inner single-wall carbon nanotube (SWCNT) trapped inside a single-wall boron nitride nanotube (SWBNNT) nanotube host. Representative structure of optimized (5,5)@(10,10) CBN nanotube is shown in Fig. 1.

A Lennard-Jones potential: $U_{ij} = 4\epsilon [(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^{6}]$ is used to describe the van der Waals interactions between the outer and inner nanotubes, where $r$ is the atom-atom distance, the values of the Lennard-Jones $\sigma_{ij}$ parameter is given by 4.116, 6.281 and 2.635 meV, whereas the $\epsilon_{ij}$ parameter is 0.3453, 0.3365 and 0.3369 nm, for boron, nitrogen and carbon atoms, respectively [20–22]. The parameters $\sigma_{ij}$ and $\epsilon_{ij}$ between different atoms are calculated by the following Lorentz-Berthelot rules: $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\epsilon_{ij} = (\epsilon_i + \epsilon_j)/2$.

The interlayer distance $d$ between the outer and inner nanotube is close to 0.34 nm, this value obtained by minimum energy calculations. Which is in good agreement with that calculated by the density functional theory method [18].

The SWBNNT B-N intratube interactions are described using the same force constant used in recent calculations of the infrared spectra of SWBNNTs [16]. The SWCNT C–C intratube interactions are described by using the same force constants set that the one used in our calculation of the Raman spectrum of isolated SWCNT [23]. The dynamical matrix of SWCNT inside SWBNNT is calculated by block. The system under study contains a large number of atoms, the diagonalization of their dynamical matrix requires long computing time or fails. The most effective way of computing directly the infrared spectra without diagonalizing the dynamical matrix is the spectral moments method [24]. In order to enhance the IR response of both CNT and BNNT nanotubes, dynamical effective charges on tied atoms were fixed at $q_A=+1$ and $q_B=-1$ for a given A-B bond. Please follow these instructions as carefully as possible so all articles within a conference have the same style to the title page. This paragraph follows a section title so it should not be indented.

3. Results and discussions
In all of this study we apply a periodic conditions on the unit cells of nanotubes to obtain the infinite system, also we consider the common Z axis of inner and outer nanotubes to be along the z-axis and the X axis of each nanotube to be along the x-axis of the laboratory reference frame. The symmetries of the infrared-active modes are directly derived from the polarized IZ($\omega$) and IX ($\omega$) spectra.

In a first section, we present the results of calculated infrared spectra for infinite hybrid system of CNT@BNNT of armchair@armchair chirality. Next, we report the boron nitride nanotube, carbon nanotube and hybrid system diameter dependence on the frequencies IX($\omega$) infrared active modes.
Then we also study the influence of the finite length of the inner and outer zigzag tubes on their infrared responses.

3.1. Infinite length of CBN nanotube

We report the calculations of the infrared responses of (10,10)@(15,15)CBN with their corresponding single (10,10)CNT and (15,15)BNNT. The results are displayed in Fig. 2 for three frequency regions: (i) Below 600 cm\(^{-1}\) where the breathing-like modes (BLM) dominate, (ii) Intermediate region between 600 and 1000 cm\(^{-1}\) where the intermediate-like modes (ILM) are located, and (iii) above 1000 cm\(^{-1}\) where the tangential-like modes (TLM) are dominated.

Concerning the \(I_Z(\omega)\) polarization, in both BLM and ILM regions no infrared bands are observed in CBN nanotube and also in the corresponding isolated nanotubes. The TLM region is dominated by two bands coming from the corresponding isolated tubes.

Concerning the \(I_X(\omega)\) polarization, in the BLM region, the infrared spectrum of the (10,10)@(15,15)CBN displays peaks located at 144 and 237 cm\(^{-1}\). The frequencies of the breathing modes in isolated (10,10) and (15,15) armchair tubes are calculated at 140 and 233 cm\(^{-1}\) respectively. Our calculations state a systematic upshift (4 cm\(^{-1}\)) of the frequencies of the breathing-like modes with respect to the frequencies of the breathing modes in SWBNNTs and SWCNTs, respectively. In the ILM region, the same behaviour in BLM region is observed. We observe an upshift (2 cm\(^{-1}\)) of the infrared bands in CBN nanotube with respect to their positions for single nanotubes. In the TLM region, there are two active modes around 1393 and 1587 cm\(^{-1}\). They are associated with the in-phase and counter-phase coupled motions of the tangential modes of the inner and outer tubes.

3.2. Diameter dependence

To illustrate the diameter dependence of the infrared-active modes, the calculated \(I_X(\omega)\) spectra are displayed for three values of the diameter 1.35, 2.03 and 2.71 nm of (10,10), (15,15) and (20,20) SWCNT inside 2.05, 2.74 and 3.42 nm of (15,15), (20,20) and (25,25) SWBNNT, respectively (Fig. 3).
Figure 3. $I_x(\omega)$ calculated IR spectra of infinite (n,n)@(n+5,n+5) CBN nanotube, for n = 10, 15 and 25 from bottom to top in BLM (left), ILM (middle) and TLM (right) regions. The stars and plus give the position of the active modes of carbon and boron nitride isolated tubes, respectively.

In the intermediate mode region, all spectra are dominated by two strong bands around 800 and 870 cm$^{-1}$. These bands are associated with the counter-phase and in-phase coupled motions of the intermediate modes of the outer and inner tubes.

In the TLM region, spectra are dominated by two strong bands around 1393 and 1587 cm$^{-1}$ when the diameter increased. They are associated with the in-phase and counter-phase coupled motions of the tangential modes of the inner and outer tubes.

In the BLM region, the results indicate two modes low frequency (LF-BLM) and high frequency (HF-BLM). We observe a frequency downshift with increasing tube diameter, for their modes, whereas the intensities decrease. One can see that the BLM modes are strongly dependent on the diameter in comparison with ILM and TLM modes.

We have reported in figure 4 the BLM frequencies for CBN system versus diameter D. From these results, and for CBN in the diameter range 0.6–2.6 nm, phenomenological relations which describe the diameter dependence of the IR-active-mode frequencies have been derived.

The dependence of the frequency of the LF-BLM mode as a function of tube diameter is described by an $a/D$ scaling law with the $a$ parameter depending on the mode symmetry (see Table 1) but the HF-BLM mode is well fitted by the phenomenological relation:

$$\omega = a/D + b/D^2 + c$$

Where $D$ is the outer nanotube diameter. The $a$, $b$, and $c$ parameters are given in Table 1 for armchair.

It must be emphasized that this previous expression has a useful application for deriving the diameter of tubes from the experimental infrared-active-mode wave numbers. No physical meaning is attached to the values of the different parameters of the fit.
Figure 4. Diameter dependence on the wavenumber $\omega$ infrared active modes for SWBNNT@SWCNT in the low wavenumber region.

| Modes     | Parameters                  |
|-----------|-----------------------------|
| LF-BLM    | $a=283$ nm cm$^{-1}$        |
| HF-BLM    | $a=110$ nm cm$^{-1}$, $b=-199$ nm$^2$ cm$^{-1}$, $c=940$ cm$^{-1}$ |

Considering the diameter dependence of the specific modes in BLM regions, we present in Fig. 5 the eigendisplacement vectors of BLM lines in a (5,5)@(10,10) CBN nanotube obtained from the direct diagonalization of the dynamical matrix. The eigenvector displacements of the modes located around 212 and 458 cm$^{-1}$ (see figure 4 b and d) are assigned to hybridation between the modes of the outer BN (208 cm$^{-1}$) and inner carbon (464 cm$^{-1}$) nanotube (see figure 4a and 4b). All this modes correspond to a mixing of tangential and radial displacement of atoms, as shown in Fig. 5. There are two nodes along the circumference, and all atoms move inward (outward) for the radial component and upgrade (downgrade) for the tangential one on both sides of the two nodes.

3.3. CBN nanotubes with a finite length

Because experiments have been shown a short portions of the inner tube inside the outer tube, we investigate the dependence of the infrared spectra on the lengths of the inner (Li) and outer (Lo) tubes. Thanks to spectral moments method, we can calculate the infrared spectra for finite (9,0)@(18,0) CBN nanotube. In this study, we consider five cases when Li/Lo ratio can take 0.25, 0.5, 1, 1.5 and 2. (figure. 6).
**Figure 5.** Infrared-active-mode atomic displacements for selected normal modes in the (a) (10,10) BNNT, (c) (5,5) CNT and (b,d) (5,5)@(10,10) CBN nanotube.

**Figure 6.** Calculated $I_x(\omega)$ infrared spectra of the (9,0)@(18,0) CBN as a function of the $L_i/L_o$ ratio.

In the x-polarization, and for usual CBN nanotubes ($L_i = L_o$), in the TLM region the infrared spectrum is dominated by two bands located at 1391 and 1579 cm$^{-1}$ in the (9,0)@(18,0) CBN nanotubes. For $L_i > L_o$, the intensity of mode at 1579 cm$^{-1}$ increases and is assigned to the TM of the
part of the inner carbon tube, which does not interact with the outer boron nitride tube (the TM of the corresponding (9,0) SWCNT is calculated at 1580 cm\(^{-1}\)). For Li < Lo, the intensity of mode at 1391 cm\(^{-1}\) increases and is assigned to the TM of the part of the outer boron nitride tube that does not interact with the inner carbon tube (the TM of the corresponding (18,0) SWBNNT is calculated at 1391 cm\(^{-1}\)). BLM and ILM range shows the same dependence of the Li/Lo ratio than the TLM range and the above discussion is also valid. The intensity of the lines at 83 and 797 cm\(^{-1}\) (respectively 225 and 887 cm\(^{-1}\)) decreases when the Li/Lo ratio increases (respectively decreases).

4. Conclusion
We have outlined the construction of double wall nanotube consisted of carbon nanotube inside BN nanotube. For this obtained system, the dependence of the infrared spectra as a function of the diameter and finite lengths of outer and inner nanotubes have been analyzed using the spectral moments method. First, we calculated the infrared spectra of infinite length of CBN nanotubes as a function of their diameters, we observed that the mode located in BLM region decrease when the diameter increase. We also calculated the infrared spectra of CBN nanotubes with a finite length. We observed additional infrared bands as a function of the relative lengths of the inner and outer tubes in the whole infrared spectrum. By varying the length of the CBN sub-system only bands located in the BLM and ILM regions have changed.

References

[1] Chopra N G, Luyken R J, Cherrey K, Crespi V H, Cohen M L, Louie S G and Zettl A 1995 Science. 266 966-67
[2] Iijima S 1991 Nature. 354 56-58
[3] Chang C W et al 2006 Phys. Rev. Lett. 97 085901
[4] Stewart D A, Savic I, Mingo N 2009 Nano Lett. 9 81–84
[5] Chen Y et al 2004 Appl. Phys. Lett. 84 2430–32
[6] Blase X, Rubio A G, Louie S and Cohen M L 1994 Europhys. Lett. 28 335
[7] Zhi C et al 2009 Adv. Func. Mater. 19 1857–62
[8] Lauret J S et al 2005 Phys. Rev. Lett. 94 037405
[9] Mickelson W, Aloni S, Han W Q, Cumings J and Zettl A 2003 Science. 300 467–69
[10] Trave A, Ribeiro F J, Louie S G, Cohen M L 2004 Phys Rev B. 70 205418
[11] Walker K, Rance G A, Pekker A, Tohati H M, Nemeth G, Fay M W, Lodge R W, Stoppiello C T, Kamaras K and Khlobystov A N 2017 Small Methods. 1 1700184
[12] Lee C H, Wang J, Kayatsha V K, Huang J Y and Yap Y K 2008 Nanotechnology. 19 455605
[13] Guo L and Singh R N 2009 Phys. E. 41 448
[14] Lim S H, Luo J, Wei J and Lin J 2007 Catalysis Today. 120 346-50
[15] Bi J Q, Wang W L, Qi Y X, Bai Y J, Pang L L, Zhu H L, Zhao Y and Wang Y 2009 Mater. Lett. B. 63 1299-1302
[16] Fakrach B, Rahmani A, Chadli H, Sbai K, Bentaleb M, Bantignies J L and Sauvajol J L 2012 Phys. Rev. B. 85 115437
[17] Bantignies J L, Sauvajol J L, Rahmani A and Flahaut E 2006 Phys. Rev. B. 74 195425
[18] Rahmani A, Sauvajol J L, Rolsand S and Benoit C 2002 Phys. Rev. B. 66 125404-12
[19] Fakrach B, Fergani F, Boutahir M, Rahmani AH, Chadli H, Hermet P and Rahmani A 2018 Crystals. 8 118
[20] Darkrim F and Levesque D 1998 J. Chem. Phys. 19 4981-84
[21] Lee C H, Wang J, Kayatsha V K, Huang J Y and Yap Y K 2008 Nanotechnology. 19 455605
[22] Yuan J and Liew K M 2011 *Carbon*. 49 677–683
[23] Saito R, Takeya T, Kimura T, Dresselhaus G, Dresselhaus M S 1998 *Phys. Rev. B*. 57 4145
[24] Benoit C, Royer E and Poussigue G 1992 *J Phys. Condens Matter*. 4 3125