



Vibrational and electronic properties of single-walled and double-walled boron nitride nanotubes

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ABSTRACT

We calculated IR, nonresonance Raman spectra and vertical electronic transitions of the zigzag single-walled and double-walled boron nitride nanotubes ((0,*n*)-SWBNNTs and (0,*n*)@(0,2*n*)-DWBNNTs). In the low frequency range below 600 cm⁻¹, the calculated Raman spectra of the nanotubes showed that RBMs (radial breathing modes) are strongly diameter-dependent, and in addition the RBMs of the DWBNNTs are blue-shifted reference to their corresponding one in the Raman spectra of the isolated (0,*n*)-SWBNNTs. In the high frequency range above ~1200 cm⁻¹, two proximate Raman features with symmetries of the A_{1g} (~1355 ± 10 cm⁻¹) and E_{2g} (~1330 ± 25 cm⁻¹) first increase in frequency then approach a constant value of ~1365 and ~1356 cm⁻¹, respectively, with increasing tubes' diameter, which is in excellent agreement with experimental observations. The calculated IR spectra exhibited IR features in the range of 1200–1550 cm⁻¹ and in mid-frequency region are consistent with experiments. The calculated dipole allowed singlet–singlet and triplet–triplet electronic transitions suggesting a charge transfer process between the outer- and inner-shells of the DWBNNTs as well as, upon irradiation, the possibility of a system that can undergo internal conversion (IC) and intersystem crossing (ISC) processes, besides the photochemical and other photophysical processes.

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1. Introduction

Carbon nanotubes (CNTs) were discovered in 1991 [1], and their unique physical, chemical, and electronic properties have led to a variety of technological uses in functional nanodevices, especially as transistors and sensors [2–7], in heat conduction systems [8,9], in specialty electronics [10,11], molecular memories [12], optics [13–15], electrically excited single-molecule light sources [16–19], to functionalized DNA [20,21], high-performance adsorbent electrode material for energy-storage device [22], and protein functionalization [23,24]. In recent years there have been numerous experimental and theoretical studies to realize the structural and optical properties of single-walled, double-walled and multi-walled nanotubes, such as BN [25,26], BC₃ [27], BC₂N [28], CN [29], AlN [30] GaN [31], SiC [32], and WC [33] nanotubes, have been predicted theoretically, and some of them have been synthesized, such as BN [34] and B_xC_yN_z [35], doped and functionalized nanotubes.

As it is well known, carbon nanotubes can be visualized as being formed by rolling up a defined projected area from within the hexagonal lattice of a graphene sheet in a seamless fashion such that all carbon–carbon (C–C) valences are satisfied, and the direction in which the roll up is performed transforms into the

circumference of the tube. The projected area is in fact a homomorphic representation of a particular carbon nanotube [51]. Carbon nanotubes can be metallic or semiconducting depending on their structures. This is due to the symmetry and the unique electronic structure of graphene. If the chiral indices are equal, $n = m$, the nanotube is metallic; if $n - m$ is a multiple of 3, then the nanotube is semiconducting, with a very small band gap; otherwise, the nanotube is a moderate semiconductor [36]. Interestingly, some nanotubes have conductivities higher than that of copper, while others behave more like silicon.

More recently, boron nitride nanotubes (BNNTs) can be counted among the modified CNT that have been synthesized [37–39]. The electronic properties of boron nitride nanotubes differ from carbon nanotubes: while carbon nanotubes can be either metallic or semiconducting, depending on their chirality and radius [40], all boron nitride nanotubes (BNNTs) are found to be semiconducting materials with a large band gap [41,51]. In addition, since the band gap is large, the gap energy is only weakly dependent on the diameter, chirality, and the number of walls of a multi-walled tube structure. It is to be noted that single-walled and multi-walled nanotubes generally have properties that are significantly different, while double-walled nanotubes (DWNTs) can be viewed as representing the key structure that defines the transition between SWNTs and MWNTs. Moreover, because of their semiconducting character, BNNTs like CNTs themselves are also very interesting materials for application in nanoscale devices, and have been

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considered as alternatives to CNTs [42,43]. Like CNTs the modification of the electronic properties of BNNTs by doping and functionalization is an important avenue for making nanodevices. The doped BNNTs nanotubes may exhibit a dramatic change relative to the pristine nanotube. Furthermore, because of the strong interactions between electrons and holes in BNNTs [44,45], the excitonic effects in BNNTs have proven more important than in CNTs. Bright and dark excitons in BNNTs qualitatively alter the optical response [46].

As it is well known, the optical properties of nanotubes are implicitly connected with the absorption, photoluminescence, and Raman spectroscopy of nanotubes. Such optical measurements permit a reliable characterization of the quality of nanotube such as chirality, size, and structural defect. In the case of Raman measurements, even though a large number of phonon modes of carbon nanotubes would be expected, most of them are Raman inactive due to the selection rules that emanate from the high symmetry properties of the nanotubes. The Raman spectrum of a nanotube exhibits a few characteristic modes that can be used to determine the size of nanotubes and to classify the type of the nanotubes, such as semiconducting and metallic. For example, in the low frequency region, one type of characteristic vibration is called the radial breathing mode (RBM); this movement of the atoms is in the radial direction with the same phase, and corresponds to vibration of the entire tube, which is strongly diameter-dependent [47,48]. The RBM is used to determine the size of the nanotube. Additionally, there are two other characteristic Raman bands that lie in the range of 1300–1650 cm^{-1} , which are called tangential modes. The line shape of these Raman modes may be used to classify whether the nanotube is metallic or semiconducting. These Raman modes in the high energy region are also slightly diameter dependent [47,48].

For a better understanding of the physical and optical properties of nanotubes, quantum mechanical calculations have been extremely helpful. In this work, we provide theoretical results on double-walled boron nitride nanotubes (DWBNNs) using DFT; this report extends the quantum chemical computational approach that we have used earlier [47–49]. The results of calculations not only indicate the shift in the spectral peak positions of the RBM and G-modes in Raman spectra of DWBNNs relative to their corresponding isolated SWBNNs, but also indicate a charge transfer from the outer-shell to the inner-shell when DWBNNs are excited, as discussed in Section 3.4. Furthermore, the plots of the frequencies of vibrational radial breathing modes (RBM) versus $1/d_t$ for the zigzag double-walled boron nitride nanotubes $(0,n)@(0,2n)$ -DWBNNs exhibit a strong diameter dependence.

2. Computational methods

The ground state geometries of single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs), and single-walled boron nitride nanotubes (SWBNNs) were optimized without symmetry restriction on the initial structures. Both structure optimization and vibrational analysis calculations were implemented using DFT with functionals, specifically, B3LYP, in which the exchange functional is of Becke's three parameter type, including gradient correction, and the correlation correction involves the gradient-corrected functional of Lee, Yang and Parr. The basis set of split valence type 6-31G, as contained in the Gaussian 03 software package [50], was used. The results of the calculations did not produce any imaginary frequencies. It is worth nothing that during the vibrational calculations, in order to eliminate the contributions to the peaks intensity in the vibrational spectra from the motion of the hydrogen atoms (on the open end point of the nanotube), their internal motions were fixed. The vibrational mode descriptions were made on the basis of calculated

nuclear displacements using visual inspection of the animated normal modes (using GaussView03) [50], to assess which bond and angle motions dominate the mode dynamics for the nanotube. The DFT method was chosen because it is computationally less demanding than other approaches as regards inclusion of electron correlation. Moreover, in addition to its excellent accuracy and favorable computation expense ratio, the B3LYP calculation of Raman frequencies has shown its efficacy in numerous earlier studies performed in this laboratory and by other researchers, often proving itself the most reliable and preferable method for many molecular species of intermediate size, including anions and cations [47,48,51–56]. In our calculations, hydrogen atoms have been placed at the end points of the unit cells. Furthermore, the time-dependent density functional theory at TD-B3LYP/6-31G level were applied to calculate the vertical electronic transitions for the $(0,n)@(0,2n)$ -DWCNTs and -DWBNNs, and $(0,n)$ - and $(0,2n)$ -SWCNTs and -SWBNNs.

3. Results and discussion

3.1. Structure results

Calculated diameters of the $(0,n)@(0,2n)$ -DWCNTs (zigzag double-walled carbon nanotube) and $(0,n)@(0,2n)$ -DWBNNs (zigzag double-walled boron nitride nanotubes), for $n=6$ –10, were found to decrease for the inner-nanotube and increase for the outer-nanotube, referenced to the corresponding diameter of the zigzag single-wall nanotube $((0,n)$ -SWNT) which changes with n . A fit to the calculated individual tube diameters for each inner- and outer-shell of the DWCNTs and DWBNNs using a functional form that depends inversely on single-walled nanotube's diameter: the fitting parameters are shown in Eqs. (1a)–(2b)

$$D_t \text{ (outer-shell-DWCNT), in nm} = -0.040 + \frac{0.147}{d_t} + \frac{0.138}{d_t^2} \quad (1a)$$

$$D_t \text{ (inner-shell-DWCNT), in nm} = -0.039 + \frac{0.037}{d_t} + \frac{0.005}{d_t^2} \quad (1b)$$

$$D_t \text{ (outer-shell-DWBNN), in nm} = -0.009 + \frac{0.114}{d_t} + \frac{0.143}{d_t^2} \quad (2a)$$

$$D_t \text{ (inner-shell-DWBNN), in nm} = -0.069 + \frac{0.081}{d_t} + \frac{0.021}{d_t^2} \quad (2b)$$

A comparison of the diameters of the inner- and outer-shells of the DWNTs with their corresponding SWNTs diameters show that the inner-shells diameters decrease and the outer-shells diameters increased. These predictions explicitly indicate the existence of intertube interactions in DWCNT systems. As seen in Fig. 1, the diameter dependence of the curvature energies of the DWCNTs and DWBNNs referenced to the global energies per hexagon of the $(0,10)@(0,20)$ -DWCNTs and -DWBNNs is well fitted by a Lennard–Jones potential expression $E_{LJ} = -((A/r^6) - (B/r^{12}))$ where parameters of the are A and B are van der Waals interaction parameters in Lennard–Jones potential as given in Eqs. (3a) and (3b):

$$\Delta E \text{ (DWBNNs, in eV)} = -\left(\frac{0.503}{D_t \text{ (nm)}}\right)^6 \left\{1 - \left(\frac{0.266}{D_t \text{ (nm)}}\right)^6\right\} \quad (3a)$$

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