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Raman spectrum of single-walled boron nitride nanotube

B. Fakrach [a], A. Rahmani [a,*], H. Chadli [a], K. Sbai [a], J.-L. Sauvajol [b]

[a] Laboratoire de Physique des Matériaux et Modélisation des Systèmes (Unité Associée au CNRST-URAC), Université MY Ismaïl, Faculté des Sciences, BP 11201, Zitoune, Meknes, Morocco

[b] Laboratoire des Colloïdes, Verres et Nanomatériaux (UMR CNRS 5587), Université Montpellier II, 34095, France

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ABSTRACT

Using the spectral moments method, the calculations of the Raman spectra of single-walled boron nitride nanotubes (SW-BNNTs) were performed in the framework of the force constants model. Spectra were computed for chiral and achiral nanotubes for different diameters and lengths. The Raman scattering intensities were determined using the bond-polarizability model and a good agreement with group theory analysis was found. We show that the modes in the low frequency region are very sensitive to the nanotube diameter variation, whereas the ones associated to the tangential region are chirality dependent. The number of Raman active modes, their frequencies, and intensities depend on the length of the nanotube.

1. Introduction

After the emergence of single walled carbon nanotube (SWCNT) [1], the existence of other tubular structure of different materials was anticipated. From tight-binding [2] and first-principal calculations [3], boron nitride nanotube (BNNT) was predicted to be a stable nanostructure. The BNNT is diatomic specie with its geometrical structure identical to that of SWCNT where boron and nitrogen atoms occupy the alternate nodes. The possibilities for technological applications of SW-BNNTs motivated the development of various methods for their production: arc discharge [4,5], laser ablation [6,7], and chemical vapor deposition [8]. A continuous laser vaporization process under a nitrogen atmosphere that produced BNNTs in gram quantities reported [9]. The produced tubes have a finite length typically between 100 and 400 nm and appear either as individual tubes or as bundles where they are packed together through van der Waals inter-tubes interactions.

Vibrational spectroscopy especially Raman spectroscopy, has been shown to play a major role in carbon nanotube science [10]. At a theoretical level, the nonresonant Raman spectra of SWCNTs have been calculated within the bond polarizability model [11,12]. It is expected that the combination of Raman and infrared spectroscopies will be a standard characterization tools for BNNTs. However, due to difficulties with the sample purification no experimental data on contamination-free samples have been reported. Electronic structure calculations indicated that the band gaps of BNNTs are insensitive to the diameter, chirality, and whether the tube is single walled, multi walled or packed into bundles [2,3]. Measurements of the optical properties on a synthesized BN nanotube sample by means of absorption [13] and low-loss EELS [14,15] were performed and confirmed the predicted large band gap. Due to this latter large electronic band gap of the BNNTs, the Raman scattering of light is expected to be nonresonant in contrast to carbon nanotube in which the process is resonant. Raman experiments on unpurified BNNTs prepared by laser vaporization process have been reported [16]. Raman spectrum was measured at different laser energies (457.9, 488, and 514.5 nm) [17]. Therefore, the resulting spectra are weaker in intensity and must be carefully separated from a possible overlap by resonant Raman scattering from contaminants. More recently, Raman spectroscopy of SW-BNNTs have been performed using visible and UV excitation energies [18]. The authors show that in the visible range, the effect of contaminants is important, since it can hide the spectroscopic response of BNNTs. In the UV range, Raman scattering at 229 nm excitation wave length provides preresonant conditions and allows to identify the tangential modes at high frequency (1370 cm^{-1}). In contrast to SWCNTs, no dependence on the excitation wavelength was observed confirming the insulating character of BNNTs.

* Corresponding author. Tel.: +212 35 55 62 10; fax: +212 35 43 94 82.
E-mail address: rahmani@fs-umi.ac.ma (A. Rahmani).

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Using a force constants model in which the interatomic force constants up to the fourth-nearest-neighbor interaction are fitted to experimental data, many calculations of phonons have been performed for graphite and carbon nanotubes [19,20]. These approaches are very fast and allows a good understanding of phonon in carbon nanotubes. The same approach was developed recently by Xiao et al. for phonons in boron nitride [21] and BC3 [22] nanotubes. Group-theoretical analysis of single BNNTs [23] reveals that four A, five E_1 and six E_2 modes for chiral nanotubes, three A_1, five E_1, and six E_2 modes for zigzag nanotubes, and three A_g, two E_{1g}, and four E_{2g} modes for armchair nanotubes are Raman active. The infrared and Raman active modes of individual single BNNTs have been predicted by different theoretical approaches: zone-folding [24] combined with bond polarizability parameters of carbon [3,4], tight binding approach [25], and *ab initio* calculations [26,27]. From these studies, it is confirmed that the radial breathing mode (RBM) in carbon nanotubes is inversely proportional to the tube diameter [20]. In BN nanotube, note only the RBM, but most of the low frequency modes display the same behavior, i.e., $\omega_{RBM} = A/D$, the constant A is model dependent, $A \approx 218.2\,\mathrm{cm^{-1}\,nm^{-1}}$ from tight-binding model [25], $A \approx 190.2\,\mathrm{cm^{-1}\,nm^{-1}}$ from force constants model [21], $A \approx 170.2\,\mathrm{cm^{-1}\,nm^{-1}}$ from valance shell model [24] and $A \approx 205$ and $209.8\,\mathrm{cm^{-1}\,nm^{-1}}$ for the zigzag and armchair tubes respectively, from potential linear combination of atomic orbitals approach [28].

In this work, we present calculation results of the nonresonant Raman spectra in the breathing modes (BM), intermediate and tangential modes (TM) ranges of single-walled boron nitride nanotube. These calculations have been performed for a large collection of infinite nanotubes with various diameter and chirality. Thanks to the spectral moments method, we have investigated the finite length effects on SW-BNNT Raman spectrum.

2. Model and formalism

A SW-BNNT structure can be considered in quite the same way as it was done for SWCNT [19] by rolling a single hexagonal BN sheet. Such a tube can uniquely be specified by the pair of integers (n,m) that define the lattice translation vector. In this work, the interatomic interactions at the surface of the SW-BNNT are described by using the force constants model (Table 1) introduced by Xiao [21].

The spectral moments method (SMM) was shown to be a powerful tool for determining infrared absorption, Raman scattering, and inelastic neutron-scattering spectra of harmonic systems [30]. In our previous work on the nonresonant Raman spectrum on finite and infinite SWCNTs, we have successfully calculated the Raman spectra for achiral and chiral SWCNTs in a large range of diameters and lengths (up to 80 nm) [12]. This same approach was recently used to calculate the dependence of the Raman spectrum of double-walled carbon nanotubes as a function of the diameter and chirality of the inner and outer tubes [12].

Table 1
Force-constant parameters for 2D h-BN in units of 10^4 dyn/cm.

Radial	Tangential	
$\phi_r^1 = 31.00$	$\phi_{ti}^1 = 18.50$	$\phi_{to}^1 = 5.60$
$\phi_r^{B-B} = 7.00$	$\phi_{ti}^{B-B} = -3.23$	$\phi_{to}^{B-B} = -0.70$
$\phi_r^{N-N} = 8.00$	$\phi_{ti}^{N-N} = -0.73$	$\phi_{to}^{N-N} = -0.55$
$\phi_r^3 = -1.00$	$\phi_{ti}^3 = -3.25$	$\phi_{to}^3 = -0.65$
$\phi_r^4 = -1.90$	$\phi_{ti}^4 = 1.29$	$\phi_{to}^4 = -0.30$

Here the subscripts *r*, *ti*, and *to* refer to radial, transverse in plane, and transverse out of plane, respectively.

The Raman scattering of light is expected to be nonresonant for BN nanotubes. Therefore, the Raman scattering cross section can be calculated assuming the induced polarization tensor is known [31–33]. In this paper, the Raman cross section was calculated assuming that scattering can be described within the framework of the bond polarizability model and the Raman intensities are calculated using the bond polarizability parameters of carbon [29].

3. Results and discussions

In this section we report calculations result for the polarized nonresonant Raman spectra of achiral and chiral single-wall boron nitride nanotubes of different diameters and chiralities using the spectral moments method. The mode frequency is directly obtained from the position of the peak in the calculated Raman spectrum. In all our calculations, we consider the Z nanotube axis is to be along z axis, and the X nanotube axis is to be along the x axis of the laboratory reference frame. The laser beam is kept along the y axis. Three geometrical configurations are considered: in the ZZ configuration, both incident and scattered polarizations are along the Z axis and, for ZX (XY) configuration, the incident and scattered polarizations are along the $Z(X)$ and $X(Y)$ axes respectively.

3.1. Polarized Raman spectra of infinite SW-BNNTs

The calculations of the Raman spectra for achiral (armchair and zigzag) and chiral nanotubes are performed for infinite crystal of nanotubes by applying periodic conditions of nanotube unit cell. In Fig. 1, we show the polarized calculated ZZ (top), ZX (middle) and XY (bottom) Raman spectra of infinite (10, 10), (17, 0) and (14, 5) nanotubes, whose diameters are 1.37, 1.35 and 1.35 nm, respectively. The spectra are displayed in the BM, intermediate and TM regions.

In the BM region (lower than $500\,\mathrm{cm^{-1}}$), one can see that for (10, 10) armchair BNNT, a single A(RBM) radial-breathing mode is observed in the ZZ polarization, a single longitudinal $E_1(L)$ mode in ZX and two radial and tangential ($E_2(R)$, $E_2(T)$) modes in YX. The number and the symmetry of these modes are the same as for infinite SWCNT [12]. For (17, 0) zigzag and (14, 5) chiral tubes, a single A(RBM) mode is active in the ZZ polarization, two ($E_1(L)$, $E_1(T)$) modes in ZX and three ($E_2(R)$, $E_2(L)$, $E_2(T)$) modes in YX. The chiral and zigzag BN tubes show one E_1 and E_2 additional Raman active modes in comparison with SWCNTs.

In the ($600–1200\,\mathrm{cm^{-1}}$) intermediate-frequency region, three weak A_1, E_1 and E_2 modes are observed respectively in ZZ, ZX and YX spectra of zigzag and chiral nanotubes. For (10, 10) armchair nanotube, only two weak A_g and E_{2g} modes are Raman active.

Concerning the TM region, the ZZ polarized calculated spectra show two peaks for chiral and one peak for achiral SW-BNNTs. In the case of zigzag tube, the spectra show one weak peak for ZX and XY polarizations.

The number of active modes is in agreement with group theory calculations [23] and the calculated wave numbers of these active modes are given in Table 2. Our calculations predict that all BM (except the E_2 very low frequency mode) and TM modes have sufficient intensity to be detected in Raman experiments.

Considering now the chirality dependence of the TM Raman spectra profile (Fig. 1: TM region). As mentioned, for zigzag ($\theta = 0^\circ$) and armchair ($\theta = 30^\circ$) tubes, each polarized spectrum is featured by a strong peak assigned to A_1, E_1, and E_2 tangential modes in ZZ, ZX and YX configuration, respectively. For each symmetry, let us call ω_z and ω_a the wave number of the zigzag