A Comparative Theoretical Study of Carbon and Boron-Nitride Single-wall Nanotubes

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ABSTRACT

In this study we report the results of a theoretical study of vibrational and electronic properties of single-wall BN and C nanotubes (BN-NTs and CNTs), taking into account the effects of intertube coupling, by using a full potential linear combination of atomic orbitals method, as well as a planewave pseudo-potential density functional theory approach. Up-shifts in the values of the radial breathing modes (RBMs) due to intertube coupling were calculated, and found to be small and systematic, for both BN-NTs and CNTs. An understanding of the observed behavior was obtained in terms of the effects of intertube interactions on the van Hove singularities. We conclude that our approach provides a reasonable tool for accurate predictions of RBMs in carbon, and possibly BN nanotubes.

Keywords: Boron Nitride and Carbon Nanotubes, Density Functional Theory, Radial Breathing Mode, Intertube Coupling.

1. INTRODUCTION

From the time of their discovery, CNTs [1] and BN-NTs have been receiving ever-increasing interest due to their unique properties and potential application in nano-devices. CNTs can be either metallic or semiconducting, depending on the tube chirality and diameter, suggesting a variety of applications [2]. BN-NTs have a wide band gap [3] regardless of chirality and diameter.

However, applications are still hampered by the diversity of tube diameters and chirality, due to various preparation methods, thus leading to studies on separation and characterization [4], and rendering theoretical predictions important. Resonant Raman spectroscopy is an important technique in probing and characterizing the structure of nanotubes [5], which can be explained in terms of the van Hove singularities (vHs) in the electronic density of states. Also, the relationship between the RBMs and tube diameter is well known [6].

However, simpler models may not be appropriate for predicting RBMs, especially for small diameter tubes, and to provide insight into the effects of intertube interactions. Indeed, an extensive study of single-wall carbon nanotube properties was recently carried out [7], where CNTs were modeled as isolated tubes or crystalline-ropes, using a full-potential linear combination of atomic orbitals (FP-LCAO) density functional theory approach. Although this approach is computationally intensive, the accuracy in modeling single-wall CNTs was evident in comparison to other theoretical work and experiment. In a related paper [8] we reported an extensive and rigorous investigation using FP-LCAO and planewave pseudopotential methods (PW-PP), as the first step towards establishing an approach for accurate properties predictions, while in this study we highlight the results for RBMs that could provide a useful tool to assist nanotubes characterization. Calculations were carried out using DMOL3 and CASTEP [9] (computational details are reported elsewhere [8]). Note that the geometry and cell parameters were optimized in all calculations to take into account intertube coupling effects.

2. RESULTS AND DISCUSSION

Theoretical and experimental [10,11] studies of CNTs RBMs are well known, but values for BN-NTs are still not readily available. Our calculations were carried out for both isolated tubes and ropes with optimized intertube distances (Table 1), fitting the RBM values to A/R, where R is the radius and A the fitting constant (*cf.* Table 2). The results are consistent with previous calculations [12] and experimental data. In order to assess the reliability of the A/R relationship, in terms of extrapolating results to larger diameter tubes, a calculation for the isolated armchair C(20,20) tube (which has 80 atoms per unit cell) was carried out, obtaining a value of 84 cm^{-1}, in good agreement with the extrapolated value of 86 cm^{-1}. These results imply that our fitting constants could be used to predict RBMs. A similar behavior is noted for BN-NTs. Note that the fitting constants in CNTs are higher than those in BN-NTs by 8% and 10%, for zigzag and armchair tubes, respectively.

Chirality	Carbon			BN		
	Isolated tube	Rope	Up-Shift	Isolated tube	Rope	Up-shift
(6,0)	453.6	460.7	1.5%	414.5	420.0	1%
(8,0)	361.0	366.5	1.5%	317.1	320.6	1%
(9,0)	---	---	---	279.8	283.6	1%
(10,0)	291.4	299.5	2%	---	---	---
(4,4)	426.0	435.0	2%	---	---	---
(6,6)	287.0	297.0	3.5%	251.1	261.6	4%
(8,8)	215.0	229.0	6.5%	188.8	203.6	7%
(9,9)	---	---	---	168.6	177.7	5%
(10,10)	171.0	181.0	6%	153.0	156.4	2%

Table 1: Radial breathing mode values (cm^{-1})

SWNT	Fitting constants	
	Isolated tube	Rope
C(n,0)	1120 (1160) [12]	1140
C(n,n)	1167 (1180) [12]	1207
BN(n,0)	1025	1038
BN(n,n)	1049	1101

Table 2: RBM fitted constants (A [Å cm^{-1}]) to 1/R

van der Waals interactions alter the RBMs, as observed (Table 2). In testing the sensitivity of the RBMs with respect to the intertube distance we find that the intertube distance values are about 3%, on average, smaller than (2R+3.4Å); indeed,, the calculated RBM for a C(6,6) tube at the graphite interlayer distance (3.4Å), for example, equals that of an isolated tube. Thus, RBM calculations were performed at the optimized intertube distances. Other theoretical work [13,14] reported up-shifts of 8% and 12% in the RBM values for C(9,9) and C(10,10) nanotubes. Our results show lower up-shifts, especially in the zigzag tubes, where the up-shift is found to be small and systematic, about 2% in CNTs and 1% in BN-NTs, whereas it varies from 2% - 7% in the armchair CNTs and BN-NTs.

Calculations of the electronic density of states of CNTs to study the change of the first and second vHs due to the intertube coupling, were compared to previous theoretical studies, which reported the effects of van der Waals interactions on the electronic structures, such as the opening of a pseudo-gap due to the broken symmetry [15] in the metallic C(10,10) nanotubes. A study using tight binding [16] suggested that the pseudo-gap expands the vHs, concluding that the expansion needs to be taken into account in the Raman spectroscopy tubes characterization. Our calculations show an opening of a pseudo-gap in all cases [8], appearing exactly at the equilibrium intertube distance. Also, the E_{22}/E_{11} values were found to be 1.7 and 2.0 for the armchair and zigzag nanotubes, respectively, generally in agreement with experiment.

3. CONCLUSIONS

A comparative study of BN and C nanotubes using first-principle calculations revealed interesting features and trends for RBMs, particularly the effects of intertube coupling. This study may serve as the first step towards establishing an approach for accurate properties predictions in nanotube materials.

4. REFERENCES

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