Chemical Physics Letters 679 (2017) 45–51

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Raman intensity and vibrational modes of armchair CNTs

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ARTICLE INFO

Article history:
Received 6 March 2017
In final form 22 April 2017
Available online 24 April 2017

Keywords:
Bond polarizability change
$\sigma-\pi$ hybridizations
Structural distortion
Edge effect
Vibrational density of state (VDOS)

ABSTRACT

Raman intensity changes and frequency patterns have been studied using the various armchair (n,n) to understand the variations of bond polarizability, in regard to changing diameters, lengths, and the number of atoms in the (n,n). The Raman intensity trends of the (n,n) are validated by those of C_n isomers. For frequency trends, similar frequency patterns and frequency inward shifts for the (n,n) are characterized. Also, VDOS trends of the (n,n) expressing Raman modes are interpreted. The decomposition of vibrational modes in the (n,n) into radial, longitudinal, and tangential mode is beneficially used to recognize the distinct characteristics of vibrational modes.

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1. Introduction

Carbon nanotubes (CNTs) have been characterized experimentally and theoretically, since they were discovered [1]. To identify the various properties such as electronic [2], vibrational [3], or mechanical [4] properties of CNTs, many researches have been performed. Theoretical approaches have been fulfilled to explore vibrational characteristics of CNTs, for example, zone folding model [5], force constant models [6,7], tight binding calculations [8–10], and *ab-initio* calculations [11–16].

Among types of CNTs, all armchair (n,n) show a symmetric mirror plane along the principal nanotube axis that we label the z direction, and the (n,n) are known as achiral nanotubes [17]. With a group theory, all the (n,n) display Raman active modes which are A_{1g}, E_{1g}, and E_{2g} vibrational modes corresponding to $\{x^2 + y^2\}$, $\{xy, yz\}$, and $\{x^2 - y^2, xy\}$ basis functions of the irreducible representations. The amplitudes of vibrations based on these basis functions exhibit zero, two, and four nodes in the xy plane, respectively [18]. As a good example of vibrational modes in the (n,n), radial breathing mode (RBM) having strong A_{1g} active modes at the low frequency range was reported by Rao et al. [19]. By using tight binding models or *ab-initio* models, the frequencies of RBMs have been identified and shown to be inversely proportional to diameters of the (n,n), showing strong A_{1g} symmetry. D-band is featured by the defects and the finite size effects of the (n,n), and G-band modes showing tangential vibrations are widely known [20].

To date, little attention has been paid to characterizing Raman intensity variations, frequency shifts, and vibrational density of states (VDOSs) with respect to a series of the (n,n), whose characteristics have a strong correlation with the changes of tube diameters, lengths, and the number of carbon atoms. In this sense, main purpose of this study is here to examine Raman intensity and frequency characteristics, to analyze VDOSs of the (n,n) including 3-decomposed vibrational modes, and to explore unknown vibrational mode frequencies in the high frequency range, regarding to the (n,n).

The Raman intensity changes are dependent on polarizability changes in a bond of the CNT structure as increasing the tube diameters, representing that $\sigma-\pi$ hybridizations are changed from more like sp^3 to sp^2 structures by bond angle changes. It is found that the magnitude of Raman intensities associated with the most symmetric vibrations (A_{1g} symmetric modes) increases as the magnitude of bond polarizability changes is increased in the CNT matrix structure. Bond polarizability changes come from the distortion of electron distributions in a bond of the CNT structure, meaning that $\sigma-\pi$ hybridizations originated in smaller bond angles of the CNT matrix more likely cause electric bond polarizability changes. For calculations, we used the (n,n); $n = 2$–15 to see the sequential trends of Raman intensities showing the bond polarizability changes as a function of the tube diameters, lengths, and the number of the tube atoms. We suspect that Raman intensities for purely symmetric A_{1g} modes (radial atom displacements) become stronger for smaller tubes whose $\sigma-\pi$ hybridizations are consistent with their more sp^3-like hybridization structures. The hypothesis is supported by the results obtained from characteriz-

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http://dx.doi.org/10.1016/j.cplett.2017.04.078
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ing the Raman intensity trends of carbon isomers, C_{20}, C_{28}, C_{60}, and C_{70}, which show similar intensity trends to those of the (n,n). It is also valuable to see interesting frequency variations of the (n,n); n = 5–15 with l = 2 in D–band like and G–band like frequency range. Specifically, frequency inward shifts and intense peaks discovered in the two frequency ranges mentioned above might be useful for some of the (n,n) to distinguish their characteristics.

VDOS of the (n,n) is another important subject to be considered when changing the various armchair indice (n,n), because the vibrational mode distributions of the (n,n) represent the vibrational motions of each atom inside of the CNT matrix and are related to the physical properties such as the electronic structure. In this point, the decompositions of the vibrational modes into radial, longitudinal, and tangential components in VDOS are definitely useful to characterize the variations of the electronic structure, derived from the curvature effects on frequency patterns as changing the diameters of the (n,n). The $\sigma-\pi$ hybridization deviations and smaller tube radii that lead to more CNT curvatures should be an determinant of the decrease of π interactions in the CNT structure. In using the eigenvectors of each carbon atom in the (n,n), 3-decomposed vibrational modes are distinguished, and these modes of the selected (n,n) are characterized, which obviously show the distinct frequency patterns as increasing the tube diameters and unit cell lengths. Consistent VDOS patterns and frequency shifts observed in some decomposed modes are necessarily taken into account. Exceptional VDOS patterns above $\sim$1900 cm^{-1} in tangential mode are considered as particular characteristics of the (n,n), and it is presumably suggested that the VDOSs above the high frequency are formed from the edge of the (n,n) as edge modes.

To better understand Raman intensity features related to bond polarizability and the π interactions in the $\sigma-\pi$ hybridizations, which are induced by the tube curvatures, the trends of RBM, D-band like, and G-band like frequencies are characterized. VDOS patterns of the (n,n) are interpreted by using Gaussian density functions. Further, the changes in symmetry-decomposed vibrational modes with respect to the various diameter changes of the (n,n) are valuably studied. For the trends of 3-decomposed vibrational modes, two of the armchair (n,n) were selectively chosen to see the most obvious frequency trends in this work.

2. Methods

Armchair carbon nanotube fragments with a variety of diameters and lengths were prepared. Their geometry is optimized with Gaussian 09, revision B.01 [21], using density functional theory with the B3LYP functional [22,23] and the 6-31G basis set [24,25] whose accuracy is enough to calculate Raman spectra of the (n,n) only consisting of carbon atoms, and computation time is reasonably fast. Raman intensities with A_{1g} symmetry and eigenvector values for the (n,n); n = 2–15 are calculated, and all vibrational mode frequencies from 0 cm^{-1} through 2500 cm^{-1} are calculated with the finite-sized nanotubes.

Length (l) of the tube is defined here as the number of length unit cells of the armchair (n,n) in the longitudinal direction (z-axis). For example, the (5,5), an armchair tube with one length unit cell (l = 1) contains 20 carbon atoms. Length unit cells of the (n,n) are used from l = 2 up to l = 25, and the armchair indice (n,n) from the (2,2) to the (15,15) are applied. Non-periodic boundary conditions of the finite-sized (n,n) are used without hydrogen terminations. Finite size of the non-periodic (n,n) ranges from a minimum of 24 atoms to a maximum of 200 atoms.

Table 1 shows all the armchair (n,n) used in here. Each of the geometry-optimized tubes with DFT calculations provides a stable geometry that has a minimum energy. Among the (n,n), a minimum diameter is 2.8 Å for the (2,2) tube and a minimum length is 3.69 Å for the (15,15) when using only 2 length unit cells. A maximum diameter is 20.35 Å for the (15,15) tube and a maximum length is 61.6 Å for the (2,2) when using 25 length unit cells.

Table 1
All armchair (n,n) used for the Raman intensities, frequency trends, and vibrational modes.

(n,n)	Length unit cells (l)	Atoms used
(2,2)	l = 2, 5, 7, 13, 20, 25	16–200
(3,3)	l = 2, 3, 4, 5, 9, 10, 12, 13, 15, 16	24–192
(4,4)	l = 2, 3, 4, 6, 7, 9, 10, 12	32–192
(5,5)	l = 2, 3, 4, 5, 6, 7, 8, 9, 10	40–200
(6,6)	l = 2, 4, 5, 6, 7, 8	48–192
(7,7)	l = 2, 3, 4, 5, 6, 7	56–196
(8,8)	l = 2, 3, 4, 5, 6	64–192
(9,9)	l = 2, 3, 4, 5	72–180
(10,10)	l = 2, 3, 4, 5	80–200
(11,11)	l = 2, 3, 4	88–176
(12,12)	l = 2 and 3	96 and 144
(13,13)	l = 2 and 3	104 and 156
(14,14)	l = 2 and 3	112 and 168
(15,15)	l = 2 and 3	120 and 180

All eigenvector values using Cartesian (x,y,z) coordinate for each vibrational mode are used to decompose the vibrational modes into their radial, tangential, and longitudinal components. Here, we define the calculation of each decomposed vibrational mode. The calculation of vibrational mode frequencies results in $3N$ different eigenvectors $\mathbf{e}_i = (\vec{e}_{i1}, \vec{e}_{i2}, \cdots, \vec{e}_{iN})$, where $\vec{e}_{ij}$ describes the three dimensional motion of atom j in eigenmode i. Typically, these displacements are calculated in Cartesian coordinates. However, given the cylindrical symmetry of the CNT systems, it is convenient to express the atomic displacements in cylindrical coordinates, with a distinct coordinate system for each atom, using its position vector to define the radial direction. That is, for any atom j we can define a cylindrical coordinate system with mutually orthogonal unit vectors $\hat{\rho}_j, \hat{\theta}_j, \hat{z}$ where

$$\hat{\rho}_j = \hat{r}_j - (\hat{r}_j \cdot \hat{z})\hat{z} \tag{1}$$

is the projection of the position of atom j into the x–y plane and

$$\hat{\rho}_j = \frac{\hat{\rho}_j}{|\hat{\rho}_j|} \tag{2}$$

is the unit vector pointing in the same direction. The $\hat{z}$ vector is the same in cylindrical coordinates as in Cartesian coordinates (and does not vary with atom position), and the tangential direction is defined as

$$\hat{\theta}_j = \hat{z} \times \hat{\rho}_j \tag{3}$$

Using these coordinates, we define the radial component of eigenvector $\mathbf{e}_i$ as

$$\phi_{rad,i} = \frac{\sum_{j=1}^{N} (\vec{e}_{ij} \cdot \hat{\rho}_j)^2}{\sum_{j=1}^{N} |\vec{e}_{ij}|^2} \tag{4}$$

Likewise, the tangential and longitudinal components are defined as

$$\phi_{tang,i} = \frac{\sum_{j=1}^{N} (\vec{e}_{ij} \cdot \hat{\theta}_j)^2}{\sum_{j=1}^{N} |\vec{e}_{ij}|^2} \tag{5}$$

and

$$\phi_{long,i} = \frac{\sum_{j=1}^{N} (\vec{e}_{ij} \cdot \hat{z})^2}{\sum_{j=1}^{N} |\vec{e}_{ij}|^2} \tag{6}$$

respectively. Note that since the $\hat{\rho}_j, \hat{\theta}_j$, and $\hat{z}$ vectors are mutually orthogonal for each atom j, we are assured that

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