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Empirical Ratio of Higher Optical Transitions in Semiconducting SWCNTs

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***Abstract*—In this work, the 'ratio problem' among higher optical transition energies (4th, 5th and 6th transitions) of semiconducting single-wall carbon nanotube is discussed. A number of semiconducting single-wall carbon nanotubes having (n – m) familyrange 2 to 32 with mod (n-m, 3) ≠0 and having diameter range 1.48nm to 3.44nm are considered. Higher optical transition energies of all those tubes are recorded from various experimental reports based on fluorescence and Raman spectroscopy. Based on that observation, ratio between consecutive higher transition energies for all semiconducting tube is expressed empirically through some empirical expressions in terms of diameter, (n- m) family and mod value. The empirical ratio matched very well with experiment ratio over the full diameter range. The proposed empirical way to expressing this ratio may greatly help in finding the proper ratio of higher optical transitions without depending on experimental values of these transitions.The generated pattern from the plot of this empirical ratio can also help in Photoluminescence based chirality assignment.**

***Keywords*—Single Wall Carbon Nanotube, Ratio Problem, Optical Transition, Diameter, Chiral Index.**

I. Introduction

Electronic and optical properties of single-wall carbon nanotubes (SWCNT) are directly associated with their geometrical structures [1, 2] which are uniquely specified by a pair of chiral index (n, m). A SWCNT (n, m) will be metallic if its n-m = 3k (k is integer), i.e. mod (n-m, 3) = 0 and it will be semiconducting if its n-m ≠ 3k, i.e. mod(n-m, 3) = 1 or 2 [3]. This relation gives two types of semiconducting SWCNTs, mod 1 type and mod 2 types.

The one-dimensionality of the Single Wall Carbon nanotubes (SWCNT) gives rise to 1D sub-bands instead of one wide electronic energy band in nanotube density of states (DOS). Each SWCNT (*n*, *m*) has a unique set of interband transition energies E_{ii}denoting the energy differences between the *i*-th conduction and valence bands and optical transitions can only occur between these mirror sub-bands [1, 2, 4-6].

The tight-binding (TB) model of π-bands of graphene using the zone-folding approximation has been widely used for modeling electronic band structure of single-wall carbon nanotube (SWCNT) due to its simplicity, low computational cost, and qualitative agreement with experimental results [7-9]. TB model with the nearest-neighbor approximation provides following simple expression to calculate optical transitions of a SWCNT [1, 2, 10]:

$$E_{ii} = 2ja_{cc}\gamma_0 / d_t \qquad (1)$$

Where, γ_0 is the nearest-neighbor hopping parameter, $a_{cc} = 1.44$ Å is carbon-carbon bond length, d_t is nanotube diameter in nm, given by $d_t = \sqrt{3\left(n^2 + nm + m^2\right)}a_{cc} / \pi$ and *j* is an integer. E_{ii}corresponds to the first, second, third, fourth… interband transitions (E_{11}^S, E_{22}^S, E_{33}^S, E_{44}^S….) of semiconducting SWCNT when *j* = 1, 2, 4, 5… respectively. This inverse proportional trend of transition energies with SWCNT diameter, given by Eqn. (1), is also observed from the Kataura plot [11, 12] and from other optical spectroscopic experiments [6, 13].

Basic tight binding model has a number of limitations due to which Eqn (1) cannot give complete description of different optical transition energies in SWCNTs.These limitations are attributed to many factors. One major factor is nanotube 'curvature effect' induced band structure deviation from simple π-orbital graphene picture [11-14]. Other factors are 'chirality effect' [15], 'trigonal warping effect' [9, 11, 16] and many body effect (electron-electron interaction) comprising self-energy and exitonic effect [17-22].

One effect of such limitation is basic TB model predicts inaccurateratio of first two optical transitions [14]. For example, it has been observed from some optical spectroscopic experimentsthat basic TB model fails to explain experimentally observed ratio of first two optical transition energies of semiconducting SWCNTs (E_{22}^S/E_{11}^S). Nearest neighbour TB modeland the corresponding Eqn (1)predicted this ratio to be 2. Extended TB model later predicted that this ratio will be lesser than 2 at small diameters but will approach 2 asymptotically for large diameters [21]. In practice, experimentally observed ratio was found to oscillate below and above 2 for different chiralities and converge to only around 1.8 for large diameters [21-26]. This problem is often referred as 'ratio problem' in literatures [21]. Neither the simple TB model nor the extended TB model could account this observation fully.Kane *et al* [21] and Mele*et al* [22] reported 'blue shift' of transition energies which is also not reflected through Eqn (1). They observed this problem after

scrutinizing fluorescence spectroscopy results reported by Bachilo*et al* [14] and O' Connel *et al* [27].

One of the reasons behind deviation of simple tight binding model from experimental results is many body effect (electron-electron interaction) [21-26, 28-32]. The many body effect comprises an exciton binding energy and a self-energy. Kane *et al* [21], Mele*et al* [22], Lin *et al* [23], Spataru*et al* [24, 32], Zhao *et al* [25], Dukovic*et al* [26], Samsonidze*et al* [33], Jiang *et al* [28], Sato *et al* [29], Ando *et al* [30], and Pedersen *et al* [31] studied the many body effect on electronic properties of SWCNTs. It is believed by some authors that the main explanation for the 'ratio problem' and 'blue shift problem' can be given by showing the effect of many body interaction in SWCNTs [21-23, 25, 26], even if the relative contributions of self-energy and excitonic effects are not precisely known yet.

In 2015, G. R. A. Jamal *et al.* [34] discussed empirical ratio of 1st and 2nd optical transition energies in semiconducting SWCNTs. In this work, we will find the empirical relation for ratio of next higher optical transitions namely 3rd, 4th, 5th and 6th optical transition energies.

II. Method and Results

We collected experimental values of 3rd, 4th, 5th and 6th optical transition energies, represented by E_{33},E_{44},E_{55} and E_{66}, respectively, of 200semiconducting SWCNTs from various reports of optical spectroscopic experiments [15,16]with a special focus on the work of Liu *et al* [35] which is most recent and provides most comprehensive data.

Earlier, it was observed by Weisman *et al.* [12] and Bachilo *et al.* [14] that the ratio of first two optical transitions in semiconducting SWCNT show symmetric pattern with (n-m) family where the value of (n-m) family decrease with increasing diameter of SWCNT. We will use this observation to formulate our empirical relation for higher optical transitions.We aligned experimental optical transition energies value according to (n-m) family and computed the Ratio $\frac{E_{44}}{E_{33}}, \frac{E_{55}}{E_{44}}, \frac{E_{66}}{E_{55}}$. Then we computed mod|(n-m)/3|=K ; For K=1 and K=2 and separate both types of data.Here, K=1 and K=2 are mod-1 type and mod -2 type semiconducting SWCNTs, respectively. After separating hem according to their mod type we computedthe diameter of each tube and sorted data according to ascending value of tube diameter.

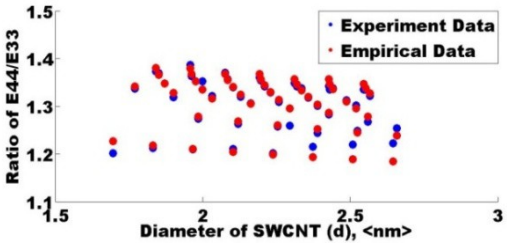
Then, to formulate the relation between optical transition energy ratio and structural parameter of semiconducting SWCNTs, we closely observed the pattern of data change according to diameter and (n-m) family value. Based on our observation, we used exponential term along with (n-m) family and diameter including two numerical fitting parameters A and B. After adjusting all these structural and numerical parameters through trial and error, we devised a set of symmetrical empirical relations for ratio of these higher optical transitions.

Ratio between 3rd and 4th Optical transitions $(\frac{E_{44}}{E_{33}})$:

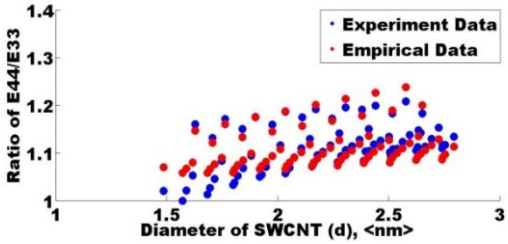
For mod 1 type (K=1):

$$r_1\left(\frac{E_{44}}{E_{33}}\right) = A - Be^{\left(\frac{\sqrt{\frac{n-m}{2}+K}}{d_t}\right)^{0.3}} \quad \ldots\ldots\ldots (1)$$

Where A=1.75, B=0.65.



(a)



(b)

Fig. 1. Plot of experimental E_{44} to E_{33} ratio with empirical ratio vs d_t from (1) for (a) Mod-1 type and (b) Mod-2 type semiconducting SWCNTs.

For mod 2 type (K=2):

$$r_2\left(\frac{E_{44}}{E_{33}}\right) = A - Be^{\left(\frac{-d_t}{\sqrt{\frac{n-m}{2}+K}}\right)^{0.3}} \quad \ldots\ldots\ldots (2)$$

Where, A=1.75, B=0.8.

Ratio between 4th and 5th optical transitions $(\frac{E_{55}}{E_{44}})$:

For mod 1 type (K=1):

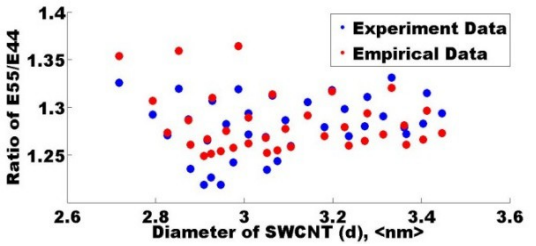
$$r_1\left(\frac{E_{55}}{E_{44}}\right) = A - Be^{\frac{-0.4\,d_t}{n-m}} \ldots\ldots\ldots (3)$$

Where A=1.75, B=0.52.

For mod 2 type (K=2):

$$r_2\left(\frac{E_{55}}{E_{44}}\right) = A - Be^{\frac{-2\,d_t}{n-m}} \quad \ldots\ldots\ldots (4)$$

Where A=1.75, B=0.47.



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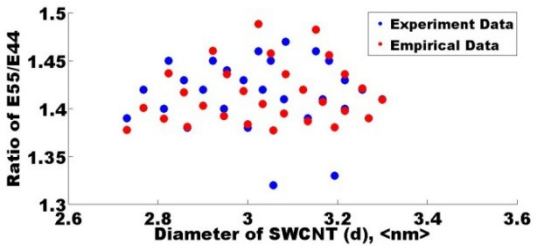
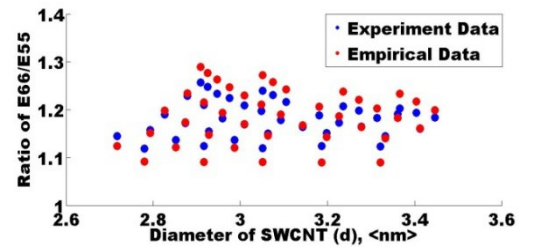
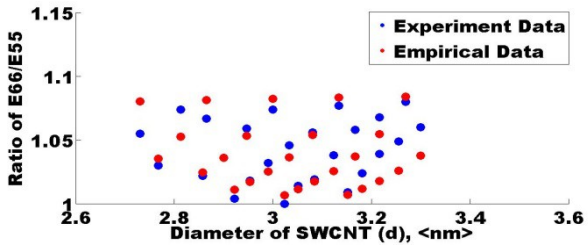


(b)

Fig. 2. Plot of experimental E_{55} to E_{44} ratio with empirical ratio vs d_t from (1) for (a) mod-1 type and (b) mod-2 type semiconducting SWCNTs.



(a)



(b)

Fig. 3. Plot of experimental E_{66} to E_{55} ratio with empirical ratio vs d_t from (1) for (a) mod-1 type and (b) mod-2 type semiconducting SWCNTs.

Ratio between 4th and 5th optical transitions ($\frac{E_{66}}{E_{55}}$):

For mod 1 type (K=1):

$$r_1\left(\frac{E_{66}}{E_{55}}\right) = A - Be^{\frac{0.1(n-m)}{d_t}} \quad \ldots\ldots(5)$$

Where A=1.4 and B=0.32.

For mod 2 type (K=2):

$$r_2\left(\frac{E_{66}}{E_{55}}\right) = A - Be^{\left(\frac{-d_t^{0.2}}{n-m}\right)} \quad \ldots\ldots(6)$$

Where A=1.75 and B= 0.78.

Table I. Comparison between experimental and empirical ratio of different optical transitions in terms of average error.

Ratio	Mod Type	Average Error, $\lvert\Delta E\rvert$	% Average Error, $\lvert\%\Delta E\rvert$
$\frac{E_{44}}{E_{33}}$	Mod -1	0.006	0.60
	Mod -2	0.0143	1.43
$\frac{E_{55}}{E_{44}}$	Mod -1	0.0117	1.117
	Mod -2	0.00947	0.947
$\frac{E_{66}}{E_{55}}$	Mod -1	0.0146	1.46
	Mod -2	0.0095	0.95

Table-I gives the deviation of empirical data from experimental values of optical transitions. It can be noticed that the average error and average absolute error is less than 1.5% for diameter between 1.48 nm to 3.44 nm. This means our empirical formula can predict the experimental ratio with more than 98% accuracy over a wide diameter range.

Figure 1, 2 and 3 show the experimental and empirical optical transition ratio vs d_t for $\frac{E_{44}}{E_{33}}$, $\frac{E_{55}}{E_{44}}$ and $\frac{E_{66}}{E_{55}}$, respectively, both for mod 1 type and mod 2 type semiconducting SWCNTs. From these figures it can be observed that the empirical values calculated using (1) to (6) is very close to experimentally reported value. This again proves the strength of the devised empirical relations.

III. CONCUSIONS

In this work, we have proposed a set of empirical expression to represent the 3rd, 4th, 5th and 6th optical transition energies ratio for semiconducting SWCNT with any chirality. In our proposed empirical expression the (n-m) family, mod values and the nanotube diameter d_t are included so as to incorporate curvature effect and mod type effect on optical transition energies ratio. The empirical ratio was found to match quite accurately with experimental ratio in every cases and also found to be approaching 1.75 at higher diameters like the experimental ratio. The % average deviation of empirical result is lesser than 1.5% for diameter between 1.48 nm to 3.44 nm which in turn proves the strength of the devised equations to understand the internal structural symmetry.

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