

A Theoretical Study of Raman Spectroscopy of Carbon Nanotubes and Evaluation of Energy Separation as a Function of Nanotube Diameter

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(Received on: October 5, 2018)

ABSTRACT

Using the theoretical formalism of P T Araujo *et al.* [Physica E, 42, 1251 (2010)] and M S Dresselhaus *et al.* {Phys. Rep. 409, 47 (2009)}, we have theoretically studied the Raman spectroscopy of carbon nanotubes. We have evaluated separation energy between valence band and conduction band of both semiconducting and metallic nanotubes as a function of nanotube diameter. Our theoretically obtained results show that separation energy decrease with increase of diameter for both the systems. We have compared our evaluated results with the results of other theoretical workers and found that the agreement between our results with other workers are good so far trend of the results concerned. However the magnitude of our values is less than their values. We have also reported an experimental result of Raman radial breathing mode frequency as a function of reciprocal of the nanotube diameter. The measured frequency increases with reciprocal diameter. The observation is consistent with the two laser source 635nm and 785nm lasers. We have also reported an experimental result and theoretical result³⁴ of transition energy E_{ii} as a function of nanotube chiral number (n, m) for the isolated semiconducting SWNT for two laser source 635nm and 785nm. The reported both measured and evaluated are in good agreement to each other.

Keywords: Raman spectroscopy of carbon nanotube, Raman radial breathing mode frequency, Single Wall carbon nanotubes (SWNTs), Multiwall carbon nanotubes (MWNTs), Laser sources, separation energy, transition energy, Reciprocal of nanotube diameter, G-band.

INTRODUCTION

Over the past decade, a huge scientific interest, both theoretically and experimentally, has been focused on carbon nanotubes (CNTs). This is due to their unprecedented properties arising from their unique one-dimensional character. The combination of superb mechanical, electrical and thermal properties makes CNTs ideal reinforcing fillers for advanced composite materials. But one of the major problem is the fact that the nanotubes aggregate in bundles. This is the result of substantial van der Waals attraction and homogeneous dispersion of CNTs. Similarly the host matrix is probably the most fundamental issue for efficient load transfer and good reinforcement¹⁻⁶.

Raman spectroscopy has been shown to be a powerful and non-destructive technique for the characterization of carbon based materials including carbon black (CB) and carbon nanotubes (CNTs). It has become an invaluable tool for understanding many fundamental aspects of all sp^2 carbons^{7,8}. The diameter of nanotube⁹, the presence of disorder in sp^2 hybridized carbon systems¹⁰ as well as the effect of nanotube-nanotube interactions¹¹ on the vibrational modes have been assessed using Raman spectroscopy. Specific features such as the strong frequency dependence on the excitation laser energy of some Raman bands¹²⁻¹⁷ or laser radiation –induced effects¹⁸⁻²¹ have been the subject of extensive studies.

Raman spectroscopy of CNT-based composite materials has been used to evaluate the states of dispersion and the polymer-filler interaction reflected, by shifts or width changes of the peaks. On the other hand, the sensitivity of some bands of CNTs to an application of mechanical deformation to the composite²²⁻²⁵ has been used.

Confocal optical microscopy was employed to study the effect of surface-enhanced Raman scattering on individual single-walled carbon nanotubes (SWNTs) covered with isolated gold particles. The gold particles with diameters between 10 and 130 nm were deposited on low densities on the tubes sidewalls by an electrochemical method. In the spectra, Raman peaks associated with the nanotubes were found to be superimposed on the broad luminescence background originating from the metal particles. With increasing particle size both the luminescence intensity as well as the Raman enhancement increased at longer wavelengths. This finding is consistent with size –dependent broadening of the gold Plasmon frequency and a corresponding extension of the energetic range for the local field enhancement on the particle surface. In addition, wavelength dependent experiments revealed a maximum Raman intensity when both nanotube and metal particle were in optical resonance^{26,27}

In this paper using the theoretical formalism of P T Aranja *et al.*²⁸ and M S Dresselhaus *et al.*²⁹, we have theoretically studied the Raman scattering of carbon nanotubes. We have evaluated separation energy between valence band and conduction band of both semiconducting and metallic nanotubes as a function of nanotube diameter. Our theoretically obtained results show that separation energy decrease with increase of diameter for both the systems. We have compared our evaluated results with the results of other theoretical workers^{30,31} and found that the agreement between our results with other workers are good so far trend of the results concerned. However the magnitude of our values is less than their values. We have also reported an experimental result of Raman radial breathing mode

frequency as a function of reciprocal of the nanotube diameter. The measured frequency increases with reciprocal diameter. The observation is consistent with the two laser source 635nm and 785nm lasers. We have also reported an experimental^{32,33} result and theoretical result³⁴ of transition energy E_{ii} as a function of nanotube chiral number (n, m) for the isolated semiconducting SWNT for two laser source 635nm and 785nm. The reported both measures and evaluated are in good agreement to each other.

MATHEMATICAL FORMULA USED IN THE EVALUATION

Calculation of energy separation as a function of nanotube diameter

The structure of SWNT is defined by the chiral vector C_h

$$C_h = na_1 + ma_2 = (n, m) = (n, m)$$

Here a_1 and a_2 are the unit vectors of the hexagonal lattice. The diameter of the nanotube is given by

$$d_t = C_h / \pi = \sqrt{3}a_{C-C}(m^2 + mn + n^2) / \pi \quad (1)$$

Here a_{CC} is the nearest neighbor C-C distance (1.42 Å) in graphite. C_h is the length of the chiral vector. The chiral angle is given by

$$\theta = \tan^{-1}[\sqrt{3}m / (m + 2n)] \quad (2)$$

The 3D energy dispersion relation of graphite is calculated by solving the eigenvalue problem for a (2x2) Hamiltonian H and (2x2) overlap integral matrix S with two carbon atoms in 2D graphite.

$$H = \begin{pmatrix} \varepsilon_{2p} - r_0 f(k) & \\ & -r_0 f(k) \varepsilon_{2p} \end{pmatrix} \quad (3)$$

The overlap integral matrix S is given by

$$S = \begin{pmatrix} sf(k) & \\ & 1 \end{pmatrix} \quad (4)$$

Here $f(k)$ is given by $f(k) = e^{ik_x a / \sqrt{3}} + 2e^{-ik_x a / 2\sqrt{3}} \cos(k_y a)$. ε_{2p} is the site energy of the 2p atomic orbitals. The eigen value equation is given by

$$E_{g2D}^{\pm}(k) = \frac{\varepsilon_{2p} \pm r_0 w(k)}{1 \mp sw(k)} \quad (5)$$

Here the c-c transfer energy $r_0 > 0$, s denotes the overlap of the electronic wave function on adjacent sites. E^+ and E^- corresponds to π^* and π energy bands respectively. One takes $r_0 = 1$. The $w(k)$ is given by

$$w(k) = [1 + 4 \cos \frac{\sqrt{3}k_x a}{2} \cos \frac{k_y a}{2} + 4 \cos^2 k_y a / 2]^{\frac{1}{2}} \quad (6)$$

The expansion of equation (5) for small k yields

$$E_{g2D}(k) = \varepsilon_{2p} \pm (r_o - s\varepsilon_{2p})w(k) + \dots \quad (7)$$

The 1D energy dependence for SWNT is given by

$$E_{\mu}^{\pm}(k) = E_{g2D} \left[k \frac{k_2}{|k_2|} + \mu k_1 \right] \quad \text{for } \left(-\frac{\pi}{T} < k < \frac{\pi}{T} \right), \mu = 1 \dots N \quad (8)$$

Here T is the magnitude of the translational vector, k is 1D wave number along the nanotube axis and N is the no of hexagon of the graphite honey comb lattice that lies within the nanotube unit cell. k_1 and k_2 are defined as

$$k_1 = [(2n+m)b_1 + (2m+n)b_2] / Nd_R \quad \text{and} \quad k_2 = (mb_1 - nb_2) / N \quad (9)$$

Here b_1 and b_2 are the reciprocal lattice vector of graphite and are given by

$$b_1 = (1/\sqrt{3}, 1)2\pi/a \quad b_2 = (1/\sqrt{3}, -1)2\pi/a \quad (10)$$

DISCUSSION OF THE RESULTS

Using the theoretical formalism of P.T. Aranja *et al.*²⁸ and M S Dresselhaus *et al.*²⁹, we have theoretically studied the Raman scattering of carbon nanotubes. The essential features of this studies are the evaluation of frequency of the Raman radial breathing mode (RBM). This mode is dependent on nanotube diameter through the relation $\omega_{RBM} = A/d_t + B$. The various values for the parameter A and B have been suggested in the literature. This means a systematic study of the effect of the environment required if Raman spectroscopy is to be used in assessing the dispersion state and the composition of the sample. Deforming a nanotubes can change the C-C bond length and the E_{ii} the transition energy. The deformation process, if followed using resonance Raman spectroscopy can give insight into the electronic properties of the nanotubes. This is made even more powerful when deformation tests are performed on individual nanotubes. Moreover, when the strain is applied through deforming a nanocomposite in which nanotubes are embedded. The shift of the nanotubes Raman bands allows the efficiency of strain transfer. In **table T1 and T2**, we have shown the evaluated energy separation ΔE (eV) as a function of nanotube diameter d_t . In fact the energy separation $E_{pp}^S(d_t)$ and $E_{pp}^M(d_t)$ have been evaluated as a function of nanotube diameter d_t . Here S stands for semiconducting and M for metallic nanotubes. The evaluation has been done for all the (n, m) values for diameter from 0.7nm to 3.0 nm. Actually the term $E_{pp}^M(d_t)$ is the energy separation between the valence and conduction bands of metallic nanotube. The result is based on the tight binding model. Here C-C is the transfer energy r and we have fixed $r > 0$. In the actual calculation the value of $r=2.9$ eV and $s=0.129$ were taken. Our theoretically obtained results indicate that energy separation for both semiconducting and metallic decrease with increase of nanotube diameter. We have compared our theoretically evaluated results with other theoretical workers and found that trend is the same although the magnitudes differ from ours. In **table T3**, we have presented the experimental results of frequency of Raman radial breathing mode ω_{RBM} as a function of nanotube diameter measured from two different laser

sources. The result shows that ω_{RBM} (cm^{-1}) increase with $(d_t)^{-1}$. The results are consistent with both laser 635nm and 785 nm respectively. In **table T4**, we have shown the evaluated results of transition energy E_{ii} (eV) with different chiral number (n, m) nanotubes. In fact the transition energy E_{11}^s and E_{22}^s has been evaluated with different [n,m] values for 635 nm laser source. In **table T5**, we reported the similar calculation for another laser source 785 nm laser. The identical results were observed in this laser source also. There is some recent calculations³⁵⁻⁴⁰ which also reveals the similar findings.

Table T1: An evaluated results of energy separation ΔE (eV) as a function of nanotube diameter d_t (nm) for semiconducting nanotube with parameter $r_0=2.20\text{eV}$ and $s=0.129$

d_t (nm)	< ----- ΔE (eV) ----- >		
	Ours	Other's	Other's
0.7	3.25	4.28	3.42
0.8	3.16	4.05	3.31
0.9	3.12	3.86	3.16
1.0	3.05	3.73	3.08
1.2	2.98	3.54	2.87
1.4	2.84	3.44	2.69
1.6	2.78	3.32	2.58
1.8	2.65	3.20	2.39
2.0	2.82	3.16	2.18
2.2	2.43	3.08	2.02
2.4	2.32	2.86	1.88
2.6	2.22	2.72	1.75
2.8	2.14	2.58	1.59
3.0	1.86	2.35	1.42

Table T2: An evaluated results of energy separation ΔE (eV) as a function of nanotube diameter d_t (nm) for metallic nanotube with parameter $r_0=2.20\text{eV}$ and $s=0.129$

d_t (nm)	< ----- ΔE (eV) ----- >		
	Ours	Other's	Other's
0.7	2.82	3.02	2.64
0.8	2.46	2.90	2.58
0.9	2.18	2.82	2.37
1.0	2.03	2.76	2.24
1.2	1.84	2.57	2.12
1.4	1.73	2.49	1.94
1.6	1.60	2.37	1.85
1.8	1.48	2.18	1.79
2.0	1.34	2.08	1.67
2.2	1.23	1.97	1.58
2.4	1.17	1.88	1.46
2.6	1.14	1.79	1.38
2.8	1.08	1.68	1.22
3.0	0.92	1.52	1.13

Table T3: An experimental result of frequency ω_{Rm} (cm^{-1}) RBM (Raman radial breathing Mode) as a function of reciprocal of nanometer diameter taken with two laser source 635nm and 755nm

$(d)^{-1}$ ($\text{nm})^{-1}$	<----- ω_{Rm} (cm^{-1})----->	
	635 nm laser	785 nm laser
0.4	198.2	200.4
0.6	203.5	209.8
0.8	210.8	213.2
1.0	212.3	217.5
1.1	218.7	222.4
1.2	222.9	227.9
1.3	238.5	242.6
1.4	247.9	258.3
1.5	268.7	279.9
1.6	279.4	282.7

Table T4: An evaluated theoretical and experimental result of transition energy E_{ii} as a function of chirality (n,m) of isolated semiconducting SWNTs using IR785nm laser.

Chirality (n, m)	E_{ii} (Theoretical)(eV)		E_{ii} (experimental)(eV)	
	E_{11}^s	E_{22}^s	E_{11}^s	E_{22}^s
13,3	0.70	1.47	0.83	1.62
9,7	0.76	1.48	0.94	1.58
10,5	0.80	1.54	0.99	1.58
11,3	0.84	1.57	1.04	1.57
12,1	0.86	1.59	1.06	1.55
10,2	0.96	1.78	1.18	1.68

Table T5: An evaluated theoretical and experimental result of transition energy E_{ii} as a function of chirality (n,m) of isolated semiconducting SWNTs using 633nm laser.

Chirality (n, m)	E_{ii} (Theoretical)(eV)		E_{ii} (experimental)(eV)	
	E_{11}^s	E_{22}^s	E_{11}^s	E_{22}^s
10,3	0.70	1.47	0.83	1.62
11,1	0.76	1.48	0.94	1.58
7,6	0.80	1.54	0.99	1.58
11,3	0.84	1.57	1.04	1.57
12,1	0.86	1.59	1.06	1.55
10,2	0.96	1.78	1.18	1.68

CONCLUSION

From the above theoretical investigations and analysis, we have come across the following conclusions:

- (1) One can study characterization of carbon nanotubes by Raman scattering.
- (2) From resonance Raman scattering, one can probe the variety of nanotube parameters like (a) (n, m) values, diameter and chirality (b) laser energy (c) polarization of light (d) sample orientation relative to the polarization (e) Stokes and anti-Stokes Raman lines etc. Micro-Raman spectroscopy has become a powerful tool for characterizing nanotubes and nano-materials.

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- (3) In a single nanotube spectroscopy, all Raman peaks come from the same SWNTs, so that the total Raman spectra contains a wealth of information which needs to be interpreted for self-consistency.
- (4) The investigation and analysis were performed by two formalisms namely P T Aranji *et al.* and M S Dresselhaus *et al.* It appears that both the formalisms work quite well in explaining many observed facts of nanotubes.

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