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# *Thermal Expansion Properties of Single-Walled Carbon Nanotubes by Raman Spectroscopy at 780 nm Wavelength*

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*Abstract*— **Single-walled carbon nanotubes are predicted to significantly impact semiconductor physics, owing to their unique electronic properties and reduced dimensionality. Some of the semiconductor technologies in which carbon nanotubes (CNTs) are expected to hold significant promise are in super-capacitors, hydrogen storage materials, nanoprobes, and bio-chemical sensors. For future applications there is a great need for understanding their thermal properties, since nano-devices based on single-walled and/or multi-walled nanotubes may have to experience high temperatures during the manufacturing process, or while being operated. This, in turn, affects the reliability of the devices due to thermal expansion and the ensuing strain. The coefficient of thermal expansion (CTE) is a key property for nano-electronic applications based on the use of CNTs. We utilize Raman Spectroscopy, with a 780 nm laser, to characterize our carbon nanotube samples and determine vibrational modes and bond lengths. Raman spectroscopy is applied to the various sp2 carbonaceous materials primarily as a characterization tool since these materials each exhibit structural differences. In our CNT samples, we have been able to identify the main features seen in CNTs for our purified and unpurified High Pressure Carbon Monoxide Process CNTs. The values of these features have been well studied and our results match well with known literature, and we have been able to properly characterize the vibrational modes of our samples. Though CNTs come in a variety of sizes and shapes, this study serves as the first step in finding a generalized way to categorize the thermal properties of CNTs. This work, along with Molecular Dynamic simulations, will provide us with insight on the thermal properties of single-walled carbon nanotubes.**

***Keywords: raman spectroscopy; carbon nanotubes; thermal expansion; near infrared***

## I. INTRODUCTION

Carbon nanotubes are honey-combed lattices rolled up into cylinders with nanometer sized diameters and lengths on the order of microns. Actively studied for over thirty years, with a now greater availability, single walled nanotubes are predicted to significantly impact semi-conductor physics, owing to its unique electronic properties and reduced dimensionality. Some of the semi-conductor technologies in which carbon nanotubes (CNT's) are expected to hold significant promise are in super-capacitors, hydrogen storage materials, nanoprobes, and bio-chemical sensors [1]. Necessary in many future CNT applications is an understanding of their thermal properties, as nano-devices based on single walled and or multi-walled nanotubes may have to experience high temperatures during the manufacturing process, or while being operated [2]. This in turn affects the reliability due to thermal expansion and the ensuing strain in the devices. The coefficient of thermal expansion (CTE) is a key property for nano-electronic applications based on CNT's. However, there is still a controversial widespread discrepancy among the theoretical results of this quantity in terms of its temperature dependence and certain magnitudes, such as the temperature at occurrence of maximum contraction of the carbon nanotube and at the transition from contraction to expansion in some studies.

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## II. CARBON NANOTUBE STRUCTURE

The conceptual description of a single-walled carbon nanotube (SWNT) is a graphene sheet rolled into a cylinder. Based solely on this geometric definition, the diameter can be arbitrarily large; however, it has been shown that for tubes with diameters larger than ~ 2.5 nm, collapsing into two flattened ribbons is the more energetically stable configuration [3]. At the other extreme, in the case of small diameters, SWNT diameters of 0.4 nm have been realized despite the higher stresses and greater energy requirements in a tube like structure with very small radii of curvature. Carbon nanotubes with diameters of approximately 1.3 nm are usually the most abundant in SWNT samples produced by any method, as diameters close to this value result in a compromise between the two extremes in the energy requirements mentioned above.

An essential structural property of a resultant nanotube after the rolling up process is the orientation of the initial honey-comb lattice relative to the tube axis. The two resulting classifications, depending on whether the nanotubes' plane of symmetry is parallel or perpendicular to the axis or not, are achiral and chiral, respectively. In the case of achiral nanotubes there are only two sub-categories, armchair and zigzag nanotubes [4].


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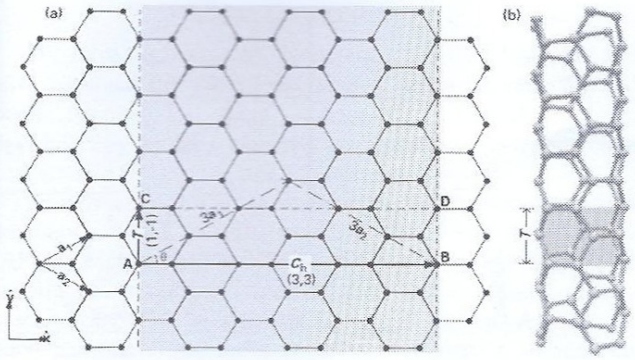


**Figure 1. (a) Illustration of the conceptual formation of a single-walled armchair nanotube. The lattice is rolled along the line Ch, with points C and A coinciding with points D and B, respectively. (b) The resulting nanotube and its cylindrical unit cell. Adapted from ref. [1].**

The various ways of rolling up a graphene sheet is all contained in the chiral vector and the chiral or helical angle, labeled $\mathbf{C_h}$ and $\boldsymbol{\theta}$, respectively in Figure 1. The length of the chiral vector $\mathbf{C_h}$ is

$$|C_h| = a\sqrt{n^2 + nm + m^2} \qquad (1)$$

where n and m are integers such that, $0 \le m \le n$, and the basis vectors of the honey-comb lattice follow.

$$\boldsymbol{a_1} = \frac{\sqrt{3}a}{2}\hat{x} + \frac{a}{2}\hat{y} \qquad (2)$$

$$\boldsymbol{a_2} = \frac{\sqrt{3}a}{2}\hat{x} - \frac{a}{2}\hat{y} \qquad (3)$$

a is the Bravais lattice constant, which in terms of the Carbon-Carbon bond length, ($a_{C\text{-}C}$ = 1.42Å), equals

$$a = \sqrt{3}a_{C-C} = 2.46\ \text{Å}$$

Since the length of the chiral vector is the circumference of the nanotube, the nanotube's diameter is given by

$$d_t = \frac{a}{\pi}\sqrt{n^2 + nm + m^2} \qquad (4)$$

Also for the chiral angle we have

$$\cos\theta = \frac{C_h \cdot a_1}{|C_h||a_1|} \qquad (5)$$

The three nanotube parameters mentioned above, namely $C_h$, q, and $d_t$, in addition to those listed in Table I, are all functions of the ordered pairs (n, m). Hence, these integer pairs are used to label SWNT's. Also note that chiral vectors constructed solely from lattice vectors, i.e. (n, 0) result in zigzag cross-sectional tubes, and chiral vectors constructed from equal numbers of graphene lattice bases, i.e. (n,n) nanotubes result in armchair nanotubes. All other (n, m) pairs result in chiral nanotubes.

TABLE I. PROPERTIES OF CHIRAL (CCNT), ARMCHAIR (ACNT), AND ZIG ZAG (ZCNT) CARBON NANOTUBES, ADAPTED FROM WONG ET AL. [1].

| Parameter | cCNT | aCNT | zCNT |
|---|---|---|---|
| $C_h$ chiral vector | $C_h = n\mathbf{a_1} - m\mathbf{a_2} = (n,m)$ | $C_h = (n,m)$ | $C_h = (n,0)$ |
| $C_h$ length of chiral vector | $C_h = \lvert C_h\rvert = a\sqrt{n^2 + nm + m^2}$ | $C_h = a\sqrt{3n}$ | $C_h = an$ |
| $d_t$ diameter | $d_t = \frac{a}{\pi}\sqrt{n^2 + nm + m^2}$ | $d_t = \frac{an}{\pi}\sqrt{3}$ | $d_t = \frac{an}{\pi}$ |
| $\theta$ chiral angle | $\cos\theta = \frac{2n+m}{2\sqrt{n^2+nm+m^2}}$ | $\theta = 30°$ | $\theta = 0°$ |
| $g_d$ greatest common divisor | $g_d \equiv \gcd(2m+n, 2n+m)$ | $g_d = 3n$ | $g_d = n$ |
| $T$ translation vector | $T = \frac{2m+n}{g_d}\mathbf{a_1} - \frac{2n+m}{g_d}\mathbf{a_2}$ | $T = \mathbf{a_1} - \mathbf{a_2}$ | $T = \mathbf{a_1} - 2\mathbf{a_2}$ |
| $T$ length of translation vector | $T = \lvert T\rvert = \frac{\sqrt{3}C_h}{g_d}$ | $T = a$ | $T = a\sqrt{3}$ |
| $N$ Number of hexagons/cell | $N = \frac{2C_h^2}{a^2 g_d}$ | $N = 2n$ | $N = 2n$ |

## III. RAMAN SPECTRA OF SWNT

Resonance Raman spectroscopy, being one of the most sensitive techniques is now commonly used in characterizing single-walled nanotubes. It is possible to obtain rich detailed spectra from SWNT samples with little to no work in the way of sample preparation. It is due primarily to the resonance Raman Effect where the excitation wavelength is near in energy to the van Hove singularities in the density of states of nanotubes of various chiralities that make this possible.

The primary first order feature in the Raman spectrum of graphene is the G band usually located at approximately 1582 $cm^{-1}$. However, due to the symmetry breaking involved in rolling a graphene sheet to form a nanotube this Raman feature is split into two peaks, labeled G+ and G- in Figures 2 and 3. These two most prominent features arise mainly for displacements now along the tube axis, and circumference, respectively. The semiconducting or metallic nature of nanotubes can be obtained from the $G^-$ feature, which is broadened for metallic single-walled nanotubes.

In graphene and graphite, introduction of disorder to the crystal symmetry creates certain vibrational modes that would not be present otherwise. This in turn leads to modes in the spectral range labeled as the D or "Defect" mode. However, it is still uncertain if this feature can be used for defect characterization in all $sp^2$ materials, nanotubes included [5]. Two key traits distinguish the D band feature of single walled nanotubes from that of defective graphite. The first is the small line-widths associated with this feature in carbon nanotubes. Raman spectroscopy done on individual tubes shows line-widths of this feature varying in the 7-40 $cm^{-1}$ range. In single-walled nanotube samples the Raman spectra are usually composed of broad peaks with sharper features from nanotubes superimposed on them. The second trait is the lower frequencies of the D band in nanotubes compared to other bulk



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$sp^2$ carbons; this downshift also increases with increasing diameter.

The strong feature at 2578 $cm^{-1}$ in Figure 2 denoted as the 2D band is characteristic of all types of $sp^2$ hybridized carbon [6]. This peak, which is usually anywhere in the range 2500-2800 $cm^{-1}$, is the result of a second-order scattering process involving the activation of a phonon near the K point in graphene's Brillouin zone by a double resonance process. It is also surprisingly dispersive, which makes this a useful feature in characterizing SWNTs and other nanocarbon materials.

Single-walled nanotubes display Raman features in the range 120 – 250 $cm^{-1}$, corresponding to the coherent vibration of the tube along the radius, as if the tube is breathing [7]. Such features are useful in the characterization of the diameters due to their inverse relationship with this geometrical property.

$$\omega_{RBM} = A/d_t + B \quad (6)$$

$\omega_{RBM}$ is the radial breathing mode frequency and the coefficients A and B are determined experimentally, with typical values of A = 234 $cm^{-1}$ nm and B = 10 $cm^{-1}$ for single-walled nanotube diameters in the range 1.5 ± 0.2nm. The parameter B is an up shift included for interactions between different carbon nanotubes in a bundle.

## IV. RESULTS AND DISCUSSION

The sample analyzed was carbon nanotube powder from Unidym™ Carbon Nanotubes. The SWNTs were produced by the High Pressure Carbon Monoxide Process (HiPco), followed by purification. According to the manufacturer, the diameter of the nanotubes was in the range 0.8 – 1.2 nm, and the lengths varied from ~ 100–1000 nm. After thermogravimetric analysis, the manufacturers also claimed to have less than 15% residual Fe catalyst by weight.

The Raman characterization of SWNT samples was done with a DXR Smart Raman spectrometer from Thermo Scientific. The samples were compressed and the spectra were taken in the 180-degree geometry. The excitation source was a 780 nm diode laser, and the spectra were obtained using a full range grating and a triplet spectrograph.

Figure 2 shows the Raman features from a purified sample of single-walled carbon nanotubes produced by the HiPCO technique. We have been able to identify the main features seen in CNTs: the 2D band (2578.61 $cm^{-1}$), the D band (1290.22 $cm^{-1}$), the G+ band (1585.95 $cm^{-1}$), the G- band (1559.88 $cm^{-1}$) and the Radial Breathing Mode (222.81 & 264.81$cm^{-1}$). The values of these features have been well studied and our results match well with known literature, and we have been able to properly characterize the vibrational modes of our samples.

Using Eqn. (6) for the 222.81 $cm^{-1}$ radial breathing mode peak, the estimated diameter that is in resonance with this excitation energy is ~ 1.09 nm, corresponding to either a (14, 0) zig-zag or (10, 6) chiral nanotube.

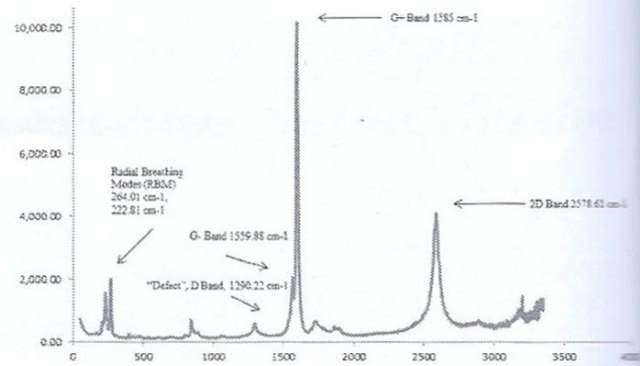


**Figure 2. Raman Spectrum of Purified SWNT using a 780 nm laser source.**

Figure 3 is the Raman spectrum for unpurified SWNTs under the same conditions. For these, we have obtained the following features: the 2D band (2575.61 $cm^{-1}$), the D band (1293.27 $cm^{-1}$), the G+ band (1589.82 $cm^{-1}$), the G- band (1561.43 $cm^{-1}$) and the Radial Breathing Mode (230.69 & 263.99 $cm^{-1}$). With an RBM of 230.69 $cm^{-1}$ we obtain an estimated diameter of ~1.06 nm, which corresponds to the same nanotube configurations as in Figure 2.

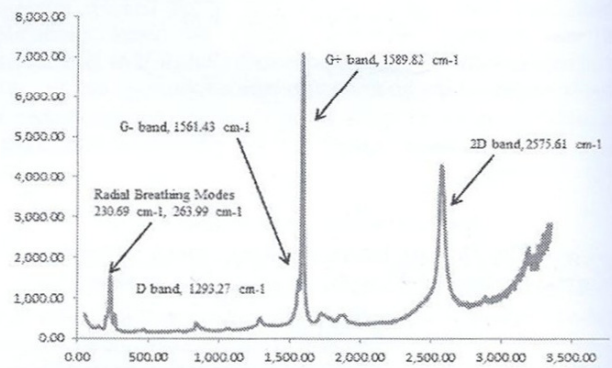


**Figure 3. Raman Spectrum of an Unpurified SWNT using a 780 nm laser source.**

According to reference [8], infrared excitation sources can also be used to determine the extent of aggregation of nanotubes in a sample. By using varying laser excitation energies to excite both individualized and bundled nanotube samples the authors of [8] were able to create a distribution of radial breathing mode intensities. In the case of bundled tubes, the point in the distribution corresponding to the 785 nm laser excitation was the peak of this distribution, corresponding to a chirality of (10, 2) being in resonance with this laser wavelength. The radial breathing mode band that the authors used in this analysis was located at 264 $cm^{-1}$, termed the "roping" peak. An RBM band, at almost the same location in Figures 2 and 3, is also observed in the case of our 780 nm excitation.



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## V. Conclusions

We have been able to characterize our CNT samples and have obtained the vibrational modes, diameter, chirality and bond lengths for them successfully. Through Raman Spectroscopy we have obtained a majority of the features that characterize CNTs to a satisfying degree.

Experimental CTE measurements on individual carbon nanotubes could benefit from Atomic Force Microscopy (AFM), high resolution TEM, nanolithography, and other techniques requiring specialized surface and sample preparations, and would also be subject to size restrictions. Such considerations make Molecular Dynamics simulations the next logical step, after our Raman Spectroscopy work, in the examination of the thermal properties of carbon nanotubes.

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