VIBRATIONAL MODES AND THERMAL TRANSFORMATION OF PURIFIED
SINGLE WALLED CARBON NANOTUBES

A Thesis in
Physics
by
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Vibrational modes of single-walled carbon nanotubes (SWNTs) and graphitic nanoribbons (GNRs) were studied using Raman scattering and/or Fourier Transform Infrared Spectroscopies, Variations in a three-step purification scheme to remove amorphous carbon and residual catalyst were studied: (step 1) Oxidation, (step 2) Acid Reflux, and (step 3) Thermal Annealing were found to remove most amorphous carbon (oxidation step) and residual metal catalyst (acid reflux step) which were the major impurity phases. By combining IR and Raman, we found considerable wall damage and functional groups (e.g., -COOH and -OH) could be introduced via H₂O₂ and HNO₃ reflux. Surprisingly, vacuum annealing at ~1100°C for a few hours was found to remove most wall damage and functional groups.

Methods to break up large (purified) bundles of single-walled carbon nanotubes (SWNTs) to individual tubes were also investigated. Amide solvents with ultrasound were found to be very effective in debundling; initial purification treatment strongly impacted the outcome. SWNT material decorated with functional groups (e.g., -COOH) tended to produce higher yields of single tubes. Length and diameter distributions of individual tubes were measured using Atomic Force Microscopy. Aggressive chemical debundling processes were found to lead to more functionalization, higher degree of debundling and shorter tubes.

The IR-active modes of SWNTs was observed for the first time by transmission method, some ten years after the discovery of the Raman-active modes. In concert with
theoretical calculations, we were able to assign much of the sharp structure in the IR with anticipated one- and two-phonon lattice mode bands.

Thermal evolution of bundled SWNT materials produced in the electric arc (ARC) and by CVD in CO gas (HiPCO) was also investigated. Although both ARC and HiPCO evolved thermally to multi-walled tubes (MWNTs), we found using electron microscopy that for $T>2000^\circ C$ ARC SWNTs (with significantly narrower diameter distribution) evolved beyond MWNTs to a new dominant form of carbon termed “graphitic nanoribbons” (GNRs). A strong increase in D-band Raman intensity in ARC SWNTs was observed after the formation of GNRs and identified with lateral phonon confinement.
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Chapter 1
Introduction

An ideal nanotube can be thought of as a hexagonal network of carbon atoms that has been rolled up to make a seamless cylindrical shell, one atom thick. They can be as small as a nonometer across, and tens of microns long. Each end is "capped" with half of a fullerene molecule. Single-wall nanotubes can be thought of as the fundamental cylindrical shell structure, and these form the building blocks of both multi-wall nanotubes and ordered arrays of single-wall nanotubes called ropes.

In 1991, Multi-walled carbon nanotubes (MWNTs) were discovered by Iijima and co-workers from arc discharge-produced carbon soot[1]. Some controversy exists regarding whether or not Morinobu Endo may have first discovered concentric cylindrical carbon tubes[2]. Fig. 1-1 shows the MWNTs reported by Iijima’s group showing an inner nuclear diameter d_o ~6nm and structures with 2-7 walls[1]. MWNTs can exhibit as many as 20-50 closed shells per filament, and usually have a large inner tube diameter (~10nm). Recently, Ando’s[3] and Iijima’group[4] have reported that a 0.3-0.4nm nanotube can be centered inside a MWNT, as observed by high resolution transmission electron microscopy (HRTEM). Usually, the spacing between the shells in a MWNT is almost the same as the layer spacing in graphite[3]. Direct stimulus to study very small diameter carbon filaments came from the discovery of fullerenes by Kroto and Smalley[5]. In 1993, single walled carbon nanotubes (SWNTs) were discovered in arc soot by Iijima and Bethune and coworkers[6, 7]. These results were published back to
back in Nature. All carbon nanotubes require the presence of small metal particles, usually containing Fe, Co or Ni. They act as “growth seeds”. This will be discussed further below. Fig. 1-2(a) shows a typical low resolution TEM image of bundled SWNTs. These tubes happen to be grown by Pulsed Laser Vaporization (PLV) method reported first by Smally’s group[8]. Each filament is a bundle of tubes. SWNT materials produced by ARC discharge and the chemical vapor deposition (CVD) method are harvested as loose powders and have images similar to Fig. 1-2(a). Interestingly, SWNTs can be grown nearly parallel to each other, forming crystalline-like bundles or ropes of nanotubes, perhaps 10-50nm in diameter as shown in Fig. 1-2(b). SWNTs formed by ARC discharge method or PLV are usually closed packed forming an approximate triangular lattice. The diameter distributions of the individual tubes can be narrow. These bundles typically contain from tens to hundreds of carbon nanotubes. Isolated SWNTs can also be grown by using well isolated small catalyst particles supported on the substrates by CVD[9]. X-ray diffraction measurements also showed that single-wall nanotubes grown by ARC discharge[10] and Pulsed Laser Vaporization (PLV) method[8] tend to form in bundles described by a two-dimentional triangular lattice. The bundle is held through van der Waals bonding. However, for SWNTs grown by HiPCO process, the diameter distribution of SWNTs is very wide and the tube packing in the bundle is imperfect, i.e., they are not in a triangular lattice.

Currently, many groups have been trying to improve the nanotube growth process for applications requiring larger quantities [11-14], or to obtain higher purity as grown SWNT material(i.e., amorphous carbon is an important impurity phase.) [15]. For example, Choi et al.[14] have been growing vertically aligned MWNTs in prepatterened
porous anodic aluminum oxide (AAO) templates to produce tera level density 
\(2 \times 10^{11}/\text{cm}^2\) Field Effect transistors (FETs) by CVD method. Some groups have been 
trying to grow SWNTs on the prepatterned catalyst particles\[11-13\]. Others have been 
trying to lower the growth temperature of SWNTs or MWNTs to be compatible with 
device integration\[16-18\]. Iijima’s group has reported that ultra high purity SWNTs can 
be grown by water vapor assisted CVD (supergrowth CVD) method\[15\]. There have 
been some reports to separate metallic tubes and semiconducting tubes by various 
chemical protocols\[19-21\].

Due to its unique 1-D structural nature, carbon nanotubes have captured the 
attention of the international research community who investigate their fundamental 
properties as well as novel devices, e.g., single electron transistors\[14, 22, 23\], ballistic 
charge/heat transport\[24\]. SWNTs are also of interest because of their promise for 
applications as transistors \[14, 22, 23\], logic gates\[25\], gas storage\[26\], sensors\[27, 28\], 
field emission devices\[29, 30\] and high-strength, conductive additives for structural 
materials\[31, 32\].
Fig. 1-1: three MWNTs reported by Iijima’s group (a) the inner modes tube diameter $d_o \sim 6$nm with 5 walls, (b) $d_o \sim 5.5$nm with two walls, (c) $d_o \sim 6.5$nm with 7 walls [1]

Fig. 1-2: (a) typical SEM image of bundles of SWNTs, (b) the HRTEM image of a SWNT bundle cross-section
1.1 Structure of graphite and SWNTs

1.1.1 Graphite

The crystal structure of single crystal graphite is hexagonal, in which planes of carbon atoms (two atoms (A, A’) per unit cell) in each layer exist in two inequivalent layers. These layers are labeled A and B (Fig. 1-3(a)). The three dimensional structure has an ABAB…stacking sequence. This crystal structure is consistent with the $D_{6h}^4$ (P63/mmc) space group and has four carbon atoms per unit cell (two atoms in each layer), as shown in Fig. 1-3(a). Accepted values of the lattice constants are $a_0=0.2462\text{nm}$ and $c_0=0.6707 \text{ at room temperature, so that the in-plane bond length is } 0.1421\text{nm and the interplanar separation, } c_0/2 \text{ is } 0.3354\text{nm.}$ Since the in-plane covalent C-C bond is very strong and the nearest-neighbor spacing between carbon atoms in graphite is very small, the in-plane lattice constant is quite stable against external perturbation. The graphene layers are bonded by a weak van der Waals force. Fig. 1-3(b) shows a typical STM image of highly oriented pyrolytic graphite (HOPG) basal plane. The STM image shows a trigonal network of C-atoms in which only one site of the carbon hexagonal network appears, as for example, the A’ site, denoted by black balls in (a). The black balls (A’) represent carbon atoms that lie directly above atoms in the plane below. The white balls lie above voids in the lower plane. Because the electron density is higher above the filled atoms, they appear as the bright spots in the image, which explains why trigonal pattern is observed in the STM image for HOPG instead of honeycomb lattice pattern. The following interpretation of the STM image has been proposed[33].
Fig. 1-3: (a) The crystal structure of hexagonal single crystal graphite, in which the two distinct planes of carbon hexagons called A and B planes are stacked in an ABAB, sequence with the $D_6h$ symmetry. (b) An STM image showing the trigonal network of highly oriented pyrolytic graphite (HOPG) in which only one site of the carbon hexagonal network appears, as for example, the A’ site, denoted by black balls in (a).

Fig. 1-4: The vector, $\vec{OA}$ is the chiral vector, $\vec{C}_h$ for a (4,2) tubule. The vector, $\vec{OB}$ is the translational vector; $\vec{r}$ orthogonal to $\vec{C}_h$. $\theta$ is the chiral angle for (4,2) tubule and OBB’A is a unit cell of a (4,2) tubule.
1.1.2 Structure of Carbon Nanotubes

Carbon nanotubes are cylindrically rolled graphene sheet with dominant sp² hybridization [34]. The structure of the nanotube can be defined by the integers n and m, the honey comb lattice vectors; \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \). The chiral vector \( \mathbf{C}_h \) is defined as a linear combination of the honey comb lattice vectors, \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \)

\[
\mathbf{C}_h = n \mathbf{a}_1 + m \mathbf{a}_2 \quad (0 \leq |m| \leq n)
\]

Eq 1.1

The relationship of \( \mathbf{C}_h \) to the circumference of the carbon nanotube is evident in Fig. 1-4 which shows a graphene sheet and the outline OAB’B of a nanotube unit cell. The combination, (n,m) of these integers determines the type of carbon nanotube: achiral or chiral. When \( n \neq m \neq 0 \), the tube is chiral, otherwise it is achiral. Achiral tubes can be \((n,0)\) or \((n,n)\). Zigzag tubes and armchair tubes refer to \((n,0)\) and \((n,m)\), respectively. On the other hand when, \( n = m \neq 0 \), the tube is called armchair. Fig. 1-5 shows (a) \((5, 5)\) armchair tubule, (b) \((9, 0)\) zigzag tubule and (c) \((10, 5)\)[36]. The experimental verification of the honeycomb structure of a carbon nanotube was made via scanning tunneling microscope (STM) images.

Fig. 1-6 shows atomically resolved STM images of various carbon tubes reported by Dekker’s group[35]. Dashed arrows represent the tube axis \( \mathbf{T} \) and the solid arrows indicate the direction nearest-neighbor hexagon rows \( \mathbf{H} \). Tubes (a), (b) and (c) are chiral, whereas tubes (d) and (e) have a zigzag and armchair structure, respectively. The tube labeled as (a) in Fig. 1-6 has a chiral angle \( \phi = 7^\circ \) and a diameter \( d=1.3\text{nm} \), which corresponds to the \((11, 7)\)[35].
To construct a nanotube from a flat honeycomb lattice (c.f. Fig. 1-4), an arbitrary origin O is chosen with three other equivalent crystallographic sites; such as A, B and B' such that the chiral vector $\overrightarrow{OA}$ or $\vec{C}_h$ is orthogonal to the translational vector $\vec{T}$ or $\overrightarrow{OB}$ which is parallel to the tube axis. $\vec{C}_h$ and $\vec{T}$ define the unit cell of the nanotube; Fig. 1-4. By rolling up the graphene sheet so that the origin, O coincide with lattice point A and B coincide with B', a cylindrical unit cell of the nanotube is formed. Fig. 1-4 shows a unit cell of a (4,2) chiral nanotube. The diameter ($d_t$) of a nanotube is given by the equation,

$$d_t = \frac{C_h}{\pi} = \frac{\sqrt{3}}{\pi} a_{cc} n m (n^2 + m^2 + 2nm)^{\frac{1}{2}}$$  \hspace{1cm} \text{Eq 1.2}$$

where $|\vec{C}_h|$ is the circumference of the tube.

The chiral angle $\theta$ is the angular separation between a vector in the zigzag direction and the chiral vector. Thus, $\theta$ is $0^\circ$ and $30^\circ$ for zigzag and armchair respectively, while the chiral angle for all chiral tubules range between these two angles.

The translational vector, $\vec{T}$ is perpendicular to the chiral vector and is parallel to the nanotube axis. $\vec{T}$ is the length of the 1D nanotube unit cell. $\vec{T}$ can be expressed in terms of the honeycomb lattice vectors as

$$\vec{T} = t_1 a_1 + t_2 a_2$$  \hspace{1cm} \text{Eq 1.3}$$
where $t_1$ and $t_2$ are integers with no common divisor. Since $\vec{T}$ is perpendicular to $\vec{C}_h$, the integers $t_1$ and $t_2$ can be found by the dot product of $\vec{T}$ and $\vec{C}_h$ as $\vec{C}_h \cdot \vec{T} = 0$.

Fig. 1-5: (a) (5,5) armchair tubule, (b) (9,0) zigzag tubule and (10,5) chiral tubule.[36]

Fig. 1-6: Atomically resolved STM image of SWNTs: (a), (b), (c) chiral tubes, (d) zigzag tube, (e) armchair tube

For any (n,m) tube,
Here, \( d_R \) is the greatest common divisor of \((2m+n)\) and \((2n+m)\).

\[
T = \frac{\sqrt{3}|C|}{d_R} = \frac{\sqrt{3}d_r \pi}{d_R} \quad \text{Eq 1.4}
\]

1.1.3 Organization for the thesis

An effective chemical process to obtain clean nanotube bundles and/or clean individual single-walled carbon nanotubes (SWNTs) in a stable solution is an important step needed for fundamental science and developing many large scale applications for these molecular filaments. In Ch.4, we describe how we purified raw soot containing SWNT produced by the electric arc discharge. Next, we discuss how to break up the bundles in amide solvents in Ch.5. By using Raman and IR spectroscopy, the chemical changes in the tube wall caused by the chemical purification process have been followed, e.g., missing C-atoms or wall damages covalently bonded functional groups. It will be shown in Ch.5 that tube wall defects, such as missing carbon atoms, functional groups, and etc., can be removed by annealing purified arc discharge SWNTs at 1100-1400°C. In Ch.6, we describe the first systematic experimental attempts to observe the IR-active modes of SWNTs. In Ch.7, we will discuss the temperature-driven morphological changes in SWNT samples such as coalescence, transformation to MWNTs and transformation to new multishell carbon filaments, \(i.e.,\) graphitic nanoribbon (sGNRs) by annealing the bundles of SWNTs at a successively higher temperature.
Chapter 2

Theoretical background on SWNT electronic and phonon states
– Zonefolding: graphene to SWNT

2.1 Unit cells and Brillouin zones of graphite and SWNTs

Fig. 2-1 shows the unitcell(a) and the Brillouin zone(b) of two dimensional graphite(graphene) as a dotted rhombus and shaded hexagon, respectively. The vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are the real space primitive translation vectors, and \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \) are the corresponding reciprocal lattice vectors. In the \( x, y \) coordinates shown in Fig. 2-1, the real space unit vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) of the hexagonal lattice are expressed as

\[
\mathbf{a}_1 = \left( \frac{\sqrt{3}}{2}, \frac{1}{2} \right) a, \quad \mathbf{a}_2 = \left( \frac{\sqrt{3}}{2}, -\frac{1}{2} \right) a, \quad \text{Eq } 2.1
\]

where \( a = |\mathbf{a}_1| = |\mathbf{a}_2| = 1.42 \, \text{Å} \times \sqrt{3} = 2.46 \, \text{Å} \) is the lattice constant of graphene.

Correspondingly, the unit vectors \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \) of the reciprocal lattice are given

\[
\mathbf{b}_1 = \left( \frac{1}{2}, \frac{\sqrt{3}}{2}, \frac{4\pi}{\sqrt{3}a} \right), \quad \mathbf{b}_2 = \left( \frac{1}{2}, -\frac{\sqrt{3}}{2}, \frac{4\pi}{\sqrt{3}a} \right) \quad \text{Eq } 2.2
\]

corresponding to a lattice constant of \( 4\pi/\sqrt{3} \, a \) in reciprocal space.
The unit cell for a carbon nanotube in real space is given by the rectangle generated by the chiral vector \( \mathbf{C}_h \) and the translational vector \( \mathbf{T} \) as is shown in OAB’B in Fig. 1-4 for (4,2) nanotube. Expressions for the reciprocal lattice vectors \( \mathbf{K}_2 \) along the nanotube axis and \( \mathbf{K}_1 \) in the circumferential direction are obtained from the relation

\[
\mathbf{R}_i \cdot \mathbf{K}_j = 2\pi \delta_{ij},
\]

where \( \mathbf{R}_i \) and \( \mathbf{K}_j \) are, respectively, the lattice vectors in real and reciprocal space. Then, using Eq. 1.1 for \( \mathbf{C}_h \) and the relations by using \( \mathbf{R}_i \cdot \mathbf{K}_j = 2\pi \delta_{ij} \)

\[
\mathbf{C}_h \cdot \mathbf{K}_1 = 2\pi, \quad \mathbf{T} \cdot \mathbf{K}_1 = 0, \quad \mathbf{C}_h \cdot \mathbf{K}_2 = 0, \quad \mathbf{T} \cdot \mathbf{K}_2 = 2\pi \quad \text{Eq 2.3}
\]

We can therefore arrive at the following expressions for \( \mathbf{K}_1 \) and \( \mathbf{K}_2 \):

\[
\mathbf{K}_1 = \frac{1}{N} ( -t_2 \mathbf{b}_1 + t_1 \mathbf{b}_2 ), \quad \mathbf{K}_2 = \frac{1}{N} ( m\mathbf{b}_1 - n_1 \mathbf{b}_2 ),
\]

\( \text{Eq 2.4} \)

where \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \) are the reciprocal lattice vectors of 2-D graphite given by Eq. 2.2, and \( N \) is the number of hexagons per unit cell.
In Fig. 2-2, we show the reciprocal lattice vectors $\mathbf{K}_1$ and $\mathbf{K}_2$, for a $C_h = (4, 2)$ chiral nanotube. The first Brillouin zone of this one-dimensional material is the line segment $WW'$. Since $N \mathbf{K}_1 = -t_2 \mathbf{b}_1 + t_1 \mathbf{b}_2$ corresponds to a reciprocal lattice vector of two-dimensional graphite, two wave vectors which differ by $N \mathbf{K}_1$ are equivalent. Since $t_1$ and $t_2$ do not have a common divisor except for unity, none of the $N-1$ vectors $\mu \mathbf{K}_1$ (where $\mu = \ldots, N-1$) are reciprocal lattice vectors of two-dimensional graphite.

![Fig. 2-2: The Brillouin zone of a carbon nanotube is represented by the line segment WW’ which is parallel to $\mathbf{K}_2$. The vectors $\mathbf{K}_1$ and $\mathbf{K}_2$ are reciprocal lattice vectors corresponding to $C_h$ and $T$, respectively.[36]

Thus the $N$ wave vectors $NK_1$ give rise to $N$ discrete $k$ vectors, as indicated by the $N=28$ parallel line segments in Fig. 2-2, which arise from the quantized wave vectors associated with the periodic boundary conditions on $C_h$. The periodic boundary condition on $C_h$ is shown is Eq. 2.8. The length of all the parallel lines in Fig. 2-2 is $2\pi / T$ which is the length of the one-dimensional first Brillouin zone. Note that $T$ is the magnitude of the translation vector shown in Eq. 1.3.


2.2 Electronic structure

2.2.1 Electronic structure of 2-D graphite

In 3-D graphite, the interaction between two adjacent layers is small compared with intra-layer interactions, since the layer-layer separation of 3.35Å is much larger than nearest-neighbor distance between two carbon atoms, $a_{C-C} = 1.42Å$. Thus the electronic structure of 2-D graphite (graphene) is a first approximation of that for 3-D graphite.

The electronic energy band dispersion of the energy bands closest to the Fermi level in 2D graphite as obtained by the tight binding method is described by[34, 36]

\[
E_{g2D}^2(k) = \frac{\varepsilon_{2p} \pm \gamma_0 w(k)}{1 \mp \sqrt{\omega k}}
\]

Eq 2.5

\[
w(k) = \sqrt{1 + 4 \cos \frac{k_x a}{2} \cos \frac{k_y a}{2} + 4 \cos^2 \frac{k_z a}{2}}
\]

Eq 2.6

Fig. 2-3: (a) The energy dispersion relations for 2-D graphite throughout the whole region of the Brillouin zone. (b) The energy dispersion along the high symmetry direction of the triangle $\Gamma$, M, and K shown in Fig 2.1(b).

In 3-D graphite, the interaction between two adjacent layers is small compared with intra-layer interactions, since the layer-layer separation of 3.35Å is much larger than nearest-neighbor distance between two carbon atoms, $a_{C-C} = 1.42Å$. Thus the electronic structure of 2-D graphite (graphene) is a first approximation of that for 3-D graphite.

The electronic energy band dispersion of the energy bands closest to the Fermi level in 2D graphite as obtained by the tight binding method is described by[34, 36]
where $s$ is overlap integral, and $\gamma_0$ is carbon-carbon interaction energy. These bands are referred to as the $\pi$(bonding) and $\pi^*$ (anti-bonding) bands; the $\pi^*$ band, of course, lies at higher energy.

Fig. 2-3(a) represents the energy dispersion relations of 2-D graphite are shown throughout the Brillouin zone where $\epsilon_{2p} = 0$, $\gamma_0 = -3.033 \text{eV}$, and $s = 0.129$ are chosen. Fig. 2-3(b) shows the electronic dispersion along the high symmetry axes along the perimeters of the triangle shown in Fig. 2-1(b). The energy dispersion relations in the case of $s = 0$ are commonly used as a simple approximation for the electronic structure of graphene layer[36]:

$$E_{2D} = \gamma_0 w(k) = \pm \gamma_0 \sqrt{1 + 4 \cos \frac{\sqrt{3}k_xa}{2} \cos \frac{k_ya}{2} + 4 \cos^2 \frac{k_ya}{2}}$$ \hspace{1cm} Eq 2.7

This simple approximation will be used to obtain the electronic dispersion relations for carbon nanotubes.

\subsection*{2.2.2 Zone folding of Energy Dispersion Relations}

The electronic structure of a single-wall nanotube can be obtained simply from that of 2-D graphite(graphene)[36]. By using periodic boundary conditions in the circumferential direction denoted by the chiral vector[34],

$$\left| \vec{k} \cdot \vec{C}_k(n,m) \right| = 2q\pi \ (q = 1, \ldots, 2n)$$ \hspace{1cm} Eq 2.8
the wave vector associated with the circumferential direction becomes quantized, while
the wave vector associated with the direction of the translational vector $T$ (or along the
tube axis) remains continuous for a nanotube of infinite length.

The 1D energy dispersion relations are then given by [36]

$$E_q = E_{g2D}(k\frac{\bar{K}_2}{K_2} + \mu\bar{K}_1), \ (\mu = 0, \ldots, N-1, \text{and} \ -\frac{\pi}{T} < k < \frac{\pi}{T}), \quad \text{Eq 2.9}$$

The $N$ pairs of energy dispersion curves given by Eq. 2.9 correspond to the cross
sections of the two-dimensional energy dispersion surface shown in Fig. 2-3(a), where
cuts are made on the lines of $k\frac{\bar{K}_2}{K_2} + \mu\bar{K}_1$. For a particular $(n, m)$ nanotube, one cutting
line passes through a $K$ point of the 2D Brillouin zone, where the $\pi$ and $\pi^*$ energy bands
of two-dimensional graphite are degenerate. The one-dimensional valence and
conduction bands therefore have a zero gap. As will be shown later, these nanotubes
have a finite value of the electronic density of states at the Fermi level. These tubes are
therefore metallic. If, however, the cutting line does not pass through a $K$ point, then the
carbon nanotube is expected to show semiconducting behavior, with a finite energy gap
between the valence and conduction bands.

Fig. 2-4(a) and (b) shows part of the unit cells and Brillouin zones for the highly
symmetric (achiral) nanotubes, namely for (a) an armchair nanotube and (b) a zigzag
nanotube.
The appropriate periodic boundary conditions Eq. 2.8 used to obtain the energy
eigenvalues for the (n,n) armchair nanotube define the small number of allowed wave
vectors $k_{x,q}$ in the circumferential direction [34]

$$n\sqrt{3}k_{x,q}a = 2\pi q, (q = 1, \ldots 2n).$$  

Eq 2.10

The $k_{y}$ direction is parallel to the tube axis. Substitution of the discrete allowed
value for $k_{x,q}$ given by Eq. 2.10 into Eq. 2.7 yields the energy dispersion relations
$E^{a}_{q}(k)$ for the armchair nanotube, $C_{a} = (n,n)$,[34, 36]

$$E^{a}_{q}(k) = \pm \gamma_{0} \{1 \pm 4 \cos(\frac{qa\pi}{a}) \cos(\frac{ka\pi}{a}) + 4 \cos^{2}(\frac{ka\pi}{a})\}^{1/2}, (-\pi < ka < \pi),$$

$$\left(q = 1, \ldots, 2n\right)$$  

Eq 2.11

which the superscript ‘a’ refers to armchair and $k$ is a one-dimensional vector in the
direction of the $\overrightarrow{K_{2}} = \left(\overrightarrow{b_{1}} - \overrightarrow{b_{2}}\right)/2$. This direction corresponds to the $\Gamma$ to K point vector in
the two-dimensional Brillouin zone of graphite. From the Eq. 2.10, the line spacing
($\Delta k$) in the 2D reciprocal grapheme space for an armchair tube is $\Delta k_{y} = 2\pi/(\sqrt{3}a)$.

Fig. 2-5(a) shows the resulting 1D dispersion relations $E^{a}_{q}(k)$ for (5, 5) armchair
nanotube. The valence and conduction bands in Fig. 2-5(a) for the armchair nanotube
cross at a $k$ point that is two thirds of the distance from $k=0$ to the zone boundary at $k = \pi / a$. The crossing takes place at the Fermi level and the energy bands are symmetric for $\pm k$ values.

Fig. 2-5: One-dimensional energy dispersion relations for (a) armchair(5,5),(b) Zigzag(9,0) ,(c) Zigzag (10,0) carbon nanotubes

For zigzag tubes, $C_{h} = (n,0)$, the periodic boundary condition on $k_{y}$ is [34]

$$nk_{x,q}a = 2\pi q , \ (q=1,\ldots,2n) \ \text{Eq 2.12}$$

In this case, $k_{x}$ is the tube direction. By inserting this relation into Eq. 2.7, the energy bands for zigzag tubes can be obtained as [34]

$$E^{Z}_{q}(k) = \pm \gamma_{0} \{1 \pm 4 \cos(\frac{nk_{x}}{a}) \cos(\frac{2\pi q}{a}) + 4 \cos^{2}(\frac{\pi q}{a})\}^{1/2} , \ (-\frac{\pi}{\sqrt{3}} < ka < \frac{\pi}{\sqrt{3}}) , \ (q=1,\ldots,2n) \ \text{Eq 2.13}$$
The resulting calculated 1D dispersion relations \( E^Z_q(k) \) for the (9,0) and (10,0) zigzag nanotubes are shown in Fig. 2-5(b) and (c), respectively. There is no energy gap for the (9, 0) nanotube at \( k=0 \), whereas the (10,0) nanotube indeed shows an energy gap.

For the case of chiral nanotubes, the periodic boundary condition becomes[34, 36]

\[
n\sqrt{3}k_{x,q}a + mk_{y,q}a = 2\pi q.
\]  

Eq 2.14

The general dispersion relation can then be obtained as[34, 36]

\[
E^Z_q(k) = \pm t\{1 \pm 4 \cos(\frac{2\pi k a}{n-m}) \cos(\frac{2\pi q}{n}) + 4 \cos^2(\frac{2\pi q}{n})\}^{1/2}
\] where

\(-\pi < ka < \pi\) where \( q = 0, \ldots , N-1 \).

Eq 2.15

For a general \((n, 0)\) zigzag nanotube \((n, m)\) chiral nanotube), when \( n ((n-m) \) for chiral tubes) is a multiple of 3, the energy gap at \( k=0 \) becomes zero; however \( n ((n-m) \) for chiral tubes) is not a multiple of 3, an energy gap opens at \( k=0 \) as explained earlier.

**2.2.3 Density of States, Energy gap**

The electron density of states (DOS) can be derived from the energy band diagram. Due to the one-dimensional nature of the nanotube structure, sharp van Hove singularities appear in the DOS at energies associated with band minima and maxima. Fig. 2-6 shows the density of states for metallic (9,0) and semiconducting (10,0) zigzag nanotubes. Of particular interest is the density of states near the Fermi level \( E_F \) located at \( E=0 \). This density of states at \( E_F \) has a value of zero for semiconducting nanotubes, but is non zero (and small) for metallic nanotubes. The energy gaps of SWNTs depend on its diameter which will be shown in Eq. 2.16 -Eq. 2.18
The $\pi\pi^*$ bands of a single graphene sheets can be approximated by $E = \pm \frac{1}{3} \gamma_0 a \Delta k$ in the vicinity of Fermi points K and K' where they cross each other. For the case of semiconducting tubes, it can be shown that the distance from the K point to the nearest or second nearest allowed k-line is always $1/3 \Delta k$ or $2/3 \Delta k$, respectively, where $\Delta k$ is the spacing between allowed k lines imposed by the periodic boundary conditions[37]. Also it is shown earlier that $\Delta k$ is $2/d(n,m)$ as can be inferred in Eq. 2.8 (Note that $|C_{a}(n,m)| = \pi \times d(n,m)$, where $d(n,m)$ is the diameter of the nanotube). Then we can derive the first and second energy band maxima and minima for the semiconducting nanotubes, i.e., [37]

$$E_1^S = \pm \frac{1}{3} (\frac{\sqrt{3} \gamma_0}{2}) \frac{2}{d(n,m)} = \frac{\alpha \gamma_0}{\sqrt{3d(n,m)}}$$, when $k - k_F = \frac{1}{3} \Delta k$ \hspace{1cm} \text{Eq 2.16}

and

$$E_2^S = \pm \frac{2}{3} (\frac{\sqrt{3} \gamma_0}{2}) \frac{2}{d(n,m)} = \frac{2\alpha \gamma_0}{\sqrt{3d(n,m)}}$$, when $k - k_F = \frac{2}{3} \Delta k$ \hspace{1cm} \text{Eq 2.17}
The gaps between these mirror image bands is denoted \( \Delta E_{11}^S = 2|E_1^S| \) and \( \Delta E_{22}^S = 2|E_2^S| \).

For metallic nanotubes, there is always an allowed k-line crossing the Fermi point. The two points that closest to the Fermi(K) point are exactly a distance \( \Delta k \) away. The van Hove singularities thus overlap and the energy maxima (-) and minima (+) is[37]

\[
E_i^M = \pm \left( \frac{\bar{\gamma}_0}{2} \right) \frac{g}{d(n,m)} = \frac{3\bar{\gamma}_0}{\sqrt{d(n,m)}}, \text{ where } k - k_F = \Delta k
\]

Eq 2.18

The energy band overlap gap for metallic tube is therefore \( \Delta E_{11}^M = 2|E_1^M| \).

It can be noticed that the energy gap for both metallic and semiconducting nanotubes inversely depends on the reciprocal nanotube diameter \( d(n,m) \).

Fig. 2-7 shows the diameter dependence of the splitting between mirror image van Hove singularities for all \((n, m)\) carbon nanotubes for \( \gamma_0 = 2.9 \). Blue circles with cross at the center and red circles denote the values for semiconducting and metallic tubes, respectively. The diagram in Fig. 2-7 clearly shows that the splittings \( \Delta E_{ij} \) are inversely proportional to the tube diameter \( d(n,m) \) as predicted by theory in Eq. 2.17 and Eq. 2.18. This diagram is the so-called Kataura plot. It is very important to understand the nature of the resonant Raman scattering in carbon nanotubes, which will be discussed in Ch.3.
2.3 Phonons of graphite and Single Walled Carbon nanotube

Infrared and Raman spectroscopy probe predominantly zone-center modes, while inelastic neutron scattering is capable of exploring the entire Brillouin zone. Because of the small wave vector of light relative to Brillouin zone dimensions in solids, first-order light scattering is confined to the excitation of phonon modes close to the zone center. Information on the phonon dispersion relations for other points in the Brillouin zone can be obtained from second-order Raman spectra, where contributions are made by pairs of...
phonons with vectors q and –q, the major contribution coming from those regions in the Brillouin zone having high densities of states.

Because a carbon nanotube may be thought of as a graphene sheet rolled up to form a seamless tube, a carbon nanotube should be expected to have many properties derived from the energy bands and lattice dynamics of a graphene sheet. We have discussed this idea from the perspective of the electronic states near the Fermi energy. Now we carry the ideas forward to the case of phonons. We first explain how to calculate phonon dispersion relations in 2D graphite by a simple force constant model. Then phonon dispersion relations for carbon nanotubes can be obtained by the same zone-folding method used for electronic states in the previous section. Finally, we will discuss how to obtain the phonon dispersion relations by solving the three-dimensional dynamical matrix.

2.3.1 phonon dispersion relations for 2-D graphite

We start with an approach for calculating the phonon dispersion relations of 2-D graphite with a force constant model, in which inter-atomic forces are represented by spring constants (See Eq. 2.25.)

The equation of motion for the displacement of the $i^{th}$ coordinate, $u_i=(x_i,y_i,z_i)$ for $N$ atoms in the unit cell is given by
where $M_i$ is the mass of the $i^{th}$ atom and $K^{(i,j)}$ represents the $3\times3$ force constant tensor between the $i^{th}$ and $j^{th}$ atoms. In a periodic system we can perform a Fourier transform of the displacement of the $i^{th}$ atom with the wave number, $k'$, to obtain the normal mode displacements $u_k^{(i)}$

$$u_i = \frac{1}{\sqrt{N\Omega}} \sum_{k'} e^{-i(k',R_i-R_i)} u_k^{(i)}$$ \hspace{1cm} \text{Eq. 2.20}$$

where the sum is taken over all the wave vectors in the first Brillouin zone and $R_i$ denotes the origin of the $i^{th}$ atom. When we assume the same eigen frequencies $\omega$ for all $u_i$, that is $\ddot{u}_i = -\omega^2 u_i$, then Eq. 2.19 becomes

$$\left( \sum_j K^{(i,j)} - M_i \omega^2 \right) \sum_k e^{-i(k',R_i-R_i)} u_k^{(i)} = \sum_j K^{(i,j)} \sum_k e^{-i(k',R_i-R_i)} u_k^{(j)}$$ \hspace{1cm} \text{Eq. 2.21}$$

By simple mathematical treatment [36], Eq. 2.21 can be formally written as follows by defining a $3N\times3N$ dynamical matrix $D(k)$

$$D(k) u_i = 0$$ \hspace{1cm} \text{Eq. 2.22}$$

To obtain the eigenvalues $\omega^2(k)$ for $D(k)$ and non-trivial eigenvectors $u_k \neq 0$, we solve the secular equation $\det[ D(k) ]=0$ for a given $k$ vector. Each component of the density matrix $D(k)$, (i.e. $D^{ij}(k)$), is expressed as

$$D^{ij}(k) = \left( \sum_j K^{(i,j)} - M_i \omega^2(k) I \right) \delta_{ij} - \sum_j K^{(i,j)} e^{i(k,R_j)} = 0$$ \hspace{1cm} \text{Eq. 2.23}$$
where $I$ is a $3 \times 3$ unit matrix and $\Delta R_{ij} = R_i - R_j$ is the relative coordinate of $i^{th}$ atom with respect to the $j^{th}$ atom. The first two terms of Eq. 2.23 have non-vanishing values only when $i=j$, and the last term appears only when the $j^{th}$ atom is coupled to the $i^{th}$ atom through $K^{(ij)} \neq 0$.

In two-dimensional graphite, since there are two non-identical carbon atoms, A and B, in the unit cell, we must consider six coordinates $u_k$ in Eq. 2.22. The secular equation to be solved is thus a $6 \times 6$ dynamical matrix $D$. The dynamical matrix $D$ for 2-D graphite is written in terms of the $3 \times 3$ matrices $D^{AA}$, $D^{AB}$, $D^{BA}$, $D^{BB}$ for the A and B atoms within the unit cell, and the coupling between them[36]

$$D = \begin{pmatrix} D^{AA} & D^{AB} \\ D^{BA} & D^{BB} \end{pmatrix} \quad \text{Eq 2.24}$$

When we consider an A atom, the three nearest-neighbor atoms are $B1$, $B2$, and $B3$ whose contributions to $D$ are contained in $D^{AB}$, while the six next-nearest-neighbor atoms denoted by solid squares in Fig. 2-8(a) are all A atoms, with contributions to D that are contained in $D^{AA}$ and so on. In Fig. 2-8(a) and (b), we show neighbor atoms up to 4th nearest neighbors for the A and B atoms, respectively.
The remaining problem is how to construct the force constant tensor \( K^{(ij)} \) for 2-D graphite. First, we consider the force constant between an A atom and a nearest-neighbor B atom on the x axis as shown in Fig. 2-9. The force constant tensor is given by

\[
K^{(A,B)} = \begin{pmatrix}
\phi^{(1)}_r & 0 & 0 \\
0 & \phi^{(1)}_n & 0 \\
0 & 0 & \phi^{(1)}_{to}
\end{pmatrix}
\]  
Eq 2.25

where \( \phi^{(n)}_r \), \( \phi^{(n)}_n \), \( \phi^{(n)}_{to} \) represent the force constant parameters in the radial (bond-stretching), in-plane and out-of-plane tangential (bond-bending) directions of the \( n^{th} \) nearest neighbors, respectively.

The force constant matrices for the two other nearest-neighbor atoms, B2 and B3 are obtained by diagonalizing the matrix in Eq. 2.25 according to the rules for a second-tensor:

\[
K^{(A,B_m)} = U_m^{-1} K^{(A,B)} U_m \quad (m=2, 3)
\]  
Eq 2.26
where the unitary matrix $U_m$ is here defined by a rotation matrix around the x axis in Fig. 2.8, taking the B1 atom into the Bm atom,

$$
U_m = \begin{pmatrix}
\cos \theta_m & \sin \theta_m & 0 \\
-\sin \theta_m & \cos \theta_m & 0 \\
0 & 0 & 1 \\
\end{pmatrix}
$$

**Eq 2.27**

In the case of the phonon dispersion relations calculated for 2-D graphite, the interaction between two nearest-neighbor atoms is not sufficient to reproduce the experimental results, but up to at least the 4th nearest-neighbor interactions are necessary.

---

**Fig. 2-9**: Force constants between the A and B1 atoms on a graphene sheet. $\phi_r$, $\phi_t$, and $\phi_o$ represent forces for the nearest-neighbor atoms in the radial (bond stretching), in plane and out of plane tangential (bond-bending) directions, respectively. B2 and B3 atoms are equivalent to B1.[36]

In Fig. 2-10, the phonon dispersion relations for 2-D graphite by force constant model are shown by Gruneis et al (solid lines)[38]. For comparison, dotted lines were obtained by Jishi et al, where values for the force constants are obtained by fitting the 2D phonon dispersion relations over the Brillouin zone as determined experimentally, from inelastic neutron scattering or electron energy loss spectroscopy measurements along the
\( \Gamma \)-M direction. However, the new phonon dispersion relations (solid lines) are fitted to the various sources of data, such as Raman data of highly ordered pyrolytic graphite (HOPG) (solid dots), single-walled carbon nanotubes (solid squares), HOPG and SWNTs (crosses), and graphite whisker (triangles), and also inelastic neutron scattering (open circles). In Table 2-1, 12 calculated force constant parameters for 2-D graphite are shown. The values in parenthesis are from the old fitting results (dotted lines).

---

**Fig. 2-10:** Phonon dispersion relations for 2-D graphite calculated by force constant model. The solid lines are the fits to the Raman data of highly ordered pyrolytic graphite (HOPG) (solid dots), single-walled carbon nanotubes (solid squares), HOPG and SWNTs (crosses), and graphite whisker (triangles), and also inelastic neutron scattering (open circles). Broken lines are the fits to inelastic neutron scattering or electron energy loss spectroscopy measurements along the \( \Gamma \)-M direction.[38]
As seen in Fig. 2-10, there are 6 phonons for 2-D graphite, since it has only 2 carbon atoms in the unit cell. The three phonon dispersion curves, which exhibit $\omega=0$ at $q=0$ (Γ point) of the Brillouin zone, correspond to acoustic modes: an out-of-plane mode (oTA), and in-plane tangential (bond-bending) mode (iTA) and an in-plane radial (bond-stretching) mode [39], listed in order of low to high energy, respectively. The remaining three branches correspond to optical modes: one out-of-plane mode (oTO) and two in-plane modes (iTO, iLO). L and T stand for longitudinal and transverse.

However, in reality, 3-D graphite with four carbon atoms in the unit cell is much more common. Fig. 2.11(a) and (b) shows the 3-D Brillouin zone of 3-D graphite, and the phonon dispersion relations and the density of states (right), respectively[40]. The dispersion calculated from a Born-von Karman lattice dynamical model and a similar calculation[40]. As seen in Fig. 2-11(b), there is little dispersion in the $k_z$ direction (Γ to A) due to the weak interplanar interaction in 3D graphite. Pristine graphite crystallizes according to the $D_{6h}^4$ space group and has twelve vibrational modes at $q=0$ since 3-D graphite has 4 carbon atoms in the unit cell. The eigenvectors for the optically allowed

<table>
<thead>
<tr>
<th>Radial</th>
<th>Tangential</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_1^{(1)}=40.37(36.50)$</td>
<td>$\phi_1^{(1)}=25.18(24.50)$</td>
</tr>
<tr>
<td>$\phi_2^{(1)}=2.76(8.80)$</td>
<td>$\phi_2^{(2)}=2.22(-3.23)$</td>
</tr>
<tr>
<td>$\phi_3^{(1)}=0.05(3.00)$</td>
<td>$\phi_3^{(2)}=-0.08(-0.40)$</td>
</tr>
<tr>
<td>$\phi_4^{(1)}=1.31(-1.92)$</td>
<td>$\phi_4^{(2)}=0.22(2.29)$</td>
</tr>
</tbody>
</table>
Γ-point vibrations for graphite (3D) shown in Fig. 2-10(c) are two, doubly degenerate, Raman-active modes ($E_{2g}^{(1)}$ at 42 cm$^{-1}$, $E_{2g}^{(2)}$ at 1582 cm$^{-1}$); a doubly degenerate, infrared-active $E_{iu}$ mode at 1588 cm$^{-1}$; a nondegenerate, infrared-active $A_{2u}$ mode at 868 cm$^{-1}$; and two doubly degenerate $B_{2g}$ modes (127 cm$^{-1}$, 870 cm$^{-1}$) that are neither Raman- nor infrared-active. Because of the strong intralayer force constants relative to the interlayer force constants, the vibrational frequencies of the $E_{2g}^{(2)}$ and $E_{2g}^{(1)}$ modes are nearly
Fig. 2-11: (a) 3D Brillouin Zone for 3-D graphite, (b) 3D Phonon dispersion curves along several high symmetries axes. The Γ-point symmetries for the graphite structure are indicated, (c) Zone center q=0 modes for 3D graphite.[40]
degenerate. The small frequency difference of $\sim 6\text{cm}^{-1}$ between these two modes is associated with interlayer force constants.

### 2.3.2 Single-Walled Carbon Nanotube (SWNT) phonon dispersion relation by Zone folding method

The first work to calculate SWNT phonon dispersion relations was obtained from those of the 2D graphene sheet by using the same zone folding approach as was used to find the 1D electronic dispersion relations by Jishi et al[41]. By zone folding method, the one-dimensional phonon energy dispersion relations for $\omega_{1D}^{m\nu}(k)$ for SWNTs are related to the [41].

$$
\omega_{1D}^{m\nu}(k) = \omega_{2D}^{m}(k) \left( \frac{\vec{K}_2}{|\vec{K}_2|} + \mu \vec{Z}_1 \right) \text{ (m=1,…6, } \mu=0,…,N-1 \text{ , and}
$$

$$
-\frac{\pi}{T} < k < \frac{\pi}{T}, \left( m=1,...,6, \mu=0,...,N-1 \text{ and } -\frac{\pi}{T} < k < \frac{\pi}{T} \right), \text{ Eq 2.28}
$$

where $k$ is a one-dimensional wave vector, $\vec{K}_2$ is the reciprocal lattice vector along the nanotube axis, $\vec{Z}_1$ is the reciprocal lattice vector in the circumferential direction, and $T$ is the magnitude of the one-dimensional translation vector $\vec{T}$.

Zone-folding of the graphene phonon branches does not always give the correct dispersion relation for a carbon nanotube, especially in the low frequency region, and some additional physical concepts must be introduced[36, 41]. For example, when the
out-of-plane tangential acoustic (TA) modes of a graphene sheet shown in Fig. 2-11(a) on the left are rolled into a nanotube as shown on the right, the radial breathing mode is formed and the resulting vibration does not have $\omega \rightarrow 0$ as $k \rightarrow 0$. Therefore the radial breathing mode is not an acoustic mode, but rather is an optical mode with a non-zero frequency at $k=0$.

Fig. 2-12: (a) The out of plane tangential acoustic modes at $k=0$ (left) in graphene give rise to a radial breathing mode in the carbon nanotube with non-zero frequency. (b) An acoustic mode of a carbon nanotube whose vibration is perpendicular to the nanotube axis (right) corresponds to a linear combination of both in plane and out of plane graphite-derived modes (left). These modes do not couple in the case of a graphene layer, but do couple for the nanotube because of the curvature that is introduced by rolling up the sheet[36]

While the acoustic vibrations of a carbon nanotube in the longitudinal direction correspond to acoustic vibrations in the graphene sheet, the two acoustic modes in the directions perpendicular to the nanotube axis do not directly correspond to any two-dimensional graphene phonon modes. In a graphene sheet, the in-plane and out-of-plane modes are decoupled from each other. However, when the graphene strip is rolled up into a nanotube, the graphite-derived in-plane and out-of-plane modes do couple to each other as shown on the left-hand side of Fig. 2-12(b).
In order to avoid these difficulties, the phonon dispersion relations for carbon nanotubes can be obtained by solving the 3-D carbon nanotube dynamical matrix problem directly using the force constant parameters listed in Table 2.1. Since there are $2N$ carbon atoms in the unit cell, the dynamic matrix $D(k)$ in Eq. 2.22 for a carbon nanotube to be solved becomes a $6N \times 6N$ matrix.

Fig. 2-13: (a) the calculated phonon dispersion relations of an armchair carbon nanotube with $C_h=(10,10)$, (b) the corresponding phonon density of states for a (10,10) nanotube, (c) a comparison between the phonon density of states $g_{1D}(\omega)$ for a (10,10) nanotube shown as the solid curve and $g_{2D}(\omega)$ for a graphene sheet shown by the points.

Fig. 2-13 shows the calculated phonon dispersion relations of an armchair carbon nanotube with $C_h=(10,10)$ (a), the corresponding phonon density of states in units of states per C atom per cm$^{-1}$ (b), and a comparison between the phonon density of states $g_{1D}(\omega)$ for a (10,10) nanotube shown as the solid curve and $g_{2D}(\omega)$ for a graphene sheet shown by the points (c). For the $2N=40$ carbon atoms per circumferential strip for the (10,10)
nanotube, there are 120 vibrational degrees of freedom, but because of mode degeneracies there are only 66 distinct phonon branches, of which 12 modes are non-degenerate and 54 are doubly degenerate. The comparison given in Fig. 2-13(c) shows that the phonon density of states for the (10,10) nanotube is close to that for 2D graphite. The differences in the nanotube phonon density of state relative to that for 2D graphite pertain to the one-dimensional van Hove singularities for the optical phonon subbands and to the 4 acoustic modes of the nanotubes and their special properties at low \( \omega \).

Table 2-2: The number and symmetries of the Raman-active and IR-active phonon modes for all the possible different types of carbon nanotube (achiral and chiral)

<table>
<thead>
<tr>
<th>Nanotube structure</th>
<th>Point group</th>
<th>Raman-active modes</th>
<th>IR-active modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>armchair ((n,n))</td>
<td>(D_{oh})</td>
<td>(4A_{1g} + 4E_{1g} + 8E_{2g})</td>
<td>(A_{2u} + 7E_{1u})</td>
</tr>
<tr>
<td>armchair ((n,n))</td>
<td>(D_{hf})</td>
<td>(3A_{1g} + 6E_{1g} + 6E_{2g})</td>
<td>(2A_{2u} + 5E_{1u})</td>
</tr>
<tr>
<td>zigzag ((n,0))</td>
<td>(D_{oh})</td>
<td>(3A_{1g} + 6E_{1g} + 6E_{2g})</td>
<td>(2A_{2u} + 5E_{1u})</td>
</tr>
<tr>
<td>zigzag ((n,0))</td>
<td>(D_{hf})</td>
<td>(3A_{1g} + 6E_{1g} + 6E_{2g})</td>
<td>(2A_{2u} + 5E_{1u})</td>
</tr>
<tr>
<td>chiral ((n,m))</td>
<td>(C_{N})</td>
<td>(4A + 5E_{1} + 6E_{2})</td>
<td>(4A + 5E_{1})</td>
</tr>
</tbody>
</table>

Among the 6N calculated phonon dispersion relations for carbon nanotubes whose unit cell contains 2N carbon atoms, only a few modes are Raman or infrared (IR) active, as specified by the symmetry of the phonon modes. The numbers of the Raman-active (\(A_{1g}, E_{1g}, E_{2g}\) symmetries) and IR-active (\(A_{2u}, E_{2u}\) symmetries) modes for the nanotubes can be predicted by group theory, once the lattice structure and it symmetry are specified. In Table 2-2, the number and symmetries of the Raman-active and IR-active phonon modes for all the possible different types of carbon nanotube (achiral and chiral). From Table 2-2, we deduce the remarkable Raman and infrared selection rules for SWNTs, that the numbers of Raman and infrared-active modes do not depend on the
nanotube diameter and chirality, though the total number of finite frequency phonon modes (6N-4) is very different for different chiralities and diameters. Group theory selection rules indicate that there are only 15 or 16 Raman-active modes and 7 to 9 IR-active modes for a single-wall carbon nanotube, despite the large number of vibrational modes.

The eigenvectors of the Raman active modes for a (10,10) tube, which show strong intensity, are shown in Fig. 2-14 based on the calculations involving a bond polarizability model. The three higher frequencies (1585, 1587, 1591cm⁻¹) are out of

![Fig. 2-14: Calculated eigenvectors of the Raman-active modes, which show strong intensity for a (10,10) carbon nanotube. Only one eigenvector is shown for each doubly degenerate E₁g and E₂g mode.](image)
phase motions, while the four lower modes (17, 118, 165, 368 cm$^{-1}$) are in phase motions. The eigenvector labeled as $A_{lg}$ in Fig. 2-14(c) is called ‘radial breathing mode’. As can be seen, carbon atoms are moving in and out against the carbon nanotube axis. This mode is sensitive to the diameter of the carbon nanotube, not to its chirality. The high frequency modes (1585, 1587, 1591 cm$^{-1}$) are so called ‘tangential modes’. Carbon atoms are moving along the tube direction or circumferential direction. The eigenvectors of the IR active modes for a (10,10) tube will be shown in Ch.7. In the chapter, we will discuss more about the theoretical calculations on phonon modes of SWNTs by force constant model. That will be compared with the results from zonefolding method by Jishi et al.
Chapter 3
Introduction to Raman scattering and Infrared spectroscopy from sp2 carbon and carbon nanotubes Replace with Chapter Title

3.1 sp2 Carbons

3.1.1 Raman scattering from sp2 carbons

The Raman spectrum (300 cm⁻¹ < \( \omega \) < 3300 cm⁻¹) for highly oriented pyrolytic graphite (HOPG) is shown in Fig. 3-1(a), together with spectra for other forms of sp²-bonded carbons. As we discussed on p 30, there are two doubly degenerate, Raman-active modes \( (E_{2g}^{(1)} \text{ at } 42 \text{ cm}^{-1}, E_{2g}^{(2)} \text{ at } 1582 \text{ cm}^{-1}) \) for 3-D graphite. Strong scattering from the \( E_{2g}^{(2)} \) mode at 1582 cm⁻¹ is observed in Fig. 3-1(a) for HOPG. However, the scattering from the \( E_{2g}^{(1)} \) at 42 cm⁻¹ is not in the scale of Fig. 3-1. Two relatively strong second order Raman bands are observed in the 3-D graphite spectrum, one at 3248 cm⁻¹ and the other at 2720 cm⁻¹ with a shoulder, which are overtone of \( E_{2g}^{(2)} \) and 1360 cm⁻¹, respectively.

Fig. 3-1(b) shows the Raman spectrum of B-doped highly oriented pyrolytic graphite(BHOPG)[42]. Boron-doped HOPG is made by substituting 0.5% carbon atoms in the honeycomb network by boron atoms creating in-plane disorder, without disrupting the overall AB stacking of the layers or the honeycomb arrangement of the remaining C-
atoms in the graphitic planes. Fig. 3-1(e) is the Raman spectrum of glassy carbon. High resolution transmission electron microscopy HRTEM shows that glassy carbon exhibits short range sp$^2$ order and no long range order. Fig. 3-1(d) and (c) are the Raman spectra of as-grown and annealed at 2820°C sp$^2$ bonded carbon nanoparticles, respectively[40]. The disordered sp$^2$ carbon nanoparticles were prepared by a CO$_2$ laser-driven pyrolysis of a mixture of benzene, ethylene, and iron carbonyl.[40] TEM images show that the average size is ~20nm.

---

Fig. 3-1: Raman spectra from various sp$^2$ carbon using Ar-ion laser excitation: (a) HOPG, (b) boron-doped HOPG(BHOPG), (c) carbon nanoparticles derived from the pyrolysis of benzene and graphitized at 2820°C, (d) as-synthesized carbon nanoparticles, (e) glassy carbon.[40]
The disorder in sp$^2$ carbons relaxes the $q=0$ optical selection rule for one phonon scattering\cite{42}, which enhances the 1$^{\text{st}}$ and 2$^{\text{nd}}$ order Raman activity away from the $\Gamma$ point. The $E_{2g}^{(2)}$ is broader with higher disorder in sp$^2$ carbon. And more 1$^{\text{st}}$ and 2$^{\text{nd}}$ order Raman bands are observed in the disorder sp$^2$ carbon system. Instead, disorder drives the 1$^{\text{st}}$ order Raman spectrum toward the 1-phonon DOS.

Except for the Raman spectra of HOPG, all of the other carbon materials show disorder induced D-band at $\sim1360\text{cm}^{-1}$. The D-band is present in all known forms of

Fig. 3-2: First-order Raman spectra for benzene derived carbon fibers heat treated at various heat treatment temperature. $1100^\circ\text{C}<T_{HT}<2900^\circ\text{C}$\cite{43}
disordered sp$^2$ carbons, and has been identified with C-atom vacancies, substitutional impurities (boron)[42, 44], finite grain[45] or particle effects, or any other symmetry-breaking phenomena. This band is dispersive, which means that the frequency changes with the laser excitation frequency. Experimentally, it has been determined that D-band frequency shifts with excitation energy at a rate of 40-50cm$^{-1}$/eV over a wide excitation energy range[42, 46, 47]. The unusual phenomena have not been understood for 20 years. There have been attempts to assign this phenomena to a resonant coupling of the laser excitation with electronic states around K point.[46, 48] This assumption has shortcomings. For example, this assumption cannot explain why Stokes and anti-Stokes frequencies are different[49]. Thomsen et al.[50] recently proposed that D band is due to double resonance process. Their theoretical calculation can reproduce the experimentally observed D-band frequency shift with a rate of 50cm$^{-1}$/eV, and also can explain the different D-band frequencies for Stokes and anti-Stokes frequencies.
Another band at ~1610 cm\(^{-1}\) can be observed easily for example in Fig. 3-1(b) and (c) as a side band of \(E_{2g}^{(2)}\) at 1582 cm\(^{-1}\). This is called G* band which corresponds to the mid-zone maximum in the phonon density of states in the optical branch[52]. As seen in the phonon density of states of 3-D graphite in Fig. 2-11(b), there is strong density of states at ~1610 cm\(^{-1}\). It can be noticed that the intensity and the width of D-band and G*-band grows with the degree of disorder in sp\(^2\) carbon. One prominent new second order band at 2973 cm\(^{-1}\) is known as a combination mode \((\omega_1+\omega_2)\) of D-band(\(\omega_1\)) and G*-band(\(\omega_2\)).

Fig. 3-2 shows the Raman results from materials subjectsted to typical graphitization experiment conditions. The starting material exhibits significant disorder. In this study, the disordered sp\(^2\) carbon is carbon fibers produced by the thermal decomposition of benzene at 1100°C[43]. It can be seen that the intensity of D-band and
G*-band decreases with higher annealing temperatures. In addition, the width of G-band \( E_{2g}^{(2)} \) becomes narrower. At the highest annealing temperature, 2900°C, the Raman spectrum is almost identical to that of HOPG. The second order bands at high frequency region are also observed to transform into bands closely resembling those of HOPG (not shown here)[43].

One can interpret this result as affected by the size of the basal plane \( (L_a) \) crystallites and also interplanar correlation. [43, 45, 46, 53] X-ray studies to determine the size of basal plane \( (L_a) \) have been correlated with the integrated intensity ratio of the D-band to the G-band, \( (I_D/I_G) \). Perfectly ordered 3-D graphite will exhibit zero value of \( I_D/I_G \).[43, 45, 46, 53] We apply the results of these studies to graphitic nanoribbons(GNRs) in Ch.8.

### 3.1.2 Infrared spectra from sp\(^2\) carbons

Fig. 3-3 shows the IR spectra of HOPG, microcrystallite graphite and multiwalled carbon nanotubes(MWNTs) reported by Kastner et al[51]. The IR spectrum of HOPG(a) was measured by reflectance and the rest was measured in transmission using a KBr pellet. The IR spectrum of HOPG shows the two known modes at 868cm\(^{-1}\)(A\(_{2u}\)) and 1587cm\(^{-1}\)(E\(_{1u}\)). These frequencies are in good agreement with the theoretical results shown in Ch.2. In the case of graphite microcrystallites of Fig. 3-3(b), A\(_{2u}\) is in the same position as in HOPG, whereas the E\(_{1u}\) mode is softened by 15cm\(^{-1}\) to about 1575cm\(^{-1}\) and considerably broadened with an asymmetric tail in the low energy region. Kastner et.
al.[51] have suggested that the shift of the $E_{iu}$ in MWNTs can be due to several reasons. Firstly, a change of the interplane bonding leads to a change of the $E_{iu}$ line because its energy is associated with an interlayer force constant. Secondly, introduced disorder and finite size effect may lead to a line broadening and shifting as well. Finally, the curvature or bending of the graphite sheets might lead also to the same effect. Since the diameter of the individual tubes in MWNTs is large (>5nm), it can be expected that the IR spectrum will not be significantly different from that of HOPG or graphite microcrystallites. It will be shown in Ch.7 that small diameter SWNTs will exhibit many more IR active modes[54].

3.2 SWNTs

3.2.1 Raman scattering from SWNTs

As discussed in Ch.2, Among the $6N$ calculated phonon dispersion relations for carbon nanotubes whose unit cell contains $2N$ carbon atoms, only a few modes are Raman-active($A_{1g}$, $E_{1g}$, $E_{2g}$ symmetries) or infrared (IR) active($A_{2u}$, $E_{2u}$ symmetries), as specified by the symmetry of the phonon modes. Group theory selection rules indicate that there are only 15 or 16 Raman-active modes. The eigen vectors of Raman active modes of (10, 10) carbon nanotubes with relatively high intensity are shown in Fig. 2-14. The eigen vectors of IR active modes of (10, 10) tube will be shown[54].
Fig. 3-4 shows the Raman spectra of SWNT bundles produced by pulsed laser vaporization (PLV) excited by 514.53nm. The four bottom panels in the figure indicate the theoretically calculated Raman intensities for different (n,n) armchair nanotubes, where n=8, 9, 10 and 11, respectively\[55\]. Only a few intense Raman peaks can be seen clearly in the figure.

Similar to general sp² carbon, SWNTs exhibits two Raman bands; [30] disorder in the sp² network, \textit{i.e.}, the broad “D-band” scattering between 1230 - 1370 cm⁻¹; and [30] a first-order-allowed nanotube “G-band” (sometimes referred to as the T-band) with substructure appearing in the ~ 1500 - 1600 cm⁻¹ region. In addition, there is a unique mode for carbon nanotubes in the low frequency region (~100 – 300 cm⁻¹), so called the radial breathing mode (R-band; radial C-atom displacement). Because some experiments study many different diameter tubes at the same time, the diameter distribution broadens the Raman spectrum. The low frequency modes are much more sensitive to diameter than the high frequency modes. This mode is approximately related to the tube diameter by the relation, \( \omega_{RBM} \sim 224(\text{cm}^{-1}\text{·nm})/d_t(\text{nm}) \), where \( d_t \) is the tube diameter in nanometer and \( \omega_{RBM} \) in wave number.\[55, 56\]. (A small constant of 10-12 cm⁻¹ is sometimes added to approximate an additional restoring force due to the effects of tube–tube interactions within a bundle\[56, 57\].) However, this mode is not sensitive to the chirality of nanotubes.
Different from G-band of other forms of sp² carbons (single band at 1582cm⁻¹),
G-band or T-band of SWNTs exhibits substructures due to its cylindrical symmetry (see
the deconvoluted Lorenzian individual peaks displaced under the experimental G-band in
high frequency region in Fig. 3-3). For large nanotubes (d_t > 3nm), the sub-structure in
the G-band, observed in small diameter SWNTs, collapses into a single Raman peak at
~1582 cm⁻¹.

Fig. 3-4 shows the room temperature Raman spectra for purified SWNTs excited
at five different laser frequencies. All of the spectra exhibit the G-, D- and R-band with
slightly different peak position or line shape. As discussed earlier, ω_{RBM} is inversely
proportional to the tube diameter d_t(nm). Fig. 3-4 tells us that different laser excitation
energy excites different sets of tubes as first proposed by Rao et al.[55]
phenomenon can be explained by resonant Raman scattering. When the photon involved in the Raman process is in resonance with an electronic state in this highly one dimensional material, it results in the unusual Raman intensity enhancement, which is called resonant Raman scattering.

The integrated intensity of Raman band \( I(E_{\text{laser}}) \) is a function of \( E_{\text{laser}} \). It can be evaluated from the joint density of states \( g(E) \) according to the theory for incoherent light scattering[58]. In Eq. 3.1 we display the integrated Raman intensity[58]

\[
I(E_{\text{laser}}) = \left| \mathbf{M} \frac{g(E)}{(E_{\text{laser}} - E_i - i\Gamma_r)(E_{\text{laser}} + E_{ph} - E_i + i\Gamma_r)} \right|^2 dE
\]

Eq. 3.1

where the \( E_i \) = the electronic energy gap, and \( E_{ph} \) = the phonon energy to be excited. The first and second factors in the denominator, respectively, describe the resonance effect with the incident and scattered light, where the +(-) applies to the anti-Stokes(Stokes) process for a phonon of energy \( E_{ph} \). \( \Gamma_r \) is a damping factor, which gives the inverse finite life time for the scattering process. \( \mathbf{M} = M_i M_{ph} M_s \) represents the abbreviated matrix element, which is considered constant in the small energy range of the resonance. \( M_i, M_s \) and \( M_{ph} \) are, respectively, the matrix elements for the electron-radiation absorption, the electron-radiation emission, and the electron-phonon interaction.

The joint density of states(JDOS) of SWNTs \( g(E) \) can be approximated by [58, 59]

\[
g(E) = \text{Re} \left[ \sum_i a_i \frac{E}{d_i \gamma \gamma_0 (E - E_i - i\Gamma)(E + E_i + i\Gamma)} \right]
\]

Eq. 3.2
where \( a_{c,c} \) is the nearest-neighbor distance between carbon atoms, \( \gamma_0 \) is the tight binding energy overlap integral, and \( \Gamma_j \) is introduced as a measure of the effect of the finite nanotube size effect. The sum \( \sum_i \) takes into account the different van Hove singularities of one SWNT (see Fig. 2.6). From Eq. 3.1 and Eq. 3.2, it can be shown that the Raman scattering will be resonantly enhanced when the laser excitation energy satisfy the equation \( E_{\text{laser}} = E_{\text{a}} \) or \( E_{\text{laser}} = E_{\text{a}} \pm E_{\text{ph}} \). In Fig. 2-7, we show Kataura plot, electronic gap \( E_{\text{a}} \) vs. tube diameter. If we know diameter distribution of the tubes in the sample and the laser excitation energy, it can be guessed that which kind of tubes will be excited.

Interestingly, in Fig. 3-4, the Raman spectrum of SWNTs excited by 647.1nm has a very broad and asymmetric band at \( \sim 1540 \text{cm}^{-1} \). This is interpreted as a Fano or Breit-Wigner-Fano resonance[60]. The line shape[60-62] is typically found in doped semiconductors or metallic samples when a Raman –active electronic continuum and a phonon excitation are coupled. The asymmetric Breit-Wigner-Fano(BWF) line shape is described by the equation[60-62]

\[
I(\omega) = I_0 \frac{[1 + (\omega - \omega_{\text{BWF}})/q\Gamma]^2}{1 + [(\omega - \omega_{\text{BWF}})/\Gamma]^2}
\]

where \( 1/q \) is a measure of the interaction of the phonon with a continuum of states, and \( \omega_{\text{BWF}} \) is the BWF peak frequency at maximum intensity \( I_0 \), and \( \Gamma \) is a peak width parameter. Since the average tube diameter of SWNTs produced by PLV method is \( \sim 1.3 \text{nm} \), it can be seen from Fig. 2-7 (Kataura plot) that mostly metallic tubes are excited by 647.1nm (1.9eV). In Ch.8, it will be shown how BWF lineshape analysis can be used.
to study the population change of small metallic nanotubes in the sample at high
temperature annealing.

Fig. 3-5: Room temperature Raman spectra for purified SWNTs excited at five different laser frequencies. The laser frequency and power density for each spectrum is indicated, as are the vibrational frequencies[55].
3.2.2 Infrared spectrum from SWNTs

It was shown that large diameter carbon nanotubes exhibit similar IR spectrum to that of HOPG or graphite micro crystallites in Fig. 3-2. According to group theory 6-9 modes are IR active for SWNTs as discussed in Ch.2. The first systematic experimental attempts to observe the IR active modes of SWNTs by transmission will be discussed in Ch.7.
Chapter 4
Experimental techniques

4.1 Sample characterization

4.1.1 Atomic Force Microscope (AFM)

Atomic Force Microscopy (AFM) was been developed in 1986 by Binnig, and Gerber as a collaboration between IBM and Stanford University. By AFM, one can measure surface roughness almost at the atomic scale. The basic structure of the AFM is a flexible cantilever with a sharp tip (Fig. 4-1). It can operate in either the “contact” or the “tapping” modes. In the contact mode, the tip of the AFM can also be used to manipulate (translate, bend and rotate) nanowires or nanotubes[63, 64]. In the tapping mode, the tip is maintained at a few Å from the surface. Tapping mode AFM operates by scanning a tip attached to the end of an oscillating cantilever across the sample surface. The cantilever is oscillated at or near its resonance frequency with amplitude ranging typically from 20nm to 100nm. The tip lightly “taps” on the sample surface during scanning. The Van der waals force between the sample surface and the tip of the cantilever cause a very small additional deflection of the cantilever when the tip is over an atom. This additional deflection is measured optically.

AFM scanners are used to move the tip. They are made from piezoelectric materials that expand or contract proportional to an applied voltage. The feedback loop
maintains a constant oscillation amplitude of the tip. In this work, a Multimode Scanning
Probe AFM (Nanoscope III, Veeco Digital Instruments) was used to measure the SWNT
filament size distribution (Length and diameter) after debundling SWNT bundles in
amide solvents. These filaments were imaged by measuring the change in the tip position
relative to the plane of the substrate supporting the filaments.

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4.1.2 High Resolution Transmission Electron Microscopy (HRTEM)

Transmission Electron Microscopy (TEM) is based on the interaction of a high-
energy electron beam (in our case 200 keV) with the material to be analyzed. In our
studies, we primarily used the TEM operated by the Penn State, MRI. The beam is
generated in the electron gun and transmitted to the specimen through a system of
primary magnetic lenses (condenser). In the plane of the specimen the electron beam can

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Fig. 4-1: Schematic representation of an AFM showing most of the important components: the laser, the
photo diode, the cantilever, the tip, the oscillator and scanning piezoelectric tube
be broad or focused (convergent beam) depending on the experiment. For conventional TEM (including HRTEM and diffraction) the beam is broad in the plane of the sample in such a way that the system works as a “slide projector”. The convergent beam is used as a probe when signals coming from the specimen need to be localized in a very small region (i.e. Convergent Beam Diffraction and Energy-Dispersive Spectroscopy). The typical sample thickness is tens of nanometers. The electrons transmitted through the sample are redirected by a secondary system of magnetic lenses (objective, intermediate and projector). Changing the strength of the intermediate lens either a diffraction pattern (reciprocal space) or a direct image (real space) can be obtained in the viewing screen.

Fig. 4-2: Secondary signals generated from the interaction between a high-energy electron beam and the sample.[65]
The interaction between electrons and the sample can generate many different secondary signals as show in Fig. 4-2. The generation of all these signals combined with the high energy of the electrons (~high resolution of the equipment) make possible obtaining information related to strain fields, defects, crystalline structure and chemical composition in a sub-nanometer scale. In this work, we intensively studied the structural transformation of carbon allotropes by using high-resolution TEM.

4.1.3 Micro-Raman spectrometer: Jobin-Yvon T64000

Raman spectra of samples studied in this thesis were carried out with a JY Horiba T64000 Raman spectrometer. This state-of-the-art instrument has a multichannel (CCD) detector. Light is sorted by three monochromators in which the first two monochromators (filter stage) can be coupled additively or subtractively. The triple monochromator is equipped with holographic gratings (1800 lines/mm). This instrument can be used both in micro as well as macro scattering geometry. In the micro-Raman arrangement the laser is focused onto the sample using a microscope objective (100x, 50x or 10x) and the scattered light is collected by the same objective. A confocal aperture in the path of the scattered beam allows us to have a high spatial resolution of ~1µm. The microscope stage is equipped with a motorized XY stage for the precise positioning and selection of sample area.

Raman spectra are acquired by irradiating a sample with a powerful laser source. Two lasers were used to excite the Raman bands - an Ar ion laser with output
wavelengths in green and blue region and a mixed gas Ar-Kr laser which gives additional wavelengths in the red.

Fig. 4-3 is a schematic diagram for the optical path in the T64000 instrument in the micro-Raman geometry. The excitation radiation from the source (Ar or Ar-Kr laser, not shown) is passed through a plasma filter to remove the associated plasma lines. This incident laser beam then goes through an iris and a spatial filter that also defines a “crisp” circular spot that is imaged onto the sample via the objective. A beam splitter[59] is required to allow laser beam to reach the sample and the backscattering light to be collected. The laser light transmitted through the BS is

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**Fig. 4-3:** Schematic of triple grating monochrometer (JY-ISA, T6400) emphasizing the optics of the confocal microscope used to collect Raman spectra of the Nanowires. The objective is the key ingredient (100X aperture, working distance = 1mm) spot size ~ 1.0µ. The confocal aperture is used to redefine the scattering volume and remove spurious or stray light. In effect, the size is chosen to be M×1µ, where M is the optical magnification of the Raman volume produced by the objective in concert with L3.[59]
blocked while the reflected part is focused onto the sample by the microscope objective. The backscattered Raman light that is transmitted by the BS proceeds through the triple monochromator to the detector. The heart of the microRaman apparatus is the confocal microscope (Olympus BX 40) that allows a high lateral resolution. The objective therefore serves two purposes: to focus the beam on the sample and to collect the backscattered light.[59] The collected back scattered light passes through the beam splitter and then through lens L3 to the adjustable confocal aperture. The confocal aperture “re-defines” the scattering volume, rejecting stray light coming from elsewhere. In effect, the aperture size is chosen to be \( M \times 1 \mu \), where \( M \) is the magnification given by \( M \) is the optical magnification of the \( \sim 1 \mu \) diameter beam spot on the sample produced by the objective in concert with the lens L3. The \( 1 \mu \) spot size is limited by the lateral resolution of the microscope. After the confocal aperture, the Raman scattered light is
then focused by lens L5 onto the entrance slit of the subtractive dispersion monochromator (details are shown in Fig. 4-3).

Fig. 4-4 is the schematic diagram for the internal optics in T6400. The polychromatic radiation scattered from sample enters the first monochromator through entrance slit S1, which determines the instrument resolution. The grating G1 disperses the light and the exit slit S2 selects the bandpass ($\lambda_1 < \lambda < \lambda_2$). In the second monochromator, G2 recombines the dispersed radiation into a polychromatic onto the slit S3. This configuration is used as a tunable filter in the spectral range defined by the scanning mechanism and the gratings. This polychromatic radiation is then dispersed by G3 of the spectrograph. The spectrum is acquired with a liquid nitrogen cooled CCD.
4.1.4 ThermoGravimetric Analysis (TGA)

The TA Instruments SDT 2960 module is capable of performing both thermo gravimetric analysis (TGA) and a Differential Scanning Calorimeter (DSC) at the same time. Differential Scanning Calorimetry (DSC) is a thermal analysis technique which is used to measure the relative specific heat associated with transitions in materials. Such measurements provide qualitative and quantitative information about physical and chemical changes that involve endothermic and exothermic processes, or changes in heat capacity. Thermogravimetric Analysis (TGA) measures changes in weight of a sample with increasing or decreasing temperature. Weight changes observed at specific temperatures can correlate with volatilization of sample components, decomposition, oxidation / reduction reactions, or other changes. Computer controlled graphics can calculate weight percent losses.
In the diagram, Fig. 4-5 TA Instruments, model SDT 2960 is shown. Inside the machine, there are two alumina cups, one empty cup serves as a reference sample and the other cup contains the sample that needs to be evaluated. TGA analysis is used to test the purity of SWNTs and determine optimal dry oxidations condition needed to remove amorphous carbon in as-grown SWNT-containing soot. Dry oxidation under optimal conditions played an important role in producing purified SWNT material for this thesis work.

4.1.5 Ultra violet/Visible/Near IR Spectrometer "Lambda 900" (Perkin Elmer)

The Perkin Elmer "Lambda 900" is a double-beam and double-monochromator spectrophotometer (UV/VIS/NIR) with holographic gratings and tungsten-halogen (NIR) and deuterium lamps (UV-Vis) used as sources. The ‘Lamda 900’ is capable of measuring transmission, reflectance and absorption in solid or liquid state materials. The wavelength is from 185 to 3300nm with an accuracy of 0.08 nm in the UV-Vis region and 0.3nm in the NIR region guaranteed. Two detectors are used to collect the radiation from sample and reference arms: a photomultiplier for the UV/Vis range and a lead sulfide (PbS) detector for the NIR range.

Fig. 4-6 shows the optical path diagram in the instrument. The schematic diagram of the spectrometer shows how the beam came from the radiation source (i.e. halogen or deuterium lamp) is dispersed by double monochromators, and split into sample and reference beams.
To increase quantitative reflection or transmission coefficients of our samples, we measured the ratios \((I_T/I_{Ref})\) or \((I_R/I_{Ref})\), where \(I_R\) and \(I_T\) are respectively the intensity reflected from or transmitted through the sample. \(I_{Ref}\) in the transmitted light ratio refers to radiation transmitted through a standard aperture. \(I_{Ref}\) in the reflected light ration is that reflected from a standard mirror.

### 4.1.6 Fourier Transform[66] Intrared(IR) and Raman Spectrometer: Bomem DA3+

A BOMEM DA3+ FT spectrometer was used to take transmission and Raman spectra in this thesis work. Various light sources(Hg, Quartz and Globar), beam
splitters (BK7, CaF₂, KBr and Mylar film) and detectors (InGaAs, InSb, MgCdTe and Si Bolometer) are available for transmission and reflectance studies, which enables us to cover from the Far IR to near IR (20 cm⁻¹ - 10,000 cm⁻¹). An Nd: YAG (1064 nm) laser was used for the Raman excitation.

Fig. 4-7: Schematic optical path diagram of Bomem DA3+ FT-IR and FT-Raman[59]

Fig. 4-7 is the schematic optical path diagram for the Bomem DA3+ FT spectrometer[59]. The key component of FT spectrometer is the Michelson interferometer. The beam from the source will be split into two beams by the beam splitter. The interference pattern called the “interferogram” is created by summing beams from the two arms of the interferometer. The interferogram is the intensity sum as the path length difference in the tow arms caused by the moving mirror. The analysis of the
62

interferogram allows the spectral content of the source to be measured. Basic principle of
the FT spectrometer is that the spectrum distribution function I(\(\omega\)) are Fourier transform of
the interference intensity.

4.2 Purification

Most of the SWNT synthesis methods today produce tubes in the diameter range 1-2 nm, and they are arranged in bundles. Unfortunately, SWNT are often produced along with other unwanted materials; amorphous sp\(^2\) carbons which coat the bundle walls, and multishell graphitic carbons which cover the metal catalyst residue. It is a challenging problem to extract pure SWNTs without damaging the tube walls. Some of the proposed applications of SWNT, including electronic devices, field emitters, gas sensors, high-strength composites, and hydrogen storage require reasonably pure SWNT material.

In this thesis work, we have used a two-step purification method that was first proposed by Eklund and Pradhan[67]. The first step is an oxidation to selectively remove amorphous carbon. The Second step is an acid reaction to remove the metal growth catalyst (sometimes the metal surface is passivated by a shell of carbon). Two of the most common methods for the removal of amorphous carbon (AC) attempt to take advantage of the higher reactivity of AC with oxygen relative to SWNTs. In one case, a dry oxidation in air at elevated temperatures is carried out[68-70]. Success has also been reported using hydrogen peroxide H\(_2\)O\(_2\)[52]. We consider the changes to the tube wall
for both of these approaches. The second step of purification involves the removal of the metal with acids, usually HNO₃ [70] or HCl [67, 69, 70] is used. HNO₃ has been reported, in extreme chemical conditions, to aggressively attack the tube walls, while HCl is found to be passive with respect to attack on the carbons in the sample. If the metal catalyst in the nanotube soot is covered with a graphitic shell of carbon, the oxidation step is also important to weaken this coating for subsequent acid digestion of the metal [67, 69, 70]. It is also important to neutralize the sample after the acid step [70]. For HCl-treated samples, the neutral solution above the filtrate was observed to be light gray, but for HNO₃-treated samples, this solution was black. The black coloration has been attributed [68] to the solubilization of small polycyclic aromatic sheets, and occurs in neutral and moderately basic aqueous solutions after their functionalization with carboxyl groups by nitric acid oxidation. The larger, (presumably) carboxylic-functionalized nanotube bundles are contained in the filtrate. The light gray color for the solution derived from HCl-treated samples has been identified [69, 70] with the solubilization of small amounts of the carbonaceous materials oxidized and functionalized during our dry gaseous oxidation step.

The raw soots produced by Arc discharge were prepared by CarbonLex, Inc. as described earlier. Chemical analysis of these soots were carried out by temperature programmed oxidation (TPO) using a TA Instruments (SDT 2960). The TGA reaction conditions were a 5 °C/min heating rate (25 - 800 °C) under a flow of dry air at 100 scem. From the first derivative of the TPO curve with respect to time (or equivalently temperature). The DTPO curve is obtained. The preferential oxidation temperatures and the fractional percentages of the different phases of carbon in the soot can be learned.
from the DTPO data. The purity of purified SWNTs can also be estimated from the area under peak in the DTPO data.

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Fig. 4-8: The TGA data of Raw soot (a), DO(b), DO/HCl(c), DO/HNO$_3$(d)
In this section, we will show HRTEM images and TGA data of raw SWNT soot and SWNT materials subjected to DO as an amorphous carbon removal step and HNO₃ or HCl reflux as a metal removal step. Sample data from our laboratory are shown in Fig. 4-8 for various purification protocols.

The data in Fig. 4-8 are typical for raw and purified SWNT soot (originally produced by ARC discharge method). The TGA was ramped linearly in time up to 800°C under flowing air. The TGA data, from top to bottom in the figure, refer to raw soot (a), raw soot after dry oxidation (DO) at 355°C for 20 min (b), raw soot after DO/HCl (c), and then the sequences DO/HNO₃ (d). /HCl or /HNO₃ refers to a reflux process in which the acid is circulated via distillation over the SWNT product. The solid line is the weight loss curve (m(T)) and the dotted blue curve is the derivative of the solid line (dm(T)/dT). The DTPO data were fitted by multi Gaussians to determine the combustion temperatures of various carbon phase, e.g. amorphous carbon, SWNTs, multi shelled graphitic carbon in each sample. The composite fit is overlapped with the DTPO data, represented by the red solid line. The individual Gaussians were displaced and displayed under the DTPO curve for clarity. The sudden drop of TPO data at between 300 and 500°C is due to the oxidation of carbon turning into CO₂ gas. The leftover mass above 600°C can usually be identified with a metal oxide or carbide.

It can be speculated that the fraction of each carbon phase can be obtained from the area under each Gaussian peak. The metal content can be identified with the weight above 600°C.

First, in SWNT soot sample (a), we determine that the effective oxidation temperatures for amorphous carbon (306 and 365°C), SWNTs(423°C) and from
multishelled and graphitic carbon (~535°C). It was found that the fractional weight in the SWNT soot was 27% amorphous carbon, 31% SWNTs, 7% multishelled graphitic carbon, and 35% metal. After dry oxidation, it can be seen that SWNT peak is dominant in DTPO data. However, the peak at lower temperature region, which might be from amorphous carbon, is not completely removed after dry oxidation. As will be discussed in Chap. 5, this peak might also be identified with functional groups or physisorbed species attached to the tube walls during the dry oxidation or purification. After the metal removal step by HCl or HNO₃ reflux, the effective oxidation temperature of amorphous carbon and SWNTs is observed to upshift by ~100°C. We attribute this upshift in oxidation temperature to the removal of catalyst particles in the raw soot. Interestingly, the DTPO data after DO/HNO₃ does not fit properly with Gaussians. It can also be noticed that there is anomalous behavior at ~500°C in TPO data. The reason might be due to the high functionalization on the tube wall and physisorbed volatile species such as NO₃ molecules after HNO₃ reflux. After DO/HCl reflux, ~8% amorphous carbon, 53% SWNTs, 25% multishell carbon and 14% metal were estimated by TPO and DTPO analysis. Even though the Gaussian composite fit is not appropriate for DO/HNO₃, it is still informative to analyze the fit. After DO/HNO₃, ~7% amorphous carbon, 64% SWNTs, 22% multishell carbon and 7% metal was estimated in the purified SWNT sample. Even though DO/HNO₃ is more effective method in terms of the obtained purified than DO/HCl, it will be shown in Chap. 5 that DO/HNO₃ adds functional groups on the tube, and removes carbon atoms from the skeleton. Higher purity material can be obtained if optimal DO/HCl conditions are used.
Fig. 4-9: Low(Left) and High(Right) magnification images of Raw soot(a)(b), DO/HCl(c)(d), DO/HNO$_3$ (e)(f).
HRTEM images are shown in Fig. 4-9 to compare the purity of SWNT materials before and after purification: raw soot (a), (b), raw soot after DO at 355°C for 20 min (c), (d), raw soot after DO/HCl (e), (f), and then the sequences DO/HNO₃ (g), (h). Fig. 4-9(a) shows the low magnification TEM image of raw soot SWNT sample. It is clearly seen that three components are dominant in the sample, i.e., bundles of SWNTs, short range ordered sp² amorphous carbon, and 10-20nm metal catalyst particles imbedded in the amorphous carbon. HRTEM images showed that multi shelled graphitic layers are covering the catalyst particles. If the metal catalyst in the nanotube soot is covered with a graphitic shell of carbon, the oxidation step is also important to weaken this coating for subsequent acid digestion of the metal. The presence of a amorphous coating on the SWNT ropes is easily observed as indicated by arrows in Fig. 4-9 (b). Fig. 4-9(c),(d) shows that SWNT ropes are the more dominant form of carbon after DO/HCl purification step, consistent with TGA results in Fig. 4-9(c). Empty multi-layered graphitic shells left after removing catalyst particles by HCl reflux are easily seen in the image. Catalyst particles are still observed, consistent with TGA result (~14wt% metal). Fig. 4-9(d) shows that the amorphous coating on the bundles are thinner than that of the raw soot. In Fig. 4-9(e)(f), SWNT bundles and multi-layered graphitic shells are observed in the HRTEM images. The tube walls seem cleaner than DO/HCl purification protocol because nitric acid oxidizes amorphous carbon too. According to the result of HRTEM images and TGA, DO/HNO₃ protocol results in much cleaner SWNT material. However as will be discussed in Chap.5 and 6, nitric acid is much more aggressive than HCl, thus attaches functional groups and attacks tube alls. It is better to optimize DO/HCl protocol
to obtain cleaner tubes. We stress that the data shown here is not for the best purification procedure, but to indicate how minority phases can be recognized and removed.

4.3 Optical physics: Infrared absorption and Raman scattering

In this thesis work, Raman scattering and Infrared absorption technique have been used to study the vibrational modes of carbon nanotubes or functional groups attached on the tube wall. The vibrational modes will give information on the tube wall integrity or the structural transformation at high temperature annealing.[70, 71]

The atoms in a solid are bound to their equilibrium positions by the forces that hold the crystal together. When the atoms are displaced from their equilibrium position, they experience restoring forces, and vibrate at characteristic frequencies. These vibrational frequencies are determined by the phonon modes of crystal, which usually lie in the infrared spectral region. This contrasts with the optical properties of bound electrons, which occurs at visible and ultraviolet frequencies.

Since the wave vector ($10^5\text{cm}^{-1}$) of light can be treated at almost zero compared to the size of Brillioun zone ($10^8\text{cm}^{-1}$) of the crystal. By first order Infrared absorption and Raman scattering, we will only explore the phonons at Brillouin zone center ($q \approx 0$).
4.3.1 Infrared absorption

Electromagnetic waves are transverse, and can only apply driving forces to the transverse vibrations of the crystal. Therefore they can only couple to the transverse optic (TO) phonon modes.

The resonant frequencies of the phonons occur in the infrared spectral region, and the modes that interact directly with light are called infrared (IR) active. These optically active phonons are able to absorb light at their resonant frequency.

Photons couple to phonons through the driving force exerted on the atoms by the AC electric field of the light wave. This can only happen if the atoms are charges. Therefore, if the atoms are neutral, there will be no coupling to the light. This means that the crystal must have some ionic character in order for its TO phonons to be optically active. Conservation laws require that the photon and the phonon must have the same energy and momentum.

4.3.2 Raman scattering

Raman scattering is another way to investigate the phonon structure at the zone center. In the Raman effect, a photon is scattered inelastically by a crystal, with creation (Stokes) or annihilation (anti-Stokes) of a phonon.[72]

When visible photons are used to excite Raman scattering, they couple by and large only to electrons via the electron-radiation interaction Hamiltonian $H_{e\gamma}$ [72]
where \( \vec{A} \) and \( \vec{p} \) are vector potential and the electronic momentum. The scattering proceeds in three steps.

First, the incident photon with a frequency denoted by \( \omega_i \) excites the electrons in the ground state of the crystal into an intermediate electronic state \( |n'\rangle \) by creating an electron-hole pair (or exciton). Second, this electron-hole pair is scattered into another state by emitting a phonon via the electron-phonon interaction Hamiltonian \( H_{e-ion} \).

\[
H_{e-ion} = \sum_j \frac{\partial H}{\partial R_j} \cdot \delta R_j \]

Eq 4.2

This intermediate state will be denoted by \( |n'\rangle \). Third, the electron-hole pair in \( |n'\rangle \) recombines radiatively with emission of the scattered photon with a frequency denoted by \( \omega_s \). Thus electrons mediate the Raman scattering of phonons although they remain unchanged after process.
Fig. 4-10: Feynman diagrams for the six scattering processes that contribute to one phonon (stokes) Raman scattering[72]

Fig. 4-10 shows the 6 possible Raman processes. First process in Fig. 4-10(a) is described earlier. The other five possible permutations of the time order of the three vertices involved in this process are shown in Fig. 4-10(b)-(f).
The probability for scattering a system from the initial state $|i\rangle$ to the final state $|f\rangle$ can be derived via the Fermi Golden Rule. By translating 6 possible Feynman diagram into a term in the perturbation theory series[72], the scattering probability $P_{ph}$ can be obtained as seen in Eq. 4.3
From Eq. 4.3, the energy delta function requires that \( \hbar \omega_i - \hbar \omega_s - \hbar \omega_0 = 0 \), which is the energy conservation rule in a Raman scattering process. For the Antistokes processes, \(-\hbar \omega_0\) sign becomes positive. By solving the matrix element \( \langle n' | H_{eh} (\omega_s) | i \rangle \) [72], it can be shown that the net electronic contribution to the scattering process is zero, leaving \( k_i - k_s \pm q = 0 \) which is the conservation law of wave vector. In a typical Raman scattering experiment with visible light, its wave vector is about three orders of magnitude smaller than the zone boundary wave vector. Thus, in a first order Raman scattering processes, only phonons at \( q=0 \) will participate in the scattering process.
Chapter 5
De-bundling and Dissolution of Single-Walled Carbon Nanotubes in Amide Solvents

5.1 Introduction

It was pointed out in Ch.1 that an effective chemical process to obtain clean, individual single-walled carbon nanotubes (SWNTs) in a stable solution is important for various application purposes. The strategies for the dissolution of SWNTs, or bundles of SWNTs, have involved either the supramolecular complexation of the tube walls with surfactants[73, 74] or macromolecules[75, 76], or the functionalization of defect sites at the tube ends and side walls with amino groups and the subsequent conversion into derivatives, such as amides[77-79]. Finally, direct chemical functionalization of the side walls using addition reactions have been investigated[79]. More about functionalization of SWNTs will be discussed in Ch.6. Most of these moieties attached to the tube wall can be quite difficult to remove later, and can also alter the SWNT physical and chemical properties. Furthermore, the chemical processing may damage the nanotube walls i.e., remove C-atoms from the graphene cylinder or functionalize the tube wall. Nanotube synthesis approaches that provide large quantities of unsupported, loose powders, or “soots” of SWNTs, such as the Electric Arc[10, 80] or the
HiPCO[81] process, also produce large bundles of SWNTs. Typically, each bundle might contain 100’s of nanotubes bound together by the weak van der Waals force. Unfortunately, the powders or soots from these procedures can (and usually do) contain significant quantities of metals (growth catalyst) as well as amorphous carbon; the amorphous carbon can also be present as a coating on the outside of the nanotube bundles. Information about the degradation of the structural order or chemical functionalization of the nanotubes can be extracted from Raman scattering spectra. Unfortunately, previous studies[82, 83] to dissolve nanotubes in organic solvents, such as I have investigated as part of my thesis work, have not carried out spectroscopic investigation on their products, nor have they presented statistical information about the extent of the de-bundling, or the final length of the nanotubes. We were therefore motivated to initiate our own study to investigate these important issues.

In this chapter, results from a systematic study on the effects of chemical processing of arc-derived bundles of carbon nanotubes to generate solutions containing individual SWNTs will be presented. The impact of our chemical and ultrasonic processing on the structural order of the nanotube has been studied by Raman scattering. We have considered several different process routes involving an initial dry oxidation step, a metal removal step in involving a reflux in HNO₃, or HCl, followed by a de-bundling/dispersion step in either N-N-dimethylformamide (DMF) or N-methyl-2-pyrrolidone (NMP) and then a final centrifugation step to separate the light and heavy fractures. SWNTs refluxed in
H$_2$O$_2$ as an amorphous carbon removal step followed by HCl reflux was de-bundled in NMP for comparison with dry oxidation (DO)/HCl refluxed/ NMP sample. The details of amorphous carbon removal by H$_2$O$_2$ reflux will be discussed in Ch.6. Using Atomic Force Microscopy (AFM), we have determined the distribution of the tubes/bundle and the average filament length for several process routes. Furthermore, we have examined whether or not chemically-induced tube wall damage can be repaired by high temperature heat treatment (HTT). The goal of our study was to obtain perfect dissolution of carbon nanotubes in an organic solvent, creating as little chemical damage to the nanotube wall as possible. Similar to the approach of Ruoff and coworkers[84], we have used ultrasound to assist the de-bundling of the tubes and drive them into solution.

5.2 Experimental details, results and discussion

Fig. 5-1 shows a schematic diagram for the full purification and de-bundling process. The sample characterization performed after each step in the process is also indicated. First, we carried out a “dry” oxidation (DO) of the soot in air to “selectively” remove the amorphous carbon. In reality, one should strive to create conditions that promote a significantly more rapid oxidation of amorphous carbon relative to that of SWNTs. Conditions (temperature/time) for this process were found by thermogravimetric analysis (TGA; TA Instruments, model SDT 2960). The time and temperature in the
thermal oxidation process are somewhat different for each sample batch. It was determined that a thermal soak of the CarboLex soot at 365ºC for 90 minutes in a flow of dry air (100sccm) was required to achieve selective oxidation of the amorphous carbon, minimizing nanotube mass loss. Importantly, the carbon coating on the metal particles is also weakened during this step[69]. Next, the metal (Ni-Y) by a reflux in acid solution was removed, using either a strongly oxidizing 3N HNO₃ solution for 16 hours, or a weakly oxidizing 6N HCl solution for 24 hours. The details for the SWNT soot purification are described in Ch.4.

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**Fig. 5-1:** Schematic diagram for the carbon nanotube de-bundling and dissolution process. The sample characterization performed after each step in the process is indicated.
Ultrasound was then used to disperse and de-bundle the purified SWNT bundles in amide solvents. Careful comparison of the benefits of two amide solvents mentioned in the literature as useful in dispersing SWNTs were investigated, i.e., DMF and NMP (Aldrich, Inc., Spectral Grade). A mass of 0.02 mg SWNT was added per mL of solvent. Typically, ultrasonic dispersion was carried out for 4 hours in a low power bath (Aquasonic, Inc.; Model P250HT). The solutions were then immediately centrifuged (Eppendorf, Inc., Model 5417C) at 14000 rpm (20,800 g) for 90 minutes, and the supernatant liquid containing the de-bundled SWNTs was withdrawn for study. The centrifugation step was found important for removing large particles (amorphous carbon, multi shell carbon, etc), and the few large (> 5nm) bundles that may remain. The quality of the dispersion of isolated tubes in DMF or NMP was examined by both atomic force microscopy (AFM) using a Digital Instruments Nanoscope (Model IIIA) and also via transmission electron microscopy (TEM; JEOL 2010F; 100 kV). Samples for AFM were prepared by depositing a drop of solution between two freshly cleaved mica substrates that were then allowed to dry in contact in air for 12 hours. The substrates were then separated for AFM studies. Using this preparation, it was found that a uniform sub-monolayer distribution of SWNTs is distributed across the face of both mica substrates. The measured standard deviation in the height of a single filament on the mica was determined to be $\sim \pm 0.1$ nm, as determined by measuring the height at several points along the same filament. Several images taken from different regions of the mica were evaluated to obtain a statistically reliable estimate for the fraction of filaments identifiable as individual tubes or containing 2, 3 or $> 3$, tubes per bundle. TEM grids were prepared by placing a drop of the amide/SWNT solution on a “lacey carbon” grid.
Samples for Raman scattering studies were prepared by placing a few drops of amide/SWNT solution on a warm ~ 60°C silicon substrate. The possible benefits of a high temperature annealing (1100°C in vacuum) to restore structural order in the de-bundled and dispersed SWNTs was also studied by simply heating several of the Si substrates in flowing argon gas or high vacuum. Micro-Raman spectra were collected using a triple-grating Micro-Raman spectrometer (JY Horiba, Model T64000) equipped with a confocal microscope (Olympus BH-2) and a CCD detector. The scattering was excited using an argon ion laser (488 nm), and the power measured at the sample was 1 mW inside a ~1µm laser spot size. This particular excitation wavelength primarily couples to the semiconducting tubes in the sample[34, 55].

5.2.1 Purification

Using TGA in flowing dry air (100 scem, 5 °C/min heating to 800 °C), the raw CarboLex arc-discharge SWNT soot was found to contain ~ 20 - 30 wt% SWNT and ~ 30 - 40 wt% Ni-Y( refer to Fig. 4-8 in Ch.4). This conclusion was reached by observing both the oxidative mass loss of amorphous carbon at low T (350 – 375 °C), and attributing the final sample mass at 800 °C in air to metal oxides. After a two-step purification process (dry oxidation followed by acid reflux), the wt% of nanotubes in the sample increased to approximately 90% (HNO₃) and 85% (HCl); the remainder of the solids at this stage of purification were typically ~8 - 12 wt% amorphous carbon, and ~1 - 2 wt% metal[69].
Room temperature Raman spectra (488 nm excitation) of SWNT material at various stages of the chemical processing are shown in Fig. 5-2. From bottom to top in the figure, are the high frequency spectra for the following: as-prepared or raw arc soot (a), dry oxidized soot (b), dry oxidized soot + HCl-reflux (c), dry oxidized soot + HNO_3-reflux (d), and dry oxidized soot + HNO_3-reflux + high T annealing (e) (annealed for 1 hr under vacuum (10^-6 Torr) at 1100 °C).

Two Raman bands are typically observed for sp^2 carbon material in the 1200 - 1850 cm^{-1} range[52, 55], i.e., a relatively broad, disorder-induced band (or “D-band”) appears in the region 1300 - 1370 cm^{-1} and a first-order-allowed band with substructure appears in the region ~ 1580 - 1600 cm^{-1} as discussed in Ch.3. For small diameter carbon nanotubes (d < 2 nm), the cylindrical and chiral (n,m) symmetry produces Raman activity in related vibrations with frequencies in the range 1450 - 1620 cm^{-1}. Several of these
modes are observed as unresolved side bands to the main peak at 1591 cm$^{-1}$ [52, 55]. In the bottom three spectra of Fig. 5-2, for example, one can easily observe one main peak (1591 cm$^{-1}$) and two unresolved bands on the low frequency side of the main peak. Actually, to fit the complex bandshape of the nanotube G-band, a fourth high frequency, and unresolved Lorentzian peak at ~ 1610 cm$^{-1}$ is also required. The effects on the high frequency Raman spectrum of carbon nanotubes due to wall disorder and chemical functionalization can be anticipated. These chemical changes are expected to broaden the structure in the G-band, and to increase the integrated intensity and width of the D-band[52, 55].

Carbon nanotubes also exhibit a unique, low frequency, first-order Raman scattering feature identified with the radial breathing mode of the tube wall. The frequency of this mode is inversely related to the nanotube diameter $d$. An approximate expression based on several experiments is given by i.e., $\omega = 234$ cm$^{-1}$.nm/d [61]. In 2002, Mahan has derived a simple formula of radial breathing mode of carbon nanotubes by solving the standard wave equation[85]. It clearly shows that the radial breathing mode of carbon nanotubes is inversely proportional to its diameter, which is consistent with the empirical law, $\omega = 234$ cm$^{-1}$.nm/d. In the raw CarboLex arc material the main peak in the R band is located at ~ 161 cm$^{-1}$. This corresponds to a tube diameter of 1.4nm.

As discussed in Ch.3 the D-band is present in all known forms of disordered sp$^2$ carbons, and has been identified with C-atom vacancies, substitutional impurities (boron), finite grain or particle effects, or any other symmetry-breaking phenomena[44, 46]. We therefore need to be extremely careful using the D-band to assess damage to the SWNTs
caused by the purification process. For example, a contribution to the D-band spectrum can come from minority phases of disordered sp$^2$ carbon in the sample (Fig. 5-2(a)). After dry oxidation (DO) of the sample to remove the amorphous carbon (Fig. 5-2(b)), the relative intensity of the D-band is observed to decrease very slightly. However, after the acid treatment (second step of the purification process), the relative integrated intensity of the D-band intensity increases, and the D-band broadens (Fig. 5-2(c) and (d)). This is particularly evident for the HNO$_3$ refluxed material. Since the TGA data suggest that most of the amorphous carbon has been removed from the sample in the dry oxidation step as shown in Ch.4 and the NaOH wash removes oxidized carbonaceous materials derived from dry or acid oxidation, we interpret the increase of the D-band intensity and width after acid treatment as evidence for a decrease in structural order in the SWNT bundles as a result of the reflexing. After acid treatment, the intensity of the D-band relative to the G-band was always found to be higher for the HNO$_3$-treated samples than for the HCl-treated samples. Using the D-band as a probe, it is clear from comparing the spectra in (Fig. 5-2(c) - HCl reflux) and (Fig. 5-2 (d) - HNO$_3$ reflux), that HNO$_3$ induces significantly more chemical change to the dry oxidized nanotubes. In addition to the difference in the D-band intensity, we can also see in Fig. 5-2 (c), (d) that the features in the G-band are also broadened as a result of reflexing. For the case of HCl reflux, the nbn effect is somewhat subtle, yet it can be observed with careful curve fitting. In the case of HNO$_3$ reflux, however, the broadening is obviously quite strong, and the substructure within the G-band almost disappears. We believe that it is very significant that in the case of HCl-reflux, no significant change in the FWHM for the G-band was observed. For the HNO$_3$-treated sample, a fit to the experimental G-band shows the
presence of a new Raman peak near \(~1620\) cm\(^{-1}\). The unresolved shoulder near \(~1620\) cm\(^{-1}\) has a counterpart in disordered sp\(^2\) carbons, and is referred to in the literature as the G*-band\([52]\). The frequency of the G*-band in graphite corresponds to the mid-zone maximum in the phonon density of states in the optical branch\([52]\). As structural disorder tends to introduce structure in the Raman spectrum near positions of maxima in the one-phonon density of states of the ordered (parent) material, the G*-band is therefore another anticipated signature of wall disorder, or functionalization or wall defects after processing.

There have been several reports that chemical oxidation and processing leads to the formation of oxygen-containing functional groups on the tube walls, such as carboxylate, hydroxyl, ether and quinone groups, etc.\([86-89]\). The fractional abundance of each of these functional groups is variable, and should depend on the details of the particular chemical process. For the HNO\(_3\)-based treatment, carboxylic groups have been reported as the most abundant functional group on the carbon nanotube surface\([86, 88]\).

The identification of functional groups attached to the tube walls after HNO\(_3\) reflux will be discussed in Ch.6. Using infrared spectroscopy, Zhang et al.\([86]\) have proposed that the oxidation process begins with the oxidation of initial wall defects (step 1) (e.g., at \(-CH_2\) and \(-CH\) groups, or pentagon-heptagon pair defects). These defects might be present, to some extent, after growth, i.e., before or after chemical processing. After these defects are oxidized, they have suggested two more successive steps in the evolution of the defect structure: the defect-generating step (step 2) and the defect-consuming step (step 3). In step 2, an electrophilic addition to the wall begins at the bond
defined by the fusion of adjacent six-membered rings in the wall, generating more active sites, such as –OH and –C=O. The third, or final step is the defect-consuming step (step 3), whereby the graphene structure of the wall is locally destroyed by the oxidation of the generated active sites in step 1 and 2. According to Zhang et al.[86], steps 2 and 3 compete and cooperate with each other; they require special, strong oxidation conditions. According to these authors, refluxing in dilute (2.6 M) nitric acid under similar conditions (3 M) to those used here should be considered a mild oxidation for SWNT, introducing carboxylic groups only at defects that existed prior to chemical processing. Also, according to their work[86], extended refluxing in dilute (2.6 M) HNO₃ for >96 hours appears to have no impact on the generation of new defect sites on the tube wall, and they propose that this extended HNO₃ digestion advances the system only as far as

Fig. 5-3: Raman spectra for HNO₃-purified SWNT sample before (a) and after (b,c) neutralization with pH 10 NaOH solution. The sample heterogeneity after removing bulk impurities is characterized by significant spot-to-spot variation in the G-band features as noted in the different spectra (b) and (c).
step 1 (above), the oxidation does not proceed to steps 2 and 3. However, in this work, our Raman scattering spectra show that dilute (3N) HNO₃ reflux for ~16 hours has a significant impact on the tube wall structure. We therefore suggest that even mild HNO₃ treatments can create defect sites on the wall.

Our Raman microprobe has a spatial resolution of 1µm, and using this resolution we can observe a highly heterogeneous character for the HNO₃-refluxed sample. The HCl-refluxed material is, by comparison, very homogeneous. In Fig. 5-3, we show the Raman spectra for the HNO₃-treated sample before neutralization (washing) with NaOH, and also the Raman spectrum from two nearby spots of the sample after neutralization with NaOH. As discussed previously, the neutralization with NaOH removes nanoparticulate impurities by solubilizing the carboxylic acid functionalized carbonaceous materials. As a consequence of their removal from the sample, one would expect the contributions of disordered nanoparticulate carbons and small polycyclic sheets to the D- and G*-band to be decreased. The anticipated outcome of their removal is seen in the Raman spectrum of spot 2 in Fig. 5-3, but not for spot 1 on the same sample. This sample heterogeneity was also observed in TEM images, as discussed by other authors[84].

It is interesting to observe that chemical changes and structural damage induced by HNO₃-reflux is largely reversible at moderate temperatures. By annealing the refluxed material at ~ 1100 °C under vacuum, or in Argon, the tube wall disorder is largely repaired. We present that chemical functional groups associated with wall defects are also removed. This can be seen by comparing the Raman spectrum in Fig. 5-2 (e)(annealed) to that after refluxing (Fig. 5-2(d)). For example, after annealing, we find
that the G* peak at 1620 cm\(^{-1}\) disappears, and that the D and G band’s positions, widths and relative intensities return to those observed for the SWNTs in raw soot (Fig. 5-2(a)).

### 5.2.2 De-bundling and Dispersion into Organic Solvents

The final step of the chemical processing to produce individual (de-bundled) SWNTs involves the dissolution of the nanotube bundles into individual tubes in an organic solvent. Previous authors have found that this de-bundling or “dispersion” requires ultrasonic assistance[82, 83, 90]. Furthermore, it has been reported that ultrasonic dispersion in DMF introduces further damage to the tube walls[84]. We have investigated this contention using Raman scattering, and have tried to correlate any ultrasonic-related wall damage with the purification protocol prior to the de-bundling and dissolution step. To examine these phenomena, samples of purified bundled tubes were ultrasonically agitated in DMF or NMP for 4 hours. Longer sonication times were found

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Fig. 5-4: AFM image of dry oxidized SWNTs (without acid digestion step) sonicated in DMF for 4 hours

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to have no additional benefit on the dispersion. Afterwards, centrifugation was performed at 14000 rpm (20,800 g) for 90 min, and resulted in transparent, light-gray suspensions; most large particles and any remaining larger bundles were driven out of solution. The centrifugation step was used to remove large particles (*i.e.* 20nm diameter particles) and large diameter bundles from solution (*i.e.*, *d* ≥5nm). We estimate that ~15% of the SWNTs are removed as small bundles by centrifugation. The suspensions were observed to be stable; no evidence for agglomeration was observed over periods of weeks.

Interestingly, if the SWNT soot was subjected only to dry oxidation (*no acid reflux*), we found that the amide solvent with sonication produced no measurable dispersion; no isolated tubes could be found in solution. As shown in Fig. 5-4, large quantity of particles surrounding bundles of SWNTs were observed in the AFM image. This must be catalyst particles left after amorphous carbon removal step. By TGA study in Ch.4, ~70% was found to be metal particles after DO. No measurable dispersion of dry oxidized SWNTs in DMF may suggest that the catalyst particles serve as an important anchor at one end of the bundle encouraging rebundling in the absence of ultrasonic agitation. The reason that both DO *and* acid reflux (*either HCl or HNO_3*) are a required first step prior to ultrasonic debundling in the amides remains an interesting point that we cannot yet fully explain. Based on intercalation studies in graphite, one would not expect HCl to intercalate into the SWNT bundle (*i.e.*, HNO_3 forms a graphite intercalation compound, and HCl does not). Nevertheless, both the HCl- and HNO_3-treated SWNT bundles can be efficiently debundled in amide solvents. This suggests that HCl can also penetrate the SWNT bundles and the result of this penetration is to reduce the van der Waals interaction between tubes in a bundle allowing the amides to penetrate
the bundle via a displacement reaction. We suggest that ultrasound and weak charge transfer between the amide and the SWNT, and a reduced van der Waals interaction (perhaps) driven by acid penetration into the bundle may all be required to drive an efficient debundling process.

Fig. 5-5: Typical AFM images showing the dispersion of SWNTs in DMF for (a) HCl-treated and (b) HNO$_3$-treated SWNT material. (c) Shows Z scan analysis of the lines labeled [30], [30], (3), (4) in (a).

Fig. 5-5(a), (b) shows topographic AFM images of carbon nanotubes deposited from DMF solution onto cleaved mica substrates. The same AFM tip was used to acquire both figures (Fig. 5-5(a), (b)). As the tip scans over a nanotube filament, we can estimate
the filament diameter via the change in height of the tip. The diameter of all filaments for
the histogram was checked at the different positions along the filaments at least 3 times.
We will show histograms of filament diameter and length below. The apparent width of
the filaments in the figure is not significant; changes in the width at the real scale of the
nanotube diameter is not resolvable with these AFM tips. In Fig. 5-5(a) and (b) we show,
respectively, the images for dry oxidized nanotube bundles refluxed in HCl(a) and
HNO₃(b). Fig. 5-5(c) shows Z scan analysis of the lines labeled as [30], [30], (3), (4) in
Fig. 5-5(a). In Fig. 5-5(c), the data for lines. [30], [30], (3) all refer to the same tube. The
actual filament diameter measured in three locations is shown. The average filament
diameter in this case is $d = 1.45 \text{nm} \pm 0.07 \text{nm}$. The line labeled as (4) in Fig. 5-5(a) cuts
across 7 tubes and 2 small particles and the Z scan is also shown in Fig. 5-5(c); examples
of isolated tubes and very small bundles (2~3 tubes/ one bundle) can be seen. By
comparing the topographic results in Fig. 5-5(a) and (b), several results can be seen
immediately: [30] HNO₃ reflux (Fig. 5-5(b)) has produced a better dispersion, i.e., more
of the filaments are actually individual SWNT, [30] the average length of the filaments
are slightly shorter when processed with HNO₃ than with HCl. A closer inspection of
many of the filament’s topology (via z-scan) showed the following. For the HCl-refluxed
sample in DMF, we observed that the apparent thickness of some of the isolated tubes
was not uniform along the tube length, suggesting a coating had formed; this coating was
definitely less than 1/2 a tube diameter in thickness). Also, on occasion, small bundles of
3-6 tubes processed with HCl/DMF were observed that exhibited a tapering along their
length. We suppose that this might be caused by the fact that not all tubes in these small
bundles were cut at the same position.
To see the real effects of various chemical process schemes on the nanotube dispersion, we have made a detailed AFM study of various topographic images such as shown in Fig. 5-5(a),(b) to obtain the distribution of filament height (diameter) and filament length for several purification/de-bundling processes. All of the samples stemmed from the same batch of CarboLex nanotube soot; all were subjected to a standard DO step, and either an HCl reflux (6.0 N; 24 h) or an HNO₃ reflux (3N; 16), and then sonication in DMF or NMP (4 h). Finally, (in all cases) the sonicated solution was centrifuged at 14,000 rpm for 90 min and the several drops of a solution were placed on mica for the comparative AFM study. Fig. 5-6 shows the effect of centrifugation in dispersion for DO/HNO₃ purified SWNTs in DMF. (a) and (b) are the AFM images before and after centrifugation, respectively. As can be seen, after centrifugation, it has

Fig. 5-6 AFM images of DO/HNO₃/DMF before(a) and after(b) centrifugation
less large particles and bundles. As will be discussed later, centrifugations will improve the dispersion yield ($Y_D$) in the case of DO/ HNO$_3$/DMF sample. However, there was no noticeable change in $Y_D$ for DO/HCl/DMF and DO/HCl/NMP samples although less large particles are observed after centrifugation.

The results are shown in Fig. 5-7 for the processing indicated; the left hand three panels (Fig. 5-7(a)-(c)) and the three right hand panels (Fig. 5-7(d)-(f)) refer, respectively, to the filament diameter and length distributions. As can be seen, the filament diameter distributions produced via HCl/DMF and HCl/NMP are remarkably similar; both exhibit a peak in the bin (1.4-2.0 nm), consistent with the average diameter (~1.4 nm) reported for CarboLex tubes. Interestingly, the AFM data in Fig. 5-7(c) indicates that small diameter tubes are more commonly found after the HNO$_3$/DMF process than after the HCl/DMF or HCl/NMP processes. The reason for this is not clear, but we speculate it may have something to do with the higher reactivity of smaller diameter nanotubes in HNO$_3$[87]. It may be that HNO$_3$ refluxing preferentially functionalizes smaller diameter SWNTs, causing bundles containing them to be preferentially exfoliated. From Fig. 5-7(a)-(c), we can see that both HCl and HNO$_3$-refluxed material can be dispersed successfully in DMF or NMP, as bundles containing more than 3 tubes per bundle were rarely detected, but the HNO$_3$/DMF process is the most successful at generating individual tubes in solution. This better dispersion does come at a price, as Raman scattering indicates that the HNO$_3$ reflux produces considerably more wall damage (Fig. 5-2(c)).

We can define a quantitative measure of the success in de-bundling or dispersion by a “dispersion yield” ($Y_D$), defined as the fraction of the nanotubes found in the final
solution as individual nanotubes. From data in Fig. 5-7(a)-(c) we find $Y_D \approx 50\%$ for HCl/(DMF or NMP) and $Y_D \approx 90\%$ for HNO$_3$/DMF. Also we should add that comparing AFM z-scan data for sonicated solutions with and without the added centrifugation step, shows that this final step is very effective at removing large carbon particles and even larger carbon nanotubes bundles. For example, $Y_D$ for the HNO$_3$/DMF increased from $\sim 70\%$ before centrifugation to $\sim 90\%$ after centrifugation. However, for both the HCl/NMP and HCl/DMF processes, $Y_D$ was not affected by centrifugation ($\Delta Y_D < 5\%$), and remained near 50%; presumably there were only a few large bundles after sonication in these cases.

Fig. 5-7: AFM Diameter and length distributions for arc-derived SWNTs after various purification and de-bundling processes.
The optimal physical properties of organic solvents that dissolve SWNTs are still not well established[82]. Electron pair donicity (Lewis basicity) without hydrogen bond donation, a property present in amide solvents like DMF and NMP, was found to be a necessary, but not a sufficient condition for solvating HNO₃-treated SWNTs, since other solvents with the same property have failed to disperse them[82]. DMF and NMP are subject to cleavage of the CH₃-N and C-H bonds under ultrasound excitation[90], evidencing the nucleophilic character of the N-C-O group, and, therefore, increasing the possibility of physi- or chemi-sorption. The charge-stabilized colloidal nature of the HNO₃-treated SWNT suspension in DMF was also proposed by several authors[91, 92]. SWNTs in DMF were found to carry ~ 1 negative charge every 3.5 nm of length by measurements of zeta potential in electrophoretic mobility experiments[79]. The interactions between these anionically charged SWNTs in electrolyte solution before the critical coagulation concentration were found to be described by a simple model of solid spheres with van der Waals and electric double-layer interactions[91].

The difference between the high percentages of individual tubes dispersed in amide solvents from using HNO₃-treated samples to that using HCl-treated samples (Fig. 5-7(a)-(c)) might be explained by the effective interaction between the solvent and the respective (functionalized) tube surface. It is known that nitrogen-containing functional groups, like amines and amides, possess significant affinity for physi- or chemisorption with attendant weak charge transfer on the SWNT sidewalls due to the high nucleophilicity of these N-based groups, as mentioned above. In DO/HCl samples, Raman spectra indicate that the wall damage is almost not detectable. This indicates that
functionalization of the SWNT wall with oxygen containing functional groups is not expected to be extensive. Hence, the amide adsorption on the nanotube wall, stabilized by the donation of π-electrons from the aromatic rings to the N-based electronegative solvents, should be the dominant interaction that drives the tube de-bundling. After refluxing in 3N HNO₃, the pristine tube walls are functionalized with hydroxyl and carboxyl groups as will be discussed in Ch.6[71]. A dipolar interaction between the solvent and these polar groups may also provide a significant benefit to dissolution, consistent with the higher values of Yₓ ~ 90% we observe for HNO₃-processed tubes. We also suggest that polar groups added on the nanotube walls, e.g., –COOH groups, may provide a second mechanism for the debundling process.

In one experiment, to investigate the effects of HNO₃ reflux on debundling, we annealed a DO/HNO₃ SWNT sample at 1100°C in 10⁻⁶ Torr for one hour (the Raman spectrum for this annealed sample is also shown in Fig. 5-2(e), and the spectrum exhibited very narrow SWNT bands and the D-band decreased). We then tried to disperse this annealed and still bundled SWNT material in amides (DMF and NMP) using ultrasound (by our usual procedure). We found that the purified and high-T annealed material dispersed much less efficiently. We expect that this 1100 °C vacuum annealing should reduce significantly the tube wall functionalization[71], and the narrowing of the Raman lines is in agreement with this expectation. Therefore, it appears that tube wall functionalization, prior to the de-bundling step, is important. As mentioned above, the functionalization may separate the tubes in the bundle reducing the van der Waals interaction; it may also be that the functional groups enhance the SWNT
interaction with the amide solvent.

In Fig. 5-7((d)-(f)) we exhibit the length distributions for the debundled tubes obtained from AFM z-scan analysis. The samples investigated are the same as in (Fig. 5-7(a)-(c)). First, we can see that for the case of HCl reflux, there is no significant difference in the final length distribution depending on whether NMP or DMF was used with ultrasound to disperse the tubes. Second, HNO₃ reflux was found to reduce the average tube length from ~800 nm for HCl-reflux to ~300 nm, similar to lengths found previously for laser oven tubes sonicated in DMF[89]. Based on our AFM studies, we suggest that the final tube length from sonication in solvent depends significantly on the acid processing. This processing functionalizes the tube wall or creates defects (missing C-atoms) in the tube wall (as seen by Raman scattering) and these positions in the tube wall appear to locate “weak” positions at which the ultrasonic cutting can occur.

We have also dispersed H₂O₂ refluxed (as an amorphous removal step) SWNTs followed by HCl reflux(metal removal step) in NMP to compare with DO/HCl/NMP. As shown in Fig. 5-8, H₂O₂/HCl/NMP processing exhibit a peak in the bin (1.4-2.0nm) similar to DO/HCl/NMP and DO/HCl/DMF, consistent with the average diameter (~1.4nm) reported for Carbolex tubes. However, the dispersion yield Y_D and the average filament length was ~70% and 400nm, which is better in dispersion yield and shorter in length than DO/HCl/NMP and DO/HCl/DMF. We believe that it is due to the much higher functionalization occurred during the H₂O₂ reflux step than DO. We have observed G-band broadening and D-band enhancement in Raman spectrum after H₂O₂ reflux step which will be shown in Ch.6. It is interesting that functionalized tubes by
HNO₃-reflux or H₂O₂-reflux produce a higher dispersion yield in amid solvents. In Ch.6, we will discuss about the functional groups attached to the tube wall at each purification step by Raman and IR spectroscopy.

Monthioux et al. using HRTEM studied the effects of HNO₃ refluxing and sonication on the structural integrity of the tubes. Their laser oven tube soot was refluxed in 3N HNO₃ solution for 45 hours (~3 times longer than in this study) and then sonicated in DMF[84]. Much different from the results presented here, they did not report exceptional dissolution or de-bundling of their laser oven tube bundles in DMF. Consistent with our Raman results (Fig. 5-3), they reported that the HNO₃-refluxed material appears very heterogeneous. More important for this study, they reported a dramatic structural degradation in the tube wall structure. In their HRTEM images, they interpret the disappearance of evenly spaced fringes representing the tube walls within the rope as clear evidence for strongly damaged, distorted and segmented tubes. They also found that the structure was improved after the ropes were vacuum annealed at 1200 °C for 14h. After sonication of their 3N HNO₃-refluxed SWNT sample in DMF for at least 15h, Montrioux et al. found that the ultrasonic treatment induced extensive further

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**Fig. 5-8:** AFM Diameter and length distributions for arc-derived SWNTs after H₂O₂ reflux/HCl reflux
damage, with many of the ropes transformed into an amorphous material[84]. Many
SWNTs survived the ultrasonic dispersion, but they appeared segmented, or exhibited
many holes in the walls. This level of damage appears to be much more severe than what
we observed via Raman scattering in this study (for ultrasonic dispersion in DMF)
(Fig. 5-3). That is, the molecular character of the tube remains in our vibrational spectra,
as discussed further below. However, they refluxed for a factor of 3 times longer.

In Fig. 5-9, we compare the Raman spectra of the nanotubes before and after
sonication in DMF; the spectrum of the raw soot is shown for comparison. In Fig. 5-9(a),
we show results for DO/HNO\textsubscript{3} purification, and in Fig. 5-9(b) for DO/HCl purification.
Centrifugation was performed on the sonicated liquid before the Raman spectrum was
collected on tubes removed from the supernatant liquid. As already discussed (c.f.,
Fig. 5-3), the much stronger attack of HNO₃ on the tube walls is clearly evident in Fig. 5-9. However, the effects of sonication are comparatively speaking, very subtle. In both HCl and HNO₃ cases, a slight narrowing of the G-band components and D-band is observed, probably indicating that the centrifugation removed small amounts of other disordered sp² carbons still present after purification. Most important, is the clear observation that sonication certainly does not broaden the Raman features, i.e., we see no Raman evidence for wall damage during the sonication/ dispersion step. Thus, it is clear from Raman spectroscopy that HNO₃ damage is much more severe than that caused by ultrasonic processing in DMF. The same results were found for ultrasonic processing in NMP, i.e., no noticeable damage via the G- and D-band was observed. As shown in Fig. 5-9(a), annealing at 1100°C under vacuum(10⁻⁶ Torr) restores order in the tube wall of DO/ HNO₃ /DMF sample. However, in the case of HCl treatment, no Raman evidence for wall functionalization or wall damage was observed before, or after, amide processing in ultrasound. Therefore, after an 1100°C vacuum annealing the samples given the DO/HCl/DMF treatment exhibited little or no change in the Raman line shape (Fig. 5-9(b)).

Some comments about the Raman-active radial breathing modes and chemical processing are worth making here. For HCl-treated samples we saw a downshift of 3 cm⁻¹ for the SWNT radial (R) band after purification (from 161 (raw) to 158 cm⁻¹ (purified)) and then an upshift of 6 cm⁻¹ in relation to the purified sample (from 158 (purified) to 164 cm⁻¹ after the tubes were dispersed as isolated tubes in solution.). Several theoretical calculations have indicated that the tube-tube interaction in the bundle, up shifts the R-band frequency by ~12-14cm⁻¹ for tubes with diameters in the range 1.2-1.6nm. So the
upshifting we observe by de-bundling is an opposite effect to what has be predicted theoretically. This upshifting upon de-bundling has been reported earlier and attributed to a change in the resonance scattering[93].

It is interesting to compare Raman scattering and electron microscopy as probes of wall damage during purification and during de-bundling. In Fig. 5-10, we display HRTEM images of bundles of SWNTs taken by our group that have been subjected to dry oxidation and acid reflux: 16 h 3N HNO$_3$-reflux (Fig. 5-10(a)) and 24h 6N HCl-reflux (Fig. 5-10(b)). The samples were neutralized in NaOH as discussed above. Whereas the Raman spectra of these purified materials shows a clear difference due to wall damage (c.f., Fig. 5-3 and Fig. 5-9), the HRTEM evidence for damage is more subtle, but nevertheless evident. A close inspection of both images in Fig. 5-10 reveal that the fringes associated with the triangular rope lattice are much more distinct and straight after HCl-reflux (Fig. 5-10(b)) than after HNO$_3$ reflux (Fig. 5-10(a)). Furthermore, notches

Fig. 5-10: (a) HRTEM image of HNO$_3$-refluxed bundles dispersed in 2-propanol (b) HCl-refluxed bundles after dry oxidation in 2-propanol.
can be seen to form in the wall of tubes that are on the outside of the bundle (see arrows in Fig. 5-10 (a)).

Fig. 5-11: (a), (b) HRTEM images of de-bundled SWNTs dispersed in DMF after HNO$_3$-reflux, (c) SWNTs dispersed in DMF after HCl reflux. All samples were subjected to dry oxidation and centrifugation steps. The HNO$_3$-refluxed tubes (a,b) appear to be coated with carbon sheet fragments; closed-shell structures are inside circles.

Fig. 5-11, we display isolated tubes produced from ultrasonic dispersion in DMF: Fig. 5-11(a), (b) HNO$_3$ purification, Fig. 5-11(c) HCl purification. These images were
obtained by Dickey’s group[70]. In all cases, we performed the initial dry oxidation and the final centrifugation in the same way, as described above. The acceleration potential in the microscope was 100keV, i.e., the same used by Monthioux et al.[84]. First, we can see that the wall of the tube subjected to DO/HCl is cleaner, i.e., has less carbon fragments, fullerenes, etc. attached to it, than the tube walls subjected to DO/HNO₃. This coating by carbon fragments probably does not affect the nanotube Raman spectrum, although the fragments may contribute to D-band scattering and a broad G-band contribution superimposing with the nanotube G-band. Second, the HRTEM images show that the tube wall of the HCl-refluxed tube appears straighter; yet it is not perfectly straight. Monthioux et al. has proposed that defects on the tube wall make the tube more susceptible to electron beam damage[84]. They reported that a defective tube wall structure or occurrence of some reactive reaction product on the tube surface accentuates the sensitivity of the wall to the electron beam, and allows the tube wall to rapidly kink, distort, and/or segment within a time period of 5-20s. We were unable to directly support this by our HRTEM study, as we did not find images of isolated tubes before chemical processing for comparison. However, our Raman scattering data on isolated, HCl-purified tubes seems to be consistent with their proposal, in that if the tubes were as imperfect as that observed in the HRTEM image of Fig. 5-11(c), then we would expect broadened Raman bands for this material. We mention again that the HCl-purified isolated nanotube material exhibits a Raman spectrum whose linewidths are as narrow as those found in the raw soot. Thus, it is interesting to consider the possibility as proposed by Monthioux et al. that even at 100keV acceleration potential, functionalized nanotubes, or nanotubes with small defects, are subject to large wall rearrangement reactions driven
by the electron microscope beam. Closed-shell structures appear to be present on the tube walls in Fig. 5-11(b) and Fig. 5-11(c)(inside circles). Monthioux et al.[84] also observed $\text{C}_{60}$ molecules on the nanotube wall (their tubes were grown by the Pulsed Laser Vaporization technique). The closed-shell structures that appear to be on the surface of our tubes may be created during arc discharge growth, or are some reaction product from purification, ultrasonic dispersion; or they might be generated in the electron beam. We see no evidence in the Raman spectra of their existence, which means they are probably not present at the ~1%, or greater, level.

Finally, we attempted to directly observe (via HRTEM) a reversal in the wall damage created via acid reflux (recall that Raman scattering shows no evidence for wall damage via ultrasonic dispersion in the amides). First, we deposited a few drops of debundled SWNT in DMF on a Si substrate. These tubes had been subjected to an aggressive $\text{HNO}_3$-reflux, and the Raman bands were significantly broadened. The tubes on the Si/SiO$_2$ substrate were annealed at high temperature ($1100^\circ$C, $10^{-6}$ Torr, 1h). After this annealing step, we sonicated the SWNTs in ethonal to remove the SWNTs from the substrate for HRTEM study. As shown in Fig. 5-12, the structural restoration of the tube wall by HRTEM was observed, which is consistent with the Raman experiments. However, our overall impression is that Raman scattering affords a much more sensitive probe of wall damage. In the HRTEM images, the quality of the tube wall on the atomic scale is almost impossible to observe. Only the restoration of significant tube wall defects (e.g., ~0.5 nm holes) can be readily observed in HRTEM.
5.3 Summary and Conclusions

Our results show that the details of the oxidation and metal digestion step (e.g., HCl or HNO₃) by which the metal catalyst and amorphous carbon are removed is a crucial first step to de-bundling and high dispersion yield, but this step can also significantly impact the structural quality of the de-bundled isolated tubes. This is perhaps a little surprising, as many of the tubes in the interior of the bundle might be viewed as protected from the acids or oxidative clean-up by the outer tubes in the bundle. Nevertheless, this is what we have observed.

Although the use of ultrasonic dispersion in amide solvents like DMF and NMP might be expected to lead to considerable damage to the tube wall structure, we do not see evidence for this damage in this work.
We have shown that a processing scheme involving a 3N HNO$_3$ reflux can yield a final product with as much as 90% isolated tubes in amide solution. Tubes can be deposited from this solution onto substrates where they can be subsequently vacuum annealed at 1100°C to repair much of the wall damage induced in the chemical processing. We believe that this is an important result, since their deposition can be controlled in such way that isolated nanotubes can, for example, be positioned at specific locations and with a specific orientation on the substrate [17].
6.1 Introduction

An unfortunate outcome of many growth processes that produce large batches of bundled, free-standing single-walled carbon nanotubes (SWNTs) is that the product is not pure, and contains residual growth catalyst and amorphous carbon as important impurities [68, 69, 94, 95]. Furthermore, the manufacturing and post synthesis chemical purification can remove C-atoms from the tube wall and add functional groups to the SWNT surface.

Raman scattering has been used for many years as a probe of disorder in the carbon skeleton of sp² and sp³ carbon materials[52]. Disorder in the tube wall has also been studied by Raman scattering [46]. Similar to studies in other sp² carbons (including graphite), disorder in the graphene structure of the tube wall leads to the appearance of a broad disorder band or “D” band[40, 42, 45]. Many factors should affect the strength of the “D” band scattering (any change in the C-atom environment that affects the periodicity of the carbon structure, e.g., missing C-atoms, and functional groups that are either added intentionally[96, 97], or added unintentionally during growth or in post
growth purification[69, 86, 95, 98-100]). Raman scattering, although a powerful probe of the nanotube phonons and optical excitations, has not been able to detect the identity of functional groups present on the tube walls. Raman scattering, therefore, has not been found very helpful in studying the chemistry of the nanotube wall.

Infrared (IR) Spectroscopy, on the other hand, has shown significant promise for the study of SWNT wall chemistry[86, 88, 97-105]. Several examples of tube wall functionalization have been reported where IR spectra were used to identify the functional groups added to the tube wall, e.g., -COOH, -OH, other oxygen containing groups[86, 96, 97, 101, 102], C-F[99, 100], - R-oxy carbonyl nitrenes[103], C-Cl[104], -CH[105].

In Ch.5, we have learnt that different chemical protocols to purify SWNT soot affect the dispersion yield \( Y_D \). It seems to be that wall functionalization will enhance the dissolution and debundling of SWNTs. In this chapter, we investigate with Raman and IR spectroscopy, how the various protocols outlined here affect the carbon skeleton and the attachment of functional groups. Although there has been considerable work invested to learn how to purify SWNT material, to the best our knowledge, nobody has used both IR and Raman spectroscopy together to follow the evolution of the SWNT material through these purification steps.
6.2 Experimental Details

Arc discharge nanotube soot for this experiment was obtained from Carbolex, Inc (USA). The specification of arc tubes from Carbolex is described in Ch.5.

To optimize the dry oxidation (DO) step, TGA was carried out first. It was determined that a thermal soak at 355ºC for 20 minutes in flowing dry air (100sccm) was required to achieve selective oxidation of the amorphous carbon, while minimizing nanotube mass loss explained in Ch.4. Wet oxidation removal of AC was carried out by refluxing in 30 vol% of H₂O₂ in H₂O for 6 hrs. The solution was then filtered through a ~1 μm pore-size polycarbonate membrane (Whatman, Inc). It was found necessary to repeat this procedure (H₂O₂ reflux/filter/wash process) 3 times to remove most of the AC.

For metal removal (Ni-Y), we refluxed the material produced after AC removal step either in a strongly oxidizing 3N HNO₃ solution for 16 hours, or in a weakly oxidizing 6N HCl solution for 24 hours. The details of metal removal procedure can also be found in Ch.5.

In the third and final step, we performed a high temperature vacuum anneal (HTVA) at 1100ºC for 1 hr at ~10⁻⁶ Torr with a turbo-pumped vacuum system pumping on the sample kept in a open boat in an 1” diameter quartz tube centered in a furnace.

FTIR and Raman spectra were both collected using a BOMEM DA3+ FT spectrometer, equipped to do conventional FTIR spectroscopy, or FT-Raman Spectroscopy with a Nd:YAG laser (1064 nm). The nanotube material was first ultrasonicated in isopropanol using a low power bath (Aquasonic, Inc.; Model P250HT). Several drops of the solution were then deposited from solution onto ZnSe substrates.
maintained in air at ~60°C. The solvent from each drop was allowed to evaporate before the next drop was added. In this way, a film of nanotubes was built up such that the transmission of the film was ~ 60% at ~ 2000 cm⁻¹. This transmission value includes the reflection/adsorption losses due to the substrate. The IR spectrum of just the nanotube
film was obtained by removing the reflection/adsorption losses from the ZnSe substrate. This normalization was done by measuring the single beam transmission of a clean portion of substrate and when the beam passed through the SWNT film and substrate; the normalized spectrum is just the ratio of these two spectra. For the IR measurements, the spectral resolution was 4 cm\(^{-1}\); for Raman spectroscopy it was \(~ 1\) cm\(^{-1}\).

6.3 Results and Discussion

We first present the results obtained from Raman scattering that focus on the evolution of SWNT skeletal disorder obtained via chemical processing and repaired through HTVA. The scattering was excited using 1064 nm Nd:YAG radiation, which is known to couple to semiconducting nanotubes in our samples that have diameters in the range 1.2-1.6 nm[106].

Fig. 6-1 shows the Raman spectra of SWNT materials from the raw soot and processed by various protocols as discussed above. The spectra appear in two panels: 100 – 300 cm\(^{-1}\) and 1230 – 1750 cm\(^{-1}\). The intensity of all the spectra in Fig. 6-1 were normalized to yield the same intensity for the “G” band at \(\sim 1590\) cm\(^{-1}\). The Raman spectra, from bottom to top in the figure, refer to raw soot (a), raw soot after DO at 355\(^\circ\)C for 20 min (b), raw soot after H\(_2\)O\(_2\) reflux (c), raw soot after DO/HCl (d), and then the sequences DO/HNO\(_3\) (e), DO/HCl/HTVA at 1100\(^\circ\)C (f), DO/HNO\(_3\)/ HTVA at 1100\(^\circ\)C (g). The Raman-active radial breathing modes (“R”-band) are observed at low frequency in the left hand panel of Fig. 6-1. The R-band can have contributions from several tubes simultaneously in resonance with the laser photon frequency. Each component in the R-
band has a frequency approximately given by $\omega_{RBM} = 223.7\text{cm}^{-1}(\text{nm})/d_i(\text{nm})[55]$, where $d_i$ is the tube diameter. This relation is approximate in that it neglects a small (calculated) restoring force that adds 12-14 cm$^{-1}$ to the $1/d$ term[56, 57]. For more information on this detail, the readers are referred to reference[56, 57]. It is clear from the R-band that at least two distinct radii tubes exist in the CarboLex material when excited with 1064 nm radiation (i.e., $d \sim 1.24\text{nm}$ and 1.40nm). In the 1230 – 1750 cm$^{-1}$ region (right hand panel), two Raman bands are observed: a relatively broad band near $\sim 1300 \text{ cm}^{-1}$ and a stronger band with structure in the $\sim 1580 - 1600 \text{ cm}^{-1}$ region. The band with maximum near $\sim 1300 \text{ cm}^{-1}$ is common in disordered sp$^2$ carbon material and has been called the “D”-band. It is activated by disorder in the sp$^2$ carbon network. The band at $\sim 1590 \text{ cm}^{-1}$ is close to that observed for well ordered graphite (i.e., $E_{2g}$ band at 1582 cm$^{-1}$) and it is therefore often called the “G”-band. The G-band in well-ordered nanotubes actually has several components that stem from the perfect cylindrical symmetry of the nanotube. The D-band intensity, and G-band width, have both been considered as probes of SWNT wall integrity or functionalization on the tube walls[52].

We have fit the G-bands in Fig. 6-1 to a sum of four Lorentzian components. The components can be broadened by disorder in the SWNT skeletal structure. To take advantage of this link between Raman linewidth and order in the carbon skeleton of the SWNT, we have had to carry out a careful lineshape analysis. The solid line in the figure is the result of our lineshape analysis. We find that the Lorentzian linewidth parameters for the G-band components of the raw soot are not affected by either dry oxidation (DO) or by a two-step treatment involving dry oxidation followed by HCl treatment (DO/HCl). This suggests that these chemical processing steps produce little or no change in the
carbon skeleton of the SWNT. Similarly, there is no increase in intensity in the D-band after DO or DO/HCl processing. However, this is not the case for wet oxidation ($\text{H}_2\text{O}_2$) to remove amorphous carbon, or after using 3N HNO$_3$ to digest metallic particles. In the case of this chemical processing, very noticeable changes in the Raman spectrum can be observed, even by examining the Raman spectra by eye (Fig. 6-1). For H$_2$O$_2$ processing only (Fig. 6-1(c)) and DO/HNO$_3$ processing (Fig. 6-1(e)) a careful lineshape analysis was also carried out. After this chemical processing, the G-band could be well fitted by a simple rigid upshift of the 4 Lorentzian components identified in the spectrum of the raw soot (i.e., all relative intensities of the G-band components remain the same, but all the components were broadened by the same amount). The results of these G-band analyses are seen as the solid curves passing through the data in Fig. 6-1. After H$_2$O$_2$ reflux, and also after DO/HNO$_3$ processing, we find that the G-band components are broadened by factors of 1.8 and 2, respectively. Furthermore, the G-band has upshifted by $\sim 4 \text{ cm}^{-1}$ ($\text{H}_2\text{O}_2$) and $\sim 10 \text{ cm}^{-1}$ (HNO$_3$). Previous experimental and theoretical work has shown that doping SWNTs with either electron donors or acceptors[61, 62, 107] results in noticeable shifts in the high frequency vibrational modes. Removing electrons from a SWNT (i.e. p-doping or oxidizing) has been shown to result in an upshift in the G-band peak[61, 62], as observed here. This conclusion is consistent with extensive observations of chemical charge transfer reactions in graphite[60], C$_{60}$ [108] and in SWNTs[61, 62, 107]. An upshift of the G-band after refluxing SWNT samples in HNO$_3$ has been observed by several groups[95, 96]. They identified the upshift of G-band with electron transfer from the nanotube bundle to form NO$_3^-$ anions. This interpretation is consistent with work in graphite intercalation compounds[107]. For the case of H$_2$O$_2$, the identity
of the anion formed as a result of the refluxing is less clear. In fact, the G-band upshift in this case is probably associated with negative –OH groups chemically bonded to the tube walls. This proposal is consistent with our IR-results, which we discuss further below.

The intensity of the D-band in SWNT soot processed by DO/HNO₃ or just by H₂O₂ is enhanced. The band also broadens and upshifts. The upshift of the D-band is large (~ 30 cm⁻¹) for DO/HNO₃. It should be noted that the D-band is a “dispersive” Raman band whose position changes with the excitation laser frequency[46]. It is not unexpected that the D-band should also shift at the same time the G-band is upshifting; this is just another signal of charge transfer. Of course, the increase in the D-band intensity should be interpreted as a decrease in the structural order in the SWNT bundles. It is likely that the disorder stems from three factors: added functional groups, missing carbon atoms in the wall, and inhomogeneous decoration of the tube wall by NO₃⁻ anions. It is well known that introducing disorder to an sp² carbon network introduces a broad disorder-induced “D-band” at ~1350 cm⁻¹. It is less well known that a second disorder-induced band often appears as a high frequency shoulder to the G-band. This shoulder is located at ~1620 cm⁻¹ and is referred to as the G*-band[52]. In the current study, although we cannot see direct evidence for this G*-band as a shoulder to the G-band, we do observe an increase in scattering intensity on the high frequency side of the G-band. It was found necessary to incorporate a broad Lorentzian band centered near ~1600 cm⁻¹ to fit Raman spectra to account for this scattering. It could well be that the presence of this 1600 cm⁻¹ component in our fits is just a measure of new G* scattering.
We also considered the processing combination of H$_2$O$_2$/HCl for the first two steps. However, we have not shown the Raman spectrum of H$_2$O$_2$/HCl in Fig. 6-1, since the subsequent HCl step has no measurable effect on the Raman spectrum.

Finally, it is very interesting to observe the changes in the Raman spectrum associated with HTVA (high temperature vacuum annealing). As observed in the Raman spectrum of Fig. 6-1(f) and (g), a vacuum anneal at 1100 °C for 1 hr on DO/HCl and DO/HNO$_3$ processed material is very dramatic. All the lines narrow, the D-band intensity decreases, and the Raman spectrum returns to that of the raw soot. This indicates that most of the wall disorder introduced by chemical processing can be removed by the HTVA step. In fact, it appears that the skeletal “holes” (i.e., missing C-atoms) produced in the SWNT wall may drift to the open tube ends where they “evaporate”. We can observe the removal of the functional groups via IR spectroscopy, as discussed below.

Although the physical or chemical reasons are not yet clear, we find that the ratio of the scattering intensity in the R-band (I$_R$) to that of the G-band (I$_G$) is sensitive to the chemical processing. Our results show that higher ratios I$_R$/I$_G$ are more typically found in SWNT materials with low D-band intensity and narrow G-band components. In the case of DO/HCl processing, it is difficult to notice any significant change in either the D-band intensity or the G-band component width relative to that in the raw soot. However, the ratio I$_R$/I$_G$ changes noticeably. After HTVA, the I$_R$/I$_G$ ratio increases, and the ratio returns to that observed in the raw soot. We propose that the decrease in I$_R$/I$_G$ is associated with a reduction in I$_R$. I$_R$ is therefore proposed to be more sensitive to disorder than I$_G$. 
The major impact of chemical treatment on the R-band is a reduction of intensity. However, we can also say the following about the effects of chemical treatment on the R-band frequency: [30] HCl has little or no effect on the R-band frequency, [30] H$_2$O$_2$ produces a small upshift of $\sim 4$ cm$^{-1}$, (3) HNO$_3$ may produce a small ($\sim$1-2 cm$^{-1}$) upshift, but this upshift is difficult to quantify given the weak nature of the R-band after nitric acid treatment. It is interesting to consider why the shift of the G- and D-band can be so easily observed while the R-band shift is so small as to be difficult to measure. The reasons could be many, e.g., the difference in the % effects of doping on the bond bending vs bond stretching force constants, and the admixture of the bond bending and stretching in the various eigenmodes (e.g., R-, D-, G-) are different and therefore a complicating factor. However, consider the following argument. If we say that the mode frequency is simply related to the square root of the change in an effective force constant, then a 0.1 % change in the effective force constant for a particular mode leads to a 0.05% change in the mode frequency. Further, if we consider the same % change in the effective force constant for the modes at $\sim$160 cm$^{-1}$ (R), $\sim$1300 cm$^{-1}$ (D) and $\sim$1600 cm$^{-1}$ (G), then we would expect the same percentage shift in the R- D- and G- mode frequencies. However, in terms of the actual cm$^{-1}$ shift, the high frequency modes would then upshift much more than the R-bands because they have significantly higher frequency, i.e., a 10 cm$^{-1}$ upshift of the G-band is equivalent to a $\sim$ 1 cm$^{-1}$ upshift in a $\sim$160 cm$^{-1}$ R-band mode. It is difficult at this time to separate out the effects of strain due to adding functional groups to the tube wall and the effects of strain due to electron transfer to (or from) the carbon skeleton. Compressive strain of the C-C bond or a change of the bond angles can lead to an upshift in vibrational mode frequencies. We can add that studies of charge transfer-
induced strain in graphite intercalation compounds space (GICs) have found similar upshifts to what we observe in carbon nanotubes exposed to nitric acid or hydrogen peroxide. For example, the reaction of nitric acid with graphite under mild conditions is thought to lead to the intercalation of nitrate ion between the graphene layers which removes electrons from the sp² carbon network and induces an upshift in the G-band of the GIC by ~ 10-20 cm⁻¹, similar to what is observed here for SWNTs. In the case of GICs, it is thought that the reaction with nitric acid under mild conditions does not disrupt the carbon skeleton via the removal of carbon and/or the addition of functional groups.

We have also examined HRTEM images of bundles of SWNTs that were subjected to various chemical processes. Inspection of these images indicates to us that HRTEM is far less sensitive in exposing disorder in the carbon skeleton than Raman scattering. Only under extreme processing conditions in HNO₃, we were able to see evidence of large holes in the nanotube wall. We can conclude that Raman scattering is far better a probe of disorder when the tube walls are largely intact.
Next we show how the IR spectroscopy of SWNT material during processing can be used as an important complementary probe to Raman scattering. We follow the evolution of the IR spectrum with the same set of samples as discussed above. Unfortunately, the IR activity associated with added functional groups is somewhat difficult to observe. After chemical processing, the %wt fraction of the sample identified with functional groups is perhaps on the order of ~ 5 wt%, at the most. Only those groups that are most numerous, and those having strong IR activity will be detected. Furthermore, the optical absorption in the mid-IR region is dominated by electronic
contributions from the SWNTs. To see the vibrational modes of the functional groups (and the IR modes of the SWNT[ ]), the electronic contribution should be removed from the spectrum. First, we show how this electronic contribution is removed.

In Fig. 6-2 we show the actual normalized transmission spectrum for a SWNT film on a ZnSe substrate (indicated as (a)). The effects of reflection/absorption loss in the ZnSe have been removed from (a), as discussed in the experimental section. To enhance the visibility of the sharp structure, we subtract the background identified with the electronic contribution by fitting it to a cubic polynomial, shown as the dotted line (b). The difference spectrum (i.e., (a-b)) is shown at the bottom of Fig. 6-2 as (c). The parameters of the cubic polynomial are chosen to produce a flat baseline for (c).

In Fig. 6-3 we show the evolution of the mid-IR spectrum of SWNT material after processing for amorphous carbon removal (i.e., oxidation step). The spectra in Fig. 6-3 are the difference spectra; the particular electronic contribution has been removed. The difference spectrum for the raw soot appears at the bottom, and at the top we display the difference spectrum of purified material processed by DO/HCl/HTVA=1100°C and by DO/HNO₃/HTVA=1100°C. These top two spectra are for purified and annealed SWNTs. They represent the vibrational contribution of the “cleanest” material. The structure that appears in these top two spectra should either be identified with SWNT IR modes[54] which will be discussed in Ch.7, or with the most tenaciously bound functional groups, or defects. According to studies on other sp² carbons, on HTVA=1100°C treatment should remove most of the functional groups (the hydrocarbon groups are the most difficult to remove)[109]. These upper two spectra should be very helpful in setting the baseline for intrinsic SWNT IR activity, and allow the identification of functional groups that become
attached during chemical processing. We begin with a brief description of the structure in these two top spectra. First of all, there are two artifacts identified with the spectrometer in all the spectra in Fig. 6-3: a prominent triplet at 2900 cm\(^{-1}\) and a weaker narrow peak at \(~\sim 1250\) cm\(^{-1}\). These are identified by the asterisks in the figure. However, the triplet at \(~\sim 2900\) cm\(^{-1}\) has been assigned as C-H\(_n\) functional groups introduced by atomic hydrogen generated in cold plasma\[105\], or as C-H stretching mode of alkyl chain in octadecylamido [95] functionalized SWNTs[101]. In our spectra, we believe that the 2900 cm\(^{-1}\) triplet is associated with hydrocarbon contamination in our spectrometer. Most of the peaks in the top two “baseline” spectra on purified and annealed material in the range 800 – 1760 cm\(^{-1}\) have been assigned previously to 1\(^{st}\) and 2\(^{nd}\) order IR modes of SWNTs[54]. It should also be mentioned that all of the structure seen in these top two spectra have also been observed in material vacuum annealed to 1400 °C[54]. So it is unlikely that the peaks in the top two spectra in Fig. 6-3 can be identified with functional groups, as they should be removed during a 1400°C HTVA[109].

We now discuss the new IR bands that appear after chemical processing. For the case of oxidative removal of AC, the results are shown for DO and H\(_2\)O\(_2\) reflux in the middle of Fig. 6-3. The results after acid processing are shown in Fig. 6-4.
We consider first the IR spectrum of the raw soot (Fig. 6-3 (a)). Many bands from functional groups can be seen in (a) that are not present in our “baseline” spectra Fig. 6-3 (d) and (e). For example, the 1101 cm$^{-1}$ band in Fig. 6-3(a) is located within the range expected for C-O stretching modes in ethers, esters, alcohols or phenol compounds, and the 1710 cm$^{-1}$ band can be assigned to carbonyl (C=O) stretching in ketones, aldehydes or carboxylic acid groups[109-111]. For aldehyde groups, one or two bands assigned to the aldehydic C-H stretching, or the Fermi resonance between the
fundamental aldehydic C-H stretching and the first overtone of the aldehydic C-H bending vibration, should generally appear in the 2695 -2830 cm\(^{-1}\) range. However, these high frequency bands are not observed, so the 1710 cm\(^{-1}\) band is probably associated with either ketone or carboxylic acid groups. A prominent broad band (3100 -3600 cm\(^{-1}\)) can be observed in many of the IR spectra of Fig. 6-3. This broad band is assigned to contributions from a variety of O-H stretching modes. The width indicates that several different - OH containing groups are probably present in many different chemical and carbon environments. The frequency is somewhat lower than observed for free molecules and is instead characteristic of coupled acid and alcoholic hydroxyl functionalities. Since the -OH stretch band is present, the C=O band at 1710 cm\(^{-1}\) should probably be identified with carboxylic acid groups. We also should consider the presence of ketone groups. If a high frequency shoulder is seen on the ~1710 cm\(^{-1}\) band (the shoulder is apparent in the figure), we should also consider the presence of α,β-unsaturated and benzoate esters. Since there is AC and possible polyaromatic hydrocarbons in the raw soot, it must be said that the functional groups we can see by their IR signature in the raw soot are not necessarily on the tube walls, but could be elsewhere in the sample. As reported by Zhang et al[86], a very broad band at ~1100cm\(^{-1}\) was observed in the raw SWNT soot grown by the CVD process. However, they did not make any assignment for this band. Zhang et al.[86] and Kukovecz et al.[96] did not observe a band at ~1700cm\(^{-1}\) in their raw soot samples.

After dry oxidation (DO) of the raw SWNT soot at 355°C for 20 min (Fig. 6-3(b)), the IR band at ~ 1100 cm\(^{-1}\) is reduced, and the broad –OH absorption between 3100 and 3600 cm\(^{-1}\) has been removed. These observations suggest that many of the functional
groups seen in the spectrum of the raw soot (Fig. 6-3(a)) may be attached to amorphous carbon or other carbonaceous fragments which were removed by dry oxidation. One intriguing feature in Fig. 6-3(b) is the appearance of additional absorption in a broad band with structure located between ~1300 and 1600 cm\(^{-1}\); we are unable to assign this band. It is also interesting that although very little, or no change was observed in the Raman spectrum upon dry oxidation of the raw soot, a considerable change in the IR spectrum is evident. Our IR data shows clearly that oxygen containing functional groups appear after dry oxidation (~1300 and 1600 cm\(^{-1}\)). Thus IR can be seen to be a complimentary and powerful probe of chemical changes in this carbon system.

A reflux in 30% H\(_2\)O\(_2\) has also been reported to remove AC from SWNT material[95]. The AC phase can be preferentially oxidized to CO\(_2\) gas. For our H\(_2\)O\(_2\)-processed sample, the IR spectrum (Fig. 6-3(c)) exhibits enhanced absorption near ~1730 cm\(^{-1}\). This is consistent with the formation of additional carboxyl groups on the SWNT surface. The band in the H\(_2\)O\(_2\) processed material is enhanced and upshifted to 1734 cm\(^{-1}\), relative to its counterpart in the raw soot (~1710 cm\(^{-1}\)). After H\(_2\)O\(_2\) reflux, very broad bands also appear in the ~3230 – 3500 cm\(^{-1}\) range, and identified with O-H stretching modes. The broad low frequency component of this O-H band with a peak at ~3234 cm\(^{-1}\) (lower in intensity) is identified with O-H stretching from coupled carboxylic acid groups, and the higher frequency band at ~3390 cm\(^{-1}\) with alcoholic or phenolic groups. The frequency of these vibrations is sensitive to hydrogen bonding between functional groups. The low frequencies observed for both broad -OH bands in Fig. 6-3(b) may be the result of coupling to adjacent O-containing groups. The C-O stretching vibrations in alcohols and phenols also exhibit bands in the 1000- 1260 cm\(^{-1}\) range; their
frequency depends on the details of the coupling to C-C stretching vibrations. The bands
at ~ 1035 cm\textsuperscript{-1} and 1100 cm\textsuperscript{-1}, shown in the spectrum of Fig. 6-3(c), could therefore be
tentatively identified with C-C-O stretching in unsaturated hydroxyl groups, and the peak
appearing at ~ 1315 cm\textsuperscript{-1} in Fig. 6-3(c) might be associated with the characteristic
vibrational mode resulting from interaction between O-H bending and C-O stretching in
phenol groups\[112\].

There are several interesting changes in the IR spectrum at high frequency (>1500
cm\textsuperscript{-1}) after H\textsubscript{2}O\textsubscript{2} processing. We observe a broadening and intensity enhancement of the
absorption band in the 1550 – 1650 cm\textsuperscript{-1} region. A band at ~1570 cm\textsuperscript{-1} in the raw soot
(Fig. 6-3(a)) that we have identified with a fundamental SWNT mode[71] appears to have
broadened and upshifted to ~1585 cm\textsuperscript{-1} after H\textsubscript{2}O\textsubscript{2} processing. It also now contains new
structure at ~ 1620 cm\textsuperscript{-1} and 1650 cm\textsuperscript{-1}, and these higher frequency modes are likely due
to localized C=C bonds, either in conjugation with carbonyl groups, or interacted with
carboxylic acids or ketones. Of course, there are many ways to couple and shift these
high frequency modes, so it is difficult to make definite assignments. For example, both
intermolecular and intramolecular hydrogen bonding with hydroxyl groups result in
delocalization of the \(\pi\) electrons of both unsaturated groups or C=O groups. These
couplings reduce the double-bond character of the C=O bond and downshift the IR bands.
For example, the C=O stretching mode of a quinone group, without conjugation, usually
appears at ~1715 cm\textsuperscript{-1}. Quinones that have both carbonyl groups in the same ring (which
therefore has conjugation) absorb in the 1655 - 1690 cm\textsuperscript{-1} region. With extended
conjugation, in which the carbonyl groups are coupled weakly and appear in different
rings, the absorption downshifts to 1635 - 1655 cm\textsuperscript{-1} region. Hence, there are many
possibilities here, and model compound reactions with clean SWNT material will be needed to sort this out. Mawhinney et al.\[102\] reported FTIR spectroscopic studies of the oxidation and etching of SWNTs using ozone at 298K. They assigned a 1650 cm\(^{-1}\) band to the C=O stretching mode of quinone groups added preferentially to the ends of the tubes. In our case, the appearance of also O-H stretching modes after H\(_2\)O\(_2\) reflux leads us to believe that coupling effects (i.e. both intermolecular and intramolecular hydrogen bonding with hydroxyl groups) also might be responsible for the downshift in C=O stretching mode, besides the production of surface-bound quinone groups with extended conjugation.

It seems conclusive from an IR band analysis that an H\(_2\)O\(_2\) reflux approach to AC removal leads to a substantial increase in carboxylic acid and hydroxyl (phenolic and alcoholic) groups relative to the amount found in the raw soot, or after DO. At the same time, our Raman spectral analysis, discussed above, show an enhancement in the D-band scattering intensity and a broadening of the G-band for H\(_2\)O\(_2\) processing, but not for DO processing. From TGA and HRTEM, we know that H\(_2\)O\(_2\) reflux definitely removes most of the AC component from the material. So, there is a consistent picture of the difference in the outcomes from dry oxidation (DO) and H\(_2\)O\(_2\) reflux of raw SWNT material: while both oxidative processes lead to removal of AC, H\(_2\)O\(_2\) reflux yields a much stronger functionalization of the nanotube wall. For electronic applications of processed SWNTs, for example, DO should be preferred. Recall that the H\(_2\)O\(_2\) reflux was observed to upshift the G-band by \(\sim 4\) cm\(^{-1}\). The IR band that we have identified with one of the nanotube (tangential) IR modes also upshifts (by \(\sim 15\) cm\(^{-1}\)). We can see from our work here, it can be seen that band upshifting can occur both by charge transfer (NO\(_3\)) and
functionalization with negatively charged groups (-OH). In both cases, the upshifting of these tangential SWNT bands is associated with the withdrawal of π electrons.

SWNT is a macroscopic realization of a resonant C=C conjugated system. During strong chemical processing, it appears possible to create additional defects where carbon atoms are eliminated, the ring structure is now open, localized C=C bonds are created, O-containing groups can be added to this defect to stabilize the structure. This should lead to an upshifting of the IR C≡C bands and a C=O band should appear. A strong coupling between neighboring C=O functional groups will downshift the C=O band and may be a signature of a high density of C=O groups. Zhang et al.[86] observed that the band at ~1735cm⁻¹ that we identify with -COOH addition gradually downshifted to ~1720cm⁻¹.

Fig. 6-4: Difference spectra (c.f. caption to Fig. 6-2) of chemically processed SWNT materials: DO/HCl (a), DO/HNO₃ (b) and H₂O₂/HCl (c). Spectral artifacts are indicated with asterisks(*)[30].
with longer acid treatment. They suggested that longer acid treatment introduces more –COOH and –OH groups to the tube walls and ends, and this lowers the frequency of the –C=O stretching mode. Their observation supports our assignment of new structure at ~1620 cm\(^{-1}\) and 1650 cm\(^{-1}\) appears after refluxing the tubes in H\(_2\)O\(_2\).

We next turn to the analysis of the IR spectroscopic signatures of acid processing of SWNT material to remove the metal growth catalyst. The material was first processed to remove the AC. In Fig. 6-4 we show the IR spectra of DO/HCl (spectrum (a)) and DO/HNO\(_3\) (spectrum (b)) processed material. The effects on the IR spectrum from H\(_2\)O\(_2\)/HCl processing is indicated in Fig. 6-4 spectrum (c). We consider first the effect of HCl reflux on DO material. Basically, the only significant changes in the IR spectrum after HCl reflux is a reduction in the absorption near ~1400 cm\(^{-1}\) and an enhancement in absorption ~ near 1100 cm\(^{-1}\). As discussed above, we have had difficulty assigning the 1400 cm\(^{-1}\) band to a particular functionality. The fact that the 1400 cm\(^{-1}\) band intensity is reduced, certainly strengthens our opinion that the ~1400 cm\(^{-1}\) band is associated with an unknown functional group rather than a nanotube mode. Above, we assigned the ~1100 cm\(^{-1}\) band to C-O stretching; C-O containing groups appear to have been added by HCl reflux. However, the chemistry behind these C-O additions needs to be clarified in further work. Interestingly, for DO/HCl processing of raw SWNT soot, little or no changes in the Raman scattering from the D- or the G-bands were observed, i.e., the D-band intensity and the G-band component widths did not change. However, the IR spectrum shows a clear change: C-O containing functional groups have been added to the tube wall. Hence, the reduction in the Raman intensity \(I_R/I_G\) for DO/HCl processed SWNT must be due to C-O functionalization.
Processing DO material with HNO₃ can be seen in Fig. 6-4(b) to lead to the addition of carboxylic acid and hydroxyl groups (c.f., broad bands with maxima at ~3234 cm⁻¹ and ~3412 cm⁻¹). From the relative intensity of these two broad components, we can conclude that HNO₃ leads to a larger population of carboxyl relative to hydroxyl group on the SWNT wall. Several groups[86, 96, 101] have also observed the enhancement of the band at ~ 1730 cm⁻¹ after refluxing SWNT samples in HNO₃ or mixed acid such as HNO₃/H₂SO₄. They assigned this band to C=O stretching mode in carboxylic acid groups. We also observe an upshift in the SWNT band at ~1575 cm⁻¹ (DO) to ~1586 cm⁻¹ (DO/HNO₃) that is consistent with charge transfer (i.e., via the attachment of NO₃⁻ ions) and possibly mitigated by localization of C=C bonds and coupling to C=O modes, as discussed above. The band in the DO/HNO₃ material (Fig. 6-4(b)) at ~1230 cm⁻¹ probably should be assigned to O-H bending mode, or C-O stretching mode.

We next consider, from the perspective of IR spectroscopy, the effect of a completely “wet” purification of the SWNT soot, i.e., H₂O₂ reflux to remove the amorphous carbon, and a mild mineral acid reflux (HCl) to remove the metal. To see the effects of HCl on the “wet” oxidized material, we need to compare the spectrum(c) in Fig. 6-4 to that discussed previously in Fig. 6-3. From this comparison, it is clear that HCl induces replacement reactions that remove many of the O-containing functional groups. This view is consistent with two observations: i) the broad ~3390 cm⁻¹ O-H stretching band in H₂O₂ refluxed material (Fig. 6-3 spectrum(c)) (from the hydroxyl groups) is now less intense. The high frequency component is also upshifted from 3390 to 3460 cm⁻¹, indicating a decoupling of hydroxyl groups, consistent with a decrease in their population; ii) the broad strong bands in the ~1500-1700 cm⁻¹ region for H₂O₂ refluxed
material (Fig. 6-3(c)) show a significant reduction in intensity. The bands are now narrower. Similar to the IR spectrum for the DO/HNO₃ material, one relatively sharp band at ~1585 cm⁻¹ identified with the IR active tangential nanotube mode is observed, upshifted by charge transfer from its position at ~1570 cm⁻¹ in the raw soot.

Finally, we consider the IR signatures that evolve from a short term high temperature vacuum anneal (HTVA) of the DO/HCl and DO/HNO₃ material. These spectra appear at the top of Fig. 6-3. We have discussed the outcome from this anneal from the perspective of the Raman bands. As discussed above, the Raman data show that an anneal in ~1100 °C in vacuum for one hour reduces the D-band intensity and the G-band component width, returning the SWNT structure to almost the same condition as was observed for tubes in the raw soot. We expect that high temperatures should remove many of the functional groups produced by dry or wet chemical processing. Indeed, according to a review of many studies of functional groups on high surface area amorphous and graphitic carbons by Kinoshita[109], various groups leave at characteristic temperatures. Summarizing his review, carboxylic and lactone groups begin to decompose first at about 250°C and are volatilized. In the 500°C - 900°C range, phenol and quinone groups have decomposed almost entirely. And at 900°C, the -OH content decreases significantly, and other oxygen containing surface groups are almost completely eliminated. Hydrogen, on the other hand, is removed from amorphous carbon by heat treatment between 900°C and 1200°C. Based on the review by Kinoshita[109], our HTVA at 1100°C for 1h should remove all O-containing functional groups; we expect also that any –CH groups present should also be decreased drastically[54].
Comparing the IR spectra for DO/HNO$_3$/HTVA and DO/HCl/HTVA to that of the raw soot (c.f., Fig. 6-3(a), (d), (e)), we see that the broad bands in the 3000-3600 cm$^{-1}$ region are removed, as well as many of the broader and stronger bands below 1600 cm$^{-1}$ present in the starting material. Furthermore, after removal of the AC by H$_2$O$_2$ reflux (c.f., Fig. 6-3(c)) and DO (c.f., Fig. 6-3(b)), broad –OH bands remain in the material which we have attributed to functional groups. By comparing the top two IR spectra in Fig. 6-3 to those that appear below in the same figure, as well as to those for acid–processed material in Fig. 6-4, we can say that the HTVA indeed removes most of the functional groups either present in the starting material, or added by chemical processing.

However, it is clear from the top two IR spectra in Fig. 6-3 that there are some small differences in the purified HTVA material, depending on whether HCl or HNO$_3$ was used to remove the metal. Annealing of the DO/HCl material at higher temperatures (up to ~1400 °C) generated a material whose IR spectrum almost identical to that shown for DO/HNO$_3$/HTVA material in Fig. 6-3 spectrum (e). The weak structure that remains in the spectra(d) and (e) of Fig. 6-3 for HTVA purified SWNT material below ~1700 cm$^{-1}$ will be discussed in terms of the predicted one- and two-phonon IR absorption in Ch.7. The band positions for the weak structure that remain after HTVA are reported to be in reasonable agreement with theory[54].

In Table 6-1, we summarize the main IR bands observed for functional groups in the raw soot and chemical processed SWNT material, as well as our assignment for those bands. The assignments we make in Table 1 are plausible, but are by no means certain. Follow-up work on model compounds will be needed to confirm these tentative assignments.
6.4 Summery and Conclusions

This work presents a first step toward the use of IR and Raman spectroscopy as a probe for SWNT chemistry and the evaluation of purified SWNT material after reactions. We expect that much progress will now be made in understanding SWNT chemistry, as cleaner SWNT material becomes available, and these spectroscopies are applied to probe the material. Higher annealing temperatures should be avoided, however, as nanotube coalescence and other transformations begin to take place at 1400 –1600°C. This work represents an early study using both IR with Raman spectroscopy to observe the effect of several common chemical schemes to remove amorphous carbon and growth catalyst from large batches of ARC derived SWNTs. Our objective was to learn which of these processes produced the most damage to the carbon skeleton and which functionalities were added via exposure to specific chemicals. This work is one of the first, if not the
first, work to indicate which purification procedure is to be preferred based on observations of damage to the carbon skeleton or added functionalities. This work is the first of its kind to address purification from the vantage point of vibrational spectroscopy. Considerable progress, however, is needed to take this work to a higher (more quantitative) level, such as could be obtained from correlating IR intensities with % functionalization. This type of study is best done with model SWNT compounds. In the present work, we must be content to simply learn about the effects of the particular (commonly used) purification scheme by noticing how they affect the D-band Raman scattering, or for example, when the intensity from carboxyl vibrations increase or decrease. The next step, set aside for future work, is to make quantitative contact between IR spectroscopy (e.g., IR band intensities) and some other probe, e.g., TG-MS, that can tell us about the nature and quantity of functionalites present. It is hoped that this work will spark interest in model compound reactions of SWNTs with various reagents, and that IR and Raman spectroscopy can be used to characterize the reactions.
Chapter 7
Infrared-Active Vibrational Modes of Single-Walled Carbon Nanotubes

7.1 Introduction

Despite the fact that SWNTs have been produced in the laboratory and widely studied for more than ten years[34, 36, 113, 114], relatively little is known about the infrared (IR)-active vibrational modes of this important macromolecule. In contrast, Raman scattering has been used almost from the time of the discovery of the SWNT to probe the vibrational modes of carbon nanotubes[55, 115, 116]. The Raman studies have been facilitated by a strong resonance in the scattering cross section, and this resonance has been identified with interband transitions between mirror image van Hove singularities (vHs) in the quasi-1D electronic density of states (DOS) [55, 115, 116]. Recently, this interpretation of the resonance has been called into question, however, as a convincing set of experiments[117] and theoretical calculations[118-120] indicate that strong excitonic effects may overwhelm the interband dipole activity near the band edges.

SWNT IR vibrational modes, on the other hand, are much more difficult to detect than their Raman-active counterparts. The difficulty stems, in part, from the fact that SWNTs do not support a static dipole moment, and must therefore generate a dynamic dipole moment, which is usually much weaker. The nature of the dynamic dipole
formation in SWNTs, and how it depends on bond-bending and stretching, is contained in
the experimental IR intensity. Parabolic phonon dispersion in 1D must also lead to van
Hove singularities (vHs) in the one- and two-phonon DOS and, depending on the strength
of the activity, lead to sharp IR phonon features. An earlier report of phonon modes
observed by reflectance from unpurified powder containing SWNTs and graphitic
nanocarbons produced by the arc process has appeared[121]. Two dominant structures
were observed after the derivative of the SWNT powder diffuse reflectance was inspected,
one band at ~868 cm\(^{-1}\) and the other at ~1590 cm\(^{-1}\) (frequencies close to those assigned to
A\(_{2u}\), and E\(_{1u}\) modes of graphite).

In this paper, we report the first systematic experimental attempts to observe the
IR-active modes of SWNTs. In concert with theoretical calculations on free-standing
SWNTs (i.e., without nanotube-nanotube, or nanotube-solid surface interactions), we are
able to assign much of the sharp structure in the IR spectra of purified and annealed
SWNTs to one- and two-phonon lattice mode bands.

### 7.2 Experimental

Bundles of typically ~ 100 or more SWNTs with tube diameters in the range
1.2<d<1.6 nm were grown by the electric arc method (CarboLex, Inc.). The material was
purified via a three-step process, which were discussed in detail in Ch.4. The last step
involved a 4-24 hour vacuum anneal in ~1x10\(^{-7}\) Torr at 1100 or 1400°C. Transparent
bundled nanotube films were deposited from a 2-propanol suspension onto ZnSe
substrates for the IR studies. Raman spectra were also collected from these samples and showed narrow radial and tangential Raman bands, consistent with the literature[70, 71]. Room temperature transmission spectra on these films were collected using a BOMEM DA3+ Fourier Transform Infrared (FTIR) spectrometer employing a cooled MCT detector with a spectral resolution ~4cm⁻¹.

7.3 Results and discussions

The vibrational modes that are excited in a periodic structure in a 1st order IR or Raman process involve the long wavelength (or q=0) modes. The SWNT structure can be classified according to whether the tube is achiral (i.e., “zigzag” (n,0) or “armchair” (n,n)) or chiral (n,m ; n≠m)[34, 36]. Chiral nanotubes can exhibit very large (i.e., long) one-dimensional (1D) unit cells compared to achiral tubes of the same diameter. It is indeed a surprising result from the group theory of nanotubes[41, 122] that the number of IR- and Raman-active modes in a chiral tube is almost the same as that for an achiral tube with a much shorter unit cell. In a graphene sheet, the crystal symmetry forbids a q=0 IR-active optical phonon. However, this rule is broken by the cylindrical boundary condition of the SWNT. Group theory selection rules indicate that there are only 15 or 16 Raman-active modes and 7 to 9 IR-active modes for a single-wall carbon nanotube depending on the chirality of the specific tube[34, 36, 41, 122], despite the large number of vibrational modes. A different set of selection rules has been presented in ref [123]. The difference between these two sets of selection rules lies in a disagreement over the
correct set of covering operations for the specific (n,m) nanotube[36]. In an IR experiment, all the tubes in the ensemble can be probed at the same time, whereas the resonance in the Raman cross section allows only a few (n,m) to be probed in the same experiment.

Fig. 7-1: Difference spectra for raw and purified SWNT samples annealed at various temperatures:(a) as-delivered arc-derived SWNT material with degassing at 200°C, (b) after purification and degassing at 200°C, (c) after purification and HTVA= 1100°C. Spectrum (e) is that of a sample with HTVA=1400°C and a polynomial fit to a smooth background (dotted line). The inset: the entire spectrum of a sample exposed to HTVA=1100°C (from the Far IR to the UV on a logarithmic frequency scale). The asterisk (*) indicates a triplet, which is a spectral artifact.
Lattice dynamics calculations show that modes below \( \sim 400 \text{ cm}^{-1} \) exhibit significant radial character, whereas modes above \( \sim 1100 \text{ cm}^{-1} \) exhibit primarily tangential C-atom displacement\[34, 36, 41, 122\].

Two-phonon Raman and IR excitations exist above \( \sim 1600 \text{ cm}^{-1} \). These 2-phonon excitation processes must have a \( q = q_1 + q_2 = 0 \) to satisfy momentum conservation law. On the other hand, vibrational modes of functional (chemical) groups, e.g., -COOH, -OH, C-H, may also be present\[71, 109\]. The details of functional groups on the tube wall or purified SWNTs are discussed in Chap.6. It is therefore important to have some experimental basis for the assignment of the observed IR structure to intrinsic nanotube modes. Our approach to this problem has been to study the evolution of the \( T=300 \text{ K} \) IR spectra in a series of purified samples that have each been exposed to a successively higher temperature \( T \) vacuum anneal (HTVA). Eventually, \( (T \geq 1200^\circ \text{C}[109]) \) most of these groups have desorbed as gas, and the vibrational mode intensity is expected to decrease significantly as the temperature is increased from 600 to 1200°C.

In Fig. 7-1, we display the \( T=300 \text{ K} \) optical density (OD) of several SWNT films. Here the OD = - \( \log_{10} T \), where \( T \) is the transmission of the sample, and the OD is a measure of the optical absorption. The inset at the top of the figure shows the OD on a log frequency scale from the Far IR to the UV for a purified sample with HTVA=1100°C. All the strong broad features in the inset are due to electronic transitions, and their position is in good agreement with the literature \[106, 124-127\]. The broad peak (labeled \( E_c \)) at \( \sim 200 \text{ cm}^{-1} \) is consistent with electronic transitions across a range of curvature-induced small energy gaps\[125, 126\]. Between \( \sim 4000 \text{ cm}^{-1} \) and \( \sim 18,000 \text{ cm}^{-1} \), three bands are observed labeled (\( E_{11}^s, E_{22}^s \) and \( E_{11}^m \)). They have been observed previously and
identified with electronic transitions across the much larger “chirality” gaps $E_{\text{g}}^{s(m)}$ [106, 124, 127]. However, as we discussed above, strong excitonic effects need to be considered in the interpretation of this structure[118-120]. Finally, on the basis of band structure calculations[106, 127] and the observed dielectric function of graphite[66], the strongest peak at $\sim$35,000 cm$^{-1}$ in Fig. 7-1 (labeled M) is identified with the “cylindrical analog” of the $\pi-\pi^*$ electronic interband absorption of a graphene sheet.

The relatively weak IR-active vibrational structure associated with the nanotube film is barely visible on the OD scale of the inset. In Fig. 7-1(e) we display the mid-IR spectrum of a purified sample with HTVA=1400°C. Weak sharp structure can be seen riding on a smooth background. To enhance the visibility of the sharp structure, we first subtract the background identified with the electronic contribution (polynomial fit), and plot the difference spectrum, as shown in (d). We have used a 3rd order polynomial with adjustable coefficients to fit the background. The parameters of the cubic polynomial are chosen to produce a flat mid IR spectrum after subtraction. The polynomials we have used do not produce the variety of 10-20 cm$^{-1}$ wide structures observed in the difference spectra. The dotted line under the spectrum (e) shows the polynomial fit to the particular electronic background. Other vibrational (difference) spectra labeled (a), (b) and (c) (see bottom of Fig. 7-1) were obtained similarly. They correspond, respectively, to (a) as-delivered SWNT material degassed at 200°C, (b) after purification and degassing at 200°C, and (c) after purification and HTVA= 1100°C. The horizontal bars at the bottom of Fig. 7-1 identify the typical frequency intervals in which IR-active modes occur for the specified chemical groups. It is clear that some of the strong broad bands in the difference spectrum for the as-delivered and chemically-processed SWNT material match
up well with these bars[109]. Because these IR bands can be removed with HTVA, they can be assigned to the specified chemical functional groups indicated and are not SWNT modes, which was explained in Ch.6[71]. For example, in spectrum (a), a very broad band with a maximum near 3200 cm$^{-1}$ can be identified with –OH from carboxylic acid groups attached either to SWNTs or to other nanocarbons present in the as-delivered material. After selective oxidation, chemical purification and degassing at 200°C, this band is reduced in strength; it disappears completely after HTVA=1100°C. Also, the feature at ~1710 cm$^{-1}$, which is near the C=O stretching modes, is diminished by our purification and degassing at 200 °C, yet we see a growth of the feature near the C-O-C stretching mode region after chemical processing. Most of the IR activity identified with chemical functional groups in Fig. 7-1(a) can be removed by HTVA=1400°C, except for the 2900 cm$^{-1}$ triplet. This triplet has been observed previously and identified with C-H$_n$ functional groups introduced by atomic hydrogen generated in cold plasma.[105] We believe that the 2900 cm$^{-1}$ triplet is associated with hydrocarbon contamination in our spectrometer; the feature should have been removed by the HTVA=1400°C[71]. The broad asymmetric band at 1730 cm$^{-1}$ in (d) has also survived HTVA=1400°C. It lies above the maximum frequency for one-phonon excitation in SWNTs. Although this feature has a frequency close to that observed for IR bands in organic compounds with -C=O stretching modes, we find that the 1710 cm$^{-1}$ band changes very little with purification or annealing: it does undergo slight changes of shape, and is reduced somewhat in intensity and upshifts by ~20 cm$^{-1}$, and it is still present after HTVA=1400°C. Therefore, the ~1730 cm$^{-1}$ feature in Fig. 7-1 (e) appears to be a 2-phonon SWNT excitation.
In Fig. 7-2, we expand the vibrational spectrum of a HTVA=1400 °C film (Fig. 7-1(d)) in the range 600 – 1800 cm⁻¹, and fit the peaks to Lorentzians. We believe this film represents the most intrinsic SWNT sample in this study. The thin solid line through the data is the composite fit, and the individual Lorentzians are displaced below the spectrum for clarity. Their full width at half maxima (FWHM) are in the range 10-20 cm⁻¹, and these narrow features can be observed in all spectra in Fig. 7-1.

Of the 18 narrow bands in Fig. 7-2 in the 1st order region (below 1600 cm⁻¹), 8 are close in frequency to IR modes calculated for achiral SWNTs in the diameter range of 1.2nm and 1.6nm which is close to the diameter distribution of the SWNTs used in this experiment; the IR frequencies from our current model calculations from Saito’s group on achiral tubes of similar diameter appear as vertical bars below this spectrum[128]; below these bars are another set of bars representing the IR frequencies calculated by Jishi et al. previously[122] for achiral tubes with diameters similar to our sample.
However, Jishi’s result[122] shows higher scatter in frequency than current work over different sets of (n,m). The difference between Jishi’s[122] and current calculation[128] is the difference choice of force constants. The details about the choice of force constants will be discussed later. As Jishi et al. have shown previously, the diameter dependence of the frequencies for $q=0$ Raman- and IR-active modes above $\sim 1000 \text{ cm}^{-1}$ is relatively unimportant (below 400 cm$^{-1}$, however, the diameter dependence of all phonon mode frequencies is strong). So, for the high frequency modes, the fact that we have a chirality/diameter distribution does not present as serious a complication for the spectral analysis as one might expect. Based on the proximity in frequency between many of the observed narrow IR features in Fig. 7-2 below 1600 cm$^{-1}$ with calculated $q=0$ modes, we feel that we can make some tentative assignments of the bands observed in Fig. 7-2 at this stage. The results of these identifications are summarized in Table 7-1.

For this work, Saito’s group have developed a new approach for calculating phonon dispersion for specific (n,m) tubes and wave vector $q$[128]. The rotational symmetry around the nanotube axis for calculation of phonon dispersion is adopted. Thus a $6N \times 6N$ dynamical matrix (refer to section 2.3 in Ch.2) is changed to $N$ $6 \times 6$ small dynamical matrices, where $N$ is the number of atoms in a primitive cell. This reduces the computational time significantly, but no changes in the numerical results are obtained in several specific cases examined closely. The force constants are modified to reproduce the resonant Raman scattering [129, 130] or inelastic X-ray scattering for graphite especially around the K point of the 2D graphene Brillouin zone (BZ)[131]. The force constants used by Jishi et al were fitted to neutron scattering data on graphite, but these data were relevant between the $\Gamma$ and M points of the BZ. Details of our phonon
calculations are given in ref.[36]. The small differences we observe with diameter (bottom Fig. 7-2, upper set of vertical bars) are perhaps not significant at the moment, amounting to a scatter as a function of diameter for nanotubes that is $\sim 10 \text{ cm}^{-1}$, although this scatter is comparable to the FWHMs of the features in Fig. 7-2.

The q=0 eigenvectors for the mid IR modes of a (10,10) nanotube are shown in Fig. 7-3, where the frequency and symmetry labels ($A_{2u}$ or $E_{1u}$) are indicated in each case. Fig. 7-3 clearly shows that the IR active modes as above $\sim 1100 \text{ cm}^{-1}$ exhibit primarily tangential C-atom displacement as mentioned previously. Calculated phonon dispersion from pf. Saito’s group including optical, acoustic and silent modes are shown in Fig. 7-
(a) and (b), respectively for (10,10) and (15,0) nanotubes. T denotes the magnitude of the unit vector along the tube axis, which is the size of Brillouin zone. Even though the number of Raman and IR active modes at q=0 are similar for different chiralities, Fig. 7-4(a) and (b) show that the total number of vibrational modes are quite different, and the trend of dispersion curves over entire Brillouin zone are very different.

Finally, we should also consider possible 2nd order (2-phonon) SWNT features that might be responsible for the structure in the IR spectrum. Two-phonon IR absorption can occur at a frequency \( \omega(q) = \omega_1(q_1) \pm \omega_2(q_2) \), where the \( \omega_j \) are the phonon frequencies; the total wavevector of the two-phonon excitation must satisfy \( q = q_1 + q_2 = 0 \). Here, we
only consider the case where two phonons are created \((\omega=\omega_1+\omega_2)\). In one-dimensional materials, we can also expect vHs in the one- and two-phonon density of states (DOS) that stem from states near the minima or maxima in the near-parabolic phonon dispersion. Thus 2-phonon excitations involving vHS could also lead to sharp structure in the IR spectrum.

In Fig. 7-5, we compare the calculated 2-phonon DOS from Saito’s group[ ] for three selected tubes (top three curves) with the experimental IR-spectrum. The 2-phonon DOS were calculated from the 2-phonon dispersion by adding all possibly chosen two branches from one phonon dispersion, for example Fig. 7-4(a), (b). The vertical bars above the experimental spectrum locate the calculated IR-active one-phonon frequencies. Note that the three tubes chosen for Fig. 7-5 are from the three families \((n,n)\), \((n,0)\) and \((n, m)\) \(n\neq m\). Despite the difference in chirality, the 2-phonon DOS or JDOS (J=joint) for these three tubes exhibits considerable similarity. It should also be noted that two curves are present for each JDOS: solid curve is the JDOS (as calculated), and the dotted curve is the JDOS smoothed by a convolution with a Lorentzian in Fig. 7-5. Fig. 7-5 The latter is done to mimic the effects of a moderately short phonon lifetime (0.1ps).[132] From the smoothed JDOS shown in the figure, we can say that the three different symmetry tubes chosen all provide a large 2-phonon DOS near \(\sim1110-1130 \text{ cm}^{-1}\), \(\sim1455 \text{ cm}^{-1}\), \(\sim1710-1750 \text{ cm}^{-1}\), 1860-1880 cm\(^{-1}\), \(\sim2450 \text{ cm}^{-1}\), \(\sim2610-2630 \text{ cm}^{-1}\) and \(\sim2880-2910 \text{ cm}^{-1}\), in agreement with experiment (c.f., Table 7.1).
7.4 Conclusions

In conclusion, we have studied the evolution of the IR-spectrum of purified SWNT samples that were annealed to high temperatures (up to 1400°C). The higher temperatures should remove all chemical functional groups. Through comparison with
theory, 8 out of the 18 IR bands that remain in samples annealed in the range 1100 °C - 1400 °C can be assigned to first order IR modes (A_{2u} or E_{1u}). The remaining 10 bands are assigned to two-phonon excitations.
Table 7.1 Comparison of experimental and theoretical IR structure. *Purified sample HTVA=1400°C (c.f. Fig. 7.1, Fig. 7.2) † Based on JDOS for (10,10), (15,0), (14,7)

<table>
<thead>
<tr>
<th>Expt (cm$^3$)</th>
<th>Theory (cm$^3$)</th>
<th>Assignment</th>
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<tr>
<td>682</td>
<td>670-691</td>
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<tr>
<td>906</td>
<td>774-775</td>
<td>1$^{st}$ order $A_1$</td>
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<tr>
<td>854</td>
<td>870-876</td>
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<td>956</td>
<td>970</td>
<td>2$^{nd}$ order $2E_1$(295+675) (15,0)</td>
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<tr>
<td>987</td>
<td>970</td>
<td>2$^{nd}$ order $2E_1$(295+675) (15,0)</td>
</tr>
<tr>
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<td>1034</td>
<td>2$^{nd}$ order $2A_1$(346+888) (10,10)</td>
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<tr>
<td>1095</td>
<td>1110-1130</td>
<td>2$^{nd}$ order $2E$(432+681) (10,10), $2E_1$(525+605) (15,0), $2E_1$(443+670) (14,7)</td>
</tr>
<tr>
<td>1164</td>
<td>1110-1130</td>
<td>2$^{nd}$ order $2E$(432+681) (10,10), $2E_1$(525+605) (15,0), $2E_1$(443+670) (14,7)</td>
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<td>1197</td>
<td>1110-1130</td>
<td>2$^{nd}$ order $2E$(432+681) (10,10), $2E_1$(525+605) (15,0), $2E_1$(443+670) (14,7)</td>
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<td>1455</td>
<td>2$^{nd}$ order $2E_2$(339+1117) (10,10), $2E_1$(343,1112) (15,0), $2E_1$(765+692) (14,7)</td>
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<tr>
<td>1708</td>
<td>1710-1750</td>
<td>2$^{nd}$ order $2A_1$(859+859) (10,10), $2E_1$(339+1406) (15,0), $2E_1$(681+1029) and $2E_1$(159+1551) (14,7)</td>
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<td>1730</td>
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<td>2$^{nd}$ order $2A_1$(859+859) (10,10), $2E_1$(339+1406) (15,0), $2E_1$(681+1029) and $2E_1$(159+1551) (14,7)</td>
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Chapter 8

Effect of the Tube Diameter Distribution on the High-Temperature Structural Modification of Bundled Singled-Walled Carbon Nanotubes

8.1 HRTEM study on SWNTs annealed at a successively higher temperature

8.1.1 Introduction

In the last fifteen years, structural changes in carbon nanostructures due to electron irradiation[133-138] as well as thermal treatment[39, 139-145] have been intensively studied both experimental and theoretically. For example, in 1992 Ugarte [133] demonstrated that graphitic onions can be obtained by irradiating amorphous carbon with a high-energy electron beam. Subsequently, many other in situ experiments on nanocarbons using high-energy electrons have reported striking structural transformations such as: graphitic onions to nanodiamonds[134], nanopeapods to double-walled nanotubes (DWNT)[137], tube-tube coalescence in bundled single-wall nanotubes (SWNT)[136], multi-wall nanotubes (MWNT) to graphitic ribbons[135], and carbon nanostructure engineering by combining high temperature and focused electron beam[138]. Furthermore, the evolution of nanocones[39], bundles of DWNT[142, 143] and bundles of SWNTs[139-141] subjected only to high temperature environments (in inert gas or vacuum) have also been studied. In situ electron irradiation and thermal
treatment are different processes. The former is a very anisotropic non-equilibrium process and in many cases, the particular structural transformation is determined by the direction of the electron beam[135].

Two surprising morphological changes have already been observed when heating bundles of SWNTs to high temperatures in an inert gas or vacuum. The first change, a coalescence of neighboring tubes into larger diameter tubes, occurs at temperatures between ~1300-1600 °C[141]. The second morphological transformation, in which tubes undergo massive bond rearrangement and transform into MWNTs, occurs at higher temperatures ~1600-2000 °C[139, 140]. Previous experimental work in this area has been on unpurified (as-grown) material that also includes amorphous carbon (a-C) and residual growth catalyst (e.g., Ni,Fe,Co). Therefore, the role of these impurities on the structural changes is not understood and studies on purified material are needed.

Our studies presented here were made on purified SWNT material. To further elucidate the transformations of SWNT bundles, we have made a systematic study of the thermal evolution of two bundled SWNT materials (ARC and HiPCO) in vacuum up to 2200°C. These two nanotube systems were chosen for study because they have significantly different initial (as-grown) tube diameter distributions. Although both SWNT systems evolve thermally to MWNTs, we found that the ARC material with the tighter initial diameter distribution evolves beyond MWNTs into a new form of multishell carbon filament, i.e., graphitic nanoribbons (GNRs)[146] which dominate the system after heat treatment above ~2000 °C.
8.1.2 Experimental Details

8.1.2.1 Synthesis and Thermal Treatment

The HiPCO tubes (CNI, Inc.) and Arc discharge tubes (ARC) (CarboLex, Inc.) were obtained from the vendors and purified as follows. Amorphous carbon (a-C) was removed by dry oxidation at ~350°C for ~20 min and then catalyst particles (Fe; HiPCO and Ni/Y; ARC) were removed by a 24h reflux in 6N HCl. The details of the purification of as-grown HiPCO and ARC SWNTs were described in Ch.4. The purified tubes were then placed in a high temperature vacuum furnace (“Red Devil”, R.D.Webb, Inc.) and degassed at 200°C over night. This was done to remove strongly bound O₂ at temperatures below which it can react with the sample (i.e., removing carbon as CO₂). After this long-term, low-T degassing step, the furnace was then ramped to the desired final temperature (1100-2200°C) at 10°C/min. After arriving at the desired “soak” temperature, the samples were annealed at this temperature for ~4 hours and then cooled to room temperature in ~8hr. Six different high temperature heat treatment temperatures (HTTs) were studied (1100, 1400, 1600, 1800, 2000 and 2200 °C). In every experiment, the pressure in the diffusion-pumped furnace was better than 10⁻⁵ Torr. The temperature of the sample was measured using either a retractable thermocouple (below 1600 °C) or an optical pyrometer.
8.1.2.2 Characterization

Samples for transmission electron microscopy were prepared by dispersing the material in ethanol; drops of this dispersion were deposited onto lacey carbon grids (from Ted Pella, Inc.). For TEM images of the bundle cross-section, nanotube powder (without dispersion in ethanol) was applied directly to the TEM grids. This procedure seemed to increase the number of bundles aligned perpendicular to the plane of the grid and therefore parallel to the e-beam. High-resolution transmission electron microscope (HRTEM) images were obtained with a JEOL 2010F (200 kV). Although the acceleration voltage in our experiments is low, special care was taken in order to minimize the exposure time and the electron current density through the sample before and during each image acquisition.

8.1.3 Results

8.1.3.1 Diameter distribution and Coalescence

In Fig. 8-1(a)-(c) we show representative HRTEM images of SWNT bundle cross sections of purified ARC and HiPCO material that have been vacuum-degassed at HTT=200°C for ~15hr. This temperature is too low to promote any C-C bond rearrangement; thus these tubes should exhibit the as-grown diameter distribution. In Fig. 8-1(d), we show diameter distributions of ARC and HiPCO tubes with HTT = 200°C, 1600°C, 1800°C determined from HRTEM image analysis. As-grown ARC
Fig. 8-1: High resolution TEM image of as-grown SWNT bundle cross-section of (a) ARC and (b,c) HiPCO materials; insets are schematic representations of the spatial arrangement of SWNTs in the bundle for each material. (d) Diameter distributions of SWNTs after Heat-Treatment Temperature (HTT) of 200, 1600 and 1800°C for ARC (left) and HiPCO (right).
nanotubes (HTT=200°C) were found to exhibit a most probable diameter $d \sim 1.4$ nm and a relatively narrow diameter distribution largely contained between 1.2 and 1.8 nm. This narrow distribution promotes a triangular packing of the SWNT in the rope (see inset of Fig. 8-1(a)). A triangular lattice provides tubes surrounded by six nearest-neighbors. Each pair of tubes in this arrangement should have almost the same probability for coalescence (diameter doubling).

The diameter distribution for as-grown HiPCO tubes is considerably broader than as-grown ARC tubes. The HiPCO distribution ranges from 0.5 to 2 nm and the most probable diameter is $d \sim 1$ nm. A broad diameter distribution clearly obstructs the optimal packing of the SWNTs within the rope; this is illustrated in the scheme (inset) of Fig. 8-1(c). In this case, the number of neighbors in contact with a central tube can be reduced to five, or even four, depending on the diameter of the surrounding nanotubes.

We expect that a reduced number of nearest-neighbors will reduce the probability of coalescence. However, the presence of smaller diameter tubes in HiPCO might be expected to increase the coalescence probability due to their higher reactivity originated by curvature-induced strain[147, 148]. Thus, the calculation of a coalescence probability vs T should not be an easy task. The effects of specific wall defects[149], the energetic contribution due to wall curvature, and the diameter distribution of tubes within a bundle should all be considered.

We should add here that we have studied the effects of the purification process on the tube wall structure using Raman and IR spectroscopy[70]. According to our experience, we have found that the dry oxidation/HCl reflux method that we have used here causes considerably fewer (if any) defects in the tube wall and minimal addition of
functional groups relative to that produced to peroxide removal of amorphous carbon or HNO₃ removal of metal residues (as opposed to HCl). Therefore, we believe that our purification scheme is reasonably mild in so far as wall defect formation is concerned.

In Fig. 8-1(d), the effects of “diameter doubling” or coalescence on the diameter distributions are clearly visible for HTT ≥ 1600°C. Vertical dashed lines are used in the figure as visual guides. Interestingly, after HTT=1600°C, both ARC and HiPCO exhibit similar diameter distributions. However, after HTT=1800°C, the diameter distribution of ARC SWNTs is wider than that of HiPCO and includes tubes with diameter \( d = 3 \times \bar{d} \), where \( \bar{d} \) is the most probable diameter for as-grown material. It is important to notice that after annealing at 1600°C and 1800°C, both ARC and HiPCO SWNTs with \( d < 1.4 \) nm represent only a small fraction, i.e., 4 - 6% of the sample. This indeed suggests that a \( d \approx 1.4 \) nm is the smallest diameter nanotube that can withstand coalescence in the range 1600-1800°C. Our data also suggest that once the nanotubes double (or triple) their diameter, they become significantly more stable against coalescence.

For ARC tubes, the diameter distribution width increases significantly from HTT=1600°C to 1800°C (Fig. 8-1(d)); and the distribution maximum peak shifts to larger diameters. This suggests that the coalescence after HTT= 1600°C involves the smaller diameter primary nanotubes (\( d \leq 1.6 \) nm); and at 1800°C, even larger diameter primary nanotubes (e.g., \( d \geq 1.6 \) nm) appear to coalesce. By “primary” we mean tubes produced in the growth process (not by coalescence). However, the formation of tubes with \( d \geq 3.4 \) nm at HTT= 1800°C could also has been originated by the simultaneous coalescence of three SWNTs, which appears to be more probable at higher temperatures. This view assumes that two successive coalescence transformations involving the same tube has a
low probability due to the significantly higher stability of diameter-doubled tubes. The C-C bond strain is proportional to the wall curvature; higher curvature produces more strain and the tendency is to relax this strain by rearrangement of the C-C bonds, i.e. by reacting with neighboring tubes to increase the tube diameter and reduce the curvature.

Following this line of reasoning, since most of the HiPCO SWNTs are smaller than 1.4nm, HTT=1600°C is sufficient to drive almost every nanotube in a HiPCO bundle to either coalesce or evolve into fragments. This is consistent with our observation that the diameter distribution for HiPCO material annealed at 1800°C is not much different from that of HiPCO sample annealed at 1600°C.

As can be seen in Fig. 8-1(d), almost no SWNTs with diameters four times larger than the mean starting diameter were observed. This observation is in agreement with recent Molecular Dynamic (MD) simulations[150, 151] in which the simultaneous coalescence of three SWNTs in an initial triangular arrangement leads to the largest coalesced tubes (and also our proposal that diameter-doubled tubes are usually too stable to coalesce again). Their simulations suggest that strong bond rearrangement activity involving more than four close-packed tubes leads instead to the formation of a MWNT[150, 151]. Other simulations suggest that if a very large diameter SWNT is generated, the tube will collapse into a two-layer graphitic ribbon[152, 153] and will therefore not be observed to exhibit a cylindrical cross-section in the product. Also, it should be noticed that HRTEM images of these collapsed tubes might easily be misinterpreted as a two-layer graphitic sheet with “edge” atoms, depending on the orientation of the electron beam[153].
8.1.3.2 HiPCO: MWNT formation at high temperatures

For HiPCO material subjected to HTT=1600°C and 1800°C, besides SWNT coalescence, we also observed graphitic structures (i.e., a stack of graphene layers with plane spacing ~3.4-3.8Å). In Fig. 8-2, we show two bundle cross-sections ((a), (b)) and two side-views ((c), (d)) of HiPCO material with HTT=1800°C. These HRTEM pictures clearly show several large diameter SWNTs produced by coalescence that are surrounded by unclosed and defective multi-layered graphitic structures. Strictly speaking, these structures should not be considered a multi-wall nanotube (MWNT) because the number of walls is not the same on both sides of the tubule (Fig. 8-2(c)).

Because of the less organized and lower density packing of the HiPCO SWNTs in a bundle, one might expect that the thermal transformation of HiPCO tubes into MWNTs might be more disorganized and produce a wider variety of defect-laden structures. That condition is observed in the HRTEM image in Fig. 8-3(a) that shows the resulting structure of HiPCO for HTT= 2000°C. At this temperature, bundles of coalesced and defect-laden HiPCO tubes produced at lower HTT are observed to transform into non-uniform tubular structures with numerous defects. At higher HTT, these structures might eventually become well-ordered MWNTs. However, even after HTT=2000°C, most tubular structures in the HiPCO material do not exhibit equal number of shells on each side of the central pore. Large amounts of amorphous carbon and debris are also observed to cover the tubular structure.
For HiPCO subjected to HTT=2200°C, a noticeable increase in the order of the MWNT wall structure is found (see Fig. 8-3(b), (c)). Also for HTT=2200°C, the amount of amorphous carbon coating the outside of the MWNTs is lower than that observed for HTT=2000°C. We suspect that the amorphous carbon has been reorganized by diffusion, allowing the further addition and completion of MWNT shells. This growth mechanism is similar to that proposed for the island growth of new carbon layers on conical graphene surfaces by Iijima et al.[154]. It is also similar to the usual epitaxial growth of crystalline thin films. Indeed, we observed evidence for this kind of growth in the image of MWNTs shown in Fig. 8-3(b), (c) have three well-defined walls; however, a fourth discontinuous layer (indicated by arrows) is forming from mobile (amorphous) carbon on the outermost
wall of the MWNTs. More interesting may be the fact that the outer layer is epitaxially copying the wall defects, such as the kinks that occur in the innermost wall.

Fig. 8-3: HRTEM images of HiPCO material after: (a) HTT=2000°C, tubular structures with several incomplete sp²-walls can be observed, large amount of amorphous carbon covers the structures. (b,c) HTT=2200°C, two MWNTs with three well-defined walls are shown; the outer fourth wall (incomplete) is composed by two-dimensional islands of sp² material (indicated by arrows); a very small amount of amorphous carbon can be observed at the MWNTs surface.
8.1.3.3 ARC: MWNT and Graphitic Nano-Ribbons formation

ARC SWNT material exhibits a more orderly thermal transformation to other filamentary forms of carbon than HiPCO SWNTs. After HTT=1600°C, most of the MWNTs exhibit well-formed tubules with a small number of defects. Most of the SWNTs have doubled their diameter and no longer exhibit straight walls, i.e. corrugated walls are observed instead. A few graphitic nano-ribbons (GNRs) were observed in ARC material beginning at this temperature. The GNRs are detected in the HRTEM images as very long filaments of parallel sp² layers, differently from MWNTs, GNRs do not present a hollow central space and the contrast of high-resolution images is stronger than MWNTs.

After HTT=1800°C, the ARC material was found to contain a significantly higher fraction of GNRs. Three different structures, as shown in the HRTEM images of Fig. 8-4, were observed: (a) bundles of diameter-doubled SWNTs, (b) GNRs, (c) and (d) bundled MWNTs. The fraction of GNRs in the material after HTT=1800°C is considerably larger than that observed after HTT= 1600°C. After HTT=1800°C, the wall structures of SWNTs and MWNTs appear considerably straighter than those annealed at 1600°C. In Fig. 8-4(b) we display an image showing a graphitic nanoribbon that appears to be a stack of collapsed SWNTs. Those tubes have larger diameters indicating they have first undergone coalescence. Each large diameter SWNT in the stack has become flattened in cross section and has a closed end (indicated by the arrows). The bulbs have lateral dimension of ~1.6nm, slightly larger than the mean diameter for as grown material.
(\(d = 1.4\text{nm}\)). We assume the cross section of this bulb is approximately elliptical due to the collapse, and we are observing the minor diameter in the plane of the figure. We

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Fig. 8-4: HRTEM images of different carbon allotropes found on ARC samples after HTT=1800°C. (a) Bundles of SWNTs. (b) Type-I GNR, the closed ends suggest the collapse of a SWNT’s bundle. (c) and (d) Bundles of MWNTs; the inset of (d) shows a higher magnification of the MWNT walls. (e) Map of “Number of walls vs Inner diameter” for MWNTs at different HTT; dashed lines were used to enclose the region with higher concentration of data points, N is the number of equivalent SWNTs (with d=1.4 nm) that thermally transform into a MWNT at the positions indicated by arrows.
identify these GNRs as type-I, they are formed from the collapse of bundles of large-diameter SWNTs. As we shall see below, type-II GNRs appear to form via the collapse of MWNTs.

The MWNT structure we observe in ARC material for HTT=1600, 1800 and 2000 °C, is summarized in Fig. 8-4(e). In this figure, we plot the number of walls in these MWNTs, produced by thermal transformation, versus the diameter of the inner most shell \((d_i)\). The dashed vertical lines in the figure are positioned at \(d\) and \(3d\), where \(d = 1.4\) nm is mean diameter of the as-grown ARC tubes. The lower and upper dashed horizontal lines that appear in Fig. 8-4(e) represent, respectively, the estimated lower and upper bounds for the number of walls per MWNT, i.e., \(3 < n < 12\) walls. Almost all of the data points in the figure fall into the region enclosed by dashed lines. We suspect that the relatively sparse population of MWNTs with \(d_i > 3d\) may have actually been present in the as-grown material, i.e., directly produced in the arc. The intersections of the dashed vertical and horizontal lines in the figure are labeled with the number \(N\) of typical ARC tubes \((d=1.4\) nm) that would be required to transform into these MWNT structures. We have calculated that MWNTs corresponding to the lower and upper intersections require \(N=4\) and \(N=69\) SWNTs, respectively, to complete the MWNT structure. The original ARC material exhibits a typical bundle diameter of \(\sim 15-20\) nm, i.e., they contain \(\sim 100-200\) SWNTs/bundle. Therefore, using \(4 < N < 69\), we would predict that from \(\sim 2-20\) MWNTs would be created per typical SWNT bundle. This number of MWNT/bundle is also in general agreement with our HRTEM observations. So, we can
conclude that most of the thermal reorganization of C-atoms below ~ 2000 °C takes place within the same bundle. It is interesting to note that when MWNTs are grown directly by

Fig. 8-5: HRTEM images of ARC material after: (a,b) HTT=2000°C and (c,d) HTT=2200°C showing some isolated SWNT and MWNT (a and c), and type-II GNRs (b, c and d). The closed ends of type-II GNRs (different to type-I GNR) suggest the formation from a collapsed MWNT bundle. (d) Schematic representation of type-II GNR structures, three possibilities for the cross-section are proposed. The width range of GNRs was estimated from the plot in Fig. 8-4(e).
arc discharge from catalyst-free electrodes, typical inner diameters are much larger (i.e., $d_i \sim 10\text{nm}$). However, Koshio et al [155] recently reported MWNT with innermost diameter of 0.4nm produced by using a metal-free radio-frequency plasma method.

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Fig. 8-6: Low-magnification TEM images at different positions of the sample heat-treated at HTT=2200 °C. After this HTT the sample is mostly composed of GNR’s; a few isolated MWNTs can also be found, as described in the paper.

After HTT= 2000 and 2200°C, numerous type-II GNRs were observed and a small number of isolated MWNTs remain, as shown in Fig. 8-5. At HTT=2000°C, some isolated diameter-doubled SWNTs and closed-shell sp² carbon structures are also observed. The most important finding after these high temperature treatments is what appear to be closed ends on the type-II GNRs. AT HTT=2200°C, majority was found to be GNRs as can be seen in the low magnification TEM image in Fig. 8-6. These ends can be observed in Fig. 8-5(b,d) and some of them can be seen to form a multi-shell hollow bulb (Fig. 8-5(b)). This is strong evidence that the type-II GNR is formed from
collapsed MWNTs. Type-II GNR ends are different from those in type-I GNR’s that are produced at lower HTT (Fig. 8-4(b)). A schematic illustration of a closed end of a type-II GNR is shown in Fig. 8-5(c). From this cartoon one can appreciate that the HRTEM images in Fig. 8-5(b) and Fig. 8-5(d) might represent a side-view of type-II GNRs. Fig. 8-5(c) also includes three distinct possibilities for the cross sectional structure of a type-II GNR. Future research will be oriented to isolate a single GNR and obtain an unobstructed end (or cross sectional) view. Knowledge of the GNR cross section is important, because depending on whether the edge of the GNR is open, or closed, or a combination of open and closed, different interesting electronic and magnetic properties can be expected for the system[156-159]. A final comment should be made, the fact that type-II GNRs are observed to increase significantly after the formation of MWNTs, suggests that the former arise from the collapse of MWNTs. Then from the plot in Fig. 8-4(e), we can estimate the lateral dimension of the GNRs to be between 4-20nm in width.

It will be interesting to know the exact interlayer spacing value of GNRs. As explained in Ch.1, each graphene layer in HOPG is stacked in an ABAB.. sequence. The interplanar separation is $c_0/2$ is 0.3354nm. The graphene layers are bonded by a weak van der Waals force. Another kind of graphite is turbostratic graphite, which is not stacked in a regular sequence. The interlayer spacing of turbostratic graphite can vary from 0.3354nm to more than 0.344nm for low temperature treated carbon fibers.[160] Jenkins and Kawamura[161] have reported in 1974 similar ribbon like graphitic structure to our GNR material as shown in Fig. 8-6. They called it ‘microfibrils’ structure produced by annealing phenolic resin fibers at 2800°C. As they described in the
literature, it is more like ‘confluences’ in the network of microfibrils than isolated or well-defined graphitic nanoribbons.

In Fig. 8-7, we show our attempt to obtain the interplanar separation of GNRs. Fig. 8-7(a) is a HRTEM image of a type-II GNR bundle observed after HTT=2200°C.
(b) is Fourier Transform [66] of (a). Low frequencies in the FT image correspond to the overall background in the real space. (c) is a filtered image of (a), which shows enhanced contrast of the graphite structure in the original HRTEM image(a). (d) is a FT of the filtered image showing the selected spatial frequencies corresponding to the interlayer spacing of graphene sheets in a GNR. The spacing between graphene layers (3.4 ± 0.2 Å) was obtained from the inverse radius of the FT ring in (d), the uncertainty (± 0.2 Å) was estimated from the width of the ring. This uncertainty should not be confused with the point-to-point resolution (Rayleigh criterion) of the instrument (1.9 Å) that represents the upper limit to which intuitive image interpretation can be made. For more information about the definition of resolution and information limits on HRTEM read [162]. HRTEM is not the right tool to distinguish whether the GNRs are formed by turbostratic graphite or not. In this sense, X-rays techniques provide more accurate values of interplanar spacing.

8.1.4 Discussion

8.1.4.1 Coalescence mechanisms

Using the schematic illustrations in Fig. 8-8, we now summarize our observations about the thermal transformation of bundled ARC and HiPCO SWNTs. Based on our study, we believe that two distinct pathways (i and ii) for tube coalescence can occur, as
shown in Fig. 8-8(a): chain-like (i) and close-packed (ii). These pathways are also

Fig. 8-8: (a) Schematic representation of chain-like (i) and close-packed (ii) coalescence processes. (b) and (c) are diagrams of the thermal evolution of SWNT bundles of HiPCO and ARC, respectively. (b) HiPCO SWNT bundles transform into isolated MWNTs. (c) ARC: Large SWNT bundles evolve forming MWNT bundles that collapse at higher temperatures to form type-II GNR; small SWNT bundles can produce isolated MWNT or diameter-doubled SWNT bundles that eventually collapse to form type-I GNR.
motivated by the MD simulations of Lopez et al.[150, 151]. For example, they have found that in the close-packed configuration, three SWNTs are the maximum number that can coalesce to produce one triple-diameter SWNT[151]. Their MD simulations also suggest that simultaneous reaction and bond rearrangement involving more than four SWNTs can produce a MWNT. Lopez et al. also could produce chain-like processes by “artificially” introducing wall defects on the outer SWNT’s in small 7-tube bundles (the defects were not on the central SWNT). However, their simulation did not reproduce the usual experimental result of tightly nested tubes in a MWNT (i.e., with wall spacing Δd=0.34 nm). In fact, their MWNTs were very open, with much larger intershell spacings than observed here, or in previous work[163, 164]. However, they were able to simulate the basic thermal transformation of a SWNT bundle to MWNTs, and argued that this was due to chain-like coalescence.

The probability of chain-like and simple pair-wise coalescence in poorly packed bundles (e.g., HiPCO) and tightly packed bundles (e.g., ARC) may be very different. In Fig. 8-8(b) and (c) we illustrate the concepts that the diameter-distribution, and the bundle size, can affect the carbon structures produced from bundled SWNTs at high HTT.

For HiPCO samples, with a wider diameter distribution and smaller bundle size, a mechanism similar to that illustrated in Fig. 8-8(b) should be considered, i.e., a chain-like coalescence of small-diameter nanotubes trapped in between larger tubes. This transformation might be preferentially activated at lower HTT due to the strain energy in the smaller diameter tubes. Driven by the van der Waals interaction, we propose that a chain coalesced filament might collapse into two closely spaced graphene sheets. In this case, up to four layered-graphite structures inside the bundle might be observed,
depending on the e-beam direction. Moreover, as shown in $(ii)$ of Fig. 8-8(a), three tubes in contact can also coalesce into a single much larger tube (close-packed transformation). We observe this structure in our HRTEM images, e.g., large-diameter tubes surrounded by unclosed graphitic structures, c.f., Fig. 8-2.

In the case of ARC tubes, with a much narrower diameter distribution, the probability for chain-like and close-packed coalescence, at high HTT, should be similar. However, van der Waals forces in the core of large bundles might drive their collapse, providing highly curved[165] and reactive edges. This may increase the probability of chain-like coalescence (c.f., Fig. 8-8(c)), leading to MWNT bundle formation for reasons given above. Ruptured tube walls with dangling bonds, mobile C$_2$ species, polymerization, etc., are all possibilities that may contribute to the details of the transformation.

### 8.1.4.2 Collapsed SWNT and MWNT

As we proposed above, the collapse of SWNT’s and MWNT’s bundles due to van der Waals forces may drive the formation of type-I and type-II GNRs, respectively. In Fig. 8-8(c) we suggest that small bundles of ARC material are more likely to form isolated MWNTs or small bundles of coalesced SWNTs that subsequently collapse in type-I GNRs. Only bundled MWNTs, formed from large bundles of ARC material, are expected to collapse at high HTT into type-II GNRs. In HiPCO material (Fig. 8-8(b)), HTT produced isolated MWNTs that were stable against collapse up to HTT=2200°C.
The high temperature formation of carbon loops connecting adjacent graphene was reported previously by Endo et al. [166] and Lim et al. [167]. They found that single loops are unstable at high temperature and transform into multi-loops above 2100°C. The shape of the end of type-I (Fig. 8-4(b)) and type-II (Fig. 8-5) GNRs are similar to the single loop and multi loop structures discussed by Endo et al. We have proposed here that the collapse of coalesced SWNTS and bundled MWNTs to form, respectively, type-I and type-II GNRs is driven by van der Waals forces. If after collapse, the GNR presents open (unstable) edges of graphene, they may well close by loop formation. Of course, SWNTs and MWNTS often exhibit fullerene-like closed ends. We do not know whether these closed ends survive collapse and/or simply distort and undergo some bond rearrangement to form the stable GNR end, or the stable end forms by loop formation, or a related process. It is possible that computer simulations may shed light on this issue.

Chopra and co-workers observed ribbon-like structures, i.e. fully collapsed carbon nanotubes together with the more common MWNTs in material synthesize in a metal-free carbon arc [168]. They suggested that the ribbon-like structures form when hollow cylindrical nanotubes are locally deformed (for example, kinked or twisted) by external mechanical forces. They proposed that on kinking, the inner tube wall collapses locally and starts a “zipper” effect, in which the flattening propagates down the entire length of the tube. In their work, the collapse of a single (i.e., isolated) MWNT was observed and the collapse was driven by mechanical deformation and not a thermal transformation. Gao et al. [152], and more recently Tang et al. [169], showed theoretically that there are two critical tube radii (R_{\text{min}} and R_{\text{max}}) important for SWNT collapse. For R < R_{\text{min}}, they
found that the cylindrical shape is stable; for $R > R_{\text{max}}$, the collapsed shape is energetically favored, and for $R_{\text{min}} < R < R_{\text{max}}$ the collapsed shape is metastable.

Crespi et al. reported that the irradiation of MWNTs in an 800-keV TEM beam induces an anisotropic collapse of an isolated MWNT. However, this structural transformation is a very anisotropic and non-equilibrium process[134, 135]. The thermal collapse of a cylindrical SWNT or MWNT, as observed in our experiments, is probably driven by non-compensated van der Waals forces due to tube-tube interactions within a bundle. This is supported by the fact that isolated MWNTs are stable (without collapsing) at these temperatures and even higher ($2800^\circ$C) as recently reported by Kim et al[170].

8.1.5 Conclusions

We have studied two purified bundled SWNT systems: purified ARC and HiPCO nanotubes. The large differences in the as-grown diameter distribution and spatial arrangement of tubes within a bundle, as well as the number of tubes per bundle, result in very different thermal transformation behavior. For bundled SWNT with a very wide diameter distribution and small size bundles (i.e., HiPCO), the C-C bond rearrangement can be chaotic, producing a large amount of sp$^2$ fragments and amorphous carbon (a-C). At higher temperatures, these fragments and a-C help to form individual MWNTs. Tightly packed bundled SWNTs with a more homogeneous diameter distribution (ARC) were found to exhibit a more organized thermal transformation. Depending on HTT and the starting bundled size, the observed structures include coalesced SWNTs, individual
MWNTs, bundled MWNTs, and type-I and type-II GNRs. Our observations suggest that type-I and type-II GNRs can be formed from the collapse of coalesced (larger diameter) SWNTs and bundled MWNTs, respectively. In this thermal process, we propose that the collapse of SWNTs and MWNTs into GNRs is driven by inter-tube van der Waals forces within bundles.
8.2 Raman Scattering Study of the Thermal Conversion of Bundled Carbon Nanotubes into Graphitic Ribbons

8.2.1 Introduction

In Ch.8.1, we have followed the thermal evolution of SWNTs at a successively higher temperature up to 2200°C by HRTEM. Here, we present results of Raman scattering studies on the thermal transformation of purified SWNT materials. We will show the Raman spectra of GNRs observed for the first time.

8.2.2 Experimental Details

After HTT, the materials were dispersed in spectroscopically pure ethanol using weak ultrasound and thin films were deposited by placing a few drops of the solution onto a glass slide. The samples were then degassed in vacuum at 200°C for ~2 hr before Raman measurements.

Raman spectra were collected under ambient conditions with a JY Horiba T64000 microRaman spectrometer equipped with an Olympus BX40 confocal microscope front end and cooled CCD detector. Excitation was provided by an Ar-Kr laser at 1-3 mW.
incident power, as measured by a handheld radiometer at the sample position. Both H- and V-polarized light were accepted in the scattered radiation. The same set of samples that were characterized by extensive HRTEM analysis in Ch.8.1 were studied via Raman scattering in this work.

8.2.3 Results and Discussion

Raman scattering has been shown to be a powerful probe of carbon materials, sensitive to structural changes, defects and doping[34]. In contrast to TEM, Raman scattering probes a large sample area. It is therefore easier to obtain a sense of the ‘average’ sample properties. In small diameter d<2nm SWNTs, Raman scattering is known to be “resonant”[55]. A small fraction of the full variety (n,m) nanotubes dominate the spectrum; the excitation wavelength (or photon energy) determines which tubes will dominate the scattering[55]. Metallic and semiconducting nanotubes have been found to exhibit different Raman lineshapes for the high frequency SWNT G-bands. A Breit-Wigner-Fano lineshape is observed in the G-band of metallic tubes, and Lorentzian lineshapes are observed in the G- and R-bands of semiconducting tubes and in the R-band of metallic tubes[55].

In this work, we have used 647.1nm, 514.5nm, 488.0nm, 457.9nm excitation to probe our samples. According to the Kataura plot [106] shown in Fig. 2-7, 514.5nm and 647.1nm excitation can excite both semiconducting and metallic tubes in the ARC sample, and in HiPCO material, 514.5nm and 647.1nm excitation probes both metallic
and semiconducting nanotubes. New theoretical results[118-120] support the view that the Raman scattering resonance in SWNTs involves excitons rather than direct interband transitions. The energetics in the Kataura plot are nevertheless useful because the exciton binding energy should be small. Our discussion of the Raman spectra here is really not affected by the exciton issue: one only needs to appreciate that the exciton energy and/or the van Hove singularity spacing both increase like \( \sim 1/d \). Different subsets of the tube population are probed at different laser excitation as shown beautifully in the Kataura plot. The frequency of the disorder-induced or D-band scattering in \( \text{sp}^2 \) carbons can also be sensitive to the excitation wavelength; this will be discussed later.

In Fig. 8-9 and Fig. 8-10, we show a series of Raman spectra collected under ambient conditions. Fig. 8-9 and Fig. 8-10 collect, respectively, spectra excited at 514.5 nm and 647.1nm. The spectra in both figures are stacked according to HTT, with the spectrum of raw SWNTs (as-delivered material) on the bottom. In each figure, the Raman spectra in the left panel are from ARC material and in the right panel from HiPCO material. Because of an enhanced SWNT Raman cross section, the Raman spectrum of the raw ARC and HiPCO soot exhibits features primarily associated with the SWNTs: [30] 1st order-allowed “R-band” components in the range \( \sim 100 – 300\text{cm}^{-1} \) are associated with radial SWNT modes; the radial mode frequency \( \omega_R \) of a SWNT with diameter \( d \) is proportional to \( 1/d \); coalescence should produce new R-bands downshifted considerably from the position of the original bands. [30] weak disorder-induced “D-band” scattering between \( 1230 – 1370\text{cm}^{-1} \) (whose frequency depends on the excitation frequency); increasing disorder should increase the intensity of this band, and (3) a 1st order-allowed “G-band” with substructure in the \( \sim 1500 – 1600\text{cm}^{-1} \) region associated
Fig. 8-9: The spectra (dotted lines) excited by 514.5nm are organized in the left panel for ARC tubes and the right panel for HiPCO tubes: (i) as-delivered soot, and in (ii-vii) vs temperature in purified material for a series of increasing HTT=1100°C-2200°C. The solid line is a composite Lorentzian (plus one Fano component for G-band of HiPCO) fit to the data. Individual Lorentzians (and one Fano for HiPCO) for G-band are plotted separately.
Fig. 8-10: The spectra (dotted lines) excited by 647.1nm are organized in the left panel for ARC tubes and the right panel for HiPCO tubes: (i) as-delivered soot, and in (ii-vii) vs temperature in purified material for a series of increasing HTT=1100°C-2200°C. The solid line is a composite Lorentzian (plus one Fano component for G-band of both ARC and HiPCO) fit to the data. Individual Lorentzians and one Fano for the G-bands are plotted separately.
with new tangential displacement modes activated by the nanotube cylindrical symmetry (i.e., graphite has only one G-band component at 1582 cm$^{-1}$). A transformation to MWNTs is observed at higher HTT after coalescence. From earlier Raman studies on MWNTs[171], we know that well-formed large diameter MWNTs exhibit a Raman spectrum almost identical to graphite: notably a 1$^{\text{st}}$ order-allowed G-band at 1582 cm$^{-1}$ and, because of their large diameter, R-bands too low in frequency to be observed without considerable effort. The analog of the Raman-active shear mode in graphite observed at 42 cm$^{-1}$ [172] has not been reported for MWNTs[40].

All Raman spectra in Fig. 8-9 and Fig. 8-10 have been normalized (or scaled) to yield the same G-band peak intensity. We have fit the semiconducting SWNT G-band and R-band spectra with Lorentzians. One Breit-Wigner-Fano (BWF) component was added in our G-band analysis for metallic tubes. The calculated spectral lines (least squares fits) are shown as solid lines in the figures. The BWF line shape is typically found in doped semiconductors or metallic samples when a Raman–active electronic continuum and a Raman-active phonon are coupled. The asymmetric BWF lineshape is given by [173]

$$I(\omega) = I_0 \frac{[1 + (\omega - \omega_{BWF})/q \Gamma]^2}{1 + [(\omega - \omega_{BWF})/\Gamma]^2}$$  \hspace{1cm} \text{Eq 8.1}

where 1/q is a measure of the interaction strength between the phonon and electronic continuum, $\omega_{BWF}$ is frequency at maximum intensity $I_0$, and $\Gamma$ is a width parameter. In the limit of 1/q $\rightarrow$ 0, the BWF lineshape becomes a Lorentzian riding on top of the electronic background; the Lorentzian then represents the decoupled phonon[62].

\textbf{R-band Analysis}
It is well established that the R-band frequency for an isolated SWNT is inversely proportional to its diameter, i.e., $\omega_R \sim 1/d[85]$. There is, however, some argument in the literature over the exact value of the proportionality constant[174]; values in the range 224-240 cm$^{-1}$ nm have been proposed on theoretical grounds and on experiments on individual tubes[175]. If the tubes are bundled, then a tube-tube interaction is present that is calculated to upshift the R-band by a nearly constant factor of $\sim$10-12 cm$^{-1}$ (for tubes in the diameter range 1 nm < $d$ < 3 nm)[56, 57]). The exact relationship between $\omega_R$ and $d$ is not so important here, as will be seen, because we are primarily in search of large changes in R-band position due to tube coalescence (diameter-doubling) as well as the loss of R-band scattering due to coalescence and the subsequent transformation to MWNTs.

To fit the R-bands vs HTT in Fig. 8-9 and Fig. 8-10, we have used the minimum number of Lorentzian peaks required to achieve a reasonable fit. For simplicity, the frequency and linewidth of each component in the R-band was fixed to that observed in the raw material, i.e., before any purification or HTT. The value of the frequency of these components is indicated once in the figure. With increasing HTT, only the amplitude of the individual peaks in the R-band region was made an adjustable parameter. After coalescence, new R-bands were observed at lower frequencies (i.e., corresponding to larger diameters) and these peaks were also fit to Lorentzians. After higher HTT, the frequency and linewidth of these new peaks did not change much from the values at which they first were detected, so we kept them constant. The result of each composite fit to the R-band region is shown as a solid line superimposed on the experimental data (dotted line). This simplified fitting procedure to the R-band region with minimal
Lorentzian parameters can be seen in Fig. 8-9 and Fig. 8-10 to be successful. Based on the Kataura plot[106], we have also added shaded regions in Fig. 8-9 and Fig. 8-10 to indicate whether the R-band should be tentatively assigned to metallic or semiconducting tubes.

With increasing HTT, both ARC and HiPCO tubes first exhibit a relative decrease in the intensity of the high frequency R-band components. This behavior is interpreted as evidence that the smaller tubes are relatively more unstable, i.e., they have a higher tendency toward coalescence. As can be seen in Fig. 8-9 and Fig. 8-10, after HTT=1600-1800°C, the higher frequency R-band components are lost in both ARC and HiPCO spectra and new R-bands are observed at ~90 cm\(^{-1}\) (ARC) and 116, 127, 155 cm\(^{-1}\) (HiPCO). Using the expression \(\omega_R \sim 224cm^{-1}/d\), these new low-frequency bands are identified with coalesced SWNTs with diameter \(d \sim 2.4\) nm (ARC) and \(d \sim 1.9, 1.8\) and 1.4 nm (HiPCO). The reasonably narrow lineshape of these coalescence-induced R-bands indicates that the diameter-doubled tubes are reasonably defect-free. This indicates that a rapid annealing of the many wall defects first formed after tube fusion can be achieved. From the evolution of the R-band region with HTT, it is clear that smaller diameter tubes are more thermally unstable. Weak R-band scattering remains to HTT=2000°C in ARC and to HTT=2200°C in HiPCO material. Thus, some SWNTs can survive these very high HTTs. According to our HRTEM images shown in Ch.8.1, these tubes probably reside in the core of small diameter MWNTs.

**G-band Analysis**

In SWNTs, the high frequency tangential C-atom displacement bands with frequencies ~1400-1600 cm\(^{-1}\) contribute to the G-band. These mode frequencies are
relatively insensitive to tube diameter, except for small diameter tubes, i.e., \( d < 1.0 \text{nm} \). We have fitted the SWNT G-band region in Fig. 8-9 and Fig. 8-10 with only three components; for simplicity; a fourth weaker component was not added. If metallic tubes were excited, an asymmetric BWF lineshape was used to fit one of the three G-band components, while the other two were fit by Lorentzians[173]. If semiconducting tubes were excited, the G-band spectrum can be reasonably well fit by 3 Lorentzians. The composite fit (solid line) in Fig. 8-9 and Fig. 8-10 in the high frequency region is shown superimposed on the experimental spectrum; for clarity, the individual Raman lines used in the composite fit are shown displaced below the spectrum. The BWF component is seen to be relatively broad.

To minimize the number of fitting parameters, we have fit all the G-band components to fixed-frequency bands and we also fixed the relative amplitudes of the components within the SWNT G-band. If needed, the peak width was adjusted to fit the data. If this width adjustment was needed, all related component widths were increased by the same amount. The fractional increase of the width is indicated in Fig. 8-9 and Fig. 8-10 by the values listed for \( \Delta \Gamma \). For example, the notation \( \Delta \Gamma = 0.14 \Gamma_0 \), indicates that a 14% increase in the G-band component width was required to fit the data. As is well known, the peak width of 1st order lines is related to the disorder in the \( \text{sp}^2 \) network[43]. Thus, inspection of the HTT-dependence of \( \Delta \Gamma \) in Fig. 8-9 and Fig. 8-10 shows the effect of HTT on the structural order of the carbons. It can be seen that \( \Delta \Gamma \) of HiPCO exhibits a lower threshold temperature for HTT change in linewidth than ARC. Significant changes in \( \Delta \Gamma \) for HiPCO tubes were observed first at HTT=1100° C,
consistent with crosslinking between tubes (formation of new intertubule bonds). This is the anticipated precursor to coalescence. However, for ARC material, with larger tube diameters, the first observable changes in the G-band Γ’s were found at 200°C higher (at least) HTT.

For the ARC and HiPCO spectra collected after HTT=1800°C and 2000°C, two additional Lorentzian components were required to fit the G-band region: they are centered at ~1580 cm\(^{-1}\) and ~1620 cm\(^{-1}\). The band at ~1580 cm\(^{-1}\) signals the evolution to graphitic or MWNT carbons, while the band at ~1620 cm\(^{-1}\) is often associated with disorder in the sp\(^2\) carbon network. Scattering at ~1620 cm\(^{-1}\) is sometimes referred to as the G* band, the frequency is close to a maximum in the one-phonon density of states [52]. As crystalline materials become disordered, the Raman spectrum usually evolves into something similar to the one-phonon density of states.

Brown et al.[173] has reported that BWF G-band frequency \(\omega_{BWF}\) for metallic SWNTs shifts monotonically to lower frequencies as the diameter of SWNTs decreases. However, we did not observe any clear changes in \(\omega_{BWF}\) after coalescence. They proposed that the curvature of metallic SWNTs facilitates increased the BWF coupling of the lower frequency metallic G-band component to a plasmon-based electronic continuum. This, they say, would result in a downshifting and broadening of the BWF band as the tube diameter decreases. However, reasonable BWF fits are obtained here with constant \(\omega_{BWF}\) when the diameters double. It could be that none of the tubes participating in the BWF scattering we observed was small enough in diameter to show these shifts.
After very high HTTs, we observed significant broadening of the SWNT G-band features (note the values of $\Delta \Gamma$ at high HTT in Fig. 8-9 and Fig. 8-10). For example, after HTT=2000°C, the fine structure of the SWNT G-band (i.e., peaks at ~1550 and ~1530 cm$^{-1}$) has almost disappeared from the G-band, and the G* band at 1620 cm$^{-1}$ (signaling disorder) now appears clearly as an unresolved shoulder. After HTT=2200°C, the fine structure of SWNT G-band has completely disappeared in both ARC and HiPCO material. The weight of the G-band has then downshifted to ~1583 cm$^{-1}$ with a clear shoulder at ~1620 cm$^{-1}$. For HiPCO, this behavior is consistent with the further loss of SWNTs, conversion of coalesced tubes to MWNTs and some annealing of wall defects in MWNTs. In ARC, the changes in the G-band are consistent with the loss of the last surviving nanotubes, the annealing of MWNTs and the further formation of GNRs.

In Fig. 8-10, our G-band analysis shows that the BWF band intensity gradually disappears with increasing HTT. This can be interpreted as either a disappearance of small diameter metallic tubes, or a decrease in conduction electron density in metallic tubes with growing defect concentration. Our analysis of the SWNT G-band in HiPCO excited by 514.5 nm radiation shows that, with increasing HTT, the SWNT G-band evolves from one containing a noticeable BWF component to one well-described by Lorentzian components whose frequencies and widths are characteristic of semiconducting tubes. Similar to ARC material, the intensity in the BWF band is found to gradually decrease with increasing HTT. Interestingly, the SWNT G-band of HiPCO excited with 647.1 nm excitation exhibits the opposite trend, i.e., the BWF component gains strength with increasing HTT, becoming more metallic at higher annealing temperature.
Fig. 8-11: (a) The frequency of D- and G-band of ARC(○) and HiPCO(Δ) material excited by 457.9, 488, 514.5 and 647.1nm vs annealing temperature, (b) The integrated intensity ratio of D band to G band ($I_D/I_G$) excited by 514.5nm for ARC(○) and HiPCO(Δ) material as a function of annealing temperature.
As summarized by the shading in the R-band region of HiPCO samples in Fig. 8-9 and Fig. 8-10, small tubes excited by 514.5 nm and 647.1 nm are tentatively considered (via the Kataura plot in Fig. 2-7) as metallic and semiconducting, respectively. Thus, as small diameter tubes are lost via increasing HTT, the lineshape of the HiPCO SWNT G-band becomes more semiconducting or more metallic in nature, depending on the laser excitation. SWNTs coalescence of HiPCO is expected to change the SWNT G-band lineshape. As discussed above, HiPCO has many small tubes and they should exhibit a slightly downshifted set of tangential mode frequencies relative to larger tubes.

We next consider the HTT dependence of the G-band maximum $\omega_G$ ($\omega_G$ is the frequency of the maximum intensity within the G-band). This data, collected using four different excitations, is plotted in Fig. 8-11(a). As can be seen in Fig. 8-11(a), both ARC and HiPCO exhibit a similar behavior for $\omega_G$ vs HTT. With increasing HTT, $\omega_G$ first exhibits almost no change over most of the range and then a significant (sudden) decline at the highest HTT=2200°C. The sudden decline is associated with the loss of SWNTs which exhibit higher frequency G-band frequencies. The 1580 cm$^{-1}$ band remains, and has been growing in intensity with HTT. This growth is associated with the evolution to MWNTs (ARC and HiPCO) and GNRs (ARC).

**D-band Analysis**

Raman scattering intensity in the range ~1300-1400 cm$^{-1}$ is present in all known forms of disordered sp$^2$ carbons[52]. This so-called “D-band” scattering has been identified with C-atom vacancies, admixtures of sp$^3$ bonding, substitutional impurities (boron), and finite basal plane grain size or particle size effects, [44-46, 53, 71]. It therefore can generally be associated with many factors that break the long range order in
the sp² carbon network. D-band intensity is usually identified with the degree of the disorder. The “D-band” is associated with scattering involving a collection of short wavelength vibrational modes (phonons) in the range ~1300-1400 cm⁻¹. These modes are not Raman-allowed in 1st order. Different from 1st-order allowed Raman scattering, the D-band has been known for some time to exhibit a band maximum that depends on the excitation frequency. This behavior is called “dispersive”, and recent work has shown that it should be considered as a double-resonance process involving when either the incident or scattered photon is resonant with an electronic π to π* state transition [50, 130, 176]. In the case of one phonon second order process, i.e. D-band, electrons in the state \( k + q \) (where \( q \) is the phonon wave vector), which were initially in the state \( k \) and scattered by phonons, are elastically scattered by an impurity or defects to a final state with the wave vector \( k \).

The D-band is observed near ~1350 cm⁻¹ in Fig. 8-9 (514.5nm excitation) and Fig. 8-10 (647.1nm excitation). For ARC material, the integrated intensity of the D-band (measured relative to the G-band intensity) exhibits interesting non-monatomic behavior with increasing HTT. Relative to purified ARC material degassed at 200°C, an increase in the D-band intensity is first observed after HTT=1400°C (i.e., after coalescence), and the D-band intensity continues to increase with increasing HTT, even after HTT= 1600°C. Finally, after HTT=1800°C, we see the D-band intensity beginning to decrease. This behavior can be understood as first being driven at lower HTT by the onset of disorder due to coalescence and at higher HTT the D-band intensity is diminished via structural annealing of the disorder created at lower HTT.
For HiPCO material, the HTT dependence of the integrated D-band intensity with HTT is somewhat different than that found for ARC material. In the range $1100^\circ<HTT<1800^\circ$, the D-band scattering in HiPCO material exhibits a clear maximum at HTT=1400$^\circ$. This difference between ARC and HiPCO is understandable given our HRTEM result that indicates ARC tubes transform at lower HTT to MWNTs and furthermore exhibit better MWNT structural order than we observed in HiPCO material. Secondly, we observed by HRTEM that a noticeable corrugation in the wall structure of coalesced ARC and HiPCO tubes; this can be largely removed by HTT=1800$^\circ$ in Ch.8.1[146, 177].

As can be seen directly in the Raman spectra of Fig. 8-9, Fig. 8-10 and more quantitatively in Fig. 8-11, with increasing HTT the frequency $\omega_D$ identified with the D-band maximum begins to upshift above HTT~1500$^\circ$. Even though the Raman band is dispersive [46], this behavior is seen to be independent of excitation frequency and is similar for ARC and HiPCO material. Since the scattering is a double resonance, it is difficult to identify the upshift as purely associated with changes in the phonon dispersion. It is also difficult to assign the D-band to one form of carbon or another, particularly when so many structural transformations are taking place and with attendant disorder.

Perhaps the most interesting difference between HiPCO and ARC, as seen clearly in HRTEM images, is the thermal production of GNRs from bundled MWNTs which begins at HTT~1800$^\circ$. Our HRTEM images indicate that after 4 hours of HTT~2200$^\circ$, the ARC material has almost completely transformed to GNRs and in sharp contrast to this discovery in ARC material, we could not find any examples of
Fig. 8-12: The ratio of integrated area of D band and G-band ($I_D/I_G$) v.s. laser wave length for HiPCO(triangles) and ARC(circles) material annealed at 2200°C. The dotted line is a fit to the modified Knight formula.
GNRs in HRTEM images of HiPCO with the same HTT[177]. It is therefore interesting that this significant difference in the endpoint carbons in these two starting materials cannot be seen in a plot of \(\omega_D\) or \(\omega_G\) vs HTT, as shown in Fig. 8-11(a). However, we can find Raman support for a MWNT-GNR transformation in ARC, as seen in Fig. 8-11(b). There we plot the Raman intensity ratio \(I_D/I_G\) vs HTT. The difference in behavior between HiPCO and ARC at high HTT is evident in this plot. After HTT=2000°C, there is a much stronger upturn in \(I_D/I_G\) for ARC relative to HiPCO material. We can tentatively explain this difference as the result of the production of the large fraction of GNRs produced in ARC material during the HTT=2000°C. The increased D-band scattering in GNRs may, however, stem from a “finite basal plane crystallite effect” associated with the narrow width of the GNRs, as we discuss in detail below. A smaller downturn in \(I_D/I_G\) is observed after the highest HTT=2200°C in both HiPCO and ARC which probably is associated with an annealing of defects, i.e., MWNTs in HiPCO and GNRs in ARC.

The effect of the basal plane crystallite size on the intensity ratio \(I_D/I_G\) has been studied in many graphitic systems. This has been done by correlating the basal plane coherence length \(L_a\) obtained from the width of (hk0) x-ray peaks with \(I_D/I_G\), as discussed in detail by Knight and White[53]. For a GNR, \(L_a\) would correspond to the average width of the ribbon. After studying several graphitic systems using different laser excitations, Matthew et al. [46], proposed the following empirical relationship between \(I_D/I_G\) and \(L_a\)

\[
\frac{I_D}{I_G} = C_0 + C_1\frac{\lambda_L}{L_a}
\]

Eq 8.2
The excitation wavelength $\lambda_L$ must enter the relationship because the D-band is dispersive. For example, a careful fit of Eq. 8.2 to data on poly-paraphenylene-derived carbons for HTT up to 2000°C has been found to yield $C_0 = -12.6$nm and $C_1 = 0.033$, respectively[46]. According to previous reports [42, 46, 178-180], Knight plots of $I_D/ I_G$ vs $\lambda_L$ for various type of sp$^2$ carbon material produces approximately linear data for 400$<\lambda_L<$700nm.

To further investigate the D-band scattering from HiPCO and ARC material after HTT=2200°C, we make a Knight plot in Fig. 8-13 for the intensity ratio $I_D/ I_G$ vs $\lambda_L$. The dotted lines in the figure are the result of a least squares fit of Eq. 8.2 to the data using the values of the constants $C_j$ obtained for poly-paraphenylene-derived graphitic carbons. The in-plane structural coherence length $L_a$ is the only fitting parameter. The HiPCO-derived MWNTs exhibit a linear Knight plot and the slope leads to the value $L_a = 10$nm. Interestingly, this value is close to the value we estimate for the average HIPCO MWNT circumference, i.e., $\pi <d> \sim 12.7$nm. When the ARC-derived GNR data is presented in a Knight plot, all data but one point at $\lambda_L = 514.5$nm falls on a straight line that yields $L_a = 5.9$nm for the GNRs. However, the point at 514.5nm falls far above the best-fit Knight line. The departure cannot be ascribed to experimental error which is estimated conservatively to be $\sim 5\%$ for $I_D/I_G$. 
The details of the GNR cross section are not yet known. We have proposed that GNRs form from the cross sectional collapse of a MWNT in Ch.8.1[146, 177]. We have been unable to isolate one of these filaments perpendicular to the focal plane of the TEM and directly observe the cross section. The images that we have seen are side views of the GNRs along its length that can be interpreted as a stacking of graphene ribbons with closed fullerene-like ends (c.f., Fig. 8-6).
In the upper right hand corner of Fig. 8-14, we show three possible schematic cross sectional views of a GNR consistent with our TEM observations. Each of three possibilities would have approximately the same lateral dimensional $L_a$. In fact, we can estimate the $L_a$ distribution for the GNRs using the proposal that GNRs are just collapsed MWNTs. We use the cross sectional diameter distribution found from TEM for the ARC MWNTs produced at lower HTT[146, 177], and then compute the $L_a$ distribution in our final GNR material (after HTT=2200°C). The final simplifying geometrical assumption is that each shell of the MWNT collapses into two long graphene sheets each with width $L_a \sim \pi d/2$, where $d =$diameter of the respective MWNT shell. The long dimension of ribbon is ~microns and is not important. By using this simplifying assumption, we can generate the $L_a$ distribution shown in Fig. 8-13 (histogram plot) that we also fit to a log-normal function $F(d)$ given by;

$$F(d) = \frac{1}{\sigma} \exp\left[-\frac{(\log d - \log \bar{d})^2}{2\sigma^2}\right]$$

Eq 8.3

where $\bar{d}$ and $\sigma$ are, respectively, the most probable value and width of the distribution[34]. We find $\bar{d}=7.6\text{nm}$ and $\sigma = 3.3\text{nm}$. This value for $\bar{d}$ is somewhat larger than the value $L_a=5.9\text{nm}$ obtained from our Knight analysis, yet the two values are in reasonable agreement given the sheet distribution width ($\sigma = 3.3\text{nm}$)

Finally, we return to the issue of the high lying point in the Knight plot for ARC generated GNRs. Brown et al.[180] found that SWNTs ($d_{\text{ave}} \sim 1.35$ and 1.49nm) also exhibited a different behavior for $I_D/I_G$ vs $\lambda_L$ than predicted by the Knight equation. In their report, when the laser excitation reached the band gap of metallic tubes at $\sim 1.9\text{eV}$ (647.1nm) for samples with $d_{\text{ave}} \sim 1.35$ and 1.49nm, they found that $I_D/I_G$ displayed a
higher value than expected in the Knight plot. They mentioned that the special behavior might be connected with phonon-plasmon coupling in the metallic tubes. Their suggestion may be applicable in our results as well if we consider that Nakada et al. [158] have reported that armchair symmetry graphene nanoribbons can be metallic and exhibit van Hove singularities in a 1D electronic density of states. Thus we are led to speculate that the departure from Knight behavior in GNRs that we observe may be due to metallic GNRs, or metallic sheets within GNRs, that have a van Hove singularity spacing that is in resonance with our laser at 514.5 nm, i.e., $E_g \sim 2.4$ eV.

**Second order Raman Scattering Analysis**

In Fig. 8-14, we compare second order scattering in the region of $2400\text{cm}^{-1} < \omega < 3400\text{cm}^{-1}$ for HOPG, MWNTs and GNRs. All spectra were excited by 514.5 nm radiation and the spectra were normalized to have the same G-band intensity. The MWNTs are thermally produced from HiPCO using HTT=2200°C, whereas the GNRs were produced from ARC using HTT=2200°C. Structure is observed at $\sim 2450\text{cm}^{-1}$, $\sim 2700\text{cm}^{-1}$, $2950\text{cm}^{-1}$ and $3250\text{cm}^{-1}$. The scattering near $\sim 2700\text{cm}^{-1}$ sp$^2$ carbons is referred
to as the G’ band, and this scattering in sp² carbons has been interpreted as an overtone for D-band scattering (i.e. \(2700 = 2 \times 1350 \text{cm}^{-1}\))[40, 45]. However, the G’-band is an

Fig. 8-14: Raman spectra of second order mode region (2400 cm\(^{-1}\) < \(\omega\) < 3400 cm\(^{-1}\)) of HOPG (a), MWNTs produced by annealing HiPCO materials at 2200°C (b), GNRs produced by annealing ARC materials at 2200°C (c)
intrinsic property of well-ordered sp\(^2\) carbons and is present in high-quality graphite crystals, where the D-band is completely absent [40, 45].

HOPG (bottom spectrum) exhibits structure in the G’ band with a main peak at \(~2754\) cm\(^{-1}\) and a weaker peak (shoulder) at a lower frequency, \(2720\text{cm}^{-1}\). This structure is associated with the details of the 2-phonon density of states near the K- and M-points in the Brillouin zone. It has been reported that disorder broadens and downshifts the G’-band by \(~10\text{cm}^{-1}\)[40]. With extensive disorder or defects in the honeycomb network, the G’-band has been reported to almost disappear. In other words, it has the opposite behavior to the D-band. For MWNTs, depending on the MWNT diameter distribution, the G’ band is found between \(~2710 - 2734\text{cm}^{-1}\)[40, 51]. The G’-band of the ARC-derived GNRs and the HiPCO-derived MWNTs is similar, as can be seen in Fig. 8-14. The GNR G’ band is somewhat narrower (FWHM) by \(~10\text{cm}^{-1}\). This is consistent with a higher structural integrity (as seen in a HRTEM side view of GNRs) than observed in the wall structure of HiPCO-derived MWNTs. The narrower G’ bandwidth in GNRs strengthens our argument that GNR D-band is activated by the lateral confinement, not by defects in the honeycomb carbon network.

The 2\(^{nd}\) order band at \(~2951\text{cm}^{-1}\) is combination mode scattering involving states associated with G- and D-bands. This band was observed in the disordered sp\(^2\) carbon system. The second order band at \(~3250\text{cm}^{-1}\) is assigned to overtone scattering from modes near \(~1620\text{cm}^{-1}\) in between \(\Gamma\) and M point in the Brillouin zone.
8.2.4 Summary and Conclusions

In this study, Raman scattering has been used to follow the thermal evolution of purified and bundled ARC and HiPCO SWNTs subjected to a ~ 4 h HTT in ~10^{-5} Torr vacuum. The effects of tube coalescence were observed via changes in the R- and G-bands. We also observed new R-bands in the region ~ 100-130 cm^{-1} after HTT=1400°C that can be identified with diameter-doubled tubes. From the R-band components, we can conclude that small diameter tubes (d<1.4nm) are preferentially lost in the range HTT~1600-1800°C. At the highest HTTs, ARC and HiPCO material were observed to convert to MWNTs, as observed by the addition of new Raman scattering at ~ 1580 cm^{-1}. Arc material subjected to HTT≥ 2000°C was found to exhibit a strong increase in the intensity scattering ratio $I_D/I_G$ that was identified with additional D-band scattering associated with lateral confinement in the GNR width (basal plane confinement). The Raman spectrum of GNRs was found to consist of three broad peaks that can be well fit by Lorentzians: 1320, 1580 and 1620 cm^{-1}. The GNR D-band is also weakly dispersive. The 2nd order Raman G’band for GNRs and MWNTs derived from HTT=2200°C are very similar, with the G’band in GNRs being somewhat. These differences indicate subtle differences in structural order and phonon dispersion in these two thermally transformed carbon filaments.
Chapter 9
Conclusions and Future work

Due to its unique 1-D structural nature, carbon nanotubes provide great opportunities for fundamental science and applications as described in Ch.1. As discussed, SWNT are often produced along with other unwanted materials; amorphous sp$^2$ carbons which coat the bundle walls, and multishell graphitic carbons which cover the metal catalyst residue. It is challenging to remove selectively unwanted materials in the raw soot with a minimum loss SWNT bundles. It was shown how to obtain purified SWNTs involving amorphous carbon removal step and catalyst particle removal step in Ch.4. Depending on the purification protocol, the degree of wall damage or functionalization on the tube walls was shown to be different by combining Raman and IR spectroscopy, which is sensitive to carbon skeleton and functional groups on the tube wall, respectively. It was also shown that wall damage and functional groups can be completely recovered and removed by high temperature annealing (1100°C < T < 1400°C).

Also, by the evolution of the IR-spectrum of purified SWNT samples that were annealed to high temperatures (up to 1400°C), we were able to observe the IR active modes of carbon nanotubes. Through comparison with theory, 8 out of the 18 IR bands that remain in samples annealed in the range 1100 °C -1400 °C can be assigned to first order IR modes (A$_{2u}$ or E$_{1u}$). The remaining 10 bands are assigned to two-phonon excitations.
Beyond 1400°C, thermal transformation of SWNT bundles were observed. For bundled SWNT with a very wide diameter distribution and small size bundles (i.e., HiPCO), the C-C bond rearrangement can be chaotic, producing a large amount of sp² fragments and amorphous carbon (a-C). At higher temperatures, these fragments and a-C help to form individual MWNTs. Tightly packed bundled SWNTs with a more homogeneous diameter distribution (ARC) were found to exhibit a more organized thermal transformation. Depending on HTT and the starting bundled size, the observed structures include coalesced SWNTs, individual MWNTs, bundled MWNTs, and type-I and type-II GNRs. Our observations suggest that type-I and type-II GNRs can be formed from the collapse of coalesced (larger diameter) SWNTs and bundled MWNTs, respectively. In this thermal process, we propose that the collapse of SWNTs and MWNTs into GNRs is driven by inter-tube van der Walls forces within bundles. By Raman scattering, GNRs exhibited much higher integrated D-band intensity than MWNTs transformed from HiPCO sample. However, the width intensity of the overtone of D-band (i.e. G’-band) is somewhat narrower. This suggests that D-band is activated by the lateral width of GNRs, not by defects in the honeycomb network.

There are several interesting issues to consider for the future work. First, We have suggested the three possible configurations of type II GNRs in Fig. 8-6(e). The cross-section of GNRs should be investigated by HRTEM measurement to see what the configuration at the edge is. Second, if GNRs are produced by collapse of MWNTs, the chirality of each layer would be random. Thus there will be no correlation between layers, which is called turbostratic graphite, unless in plane carbon atoms reorganize themselves to obtain ABAB stacking. HRTEM is not the right tool to obtain the accurate spacing.
between the layers to distinguish whether it is 3-D graphite or 2-D graphite (i.e. turbostatic). However, X-ray diffraction would be a candidate as a tool to check if GNRs are in a turbostratic structure. Third, the annealing has been done only up to 2200°C in this thesis work. However, it will be interesting to see the further transformation of GNRs at HTT=2800°C.
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