Laser induced effects in carbon nanotubes
Implications for Raman characterization of functionalized systems

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Preface

The work presented in this Licentiate thesis has been performed at the Division of Physics at Luleå University of Technology and to some extent at Henri Poincaré University in Nancy. The work was funded by the international PhDPolis program, to which I am grateful. Although many people have supported me in this work I will only name a few, but I hope all of you others know my gratitude.

My deepest thanks go to

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My co-supervisor Associate Professor Nils Almqvist, for motivation.
Dr Edward McRae, for pleasant discussions giving me new perspectives.
My parents, for your support whenever I need it.

Most importantly, thank you Liz for putting up with me.

Last, consider a few words from Ernest Rutherford from J. B. Birks “Rutherford at Manchester” (1962):

"All science is either physics or stamp collecting."

David Olevik

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Cover page: Functionalized single-wall carbon nanotube.
Abstract

Carbon nanotubes (CNTs) have attracted attention over the past decade because of their outstanding mechanical and electronic properties. These tiny tubular shells made of carbon atoms can be metallic or semiconducting and while having diameters of only about one nanometer ($10^{-9}$ m), they can be up to centimeters in length, making them quasi one dimensional (molecular wires). Along with a Young’s modulus several times that of steel, CNTs are close to perfect (ballistic) electric conductors and conduct heat better than diamond. This makes them candidates for a variety of applications from nanoscale electronics and composites reinforced with CNTs on the molecular level to nano-actuators and high performance flatscreen displays.

Beside electron microscopy, no other experimental method has been employed more in research on carbon nanotubes than Raman spectroscopy since it can noninvasively probe single CNTs and provide direct information about their molecular properties, for example, diameter and chirality. That is possible because in the case of CNTs Raman scattering is resonantly enhanced, giving an increase in signal by a factor of $10^6$. Due to their high surface energy and the van der Waals inter-tube interactions, carbon nanotubes naturally form bundles of up to hundreds of tubes. Heat dissipation in CNT bundles is inefficient and, as a result, their exposure to high incident laser power causes overheating and results in several thermal effects dominating the Raman spectrum. The high cost of CNT production has strongly impeded design of “pure nanotube” functional materials, thus shifting the focus of CNT materials research to creation of CNT-based composites. Such new multifunctional materials, based on the outstanding physical properties of nanotubes, are created by mixing relatively small amounts of CNTs with polymers or metals (matrix). This is still a big challenge because of poor dispersion of CNT bundles in the matrix and weak bonding of the nanotubes
to the surrounding host (matrix) molecules. One proposed solution to solve the latter problem is to establish bonding of CNTs to the matrix via functional groups covalently attached to the CNT surface, i.e., to use so-called "functionalized" CNTs in composites.

The aim of this work is to explore the possibilities of using Raman spectroscopy for expressive characterization of functionalized CNTs, the source material for synthesis of CNT-based composites. CNTs produced by two synthesis techniques, with different diameter distributions, were probed using several laser excitations. Evaluating the efficiency of the functionalization process requires first determination of the intrinsic spectroscopic properties of the pristine (non-functionalized) CNTs. Because functionalization is carried out on bundled CNTs, a detailed investigation of whether the incident laser irradiation causes thermal effects in the sample during Raman experiments was performed in order to find experimental protocols for recording the intrinsic (unperturbed by heating) spectrum of the CNT bundles. From this study a set of "reference conditions" defining laser irradiance levels that do not result in overheating of the CNT bundles was established. Exceeding these laser irradiation levels (thresholds) first results in reversible changes of the Raman spectrum due to heating, while further increase of the laser irradiation leads to irreversible changes in the spectra and, hence, destruction of the CNTs in the sample. Evaluation of this destruction demonstrates its dependence on CNT diameter and high sensitivity to photon energy. Additional experiments show that in some cases a similar instability of the Raman spectra and irreversible destruction of the CNTs occur at laser irradiation levels below those that increase sample temperature. Finally, we used the "reference" laser irradiation regimes to characterize the effects of CNT sidewall functionalization. Specifically, HiPCO-produced, single-walled CNTs functionalized by methoxypenyl functional groups were studied in detail and the influence on the three main vibrational bands investigated. Results from analysis of the radial breathing mode band show that the functionalization process is selective and depends on both nanotube diameter and type.
Appended papers

**Paper I**
Low laser power induced temperature instability of single-walled carbon nanotubes: A Raman study.
David Olevik, Alexander V. Soldatov, Edward McRae, Manuel Dossot.
Manuscript for publication

**Paper II**
Stability of carbon nanotubes to laser irradiation probed by Raman spectroscopy.
David Olevik, Alexander V. Soldatov, Manuel Dossot, Brigitte Vigolo, Bernard Humbert, Edward McRae.

**Paper III**
Preferential functionalisation of carbon nanotubes probed by Raman spectroscopy.
Jie Liu, Manuel Dossot, David Olevik, Victor Mamane, Brigitte Vigolo, David Abrahamsson, Henrik Jonsson, Yves Fort, Bernard Humbert, Alexander V. Soldatov, Edward McRae.
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Chapter 1

Introduction

Carbon nanotubes are single molecules made entirely of carbon atoms covalently bonded through \( sp^2 \) hybridization, which form a honeycomb pattern. The first carbon nanotubes (CNTs) were observed by Sumio Iijima in 1991 [1]. His transmission electron micrographs showed tubular structures with several concentric layers of carbon, i.e., several tubes inside one other, which were named multi-walled carbon nanotubes (MWNTs). While this type of tubes have many excellent properties they are not easily characterized by spectroscopy, which severely limited the widespread of the research. For this reason the discovery of the single-walled carbon nanotube (SWNT) in 1993 [2] was the start of extensive interest in the field by scientists worldwide. Raman spectroscopy in particular is simple and inexpensive in comparison to electron microscopy and has been employed in a tremendous amount of research on CNTs over the past decade.

1.1 Motivation of work

SWNTs have diameters of about 0.5 – 2 nm but their lengths can be from tens of nanometers up to centimeters, making them quasi-one-dimensional. Depending on its structure, a SWNT can have a tensile strength 20-100 times, and a Young’s modulus 5-20 times, that of steel. Also, when released from strain, nanotubes recover their original form without fracture. SWNTs are exceptional electric and thermal conductors, incomparable to metals, and can be of metallic or semiconducting type. These exceptional properties have inspired many proposed appli-
cations such as nano-electronics (including transistors and logic gates), conductive films, field emission sources (for use in LEDs and flat screen displays), different types of sensors or probes, nano-electro-mechanical devices (NEMS), nanomaterials and fuel-cell hydrogen storage to name just a few. The vision of macroscopic materials that inherit the strength of the CNTs is, however, hindered by the fact that CNTs bond weakly to each other and to their surroundings. Therefore, creation of CNT based nanomaterials proposes incorporating either polymerizing the nanotubes or having them form composites where they reinforce a matrix on the molecular level. Due to the high cost of synthesis and purification (about $500/gram) the composite route looks more promising. The problem of forming a strong link between the nanotubes and its surroundings still remains to be solved. A proposed solution is to covalently attach other molecular groups to the CNTs, which can interact strongly with the composite matrix. This is known as functionalization. Double-walled nanotubes (DWNTs) consisting of two tubes, one inside another, have lately gained a lot of attention. Their inner tubes increase their ability to withstand high pressures but, unlike MWNTs, they can still be characterized by Raman spectroscopy making them good candidates for polymerization. In order to make progress in research on composite carbon-based nanomaterials, fast and simple methods for their characterization are required. Raman spectroscopy fits these requirements. The main motivation for this thesis has been to develop completely

Figure 1.1: Single-walled carbon nanotube (SWNT).
Figure 1.2: Double-walled carbon nanotube (DWNT).

nondestructive experimental parameters for evaluating the efficiency of functionalization of SWNTs for the purpose of their further use in manufacturing (synthesis) of nanocomposites.

1.2 Thesis outline

In the first chapter of the thesis, Carbon nanotubes, an introduction to the structure and properties of single-walled carbon nanotubes and their synthesis and characterization is given and description of the CNT functionalization concept. In the next chapter the theory of Raman scattering in SWNTs is explained along with a detailed literature review of thermal influence on their electronic and vibrational properties. In the Methods and Materials chapter the pristine SWNT materials are presented along with the protocol used for their functionalization. The description of the Raman measurement system is also included in this part. The results part of the thesis includes experimental conditions for probing the intrinsic properties of SWNT bundles while avoiding thermal effects completely, discussed in the section Laser heating effects. Further, the problem of laser induced degradation of the Raman spectrum is considered, which is identified as destruction of the SWNTs. In the last part of the Results and discussion chapter, the efficiency and selectiveness of the CNT functionalization process is evaluated using the established experimental conditions. Finally, the results and conclusions
are summarized along with suggestions for future work.
Chapter 2

Carbon nanotubes

2.1 Structure

A single-walled carbon nanotube can be described as a rolled up layer of graphene, which is a single atomic layer of graphite. In figure 2.1 the 2D honeycomb lattice of graphene is shown. Connecting the sides $OB$ and $AB'$ will create the nanotube displayed on the right. The two vectors $C_h$ and $T$, which span the SWNT unit cell, are called chiral vector and translation vector, respectively. Depending on diameter and chiral angle, the unit cell can contain just a few carbon atoms or several hundreds. Since the bond-length between two carbon atoms is fixed, the nanotube can be defined by its diameter and helicity, which are both incorporated in the chiral vector, $C_h$. The vector is defined as

$$C_h = n\mathbf{a}_1 + m\mathbf{a}_2 \equiv (n, m), \quad (2.1)$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit vectors of the 2D unit cell of graphene. This means that the two indices $(n, m)$ uniquely describe the structure of the nanotube. As mentioned, SWNTs typically have diameters of $0.5 - 2$ nm and the diameter of a tube can be found from the $(n, m)$ indices using the equation

$$d_t = C_h/\pi = \frac{a_0}{\pi} \sqrt{m^2 + mn + n^2}, \quad (2.2)$$

where $C_h$ is the length of the chiral vector and $a_0$ is the graphene lattice constant ($a_0 = 2.460$ Å). Equation 2.2 is valid for $d_t > 0.8$ nm to an accuracy of about 2% [4]. It might be expected that diameter play the
Figure 2.1: Left: The 2D lattice of graphene with the chiral and translation vectors of a carbon nanotube presented. Right: Connecting the sides $OB$ and $AB'$ result in the nanotube presented. Reproduced from [3].

A major role for the properties of a SWNT, but there is another structural property which is just as important. As an example, the (10,6) and (10,5) nanotubes differ in diameter by only 5% and their difference in atomic structure is almost undetectable. Yet they show completely different electronic properties, with the (10,6) being semiconducting and the (10,5) metallic. The difference is caused by their different chiral angles (helicities). The chiral angle of a nanotube is defined as the angle between the chiral vector and the zig-zag direction, indicated in figure 2.1, and is found as

$$\theta = \tan^{-1} \left[ \frac{\sqrt{3} m}{m + 2n} \right].$$  \hspace{1cm} (2.3)

Due to symmetry of the hexagonal lattice $0 \leq \theta \leq 30^\circ$. Different chiral angles result in the nanotube being of metallic or semiconducting character and belonging to one of three different families depending on the $(n,m)$ indices. The family is determined by taking the remainder, (MOD), of $(2n + m)/3$, which can be 0, 1 or 2 [5]. If MOD=0 the nanotube belongs to the metallic family. Due to the curvature of the nanotube surface, however, only tubes where $n = m$ are truly metallic (corresponding to a chiral angle $\theta = 30^\circ$). These tubes are called armchair type, due to the resemblance of the carbon atoms along the circumference of the tube (see figure 2.2), and have a bandgap that is
strictly zero. In the cases where MOD=0 and n > m, the tubes are quasimetallic with bandgaps in the range 10 – 100 meV. Such tubes are only metallic at room temperature. If, on the other hand, MOD=1 or 2, the nanotube is of semiconducting type. In cases when the chiral indices are (n, 0), the atoms on the circumference form a zig-zag pattern and the tube is hence called zig-zag type, with a chiral angle $\theta = 0^\circ$. The zig-zag type and armchair type tubes are called achiral, in contrast to chiral tubes which have $0 < \theta < 30^\circ$. The achiral tubes have fewer numbers of atoms in the unit cell compared to chiral tubes of similar diameter. In table 2.1 the different structural properties of SWNTs are summarized.

<table>
<thead>
<tr>
<th>Structure type</th>
<th>Chiral indices (n,m)</th>
<th>Chiral angle $\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Armchair</td>
<td>n,n</td>
<td>$30^\circ$</td>
</tr>
<tr>
<td>Zig-zag</td>
<td>n,0</td>
<td>$0^\circ$</td>
</tr>
<tr>
<td>Chiral</td>
<td>n,m</td>
<td>$0 &lt; \theta &lt; 30^\circ$</td>
</tr>
</tbody>
</table>

Table 2.1: Chiral indices and angles for different types of nanotube structures.
2.2 Properties

The SWNT can be considered a ladder polymer meaning that in order to break the backbone, more than one bond must be broken. Typical ladder polymers have two such bonds, while in the case of SWNTs 10-20 bonds must be broken to cause failure. Since the $sp^2$ carbon-carbon bond is one of the strongest known, this gives SWNTs incredible mechanical properties. With a tensile strength of $50 - 200 \text{ GPa}$ (which is 20-100 times that of steel) and a Young’s modulus of $1 - 5 \text{ TPa}$ (5-20 times that of steel) they are even stronger than diamond (which has $sp^3$ hybridization). Metallic SWNTs are also close to perfect electrical conductors in their axial direction. In normal conductors the charge carriers are electrons or holes in the valence band and scattering events take place which dissipate the carrier momentum. SWNTs, on the other hand, are so-called ballistic conductors, meaning that the charge carrier moves without being scattered, hence avoiding the carrier momentum to be dissipated [7]. One can compare ballistic conduction in a nanotube to sending light in an optical fiber, where the complete internal reflection leads to minimal attenuation. In theory metallic nanotubes can carry a current density of $4 \times 10^9 \text{ A/cm}^2$ which is more than 1,000 times greater than that of copper. Further, the ballistic conduction of low energy phonons also aids in giving SWNTs a thermal conductivity of $6000 \text{ W/mK}$ [8] in their longitudinal direction, which is six times better than diamond and well exceeding that of copper (400 W/mK). A very

Figure 2.3: SEM micrograph of SWNT bundles.
important physical property of carbon nanotubes is that due to their high surface energy and van der Waals inter-tube interactions, they naturally form bundles of tens to hundreds of tubes. A scanning electron microscope image of bundled up tubes is shown in figure 2.3. This form of aggregation causes problems for applications and characterization, as will be discussed further in the text.

2.2.1 Electronic properties

In first approximation, SWNTs owe their electronic structure to the parent material graphene, but the one-dimensional nature of SWNTs causes interesting behavior and completely determines their electronic properties. In the $sp^2$ hybridization the $\sigma$-bonds form the hexagons on the nanotube walls and leave the $\pi$-bonds pointing perpendicular to the surface [9]. The electronic structure of SWNTs can therefore be derived from simple tight-binding calculations for the $\pi$-electrons of carbon atoms [3]. 1D systems are characterized by their electronic spectra exhibiting sets of singularities ($1/\sqrt{E}$) called van Hove singularities (vHSs) [10], shown in figure 2.4. These peaks occur due to quantum confinement of the electronic states and each $(n,m)$ SWNT has a unique DOS. The energy

![DOS Diagram](image)

Figure 2.4: The DOS of a (10,10) metallic SWNT. The Fermi level is set as zero energy and the peaks are van Hove singularities.
gap between vHSs symmetric about the Fermi energy is called the electronic transition energy $E_{ii}$, where $i = 1, 2, \ldots, n$ depending on its order (indicated in figure 2.4). Plotting these energies versus nanotube diameter for a large selection of different SWNTs builds a so-called Kataura plot [11], presented in figure 2.5. Hence each point in the Kataura plot represents a specific (n,m) nanotube [11]. Different bands can be seen corresponding to increasing order of the separation of the vHSs in the DOS ($E_{11}^S$, $E_{22}^S$, $E_{11}^M$ and so on). This band structure shows the relation of the electronic properties and the atomic structure or the nanotubes. The superscript indicates that the tubes in the band are metallic (M) or semiconducting (S). The Kataura plot is useful when employing Raman spectroscopy since when the laser photon energy matches the difference in energy of the vHS of a SWNT, the process becomes resonant (discussed in detail in section 3.1 and 3.2). In the bundled state, the vHSs are broadened and downshifted in energy.

### 2.2.2 Vibrational properties

The phonon structure affects many important processes in crystals. The phonons are carriers of thermal energy, participate in electron transfer and determine elastic and mechanical properties [3]. Shown in figure

![Figure 2.5: Kataura plot showing the electronic transition energies $E_{ii}$ as a function of nanotube diameter.](image)

Figure 2.5: Kataura plot showing the electronic transition energies $E_{ii}$ as a function of nanotube diameter.
2.6a, the phonon dispersion curve of graphene (2D graphite) has six phonon branches. Two dimensional solids have three acoustic branches, in this case the out-of-plane transverse acoustic (oTA), in-plane transverse acoustic (iTA) and the longitudinal acoustic (LA). Further, the out-of-plane transverse optic (oTO), in-plane transverse optic (iTO) and longitudinal optic (LO) phonon branches are also indicated. Imposing a Brillouin Zone-folding method on the phonon dispersion curve of graphene (figure 2.6a) produces the corresponding curve for a (10,10) nanotube [3]. This specific nanotube has 120 degrees of freedom, resulting in 66 distinct branches shown in figure 2.6c. Further, comparison of the phonon density of states (PDOS) of the 2D solid graphene (2.6b) to the one for the (10,10) nanotube (2.6d) exhibits the result of the 1D quantum confinement of the phonon states in the nanotube, with the familiar vHIs visible. The nanotube phonon dispersion curve and PDOS will approach that of graphene as the nanotube radius increases ($R \to \infty$). The Raman active vibrational modes of SWNTs are discussed in detail in section 3.2.1.
2.3 Synthesis

In all synthesis methods of SWNTs, a metal (Fe, Co, Ni or Y) or a bimetal (CoMo or FeRu) which favors the growth of carbon nanotubes is used as process catalysts. In addition a feedstock of carbon is required along with high temperature and pressure [6]. Synthesis of carbon nanotubes can be divided into three categories.

- **Laser ablation.** A target consisting of a graphite rod with a metal catalyst core is vaporized using a laser. The vapor is condensed on a substrate. Lithography can be used for placing catalyst particles on the substrate allowing for highly controlled growth.

- **Arc discharge.** Two catalyst doped graphite rods are used as electrodes and brought close together until a stable electric arc is formed (ignited). The anode is consumed and the rods are moved closer continuously to uphold the process.

- **Chemical vapor decomposition.** In the CVD method nanotubes are formed due to decomposition of a carbon-containing gas. The metal catalyst particles act as nuclei for the SWNT synthesis. The most commonly used CVD process is high-pressure carbon-monoxide conversion (HiPCO) where SWNTs with up to 97% purity are produced by CO and Fe(CO)$_5$ flowing at high pressure (30 – 50 bar). This creates single-walled carbon nanotubes of very small diameters, as low as 0.7 nm, with an average of 1.1 nm.

All current synthesis techniques yield a mixture of diameters and chiralities and on average about 1/3 metallic type tubes.

2.4 Characterization

There are several techniques available for characterizing carbon nanotubes and the choice depends on what information is of interest.

- **Scanning tunneling microscopy (STM) or scanning force microscopy (such as AFM) are used for determining diameter, and in some cases even chirality, and studying dispersion and aggregation of the nanotubes.**

- **Transmission electron microscopy (TEM) has the resolution to image even the hexagonal structure on the nanotube sidewalls.** It
can be used to find the number of walls and intershell spacing in MWNTs and to investigate structural details such as diameter and chirality.

• X-ray diffraction (XRD) is used to obtain information on the inter-tube spacing of nanotube bundles along with structural strain and impurities.

• Infrared spectroscopy is used to determine the presence of impurities remaining from synthesis.

• X-ray photoelectron spectroscopy (XPS) uses X-ray bombardment to allow electrons on the CNT surface to escape and their kinetic energy to be measured. This allows analyzing the bonding state and morphology state of the surface as well as carbon modification and contaminations.

• Photoluminescence techniques can be used to determine the chirality and diameter of a CNT as well as to find the optical transition energies $E_{ii}$. While signal strength is comparable to resonant Raman scattering in the case of carbon nanotubes, avoiding non-radiative decay of excited states (quenching) requires the bundles to be separated into individual tubes in order to measure their fluorescence. Further, metallic tubes can not be probed using photoluminescence.

• Raman spectroscopy is a powerful technique for characterizing single-walled carbon nanotubes due to their resonant enhancement. It probes vibrational properties of carbon nanotubes. Minimal sample preparation is necessary and the technique is fast and non-destructive.

2.5 Functionalization of carbon nanotubes

The concept of functionalization is to attach a molecule or a chemical group to a macro-molecule such as, for instance, a polymer chain or a nanotube. There are several ways a nanotube can be functionalized, i.e. via end-caps, open-ends or sidewalls as possible targets for the functional groups [12]. Of these strategies, the most interesting is sidewall functionalization which can result in increased CNT solubility, leading
to their better dispersion in solvents and polymeric systems. Stronger interactions between the nanotubes and their surroundings (such as a composite/polymer matrix) can also be achieved. Another interesting property of functionalization of CNTs is that the surface tension of the tubes can be modified. Pristine nanotubes are hydrophobic in nature due to the van der Waals interaction but functionalization can transform the surface to become hydrophilic by ionizing the CNT surface [13]. Sidewall functionalization of CNT can be performed in two ways, resulting in different types of bonds attaching the functional group to the nanotube. The first case is non-covalent functionalization, where the functional group binds to the nanotube surface through van der Waals forces. This effect is commonly used to individualize nanotubes for Raman experiments [14], in which case a surfactant is used to cover the nanotube surface, preventing bundling (see also section 4.3). However, non-covalent functionalization used for dispersion of nanotubes into a composite matrix does not provide a strong bond to the matrix itself. Further, the additives are difficult to remove and thus can have negative effects on the properties of the composites [12, 15], including fiber pull-out causing failure. A better candidate for CNT-composites is covalent functionalization. This requires breaking $sp^2$ bonds and replacing them with $sp^3$ bonds for attaching the functional groups to the nanotube sidewall. A schematic description of a functionalized single-walled carbon nanotube is seen on the cover page of this thesis. Since covalent bonds are very strong, unlike the van den Waals interaction, the created "handle" on the nanotube can be used to transmit its mechanical strength to the surrounding matrix. Further, since the chemical properties of the attached groups are well known, this can make the functionalized nanotube fit into established protocols and facilitate creation of composite materials. The functional group can hence be selected to match the chosen matrix. Moreover, covalent sidewall functionalization can be performed selectively, modifying metallic nanotubes while leaving the semiconducting ones unaffected [16, 17]. This can aid separation of semiconducting tubes from metallic tubes and is hence of interest for nano-electronic construction. Analysis of functionalized nanotubes employs some different experimental techniques. Absorption spectroscopy and resonance Raman spectroscopy are used to ensure that the functionalization is covalent and occurs at the sidewalls. Thermal gravimetric analysis (TGA) and X-ray photoelectron spectroscopy are employed to estimate the degree of functionalization by finding the weight fractions of the different
elements in the samples. Atomic force microscopy, scanning electron microscopy and transmission electron microscopy are mainly used to visualize structural changes in the samples, including aggregation.
Chapter 3

Theory of Raman scattering

Discovered by Sir Chandrasekhara Venkata Raman in the 1920s, which awarded him the Nobel prize in physics in 1930, the Raman effect is inelastic scattering of light on vibrational excitation (phonons). In Raman experiments a laser is used to excite atoms or molecules, changing their vibrational state. In figure 3.1 some different scattering processes involving phonons are shown. The width of the arrows symbolize the probability of the scattering events. Most likely to occur is Rayleigh scattering, where the photon is scattered elastically, resulting in emission of a photon with the same wavelength as the incident one. If the molecule is initially in its ground state and after scattering ends up in an excited (higher) energy vibrational state, the process is called Raman Stokes scattering. Oppositely, with the molecule initially in an excited state ending up in the ground state is called Anti-Stokes scattering. The probability (cross section) for Raman scattering is in the order of one in $10^6$. The cross section of these different scattering events depends on the number of molecules initially in the excited state, which in turn depends on temperature (according to the Boltzmann distribution). Hence the relative intensity of the Stokes/Anti-Stokes peaks in the Raman spectrum can be used for temperature estimations.
3.1 Resonance Raman scattering

Normally the molecule is excited to a virtual energy state before relaxing and resulting in a photon being emitted. A scattering process is called resonant if one or more transitions involves a real energy state of the molecule. More specifically, if there exists an actual electronic-vibrational energy state of the molecule matching the incident photon energy (instead of the virtual state), the process will be much more likely to occur. This effect is schematically shown in figure 3.1 along with the increase in probability of the scattering by a factor $10^3$, indicated by the thicker line.

3.2 Raman scattering in single-walled carbon nanotubes

In SWNTs, resonance occurs when the excitation photon energy matches the energy difference between the electronic-vibrational states (vHISs).
The excitation energy must match the transition energy by approximately $\pm 50 - 100\,\text{meV}$ in order for resonance to occur [18]. This span is called the resonance window. While this resonance effect will increase the probability of scattering, the number of electronic states will also contribute greatly to the signal strength. The van Hove singularities in the DOS of SWNTs exhibit a large number of allowed electronic states with nearly the same energy. It is this fact that makes it possible to detect the Raman signal of SWNTs at all. Since different $(n,m)$ nanotubes are in resonance at different excitation energies, it is not possible to measure signal from all tubes present in a sample using only one laser wavelength. The Kataura plot (figure 2.5) indicates which tubes are in resonance with a certain excitation energy (since it must match the transition energies $E_{ii}$ in the plot). Thus, to probe all possible resonance excitations corresponding to all nanotubes present in the sample, a laser system with tunable wavelength is required.

### 3.2.1 Raman active phonon modes

As discussed in section 2.2.2 there can be more than a hundred phonon branches in carbon nanotubes (an exact number depends on the chirality), but only less than twenty of these are Raman active. Of these vibrations we consider only the most important ones which fall into four bands. A low-energy range where radial vibrations are observed, a high-energy range with in-plane carbon–carbon vibrations and an intermediate-frequency range and its second order feature. These Raman modes are indicated in the typical SWNT Raman spectra of figure 3.2. The low- and high-energy phonons have received the most attention since their Raman signal is very strong. They give information about tube diameter, chirality, phonon confinement, semiconducting or metallic character, optical transition energies and more. We consider them in turn below.

**Tangential mode**

This first order mode comes from in-plane vibrations of adjacent carbon atoms in the hexagonal lattice involving both stretching and bending of the carbon-carbon bonds. The mode is inherited from graphite and is therefore often called the G-band. While Raman scattering in graphite produces a single G-band mode with a frequency of about $1590\,\text{cm}^{-1}$, a second mode with lower energy of about $1560 - 1580\,\text{cm}^{-1}$ is present.
in nanotubes. The different modes are due to vibrations in the circumferential or the longitudinal direction of the nanotube, as shown in the right part of figure 3.3. The higher energy mode is named $G^+$ and the lower energy mode $G^-$. If the nanotube is of metallic type, the $G^-$ and $G^+$ will correspond to the circumferential and transversal vibrations, respectively, while if the type is semiconducting the assignment of these modes is reversed [19]. The splitting of the graphite high energy phonon mode into two components is a sign of nanotubes present in the sample. 

The G-band Raman lineshapes in carbon nanotubes are of Lorentzian type with the exception of the $G^-$ component in metallic tubes. Here an asymmetry is present due to interactions between the phonons and the continuum of electronic states and a Breit-Wigner-Fano (BWF) lineshape is required to describe the mode profile:

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

(3.1)

where $1/q$ is the asymmetry of the lineshape, $\omega_{BWF}$ is the center frequency at the maximum intensity $I_0$ and $\Gamma$ is a broadening parameter [3, 20, 21]. The presence of the BWF component is a definite sign of metallic tubes being probed. While the $G^+$ component is diameter independent, the $G^-$ component depends on diameter and due to increasing

Figure 3.2: Typical Raman spectrum of a SWNT sample acquired using two different laser excitations. a) 1.96eV. b) 2.33eV.
curvature of smaller diameters, the phonon frequency decreases [22]. Further, the tangential Raman features are sensitive to environmental effects such as subjection to increased hydrostatic pressure which upshift the phonon frequencies [23, 24]. Mechanical tension or stress cause upshift or downshift depending on the direction it is applied in. The G-mode is also sensitive to charge transfer to or from the SWNT surface, achieved by dopant particles or functionalization to name a few. Negative or positive charge transfer to the SWNT causes downshift or upshift the G-modes, respectively.

Radial breathing mode

Due to the boundary conditions implied by rolling up a graphene sheet into a tube, a vibrational mode where all the carbon atoms in the circumference are vibrating coherently in the radial direction is possible (described in the left panel of figure 3.3). This mode is called radial breathing mode (RBM) with a frequency around 100 – 500 cm\(^{-1}\) and Lorentzian lineshape. While a tangential mode is present for graphene, graphite and nanotubes, RBM signal is a definite sign that the sample contains nanotubes. Since the mass of the carbon atoms on the circumference of a SWNT is proportional to its diameter, the frequency of the
RBM is related to the diameter of the tube as:

\[ \omega_{RBM} = \frac{A}{d_t} + B. \quad (3.2) \]

One set of experimentally determined coefficients are \( A = 234 \text{ nm cm}^{-1} \) and \( B = 10 \text{ cm}^{-1} \) which are valid for \( 1 \text{ nm} < d_t < 2 \text{ nm} \) [3]. The constants \( A \) and \( B \) depend on the tubes interaction with its environment and hence vary for tubes in bundles compared to individual tubes. They further also depend on whether the tubes are on a substrate, in solution or suspended. For diameters below 0.7 nm, lattice distortion causes the diameter to wavenumber relation to start deviating from equation 3.2. Since the RBM frequency depends on the nanotube diameter, signals from different diameter tubes do not overlap in the Raman spectrum (as they do for the \( G^+ \) mode). The RBM band hence reveals which diameters are present in the sample probed. The intensity of the RBM becomes weaker for larger diameters and is not visible for diameters above 3 nm. The RBM frequency is, like the tangential modes, sensitive to hydrostatic pressure, shifting to higher frequency upon increase of pressure.

All the first order Raman features depend on the bond length of the carbon-carbon bonds. Increasing bond length causes downshifts in the energy of the vibrational modes. Further, decreasing diameter causes increased curvature and hence the \( sp^2 \) hybridization to be distorted towards \( sp^3 \) character.

### Disorder band

The disorder or defect band, D-band, is also inherited from graphene and involves double resonant Raman scattering (two of the transitions to intermediate states of the system involve real energy states of the nanotube). The intensity of the D-mode is related to the number of defects on the nanotube surface. The scattering process involves one scattering of a phonon and also an elastic scattering off a crystal-defect. If the scattering off a defect is replaced with an inelastic scattering with an additional phonon, this leads to a Raman signal at twice the phonon energy, producing the second order mode of the D-band: \( G' \) [4]. This band, hence, does not depend on crystal defects. The double resonance further results in the D-band and \( G' \)-band lineshapes being non-Lorentzian [4]. The frequency of both the D-band and the \( G' \)-band are highly dependent on excitation energy. The D-band can upshift by 50 cm\(^{-1} \) upon
increasing the laser energy by 1 eV [3], and the corresponding upshift for the $G'$ will be twice as large.

### 3.2.2 Raman detectable signs of functionalization

As mentioned in section 2.4, sidewall functionalization of nanotubes breaks $sp^2$ bonds on the nanotube surface, creating defects in the structure. A sign of functionalization is therefore an increase in the D-band intensity. No change in the intensity of the tangential mode bands have been reported and it is therefore customary to use the ratio of the intensity of the D-band compared to the intensity of the $G^+$ component of the G-band. Hence the $D/G^+$ ratio of the functionalized sample should be compared to the one for the pristine sample [12]. Covalent functionalization also deteriorates the optical, electrical and thermal properties of the SWNTs (since these properties are $\pi$-conjugation dependent). The changes in the electronic states result in broadening (and eventually loss of) the van Hove singularities. This results also in decrease in the intensity of the RBMs [12, 16]. If the sample has been selectively functionalized, this can be investigated through the RBM band by comparing changes in relative intensities of the different components that correspond to different diameter nanotubes.

### 3.2.3 Monodispersion

In order to study the physical properties of single carbon nanotubes a vast amount of research has been performed on dispersing tubes as individuals. A variety of solvents have been proposed [25, 26], with varying results. The commonly accepted method for monodispersion is to use a surfactant such as sodium dodecyl sulfate (SDS) or sodium dodecylbenzene sulfonate (SDBS) [14, 27, 28] in solution (usually H$_2$O or D$_2$O). Applying high powered tip sonication breaks the bundles, allowing the surfactant to surround the tubes and hinder subsequent rebundling. The sonication, however, does not break all bundles completely, but leaves both individual tubes and small bundles to be non-covalently functionalized by the surfactant. The resulting particles in the suspension have different sedimentation coefficients while the solution is a constant density medium. Ultra-centrifugation (over 100,000 × g) of the suspension will cause the small surfactant-coated bundles to sediment, while the individually coated tubes have a density equivalent to the solution medium and are hence unaffected. After centrifugation, the supernatant can be
decanted, producing a stable suspension of individual tubes. For Raman experiments when studying individual tubes separately, spin-coating is used to reduce surface density on the substrate. This is required since having several tubes present under the laser spot on the sample will result in signal from all of them contributing and overlapping in the Raman spectrum. In contrast to bundled tubes, isolated nanotubes exhibit narrower vHSs in the electron spectra, with a slight increase of spacing between the energy levels.

3.2.4 Temperature effects in vibrational and electronic properties of single-walled carbon nanotubes

A change in temperature has been reported to have a strong influence on the electronic and vibrational properties of SWNTs [18, 29–40].

Influence on the vibrational properties

Increase of nanotube diameter due to thermal expansion should cause downshift of the RBM frequency according to equation 3.2. However, the expansion coefficients for SWNTs are too small for this to have effect due to the bond stretching and out-of-plane bond-bending contractions almost completely cancelling each other out [30]. Further, the RBM frequency does not only depend on diameter but also strongly on the stiffness of the carbon-carbon bonds. The same is true for the energy of the vibrations of the hexagons in the 2D graphene lattice responsible for the tangential Raman modes. Softening of the intra-tubular carbon-carbon bonds with temperature increase, decreases the energy of these vibrations and therefore causes downshift in the phonon frequencies [30]. The bond softening is the sole reason for the frequency downshift when dealing with an unperturbed SWNT, freely suspended between two supports, without any other mechanisms at work due to interaction with a surrounding [37]. If the nanotubes are individually dispersed on a substrate using a surfactant, increase of temperature will cause thermal expansion of the surfactant, resulting in increased pressure exerted on the tube [33, 36]. Increased pressure has been reported to upshift phonon frequencies [24], hence working against the effect of bond softening. It has further been shown that also the intra-tubular van der Waals interactions are softened upon increase of temperature [30, 36]. Decreasing the forces holding the SWNTs in the bundle together causes large thermal expansion of the bundles. This, along with
negligible increase of the nanotube diameters, result in decrease in the pressure asserted on the nanotubes by its surrounding tubes. This is opposite to the effect in surfactant-coated tubes.

Influence on the electronic properties

A temperature increase causes shifts of the vHSs in the electronic DOS and hence shifts of the electronic transition energies $E_{ii}$. In the case of individually suspended SWNTs, where no interaction with the surroundings occurs, the influence of temperature on the electronic properties are merely due to electron-phonon coupling [36], causing the transition energies to downshift. Further, the shifts in $E_{ii}$ for surfactant-covered monodispersed tubes show blueshift or redshift for semiconducting tubes depending on whether they belong to MOD=1 or MOD=2 families, respectively [18]. This is explained by the increase in pressure exerted by the tube environment upon heating as mentioned previously. The same effect, causing shifts of $E_{ii}$, occurs for SWNT bundles due to decrease in the intra-tubular van der Waals interactions, causing pressure decrease. Since shifts of the transition energies $E_{ii}$ result in altered resonance conditions for the SWNTs which are currently in resonance with the incident laser excitation, this leads to increase or decrease in intensities of different RBM peaks in the Raman spectrum. This is equivalent to changing the excitation wavelength slightly and these effects can dominate the spectrum. Hence temperature-induced shifts of the vHSs are very important to consider in analysis of the Raman spectrum.

Laser heating

SWNTs have remarkably high optical absorption and the incident photons cause lattice vibrations. Not all phonon scattering events result in a new photon being emitted and the energy of the remaining absorbed photons will find other ways of decay (non-radiative). If the power of the incident irradiation is high, such decay will result in heating of the nanotube. Hence, primarily tubes that are in resonance are heat absorbers [32]. Experiments on individual SWNTs suspended over trenches have been performed and have shown that, even with their impressive thermal conductivity, such nanotubes are incapable of dissipating high power incident irradiation causing downshifts of the tangential modes of around $-0.025 \text{cm}^{-1}/\text{K}$ depending on tube diameter [37, 38]. Corresponding downshift for the RBMs are diameter- and chirality-dependent, with
shifts between $-0.0002$ and $-0.025 \text{ cm}^{-1}/\text{K}$. However, if a nanotube is placed on a substrate which can act as a heat sink, its temperature does not increase until exposed to extremely high fluence of the excitation laser [18]. In the case of bundles, only the tubes that are in good contact with the substrate (at the bottom) have the heat sink and hence the concentration of heat absorbers compared to heat sinks is much higher than for monodispersed tubes. It is concluded that absorption of the incident laser energy can cause local increase of sample temperature and pose serious problem to the characterization of SWNTs, especially when in a bundled state. We will refer to this mechanism as *overheating*. 
Chapter 4

Methods and materials

4.1 Carbon nanotube source material

In this work, two different source materials of carbon nanotubes were investigated. The first sample was HiPCO-produced with a broad small diameter range of 0.8 – 1.2 nm and with exceptionally high purity (97%). The second sample was arc discharge-produced, containing larger diameters in the range of 1.2 – 1.6 nm. Arc discharge synthesis results in a high degree of impurities being present in the sample, mainly amorphous carbon and metal catalyst particles. The diameter ranges were established by Raman characterization. Decomposition of the RBM-band into individual frequency components led to an estimation of the diameters using equation 3.2. Further, assignment of some of the RBM frequencies to chiral indices was done using experimental\(^1\), semi-empirical \(^41\) and theoretical\(^2\) sources. These sources correlate \((n,m)\) indices, RBM frequencies and the optical transition energies in the electronic DOS of different SWNTs. Hence, knowledge of the excitation photon energy producing maximal resonance along with experimental RBM frequencies allow for explicit assignment of the \((n,m)\) indices. With chiral indices known, information on the electronic properties (metallic/semiconducting) of the tubes is obtained. The differing diameter range of the two samples allows for easier investigation of the influence of diameter on various chemical treatments.

\(^1\)http://www.fisica.ufmg.br/~adojorio/Download.htm
\(^2\)http://www.photon.t.u-tokyo.ac.jp/~maruyama/kataura/kataura.html
4.2 Functionalization of the source material

Functionalization of arc discharge- and HiPCO-produced SWNTs was performed by colleagues at Nancy University using the following protocol. Pristine SWNT material (6 mg) was placed along with 60 ml of toluene in a 100 ml round-bottom flask equipped with a magnetic stirrer and a reflux condenser. 4-methoxyphenylhydrazine hydrochloride (175 mg) was added under stirring. The mixture was sonicated for 30 min to get a visually homogeneous suspension. The temperature was then increased to 130° C and the reaction was continued for 72 hours after which the mixture was cooled to room temperature. Methanol was added to the mixture to dissolve unreacted 4-methoxyphenylhydrazine hydrochloride and the mixture was filtered through a PTFE membrane (pore size 0.2 μm). The nanotubes were washed with methanol (3 × 50 ml) until the filtrate became colorless. Collected nanotubes were dried in vacuum at 80° C for 12 hours. Further details of the functionalization procedure are presented elsewhere [15, 42].

\[
\text{NHNNH}_2^\text{HCl} \xrightarrow{(A) 130^\circ \text{C}, 72h} \text{PhCH}_3 \quad \text{SWNTs} \quad \text{OCH}_3
\]

\[
\text{OCH}_3 \xrightarrow{(B) \text{MicroWave O-xylene}} \text{n}
\]

Figure 4.1: Free radical functionalization of SWNTs through 4-methoxyphenylhydrazine hydrochloride

4.3 Dispersion

Before Raman measurements, the different sample materials were dissolved in Dimethyl Formamide (DMF), with a concentration of about 1 mg/ml, and ultrasonically dispersed for 30 minutes using a bath sonicator. A droplet of liquid SWNT suspension was deposited on a glass slide and subsequently air-dried at 50° C. The resulting sample slides show clear aggregation visible. Since no high power sonication (tip sonication) was used, nor any ultra-centrifugation, the nanotubes are in the form of large bundleds [14].
4.4 Equipment

Since spectroscopy of SWNT require the tubes to be in resonance with the excitation source, several different lasers were used for characterization. Explicitly the wavelengths 830 nm (infra-red), 632.8 nm (red), 532 nm (green), 514.5 nm (green), 488 nm (blue) and 457 nm (blue) were used, which corresponds to photon energies of 1.49, 1.96, 2.33, 2.41, 2.54 and 2.71 eV, respectively. Large part of the work was conducted using the excitation from a HeNe laser (632.8 nm or 1.96 eV) and a Nd-YAG laser (532 nm or 2.33 eV). These two lasers allow probing only metallic or only semiconducting type SWNTs for the arc discharge sample. The spectroscopic setup used was a WITec CRM-200 Raman/fluorescence confocal imaging system, schematically presented in figure 4.2. The laser beam enters the system through a single-mode optical fiber and is reflected by a holographic beamsplitter, a mirror which reflect only the laser wavelength. The laser light is then focused onto the sample stage by the objective. 20X and 100X objectives were used with estimated spot-sizes of 5.4 and 2 μm, respectively. Raman scattered light from

![Figure 4.2: WITec CRM-200 Raman imaging system.](image)

the sample is collected by the same objective, sending parallel beams
towards the beamsplitter. Since it will only reflect the laser wavelength it acts as a notch filter attenuating the Rayleigh scattered light, while allowing Stokes and Anti-Stokes scattered light to pass. A second filter (super notch filter) further attenuates the wavelengths around the laser wavelength (approximately ±150 cm$^{-1}$) in order to protect the CCD of the spectrometer. Due to the wavelength dependent properties of the notch filters, they must be changed to match the laser used. The scattered light is focused onto a multi-mode optical fiber before leaving the microscope and entering the spectrometer. The small diameter of the multi-mode fiber (25 – 50 μm) acts as a pinhole allowing for confocal microscopy, hence increasing spatial resolution. The spectrometer has three gratings with 150, 600 and 1800 grooves/mm with the latter resulting in spectral resolution of < 1 cm$^{-1}$ depending on laser wavelength. Finally, the grating reflect the scattered light onto a CCD array which registers the Raman signal. The sample stage consist of a two-axis piezotable with 2 nm resolution, allowing the sample to be scanned under the objective in order to select sample area. The laser powers used varied in the range 0.1 – 12 mW, measured directly on the sample stage using a Coherent LaserCheck power-meter.
Chapter 5

Results and discussion

5.1 Laser heating effects

Even when using a Raman system with excellent sensitivity and with the resonance effect present in SWNTs, it is still necessary to increase the power density (PD) of the incident light to get good Raman signal. Consequently, as discussed in section 3.2.4, SWNT bundles will immediately overheat upon exposure to high incident laser irradiation. Laser power densities of up to 100 kW/cm$^2$ are routinely used in Raman experiments, which is enough to increase the temperature of bundled SWNTs several hundred Kelvin. The effect on the Raman spectrum is particularly evident when probing a sample with many different (n,m)-tubes present, due to different resonance conditions. Increasing temperature can cause some tubes to come into better resonance, while others move out of resonance, altering their respective RBM intensities. The frequency downshift and broadening of the tangential modes can be seen in figure 5.1b, where Raman spectra of HiPCO-produced SWNT bundles probed by 1.96 eV excitation (632.8 nm) are shown. Increasing the laser power density from 5.7 kW/cm$^2$ (curve 1) to 340 kW/cm$^2$ (curve 6) causes the G-band components to downshift by on average 11 cm$^{-1}$ corresponding to a temperature increase just above 400 Kelvin [37]. Considering the RBM-band, decomposition of convoluted peaks in figure 5.1a reveal that it consists of six metallic components (left part of spectrum) and six semiconducting components (right part), at ambient temperature. It is important to emphasize that the frequency shifts of the RBMs upon laser PD increase are very small compared to the corresponding shifts of the G-band. However, the changes in resonance conditions due to down-
shift of the vHSs (described in section 3.2.4) result in significant changes of the relative intensities of the twelve peaks and, consequently, in RBM profile. It should also be stressed that these temperature induced shifts of the phonon frequencies and changes to the resonance conditions are reversible. Fantini et al. report complete recovery of the original, ambient temperature, spectrum upon decrease of laser power [18]. However, high PD laser irradiation has been reported to cause irreversible decrease in the Raman spectrum for SWNT bundles [32, 34, 40], identified as destruction of the nanotubes. From studying how the RBM intensities of certain (nm)-species of SWNTs decrease during laser exposure, selective destruction dependent on diameter [40] and electronic properties [34] of the nanotubes have been proposed. Claims that nanotubes in resonance with the incident radiation are preferentially destroyed have also been put forward [32]. There hence seem to be two laser induced effects present in SWNT bundles. The first is heating of the sample by the incident laser radiation, causing reversible changes to the Raman spectrum.
We call this effect overheating. The second concerns destruction of the sample by the irradiation, with the result that the original, ambient temperature, spectrum cannot be recovered upon decrease of the laser power density. Functionalization of the SWNTs used in our experiments was performed on bundled tubes, as described in section 4.2. Therefore, care has to be taken to separate changes in the Raman spectra due to functionalization from unwanted effects arising from laser heating in the analysis.

5.1.1 Overheating threshold

We performed a series of experiments on the pristine samples, aimed at determining laser power density thresholds for each different excitation wavelength that does not change sample temperature. To ensure that temperature does not increase above room temperature, shifts of the G-band and the relative intensities of the RBM-band were monitored. The experiments were performed by initially recording the Raman spectra during exposure of the sample to minimal laser power density. The power density was then increased, causing laser heating, and spectra from the same sample area were recorded again. This was repeated until clear changes in the RBM intensities and shifts of the G-band were observed. The resulting series of Raman spectra for the HiPCO sample, probed by 1.96 eV excitation, are presented in figure 5.1 showing the influence of laser heating on the spectra. Further decrease of the laser PD below 5.7 kW/cm² (not shown) does not alter phonon frequencies or relative intensities. We can hence infer that a power density of 5.7 kW/cm² does not increase sample temperature for the HiPCO-produced SWNT bundles when probed by 1.96 eV. We introduce a term overheating laser power density threshold for this value, or simply overheating threshold. We further determined such thresholds for both the HiPCO and arc discharge samples regarding 1.96 eV and 2.33 eV laser irradiation. The established overheating thresholds are presented in table 5.1 and are in the range 2 – 10 kW/cm² depending on sample and excitation wavelength.

5.1.2 Stability threshold

Overheating thresholds yield experimental conditions that are satisfying in not increasing sample temperature. In the progress of establishing these thresholds, experiments indicated that the Raman spectrum
can show instability over time even at laser PDs below those which cause overheating. Since irreversible changes of the Raman spectrum are associated with destruction of the SWNT being probed, we performed further experiments to investigate this matter. Time evolution studies of the Raman spectra of the SWNT bundles at different laser PDs (held constant in each experiment) were performed in order to determine the maximum PD at which irreversible changes in the Raman spectra do not occur. This we define as a threshold for stability. The acquisition-times needed to produce high quality spectra using such extremely low laser power densities (in some cases <2 kW/cm²) are up to 30 minutes using our Raman setup. It should be realized that during an acquisition we in fact record a mean spectrum over that period of time. Hence, to notice any changes in the Raman spectrum of the sample, we acquired a 20 minute RBM spectrum followed by a 10 minute G-band spectrum. The procedure was repeated back-to-back for 1.5 hours probing the same area on the sample. Considering the HiPCO sample, probed using 1.96 eV excitation, we have previously established that exposure to a PD of 5.7 kW/cm² does not increase sample temperature. The temporal stability for this PD is shown in figure 5.2a. As can be

![Figure 5.2](image)

**Figure 5.2:** Influence of low laser power density on the Raman modes of HiPCO-produced SWNT bundles. a) 1.96 eV irradiation using 5.7 kW/cm² PD. b) 2.33 eV irradiation using 0.9 kW/cm² PD. M and S in the figures indicate which RBMs correspond to metallic and semiconducting tubes, respectively.
seen, no changes to the RBMs are induced during 1.5 hours of exposure. Neither is any shift of the G-band noticed (not shown). We have thus found a power density that allows acquiring the intrinsic spectrum of the HiPCO SWNT bundles for this excitation wavelength. We name these conditions as reference conditions and the corresponding Raman spectrum as reference spectrum. Moving on to exposure of the HiPCO sample to the higher photon energy of 2.33 eV. Overheating effects are avoided using a PD of 2.5 kW/cm² in this case (table 5.1). However, it turns out that this PD does not produce temporal stability of the RBM spectrum. Decreasing the laser power to the sensitivity limit of our Raman setup, we acquired a time-series of spectra at 0.9 kW/cm², presented in figure 5.2b. As can be seen, the absolute RBM intensities decrease with time for this photon energy even at this minimal PD. Metallic tubes are reported to be more sensitive to irradiation [34], yet the HiPCO sample have both metallic and semiconducting tubes in resonance at both excitation energies, indicated in figure 5.2 by M and S respectively. Comparing the influence on the RBMs of the metallic tubes for the two different excitations, we find that for 1.96 eV irradiation, the larger diameter tubes (peaks between 195 – 235 cm⁻¹) are stable. On the contrary, we observed instability of smaller diameter metallic tubes (peak at 275 cm⁻¹ in figure 5.2b) to irradiation with a photon energy of 2.33 eV. The destruction may therefore be determined by nanotube diameter or photon energy. Considering next the semiconducting tubes we find that all phonon modes are stable to 1.96 eV exposure, specifically also the smallest diameter tubes at 285 cm⁻¹. However, under exposure to 2.33 eV the peak at 290 cm⁻¹, also consisting of small diameter semiconducting tubes, decreases. So does the peak at 190 cm⁻¹ corresponding to larger diameter tubes. We therefore conclude that the photon energy plays a considerably more important role in the temporal stability of the spectrum at low laser power densities than the electronic properties. In the case of the arc discharge-produced SWNT bundles, probed by 1.96 eV excitation, the overheating threshold was determined to lie between 4.6 – 7.3 kW/cm² (stating that 4.6 kW/cm² is a safe PD). The results of the time study at this PD (4.5 kW/cm²) are shown in figure 5.3b, displaying unstable timedependance of the phonon modes. We are in this case probing only metallic tubes and can clearly see that the peak at 190 cm⁻¹, corresponding to smaller diameters, is influenced to a greater extent. Decreasing the PD to 3.4 kW/cm² results in stability of the spectrum as can be seen from 5.3a. Comparing these results with
Figure 5.3: Influence of low laser power density on the Raman modes of arc discharge-produced SWNTs, irradiated with HeNe laser (1.96 eV) with exposure times indicated: a) laser power density 3.4 kW/cm². b) power density 4.6 kW/cm².

those obtained on the HiPCO sample, we can conclude that in the case of metallic tubes, smaller diameter tubes are more sensitive to incident laser irradiation and higher photon energy further enhance this effect. To finally elude the influence of laser irradiation on semiconducting tubes we consider the thresholds for the arc discharge sample exposed to 2.33 eV photon energy. The changes in phonon mode frequencies and intensities due to rising temperature occur when PD is increased from 4.4 to 9.1 kW/cm², constituting the overheating threshold. This threshold is quite similar to the one for the lower excitation energy (4.6–7.3 kW/cm² for 1.96 eV), which probes only metallic tubes for this sample. This indicates that the thermal absorption does not depend on photon energy for the larger diameter tubes in the arc discharge sample. Surprisingly, the arc discharge-produced SWNT bundles have higher stability thresholds compared to their HiPCO-produced counterparts, despite higher degree of metal catalyst impurities present in the sample. This indicates that the impurities have inefficient heat absorption. The stability threshold for the combination arc discharge-produced SWNT bundles and 2.33 eV excitation was established to be in the range 3 to 3.7 kW/cm². It hence turns out the stability threshold is essentially the same regardless of
photon energy in the case of the larger diameter, arc discharge SWNTs. This is completely opposite to the result we obtained for HiPCO tubes, having smaller diameters, where increased photon energy cause considerable decrease in the stability threshold. Thus, we argue that smaller diameter tubes (HiPCO) in bundles are more sensitive to high energy photons than larger diameter tubes (arc discharge). Furthermore, no dependence of the thresholds on the SWNT electronic structure was found (metallic or semiconducting nanotube type). The stability power density thresholds are summarized in Table 5.1 along with the overheating thresholds. The reference conditions for each sample/excitation are in all cases defined by the lower stability threshold. A more detailed analysis of these experimental series is presented in Paper I.

### 5.1.3 Selective destruction

The reference regimes established can be used for probing the intrinsic, temperature unperturbed, Raman spectra of SWNT bundles. Nevertheless, the phenomenon of laser heating itself is interesting and requires further attention. It is of interest to examine in more detail which types of tubes are primarily affected by laser irradiation since contradictory results on preferential destruction of SWNTs have been reported. Increased sensitivity to laser irradiation due to small diameter [40] and metallic type [34] have been proposed. Huang et al. exposed HiPCO SWNT bundles to 632.8 nm laser power irradiation using 100 kW/cm$^2$ power density [34]. Since at such conditions the reaction occurs rapidly we chose to perform an experiment where the HiPCO sample was exposed to a fairly high laser PD of 47 kW/cm$^2$ (632.8 nm), still well ex-

<table>
<thead>
<tr>
<th>Sample</th>
<th>Excitation</th>
<th>Stability threshold</th>
<th>Overheating threshold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc dis.</td>
<td>1.96 eV</td>
<td>3.4 – 4.6 kW/cm$^2$</td>
<td>4.6 – 7.3 kW/cm$^2$</td>
</tr>
<tr>
<td>Arc dis.</td>
<td>2.33 eV</td>
<td>3 – 3.7 kW/cm$^2$</td>
<td>4.4 – 9.1 kW/cm$^2$</td>
</tr>
<tr>
<td>HiPCO</td>
<td>1.96 eV</td>
<td>&gt; 5.7 kW/cm$^2$</td>
<td>&gt; 5.7 kW/cm$^2$</td>
</tr>
<tr>
<td>HiPCO</td>
<td>2.33 eV</td>
<td>&lt; 0.9 kW/cm$^2$</td>
<td>2.5 – 4.4 kW/cm$^2$</td>
</tr>
</tbody>
</table>

Table 5.1: Laser power density thresholds for SWNT bundles of arc discharge- and HiPCO-produced samples when probed by 1.96 eV and 2.33 eV excitation. In the case of HiPCO SWNTs, no actual thresholds have been established for 1.96 eV.
ceeding the stability threshold. Figure 5.4 shows the results of this experiment where all data were collected from the same spot on the sample. Initially a spectrum using a PD well within the reference conditions, 4.4 kW/cm², was recorded (curve 1 in figure 5.4a). We then immediately increased the PD to 47 kW/cm² and collected Raman data under these conditions (curve 2 in figure 5.4b). The sample was irradiated at this elevated, but constant, PD for about 16 hours and Raman spectra were recorded at certain time-points (curves 3 and 5 in figure 5.4b). Importantly, we wished to simultaneously monitor the nanotube population under reference conditions. Therefore, the laser annealing of the sample was interrupted and the sample allowed to cool to ambient temperature. The reference spectra (curve 4 in figure 5.4a) was then recorded at the PD (4.4 kW/cm²). Thereafter, the sample was immediately brought back to high PD (47 kW/cm²) and irradiation resumed until the next measurement sequence (spectra 5-6 in figure 5.4). From the temporal evolution of the RBM spectra at 47 kW/cm², shown in figure 5.4b, it follows that: i) the Raman band and a shoulder around 215 cm⁻¹ and 240 cm⁻¹, respectively, decreased substantially in intensity, ii) the band at 255 cm⁻¹, originating from semiconducting SWNTs, remains essentially unchanged, and iii) the metallic band at 215 cm⁻¹ gradually shifted to higher wave numbers which is a signature of a temperature decrease due to changes in resonance conditions [18]. The latter is also evidenced by the downshift of the G-band in the correspondent tangential mode spectra (not shown) acquired using the elevated PD at the same times as the RBM spectra of figure 5.4b. We estimated the SWNT bundle temperatures at different exposure times using the shifts of the G⁺ mode frequencies combined with an average value for the temperature coefficients of this mode (−0.025 cm⁻¹/K), reported by Zhang et al. [37]. During the first 6 h of laser irradiation, sample temperature dropped from 410°C to 290°C. An additional 10.5 h of exposure, however, resulted only in a temperature decrease to 260°C. Such temperature decrease of SWNT bundles exposed to constant high PD laser irradiation is an interesting effect which has not been previously reported. We associate it with a decrease in the number of heat absorbers (SWNTs in resonance with the incident photons at 47 kW/cm² PD, as discussed in section 3.2.4) due to destruction of the most overheated tubes. A predominant decrease of the Raman signal at 210 – 225 cm⁻¹ from the metallic tubes is consistent with results reported in [34]. Turning to the RBM spectra acquired at the reference condition (figure 5.4a),
Figure 5.4: RBM spectra for HiPCO SWNT bundles recorded using 632.8 nm laser excitation at a) ambient temperature using a PD of 4.4 kW/cm² and b) during laser heating at a PD of 47 kW/cm². The spectra were recorded in order (1) through (6) at the indicated times. After acquisition of the initial spectrum (1) the PD was increased to 47 kW/cm² and maintained at this level during the experiment with only short interruptions for acquiring the spectra (4) and (6) at ambient temperature. M and S in the figures indicate which RBMs correspond to metallic and semiconducting tubes, respectively.

we notice the irreversible intensity-decrease of the Raman modes after exposure to 47 kW/cm² PD. Remembering the inverse relation between Raman frequency and tube diameter (equation 3.2), the decrease clearly depends on tube diameter. SWNTs with smaller diameters are hence more sensitive to laser irradiation. This result is in line with the findings of Bokova et al. [40]. A remarkable conclusion following from our data is that the smallest diameter tubes (peak at 285 cm⁻¹) exhibit the largest decrease despite not being in resonance at the damaging PD. Evidently, they were destroyed via indirect overheating, i.e. through heat dissipation from the heat absorbing SWNTs in good resonance at high temperatures. Furthermore, the intensity of the peak at 285 cm⁻¹ hardly decreases after 6 h of irradiation, i.e. when the nanotube temperature dropped below 300° C. We infer that at this temperature the heat
dissipation from the tubes in resonance is insufficient to cause further damage. Further, the Raman intensity of the peaks around 215 and 255 cm\(^{-1}\), originating from the SWNTs in resonance at high PD, continues to decrease below 300° C, supporting our claim. The conclusions regarding nanotubes which undergo preferential destruction under high laser irradiation drawn from the analysis of data shown in figure 5.4 may seem inconsistent. Data collected at high PD indicate no destruction of the semiconducting band at 255 cm\(^{-1}\) in contrast to data recorded under reference conditions which unambiguously show substantial degradation of the Raman signal. There is actually no inconsistency in the presented data, since the temporal evolution of the RBM spectra at high PD depends on two factors. First, the actual population of nanotubes being probed is changing due to destruction. Second, the change in sample temperature will alter the resonance conditions for the nanotubes left in the sample, as discussed in section 3.2.4. It is therefore impossible to make a reliable conclusion about damage of nanotubes from spectra acquired using high PD (resulting in elevated temperature) unless the contributions of these factors to the RBM intensities are separated. On the contrary, the ambient temperature data (figure 5.4a) depend only on the SWNT population in resonance. Therefore the reference conditions proposed should be used when considering information about nanotube damage due to high laser PD exposure. We again find that laser power densities must be carefully selected when studying SWNT bundles. The reasons for the destruction of the nanotubes, and resulting deterioration of the RBM spectrum, can be their oxidation in air and/or pure overheating since our experiments were performed in air. Oxidation has been previously suggested [34]. Additional experiments under protective atmosphere, or in vacuum, are required in order to separate pure temperature effects and oxidation in SWNT bundle destruction due to laser irradiation.

5.2 Characterization of functionalized carbon nanotubes

Functionalization of the source materials described in section 4.2 was evaluated with respect to its efficiency and selectivity. Raman characterization was performed and spectra of the pristine (unfunctionalised) and functionalized samples were compared to reveal possible changes
in the spectra. Considering the intensities of the RBMs and D-band in particular. The D-band intensity depends on the crystal disorder and increase when $sp^2$ bonds on the SWNT walls are replaced with $sp^3$ bonds as a result of the functionalization process. We conduct the experiments on SWNT bundles, so the intensity of the D-band reflects the overall crystal disorder for all different (n,m)-nanotubes currently in resonance with the excitation laser. The RBMs decrease in intensity upon functionalization is associated with broadening of the vHSs, causing reduced resonance enhancement of the signal. The broadening can also allow SWNTs not in resonance in the pristine sample case to come into resonance once functionalized. Due to the separation in RBM frequency for tubes of different diameters, probing the response of different nanotube species separately without monodispersion is possible. The D-band and RBM features do not, however, unambiguously indicate what causes the appearance of sidewall defects. The presence of the hydrazine functional groups were therefore verified by X-ray photoelectron spectroscopy and thermal gravimetric analysis. The latter found the degree of functionalization to be, for instance, one functional group per 72 carbon atoms in the case of the HiPCO produced sample. Detailed information of the procedures for the supporting characterization techniques was published elsewhere [15]. Finally, to ensure the absence of thermal effects, the reference conditions previously established were used when acquiring the Raman spectra.

**5.2.1 Preferential functionalization**

Two structural parameters of the SWNTs were investigated regarding selectivity of the functionalization process: diameter and electronic type. Considering first the information available from increase in the D/G$^+$-ratio upon functionalization for the different samples. The influence of diameter could be investigated by comparing the results for the HiPCO- and arc discharge-synthesized tubes, which have different diameter distributions. Further, for the larger diameter arc discharge-produced SWNTs, 1.96 eV and 2.33 eV laser excitations probe only metallic or only semiconducting tubes respectively, as previously mentioned. That allows us to separate two factors influencing functionalization of carbon nanotubes. In figure 5.5 the Raman spectra of the arc discharge SWNTs before and after functionalization are shown. The left two spectra (a) and (b) show the result for the semiconducting tubes, probed using
2.33 eV excitation. The right spectra (c) and (d) are acquired using 1.96 eV and show the effect on the metallic tubes. We compare the

D/G⁺-ratios before (upper panels) and after functionalization (lower panels) for the two excitations and find them to increase by 28% for the semiconducting tubes and by 22% for the metallic ones. This reveals no evident dependence on the electronic properties for the larger diameter tubes. To find the influence due to diameter we turn to the corresponding spectra for the HiPCO SWNTs in figure 5.6. Again the spectra of the pristine samples are in the upper panels and the functionalized in the lower. In this case, the increase in D/G⁺-ratios are more profound: for 1.96 eV excitation (figure 5.6a and b) the increase
Figure 5.6: Influence of functionalization on the Raman modes of HiPCO-produced SWNTs. Left: pristine (a) and (b) functionalized sample, probed by 1.96 eV excitation. Right: pristine (c) and (d) functionalized sample, probed by 2.33 eV excitation.

is 350% and at 2.33 eV excitation the corresponding increase is 165% (figure 5.6c and d). We can therefore infer that the smaller diameter tubes (HiPCO) are more likely to be functionalized than the larger diameter ones (arc discharge). That indicates that nanotube diameter is a key parameter in the process. Since we have both metallic and semiconducting tubes in resonance for both used excitations in the case of the HiPCO sample, we need to study in detail the RBM spectra in order to find any dependence of electronic properties on functionalization. Figure 5.7a demonstrates the RBM spectra of the SWNTs before and after functionalization, probed using 2.33 eV excitation. At this excitation wavelength, almost the entire spectrum is formed from the resonance
signals from metallic tubes (area indicated by M). The decrease to the main band at 273 cm$^{-1}$ (metallic) is almost 60% upon functionalization. Parts of the spectrum which originate from semiconducting tubes are too low in intensity (due to poor resonance) to be analyzed. We can therefore only conclude that the small diameter metallic tubes are highly sensitive to functionalization.

![Figure 5.7: Influence of functionalization on the Raman spectra of HiPCO-produced SWNTs. Data for: a) pristine (upper curve) and functionalized (lower curve) sample probed by 2.33 eV excitation; b) pristine and c) functionalized sample probed by 1.96 eV excitation. In panels b and c, decomposition of the spectra into signal from specific (n,m)-SWNTs is shown. M and S in the figures indicate which RBMs correspond to metallic and semiconducting tubes, respectively.](image)

It should be emphasized here that we investigate the HiPCO sample us-
ing 2.33 eV even though we have not established reference conditions for this excitation. Fortunately, the changes imposed on the RBM spectrum by functionalization are substantially greater than those originating from the temporal instability of the Raman spectrum of the pristine sample caused by laser irradiation (figure 5.2). Considering again the influence of functionalization, we turn to the HiPCO sample probed using 1.96 eV. The spectrum for the pristine sample is displayed in figure 5.7b and the spectrum for the functionalized sample in 5.7c. The influences on the different RBM components are less evident and decomposition of the spectra has been performed. We separate our analysis and compare the changes in relative intensities originating from metallic tubes compared to each other and do the same for the semiconducting ones. For the metallic components the most prominent changes are to the smaller diameter components located between 210 and 230 cm$^{-1}$ compared to the larger diameter ones between 190 and 205 cm$^{-1}$. The combination metallic and smaller diameter hence favor functionalization, supporting our conclusions drawn from the experiments with 532 nm excitation. In the case of the semiconducting tubes, components from the smaller diameter tubes (260, 266 and 284 cm$^{-1}$) again decrease in intensity compared to the the signal from larger diameter one (250 cm$^{-1}$). We again confirm that smaller diameters are more reactive and increase the efficiency of functionalization. In order to finally decide the influence of the electronic properties on functionalization we must compare changes in the RBM spectra of semiconducting tubes and metallic tubes with similar diameters. This is possible when looking in the region between 255 and 285 cm$^{-1}$ in figure 5.7. Comparing the change in intensity of the metallic-band in 5.7a, to the intensity changes of the semiconducting peaks (in 5.7b and 5.7c), we find that the former SWNTs are much more affected by functionalization. We conclude that smaller diameter SWNTs are more easily functionalized than their larger diameter counterparts. Further, for tubes of small diameters, metallic tubes will be favored over semiconducting ones. Preferential functionalization of the HiPCO-produced sample is discussed in detail in Paper III.
5.3 Summary of papers

5.3.1 Paper I
The influence of low power laser irradiation (<5 kW/cm²) on arc discharge- and HiPCO-produced single-walled carbon nanotube bundles is investigated. Changes in sample temperature and temporal stability of the radial breathing mode part of the Raman spectrum under exposure to 632.8 nm and 532 nm is studied in detail. Experimental laser power density thresholds are established for which the undesired effects can be avoided.

5.3.2 Paper II
Stability of HiPCO-produced single-walled carbon nanotube bundles under exposure to 632.8 nm laser irradiation at a high power density is investigated. We specifically study irreversible changes to the radial breathing modes in the Raman spectrum due to CNT destruction and analyze its dependence on CNT electronic properties and diameter.

5.3.3 Paper III
The selectivity of HiPCO-synthesized single-walled carbon nanotube functionalization (chemical grafting of methoxypheny functional groups to the sidewalls) is investigated. Influence of nanotube diameter, chirality and electronic properties on this process is discussed.
Chapter 6

Conclusions

6.1 Raman study of laser induced effects in carbon nanotube bundles

We have shown that laser induced temperature effects in single-walled carbon nanotube bundles pose problems for Raman characterization of their intrinsic properties. Reversible effects caused by increased sample temperature result in shifts of the Raman resonance window and shifts of the phonon frequencies. Irreversible decrease of the intensity of the radial breathing modes in the Raman spectrum can occur even at power densities below 1 kW/cm² for 532 nm. The irreversible changes in the spectrum are attributed to destruction of the nanotubes by the incident light. Small diameter SWNTs are more sensitive to laser irradiation, in particular to high energy photons. Experiments conducted at elevated laser power density exposure (47 kW/cm²) indicated that nanotubes in resonance with the incident light are preferentially destroyed and also confirm earlier findings that diameter is the most sensitive structural parameter of the process. We have established the following power density thresholds:

- **Overheating threshold.** To avoid local increase of the sample temperature due to laser heating the laser power density must be kept below this threshold.

- **Stability threshold.** Determines the maximum laser power density that results in temporally stable Raman spectrum for the exposure time required for acquisition.
The thresholds determined are in the region $2 - 10\, \text{kW/cm}^2$ for most sample/excitation combinations used, and the stability threshold is generally lower. Thus, in order to avoid these temperature effects the laser power density should not exceed the lower of the two thresholds when collecting high resolution Raman spectra, constituting a proposed reference regime for probing the intrinsic properties of SWNT bundles.

6.2 Evaluation of carbon nanotube functionalization

Raman investigations of both pristine and functionalized SWNT bundles of two different diameter distributions were performed. Analysis of the D-band and RBM-band of the Raman spectra led to the conclusions that smaller diameter SWNTs are preferentially functionalized. For SWNTs of similar small diameters, metallic tubes are more likely to be affected than semiconducting ones. Further, the influence of the electronic properties of the tubes is more subtle compared to that of tube diameter regarding efficiency of functionalization.
Chapter 7

Future work

We have shown that degradation of the Raman spectrum of SWNT bundles occurs even during their exposure to laser irradiation at low power densities (1 kW/cm$^2$). However, the reasons for the decrease in Raman signal are still unclear. In order to elucidate a possible role of tube oxidation in this degradation, laser heating experiments using high laser fluences in an inert atmosphere, or in vacuum, need to be done. Our preliminary laser heating experiments on functionalized SWNTs demonstrated a tendency for higher stability to laser irradiation. More detailed investigation is required for these systems to find temperature and stability thresholds and then compare the results to our data obtained on pristine SWNTs.
Bibliography


Paper I
Low laser power induced temperature instability of single-walled carbon nanotube bundles: A Raman study

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Abstract
Extensive Raman investigation of HiPCO- and arc discharge-produced SWNTs has been performed. We present a laser power density threshold below which reversible changes in the RBM-spectrum, originating from shifts of the optical transition energies Eii, caused by laser-induced heating of the SWNT bundles, can be avoided. We further show that the SWNT bundle spectrum can be unstable even at moderate laser power densities that fall short of causing thermally induced changes to the RBM spectrum. A second threshold is presented below which temporal stability of the spectrum is achieved. These two thresholds constitute a regime for probing the intrinsic Raman spectrum of SWNT bundles.

Keywords: Carbon nanotubes; Laser heating; Raman spectroscopy

Introduction
Progress in research on single-walled carbon nanotubes (SWNTs) has over the past years focused on studying isolated individual tubes in order to elude their fundamental properties. The benefits of removing effects of surrounding tubes, substrates and media when employing Raman spectroscopy are clear and has resulted in methods for dispersing SWNTs to the individual level now being routine [1]. In the case of photoluminescence studies, individual SWNT are required to avoid non-radiative decay of excited states. Despite these advantages there is, however, still motivation for studying the natural state of SWNTs, namely bundles. In order to evaluate effects of various protocols (chemical or other) the Raman spectrum must be compared to the intrinsic spectrum of the pristine material. It may not be desirable to subject the sample to surfactants, ultrasonication and centrifugation (which is the best way to achieve individual tubes). Moreover, successful dispersion using surfactants is time-consuming and require a high concentration of SWNTs (approximately 0.1mg/mL), with high loss in the centrifugation process. For application in carbon-based nano-materials, functionalization of SWNTs is a promising route for achieving dispersion and bonding to the matrix [2]. Spectroscopic evaluation of pristine and functionalized materials, or resulting composites, does not necessarily allow studying isolated tubes and one is restricted to probing bundles. In our previous work we have evaluated the effects of functionalization by looking at change in the relative intensities of the radial breathing modes (RBMs) [3]. This requires great care to experimental parameters since high laser power density (PD) will immediately overheat SWNT bundles, resulting in thermal effects dominating the spectrum. This is mainly caused by changes in resonance conditions, namely shifts of the optical transition energies Eii,
as previously reported [4-6]. The resulting changes on the relative intensities of the different components which constitute the RBM band are very profound [4]. While a downshift of the RBM phonon frequencies will also occur, this play a much smaller role [7-8]. For the tangential modes, downshift and broadening [9] are the dominating effects and due to the fact that the ratio of semiconducting to metallic tubes may be altered when resonance conditions change, the Breit-Wigner-Fano contribution to the G' mode may change as well. The goal of this work is to establish a protocol for finding PD thresholds for different samples and laser excitations that guarantee that the intrinsic SWNT bundle spectrum is recorded. Even with the excellent sensitivity, throughput and resonance tuning available in today’s Raman systems, increasing the power density of the photon excitation is required in order to increase signal. A threshold is therefore desired so that PD can be maximized resulting in minimized acquisition time.

Methods and Materials
In this work, two different SWNT samples were investigated. The first, a HiPCO-produced sample, has a broad, small diameter range of 0.8-1.2 nm and high purity. The second arc discharge-produced sample contains larger diameter nanotubes in the range of 1.2-1.6 nm with higher degree of impurities. The raw sample-materials were ultrasonically dispersed in DMF (Dimethyl Formamide) and drops deposited on glass substrates which were subsequently air-dried at 50°C. This procedure leaves clear aggregation visible and since neither high power sonication, nor ultra-centrifugation, was used we can be sure that the nanotubes are in bundled form [1]. Prepared samples were investigated via Raman spectroscopy with two excitation wavelengths, 1.96 eV (632.8 nm HeNe laser) and 2.33 eV (532 nm Nd-YAG laser), using a WITec CRM-200 confocal Raman imaging system. Laser light was focused on the sample through either 20X or 100X objectives, with spot-sizes of 5.4 and 2 μm respectively. The laser power was measured directly on the sample stage using a Coherent LaserCheck powermeter and was typically in the range of 0.1 – 10 mW.

Results and Discussion
Since temperature increase of SWNT bundles due to laser irradiation is a fact, it is desirable to optimize the Raman investigation of SWNT bundles and minimize laser exposure times while not increasing sample temperature. We therefore performed a series of experiments to find laser power densities that do not increase sample temperature and hence allow probing the intrinsic properties of the SWNTs at ambient conditions. A typical area on the HiPCO sample was irradiated with low laser power density (as low as 0.9 kW/cm^2) and the Raman spectra recorded. Power density was then increased and the spectra recorded again in the same spot (different spots for the two excitations). The resulting spectra for 1.96 eV and 2.33 eV excitations are shown in figure 1. Since increased photon flux results in improved Raman signal, the spectra have been normalized using the G' component of the tangential mode band, and offset, for comparison. In the case of the HiPCO sample we have both metallic and semiconducting tubes in resonance for both excitation energies, indicated by M and S respectively in figure 1. Considering 1.96 eV excitation first, it can be seen from the tangential modes displayed in the lower panel of figure 1a that the G' component shifts to lower energies and broadens upon laser power density increase. This is due to the increase in sample temperature caused by the laser irradiation [7-8]. The first step in power density from 5.7 kW/cm^2 (curve 1) to 65 kW/cm^2 (curve 2), produce a clear downshift in the G' component of the G-band. In the upper panel of figure 1a the corresponding RBM spectra are shown and the temperature induced effects on the relative intensities of the different RBM components caused by changes in resonance conditions can be seen [4].
Figure 1: Raman spectra of HiPCO SWNT bundles. For each excitation energy the spectra are recorded in the same respective spot using increasing laser power density. Spectra have been normalized and offset for clarity.

A: 1.96eV laser excitation. Curve 1-6 correspond to 5.7, 65, 130, 190, 260 and 340kW/cm² respectively.

B: 2.33eV laser excitation. Curve 1-8 correspond to 0.9, 1.6, 2.5, 4.4, 14, 31, 46 and 330kW/cm² respectively.

Consistently, changes in relative intensity of the RBM components constituting the peak at 220rel cm⁻¹ (increase) and the component at 285rel cm⁻¹ (decrease) are also evident comparing curve 1 and 2. Continued increase of PD shows further shift of the resonance window, while decreasing the power density (not shown) does not change the RBM profile nor shift the G-band to higher energies which would be consistent with further decrease in sample temperature [10]. We can hence claim that a power density of 5.7kW/cm² will not increase sample temperature above room temperature for HiPCO SWNT bundles using 1.96eV excitation. To find the corresponding threshold for 2.33eV excitation we turn to figure 1b. The initial increase in sample temperature is most evident in this case when looking at the G-band (lower panel), where a downshift is observed when the power density exceeds 2.5kW/cm² (curve 3). Closer investigation of the RBMs (upper panel) reveals a change in profile for the same step in power density. Not surprisingly we get a lower threshold for this higher photon energy. Having confirmed power density regimes that can be considered “safe” regarding laser induced sample temperature increase (overheating), we use these regimes to test the temporal stability of the RBM and G-band spectral features of the HiPCO SWNT bundles. The acquisition time needed to produce high quality spectra at such low laser power is up to 30 minutes for our Raman system. It should be realized that we in fact accumulate grating scans and record a mean spectrum over this period of time. Hence, to notice any
Raman visible changes in the sample during irradiation, we acquired a 20 minute RBM spectrum, followed by a 10 minute G-band spectrum. The procedure was repeated back-to-back for 1.5 hours in the same spot on the sample. The resulting spectra are presented in figure 2. For 1.96eV excitation and a 5.7kW/cm² PD, shown in figure 2a, no noticeable changes in RBM, D or tangential mode bands can be found for the duration of the run. This leads to the conclusion that the spectrum is in fact stable over time for this PD.

![Figure 2: Raman spectra of HiPCO SWNT bundles. For each excitation energy spectra are recorded in the same spot using constant laser power density. No normalization has been performed, but spectra are offset for clarity.](image)

A: 1.96eV laser excitation, using a PD of 5.7kW/cm².
B: 2.33eV laser excitation, using a PD of 0.9kW/cm².

To conclude the influence of photon energy on stability of the spectrum we performed the same experiment for 2.33eV. However, acquiring several spectra continuously in the same spot using the power density of 2.5kW/cm², as suggested by figure 1b not to induce any temperature effects to the spectrum, turns out does not produce a stable spectrum. The overall intensity of the spectrum unambiguously decreases with exposure time. We therefore decrease the laser power to the limit of what our Raman system can handle in terms of throughput and reasonable acquisition time and chose a new spot in the sample. The resulting series of spectra are presented in figure 2b. As can be seen, neither RBM modes (upper panel) nor tangential modes (lower panel) are stable under exposure to this extremely low laser power density of 0.9kW/cm² for 2.33eV photon energy. Looking closer at the RBM spectra, we see that the relative decrease in intensity over 5.5 hours is marginally less for the peak below 200 rel cm⁻¹, consisting of signal from larger diameter semi-conducting tubes. Further we find a drop in overall intensity by 40% of the G-band, indicating that the numbers of scatterers are
decreasing. Also, an increase in D/G' ratio by 30% indicates that the numbers of defects in the hexagonal lattice are increasing. While we can not find a completely stable spectrum in the 2.33eV case, we can use the proposed PD for 1.96eV to evaluate what influence exposure to high power density laser have on the samples. For 1.96eV excitation, increasing PD resulted in the spectral changes presented in figure 1a. During the experiment, after each PD step the laser was blocked and the sample allowed cooling for a few minutes prior to acquisition of a spectrum using a PD of 5.7kW/cm². These spectra are shown in figure 3.

![Figure 3: Spectra of HiPCO SWNT bundles acquired using 1.96eV laser excitation. Spectra are recorded after each of the spectra of figure 1a, using the proposed reference laser power density of 5.7kW/cm². Curve 1 is the initial reference spectrum and curve 2-6 correspond to reference spectra acquired after exposure 65, 130, 190, 260 and 340kW/cm² respectively. A: RBM. B: G-band.](image)

From the tangential mode spectra displayed in figure 3b we see no downshifts caused by elevated temperature and confirm that the shifts are reversible upon temperature decrease. Notably, the absolute Raman intensity decreases slightly after each step, signalling that something is happening with the sample. For this reason, RBM and G-band spectra of figure 3 have been normalized to the G' component. Looking at the figure 3a, showing the corresponding RBM spectra, we immediately see that the profound changes in the RBM band due to altered resonance conditions have been reversed, as reported by Fantini et al. [4]. We also find a relative decrease in intensity of the peak at 285rel cm⁻¹, corresponding to the smallest diameter tubes, occurring already after the first step in power density. Sensitivity of smaller diameters has been previously reported [11]. We conclude that the Raman spectrum of HiPCO SWNT bundles can be irreversibly affected by even short time exposure to high laser power density. This is due to the fact that laser irradiation can cause permanent destruction to the nanotubes, either preferential or total [12-13]. We can now define two thresholds below which the laser power density must be kept in order to record the intrinsic Raman spectrum of SWNT bundles. The first concerns increased sample temperature (overheating) and can be found unambiguously either from changes in the RBM profile or downshifts of the G-band. The second threshold states the stability of the spectrum over time and may be lower than the first threshold. For these experimental conditions we adopt the name reference conditions (used here after in the text), and the corresponding Raman spectra are hence named reference spectra.
As we now have the experimental idea clear, we move on to the SWNTs produced by the arc discharge-method. This sample contains more impurities (catalyst particles and amorphous carbon) and the nanotubes have larger diameters. Diameter and electronic properties (metallic/semiconducting) are factors reported in literature to influence stability the most. We first consider changes in the resonance conditions when probed by 1.96eV excitation, for which only metallic tubes are in resonance.

In figure 4a we find profile change in the RBM band (upper panel) when increasing the laser power density from 4.6kW/cm² (curve 2) to 7.3kW/cm² (curve 3). Interestingly, one can also see that the D/G\textsuperscript{2} ratio is reduced upon temperature increase, reported also by others [14]. Although this could theoretically be that the changes in resonance conditions result in tubes with less defects being more prominent in the spectrum, this explanation is unlikely. Further, the effect is reversible upon PD decrease so this being a temperature induced effect is evident. To conclude whether the diameter or nanotube type is the key factor, we turn to the arc discharge sample probed by 2.33eV. For this excitation only semiconducting tubes are in resonance and from the upper panel of figure 4b we find the RBMs for increasing power density. Passing 4.4kW/cm² (curve 3) we find a change in profile. Again we see the reduction of the D/G\textsuperscript{2} ratio upon temperature increase. The threshold is almost identical as for 1.96eV suggesting that the photon energy does not have great influence on inducing increased sample temperature for this larger diameter sample.
Continuing to the stability threshold, figure 5a presents the temporal behaviour of the arc discharge sample when irradiated with 2.33eV at a power density of 3kW/cm². No changes to the RBMs can be detected (upper panel), nor any decrease in overall intensity of the spectrum (lower panel) for the exposure time of just over 2 hours. A very slight increase in the intensity of the D-band is the only visible change in the spectrum. We can hence feel safe to use 3kW/cm² of 2.33eV irradiation for probing the arc discharge sample. Increasing the power density to 3.7kW/cm² will on the other hand show instability of the RBMs, as can be seen in the upper panel of figure 5b. This shows that we have crossed the stability threshold, yet no clear dependence on diameter can be seen due to the narrow diameter range in resonance at this photon energy.

Finally we consider the stability of the arc discharge SWNT bundles to 1.96eV irradiation. For a power density of 3.4kW/cm², we find from figure 6a that all spectral features remain unchanged after 1h of exposure.

Figure 5: Raman spectra of arc discharge SWNT bundles acquired using 2.33eV excitation. Each series of spectra were recorded consecutively in a fresh spot on the sample using constant laser power density. No normalization has been performed, but spectra are offset for clarity.
A: Irradiation using a PD of 3kW/cm².
B: Irradiation using a PD of 3.7kW/cm².

Finally we consider the stability of the arc discharge SWNT bundles to 1.96eV irradiation. For a power density of 3.4kW/cm², we find from figure 6a that all spectral features remain unchanged after 1h of exposure.
Figure 6: Raman spectra of arc discharge SWNT bundles acquired using 1.96eV excitation. Each series of spectra were recorded consecutively in a fresh spot on the sample using constant laser power density. No normalization has been performed, but spectra are offset for clarity.

A: Irradiation using a PD of 3.4kW/cm².
B: Irradiation using a PD of 4.6kW/cm².

Increasing the laser power density to PD 4.6kW/cm² show temporal changes in the RBMs with continuous decrease of the right peak corresponding to the smaller diameter tubes, as can be seen in the upper panel of figure 6b. The stability threshold in the case of the arc discharge-produced, larger diameter tubes is similar for both photon energies. Interestingly since this sample probed by 2.33eV excitation have only semiconducting tubes in resonance, while 1.96eV probe only metallic tubes, no dependence on electronic properties is present either. It has been reported that metallic tubes are preferentially destroyed at high power densities (100kW/cm²) [12]. We, on the other hand, conclude that temporal stability for larger diameter SWNT bundles, when exposed to low PD irradiation, is not greatly influenced by electronic properties or photon energy. Still, for the HiPCO sample, with both metallic and semiconducting tubes in resonance for both excitation energies, we could not get a stable spectrum in the 2.33eV case using a power density of about 15% compared to the 1.96eV case, which does produce stability. It would hence seem that both tube diameter and photon energy are vital parameters for the stability of the SWNT bundle Raman spectrum at low laser PDs, but for larger diameters the influence of photon energy is reduced.
Conclusions

It is established that low laser power must be used in order to make sure that sample temperatures are identical for all measurements when SWNT bundles are probed by Raman spectroscopy. Since the resonance is responsible for increasing the Raman signal by a factor $10^3$, even small shifts of the resonance window will have great impact on the intensities. Although the temperature induced effects on resonance are reversible upon temperature decrease, attempts to evaluate intensities of the RBM components are hazardous, if not impossible, under such conditions. Especially, it is incorrect to evaluate destruction of certain species from spectra recorded using high laser PD [12] since changing the population will also change the effective heat-sink, which may lead to altered sample temperature for identical PD. Also, the D/G$^*$ ratio is temperature dependent.

We have established power density thresholds for which the temperature effects can be avoided for HiPCO- and arc discharge-synthesized SWNT bundles when exposed to two laser wavelengths. This temperature PD threshold is close to 4kW/cm$^2$ in most cases. Further, extensive studies of the time dependence of the Raman spectrum have shown unambiguous decrease of Raman signal even at laser PDs below the temperature PD threshold. These instabilities can in all cases but one (HiPCO probed by 2.33eV) be avoided by further reducing the laser power. A second set of limits have been establish yielding stability PD thresholds. The lower of the two these thresholds constitute reference conditions for each sample-excitation combination. The different power density thresholds are summarized in table 1.

<table>
<thead>
<tr>
<th>Sample (Bundles)</th>
<th>Excitation</th>
<th>Stability threshold</th>
<th>Overheating threshold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc discharge SWNT</td>
<td>1.96eV</td>
<td>3.4 – 4.6 kW/cm$^2$</td>
<td>4.6 – 7.3 kW/cm$^2$</td>
</tr>
<tr>
<td>Arc discharge SWNT</td>
<td>2.33eV</td>
<td>3 – 3.7 kW/cm$^2$</td>
<td>4.4 – 9.1 kW/cm$^2$</td>
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<td>HiPCO SWNT</td>
<td>1.96eV</td>
<td>&gt;5.7 kW/cm$^2$</td>
<td>&gt;5.7 kW/cm$^2$</td>
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<tr>
<td>HiPCO SWNT</td>
<td>2.33eV</td>
<td>&lt;0.9 kW/cm$^2$</td>
<td>2.5 – 4.4 kW/cm$^2$</td>
</tr>
</tbody>
</table>

Table 1: Power density thresholds for avoiding laser heating effects in SWNT bundles and for producing temporally stable spectra.

a) No threshold for stability could be established.
b) No distinct values were established but the indicated PDs are below the thresholds.

The actual reasons for the instability of the SWNT bundle spectrum when the sample is subjected to low PD are not clear. Destruction at high laser power density is proposed to be due to oxidation of the nanotubes as a result of high temperature [12]. Since not detectable temperature increase is detected, it is unclear if there is a chemical reaction taking place. Performing the experiments in vacuum or an inert atmosphere could provide answers. Further, the exposure times in these experiments are long and investigation how they compare to short high PD exposure would be interesting. If we are dealing with an effect that is not chemical, comparing effects due to the same absorbed dose of irradiation but different exposure times would provide further information.

Decreasing diameter causes increasing instability while larger diameter tubes have a stability threshold which does not depend on either photon energy nor electronic type. Smaller diameter bundles on the other hand show huge difference in stability for altered photon energy. The stability of the Raman spectrum of SWNT bundles is hence clearly dependent on both diameterer and photon energy and smaller diameter tubes enhance the effects of increasing the photon energy.
Acknowledgments

David Olevik and Alexander V. Soldatov acknowledge the financial support from the Engineering Department, Luleå University of Technology via the International PhDPolis program. Alexander V. Soldatov greatfully acknowledge the financial grant from the Swedish Research Council (VR).

References


Correction added in proof

In Paper II and Paper III the laser probe sizes of the two objectives were calculated from the image of the laser spot registered by a CCD digital camera, used in our Raman system for sample area selection. To the best precision which this technique provides, the diameters of these spot sizes were determined to be 15 μm and 5 μm for the 20X and 100X objectives, respectively. Recently a special lithographic grating was manufactured by our collaborators at Nancy University in order to allow better precision calibration. The grating has 2.5 μm wide gold lines with 2.5 μm spacing, shown in figure 1. Scanning the laser probe across

![Image of grating](image)

Figure 1: Lithographic grating consisting of a silicon substrate with gold lines used for spectroscopic calibration of the laser probe diameter.

the grating and monitoring the intensity of the Raman line of silicon as a function of displacement resulted in determination of the probe size for the 100X objective as 2 μm. The grating has too small spacing to allow a similar calibration in the 20X objective case, and the probe size was in this case estimated by the ratio of the numerical apertures (NAs) of the objectives. This results in an estimated probe size for the 20X objective of 5.4 μm.
Power densities of the figures in Paper II and Paper III must be revised according to the new data. In Table 1 below we summarize these corrections.

<table>
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<th>Paper</th>
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<th>Corrected PD</th>
<th>Figure(s) in the paper</th>
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<td>6.5 kW/cm²</td>
<td>Figure 1a</td>
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<td>Figures 2, 3 and 4</td>
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Table 1: Corrections to the laser power densities due to more accurate estimation of laser probe diameter.

David Olevik
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Paper II
Stability of carbon nanotubes to laser irradiation probed by Raman spectroscopy

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1 Introduction Carbon nanotubes (CNTs) are unique nanomaterials with their geometric structure strongly controlling their electronic and vibrational properties. Characterization of CNTs is most often done using Raman spectroscopy. However, interpretation of results is not a trivial task since laser irradiation may lead to certain irreversible Raman-observable effects on single-walled tubes (SWCNTs), such as degassing of adsorbed species [1], ablation of carbonaceous impurities and/or annealing effects [2-4] or destruction of certain classes of nanotubes [2, 5-7]. Concerning destruction of CNTs, different authors have shown that small diameter tubes [2] or metallic tubes [1, 6] are more sensitive to irradiation effects. In earlier papers, the question was raised of whether the tube type or diameter played the principal role. Reference [6] investigated this question on small SWCNT bundles and concluded that the metallic nature was indeed the critical parameter, not the diameter. The issue of CNT tolerance to irradiation/overheating is still open. This is of particular importance in CNT bundle materials which are extremely sensitive to overheating due to inefficient cooling in this system compared to individual CNTs. Thus, for example, detection of subtle changes in the RBM profile of CNT bundles due to functionalization may be completely obscured by alteration of RBM intensities due to laser heating.

In this work, we have specifically analyzed the irreversible effects of laser irradiation on HiPco tubes in bundles at two laser energies. The aim was to investigate the destructive effects of high power density (PD) on the SWCNT bundles. High PD is defined here as exceeding 5 kW/cm², which is near or below the typical value for Raman experiments on CNTs. Therefore the results presented in this paper may be of practical help in analysis of Raman data obtained under similar experimental conditions.

2 Experimental To examine the effect of laser irradiation on SWCNT bundles, a drop of highly pure HiPco nanotubes having a relatively wide diameter distribution of about 0.8 to 1.2 nm was deposited on a glass substrate after dispersion in DMF (Dimethyl Formamide) using an ultrasonic bath and then allowed to air dry at 50 °C.

For confocal Raman studies, we used a WiTec CRM-200 imaging system having laser excitation with photon energies of 1.96 and 2.33 eV. The laser beam was focused on the sample using 20x or 100x objectives, with spot sizes of 15 and 5 μm, respectively. Incident laser power...
was measured directly on the sample stage and typical power densities were in the range of 0.15–50 kW/cm$^2$.

It has been shown that a temperature increase during laser irradiation may cause completely reversible changes in the RBM Raman spectra due to a change in the resonance conditions \[8\]. On the other hand, the concept of CNT destruction implies a decrease, or even loss of, Raman signal \[2, 5-7\]. Proof of CNT destruction should hence be based on an irreversible decrease in the Raman band intensity. If selective destruction takes place, this can be observed in detail through the RBM profile change.

In order to find a safe way for studying CNT bundles, we developed a PD regime in which no tube destruction due to laser exposure is observed over time periods exceeding 1 h, and no change occurs in bundle temperature/resonance conditions (RBM spectrum profile). Therefore it is only under these so-called “reference conditions" (term used hereafter in the text) that one can truly monitor changes in the CNT population in resonance (e.g., in case CNT damage has occurred). Corresponding “reference" PDs are below 1 kW/cm$^2$ for the CNT samples studied and depend on laser photon energies.

In the experiments described below, selected areas (spots) on the sample surface were illuminated with different laser PDs. It is important to note that within every measurement series we collected data from the same spot on the sample; therefore, a direct comparison of Raman intensities was possible. We used the following measurement protocol: before and after exposure of the HiPco CNT bundles to high laser irradiation, we recorded Raman spectra under “reference conditions." We thus could identify any eventual irreversible changes in the Raman spectra due to CNT damage/destruction. This protocol is essentially different from the majority of Raman studies of laser-induced CNT damage in which, for example, monitoring CNT damage is done only during high laser irradiation exposure \[6\].

3 Results and discussion
3.1 Damage PD threshold for short laser exposure times. To study damage of CNT in bundles, we first wanted to determine which laser PD levels could induce such damage during irradiation times typically required for recording high resolution Raman spectra. Although such problems do not exist for Raman experiments on CNT bundles suspended in a surfactant or solvent because of efficient heat dissipation through the surrounding medium, it is relevant to measurements on bundled CNTs deposited on a substrate where heat sinking is substantially more limited. First, we conducted an experiment using 1.96 eV photon energy (632.8 nm laser) excitation. After initial collection of a high resolution Raman spectrum at the “reference conditions" (labelled “start" in Fig. 1a), the PD was increased followed by an immediate recording of the Raman spectrum. This sequence was repeated for increasing PDs. The result are shown in Fig. 1a. First, an overall decrease in the intensity of the RBM modes upon CNT exposure to progressively increasing photon flux is evident. One can clearly see that the peak at 285 cm$^{-1}$ corresponding to the smallest diameter semiconducting tube is affected by the irradiation and decreases in relative intensity compared to the other peaks. We hence see that irreversible changes of the RBM spectrum are already induced by 3 min. irradiation at 10 kW/cm$^2$. This damage threshold is close to that determined by Corio et al. \[2\] for arc-discharge CNTs. Furthermore, not only is an intensity change observed but also a profile modification of the semiconducting band around 255 cm$^{-1}$ (next smallest diameters tubes).

To see the influence of photon energy on the PD threshold determined, the experiment was repeated under 2.33 eV photon energy (532 nm laser) excitation which demonstrated that CNT destruction was induced even at a PD of 0.15kW/cm$^2$. This can be seen from the time dependence of the RBM spectra under 0.15 kW/cm$^2$ irradiation in Fig. 1b. The spectral region between about 205–275 cm$^{-1}$
is comprised of the RBM modes of metallic nanotubes which dominate the CNT population in resonance at this photon energy. Destruction occurs for all tube diameters, with the main metallic peak at 270 cm⁻¹ affected to a slightly greater extent. The tangential mode (G-band) part of the Raman spectra (not shown) exhibits a slight decrease in the Breit-Wiegner-Fano component, indicating that the fraction of metallic tubes increased, which is compatible with the RBM Raman data in Fig. 1b. In conclusion, since we have both semiconducting and metallic tubes in resonance for both excitations used in this study, the excitation energy seems to play a more significant role in CNT damage than the diameter or chirality.

3.2 Temporal dependence of CNT destruction

The above described results raise the question of whether CNT destruction can be induced with longer laser exposure times at even lower PD than that determined for a 632.8 nm laser threshold (10 kW/cm²). It is also of interest to examine in more detail which types of tubes are primarily affected by laser irradiation since the alternative results on preferential destruction: small diameter [2, 7] versus metallic [6] CNTs have been reported. Therefore we conducted a separate experiment aimed at study of the time evolution of the Raman spectra of HiPco CNT bundles exposed to 632.8 nm laser irradiation at relatively high (6 kW/cm²) PD. Figure 2 shows the results of this experiment where all data were collected from the same spot on the sample. Here again, after recording a “start” spectrum at the reference PD (0.6 kW/cm²) (a) and irradiation resumed until the next measurement sequence (spectra 5–6 in Fig. 2). We must emphasize here that cooling to RT and returning to the elevated temperature (which takes about 1 min) does not perturb the CNT population which is entirely determined by the laser irradiation at high laser PD.

From the temporal evolution of the RBM spectra at 6 kW/cm² shown in Fig. 2b, it follows that: i) the Raman band and a shoulder around 215 cm⁻¹ and 240 cm⁻¹, respectively, decreased substantially in intensity, ii) the band at 255 cm⁻¹ originating from semiconducting CNTs remains essentially unchanged, and iii) the “metallic” band at 215 cm⁻¹ gradually “shifted” to higher wave numbers which is a signature of a temperature decrease due to changes in resonance conditions [8]. The latter is also evidenced by the blue shift of the G-band in the correspondent tangential modes spectra (Fig. 3) taken at the same time as the RBM spectra shown in Fig. 2b. Using our data on G⁺ mode shifts from Fig. 3 and the average value for the temperature coefficient of the G⁺ mode frequency (0.0258 cm⁻¹/K) recently determined for individual CNTs [9], we estimated CNT bundle temperatures at different exposure times.

During the first 6 h of laser irradiation, the temperature dropped from 410 °C to 290 °C, spectra (2) and (3), respectively (Fig. 2b), whereas an additional 10.5 h exposure resulted in a temperature decrease to only 260 °C (spectrum (5)). A temperature decrease of CNT bundles exposed to constant high PD laser irradiation is an interesting effect which has not been previously reported. We tentatively associate it with a decrease in the number of heat absorbers – CNTs in resonance with incident photons at high PD – due to destruction of the most overheated tubes.

A predominant decrease of the Raman signal at 210–225 cm⁻¹ from the metallic CNTs is consistent with results

Figure 2 Raman spectra for HiPCO nanotubes recorded with 632.8 nm laser excitation at room temperature (RT) under the reference conditions (PD 0.6 kW/cm²) (a) and at elevated temperatures at PD 6 kW/cm² (b). The spectra were taken in order (1) through (6) at the indicated times: after acquisition of the “start” spectrum (1) the PD was increased to 6 kW/cm² and maintained at this level during the experiment with only short interruptions for taking the spectra (4) and (6) at RT right after the spectra (3) and (5), respectively (details in the text). The spectra are offset for clarity.
reported in [6] although the effect observed in this work was more pronounced and a much higher PD (100 kW/cm²) was used to damage the HiPco CNT bundles. Turning to the RBM spectra acquired at the “reference condition” (Fig. 2a), we notice the irreversible intensity decrease of the Raman modes after irradiation at 6 kW/cm² which clearly depends on the CNT diameter: CNTs with smaller diameters are less resistant to laser irradiation. This result is in line with earlier findings [2, 7]. A remarkable conclusion following from our data is that the smallest diameters are less resistant to laser irradiation. This which clearly depends on the CNT diameter: CNTs with smaller diameters are less resistant to laser irradiation. Evidently, they were destroyed via indirect overheating, i.e. through heat dissipation from the heat absorbers (CNTs in good resonance at high temperatures). Furthermore, the intensity of the 285 cm⁻¹ hardly decreases after 6 h of irradiation, i.e. when the CNT temperature dropped below 300 °C which can be considered the temperature threshold for damage of the CNTs which are not in resonance with 1.96 eV photons. On the other hand, Raman intensity of the peaks around 215 and 255 cm⁻¹ originating from the CNTs in resonance at high PD continues to decrease down to 260 °C, the final temperature of the experiment.

The conclusions regarding CNTs which undergo preferential destruction under high laser irradiation drawn from the analysis of data shown in Fig. 2 may seem inconsistent. Indeed, data collected at high PD indicate no destruction of the “semiconducting” band at 255 cm⁻¹ while data taken under the “reference condition” unambiguously show substantial degradation of the Raman signal. Nevertheless, there is no inconsistency in the presented data because temporal evolution of the RBM spectra at high PD is determined by two factors: CNT destruction and a change in resonance conditions due to alteration of the electronic transition energies $E_i$ [8] caused by the observed temperature change. It is therefore impossible to make a reliable conclusion about damage of CNTs at high PD unless the contributions of these factors to the RBM intensities are separated, which appears to be a very challenging problem. Likewise, the statement about preferential destruction of metallic nanotubes at high PD communicated in [6] must be taken with caution as temperature effects were not analyzed in that work. On the contrary, the low PD/room temperature data (Fig. 1a) depend only on CNT population in resonance. Therefore only these data provide adequate information about CNT damage due to high laser PD exposure.

4 Conclusions In this work we presented a Raman study of HiPco CNT bundle destruction under high PD laser irradiation with different photon energies. First, we determined that the PD threshold for CNT destruction at short-time exposures does not exceed 10 kW/cm² for 1.96 eV laser photon energy and can even be lowered to 6 kW/cm² along with an increase in exposure time. Second, we observed preferential destruction of small diameter CNTs from the temporal dependence of the Raman spectra at constant temperature contrary to the previously reported preferential damage of metallic CNTs regardless of their diameters. For the first time we reported a decrease in the temperature of CNT bundles exposed to constant high PD. We show that this effect may cause unreliable interpretation of experimental data. Finally, we found that laser photon energy increase is apparently a primary factor in determining CNT destruction as such destruction can be induced at a laser PD as low as 0.15 kW/cm² using 2.33 eV photon energy.

Acknowledgements We thank Mattias Mases for help in conducting Raman measurements. A.V.S. gratefully acknowledges a financial grant from the Swedish Research Council (VR).

References
Paper III
Prefential functionalisation of carbon nanotubes probed by Raman spectroscopy

Jie Liu, Manuel Dossot, David Olevik, Victor Mamane, Brigitte Vigolo, David Abrahamsson, Henrik Jonsson, Yves Fort, Bernard Humbert, Alexander V. Soldatov, Edward McRae

Abstract

We have chemically grafted methoxyphenyl functions on HiPco single-walled carbon nanotubes through a radical procedure. To characterise the efficiency of this functionalisation, the materials have been examined via Raman spectroscopy at five laser excitation energies (1.96, 2.33, 2.41, 2.54 and 2.71 eV). This work concentrates mostly on the radial breathing mode band between 150 and 300 cm$^{-1}$. Clear evidence is put forward showing that those tubes which are preferentially functionalised are the smaller-diameter semiconducting tubes and the metallic tubes.

Keywords: Raman spectroscopy; Carbon nanotubes; Functionalisation

1. Introduction

Over the past few years, a tremendous amount of literature has been published on the use of Raman spectroscopy in the analysis of carbon nanotubes (CNTs) (for example, Refs. [1–10]). While the investigation of isolated samples is unquestionably of fundamental interest, this spectroscopy is also of great value in studying bundled samples having undergone purification or functionalisation [11]. Raman, unlike infrared or photoluminescence spectroscopy in CNTs, is resonantly enhanced, which allows selectively observing only those features specific to the CNTs themselves and thus avoiding to some extent observing spectral features of other carbonaceous impurities which may be present in the sample. Understanding intensity changes or shifts of certain spectral features during chemical treatments can be invaluable in helping to show that certain purification or functionalisation techniques do indeed result in a preferential reaction on specific kinds of tubes (metallic or semiconducting tubes, small- or large-diameter tubes). As will be shown below, for the free radical mechanism occurring in the functionalisation procedure we have developed, metallic and smaller-diameter semiconducting tubes react preferentially.

2. Experimental

Details concerning the grafting protocol and some results based on other analysis techniques can be found elsewhere [12,13]. For the confocal Raman studies using Jobin-Yvon T64000 and WiTec CRM-200 imaging systems, a drop of pristine or functionalised HiPco SWNT bundles dispersed in dimethyl formamide (DMF) was deposited on a glass substrate and then allowed to dry. In order to examine the effects of functionalisation of high-purity HiPco tubes, which have a relatively wide diameter...
distribution of about 0.8–1.2 nm, we have used five lasers. The power density on the samples was kept below 200 W cm$^{-2}$ to avoid spectral changes due to heating effects in the CNT bundles [4].

The laser excitation energies are indicated in Fig. 1, as well as the diameter range into which the majority of the HiPco tubes fall. This figure is the original Kataura plot based on a simple tight-binding analysis taking into account the nearest-neighbour interactions [3]. According to the laser energy selected, we will consequently excite different metallic or semiconducting tubes, and a proper choice of laser energy may even allow probing only a single type of nanotubes. Going beyond the nearest-neighbour approach, this original plot will be somewhat modified by considering many-body effects, excitons, the mod $[(2n,m),3]$ family considerations, the effects of chirality and going to the second- and third-neighbour interactions [1,4–10]. Taking these into account will shift the curves slightly, especially for the smaller-diameter tubes, and widen the $M_{11}, S_{12}$ and $S_{13}$ curves of interest here. Using these more refined treatments is of vital importance for assigning the chiral indices $(n,m)$, as we will do in a more detailed fashion [14]. However, for the purpose of this paper, the simpler pedagogical original Kataura plot is sufficient, as was also indicated in the review by Charlier et al. [6]. Furthermore, a plot comparing two sets of theoretical calculations by Jorio et al. [7] again shows little discrepancy for the purpose of the analysis presented here.

It can be observed on this plot that there is a clear evolution concerning the metallic or semiconducting nature of the tubes excited upon decreasing the laser energy. At 2.71 eV, we will primarily observe the signal of the smallest diameter metallic tubes ($M_{11}$ transition) and some larger-diameter semiconducting tubes ($S_{13}$ transition). As the energy decreases, a progressively greater number of larger-diameter metallic tubes will be observed, and at 2.33 eV, one should principally excite metallic tubes. At 1.96 eV, analysis of the Kataura plot reveals that one should see both larger-diameter metallic tubes and smaller-diameter semiconducting tubes ($S_{12}$ transition).

3. Results and discussion

Fig. 2 presents spectra over a wide wavenumber domain at two chosen energies (1.96 and 2.33 eV) before and after functionalisation. At both energies, the integrated intensity of the D band (sensitive to the number of defects due to the chemical treatment) with respect to that of the $G^+$ band (tangential vibration modes) is significantly increased: by fourfold at 1.96 eV and almost threefold at 2.33 eV. On the other hand, the ratio of integrated intensity of the RBM band to the $G^+$ band increases only slightly (6%) at 1.96 eV, while it even undergoes a 10% decrease when the sample is excited by 2.33 eV photons.

Fig. 3 shows the evolution of the RBM band as a function of the laser energy; one should keep in mind that, due to the inverse relation between diameter and Raman frequency, the smaller-diameter tubes correspond to the right-hand side of this figure and the larger-diameter tubes to the left-hand side. Taking the diameter range of the HiPco tubes as being between 0.8 and 1.2 nm, as illustrated in Fig. 1, implies an RBM frequency span from somewhat below 200 to about 310 cm$^{-1}$ corresponding to the range of peaks observed in Fig. 3. The exact relationship used to link the RBM frequency to the diameter is a function of many factors: tube type, diameter and environment, and the substrate to CNT interaction. At 2.71 eV, the most-intense peak can be decomposed into the contributions of many semiconducting tubes and the less-intense one at 2.33 eV.
higher Raman shifts to the metallic tubes. As the energy decreases, the metallic window broadens and downshifts. At 2.54 eV, of the three major peaks observed, only the leftmost peak is representative of the contributions of semiconducting tubes and at 2.41 eV, aside from the two most prominent peaks, the smaller two just above and below 200 cm\(^{-1}\) are for the semiconducting tubes. The most intense peak at 1.96 eV can be identified with the \(E_{22}\) transition of several semiconducting tubes.

Let us examine the two spectra relative to the functionalisation shown in Fig. 4. It should be noted here that two factors should be used to fully analyse the data. Firstly, after decomposition of the overall peak into its components (not in itself a trivial fitting procedure), one should calculate the overall integrated RBM intensity with respect to some other feature of the Raman spectrum which is less subject to change in intensity, such as that of the G\(^+\) band, for example. Secondly, one should also compare the relative integrated intensities of the different component peaks within the RBM with respect to each other. Fig. 4 allows only considering the second aspect; a more complete analysis will be provided in a forthcoming publication [14]. Analysis of these spectra brings out a number of important features. At 1.96 eV, a satisfactory decomposition of the four observed peaks can be made with 12 components (6 semiconducting, 6 metallic). Functionalisation strongly decreases the contribution of the two metallic components with smaller-diameters located between 210 and 230 cm\(^{-1}\) with respect to three larger-diameter metallic tubes located between 190 and 205 cm\(^{-1}\) (the ratio of integrated intensities of the peaks belonging to these two groups decreases from 1.76 to 1.12). There is simultaneously a strong decrease in relative intensity of the components (260, 266 and 284 cm\(^{-1}\)) due to the smallest-diameter semiconducting tubes with respect to the larger-diameter ones, which is evident from Fig. 4. At 2.33 eV, the decomposition and chirality assignment shows that almost all the spectrum can be analysed in terms of metallic tubes. The most intense peak, situated at 273 cm\(^{-1}\), undergoes an intensity decrease of almost 60% on functionalisation. This essentially determines an overall decrease of RBM integrated intensity with respect to that of the G\(^+\) band (Fig. 2) discussed above.
These results bring out then that some tubes are far more sensitive than others to the chemistry involved in the functionalisation reactions. The fact that metallic tubes are more sensitive suggests that the electronic density of states plays a role in the electron transfer processes taking place during functionalisation. The fact that two tubes of similar diameter but different chirality can be differently affected further suggests that the positioning of the different van Hove singularities with respect to the Fermi level is also one of the factors that must be considered.

4. Conclusions

This work has clearly shown that the chiral indices \((n,m)\) play a fundamental role in the functionalisation process since they determine both the geometric and electronic properties. The metallic and smaller-diameter semiconducting tubes are preferentially functionalised and within the metallic tubes, tubes of some specific \((n,m)\) react more to functionalisation than the others.

References
