Raman spectroscopy of single-walled carbon nanotubes – resonance behavior of the defect-induced Raman modes

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LIST OF ABBREVIATIONS

AC armchair
AFM atomic-force microscope
BZ Brillouin zone
C Celsius
DFT density functional theory
DGO density gradient ultracentrifugation
DOS density of states
dRRR double-resonant Raman
FWHM full width at half maximum
GCD greatest common divisor
H₂O water
HiPCO high pressure carbon monoxide
KA Kohn anomaly
KOH potassium hydroxide
LO longitudinal optical
M metallic
NaOH sodium hydroxide
NG nano graphene
NH₂O₃ nitric acid
POF Poly(9,9-di-n-octylfluorenyl-2,7-diyl)
RBM radial-breathing mode
S semiconducting
SBFC symmetry based force constant
SDS sodium dodecyl sulfate
Si/SiO₂ silicon/silicon dioxide
SWCNT single-walled carbon nanotube
TO transverse optical
ZZ zig-zag
LIST OF PUBLICATIONS

Parts of the thesis have already been published:


4. F. Herziger, J.Laudenbach, A. Vierck, J. Maultzsch, "Understanding the systematics of the defect mode in carbon nanotubes", in preparation based on Sec. 3.3 and Sec. 5.4.2.

GERMAN ABSTRACT

Raman spectroscopy of single-walled carbon nanotubes - resonance behavior of the defect-induced Raman mode
von
Jan Laudenbach

Die vorliegende Dissertation untersucht das Resonanzverhalten der defekt-induzierten Raman Mode ($D$ Mode) von einwandigen Kohlenstoff-Nanoröhren und dessen Oberton ($2D$ Mode). Dabei soll untersucht werden inwieweit die hohe, elektronische Zustandsdichte nahe einem optischen Übergang die Intensität der $D$ Mode beeinflusst.


Das verbesserte Verständnis des Resonanzverhaltens der ($2D$) Mode lässt in funktionalisierten Nanoröhren eine Aussage über den Reinheitsgrad der Probe zu. Darüber hinaus lassen sich Aussagen über eine selektive Funktionalisierung bezüglich metallischer oder halbleitender Nanoröhren ableiten.
CHAPTER I

Introduction
1 Introduction

To tune the properties of a material it is necessary to change its structure. For example to make a square stone rollable to use it as a wheel, its edges have to be ground down. However, for more advanced applications the structure of a material can be changed in the nanoscopic range to tune mechanical [1], electrical [2], or thermal properties [3] on molecular level.

For this macroscopic example of the square stone, modification and direct monitoring of the material macroscopic structure is quite simple. However, for nano materials the direct monitoring of its nanoscopic structure and structural changes is quite a challenge since the spatial resolution of an optical microscope is not sufficient [4] and for techniques using the higher diffraction limit of electrons the sample preparation is difficult and time consuming and therefore limited to small quantities of samples [5]. These limitations also apply to scanning probe techniques [6]. So both techniques are unsuitable for monitoring large scale productions. An alternative are optical spectroscopic methods for indirect monitoring of material structures for samples in bulk quantities.

Raman spectroscopy is a non-invasive technique to probe the structure related phonons of a material [7–10]. Therefore, in this work Raman spectroscopy is used to investigate the structure of a nano material and its structural changes due to chemical modifications (functionalization) [11, 12]. The basic concepts of Raman spectroscopy are summarized in Chap. II.

One important point in Raman spectroscopy is the enhancement of the Raman signal after "Fermi's golden rule", the so called resonant Raman spectroscopy [12, 13]. This enhancement occurs when the exciting laser, used for the Raman measurements, energetically matches an optical transition of the investigated material, including its high electronic density of states (DOS). This allows to investigate the optical properties of a material as well.

The nano materials investigated in this work with Raman spectroscopy are rolled up sheets of $sp^2$-hybridized carbons, so called carbon nanotubes. This nano material is of high interest for applications due to its intrinsic physical properties [14], and also due to the possibility to tune the properties of nanotubes by functionalization [15–17]. The basic properties of carbon nanotubes are summarized in Chap. III.

A special Raman mode of nanotubes is the defect-induced Raman mode ($D$ mode) [18, 19]. While this mode is absent in perfect structured nanotubes, it appears in defective material and its intensity increases with an increasing defect density [20]. Therefore, this Raman mode can be used to study changes in the structure of the nanotubes in a quite simple way. Structural changes in nanotubes can be dangling bonds of the $sp^2$-hybridized carbons which are, for example, due to holes in the nanotube structure after an oxidative functionalization [21, 22]. But they also result from $sp^3$-hybridized carbons, which occur after covalent sidewall functionalization of the nanotubes with chemical groups usable for applications [23, 24]. In both cases an increase of the $D$-mode intensity is in agreement with an increase of the functionalization degree. This will be a main parameter of the quality control for future large scale productions of functionalized nanotubes.

Beside this increase of the $D$-mode intensity by increasing defect density, it is still under discussion if resonant Raman at the high DOS also increases the $D$-mode intensity [25]. This is an important question, since it has to be clarified if the determination of the defect density depends on the excitation energy of the laser used for the Raman measurements. The right determination of the defect density in a functionalized sample is crucial for right estimation of the functionalization degree.

A reason why this question is still under discussion, is that nanotubes are commonly produced in a mixture of different kinds of tubes, possessing different optical transitions. This makes it difficult to distinguish between the different resonantly excited contributions of the $D$ mode in nanotube ensembles. With a deeper understanding of the resonance behavior of the $D$ mode it might be possible to deconvolute the Raman spectra of the $D$ mode in nanotube ensembles to different kinds of tubes with different degrees of functionalization.

With recently developed separation techniques, nanotubes can be enriched to certain chiralities [26–29]. This makes it possible to study the $D$ mode in nanotubes in more detail.

Chapter IV shows the results for the resonance behavior of the $D$ mode for such a resonance Raman study of a nanotubes sample highly enriched with single chirality. The results are interpreted with the help of numerical simulations and expanded to the overtone of the $D$ mode, the $2D$ mode.

Based on the result for the resonance behavior of the (2)$D$ mode, the Raman spectra of samples enriched to semiconducting and metallic nanotubes are analyzed to explain the different contributions of the (2)$D$ mode observed in the (2)$D$-mode dispersion in nanotube ensembles (Chap. V).
1 Introduction

This understanding of the fine structure of the (2)D mode in nanotube ensembles is used to study the strong changes in the D-mode line shape of oxidative functionalized nanotubes (Chap. VII) and to study the evaluation of the (2)D mode line shape for a sample containing selectively sidewall functionalized nanotubes (Chap. VIII).

Additionally, since the functionalization of nanotubes can lead to an unbundling of the nanotubes, changes in the Raman spectra for bundled and unbundled nanotubes are investigated (Chap. VI). These changes are interpreted concerning the resonance behavior of the (2)D mode.
CHAPTER II

Experimental methods
2.1 Raman spectroscopy

The Raman effect was discovered in 1928 by Sir C. V. Raman* [7–10] and describes the ability of materials to scatter light with a shifted frequency referred to the frequency of the incoming light. This shift is independent of the frequency of the incoming light, but strongly dependent on the atomic structure of the illuminated material. Therefore, each structure shows an unambiguous Raman spectrum.

While C. V. Raman made his first experiments with focused sunlight, the development of laser technology provides an efficient light source, which makes Raman spectroscopy a widely spread method for material characterization.

In this section I describe in short the mechanism of Raman spectroscopy according to Ref. [30–34]

2.1.1 Theory of Raman scattering

The Raman effect can be illustrated using the basics of classical physics. Raman scattering occurs if the illuminated material interacts with the incoming light. Therefore, the electric field

\[
\vec{E} = \vec{E}_0 \sin(\omega t)
\]

(with frequency \(\omega\) of the incoming light and time \(t\)) induces a polarization

\[
\vec{P} = \alpha \cdot \vec{E}
\]

in the material. \(\alpha\) is the polarizability tensor which can be approximated to the first Taylor term

\[
\alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial q} \right)_0 \cdot q
\]

with \(q\) as normal coordinate of a lattice vibration

\[
q = Q \sin(\omega_{ph} t).
\]

\(Q\) is the amplitude and \(\omega_{ph}\) the phonon frequency. Insertion of (2.1), (2.3), and (2.4) into (2.2) gives for the polarization \(\vec{P}\):

\[
\vec{P} = \alpha_0 \vec{E}_0 \sin(\omega t) + \frac{Q \vec{E}_0}{2} \frac{\partial \alpha}{\partial q} \left[ \sin(\omega t - \omega_{ph} t) + \sin(\omega t + \omega_{ph} t) \right].
\]

The first term describes the elastically scattered light (Rayleigh), the other terms describe the inelastically scattered light, whereby the frequency of the incoming light (\(\omega\)) can be decreased (Stokes) or increased (anti-Stokes) by the frequency of a lattice vibration (\(\omega_{ph}\)). Furthermore, the equation shows that a material is only Raman active if \(\partial \alpha / \partial q \neq 0\), which means the polarizability has to change during the lattice vibration. Figure 2.1 shows a sketch of the different scattering processes described in Eq. (2.5).

2.1.2 Resonant Raman scattering

The Raman shift for a lattice vibration is independent of the excitation energy\(^1\), but the intensity strongly depends on the excitation energy due to the resonance behavior of the Raman modes. Resonant Raman scattering occurs if either the excitation energy is equal to an excited state (incoming resonance), or the intermediate state after Stokes or anti-Stokes\(^2\) scattering matches an excited state (outgoing resonance). In both cases, the Raman intensity is enhanced by \(\approx 10^3\) order of magnitude. Figure 2.2 shows a sketch of both resonance conditions.

The reason for this strong enhancement is a quantum mechanical effect, known as the "Fermi Golden Rule", and can be deduced from time-dependent perturbation theory. The differential cross section and therefore the Raman scattering is proportional to \(|\mathcal{K}|^2\) [13]. Here the matrix element \(\mathcal{K}\) for the resonance Raman process is given by [19]

\[
\mathcal{K} = \sum_{a,b} \frac{M_{e-r,a} M_{e-ph,b} M_{e-r,i}}{(E - E_a + \frac{i \gamma}{2})(E - E_b - \hbar \omega_{ph} + \frac{i \gamma}{2})}.
\]

\(^*\)He awarded the Nobel Prize of Physics in 1930 for this discovery.

\(^1\)An exception is the double resonant Raman process described in Sec. 2.1.3.

\(^2\)Anti-Stokes is much more unlikely than Stokes scattering and will be neglected in further considerations.
2.1 Raman spectroscopy

![Figure 2.1: Sketch of the Raman processes. (a) Incoming and outgoing light have the same energy. (b) Incoming light has a higher or (c) lower energy than the outgoing light.](image)

![Figure 2.2: Sketch of the resonant Raman processes. (a) Incoming resonance: The excitation energy matches the excited state. (b) Outgoing resonance: After the energy loss due to a phonon the energy of the emitted light matches the excited state.](image)

$E$ is the excitation energy, $E_x^i(x = a, b)$ are the energy differences between excited and ground state of the electronic bands for wave vector $k = x$ (Fig. 2.2), $h\omega_{ph}$ is the phonon energy, and $\gamma$ is an empirical broadening factor taking into account the lifetime of the intermediate electronic states. The different $M$'s are the matrix elements for the interaction between electron and radiation ($M_{e-r,i}$ for incoming and $o$ for outgoing light), or phonon ($M_{e-ph}$). The first term in the denominator describes the incoming resonance; the second term in the denominator describes the outgoing resonance.

Besides the enhancement of the Raman intensity for $E = E_x^i$ and $E = E_x^i + h\omega_{ph}$; the matrix elements $M$ also modulate the Raman intensity. $M_{e-r,i}$ is the absorption strength; the absorption of a material is given by the imaginary part of the complex dielectric function $\epsilon(i)$ [12, 34]. In microscopic theory $\epsilon(i)$ can be calculated to [12]:

$$
\epsilon(i) = \frac{2\pi e}{m_i} \left| M_{i} \right|^2 \int \frac{dS_x}{\nabla_x |E_x(i) - E_x(i)|^2}, \quad (2.7)
$$

where $M_{i}$ is the dipole matrix element of the valence $E_x(i)$ and conduction band $E_x(i)$, and $S_x$ the joint density of states (DOS) of the observed material. The derivation in the integral shows that parallel bands at the optical transition are related to a high absorption of light and therefore Raman intensity.

$M_{e-ph}$ is the electron-phonon coupling which can change for different $k$ [35, 36]. Besides the matrix elements $M$ [Eq. (2.6)], interference effects* influence the Raman intensity [36, 37].

2.1.3 Double-resonant Raman scattering

For Raman measurements with excitation wavelength in the range of visible light, the maximal momentum for a phonon in backscattering geometry† is

$$
q_{max} = 2\pi \frac{2\pi}{\lambda_{light}} \approx 0.01 \text{ Å}^{-1} \quad (2.8)
$$

*Caused by the imaginary parts.
†The momentum conservation and the change of the wavelength in matter induce the factor $2\pi$. 

Laudenbach TU Berlin
2.1 Raman spectroscopy

![Diagram of Raman spectroscopy](image)

**Figure 2.3**: Sketch of two possible double-resonant Raman processes for the excitation energy $E_i$ in resonance with the excited state (i). (a) First, the electron is scattered resonant with a phonon with wave vector $q = k$ and frequency $\omega_{ph}(q)$ (ii); Second, the hole is scattered non resonant with a defect with wave vector $q = -k$ and the electron-hole pair recombine to emit a photon with an energy $E_o = E_i - \hbar \omega_{ph}(q)$ (iii).

(b) First, the electron is scattered resonant with a defect with wave vector $k' \neq k$ (ii); Second the hole is scattered non resonant with a phonon with wave vector $q' = -k'$ and frequency $\omega'_{ph}(q') \neq \omega_{ph}(q)$ and the electron-hole pair recombine to emit a photon with an energy $E'_o = E_i - \hbar \omega'_{ph}(q') \neq E_o$ (iii).

with $\lambda_{\text{light}} = 500 \text{ nm}$ and refractive index $n = 4$. For the Brillouin zone (BZ) of graphene with $a_0 = 2.461 \text{ Å}$ we obtain

$$k_{\text{max}} = \frac{\pi}{a_0} \approx 1.28 \text{ Å}^{-1},$$

which is more than one hundred times larger than $q_{\text{max}}$. Because of momentum conservation, a single-resonant Raman process only probes $\Gamma$-point phonons ($q = 0$), which explains the independence of the Raman shift on excitation energy. For a double resonance process, two intermediated states of the scattering process have to be real. This can be due to the fact that incoming and outgoing resonance match a real state in vertical transition ($\Gamma$-point phonons $q = 0$, compare Fig. 2.2), or because the electron (or hole) is scattered in the BZ with a phonon or a defect with $q \neq 0$ to a real state and backscattered with a phonon or defect with $-q$.

Figure 2.3 shows a sketch for the double-resonant Raman (dRR) process for (a) first, scattering the electron by a phonon and then the hole by a defect and (b) first, scattering the electron by a defect and then the hole by a phonon. Figure 2.3 further shows that for different types of scattering [(a), (b)] and for different excitation energies, the double resonance condition is fulfilled for different wave vectors $k$ ($k'$) and therefore different phonon-wave vectors $q$ with different phonon frequency $\omega_{ph}$ contributing to the Raman process.

Similar to the single resonant process [Eq. (2.6)], the matrix element $K$ for a double resonant process can be calculated from

$$K = \sum_{a,b,c} \left[ \frac{M_{x-r,o} M_{x-def} M_{x-ph} M_{x-r,i}}{(E - E_a^* - \ii \gamma)(E - E_b^* - \hbar \omega_{ph} - \ii \gamma)(E - E_c^* - \hbar \omega_{ph} - \ii \gamma)} + \frac{M_{x-r,o} M_{x-ph} M_{x-def} M_{x-r,i}}{(E - E_a^* - \ii \gamma)(E - E_b^* - \ii \gamma)(E - E_c^* - \hbar \omega_{ph} - \ii \gamma)} \right].$$

The first term describes the scattering process by, first, scattering the electron by a phonon and then the hole by a defect; the second term describes the scattering process by, first, scattering the electron by a defect and then the hole by a phonon (compare Fig. 2.3). The parameters are the same as in Eq. (2.6) with an additional state $E^*_o$ and matrix element for the interaction between electron and defect $M_{x-def}$.

2.1.4 Experimental setup

Raman measurements were performed in backscattering geometry with a Raman microscope (100x objective, <1 mW laser power) or with macro setup (<20 mW laser power). All spectra were calibrated with a neon
2.2 Atomic-force microscopy

Table 2.1: Specification of the used laser energies with related lasers and spectrometers.

<table>
<thead>
<tr>
<th>excitation energy (eV)</th>
<th>laser</th>
<th>monochromator</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.49-1.77</td>
<td>titanium-sapphire</td>
<td>Dilor XY800 (triple monochr.)</td>
</tr>
<tr>
<td>1.79-2.05</td>
<td>dye laser</td>
<td>Dilor XY800 (triple monochr.)</td>
</tr>
<tr>
<td>2.18, 2.41, 2.48, 2.63, 2.71</td>
<td>ArKr</td>
<td>Dilor XY800 (triple monochr.)</td>
</tr>
<tr>
<td>1.50</td>
<td>laser diode</td>
<td>HR800</td>
</tr>
<tr>
<td>1.96</td>
<td>NeNe</td>
<td>HR800</td>
</tr>
<tr>
<td>2.33</td>
<td>Nd:Yag frequ. doub.</td>
<td>HR800</td>
</tr>
<tr>
<td>1.58</td>
<td>laser diode</td>
<td>XploRA</td>
</tr>
</tbody>
</table>

lamp. For resonance profiles the intensity was normalized to calcium fluoride for the radial-breathing mode, and to diamond for the defect-induced Raman mode and its overtone (Sec. 3.2). The used excitation energies with related lasers and spectrometers are summarized in Tab. 2.1. Samples were measured in solution of on silicon/silicon dioxide (Si/SiO₂) substrate.

2.2 Atomic-force microscopy

In the atomic-force microscopy (AFM) a very thin and sharp tip is scanning the surface of a sample. In comparison to scanning-tunnel microscopy this method is not restricted to conductive samples, since it do not use a tunnel current to keep the required distance to the surface. For short distances between atoms, two contrary forces appear; the short-range repulsive force and the long-range attractive force. These interactions between two atoms can be described in first order approximation with the empirical Lenard-Jones potential [38]:

\[ E_{pot}(r) = \left(\frac{a}{r^12}\right) - \left(\frac{b}{r^6}\right), \tag{2.11} \]

where \( r \) is the distance between the atoms, and \( a \) and \( b \) are material constants. To monitor the structure of materials in nm scale the related force can be used in AFM [6, 39].

For AFM in non-contact mode, the cantilever of the AFM tip mechanically oscillates near its resonance frequency in free space. This provides a large amplitude of the cantilever deflection, which is monitored. Approaching the tip to the surface and bringing it into the regime of the attractive force will change the spring constant of the cantilever. Therefore, the frequency will change and the cantilever will vibrate off resonance. The resulting amplitude change is compensated by a feedback loop, which holds the cantilever in certain height above the surface. The change in height by the feedback loop provides the surface image of the sample [6, 40]. For AFM measurements aXE-100 from Park Systems was used.
CHAPTER III

Basic properties of carbon nanotubes
3.1 Structure

Carbon Nanotubes were discovered in 1991 by Iijima with multi-wall [41] and 1993 in single-wall configuration [42] [single-walled carbon nanotubes (SWCNTs)] with transmission electron microscopy. Since SWCNTs possess a lot of outstanding material properties, like thermal-, and electrical conductivity, and tensile strength [14] the interest of the scientific community is large. Furthermore, the quasi one dimensional structure of the nanotubes makes it possible to investigate and understand this material configuration in more detail.

In this section I describe in short the main properties of carbon nanotubes according to Ref. [32–34].

3.1 Structure

The structure of SWCNTs can be imagined as a rolled up graphene sheet [Fig. 3.1 (a)]. The lattice vectors \( \vec{a}_1 \) and \( \vec{a}_2 \) of this honey-comb like structure form an angle of 60° and have a length of \( a_0 = 2.461 \text{Å} \). The structure of the SWCNT is determined by the chiral vector \( \vec{c} = n_1 \vec{a}_1 + n_2 \vec{a}_2 \) with the pair of integers \( (n_1, n_2) \). \( \vec{c} \) is the circumference of the tube; the diameter \( d \) can be determined from

\[
    d = \frac{\sqrt{2}}{\pi} a_0 = \frac{a_0}{\pi} \sqrt{n_1^2 + n_1 n_2 + n_2^2}.
\]

(3.1)

The angle between \( \vec{a}_1 \) and \( \vec{c} \) is called the chiral angle and can be calculated from

\[
    \cos(\Theta) = \frac{\vec{a}_1 \cdot \vec{c}}{|\vec{a}_1| \cdot |\vec{c}|}.
\]

(3.2)

Due to the 6-fold rotational symmetry of the graphene lattice the chiral angle is equivalent for 0° to 30° and for 30° to 60°. An angle of 0° corresponds to zig-zag (ZZ) tubes and an angle of 30° to armchair (AC) tubes. These tubes are called achiral tubes, all others are called chiral. The translation period of a nanotube unit cell is given by the vector \( \vec{a} \) which is perpendicular to \( \vec{c} \), and therefore in the direction of the tube axis, and can be calculated from [43]

\[
    \vec{a} = \frac{2n_2 + n_1}{\text{GCD}(2n_1 + n_2, 2n_2 + n_1)} \cdot \vec{a}_1 + \frac{2n_1 + n_2}{\text{GCD}(2n_1 + n_2, 2n_2 + n_1)} \cdot \vec{a}_2
\]

(3.3)

\((\text{GCD}=\text{greatest common divisor})\). Its length is

\[
    a = \frac{\sqrt{3} (n_1^2 + n_1 n_2 + n_2^2)}{\text{GCD}(2n_1 + n_2, 2n_2 + n_1)} \cdot a_0.
\]

(3.4)

Furthermore, the Brillouin zone (BZ) of a nanotube can be derived from the chiral vector \( \langle n_1, n_2 \rangle \). Due to the cylindric form of the SWCNT the wave functions around the circumference \( \vec{c} \) are quantized

\[
    m \cdot \lambda = \pi \cdot d.
\]

(3.5)

A wave vector \( k_c = 2\pi / \lambda \) along the circumference (e. g. for electron or phonon) is therefore quantized to

\[
    k_c = \frac{2\pi}{|\vec{c}|} m = \frac{2}{d} m
\]

(3.6)

with \( m \in \{-q/2 + 1, \ldots, -1, 0, 1, \ldots, q/2\} \) and \( q \) the number of hexagons in the unit cell

\[
    q = \frac{2 (n_1^2 + n_1 n_2 + n_2^2)}{\text{GCD}(2n_1 + n_2, 2n_2 + n_1)}.
\]

(3.7)

This leads to \( q \) equidistant lines \( m \) of the BZ along \( \vec{k}_c \) with a distance of \( 2/d \) and a length of \( 2\pi / a \). A sketch for the \((4,1)\) SWCNT is shown in Fig. 3.1 (b). The thick, red, short lines are the \( q = 14 \) lines of the BZ. They are perpendicular to \( \vec{k}_c \) and cut the high symmetry points \( \Gamma, K, \) and \( M \), highlighted in red.

For chiral nanotubes with much higher chiral indices, this linear picture of the BZ becomes quite confusing, since the number of lines increase and the distance and length decrease. More convenient is the helical picture, here the linear bands are rearranged along the same direction as the tube axis in real space \( (\vec{k}_a) \) according the Umklapp process [34]. The number of lines \( \tilde{m} \) is given by \( \tilde{m} = \text{GCD}(n_1, n_2) \) and the length of
3.1 Structure

Figure 3.1: (a) Sketch of the graphene lattice with lattice vector $\vec{a}_1$ and $\vec{a}_2$. The chiral vector $\vec{c}$ for a (4,1) SWCNT is drawn, together with its components in $a_1$ and $a_2$ direction (dashed lines) and the chiral angle $\Theta$. The translation period $\vec{d}$ is perpendicular to $\vec{c}$ and the corresponding rectangle of both is the unit cell of the SWCNT (gray area). The high symmetry points $\Gamma$, $K$ and $M$ (red) cut by $\vec{c}$ or $\vec{d}$ are denoted. (b) Sketch of the reciprocal space of graphene with the Brillouin zone of the (4,1) SWCNT in linear picture (red, thick, short lines) along the vector $\vec{k}_c$ (which is parallel to the circumference $\vec{c}$ in real space), and the Brillouin zone in helical picture (red, thin, long line) which is along the tube axis in real space. The distance of the lines in the linear picture is denoted as well as the length of the Brillouin zones for both pictures (dark blue). Further, the quantum numbers $m$ and $\tilde{m}$ are denoted. The high symmetry points $\Gamma$, $K$ and $M$ cut by the Brillouin zone are denoted as well as the unit vectors of the later used Cartesian coordinates $\vec{k}_x$ and $\vec{k}_y$.

the helical BZ is $k_x = q/n \cdot 2\pi/a$. The helical vector $\vec{k}_n$ for the (4,1) SWCNT is shown in Fig. 3.1 (b) as a red, thin, long line. It cuts the same high symmetry points as for the linear picture. These are the same high symmetry points cut by $\vec{c}$ in real space [Fig. 3.1 (a)]. More information about the helical picture of the BZ in SWCNTs can be found in [44, 45].

By cutting the electronic band structure of graphene according to the nanotube BZ, the bang gap of a tube can be determined* (zone-folding). Figure 3.2 shows the calculated band structure of graphene using the third-nearest neighbor tight-binding approximation [47]. The high symmetry line connecting the symmetry points $\Gamma - K - M - K' - \Gamma$ is highlighted in red. The linear bands close to $K$ and $K'$ are called the Dirac cones.

As an example, Fig. 3.3 shows the zone-folding for a (4,1) nanotube in helical picture. In (a) the cutting vector $\vec{k}_n$ (red) [compare Fig. 3.1 (b)] is drawn into the two dimensional contour plot of the valence band of graphene (Fig. 3.2). The vector $\vec{k}_n$ cuts the $K$ point of graphene. At the $K$ point, the conduction band touches the valence band. Therefore, the (4,1) tube is a metallic tube. The corresponding electronic bands from zone-folding can be seen in Fig. 3.3 (b) with crossing of the conduction and valence band at the $K$ point.

With the model of zone-folding it is further possible to determine in general the species (semiconducting, metallic) of a nanotube by the chiral index $(n_1, n_2)$ by a simple approach. For a vector $\vec{k}$ which belongs to the BZ, the projection on $\vec{c}$ must fulfill the condition $\vec{k} \cdot \vec{c} = 2\pi m$. Since for a metallic nanotube the $K$ point must be cut by the BZ, and the $K$ point is at $\vec{K} = (1/3)(2\vec{k}_2 - \vec{k}_1)$, it follows:

$$\vec{K} \cdot \vec{c} = 2\pi m = \frac{1}{3}(2\vec{k}_2 - \vec{k}_1)(n_1\vec{a}_1 + n_2\vec{a}_2)$$

*(This approach neglects the curvature of the nanotube wall, which influence the band structure and is important especially for very small tubes [46]. The effect of curvature on the band structure will be discussed below.)
3.2 Raman modes

Figure 3.2: Electronic band structure of graphene calculated with third-nearest neighbor tight-binding approximation. \( k_x \) is shown in the interval \([-2\pi/\sqrt{3}a_0, 2\pi/\sqrt{3}a_0]\) and \( k_y \) is shown in the interval \([2\pi/a_0, 2\pi/a_0]\). The high symmetry line \( \Gamma - K - M - K' - \Gamma \) is highlighted in red and the high symmetry points \( \Gamma, K, K' \) and \( M \) are denoted.

with \( \vec{k}_1 = (-1,0) \cdot 4\pi/\sqrt{3}a_0 \) and \( \vec{k}_2 = (0.5,0.5\sqrt{3}) \cdot 4\pi/\sqrt{3}a_0 \) in Cartesian coordinates [34] it is easy to see that

\[
3n = (n_2 - n_1).
\]

A tube with \( n_2 - n_1 \) a multiple of 3 is therefore metallic, otherwise it is semiconducting [49]. A consequence is that for a homogeneous diameter distribution 1/3 of nanotubes will be metallic and 2/3 will be semiconducting. An even more precise definition is the classification in different families \( \nu \pm 1 \), depending on the position of the cutting line to the \( K \) point [50–52], but will not be needed for this work.

Due to its one-dimensional structure the optical transitions of nanotubes have a very high DOS with a \( 1/\sqrt{E} \)-behavior [53]. Therefore, each optical transition has a sharp resonance energy [compare Eq. (2.6)] with a very strong absorption [compare Eq. (2.7)].

The plot of diameter against optical transition shows that the optical transitions can be separated in different branches. This plot is called the Kataura plot [54]. In our previous considerations we neglected the effect of curvature. The curved nanotube walls have two effects: first, the bond lengths along the circumference are getting smaller, and second, in plane \( \pi \) orbitals of graphene can mix with the perpendicular \( \sigma \) states. Therefore, in nanotubes the pure \( sp^2 \) hybridization is partly mixed with \( sp^3 \) configuration. Both effects can shift the optical transitions [46, 55]. Popov et al. included curvature effects in his calculations of the optical transition with the help of a nonorthogonal tight-binding model [56]. A Kataura plot based on his results is shown in Fig. 3.4.

3.2 Raman modes

Similar to the electron wave vector, the phonon wave vector is quantized along the circumference of a tube. Therefore, the phonon dispersion can in principle be obtained by zone-folding of the phonon dispersion of graphene, similar to the energy bands. But this approach neglects curvature effects, which is most obvious for the radial-breathing mode (see below).

Nonorthogonal tight binding [56] includes curvature effects, but neglects the Kohn anomaly (KA). This effect describes the loss of ability of electrons to screen the lattice vibrations which induce stronger restoring force and therefore a down shift in frequency. This effect occurs for phonon wave vectors \( \vec{q} \) connecting two points on the Fermi surface \( \vec{q} = 0 \) and \( \vec{q} = 2K_F \) with \( \vec{q} \) the phonon wave vector and \( K_F \) the distance between \( \Gamma \) to \( K \) for graphene) [35, 57].
3.2 Raman modes

![Contour plot and energy band diagram](image)

**Figure 3.3:** (a) Contour plot of the valence band of graphene rotated by the angle \( \Phi \) with \( \Phi = \pi/6 - \Theta \) and \( \Theta \) the chiral vector of a (4,1) nanotube. With new coordinates \( k'_x = k_x \cos(\Phi) + k_y \sin(\Phi) \) and \( k'_y = k_x \cos(\Phi) - k_y \sin(\Phi) \). \( k'_x \) is given in units of Brillouin zone of graphene and \( k'_y \) is given in units of Brillouin zone in helical picture with \( q = 14 \), \( n = 1 \) and \( a = 6.51 \text{Å} \) [34, 48]. Drawn in red is the cutting line of the BZ for the (4,1) tube in helical picture with the high symmetry points \( \Gamma, K \) and \( M \). (b) Electronic bands obtained by *zone-folding* shown in (a) with denotation of the same high symmetry points. The Brillouin zone cut the \( K \) point of graphene. Therefore, the conduction band \( (E_C) \) touch the valence band \( (E_V) \) at the \( K \) point, which makes the nanotube metallic.
3.2 Raman modes

![Raman plot](image)

Figure 3.4: Kataura plot with the calculated data from Popov et al. [56] for energies in the range of visible light and diameters in the range of commonly used nanotubes. Denoted are the first four optical transitions for semiconducting tubes ($E_{2u}$, blue) and the first optical transition for metallic nanotubes ($E_{11M}$, red). The top axis shows the calculated Raman shift as described in Sec. 3.2.1.

![Phonon plot](image)

Figure 3.5: Calculated LO (red) and TO phonon branch (blue) for a (6,6) nanotube. Solid lines were calculated with a symmetry based force constant approach (SBFC) and dashed line were calculated with modified density functional theory (EZF-DFT) from [35]. The EZF-DFT calculations (dashed) show strong Kohn anomalies at the $\Gamma$ and $K$ point; the SBFC calculation of the TO phonon branch (blue, solid line) is only adapted to frequency related to the Kohn anomaly of graphite at the $K$ point.

More precise are calculations with density functional theory (DFT), but these calculations normally are restricted to nanotubes with a small number of atoms in the unit cell like for AC and ZZ tubes. With the \textit{zone-folding} method for the electronic band structure (Sec. 3.1), DFT calculations can be expanded to tubes with any chiral indices (EZF-DFT), but curvature effects, which are important especially for very small tubes (< 0.8 nm), have to be neglected [35].

Another fast calculation method which includes curvature effects is the symmetry based force constant approach (SBFC) [58]. Its adaption to the phonon frequencies of graphite can also provide an approximation for the KA for this calculation method.

Figure 3.5 shows a comparison of the longitudinal optical (LO) and the transverse optical (TO) phonon branch for a (6,6) nanotube between EZF-DFT (from [35]) and SBFC calculations*. In general, both calculations show the same behavior. But the EZF-DFT calculations show a distinct Kohn anomaly at the $\Gamma$ point for the LO branch and at the $K$ point for the TO branch. The KA for metallic nanotubes is quite sharp in comparison to graphene due to their one-dimensional structure [35]. The SBFC calculations show only the approximated frequency drop adapted to the KA of graphene at the $K$ point of the TO branch. This approximation provides a similar frequency, but not line shape, in comparison to the EZF-DFT

*Program: PolSym, the program was provided by the group of M. Damnjanović and I. Milošević (University of Belgrade, Serbia) [59].
3.2 Raman modes

![Graph showing Raman modes](image)

**Figure 3.6:** RBMs of an ensemble of SWCNTs for different excitation energies plotted into the Kataura plot. Spectra normalized to one with offset to excitation energies.

calculation.

### 3.2.1 Radial-breathing mode

The radial-breathing mode (RBM) stems from an acoustic mode in graphene from Γ-point phonons. For a nanotube with infinite diameter (graphene) this mode has zero frequency (like all acoustic modes) and corresponds to a translation of all atoms in out-of-plane direction. Due to the curvature of the tube walls all atoms move now in phase in radial direction, which corresponds to optical vibrations with non-zero frequencies (Sec. 3.3). Therefore, the frequency of the RBM strongly depends on the tube diameter and cannot be calculated by *zone-folding*. This dependence of the RBM frequency on diameter can be described with the equation:

$$\omega_{\text{RBM}}(d) = \frac{C_1}{d} + C_2$$

(3.10)

with the parameters $C_1$ and $C_2$. These parameters were determined theoretically and experimentally in various ways [34]. In this work I will use the parameters experimentally obtained by resonance Raman spectroscopy from Ref. [51] with $C_1 = 215 \text{ nm} \cdot \text{cm}^{-1}$ and $C_2 = 18 \text{ cm}^{-1}$. The phonon frequency of the RBM is in the region between $150 – 400 \text{ cm}^{-1}$ for diameters between $0.56 – 1.55 \text{ nm}$. Due to the low phonon energy of the RBM, the incoming and outgoing resonance is close and therefore the resonance profiles of certain tubes are quite narrow in energy. With help of resonance profiles it is possible to assign different RBMs in SWCNT ensembles to certain optical transitions, diameters, and even to different chiral indices [60]. Figure 3.6 shows the Raman spectra of the RBMs for an ensemble of SWCNTs for different excitation energies drawn into the Kataura plot. Clearly the RBM frequencies can be assigned to different optical transitions.

### 3.2.2 High-energy mode

The high-energy mode ($G$ mode) stems from vibrations along (longitudinal optical, LO) or perpendicular (transverse optical, TO) to the tube axis. In chiral SWCNTs, both LO and the TO phonons are Raman active, in contrast to ZZ or AC tubes. From the conservation of the parity, in ZZ tubes only the LO phonons are Raman active; and for AC only the TO phonons are Raman active [34]. Inside the Brillouin zone, LO and TO lose their defined longitudinal or transverse character; therefore they will be called here LO- and TO-derived phonon branches.

Similar to the RBM, the TO phonons are diameter dependent (Sec. 3.3) and the $G$ mode split into the $G^-$ mode (TO) and the $G^+$ mode (LO). The diameter dependence of the $G^-$ mode can be described with the equation:

$$\omega_{G^-}(d) = \frac{G_1}{d^2} + G_2$$

(3.11)
3.2 Raman modes

![Graph showing Raman modes](image)

Figure 3.7: Raman spectra of the $G$ mode (left panel), $D$ mode (middle) and $2D$ mode (right panel) for different excitation energies. For the $G$ mode the $G^+$ mode and the $G^-$ mode related to semiconducting ($G_s$) and metallic nanotubes ($G_m$) are denoted. Amplitudes of the spectra were normalized to 1; the spectra are plotted vertically offset.

with the parameters $G_1$ and $G_2$. These parameters were determined theoretically and experimentally in various ways [61]. In this work I will use the parameters experimentally obtained by resonance Raman spectroscopy of samples highly enriched with single chiralities [61]; with $G_1 = -27.5 \text{ nm}^2 \cdot \text{cm}^{-1}$ and $G_2 = 1582 \text{ cm}^{-1}$.

For metallic nanotubes the LO phonons are red shifted around 100 cm$^{-1}$ as compared to semiconducting tubes at the $\Gamma$ point. The reason is the Kohn anomaly [35, 57] (see above). Furthermore, the strong electron-phonon coupling broadens this mode [62].

Consequently, the line shape of the $G$ mode in SWCNT ensembles depends strongly on excitation energy (Fig. 3.7, left panel). For energies with mainly semiconducting tubes in resonance, the line shape consists of an intense $G^+$ mode and several much weaker peaks related to the semiconducting tubes ($G_s$ mode). For mainly metallic tubes in resonance, the line shape changes to an intense, broad $G_m$ mode with a weak $G^+$ mode [63–66].

### 3.2.3 Defect-induced Raman mode and overtone

In comparison to other Raman modes, the defect-induced Raman mode ($D$ mode) of nanotubes and other graphitic materials shifts in frequency with excitation energy. For SWCNTs the observed $D$-mode frequencies are in a range between 1300 – 1400 cm$^{-1}$ for excitations energies in the range of visible light. This behavior was addressed in 2000 by Thomsen and Reich [18] due to a dRR scattering (Sec. 2.1.3), and this concept was translated to SWCNTs by Maulitzsch et al. [19] with calculations of the dispersive behavior of the $D$ mode of nanotubes using equation (2.10).

Figure 3.8 shows a sketch of the dRR scattering for graphene. Due to the dRR process, the excited electron-hole pair can scatter in the whole BZ ($\vec{k}_{\text{electr.}} + \vec{k}_{\text{hole}} = 0$). A double resonant excitation occurs if the corresponding vector $|\vec{k}_{\text{electr.}}| = |\vec{k}_{\text{hole}}|$ matches twice a real state (Sec. 2.1.3) [Fig. 3.8 (a)]. For momentum conservation it must be $|\vec{k}| = |\vec{q}|$. For different excitation energies $\vec{k}$ has to change to fulfill the double resonance condition. Therefore, $|\vec{q}|$ changes together with the phonon frequency given by the phonon dispersion [Fig. 3.8 (c)]. For graphene the dRR process occurs for scattering between $K$ and $K'$, and for scattering within the same $K$ ($K''$) point. A higher excitation energy means a shorter phonon vector $|\vec{q}|$. Since the phonons for the $D$ mode stem from the TO branch near the $K$ point, for a higher excitation energy the $D$-mode frequency increases. Figure 3.7 (b) and (c) show the Raman spectra of the (2)$D$ mode for certain excitation energies with the excitation depended shift in frequency.

Furthermore, the high DOS of nanotubes near the optical transitions might influence the intensity of the $D$ mode [25]. This issue will be discussed in Chap. IV and V.
3.3 Curvature effect on phonon frequencies

To understand the dependence of the RBM and $G^*$-mode frequency on diameter, I will introduce a simple spring model of a nanotube. The use of a spring model is justified due to the results of experiments with $^{13}$C isotopes [67] and calculations using force constant models [45, 68-70]. The structure of a nanotube is approached by a simple closed ring of carbon atoms. This easy model will be sufficient to simulate the inversely-proportional relation between diameter and RBM frequency and the proportional relation between diameter and $G^*$-mode frequency*. Furthermore, this model gives the right magnitude of the frequency change to diameter.

A tube with an infinite diameter will be just a chain of carbon atoms with a constant atomic distance $a$. For this infinitely thick nanotube, the RBM is an acoustic out-of-plane vibration and therefore represents a translation with zero frequency [Fig. 3.9 (a)]. A nanotube with a given diameter is represented by a closed ring of atoms. Figure 3.9 (b) shows this for a nanotube with radius $r$ and angle $\alpha$ between radius and atomic bond $a$. The former, strict vibration orthogonal to the sigma bonds $a$ [Fig. 3.9 (a)] now becomes the breathing vibration of the nanotube, with a larger angle between vibration direction and sigma bonds. To evaluate the dependence of phonon frequency on diameter, the frequency will be calculated with classical mechanics. Figure 3.9 (c) shows the zoom to an atom with its closest neighbors in the position of equilibrium (open circles) and after displacement (gray circles). In next neighbor approximation two effective restoring forces ($F_{\text{res}}$) can be assumed for each atom, marked with red arrows for the upper atom.

In general, the restoring force $F$ is proportional to the displacement $\Delta a$ of the spring with $F = -f \Delta a$, $f$ is the spring constant. For this model, $\Delta a$ can be decomposed into a radial part $\Delta a_{\text{rad}}$ and tangential part $\Delta a_{\text{tang}}$. This leads to the effective restoring force

$$F_{\text{res}} = F_{\text{resRBM}} + F_{\text{resRBM},2} = -f(2\Delta a_1 + 2\Delta a_2)$$

$$= -2f(\Delta a_{\text{rad},1} + \Delta a_{\text{tang},1} + \Delta a_{\text{rad},2} + \Delta a_{\text{tang},2})$$

$$= 2f[2\Delta a_{\text{rad}}(\Delta a_{\text{tang}})] = f \Delta a \cdot 4 \cos(\alpha) \cdot (-\Delta a_0) .$$

*More precise is the $G^*$ mode related to the TO phonon branch.

†The introduction of different $a$s would lead to a more realistic model, but cannot be handled with this approach.

Figure 3.8: Sketch of the dRR process for graphene. The scattering of an electron-hole pair between the Dirac cones is shown in (a) [zoom into the band structure from (b)]; for two different excitation energies $E_1$ (green) and $E_2$ (blue). The corresponding phonon wave vectors $q_1$ and $q_2$ which are needed to fulfill the double resonance condition are drawn into the phonon dispersion (c) to indicate the shift in phonon frequency. The phonon frequency was calculated with POLSym for an AC nanotube.
3.3 Curvature effect on phonon frequencies

![Diagram of C atom and nanotube](image)

**Figure 3.9:** Sketch of the effective restoring force for the RBM induced by curvature. (a) Model of a nanotube with infinite diameter \( d \). All carbon atoms move perpendicular to the \( \sigma \) bonds \( a \). (b) Model of a nanotube with radius \( r = d/2 \). All atoms move in radial direction. (c) Zoom to an atom with its closest neighbors. The restoring forces are drawn in red.

The effective force constant \( f^* \) can be found by the derivation of the effective restoring force with the displacement of the atom \( \Delta r \), which is in the radial direction. With \( \Delta r \cos(\alpha) = \Delta a \) it follows

\[
f^{*}_{\text{RBM}}(\alpha) = \frac{|F^{\text{RBM}}_{\text{res}}|}{|\Delta r|} = 4f \cos(\alpha)^2. \tag{3.13}
\]

The effective restoring force changes with \( \alpha \), which is related to a change in diameter. The relation between \( \alpha \) and diameter \( d \) can be found with the cosine formula

\[
\alpha(d) = \arccos \left( \frac{a}{2r} \right) = \arccos \left( \frac{a}{d} \right). \tag{3.14}
\]

Insertion of (3.14) in (3.13) gives the dependence of the RBM frequency on diameter:

\[
\omega_{\text{RBM}}(d) = \sqrt{\frac{f^{*}_{\text{RBM}}}{m}} = 2 \sqrt{\frac{f}{m} \cdot \frac{a}{d}}. \tag{3.15}
\]

Which is the well known \( 1/d \) behavior for the RBM frequency.

Based on the same considerations and thoughts for Fig. 3.10 the effective restoring force of the \( G^- \) mode (TO phonon mode) can be determined to

\[
F^{*}_{\text{resG}^-} = f \Delta a \cdot 4 \sin(\alpha) \cdot (\varepsilon_x). \tag{3.16}
\]

With \( \Delta t \sin(\alpha) = \Delta a \) the effective spring constant can be calculated to:

\[
f^{*}_{G^-}(\alpha) = \frac{|F^{*}_{\text{resG}^-}|}{|\Delta t|} = 4f \sin(\alpha)^2. \tag{3.17}
\]

Insertion of (3.14) in (3.17) and using the relation \( \sin[\arccos(z)] = \sqrt{1 - z^2} \) the dependence of the \( G^- \) mode on diameter can be derived to:

\[
\omega_{G^-}(d) = \sqrt{\frac{f^{*}_{G^-}}{m}} = 2 \sqrt{\frac{f}{m} \cdot \sqrt{1 - \left( \frac{a}{d} \right)^2}}. \tag{3.18}
\]

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3.3 Curvature effect on phonon frequencies

Figure 3.10: Sketch of the effective restoring force for the $G^-$ mode induced by curvature. (a) Model of a nanotube with infinite diameter $d$. All carbon atoms move parallel to the $\sigma$ bonds $a$. (b) Model of a nanotube with radius $r = d/2$. All atoms move tangential to the tubes wall. (c) Zoom to an atom with its closest neighbors. The restoring forces are drawn in red.

Without curvature, the frequency of the $G^-$ mode must be equal to the frequency of the $G^+$ mode (LO phonon mode), so $2\sqrt{f/m}$ can be assigned to 1591 cm$^{-1}$. The distance to closest neighbors is set to $a = 0.213$ nm, which is the mean value for the largest and lowest possible distance of carbon atoms in a graphene hexagon.

Figure 3.11 shows the calculated diameter dependence for the RBM and Fig. 3.12 for the $G^-$ mode together with experimental data. The decrease of the RBM frequency for a diameter range between 0.6 – 1.2 nm is 49% for the calculations and 47% for the experiment. For the $G^-$ mode, the increase of frequency for a diameter range between 0.6 – 1.2 nm is 5% for the calculations and 4% for the experiment. The large difference in absolute frequencies for the RBM between calculation and experiment can be explained by an overestimation of $2\sqrt{f/m} = 1591$ cm$^{-1}$. It is known that the force constant in graphene (no curvature) is weaker for out-of-plane vibrations (RBM) than for in-plane vibrations ($G^+$ mode) [68]. Overall, a very good agreement between experiment and theory is obtained. For this model the main effect of curvature on frequency is a change in the angle between the $\sigma$ bonds and the vibration direction of the atoms, which lead to a change of the effective spring constant. Or with other words, the strict restoring force perpendicular (out-of-plane) or parallel to the atomic displacement directions (in-plane) mix due to curvature. Of course, curvature induced strain, changes in the atomic bond lengths and the rehybridization of $sp^2$ to $sp^3$ orbitals [34] might affect the frequency as well, but seem not to be the main effect for nanotubes bigger than 0.6 nm.

The opposite relation between diameter and frequency for RBM and $G^-$ mode is a consequence of the out-of-plane (RBM) and in-plane (TO phonon mode) motions of the atoms (infinite diameter). Since for the $D$ mode the atoms move in-plane direction (breathing-like vibration of the carbon hexagons) [71], a similar dependence of the $D$ mode-frequency on curvature can be assumed as for the $G^-$ mode, which will be discussed in Chap. V.
3.3 Curvature effect on phonon frequencies

**Figure 3.11:** Calculated dependence of RBM-frequency on diameter (red) from Eq. (3.15) with $a = 0.213 \text{ nm}$ and $\sqrt{f/m} = 795.5 \text{ cm}^{-1}$. For comparison, fit of experimental data (blue) from [51] is shown.

**Figure 3.12:** Calculated dependence of $G^\prime$-mode frequency on diameter (red) from Eq. (3.18) with $a = 0.213 \text{ nm}$ and $\sqrt{f/m} = 795.5 \text{ cm}^{-1}$. For comparison, fit of experimental data (blue) from [61] is shown.
CHAPTER IV

Resonance behavior of the defect-induced Raman mode
4.1 Chapter introduction

Parts of this chapter were published in Ref. [72].

4.1 Chapter introduction

The $D$-mode intensity depends on the concentration of structural defects in carbon nanotubes and other graphitic materials [20], its intensity is therefore taken as evidence for, e.g., successful covalent functionalization [23, 73]. In SWCNTs, however, the intensity and resonance behavior of the $D$ mode has not yet been fully understood [74, 75]. This is partly due to the fact that, initially, chiral-index defined SWCNT samples were not available. Moreover, most experiments on the $D$ mode of carbon nanotubes investigated the dispersion of the $D$-mode frequency with excitation energy. They were done either in nanotube ensembles, using a broad range of excitation energies [19, 25, 76, 77], or on individual SWCNTs, using only a small number of excitation energies and assuming that only those SWCNTs contribute to the $D$ mode for which the excitation energy is in resonance with an optical transition [78–80]. Numerical simulations, on the other hand, focused on the $D$-mode dispersion of both, individual nanotubes [19] and nanotube ensembles [25], showing an intensity decrease of the $D$ mode away from the optical transition of the nanotube. Ref. [25] emphasized the intensity enhancement of the $D$ mode directly at optical resonances (enhanced-IRR scattering), attributing the $D$-mode dispersion in nanotube ensembles to excitation-energy dependent contributions of different nanotubes with different $D$-mode frequencies. However, excitation-energy dependent Raman experiments following the $D$-mode dispersion and intensity on chiral-index identified carbon nanotubes have not been reported. On the other hand, knowledge about nanotube phonon dispersion [35, 81], optical transitions [82–84], and chiral-index sorting and assignment [26–28, 61] has improved significantly over recent years.

In this chapter a resonance Raman study of the $D$ mode in a sample highly enriched with (9,7) SWCNTs in the excitation energy range of $1.49 - 2.05$ eV is presented. The intensity of the $D$ mode in the sample depends strongly on excitation energy and shows a resonance behavior near the optical transition of the (9,7) SWCNT. On the other hand, the well-known dispersion of the $D$-mode frequency with excitation energy starts only above certain excitation energy, i.e. away from the resonance. Numerical simulations of the $D$-mode spectra of the (9,7) SWCNT agree with both observations, supporting the interpretation of an enhanced, only weakly dispersive double-resonant Raman scattering at excitation energies close to the optical transitions in SWCNTs.

4.2 Experimental and simulation details

SWCNTs produced by pulsed-laser vaporization were wrapped with the polymer Poly(9,9-di-n-octylfluorenyl-2,7-diyl) (POF) in toluol. After ultracentrifugation mainly individual (9,7) SWCNTs were dissolved in this solution [26] (sample received from the group of Dr. Frank Henrich). After a time of re-bundling, the sample was centrifuged again to separate the (9,7) SWCNTs from excessive POF. This was necessary to reduce the strong Raman signal of the POF in the frequency region of the $D$ mode. The obtained solution was drop casted onto a Si/SiO$_2$ (200 nm SiO$_2$) substrate [sample (9,7)]. All measurements were performed at the same spot of the sample.

The electronic bands were calculated from a third-nearest neighbor tight-binding approximation [47] (Sec. 3.1) The phonon dispersion relations were calculated with a SBFC method adapted to the experimental phonon dispersion of graphite [58, 81] with the program POLSym [59] (Sec. 3.2).

4.3 Chiral-index assignment

Figure 4.1 shows the resonance profiles of the RBM for the chiral-index assignment [51]. The profiles with the highest intensities can be assigned to the second optical transition ($E'_{22}$) of semiconducting (9,7) and (9,8) SWCNTs. Some weaker RBMs of other SWCNTs (Fig. 4.1, open symbols; bare, thick lines) are observed above the excitation energy of $1.6$ eV, however, their intensities were at least by a factor of 27 lower than for the (9,7) SWCNT and by a factor of 3 lower than for the (9,8) SWCNT.

The RBM of the (9,7) SWCNTs consists of two contributions (Fig. C.1) with slightly different frequencies ($\Delta \omega = 2.3$ cm$^{-1}$) and resonance energies ($E' = 1.5405$ eV, $E'' = 1.5336$ eV and $\Delta E = 6.9 \pm 0.8$ meV). Assigning these resonance profiles to two different chiral indices seems not suitable, because of the isolated position of the (9,7) SWCNT with respect to other SWCNTs in the Kataura plot [56]. Since similar shifts in Raman frequency and transition energy were observed between empty and water-filled nanotubes [85, 86],

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4.4 Dispersion and resonance behavior of the defect-induced Raman mode

![Diagram of Raman spectra](image)

**Figure 4.1:** RBM resonance profiles of sample (9,7) with chiral-index assignment. Circles denote semiconducting nanotubes; bare, thick lines denote metallic nanotubes. The inset shows the Raman spectra of the $G^-$ modes of the (9,7) and (9,8) SWCNTs at 1.55 eV excitation energy.

<table>
<thead>
<tr>
<th>SWCNT</th>
<th>$G^-$-mode frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>this work</td>
</tr>
<tr>
<td>(9,7)</td>
<td>1556.7±0.8</td>
</tr>
<tr>
<td>(9,8)</td>
<td>1564.4±0.7</td>
</tr>
</tbody>
</table>

Table 4.1: $G^-$-mode frequencies of the (9,7) and (9,8) SWCNTs compared with the results from Ref. [61].

the splitting might be due to empty and toluol-filled nanotubes, but cannot be explained up to know in detail.

The chiral-index assignment is confirmed with help of the $G^-$ mode (see Tab. 4.1) [61]. The Raman spectrum of the $G^-$ modes at 1.55 eV excitation energy is shown in the inset of Fig. 4.1.

4.4 Dispersion and resonance behavior of the defect-induced Raman mode

Figure 4.2 shows the Raman spectra of the $D$ mode for excitation energies between 1.49 – 2.05 eV, where the maximum amplitude was normalized to one. In these spectra, the $D$ mode consists of at least two main contributions. They are indicated by two colored stripes and denoted with the signs $+$ and $\times$. For high excitation energies, the Raman signal of POF appears in the spectra due to a decrease of the $D$-mode intensity. The spectra were fitted with two Lorentzians, after the background signal of the POF polymer was subtracted.

Figure 4.3 shows the measured $D$-mode intensity (peak area) of both contributions ($+$, $\times$) as function of excitation energy on logarithmic scale. Both contributions show a decrease in intensity by two orders of magnitude for the excitation energy between 1.49 – 2.05 eV.

The dispersion of the $D$-mode frequency with excitation energy is shown in Fig. 4.4. The frequencies are represented by $+$ and $\times$ signs, the intensities of the $D$ mode contributions are indicated by the radii of the circles. The strongest $D$-mode intensity is observed, when the RBM of the (9,7) and (9,8) SWCNTs is in resonance. Unexpectedly, the well-known dispersion behavior of the $D$ mode [19] is only observable above a certain excitation energy (1.7 eV for the SWCNTs in this sample). Here, the $D$-mode intensity is strongly decreased (Fig. 4.3); the dispersions of the two contributions can be linearly fitted to 81 cm$^{-1}$/eV and 43 cm$^{-1}$/eV.

The results can be explained tentatively by attributing the weakly dispersive, high-intensity appearance of the $D$ mode (Fig. 4.4, excitation energy between 1.49 – 1.7 eV) to an enhanced-dRRR scattering very close to the optical transition. For the dispersive, low-intensity part of the $D$ mode (Fig. 4.4, excitation energy above 1.7 eV), we are above the resonance window of the enhanced-dRRR scattering, and therefore the intensity decreases. At the same time, the electron bands of SWCNTs exhibit the nearly linear dispersion...
4.4 Dispersion and resonance behavior of the defect-induced Raman mode

![Graph showing Raman spectra and intensities](image)

**Figure 4.2:** Raman spectra of the D mode of the sample (9,7) for excitation energies between 1.49 – 2.05 eV (top to bottom). Amplitudes of the spectra were normalized to one; the spectra are plotted vertically offset. Colored stripes and signs (+, ×) indicate two main contributions of the D mode. For high excitation energies, the Raman signal of POF (bottom spectrum) overlaps with the weak D-mode intensity.

derived from the nearly linear bands close to the K points of graphite and graphene. To verify this interpretation, calculations of the resonance behavior of the D mode for the (9,7) and the (9,8) SWCNT were performed.

4.4.1 Simulations

The D mode is calculated by a numerical simulations of the dRR scattering, with the matrix element K for the scattering with one phonon and one defect, given by Eq. (2.6) (Sec. 2.1.2). Figure 4.5 shows the cutting line of the BZ of the (9,7) nanotube with the contour plot of the conduction band of graphene. Figure 4.6 shows the electron dispersion by zone-folding (Sec. 3.1) together with its phonon dispersion of the (9,7) SWCNT in units of helical quantum numbers [34, 48] (Sec. 3.2). The transition energies $E_{11}$ and $E_{22}$ in the electron dispersion, and the LO- and TO-derived phonon branches in the phonon dispersion are denoted. In the simulations, $E_{11} = 0.67$ eV and $E_{22} = 1.28$ eV *.

The simulations were performed with excitation energies in the range of both optical transitions $E_{11}$ and $E_{22}$. Therefore, up to four scattering processes for the electrons are in principle possible: $E_{11} \leftrightarrow E_{11}$, $E_{22} \leftrightarrow E_{22}$, $E_{11} \leftrightarrow E_{22}$, and $E_{22} \leftrightarrow E_{11}$. A sketch of these processes for the lowest possible excitation energy is shown in Fig. 4.7 (a). Including the two phonon branches and the four scattering processes, eight different processes contribute to the D-mode simulations [Fig. 4.7 (b)].

In contrast to Ref. [19], where it is assumed that the disorder only breaks the pure translational symmetry and not, to first approximation, the rotational symmetry of the nanotube, now the entire phonon branch with helical quantum number $\tilde{m} = 0$ is allowed. This corresponds in linear quantum numbers to a change in band index $m$, which would not be allowed if the rotational symmetry was conserved.

To analyze differences between the various contributions of the simulated Raman spectra, first, each scattering process was calculated separately, thereby neglecting possible interference effects [37]. Each spectrum of the different contributions was phenomenologically fitted with two Lorentzians (inset Fig. 4.8)

*These values are lower than the experimental ones, as the approximation does not include electron-electron and electron-hole interactions. However, only the D-mode behavior relative to the optical transition energies is considered.
4.4 Dispersion and resonance behavior of the defect-induced Raman mode

![Dispersion and resonance behavior](image)

**Figure 4.3:** Resonance behavior of the $D$ mode of sample (9,7) for excitation between 1.49 - 2.05 eV. The signs + and × denote the two contributions marked in Fig. 4.2.

**Figure 4.4:** Dispersion of the two contributions of the $D$ mode, denoted by the signs + and × (Fig. 4.2). The radii of the circles indicate the $D$-mode intensities. The arrow indicates the $E_{22}$ transition energy of the (9,7) SWCNT determined from the RBM resonance profile (Fig. 4.1). Error bars are the sum of the standard derivation of the $G^+$ mode (fitted over the whole energy range) and fitting errors of the $D$ mode.

Considering the shorter and longer phonon wave vector from the scattering processes at a given energy.

Figure 4.8 shows the fitted data of the simulated $D$ mode for each of these eight different contributions. Different colors denote the different scattering processes (color code as in Fig. 4.7) and the shapes of the symbols denote the used phonon branches. The symbol size indicates the intensity obtained from the fit. From these results, some general observations can be made. First, all scattering processes show an enhanced intensity near the corresponding optical transitions ($E_{11}$, $E_{22}$). For the symmetric scattering within the same optical transition ($E_{11} \leftrightarrow E_{11}$ and $E_{22} \leftrightarrow E_{22}$), the $D$-mode intensity of the outgoing resonance ($\approx 160$ meV) above the optical transition) is always stronger than for the incoming resonance. The reason is that for the incoming resonance, the electron scattered with a phonon will always be below the optical transition (i.e. band extrema with high density of states in the simulations), whereas for the outgoing resonance, scattering with a phonon matches the optical transition. Second, the $D$ mode becomes dispersive at energies above the outgoing resonance, as observed in experiments.

A peculiarity in the dispersion is the scattering process for the shorter wave vector of the scattering $E_{22} \leftrightarrow E_{22}$ involving the TO-derivable branch (Fig. 4.8, gray circles, lower branch). Here, an unusual negative dispersion can be observed. This is due to the fact that the phonon wave vector $q$ of the lowest possible optical transition does not correspond to the lowest frequency of the TO-derivable phonon branch [Fig. 4.7 (b), lower panel, gray arrow]. For smaller $q$ vectors (corresponding to higher excitation energy), therefore, the frequency of the $D$ mode first drops before it rises again after passing the minimum of the phonon dispersion.

A full simulation of the $D$-mode intensity of the (9,7) SWCNT with an overlap of the eight different scattering processes, necessarily including all interference effects, [37] is shown in Fig. 4.9 (a). An excitation-energy
4.4 Dispersion and resonance behavior of the defect-induced Raman mode

![Figure 4.5: Cutting line of the helical-wave vector of the (9,7) tube (red) drawn in the contour plot of the conduction band of graphene. The Cartesian coordinates are rotated by the chiral vector \( \Theta \) to \( k_x' = k_x\cos(\Theta) + k_y\sin(\Theta) \) and \( k_y' = k_y\cos(\Theta) - k_x\sin(\Theta) \). The high symmetry points \( \Gamma \) and \( M \) are denoted (Sec. 3.1).](image)

range similar to the experiment was chosen.

Similar to the experiment, the simulated \( D \) mode shows a strong intensity in a small energy range, followed by an intensity decrease and a starting dispersive behavior for higher energies. A comparison with the calculated data from Fig. 4.8 shows that the highest intensity belongs to the scattering \( E_{22} \leftrightarrow E_{22} \) with the LO-derived phonon branch (gray squares).

To deduce the dispersion of the full simulation, the Raman spectra were phenomenologically fitted with five to six Lorentzians [as an example see inset of Fig. 4.9 (b)]. The number of used Lorentzians was determined by the line shape of the simulated Raman spectra, similar to the fitting procedure for the experimental spectra. The result is shown in Fig. 4.9 (b). Here the radii of the circles correspond to the \( D \)-mode intensities.

The inset of Fig. 4.9 (b) shows that in the frequency range of the experimental data (1280 – 1330 cm\(^{-1}\)), the simulated Raman spectra consist of two main contributions. These two main contributions are due to an overlap of the different scattering processes. For these two main contributions a dispersion of 38 and 56 cm\(^{-1}\)/eV (solid lines) is obtained. Therefore, it can be assumed that the two main contributions of the measured \( D \) mode also are due to an overlap of different scattering processes with similar phonon frequencies.

For the calculation of the \( D \)-mode resonance of the (9,8) SWCNT (Fig. 4.10) a similar behavior was found as described above. For that reason and due to the much weaker RBM intensity of the (9,8) SWCNT in comparisons to the (9,7) SWCNT this contribution of the simulated \( D \) mode was neglected in the following comparison between calculation and experimental data.

4.4.2 Simulations in comparison with experimental data

In Fig. 4.11, the experimental data (Fig. 4.4) are plotted into the intensity color plot of the simulations [Fig. 4.9 (a)]. In the simulations, the energies of the optical transitions were slightly underestimated. For better comparison, the simulations were shifted by +0.28 eV to bring the theoretical optical transition energies to the same energy as in experiment.

In general, the agreement between calculation and experiment is quite good as discussed above: In both cases an enhanced \( D \)-mode intensity is visible, as well as the non-dispersive parts have similar frequencies. Furthermore, at higher excitation energies, a similar dispersion of the \( D \) mode is observed.

The two most obvious differences between simulations and experiment are as follows: First, the \( D \)-mode intensity in the simulations decreases only linearly by a factor of 2 and not exponentially by two orders of magnitude; second, the highest \( D \)-mode intensity in the simulations is shifted to higher excitation energy. This shift is caused by the strong outgoing resonance in the simulations, which is not observed in the experiment. Both differences might be due to neglecting the wave-vector dependence of matrix elements \( M \) and excitonic effects in the simulations. Also an intensity decrease of the outgoing resonance due to the non-Condon effect (recently observed for the \( G \) mode [87]) might play a role for the \( D \)-mode intensity and was not taken into account in the simulations.

A comparison of the Raman spectra between experiment and simulations is shown in Fig. 4.12. For excitation energies near the optical transition \( E_{22} \), a small difference between experiment and simulations is seen (blue shift of the simulations by about 10 cm\(^{-1}\)). This frequency difference might be caused by inaccuracies in the
4.4 Dispersion and resonance behavior of the defect-induced Raman mode

![Diagram of electron and phonon dispersion](Figure 4.6: Calculated electron and phonon dispersion of the (9,7) SWCNT. The optical transitions $E_{11}$ and $E_{22}$, and the LO- and TO-derived phonon branches are indicated. The wave vector is given in units of helical quantum numbers $[34, 48]$ with $q = 386, n = 1$, and lattice translation vector $a = 59.22$ Å.)

calculated phonon dispersion*. Since also the different contributions of the $D$ mode have slightly different frequencies (Fig. 4.8), the observed frequency deviations might also be caused by an overestimation of one of these contributions, again because of neglecting the matrix elements.

Furthermore, an additional peak appears for higher excitation energies in the range of low frequencies in the simulations (Fig. 4.12, at $\approx 1250 \text{cm}^{-1}$). This contribution corresponds to a scattering process involving the TO-derived phonon branch (Fig. 4.8, circles). Due to the anti crossing of the phonon bands near the $K$ point, the frequencies of the TO-derived phonon branch corresponds to the LO-phonon branch at the $\Gamma$-point for the (9,7) SWCNT. For $\Gamma$ point scattering (RBM and the $G$ mode) it was shown in calculations that for SWCNTs with a large chiral angle [as for the (9,7) nanotube], the Raman intensity related to the LO-phonon branch is much weaker than for the TO-phonon branch [88]. Therefore, the Raman intensity for scattering involving the TO-derived phonon branch at the $K$ point (Fig. 4.12, at $\approx 1250 \text{cm}^{-1}$) might be much smaller than in the simulations, as observed in the experiments.

The unexpected high dispersion of $81 \text{cm}^{-1}/\text{eV}$ in the experimental data (Fig. 4.4) might be explained with a jump to contributions from another scattering process as seen in the calculations in Fig. 4.9 (b), indicated with a dashed line. But we will see in Sec. 5.4.1 that in SWCNT ensembles the dispersion of the $D$ mode is strongly influenced by subsequent resonances of CNTs with different diameters. Therefore, due to the exponential decrease of the $D$-mode intensity, the still remaining metallic nanotubes (Fig. 4.1; thick, bare lines) contribute to the $D$ mode for excitation energies above 1.9 eV. This leads to an additional contribution to the $D$ mode at higher frequencies and therefore to an overestimated dispersion.

On the other hand, below 1.9 eV, significant additional contributions to the $D$ mode (from semiconducting CNTs with similar phonon frequencies; Fig. 4.1; open symbols) seem less probable due to the much weaker RBMs in comparison to the (9,7) CNT.

*For the used SBFC calculations a Kohn anomaly (KA) was approximated even for semiconducting tubes, which do not possess a KA (Sec. 3.2). For further discussion see Sec. 5.4.2.
Additional to sample (9,7) a resonance study of the (2)D mode for a sample enriched with (7,5) was done [sample (7,5)]. Since this sample was not as highly enriched as sample (9,7) (monitored by the RBM, Fig. C.2) and the excitation window was restricted to a smaller energy range, the (2)D mode of sample (7,5) does not show a significant change in intensity (C.3 and C.4). However, a comparison between the simulations of the sample (9,7) and sample (7,5) with experimental data shows a good agreement in frequency (Fig. 4.13 and 4.14); with a higher frequency for sample (7,5) compared to sample (9,7). A possible diameter dependence as reason for this higher frequency will be discussed in the Chap. V. Furthermore, an additional contribution to the 2D mode is clearly observable for the sample (9,7) (Fig. 4.14, Raman spectra: Fig. C.5). Similar to the D mode, this contribution is assigned to still remaining metallic nanotubes in the sample; discussed in more detail in Sec. 5.4.1.

4.5 Chapter summary

The defect-induced Raman mode in a sample enriched with (9,7) SWCNTs shows a strong resonance behavior. The D-mode intensity is strongest at the optical transition of the (9,7) SWCNT; the D-mode frequency, however, shows almost no dispersion with excitation energy near the resonance. The well-known dispersion of the D-mode frequency is observed only above resonance, where the intensity has dropped by approximately one order of magnitude. These results are understood based on numerical simulations of the D-mode spectra, although the intensity drop observed in experiment is even stronger than in the simulations. Further calculations therefore should include excitonic effects.

Based on the strong resonance of the D mode, it can be expected that the (2)D-mode dispersion measured in nanotube ensembles reflects not just the electron and phonon bands of a given nanotube but also a
4.5 Chapter summary

![Graph showing Raman shift vs. excitation energy with various peaks and labels E11→E11, E22→E22, E11→E22, E22→E11.]

Figure 4.8: Calculation of the different contributions of D mode for the (9,7) SWCNT. Different colors denote the scattering path; the shapes of the symbols denote the used phonon branch. The symbol size indicates the intensity. The inset shows an exemplary fit of a simulated spectrum with two Lorentzians.

diameter and chiral-angle dependence of the D-mode frequency [25, 79]. The dependence on diameter will be discussed in Chap. V.

The results further show that the D-mode intensity does not exclusively depend on the defect density of the nanotubes but also on the excitation energy. This should be considered together with the excitation-energy dependence of the G-mode intensity when taking the D/G intensity ratio as a measure for the defect density. This issue will be discussed in more detail in Chap. VIII.
Figure 4.9: (a) Simulated D-mode intensity for the (9,7) nanotube as a color plot with consideration of all interference effects.
(b) Dispersion of the simulated Raman spectra, deduced by fitting with Lorentzians (inset). The radii of the circles correspond to the simulated D-mode intensity.

Figure 4.10: Simulated D-mode intensity for the (9,8) nanotube as a color plot with consideration of all interference effects.
4.5 Chapter summary

Figure 4.11: Comparison of dispersion behavior between simulations (color intensity plot) and experimental data (symbols).

Figure 4.12: Comparison of calculated (dashed lines) and experimental (solid lines) Raman spectra. Amplitudes of the spectra were normalized to one; the spectra are plotted vertically offset.

Figure 4.13: Comparison of the D-mode dispersion between simulations (color intensity plot) and experimental data (symbols) for sample (9,7) and sample (7,5).
4.5 Chapter summary

![Figure 4.14: Comparison of the (2)D-mode dispersion between simulations (color intensity plot) and experimental data (symbols) for sample (9,7) and sample (7,5).](image)

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CHAPTER V

Dependence of the defect-induced Raman mode frequency on diameter in nanotube ensemble
5.1 Chapter introduction

As shown in Chap. IV, the high DOS at the electronic band extrema enhance the $D$-mode intensity for an excitation near this energy. A dRR scattering near this energy leads to a quasi single-resonant behavior for the $D$ mode [25]. Each contribution of the $D$ mode has a resonance window, similar to other one-phonon Raman processes. Therefore, it might be possible to correlate components of the $D$ mode to nanotube species and/or to a certain RBM and related diameter.

In this chapter, the different (2)$D$ mode contributions of samples enriched with semiconducting and metallic nanotubes are attributed to different optical transitions and the dependence of the (2)$D$-mode frequency on diameter is determined. To support this result, the determined diameter dependence is compared with measurements of samples with well-known diameter, like samples highly enriched with single chiralities [26] (Chap. IV) and measurements of individual, freestanding SWCNTs [89].

5.2 Experimental details

The samples enriched with metallic and semiconducting tubes were produced by size-exclusion chromatography [90]; the samples enriched with single chiral indices were produced by density gradient ultracentrifugation (DGU) [26] (samples received from the group of Dr. Frank Hennrich). The spectra were collected from a sample drop casted on Si/SiO$_2$ or from aqueous solution.

The individual, freestanding nanotubes were grown by catalyzed chemical vapor deposition [89]. The used catalyst particles had been adsorbed on 3 µm thick thermally oxidized polycrystalline Si supports, patterned as sharp opposing tips [91] (sample received from the group of Dr. Miroslav Haloška).

5.3 Contributions of the $D$ mode in SWCNT ensembles

Figure 5.1 shows the Raman spectra of the $D$ mode and 2$D$ mode for samples enriched with semiconducting (S-SWCNTs, blue) and metallic (M-SWCNTs, red) nanotubes for different excitation energies, where the maximum amplitude was normalized to one. Above 1.96 eV excitation energy, the line shapes of the (2)$D$ mode are different for the two samples. This reflects the resonance behavior of the (2)$D$ mode in SWCNT ensembles shown in Chap. IV, due to the subsequent resonance of semiconducting and metallic nanotubes with different optical transition energies [25]. A comparison to the experimental Kataura plot [51, 54] (Fig. 5.2) shows that above 1.96 eV metallic nanotubes become resonant; this leads to an additional contribution to the (2)$D$ mode with a slightly higher phonon frequency. Above 2.48 eV, the third optical transition of semiconducting nanotubes becomes resonant and therefore, again a new contribution

Figure 5.1: Raman spectra of the $D$ mode (left panel) and the 2$D$ mode (right panel) of sample S-SWCNTs (blue) and M-SWCNTs (red), for excitation energies between 1.5 and 2.71 eV (bottom to top). Amplitudes of the spectra were normalized to one; the spectra are plotted vertically offset.

Parts of this chapter were published in Ref. [75].
5.3 Contributions of the D mode in SWCNT ensembles

Figure 5.2: Experimental Kataura plot of the sample S-SWCNTs and M-SWCNTs, ordered by optical transitions. Crossed symbols denote transition energies gained from resonance profiles, open symbols denote transition energies gained from incomplete resonance profiles or distinct excitation energies. Solid lines are the linear fits of the different optical transitions with indication of the standard deviations (light gray areas). For transition $E_{31}^S$ an additional fit point was set to (0,0). The (9,7) and (7,5) tube is denoted.

appears in the Raman spectra of the $(2)D$ mode with an even higher phonon frequency (best visible for the 2D mode). Since the $(2)D$ mode and the RBM possess similar resonance energies (Chap. IV), this assignment to the different contributions seems evident and therefore, the resonance of the $(2)D$ mode in SWCNT ensembles follows in general the related resonance behavior of the experimental Kataura plot (Fig. 5.2). The optical transitions for this samples and excitation energies are the second semiconducting ($E_{31}^S$), the first metallic ($E_{11}^M$), and the third semiconducting ($E_{33}^S$) optical transition.

To analyze the dispersions for the different contributions, the spectra were fitted with up to three Lorentzians for the $D$ mode and with up to four Lorentzians for the $2D$ mode* (Fig. 5.3). The sum of all fits was normalized to one for each spectrum. The areas of the symbols indicate the relative peak intensities of the fits; the shape denotes the different samples. Each contribution shows a similar phonon dispersion with a mean value of $\approx 29 \pm 5$ cm$^{-1}$ for the $D$ mode and $\approx 56 \pm 6$ cm$^{-1}$ for the $2D$ mode. These dispersions are much smaller compared to single tube measurements [19] (Sec. 4.4). This behavior reflects the subsequent enhancement of the $(2)D$ mode in SWCNT ensembles of nanotubes near their optical transitions and therefore differs from the dispersion related to the phonon bands close to the $K$ point of graphite and graphene (discussed in more detail in Sec. 5.4.2).

Due to the assignment of the $(2)D$-mode contributions to semiconducting and metallic nanotubes, it is possible to evaluate the excitation windows with mainly one species in resonance. For that, the difference between the amount fractions of semiconducting ($A_S$) and metallic contributions ($A_M$), depending on excitation energy, is calculated from [92]:

$$ A = A_S - A_M = \frac{I_S}{I_S + I_M} - \frac{I_M}{I_S + I_M} = \frac{I_S - I_M}{I_S + I_M}, $$

with $I_{S,M}$ the Raman-mode intensity assigned to semiconducting or metallic nanotubes. For a value of $A = 1$ only semiconducting tubes contribute to the Raman spectrum and for $A = -1$ only metallic tubes. Figure 5.4 shows the dependence of the amount fraction $A$ on excitation energy for the $(2)D$ mode [(b),(d)] and for comparison the RBM and the $G$ mode [(a),(c)] for non-enriched nanotubes produced with the high pressure carbon monoxide method (HiPCO nanotubes) [93]. The calculations were fitted with a Gaussian function (fit parameter: Tab. B.1). For an excitation window between 1.5 - 2.0 eV only $E_{31}^S$ contributes to the $(2)D$ mode ($A = 1$). For higher excitation energies additional $E_{11}^M$ starts to contribute to the $(2)D$ mode and between 2.4 - 2.6 eV excitation energy mainly metallic tubes contribute to the $(2)D$ mode. The highest

*Chap. IV shows that the contribution of the $(2)D$ mode related to the optical transition $E_{31}^S$ consists of two Lorentzians. This leads up to four contributions for the 2D mode, for involving only three optical transitions.
5.4 (2)D-mode diameter dependence

The amount fraction for metallic nanotubes in resonance is at 2.49 eV for the D mode with $A_D = -0.7$ and at 2.47 eV for the 2D mode with $A_{2D} = -0.24$. The higher value $A$ for the 2D mode compared to the D mode can be explained with a higher phonon frequency of the 2D mode and therefore larger resonance window of the enhanced-dRR scattering (Chap. IV) of the semiconducting tubes from the $E_{22}^S$ transition. Around 2.5 eV the $E_{22}^S$ transition becomes resonant and $A$ is increasing. The different dependence of $A$ on excitation energy for the RBM compared to the (2)D mode and G mode can be explained by its low phonon frequency and therefore small resonance windows.

5.4 (2)D-mode diameter dependence

Due to the similar energy for incoming resonance for the RBM and (2)D mode (Chap. IV) it seems reasonable to deduce the dependence of the (2)D-mode frequency on diameter from a direct comparison with the diameter of the related RBM. Since $\omega_{RBM} \propto 1/d$ [Eq. 3.10] and by neglecting the fine structure of the optical transitions (branches) $E_{ii}$ is also roughly proportional to $1/d$ [51] (Fig. 3.6), it follows that $\omega_{RBM} \propto E_{ii}$. Therefore, each optical transitions of the RBM dispersion can be linearly fitted, which assigns a certain excitation energy to a RBM frequency.

Figure 5.2 shows this linear fits for the experimental Kataura plot of sample S-SWCNTs and M-SWCNTs in the diameter range of 0.6 – 1.2 nm. Because of neglecting the fine structure of the optical transitions (branches) this approximation will only lead to a mean value for the diameter dependence of the (2)D mode in SWCNT ensembles. The variance due to the different branches of the optical transitions is approximated by the standard deviations $\sigma_{RBM}$ of the fits (Fig. 5.2, light gray areas). Further, only the incoming resonance is taken into account. To compare this fits of the RBMs with the different contributions of (2)D-mode
dispersion, each contribution of sample S-SWCNTs and M-SWCNTs is also linearly fitted (Fig. 5.3). The light gray areas in the fits denote the standard deviations \((\sigma_{(2)D})\). The linear equations for the fit for RBM and \((2)D\) mode are given by:

\[
\omega_{\text{RBM}}(E_i) = m_{\text{RBM}} \cdot E_i + b_{\text{RBM}} \pm \sigma_{\text{RBM}} ,
\]

\[
\omega_{(2)D}(E_i) = m_{(2)D} \cdot E_i + b_{(2)D} \pm \sigma_{(2)D} ,
\]

with slope \(m\), intercept \(b\) and standard deviation \(\sigma\). Equations (5.2a) and (5.2b) are solved for the phonon frequency \(\omega_{\text{RBM}}(\omega_{(2)D})\) (5.3),

\[
\omega_{\text{RBM}}(\omega_{(2)D}) = m^* \cdot \omega_{(2)D}(E_i) + b^*.
\]

with a new slope \(m^*\) (5.4) and intercept \(b^*\) (5.5):

\[
m^* = \frac{m_{\text{RBM}}}{m_{(2)D}}.
\]

\[
b^* = b_{\text{RBM}} \pm \sigma_{\text{RBM}} - \frac{m_{\text{RBM}}}{m_{(2)D}} (b_{(2)D} \pm \sigma_{(2)D}) .
\]

From equation (5.3) and Ref. [51] the diameter dependence of \(\omega_{(2)D}\) can be derived to

\[
d(\omega_{(2)D}) = \frac{C_1}{m^* \cdot \omega_{(2)D}(E_i) + b^* - C_2} ,
\]

with \(C_1 = 215 \text{ nm} \cdot \text{cm}^{-1}\) and \(C_2 = 18 \text{ cm}^{-1}\) (compare Sec. 3.2.1). The parameters for the linear fits of RBM and \((2)D\) mode are summarized in Tab. B.2.
5.4 (2)D-mode diameter dependence

![Diagram](image)

**Figure 5.5:** Measured (a) and derived data (b,c) of the D mode for sample S-SWCNTs and M-SWCNTs in comparisons with samples with well-defined diameter. (d) Measured D-mode dispersion of the sample S-SWCNTs and M-SWCNTs with denotation of the related diameter (nm). Thick, gray line is a linear fit through the phonon frequencies related to nanotubes with a diameter of 1 nm.

### 5.4.1 Comparison with experimental data from nanotubes with well-defined diameter and from literature

In this section the (2)D mode diameter dependence derived from linear fits of SWCNT ensembles [Eq. (5.6)] will be compared with measurements of SWCNTs with well-defined diameter, like samples highly enriched with single chiralities [sample (9,7) and (7,5), Chap. IV] and individual, freestanding SWCNTs [89]. The obtained results confirm the derived diameter dependence from SWCNT ensembles in an excellent way. Figure 5.5 shows this comparison for the D mode. First, the D-mode frequencies are compared. Fig. 5.5 (a) shows the measurements of the samples with well-defined diameter together with the linear fits of the D-mode dispersions for sample S-SWCNTs and M-SWCNTs (Fig. 5.3). The sample (9,7) and sample (7,5) were measured with a broad range of excitation energies (denoted with line segments in the plot, compare Sec. 4.4.2). The radii of the circles indicate the relative intensities. The x indicates the frequencies for measurements with weak intensities. The phonon frequencies with the highest intensities match the linear fit for the optical transition $E_{22}^S$ quite well. Since sample S-SWCNTs and M-SWCNTs also contains (9,7) and (7,5) tubes (Fig. 5.2), this good match is evident. Furthermore, it can clearly be seen that sample (9,7) shows a contribution to the optical transition $E_{11}^H$. This leads to the conclusion that the unusually high dispersion discussed in Sec. 4.4.2 is due to contributions of remaining metallic nanotubes in the enriched sample. These contributions lead to a "jump" to $E_{11}^H$ transition in Fig. 5.5 (a).

The individual SWCNTs (blue, open circles) were measured at 2.33 eV excitation energy. The phonon frequencies of these nanotubes do not match with the frequencies measured for sample S-SWCNTs and M-SWCNTs [Fig. 5.5 (a), gray areas], but with the extension to lower frequencies for the optical transition $E_{22}^S$ (dashed line). This is in agreement with the optical transition determined from their RBM frequencies (Fig. 5.6, blue, dashed lines).

Figure 5.5 (b) shows the derived D-mode frequency as a function of the diameter for the different optical transitions (Eq. 5.6); with the inversely-proportional relation between diameter and phonon frequency for each optical transition. The solid lines are the mean values and the light gray areas indicate the standard deviations $\sigma$. The diameters of the sample (9,7), (7,5) were calculated after Eq. (3.1) and for the individual
5.4 (2)D-mode diameter dependence

![Figure 5.6](image1.png)

Figure 5.6: Katamura plot with denotation of the measured RBM frequencies of the individual tubes (dashed lines) for 2.33 eV excitation energy (green, solid line). Furthermore the optical transitions $E_{22}^M$ and $E_{22}^S$ are denoted.

![Figure 5.7](image2.png)

Figure 5.7: Derived diameter dependence of the $D$ mode (solid lines, compare Fig. 5.5) in comparison with results from literature. The red circles (Ref. [94]) are data from measurements following the optical transition $E_{22}^S$ and $E_{22}^M$. The orange diamonds (Ref. [78]), blue triangles, and blue squares (Ref. [80]) are data from measurements for different optical transitions.

SWCNTs the diameters were determined from their RBM frequencies [51]. The results for the samples (9,7) and (7,5) match the derived diameter dependence of the $E_{22}^S$ transition for the sample S-SWCNTs and M-SWCNTs (gray area). For the individual SWCNTs, which correspond to the $E_{22}^S$ transition, the Raman frequencies do not match the derived diameter dependence for the sample S-SWCNTs and M-SWCNTs (gray area), but the extended plot (dashed line). This is due to their larger diameters (in comparison with sample S-SWCNTs and M-SWCNTs) and therefore lower phonon frequencies [compare Fig. 5.5 (a)].

The same very good agreement between derived diameter dependence and measurements can be seen in Fig. 5.5 (c). Here the calculated diameter of the $D$ mode is plotted against the excitation energy.

Figure 5.5 (d) shows the correlation between $D$-mode dispersion and diameter in one plot. For each optical transition the derived diameters are denoted (unit: nm). This picture shows that it is possible to obtain two contrary relations between phonon frequency and diameter; denoted with the arrows (i) and (ii).

(i) On the one hand, if we tune the excitation energy and follow the $D$-mode frequencies along only one optical transition in a nanotube ensemble (as indicated here for $E_{22}^S$), we find an inversely-proportional diameter dependence [e.g. the $D$-mode frequencies for sample (9,7) and (7,5)].

(ii) On the other hand, if we perform measurements with a distinct excitation energy, but for samples with nanotubes of different mean diameters, there will be different optical transitions in resonance (as indicated here for $E_{22}^S$ and $E_{111}^M$), and the $D$-mode frequencies will be proportional to diameter.

Figure 5.7 shows the derived dependence of the $D$-mode frequency on diameter (solid lines, thick segments denote the range of measurement) in comparison with results from literature. Symbols are taken from


Figure 5.8: Measured (a) and derived data (b,c) of the D mode for sample S-SWCNTs and M-SWCNTs in comparisons with samples with well-defined diameter. (d) Measured 2D-mode dispersion of the sample S-SWCNTs and M-SWCNTs with denotation of the related diameter (nm).

Due to this diameter assignment, the earlier reported dispersions of \( \approx 50 \text{ cm}^{-1}/\text{eV} \) (100 cm\(^{-1}/\text{eV}\)) for the (2)D mode for SWCNT ensembles [65, 96–98] can be understood as a superposition of different contributions from different optical transitions. For nanotubes produced with the HiPCO process a mean diameter of \( \approx 1 \text{ nm} \) [93] can be assumed*. Figure 5.5 (d) shows a linear fit through the phonon frequencies related to nanotubes with a diameter of 1 nm, involving all optical transitions (thick, gray line). The found dispersion of \( 55 \pm 1 \text{ cm}^{-1}/\text{eV} \) is in good agreement to literature.

Figure 5.8 shows the same comparison between derived diameter dependence and results from nanotubes with well-defined diameter for the 2D mode, as already shown for the D mode, which show in general the same behavior. The mismatch for sample (9,7) to the derived diameter dependence [Figure 5.8 (b, c)] is due to the restricted energy range to high excitation energies in the measurements [Fig. 5.8 (a)]. The strongest intensity for sample (9,7) has to be assumed around 1.5 eV and was not measured. Here again a weak contribution to the \( E_{22}^M \) transition can be seen.

*Different mean diameters for certain batches of nanotubes [99] might explain the variance in dispersion found in literature.
A special feature is the measurement of an individual metallic SWCNTs, in resonance with the second metallic optical transition $E_{11}^M$ (closed, red circle). The measured phonon frequency is located in the area of the $E_{22}^M$ transition [Fig. 5.8 (a)]. This shows that nanotubes with a large difference in diameter can provide the same $(2)D$-mode frequency for different optical transitions in resonance [Fig. 5.8 (b)]. Therefore, the determined dependence of the $(2)D$-mode frequency on diameter (5.6) is only valid for tubes in the diameter range $0.6 \text{–} 1.2 \text{nm}$; as typical for SWCNTs produced in the HiPCO process [93]. For a larger diameter range different optical transitions overlap in frequency and the approximation of a linear dependence is no longer valid.

5.4.2 Simulation of the $D$ mode diameter dependence in SWCNT ensembles

Since the $D$-mode intensity is strongest at the optical transition (Chap. IV), it is possible to simulate the resonance behavior of an ensemble of nanotubes by, first, taking the wave vector $\tilde{k}$ involved in the dRR process at the optical transition, second, projecting this wave vector to the phonon dispersion of graphene/graphite (compare Fig. 3.8). This approximation method involves only the incoming resonance and the scattering with a defect (Sec. 2.1.3).

Figure 5.9 shows the phonon frequencies of the TO phonon branch of graphite close to the $K$ point as a contour plot from experimental data [100]. The high symmetry point $K$ and the directions to $K'$ (white lines) are denoted, as well as the directions to the high symmetry points $\Gamma$ and $M$ (arrows). Furthermore, the positions of the phonon wave vectors related to the resonantly excited $D$ mode of $E_{22}^S$ are plotted into the phonon dispersion (circles)*. All wave vectors were projected to the same $K$ point. The wave vectors were obtained from sixth-nearest neighbor SBFC calculations [101]. The calculations were done for nanotubes in a diameter range between $0.7 \text{–} 3.1 \text{nm}$; diameters are color coded. Furthermore, the positions for the (7,5) and (9,7) tube are indicated.

Similar to the optical transitions, the distance to the $K$ point is larger for tubes with a smaller diameter (color code). This can easily seen by zone-folding and geometrical considerations [101]. Since a larger distance to the $K$ point is related to a higher phonon frequency, smaller tubes have a higher phonon frequency for the same optical transition. This is in agreement with the experimental findings shown in Fig. 5.5 (a) for the (9,7) and (7,5) tubes.

Figure 5.10 shows the obtained $D$-mode frequencies by correlation of the wave vectors and the phonon dispersion of graphite for $E_{22}^S$ and $E_{11}^M$ with a diameter range of $0.6 \text{–} 1.2 \text{nm}$; as for the experiment. For these frequencies in this approach the KA of graphite affects both, metallic and semiconducting tubes, although semiconducting tubes do not possess a KA. On the other hand, the distance to the $K$ point of, for example, the (7,5) and (9,7) tube is 0.33 and 0.35 Å$^{-1}$, respectively. Metallic nanotubes with a similar diameter have a even larger distance to the $K$ point. A comparison with the phonon dispersion calculated for a metallic nanotube (Fig. 3.5) shows that for these distances to the $K$ point the KA is absent even for metallic tubes. Therefore, the KA does not strongly affect the $D$-mode frequency in experiments using

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*Simulated data of the phonon wave vectors were provided by Felix Herrneger [101].

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5.4 (2)D-mode diameter dependence

Figure 5.10: Simulated D-mode frequencies for the $E_{22}^S$ (blue circles) and $E_{11}^M$ transitions (red squares) using the TO phonons of graphite [100].

Figure 5.11: D-mode dispersion of SWCNTs (red, blue) in comparison with the dispersion of graphite (black) [102]. The arrow indicates frequencies nanotubes with different diameter but approximated the same distance to the $K$ point. The different frequencies are due to curvature effects.

HiPCO nanotubes and excitation energies in the range of visible light*. Therefore, it can be assumed that the KA of graphite might change the absolute phonon frequencies for the simulations, but not the general behavior compared to the observations from experiments.

In the simulation the metallic tubes come into resonance for the same excitation energy ($\approx 2$ eV) as observed in experiment for $E_{22}^H$ (Fig. 5.3). But there is no jump between the two contributions observable for the simulation (Fig. 5.10). As a consequence of zone-folding\(^\dagger\), nanotubes with the same transition energy have the same distance $\mathbf{q}'$ to the $K$ point, and show the same $D$-mode frequency (Fig. 5.10). In experiment, for example at 2 eV (Fig. 5.11), nanotubes with same $\mathbf{q}'$ possess different $D$-mode frequencies. Therefore, the difference in frequency $\Delta \omega_D$ is caused by the curvature of the tubes, observable for tubes with same optical transition but different diameter. The effect of curvature can be directly extracted from experimental data. To compare different excitation energies, the experimental dispersion of graphite is taken as a baseline for $\Delta \omega_D(d = \infty, eV) = 0$.

Figure 5.12 shows the relation between diameter and curvature induced frequency shift $\Delta \omega_D(d)$ extracted from Raman experiments (Fig. 5.11). The + sign represents data from sample S-SWCNTs and M-SWCNTs, the blue, open circles from measurements on individual tubes, and the gray, filled circle from measurements on sample (9,7) for an excitation at the optical transition (Chap. IV). The orange diamonds and the blue squares are data extracted from literature (compare Fig. 5.7). On the basis of the general effect of curvature

\*Therefore, the KA-induced strong electron-phonon coupling, does not broaden the $D$ mode related to metallic tubes, in contrast to the $G_{ij}$ mode (Sec. 3.2.2).

\(\dagger\)Neglecting trigonal warping and curvature effects to the electronic band structure.
5.4 (2)D-mode diameter dependence

![Graph showing frequency shift with diameter](image)

Figure 5.12: Determined frequency shift of the D mode due to curvature from experimental data; from sample S-SWCNTs and sample M-SWCNTs (+), sample (9,7) tubes (gray circle), and individual nanotubes (blue, open circles). Points are fitted with Eq. (5.7) (dashed line). For comparison, data extracted from literature are shown (orange diamonds Ref. [78], blue squares Ref. [80]).

![Graph showing Raman shift with optical transition](image)

Figure 5.13: Extracted D-mode frequencies from the TO phonons of graphite [10] for the $E_{22}^S$ and $E_{11}^M$ transitions (Fig. 5.10) with frequency correction due to curvature (Fig. 5.12). The (7,5) and (9,7) tube is denoted.

to in-plane vibrations (Sec. 3.3), the effect of curvature to the D-mode frequency can be fitted with

$$\Delta \omega_D(d) = A \left[ \sqrt{1 - \left( \frac{0.213 \text{ nm}}{d} \right)^2} - 1 \right], \quad (5.7)$$

with fit parameter $A$ and diameter $d$. The fit to experimental data is shown in Fig. 5.11 (dashed line) with $A = 593$. As expected, the effect of curvature on diameter is strongest for small-diameter tubes. For the energy range with overlap of $E_{22}^S$ and $E_{11}^M$ (see Fig. 5.10), $E_{22}^S$ will be more affected by the curvature (smaller tubes) than $E_{11}^M$ (bigger tubes). This correction to curvature is shown in Fig. 5.13. As expected, for the energy range with an overlap of $E_{22}^S$ and $E_{11}^M$ a gap opens between these branches with a width of approximately 10 cm$^{-1}$. This is in the same range as found in experiment.

In general the jump in D-mode frequency between $E_{22}^S$ and $E_{11}^M$ can be explained by the effect of curvature, but the absolute frequencies are higher in the simulations than found in experiments. This is somehow surprising, since the KA even decreases the frequencies in the simulations, but does not affect the frequencies in experiments (see above; experiments: Fig. 4.13 and Fig. 5.3). Therefore, the shift in frequency $\Delta \omega_D(d)$ due to curvature seems to be even stronger than determined form the experimental data. Since the baseline used for tubes with infinite diameter was taken from graphite, this baseline might be too low in frequency. The reason could be that the D mode of graphite is more influenced by the KA than in nanotubes [35].

In Chap. IV, the D-mode frequencies for the sample (9,7) and sample (7,5) are simulated using phonon dispersions adapted to the KA of graphite. Therefore, again a to low frequency for the simulation in
5.5 Monitoring the enrichment of nanotubes by the 2D mode

Figure 5.14: Excitation-energy dependent amount fraction [Eq. (5.1)] of the 2D mode of reference material (dashed line) in comparison with sample S-SWCNTs (blue) (a), and M-SWCNTs (red) (b). Filled circles for measurements of bulk material and open circles for measurements in solution. Fitted with a Gauss function as guide to the eyes (Tab. B.1).

comparison with the experimental data can be assumed. However, the simulations are even a little too high in frequency (Fig. 4.12). Since for the calculated phonon dispersions only a third-nearest neighbor approximation was used, there is only a weak curvature effect on the phonon frequencies (simulated frequencies therefore should be higher than for experiments). The adaption to the KA of graphite possibly simulated the neglected curvature induced down shift in frequency.

5.5 Monitoring the enrichment of nanotubes by the 2D mode

The enrichment of nanotubes to metallic or semiconducting species is essential for further applications (compare Chap. VIII). The degree of enrichment is usually monitored with absorption spectroscopy and with photoluminescence maps, which only monitor semiconducting tubes [26–29, 90, 103]. For both methods, the nanotubes have to be dissolved in solution.

For monitoring enrichment also the RBM has been used [104, 105], which can be even done in bulk material. But because of the small RBM resonance window, only a small diameter range can be monitored for a given excitation energy. Due to the assignment of the (2D)-mode frequency to diameter and its large resonance window, it might be possible to monitor the enrichment to species and mean diameter with help of this Raman mode.

Figure 5.14 shows the excitation-energy dependent amount fraction \( A \) [Eq. (5.1)] of the 2D mode of reference material (dashed line) in comparison with sample S-SWCNTs (a), and sample M-SWCNTs (b). The reference is not the same batch as used for the enriched samples. For excitation energies below \( \approx 2 \text{ eV} \) only semiconducting contribute to the 2D mode (Sec. 5.3). Therefore, the amount fractions for reference and enriched samples are the same. For higher excitation energies, also metallic nanotubes contribute to the 2D mode and the amount fraction changes according to the enrichment of the sample.

Below 2.55 eV sample S-SWCNTs shows higher value \( A \) compared to the reference [Fig. 5.14 (a)]; even for the excitation window with metallic nanotubes in resonance (2.4 – 2.6 eV, Sec. 5.3). Above 2.55 eV \( A \) is similar to the reference. For the sample M-SWCNTs [Fig. 5.14 (b)] \( A \) is always lower compared to the reference, even above 2.6 eV, where \( E_{2}^{\text{S}} \) becomes resonant.

The relation of excitation energy to diameter (Fig. 5.8) shows that the highest mismatch to the reference is for tubes in resonance with a mean diameter of 0.7 nm for sample S-SWCNTs and for 0.8 nm for sample M-SWCNTs. This results promotes the finding that surfactants (used for the enrichment process) prefer certain diameters of nanotubes [99, 106]. It has to be mentioned that the line shape of the 2D mode can change for measurements of bulk material or in solution. This change can slightly influence the calculated amount fractions (Fig. 5.14, open/filled circles). The general effect of bundling and unbundling on Raman modes will be discussed in Chap. VI.

Figure 5.15 shows the RBM Raman spectra for comparison, for certain excitation energies for reference (black, dashed), sample S-SWCNTs (blue) and sample M-SWCNTs (red), where the maximum amplitude was normalized to one. The RBMs related to the largest difference between the amount fraction for
5.6 Chapter summary

reference in comparison with enriched samples (Fig. 5.14) are denoted with a light red circle for M-SWCNTs and a light blue circle for S-SWCNTs in the background. For sample S-SWCNTs there is only a very weak difference to the reference. For the sample M-SWCNTs the difference to the reference is a bit larger, but for both samples the difference of the 2D mode (Fig. 5.14) is much more pronounced than for the RBM. The reason for that might be different matrix elements for the Raman scattering, and the different resonance windows for RBM and 2D mode.

The effect of the different resonance windows can also be seen in Fig. 5.16, which shows the amount fractions for reference and enriched samples for RBM (a), D mode (b) and G mode (c). For the RBM the amount fraction is negative ($A = -0.23$) at 1.96 eV excitation energy. For the D, G, and 2D mode the amount fraction is positive at 1.96 eV excitation energy. This is due to the larger resonance windows in comparison with the RBM (compare Sec. 5.3).

The 2D mode seems to be more sensitive to changes of species and mean diameter in a nanotube sample than the RBM. The RBMs show only minor changes in its line shape for the samples enriched with different species of nanotubes. The more pronounced changes found for the 2D mode are in agreement with the changes seen in Fig. 5.17 for absorption measurements and with the specification for this samples from Ref. [90].

In general, the 2D mode is useful as an additional tool for the characterization of the enrichment process, especially for bulk samples in low quantities, for example after a functionalization process (compare Chap. VII and Chap. VIII).

5.6 Chapter summary

The strong resonance of the $(2)D$ mode near the optical transition (Chap. IV) makes it possible to assign the different contribution of the broad $(2)D$ mode in an SWCNT ensemble to different optical transitions. This allows to distinguish between different excitation windows with mainly semiconducting or metallic tubes in resonance.

Due to the comparison to the RBM it is possible to assign the different contributions to diameters. This assignment predicts an inversely-proportional or a proportional dependence of $(2)D$-mode frequency to diameter, confirmed by simulations, depending on the experimental conditions. The findings are consistent with the contrasting predictions in literature. This diameter dependence will be very useful to investigate functionalization dependent changes of the $(2)D$ mode in nanotube ensembles, as discussed in Chap. VII and VIII.

Furthermore, the diameter dependence of the 2D mode can be used to monitor the enrichment of nanotube samples to species and a mean diameter. But the line shape of the 2D mode also depends on the aggregation...
state of the nanotubes (bundled, unbundled). Therefore, in the next section the differences in Raman spectra of bundled and unbundled nanotubes will be investigated.
Figure 5.17: Absorption spectra of sample S-SWCNTs (blue) and M-SWCNTs (red). The excitation windows for $E^S_{22}$ and $E^M_{11}$ are denoted by colored shapes in the background [107]. Spectra are normalized to one.
CHAPTER VI

Raman modes in bundled and unbundled nanotubes
6.1 Chapter introduction

<table>
<thead>
<tr>
<th>number</th>
<th>description</th>
<th>category</th>
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<tbody>
<tr>
<td>(1)</td>
<td>purified bulk material (PO-568)</td>
<td>bulk</td>
</tr>
<tr>
<td>(2)</td>
<td>solved in SDS</td>
<td>solution</td>
</tr>
<tr>
<td>(3)</td>
<td>heat re-bundled, residual solution</td>
<td>solution</td>
</tr>
<tr>
<td>(4)</td>
<td>heat re-bundled, bundle measured in solution</td>
<td>solution</td>
</tr>
<tr>
<td>(5)</td>
<td>heat re-bundled, bundle measured in H₂O</td>
<td>solution</td>
</tr>
<tr>
<td>(6)</td>
<td>bundle from (4) drop-casted on Si/SiO₂</td>
<td>bulk</td>
</tr>
<tr>
<td>(7)</td>
<td>ethanol re-bundled, bundle drop-casted on Si/SiO₂</td>
<td>bulk</td>
</tr>
<tr>
<td>(8)</td>
<td>solution (2) drop-casted on Si/SiO₂</td>
<td>bulk</td>
</tr>
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</table>

6.1 Chapter introduction

The common large scale production methods of nanotubes [93, 108] always lead to strongly attached nanotubes by van der Waals interactions [109]; they form nanotube ropes with a mixture of few hundred metallic and semiconducting tubes [110]. For a sufficient nanotube unbundling the nanotubes can be wrapped with certain materials to overcome the attractive van der Waals forces. For that purpose, the use of surfactant micelles [111], synthetic polymers [105] and the natural polymer desoxyribonucleic acid (DNA) was successful [103].

Unbundling of nanotubes is essential for subsequent separation techniques like DGU or chromatography methods, which allows a separation into different species of nanotubes (metallic, semiconducting, Sec. 5.5) [90, 103, 104] and even single chiralities [26–29]. These separations are needed for technical applications using nanotube samples enriched with metallic [104], semiconducting [112] or chiral-index sorted nanotubes [113].

Unbundling of nanotubes is normally monitored by AFM, absorption spectroscopy [114], and photoluminescence, which only occurs in individualised semiconducting nanotubes [111]. Also, a shift in the optical transition can be used in principle to monitor the unbundling of nanotubes [115, 116], for example, by recording of RBM resonance profiles [117]. Additionally, changes in the line shape of the \( G^- \) mode, due protonation [118], and changes in the \( G^+ \) mode (without explanation for these changes [119]) have been reported. A change in the \( 2D \) mode line shape due to a different size of nanotubes bundles has also been reported [118, 120], but without the knowledge that different contributions of the \( 2D \) mode belong to different species of nanotubes.

In this chapter changes in the Raman spectra between starting bulk material, unbundled and subsequently re-bundled nanotubes are investigated. The Raman spectra related to semiconducting tubes are only weakly influenced by the aggregation state of the tubes, but by the deformation of the tubes for non-dissolved samples. Additionally, the aqueous environment changes the Fermi level for the dissolved nanotubes. This can be monitored by changes in the line shape of Raman modes related to metallic nanotubes.

6.2 Experimental details

SWCNTs were unbundled and subsequent re-bundled as described in Sec. A.2 and Sec. A.3. To investigate the degree of individualization, the nanotubes were spin-casted on a Si/SiO₂ substrate as described in Sec. A.4. The free-standing nanotube film was prepared as described in Sec. A.5.
6.3 Sample categories

We will see below that the Raman spectra of the different samples can be divided into two categories according their specific ratios between $G^-$ and $G^+$ mode. The samples are numbered, described and assigned to a category in Tab. 6.1. The category bulk includes:

- the starting material (1)
- re-bundled nanotubes by heat treatment (6) or ethanol (7), subsequently drop-casted on Si/SiO$_2$
- the directly drop-casted solution of the unbundled tubes on Si/SiO$_2$ (8)

The category solution includes:

- the unbundled tubes in SDS solution (2)
- the heat treated nanotubes (Fig. A.2) measured with the laser focused into
  - the SDS solution (3) (low density of tubes)
  - a bundle of tubes, swimming in the SDS solution (4) or swimming in water (H$_2$O) (5) (low concentration of Na$^+$ ions)

6.4 Monitoring of individualization

Figure 6.1 (left) shows an AFM image of unbundled nanotubes (2) spin-casted on Si/SiO$_2$, together with amplitude profiles (right) for individual tubes (red) and small bundles (green). From this AFM measurements it can be seen that sample (2) contains individual tubes, but also small bundles.

6.5 Raman spectroscopy on bundled, unbundled and re-bundled nanotubes

6.5.1 Semiconducting SWCNTs

Figure 6.2 shows the Raman spectra of the samples described in Sec. 6.3 at 1.96 eV excitation energy; the maximum amplitude was normalized to one. Mainly semiconducting tubes contribute to the $D$, $G$, and $2D$ mode. Samples (1), (6) and (7) belong to the category bulk and samples (2)-(5) to the category solution (Tab. 6.1).

The $2D$ mode looks similar for all samples (left panel), while the RBMs (right panel) change for the sample of unbundled tubes in SDS solution (2). This change can be explained by a shift in the optical transition, caused by SDS wrapping of the tubes [115]. A heat treatment destroys the SDS micelles and the original
6.5 Raman spectroscopy on bundled, unbundled and re-bundled nanotubes

![Graph showing Raman spectra with assignments and energy level](image)

**Figure 6.2**: Raman spectra of the RBM with assignment to diameter and species [51] (left panel), D and G mode (middle panel) and 2D mode (right panel) at 1.96 eV excitation energy. Sample number and description is denoted in black for the category bulk and in blue for the category solution (Sec. 6.3). Amplitudes of the spectra were normalized to one; the spectra are plotted vertically offset.

The shape of the RBMs can be recovered for the re-bundled sample (4).

For the D and G mode there are similar changes for all Raman spectra for the samples from category solution [(2)-(5)] in comparison with the samples from category bulk; the D/G ratio, G'/G+ ratio and full width at half maximum (FWHM) of the G+ mode are changed. These changes are evaluated by fitting each mode with one Lorentzian; and plotted in Fig. 6.3 (circles). The categories solution and bulk are marked with a blue and a gray rectangle in the background of the data points. The FWHM of the G+ mode is color coded. A clear difference between the two sample categories is observable for all characteristics displayed in this plot. The D/G+ ratio*, G'/G+ ratio and FWHM of the G+ mode is much smaller for the samples from category solution [(2)-(5)] compared to the samples from category bulk [(1),(6),(7)]. These changes cannot be explained by the unbundling of the tubes due to the wrapping with SDS, because the SDS micelles are destroyed in sample (4) and (5) (monitored by the changes in the RBM) and therefore, these samples contain re-bundled tubes swimming in solution. Also the Na+ ions in the SDS solution cannot be responsible for these changes, since they are removed in sample (5). Therefore, the origin for these changes in line shape could be the surrounding H2O.

To investigate the effect of H2O on the nanotubes, a free-standing nanotube film was prepared as described in Sec. A.5. Raman measurements were performed while the film was in contact with air or H2O (Raman spectra: Fig. C.9). The analysis of the Raman spectra (Fig. 6.3, squares) shows that H2O slightly influences the Raman spectra, but the evaluated characteristics remain in the category bulk. The thickness of the film might play an important role for this experiment and was not taken into account. On the other hand, we will see later that at excitation with mainly metallic tubes in resonance, some characteristics of the Raman spectra of the free-standing film will change to category solution, when in contact with H2O.

*Not divided by the D/G+ ratio of the reference material, since only the relative ratios for this excitation energy is form interests; compare Chap. VIII.
6.5 Raman spectroscopy on bundled, unbundled and re-bundled nanotubes

![Graph](image)

**Figure 6.3:** Analysis of the Raman spectra of the samples (1)-(7) (circles) and the free-standing nanotube film (squares) at 1.96 eV excitation energy for the \(D/G\) ratio, \(G^-/G^+\) ratio and FWHM of the \(G^+\) mode (color coded).

In conclusion, the changes in the Raman spectra are observable for all nanotubes swimming in solution (individual tubes and bundles) in comparison to the samples from category bulk. Since \(H_2O\) seems not directly responsible, the changes in the Raman spectra might be due to a weaker deformation for the dissolved nanotubes.

6.5.2 Metallic SWCNTs

Figure 6.4 shows the Raman spectra for the samples described in Sec. 6.3 at 2.33 eV excitation energy; the maximum amplitude was normalized to one. Mainly metallic tubes contribute to the RBM, \(D\) and \(G\) mode. Samples (1) and (6)-(8) belong to the category bulk and samples (2)-(5) to the category solution (Tab. 6.1). For the RBMs (left panel) the samples of the category solution show a decrease of the RBM for nanotubes with a diameter bigger then 0.9 nm in comparison with the samples from the category bulk. Since all RBMs for this excitation energy belong to metallic nanotubes, the origin for this change remains unclear.

The \(D\) and the \(G\) mode (middle panel) show the same changes for the \(D/G\) ratio, \(G^-/G^+\) ratio and FWHM of the \(G^+\) mode, as already discussed in Sec. 6.5.1 for semiconducting tubes in resonance. On the other hand, now the \(G^-\) mode is related to metallic tubes and its decrease can be explained with a shift of the Fermi level, due to the aqueous environment [121]. The changes in the Raman spectra for the different samples are evaluated by fitting each mode with one Lorentzian; and plotted in Fig. 6.5 (a) (circles). The categories solution and bulk are marked with a blue and a gray rectangle in the background of the data points. The FWHM of the \(G^+\) mode is color coded. A clear difference between the two categories is observable for all characteristics displayed in this plot. The \(D/G^+\) ratio*, \(G^-/G^+\) ratio and FWHM of the \(G^+\) mode are much smaller for the samples from category solution [(2)-(5)] compared to the samples from category bulk [(1),(6)-(8)]. The \(G^+\) mode is assigned to semiconducting tubes [64, 66], but also the TO-phonons of the metallic tubes have a Raman mode with only slightly lower frequency [35, 69]. This broadens the \(G^+\) mode in comparison with the results for mainly semiconducting tubes in resonance (Fig. 6.3). As already discussed, the change in the \(G^-/G^+\) ratio can be explained by the aqueous environment.

To investigate the origin of the other changes, a free-standing nanotube film was prepared as described in Sec. A.5. Raman measurements were performed while the film was in contact with air or \(H_2O\) (Raman spectra: Fig. C.10). The analysis shows [Fig. 6.5 (a), squares] that in contact with \(H_2O\) the free-standing nanotube film remains in the category bulk for the FWHM of the \(G^+\) mode and the \(D/G^+\) ratio, whereas the \(G^-/G^+\) ratio decrease to a value related to the category solution.

The 2D mode Raman spectra (Fig. 6.4, right panel) of the starting material (1) does not show a fine structure in comparison with the re-bundled samples from category bulk [(6)-(8)]. Therefore, it seems that for the starting material the bundling is even stronger, which decreases the phonon lifetime and leads to an increase of the broadening factor \(\gamma\) [Eq. (2.10)]. Sample (1) possesses a approximately 10 cm\(^{-1}\) bigger FWHM compared to sample (6)-(8). The main difference between the samples from categories solution and bulk is a change in the ratio between the contribution related to metallic tubes and semiconducting

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*Here we do not use \(D/G^-\) and do not divided by the \(D/G^+\) ratio of the reference material, since only the relative ratios for this excitation energy is form interests; compare Chap. VIII
6.5 Raman spectroscopy on bundled, unbundled and re-bundled nanotubes

![Diameter (nm)]

Figure 6.4: Raman spectra of the RBM with assignment to diameter and species [51] (left panel), D and G mode (middle panel) and 2D mode (right panel) at 2.33 eV excitation energy. Sample number and description is denoted in black for the category bulk and in blue for the category solution (Sec. 6.3). Amplitudes of the spectra were normalized to one; the spectra are plotted vertically offset.

tubes ($2D_M/2D_S$ ratio). Furthermore, the $2D_M$-mode frequency is slightly blue shifted for the samples from category solution (Fig. 6.6). Similar to the decrease of the $G^-$ mode this blue shift can be explained with a Fermi-level shift [121, 122], strongly influencing only metallic nanotubes.

Figure 6.5 (b) shows the the $2D_M$-mode frequency plotted against the $G^-/G^+$ ratio for the samples (1)-(8) (circles), and for the free-standing film (squares) in contact to air and to H$_2$O. The categories solution and bulk are marked with a blue and a gray rectangle in the background of the data points. The $2D_M/2D_S$ ratio is color coded (logarithmic scale). As suspected, there is a strong dependence between the $2D_M$-mode frequency and $G^-/G^+$ ratio, since both changes caused by a shift in the Fermi level. In general, the $2D_M/2D_S$ ratio shows a smaller value for the samples of the category solution with exception of sample (8), which belongs to category bulk but possesses also a quite low $2D_M/2D_S$ ratio. Also the free-standing film shows a strong change in the $2D_M$-mode frequency together with a change in the $G^-/G^+$ ratio. There is also a strong change in the $2D_M/2D_S$ ratio observable, but the absolute values for contact with air and H$_2$O are much higher than for the other samples.

In conclusion, the changes in the $G^-/G^+$ ratio, $2D_M/2D_S$ ratio and $2D_M$-mode frequency for the samples from category solution compared to samples from category bulk can be explained by a shift of the Fermi level due to the aqueous environment [121]. The origin for the change of the $D/G^+$ ratio is still unclear, but might be due to a weaker deformation for the dissolved nanotubes (as seen for the semiconducting tubes, Sec. 6.5.1).
6.6 Chapter summary

The most striking change in the Raman spectra between non-dissolved and dissolved nanotubes is a decrease of the $D/G^+$ ratio for the dissolved samples. This has to be taken into account when using the $D/G$ intensity ratio as a measure for the defect density. The origin for this change is still unclear but since it is not directly correlated to the bundling of tubes, it might be due to a lower deformation of the dissolved nanotubes. In this sense, it is unclear if the $D$ mode decreases or the $G^-$ mode increases (or both) for the dissolved samples.

Besides this change in the $D/G^+$ ratio a decrease of the $G^-$ mode related to metallic nanotubes and a frequency shift of the contribution of the 2D mode related to metallic tubes is observed for the dissolved tubes. Both changes are due to a shift in the Fermi level caused by H$_2$O. Furthermore, the ratio between two contributions of the 2D mode changes, which has to be considered for monitoring the enrichment of a sample to different species by the 2D mode* (Sec. 5.5).

In general, the Raman spectra change for non-dissolved and dissolved nanotubes, but these changes are not directly related to an unbundling of the nanotubes and therefore cannot be used to investigate the unbundling of tubes due to a functionalization (Chap. VII and Chap. VIII).

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*The differences in the line shapes between dissolved and non-dissolved tubes are most prominent at excitation energies with both species in resonance.

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Figure 6.6: Raman spectra of the 2D mode of reference (1), unbundled (2) and re-bundled nanotubes (7) at 2.33 eV excitation energy. Dashed lines mark the frequencies of the different contributions of the 2D mode found for sample (7). Amplitudes of the spectra were normalized to one; the spectra are plotted vertically offset.
CHAPTER VII

Raman modes of nano-graphene flakes on carbon nanotubes after oxidation
7.1 Chapter introduction

For tuning the properties of SWCNTs and making them usable for various applications, the oxidation with acids has been well established over the last decades. The conversion of the carbon scaffold to carbon dioxide (CO₂) and a oxygen containing group, like carboxyl or carbonyl groups [21, 22] are useful as anchor groups for further functionalization [24] and for strong connections to substrates [123, 124]. Furthermore a decrease of sheet resistance in transparent, conductive films can be reached [125] due to a better connectivity between the tubes caused by interconnections of these groups [126].

In addition, the cleavage of atomic bonds by oxidation can be used for purification of the as-prepared material [127, 128] as well as for cutting the nanotubes into shorter pieces [129]. Del Canto et al. [130] showed that this cleavage also produces mostly unwanted nano-graphene flakes (NG flakes), which show a Raman mode in the frequency region of the D mode of SWCNTs. This overlap in frequency must be carefully taken into account when estimating the defect concentration based on the intensity ratio of the Raman D and G modes (D/G ratio). On the other hand, the NG-flakes Raman mode was not quantified in frequency or line shape in Ref. [130]. Therefore, to use Raman spectroscopy for the determination of the degree of impurities in an oxidized sample, the frequency, line shape and excitation energy dependent dispersion of the Raman modes of NG flakes must be determined.

In this chapter the Raman modes of NG flakes produced by oxidation of SWCNTs are analyzed. A comparison with the results from Chap. V shows that this Raman mode possess a slightly higher frequency than the D mode with a Gaussian line shape and a dispersive behavior. Furthermore, additional bands next to the G mode are observed which can be also assigned to molecular vibrations of NG flakes. Although these bands have similar frequencies as the D' mode, they cannot be used as a measure of defect concentration of oxidized samples, but as a measure of impurities through NG flakes in the sample. Additionally, the intercalation of alkali metals and its effect to the G⁻ mode is investigated.

7.2 Experimental details

The functionalization protocol for the samples is described in Sec. A.1. The spectra were collected from a sample drop casted on Si/SiO₂.

7.3 Raman spectra of oxidized nanotubes

Figure 7.1 shows the Raman spectra of oxidized nanotubes (solid lines) and a reference sample (dashed lines) for different excitation energies. In the left panel the RBM is shown. For the oxidized sample, a

Parts of this chapter are accepted for publication.
7.3 Raman spectra of oxidized nanotubes

![Raman spectra of oxidized nanotubes](image)

Figure 7.2: Raman spectra of oxidized nanotubes (solid lines) and reference sample (dashed lines) for different excitation energies. Left panel: $D$ mode; right panel: $2D$ mode. The small arrows indicate a decreased contribution of the oxidized sample. Amplitudes of the spectra were normalized to 1; the spectra are plotted vertically offset.

![Raman spectra comparison](image)

Figure 7.3: Comparison between Raman spectra of the $D$ mode for reference (dashed), oxidized tubes (red) and NG flakes (gray circles) produced by oxidation and filtration taken from Ref. [130]. Further the subtracted spectrum from NG and oxidized sample is shown.

A general decrease in the relative RBM intensities for nanotubes with small diameters can be observed, as expected [131, 132]. The right panel shows the $G$ mode with denotation of the contributing $G^\text{lo}$ mode and $G^\text{hi}$ mode. In addition, the $D'$ mode at $\approx 1620$ cm$^{-1}$ is observed as a shoulder. The $D'$ mode is due to double-resonant Raman scattering of phonons with wave vectors near the $\Gamma$ point [33]. Similar to the $D$ mode, this Raman mode increases with an increasing defect density, but is much weaker compared to the $D$ mode. In the sample it is most distinct at high excitation energies.

Figure 7.2 shows the comparison between the Raman spectra of oxidized nanotubes and reference for the $D$ mode (left panel) and $2D$ mode (right panel). In the Raman spectra of the oxidized sample, the contribution of the $2D$ mode related to small semiconducting tubes is strongly decreased (compare Sec. 5.5), indicated by small arrows. This decrease is consisted to the finding for the RBM.

7.3.1 Raman mode of NG flakes close to the $D$ mode

An additional feature is observed in the $D$ mode Raman spectra of oxidized nanotubes (Fig. 7.2, left panel): A broad contribution with a slightly higher frequency than the $D$ mode. In order to understand this additional peak, the Raman measurements were compared with the work of Del Canto et al. [130]. In their work they showed that the treatment of oxidized nanotubes with sodium hydroxide (NaOH) will only remove NG flakes possessing carboxyl groups. NG flakes without these groups can only be removed from the sample with the use of surfactants and filtration. Without such treatment, oxidized nanotubes

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7.3 Raman spectra of oxidized nanotubes

Figure 7.4: Raman frequencies of Gaussian fit (circle) and Lorentzian fit (square, example see inset) of the oxidized sample as a function of excitation energy. $D_{NG}$ is the linear fit for the peak position of the Gaussian fits (black). $D_{M/S}$ are linear fits related to the metallic/semiconducting contributions of the $D$ mode of nanotubes ensembles (red, blue, Sec. 5.3).

possess NG flakes adsorbed at their sidewalls due to $\pi-\pi$ interactions [133, 134]. Since only NaOH was used for purification, it can be assumed that NG flakes are stacked to the sidewalls of the nanotubes in the oxidized sample.

Figure 7.3 shows the Raman spectrum in the frequency region of the $D$ mode at 1.96 eV excitation energy for the oxidized sample (red) in comparison with the Raman spectrum of separated NG flakes from Del Canto et al. [130] (gray circles). For comparison also the Raman spectrum of the reference sample is shown (red, dashed line).

The spectrum of the NG flakes (gray circles) was scaled such that a good match for the slopes of the Raman spectrum of the oxidized nanotubes (red) was obtained. A Gaussian fit of the scaled spectrum of the NG flakes (gray line) was subtracted from the spectrum of the oxidized nanotubes. The resulting spectrum (NG subtracted, orange) appears similar to the reference (dashed line). The slight shift to higher frequency can be understood by the loss of small diameter tubes in the oxidized sample due to the oxidation process, similar to the observations for the $2D$ mode (Fig. 7.2, right panel).

Based on this comparison it can be concluded that the Raman spectra of the oxidized sample posses a contribution of the NG flakes with a Gaussian line shape. In the following this Gaussian fit will be assigned to a Raman mode related to NG flakes and will be call $D_{NG}$ mode.

It is now possible to deconvolute the spectra of oxidized nanotubes according to the contributions from nanotubes ($D$ mode) and from NG flakes ($D_{NG}$ mode). Therefore, each spectrum was fitted with one Lorentzian and one Gaussian (neglecting the fine structure of the $D$ mode in nanotube ensembles because of the much smaller full width at half maximum of the Lorentzian in comparison to the Gaussian fit, Chap. V).

For the Gaussian fit (NG flakes) an increase in frequency with excitation energy and an almost constant FWHM over the whole energy range was found (Tab. B.3).

Figure 7.4 shows the frequencies of the different contributions of the oxidized sample as function of the excitation energy; square for the Lorentzian fit and circle for the Gaussian fit. The inset shows a typical fit of the oxidized sample with a Lorentzian (LO) and a Gaussian (GA). In addition, the dispersions of the $D$ mode related to metallic ($D_M$, red) and semiconducting tubes ($D_S$, blue) from Sec. 5.3 are plotted.

The frequencies of the Lorentzians (squares) match the $D$ mode dispersion related to semiconducting tubes ($D_S$) for low excitation energies and the dispersion related to metallic tubes ($D_M$) for higher excitation energies. Furthermore, the Gaussian, attributed to the contribution of the NG flakes ($D_{NG}$ mode, black line), shows a dispersion of $38 \text{ cm}^{-1}/\text{eV}$. This is similar to what is found for $D_M$ (29 cm$^{-1}/\text{eV}$) and $D_S$ (30 cm$^{-1}/\text{eV}$). The $D_{NG}$ mode has a slightly higher frequency than the $D$ mode.

Since the NG flakes produced by oxidation are molecules, the $D_{NG}$ mode is defect independent* [135, 136]; furthermore, the observed dispersion cannot be explained with the double-resonance Raman process like for other graphitic materials [18, 19]. On the other hand, the dispersion can be understood as subsequent resonances for NG flakes with different size and therefore different optical transition energies and Raman frequencies [137–140].

*But the $D_{NG}$ mode depends on the size of the molecules.
7.4 Doping effect due to intercalation of alkali metals

Table 7.1: Preparation steps for producing NG flakes. Processing time for sonication and oxidation for different temperatures (RT room temperature). Samples NG 1–NG 3 were subsequently taken after denoted steps.

<table>
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<tr>
<td>tip sonication</td>
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<td>4</td>
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<tr>
<td>oxidation 120 °C</td>
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<tr>
<td>oxidation RT</td>
<td>h</td>
<td>16</td>
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7.3.2 Raman modes of NG flakes close to the G mode

Besides the $D_{NG}$ mode, NG flakes also possess a high-frequency Raman mode ($G_{NG}$ mode) with a slightly higher frequency than the $G$ mode in SWCNTs. To investigate this mode, NG flakes were produced by oxidation and the use of a tip sonicator. To keep all NG flakes within the sample, the prepared material was not washed in NaOH. Three different samples (NG 1–NG 3) for the subsequent preparation steps were obtained, summarized in Tab. 7.1.

Figure 7.5 (a) shows the evolution of the RBM for the different samples, where the maximum amplitude was normalized to one. Sample NG 1 shows a clear decrease of the RBM intensities with the expected preference to small-diameter nanotubes (semiconducting tubes for this excitation energy) due to destruction of the tubes. Because of the decrease of all RBMs in NG 3, it can be assumed that almost all nanotubes are destroyed in this sample.

Figure 7.5 (b) shows the evolution of Raman spectra for the different preparation steps in the frequency region of the $D$ and $G$ modes, where the maximum amplitude was normalized to one. In appearance of the $D_{NG}$ mode can be clearly seen. In addition, first, the $G^+$-mode intensity strongly decreases (NG 1), then the $G^-$-mode (NG 2). This decrease is consistent with the findings for the RBM, if the $G^+$-mode is attributed to semiconducting tubes (smaller diameter) and the $G^-$-mode to metallic tubes (larger diameter) [64, 66]. Additionally, two new peaks appear with slightly higher frequencies than the $G^+$-mode. The first of these new peaks is attributed to the $G$ mode related to NG flakes ($G_{NG}$ mode). This peak possesses a Raman frequency of $\approx 1604 \text{ cm}^{-1}$, which is in the frequency range found in the literature for measurements of NG flakes [135, 137]. Furthermore, a distinct peak at a frequency can be observed usually referred as the defect induced $D'$ mode of nanotubes. Since this peak is most pronounced in sample NG 3 and almost no nanotubes are in this sample, this peak is attributed instead to a defect independent Raman mode of NG flakes ($D'_{NG}$ mode) similar to the $D_{NG}$ mode [137, 139].

Figure 7.6 shows a direct comparison of the Raman spectra of the oxidized tubes and the Raman spectra related to a very high content of NG flakes (NG 3). The Raman spectra of the oxidized nanotubes is a superposition of the spectra similar to the reference material [Fig. 7.5 (a)] and the NG flakes, probably $\pi$-stacked at the sidewalls of the tubes. Therefore, without taking into account the contributions from NG flakes, the intensity of the $D$ mode of the oxidized sample would be overestimated. Furthermore, the broad shoulder next to the $G$ mode is not defect induced for this sample, but consists of two contributions related to the Raman spectra of the NG flakes.

7.4 Doping effect due to intercalation of alkali metals

For NG-flakes $\pi$ stacked on the sidewall of the nanotubes it can be assumed that alkali metals are able to intercalate between the nanotube sidewalls and the NG-flakes.

Figure 7.7 (a) shows the Raman spectra of the $D$ mode and $G$ mode before (black) and after (red) the sample was gently shaken in 30 mM potassium hydroxide (KOH) for 30 s. The treatment with KOH causes a strong decreases of the $G^-$ mode which is not observe for a reference material [Fig. 7.7 (b)]. The nearly unchanged RBMs (Fig. C.6) and topology of the oxidized sample (AFM, Fig. C.7 and C.8) before and after the treatment with KOH, let conclude that the decrease of the $G^-$ mode is not due to a loss of material. Further investigations even show that the original line shape can be recovered. Table 7.2 summarizes the different preparation steps for this experiment; after each step the sample was dried. Figure 7.8 shows the $G$ mode of the oxidized nanotubes before (gray area) and after treatment with KOH [(1) 1 red area]. As suspected the spectra shows a strong decrease of the $G^-$ mode. Spectra (2) shows the sample after a bath in $H_2O$ for 15 min, the spectra is nearly unchanged in comparison to the KOH influenced spectra (1). After
7.4 Doping effect due to intercalation of alkali metals

![Figure 7.5: Raman spectra of reference and oxidized tubes after different preparation steps (NG 1–NG 3) for (a) RBM and (b) D mode and G mode. Amplitudes of the spectra were normalized to one; the spectra are plotted vertically offset.](image)

15 h in 0.5 mM NaOH (3) the line shape of the $G^-$ mode only slightly changes. But a subsequent bath for 30 min in H$_2$O recovers the original line shape completely. This experiment shows that the effect of KOH is not irreversible due to H$_2$O in first step, but needs a intermediated step including NaOH. Assuming that the change in the $G^-$ mode line shape is due to a shift in the Fermi level [62, 121], a reason for the decrease might that $K^+$ ions intercalate between the nanotube sidewalls and the NG flakes. It is known that $K^+$ ions intercalated in graphite forming a superlattice, which is not possible for Na$^+$ ions [141]. Therefore the $K^+$ ions have to be substituted by Na$^+$ ions, before H$_2$O can remove them in a second step and the line shape of the $G^-$ mode is recovered.

Even if the role of the different alkali metals is not fully understood, the intercalation experiments promote the idea of $\pi$ stacked NG-fakes.

<table>
<thead>
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<tr>
<td>(1)</td>
<td>KOH (0.5 mM), 30 s</td>
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<tr>
<td>(2)</td>
<td>H$_2$O, 15 min</td>
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<tr>
<td>(3)</td>
<td>NaOH (0.5 mM), 12 h</td>
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<tr>
<td>(4)</td>
<td>H$_2$O, 30 min</td>
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Table 7.2: Solutions and treatment times for intercalation experiments.
7.5 Chapter summary

Nano-graphene flakes produced by the oxidation of SWCNTs show a distinct fingerprint in the Raman spectra in the frequency region of the $D$ and $G$ modes of nanotubes ($D_{NG}$, $G_{NG}$, and $D'_{NG}$ mode). The $D_{NG}$ mode can be used to identify impurities after an oxidation process [142] based on its broad Gaussian line shape and its higher frequency compared to the $D$ mode of SWCNTs (Chap. V). If not taken properly into account, the $D_{NG}$ mode influences the apparent $D/G$ intensity ratio [130] of oxidized nanotubes due to its contribution in the $D$-mode region of nanotubes. Moreover, the $D'$ mode, usually referred to defects in nanotubes, is not necessarily a defect-induced mode, but can also be due to nano-graphene flakes. Furthermore, the nature of $\pi$ stacking of the nano-graphene flakes was confirmed by intercalation experiments.
**Figure 7.7:** Raman spectra (2.33 eV) of the D mode and G mode before and after treatment with KOH for (a) oxidized nanotubes, normalized to the $D_NG'$ mode, and (b) reference material, amplitude of the spectrum was normalized to one.

**Figure 7.8:** Raman spectra (2.33 eV) of the G mode before and after treatment with KOH and further treatment with NaOH and H$_2$O, normalized to $D_NG'$ mode.
CHAPTER VIII

Intensity ratio between the $D$ mode and the $G$ mode for a sample containing selectively sidewall functionalized nanotubes
8.1 Chapter introduction

As already discussed in Chap. VI, unbundling of nanotubes is essential for their usage in technical applications, and can be achieved by wrapping the nanotubes with certain materials to overcome the strong van der Waals interactions.

On the other hand, the wrapping material makes it difficult to use the nanotubes in further applications. Therefore, functionalization of SWCNTs [23, 24] is a good alternative since it promotes unbundling [143], can be selective to metallic [144, 145] or semiconducting tubes [146], and creates the functional groups needed for the applications like sensors [124, 147, 148], electronic devices [149], or catalysts [150, 151].

For monitoring the functionalization process, the intensity increase of the $D$ mode is the most frequently used indicator. Typically, the degree of functionalization is determined by the amplitude or intensity ratio between the $D$ mode and the $G$ mode [152, 153] ($D/G$ ratio). The dependence of the $D$-mode frequency on diameter and species (Chap. V) may be used to probe a preferred functionalization related to species and diameter.

In this chapter the dependence of the $D/G$ ratio on excitation energy is investigated for selectively sidewall functionalized nanotubes. Beside changes in the $D$ mode also changes in the $G$ mode have to be taken into account when estimating the degree of functionalization by the $D/G$ ratio.

8.2 Experimental details

Covalently sidewall functionalized SWCNTs bearing carboxyl groups were prepared under reductive conditions according to Billups [146] and separated in different fractions by DGU [154]. Covalently sidewall functionalized SWCNTs bearing hydroxyl groups were prepared under modified Birch reaction [24] (samples received from the group of Dr. Frank Hauke).

8.3 Fine structure of the $D$ mode and $G$ mode in nanotube ensembles

The found diameter dependence of the $D$ mode (Chap. V) makes it is possible to correlate the often observed functionalization-induced decrease in RBM intensity to the related metallic and semiconducting contributions of the $D$ mode. For example, an excitation energy of 1.7 eV will probe the $(2)D$ mode of semiconducting nanotubes with a mean diameter of 0.9 nm (Fig. 5.5 and 5.8).

A decrease in RBM intensity can be due to two reasons: First, a functionalization process changes the $sp^2$ hybridized carbon-scaffold of the SWCNTs, which leads to a decrease in intensity of Raman modes [155]. The decrease in RBM intensity is therefore often used as a proof of selective functionalization, related to diameter [131, 156] and species [144, 146, 157]. Second, a very high degree of functionalization can alter the $sp^2$ hybridized carbon-scaffold in such an extent that the tube will be completely destroyed. This would also lead to a decrease in Raman intensity. To distinguish between these two effects, the assignment of the $D$ mode diameter and species can be used. The different contributions of the $D$ mode will increase due to functionalization and disappear on the other hand for destroyed SWCNTs.

Figure 8.1 shows the Raman spectra of the RBM, $D$, $G$ and $2D$ mode for covalently sidewall functionalized SWCNTs (red) [146] with a low degree of functionalization* and the reference material (black) for two excitation energies; normalized to power and time. For both excitation energies, the RBMs with high phonon frequencies disappear after the functionalization process (Fig. 8.1 (a)). For the shown excitation energies these RBMs belongs to small ($0.7 \text{--} 0.8 \text{nm}$) semiconducting SWCNTs [51]. The contribution of the $D$ mode related to these nanotubes has a phonon frequency in the range of 1290 -- 1320 cm$^{-1}$ (Fig. 5.5). A decrease of the RBM due to functionalization would lead to an increase of this semiconducting related contribution of the $D$ mode ($D_S$). But as seen in the inset of Fig. 8.1 (b), $D_S$ is decreased for both excitation energies. This indicates that harsh functionalization conditions have destroyed the small nanotubes in this sample1. Furthermore, the metallic contribution of the $D$ mode ($D_M$) remains constant [just like the RBM intensities related to metallic SWCNTs, Fig. 8.1 (a)] or is even slightly increased. The same decrease for the semiconducting contribution of the $2D$ mode can be observed [2D$_S$, Fig. 8.1 (c), compare Sec. 5.5].

Since the degree of functionalization is commonly deduced from the intensity ratio between the $D$ and $G$ mode [153] ($D/G$ ratio), it is also important to analyze possible changes in the $G$ mode caused by

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*The difference between low and high degree of functionalization will be discussed in Sec. 8.4.

1The alternative explanation that the small semiconducting nanotubes are removed due to the DGU can be negated by comparison of the RBMs in Fig. C.11.
8.4 Raman spectra of nanotubes with high and low functionalization degrees

![Raman spectra of nanotubes](image)

**Figure 8.1:** Raman spectra of functionalized SWCNTs (red) and reference (black) at 2.33 and 2.18 eV excitation energy; intensity normalized to power and time. (a) RBM with assignment to semiconducting and metallic tubes, (b) D and G mode, inset shows zoom to the D mode, (c) 2D mode.

the functionlization process. Fig. 8.1 (b) shows that the broad $G^-$ mode, which is related to metallic SWCNTs [63–66], is almost unchanged in intensity, whereas the $G^+$ mode is strongly decreased. This decrease is due to the destruction of the small, semiconducting SWCNTs. In consequence, the nearly unchanged $D_M$ mode in relation to the strongly decreased $G^+$ mode leads to an overestimated $D/G$ ratio. Thus a quite high degree of functionalization would be deduced, however, the absolute intensity of the $D$ mode has only slightly changed [Inset Fig. 8.1 (b)].

To overcome this problem, it is important to use different contributions of the $G$ mode to deduce the $D/G$ ratio for excitation energies with different species of nanotubes in resonance. For mainly semiconducting tubes in resonance the $G^-$ mode is favorable and for mainly metallic tubes in resonance the $G^+$ mode. The use of the $G^-$ mode can bare the problem that it can decrease due to functionalization [158, 159] caused by a shift in the Fermi level [62, 121] (compare Sec. 6.5.2), or by removal of metallic nanotubes [160]. To make the $D/G$ ratio comparable for different excitation energies it has to be normalized with the $D/G$ ratio of the reference material.

$$\frac{(D/G)_{\text{semiconducting}}}{(D/G)_{\text{reference}}} = \frac{(D/G^+_{\text{function}})/(D/G^+_{\text{reference}})}{(D/G^-_{\text{function}})/(D/G^-_{\text{reference}})}.$$  \hspace{1cm} (8.1a)

$$\frac{(D/G)_{\text{metallic}}}{(D/G)_{\text{reference}}} = \frac{(D/G^-_{\text{function}})/(D/G^+_{\text{reference}})}{(D/G^-_{\text{function}})/(D/G^-_{\text{reference}})}.$$  \hspace{1cm} (8.1b)

Furthermore, excitation energies with mainly one species of nanotubes in resonance should be preferred. For a sample of HiPCO tubes an excitation energy of $< 2\text{ eV}$ for semiconducting tubes and $2.4 - 2.6\text{ eV}$ for metallic tubes should therefore be used (Sec. 5.3).

8.4 Raman spectra of nanotubes with high and low functionalization degrees

The use of different gradient-medium concentrations in the DGU process makes it possible to separate different fractions of nanotubes with different defect densities [154]. For this method the starting material is layered in between a gradient medium with higher and lower density. After centrifugation the former starting material (now fraction 2) will lose some material to a fraction with a lower density and less defects (fraction 1) and a higher density like bundled nanotubes (fraction 3). The application of this method to covalently sidewall functionalized nanotube offers the possibility to investigate different degrees of functionalization.

Figure 8.2 shows the Raman spectra of the reference material (black), the functionalized material before DGU (red) [146] , as well as the first (green) and second fraction of the functionalized material (blue) after DGU [154] at 2.41 eV excitation energy; amplitudes of the spectra were normalized to one; the spectra are plotted vertically offset. For this excitation energy mainly metallic tubes contribute to the RBM, $D$,
8.4 Raman spectra of nanotubes with high and low functionalization degrees

![Raman spectra](image)

**Figure 8.2:** Raman spectra of reference (black), functionalized nanotubes before (red) and after the separation in different fractions with DGU (green, blue) for RBM (left panel), $D$ and $G$ mode (middle panel) and $2D$ mode (right panel); at 2.41 eV excitation energy. Amplitudes of the spectra were normalized to one; the spectra are plotted vertically offset.

and $G$ mode (Sec. 5.3).

While the RBM (left panel) shows only minor changes between the samples, the $D$ mode is narrowed for frac. 1 and broaden for frac. 2 (middle panel) in comparison with the sample before DGU (funct.).

For the $2D$ mode there is the same change in width observable as for the $D$ mode. Furthermore, the contribution related to semiconducting tubes ($2D_S$) has disappeared in the functionalized samples due to the destruction of the small, semiconducting tubes (right panel, compare Sec. 8.3). Additionally, the ratio between $G^+$ and $G^-$ mode is largest for frac. 1 (middle panel). This behavior can also be assigned to the destruction of the small, semiconducting tubes.

Figure 8.3 shows the same comparison at 1.96 eV excitation energy; amplitudes of the spectra were normalized to one; the spectra are plotted vertically offset. For this energy mainly semiconducting tubes contribute to the $D$, $G$, and $2D$ mode.

The RBM and (2)$D$ mode show the same behavior as already discussed for the measurements at 2.41 eV excitation energy, but with only semiconducting nanotubes contributing to the $2D$ mode. The changes in the ratio between the $G^+$ and $G^-$ mode are not as distinct as for 2.41 eV excitation energy.

To estimate in which quantity the different fractions contribute to the sample before DGU, the spectra of frac. 1 and frac. 2 were normalized to power and time and subsequently scaled that the sum of both fit best to the spectra of the $D$ and $G$ mode before DGU* (funct.). The spectra of the RBMs of the different fractions were modified in the same way as the $D$ and $G$ mode.

*The third fraction is neglected, since it can be assumed that this fraction contains mainly bundled tubes, which are an average of frac. 1 and frac. 2.
8.5 $D/G$ ratios at excitation with different nanotube species in resonance

![Graph showing Raman spectra of reference (black), functionalized nanotubes before (red) and after the separation in different fractions with DGU (green, blue) for RBM (left panel), $D$ and $G$ mode (middle panel) and $2D$ mode (right panel); at 1.96 eV excitation energy. Amplitudes of the spectra were normalized to one; the spectra are plotted vertically offset.](image)

Figure 8.3: Raman spectra of reference (black), functionalized nanotubes before (red) and after the separation in different fractions with DGU (green, blue) for RBM (left panel), $D$ and $G$ mode (middle panel) and $2D$ mode (right panel); at 1.96 eV excitation energy. Amplitudes of the spectra were normalized to one; the spectra are plotted vertically offset.

Figure 8.4 shows the results for measurements at 2.41 eV excitation energy for the RBM (a) and the $D$ and $G$ mode (b). The sum of frac. 1 and frac. 2 (thick, gray line) matches the functionalized sample (red) quite well. These results indicate, that the functionalized sample (funct.) consists of both fractions roughly in same share. Furthermore, the origin of the broad contribution to the $D$ mode in the functionalized sample (funct.) can be assigned to frac. 2. This broadening is due to a shorter phonon lifetime, caused by a higher defect density [compare Eq. (2.10)]. The higher defect density is confirmed by the defect induced $D'$ mode. This mode in not due to NG flakes (Sec. 7.3.2), since no contribution of NG flakes is observed to the $D$ mode (Sec. 7.3.1).

Additionally, frac. 2 does not contribute to the $G^-$ mode of the functionalized sample (funct.), since the $G^-$ mode in frac. 2 is strongly decreased (small arrow). This decrease is probably due to doping effects, caused by the functionalization [158, 159] (Sec. 7.4). On the other hand, no shift of the $2D$ mode can be observed (Sec. 6.5.2), which could be expected after the results from Sec. 6.5.2 (Fig. 6.6).

Figure 8.5 shows the same comparison for measurements at 1.96 eV excitation energy. For this excitation energy frac. 2 contributes stronger to the functionalized sample (funct.). For this excitation energy mainly semiconducting tubes contribute to the $D$ and $G$ mode, since this functionalization process is selective to semiconducting tube, the contribution of the fraction with a high degree of functionalization (frac. 2) is enhanced.

8.5 $D/G$ ratios at excitation with different nanotube species in resonance

As discussed in Sec. 8.3, to calculate the $D/G$ ratio in SWCNT ensembles it is important to use the $G^+$ mode for mainly semiconducting tubes in resonance and the $G^-$ mode for mainly metallic tubes in resonance. For excitation energies with mainly metallic tubes in resonance (2.41 eV) the $G^-$ mode for the DGU fraction

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containing highly functionalized nanotubes is strongly decreased (frac. 2, Fig. 8.4), caused by the functionalization process. Therefore, the use of both, \(G^-\) mode and \(G^+\) mode, will provide an overestimated \(D/G\) ratio for this sample. To be still able to compare the \(D/G\) ratio to other samples, the \(D/G^+\) will be used for frac. 2.

Table 8.1 shows the calculated \(D/G\) ratios using Eq. (8.1). For the \(D/G\) ratio at 2.41 eV excitation energy the overestimated \(D/G\) ratios are shown in gray. Furthermore, Tab 8.1 shows the \(D/G\) ratios for a sample functionalized with hydroxyl groups with a non-selective method [24].

Figure 8.6 shows the results from Tab. 8.1 in one graph (lines are guides for the eyes). For the selectively functionalized nanotubes (funct., frac. 1, frac. 2), the normalized \(D/G\) ratios are higher for semiconducting tubes in resonance compared to metallic tubes in resonance. Furthermore, the highly functionalized sample (frac. 2) shows an overall higher \(D/G\) ratio. The \(D/G\) ratio of the non-selectively functionalized sample (comparison, dashed line) shows the opposite relation between \(D/G\) ratio and excitation energy.

### 8.6 Chapter summary

The resonance behavior of the \(D\) mode (Chap. IV) can be used to prove selective functionalization. However, changes in the \(D/G\) ratio have to be analyzed carefully, especially for excitation energies with metallic and semiconducting tubes in resonance (Chap. V). A partial loss of the sample material can alter the \(D/G\) ratio, caused by a decrease of the \(G^+\) mode and not due to a successful functionalization. Therefore, to investigate a selective functionalization, the \(G^+\) mode has to be used to calculate the \(D/G\) ratio with mainly
semiconducting tubes contributing to the \( D \) mode and the \( G^- \) mode for mainly metallic tubes contributing to the \( D \) mode. To compare the \( D/G \) ratio at different excitation energies, it has to be normalized by a reference material. However, the \( D/G \) ratio is always an average of nanotubes with a high and a low degree of functionalization, which can be seen at the Raman spectra of the different DGU fractions.

**Figure 8.5:** Sum of the scaled components after DGU (frac. 1 + frac. 2) in comparison with the spectra of functionalized nanotubes before DGU (funct.); for RBM (a) and \( D \) and \( G \) mode (b) at 1.96 eV excitation energy.
Table 8.1: $D/G$ ratios for the different samples, excitation energies, and calculation methods after Eq. (8.1). Gray numbers indicate an overestimated $D/G$ ratio.

<table>
<thead>
<tr>
<th>sample</th>
<th>excitation energy (eV)</th>
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<tbody>
<tr>
<td></td>
<td>1.96</td>
</tr>
<tr>
<td>funct.</td>
<td>4.06 3.23 4.61</td>
</tr>
<tr>
<td>frac. 1</td>
<td>2.82 1.35 3.22</td>
</tr>
<tr>
<td>frac. 2</td>
<td>5.60 9.99 4.52</td>
</tr>
<tr>
<td>comparison</td>
<td>2.54</td>
</tr>
</tbody>
</table>

Figure 8.6: $D/G$ ratios for mainly semiconducting or metallic nanotubes in resonance for selectively semiconducting functionalized nanotubes (red) and the different fractions after DGU (green, blue). For comparison the $D/G$ ratios for non-selectively functionalized nanotubes are shown (black, dashed line).
CHAPTER IX

Summary and conclusion
Raman spectroscopy of nanotubes highly enriched with single chirality shows that the Raman intensity of the double resonant $D$ mode is strongly enhanced at excitation energies close to their optical transition. The well-known dispersion of the $D$-mode frequency is observed only above resonance where the intensity has dropped by approximately one order of magnitude. Therefore, the $D$ mode has a similar resonance behavior like a single-resonant Raman process, e.g. the RBM, but with a larger resonance window due to the higher phonon frequency of the $D$ mode. This strong resonance is explained by the high density of states at the optical transition and confirmed by simulations. Although this quasi single-resonant behavior of the $D$ mode is shown experimentally only for one particular chirality, simulations confirm this behavior for other chiralities, and also for the $2D$ mode (Chap. IV). Due to this strong resonance of the $(2)D$ mode, the well-known $(2)D$-mode dispersion behavior of graphene and graphite is not directly comparable to the $(2)D$-mode dispersions in SWCNT ensembles.

Observed contributions in the $(2)D$-mode dispersions for samples enriched to semiconducting and metallic species of nanotubes reflect the RBM dispersion of the experimental Kataura plot. This confirms the quasi-single resonant behavior of the $(2)D$ mode in nanotube ensembles and allows an assignment of the different $(2)D$-mode contributions to different optical transitions. Furthermore, excitation windows with mainly semiconducting or metallic nanotubes contributing to the $(2)D$ mode in nanotube ensembles can be assigned.

Simulations show that the experimentally observed splitting of the $(2)D$-mode dispersion into different contributions is related to a curvature induced shift in frequency as known for the RBM. However, first, the curvature-induced shift of the $(2)D$ mode is much weaker than for the RBM but in the same order of magnitude as known for the $G^-$ mode. Second, there is a blue shift in frequency with curvature for the RBM and a red shift in frequency with curvature for the $(2)D$ mode, like for the $G^-$ mode. This behavior can be understood by modeling the well-known curvature dependence of the Raman frequency of RBM and $G^-$ mode with an easy spring model and classical mechanics. Strength and direction of the curvature induced frequency shift is a direct consequence of the different vibration geometries for the different Raman modes. This means the modification of the effective spring constant with curvature behaves differently for out-of-plane vibration (RBM) and for in-plane vibrations ($G$ mode and $(2)D$ mode). All the same this model gives qualitatively a very good agreement between theory and experiment, exact calculations for the dependence of the $(2)D$-mode frequency on diameter are not possible with this simple model. But a comparison between the experimental data of $(2)D$-mode frequencies with the RBM frequencies and the well-known RBM diameter dependence makes it possible to derive the dependence of the $(2)D$-mode frequency on diameter. This dependence is confirmed by measurements of nanotubes with well-defined diameters, like samples highly enriched with single chiralities and measurements of individual, freestanding nanotubes. The derived diameter dependence predicts an inversely-proportional or a proportional dependence of $(2)D$-mode frequency on diameter, depending on the experimental set up, which explains the contrasting predictions from literature.

The assignment of the $2D$-mode contributions to different optical transitions can be used to monitor the enrichment of nanotubes to different species and with help of the found diameter dependence even to a certain diameter range (Chap. V).

Due to the advanced understanding of the $(2)D$-mode dispersion it is possible to characterize functionalized nanotube samples not only due to changes in the $D/G$ ratio, but also by analyzing the $(2)D$-mode fine structure.

Small graphitic flakes produced during oxidative functionalization of nanotubes show a broad Raman mode with a Gaussian line shape. This Raman mode partially overlaps with the $D$ mode of the nanotube sample and has to be taken into account by estimating the defect density of the oxidized nanotubes (Chap. VII). Furthermore, the assignment of the $D$ mode to diameter shows that an increase in the $D/G$ ratio is not necessarily due to a higher defect density, but can also be due to a partial loss of nanotubes. Therefore, the $D/G$ ratio has to be analyzed with great care and is not directly comparable with the behavior known from graphene and graphite. Additionally, the knowledge of excitation windows for mainly semiconducting or metallic species contributing to the $D$ mode makes it possible to show a selective functionalization of nanotubes, whereby it is important to consider the fine structure of $G$ mode to avoid misleading results (Chap. VIII).

Finally the $D/G$ ratio and the fine structure of the $G$ mode and $2D$ mode change for measurements in solution or on substrate. While for Raman modes related to metallic tubes some changes could be
9 Summary and conclusion

attributed to a shift in the Fermi level, caused by the aqueous environment, the origin of the changes for Raman modes related to semiconducting tubes are quite unclear and further experiments are needed.

In conclusion this work shows that the strong resonance behavior of the $D$ mode and $2D$ mode near the optical transitions modifies the $(2)D$-mode dispersion of nanotube ensembles in comparison to other graphitic materials like graphene and graphite. The understanding of the $(2)D$-mode dispersion behavior can be used for an advanced characterization of functionalized nanotubes, regarding sample impurities and a more accurate determination of the defect density, which also includes the proof of a selective functionalization of nanotubes.
APPENDICES
APPENDIX A

Sample preparation

All chemicals were in analytic grade.

A.1 Oxidation of SWCNTs

Purified HiPCO SWCNTs (Unidym, Batch PO355, 20 mg) were oxidized in 3 M nitric acid (HNO₃ 50 ml) for 4 hours under reflux conditions in a oil bath (120 °C, stirring 215 rpm). To the cooled down solution 200 ml H₂O was added. To remove any amorphous carbon species, the oxidized tubes were stirred in 0.1 mM sodium hydroxide (NaOH) for 12 hours. The solution was sucked through a fleece-strengthened filter membrane (pore size 200 nm) with weak vacuum. Subsequently, the oxidized SWCNT derivatives were washed with distilled water to neutral pH in the filtrate and subsequent washed with ethanol. The resulting SWCNTs possess carboxylic acid groups at the ends and at sidewall defects [22]. The SWCNTs were dissolved in 2 mM NaOH for further usage. The additional cutting of the tubes due to the acid treatment [129] is shown by the AFM statistic in Fig. A.1.

For the preparation of sample containing NG flakes, the nanotubes were treated with three steps:

NG 1 Nanotubes and HNO₃ was tip sonicated for 4 min (Tip sonicator Branson Sonifer 450, output 4; duty cycle 30; power 50 W; tip diameter 13 mm) and cooked for 4 hours under reflux conditions in a oil bath (120 °C, stirring 300 rpm) and subsequently for 16 hours at room temperature.

NG 2 The solution NG 1 was tip sonicated for 20 min.

NG 3 The solution NG 2 was refilled with 100 ml H₂O and cooked for 4 hours under reflux conditions in a oil bath (120 °C, stirring 300 rpm).

![Figure A.1: AFM statistic about nanotube length after oxidation process. The mean diameter is 520 nm. This is around half of the average length of the starting material [93].](image)

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Figure A.2: Unbundled SWCNTs (left, Sec. A.2) and after cooking (right, Sec. A.3).

A.2 Unbundling of SWCNTs

The Protocol was adapted from references [161, 162]. 5 mg of purified HiPCO SWCNTs (Nanointegris Technology Inc., Batch PO568) were sonicated in 20 ml sodium dodecyl sulfate (SDS) (1wt%) for one hour. The sonication was done with a tip sonicator (Dr. Iheihecher, UP 100) with a 10 mm diameter tip (MS10), a 0.5 s-on/0.5 s-off cycle and an amplitude of 40% (≈ 36 W/cm²) was used. The beaker was cooled in water bath to 20 °C.

The suspension was centrifuged for one hour at 13 000 g at 4 °C in 2 ml eppendorf tubes. The upper half of the suspension was used in the experiments.

A.3 Re-bundling of SWCNTs

Mixing of SDS solution containing unbundled nanotubes (Sec. A.2) with ethanol in the ratio 2:1 destroys the surfactant micelles and the nanotubes will aggregate to visible bundles.

Cooking the SDS solution with unbundled nanotubes under reflux condition (heating plate 200 °C for two hours) destroys the surfactant micelles and the nanotubes will aggregate to visible bundles (Fig. A.2).

A.4 Spin coating of SWCNTs

50 μl of unbundled SWCNTs in SDS solution (Sec. A.2) were dropped on the substrate. After one minute the velocity of the spin coater was increased slowly from 0 to 70 – 90 rpm. The substrate was subsequently washed for 30 s in H₂O and for 30 s in isopropanol. For drying the substrate was kept upright after each washing step.

A.5 Free standing SWCNTs film

10 ml of unbundled nanotubes (A.2) were sucked through a cellulose-base filter membrane (pore size 220 nm). This step was repeated three times with the each time obtained filtrate to increase the yield of nanotubes on the membrane. A weak vacuum was applied, but stopped before the filter gets dry. Subsequent 150 ml H₂O of 60 °C were run through the filter to remove the surfactant.

The still wet filter membrane was put into acetone bath. After a few minutes the nanotube film detaches form the membrane and swims on the acetone. Some acetone was partly carefully removed and refilled to wash the nanotube film.

Then the acetone was subsequently substituted with H₂O (50 μl each step) to make the film swimming on water. A glass plate with hole of 5 mm diameter was carefully moved under the swimming film and lifted.
APPENDIX B

Fit parameters

Table B.1: Fit parameters of the Gaussian fits for excitation depended amount fractions [Eq. (5.1)] of RBM $D$ mode, $G$ mode, and 2D mode for reference material and samples enriched with metallic and semiconducting nanotubes.

<table>
<thead>
<tr>
<th>sample</th>
<th>Raman mode</th>
<th>offset</th>
<th>center</th>
<th>width</th>
<th>area</th>
<th>figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference</td>
<td>RBM</td>
<td>1</td>
<td>2.320</td>
<td>0.278</td>
<td>-1.513</td>
<td>5.4 (a)</td>
</tr>
<tr>
<td>reference</td>
<td>$D$ mode</td>
<td>1</td>
<td>2.486</td>
<td>0.349</td>
<td>-0.745</td>
<td>5.4 (b)</td>
</tr>
<tr>
<td>reference</td>
<td>$G$ mode</td>
<td>1</td>
<td>2.403</td>
<td>0.427</td>
<td>-0.694</td>
<td>5.4 (c)</td>
</tr>
<tr>
<td>reference</td>
<td>2D mode</td>
<td>1</td>
<td>2.471</td>
<td>0.409</td>
<td>-0.634</td>
<td>5.4 (d)</td>
</tr>
<tr>
<td>metallic enriched</td>
<td>RBM</td>
<td>1</td>
<td>2.271</td>
<td>0.662</td>
<td>-1.579</td>
<td>5.16 (a)</td>
</tr>
<tr>
<td>metallic enriched</td>
<td>$D$ mode</td>
<td>1</td>
<td>2.486</td>
<td>0.575</td>
<td>-1.518</td>
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</tr>
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<td>$G$ mode</td>
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<td>0.508</td>
<td>-1.242</td>
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<td>metallic enriched</td>
<td>2D mode</td>
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<td>2.529</td>
<td>0.505</td>
<td>-1.104</td>
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<td>semiconducting enriched</td>
<td>RBM</td>
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<td>0.424</td>
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<td>0.384</td>
<td>-0.578</td>
<td>5.16 (c)</td>
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<tr>
<td>semiconducting enriched</td>
<td>2D mode</td>
<td>1</td>
<td>2.586</td>
<td>0.308</td>
<td>-0.447</td>
<td>5.14 (b)</td>
</tr>
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</table>

Table B.2: Fit parameters of the linear fits related to the optical transitions of RBM and (2)D mode; with slope $m$, intercept $b$ and standard deviation $\sigma$.

<table>
<thead>
<tr>
<th>Fit parameter</th>
<th>Optical transition</th>
<th>$E_{22}^S$</th>
<th>$E_{22}^{2D}$</th>
<th>$E_{11}^M$</th>
<th>$E_{11}^{2D}$</th>
</tr>
</thead>
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<td>$m_{RBHM}$</td>
<td></td>
<td>107.0</td>
<td>109.6</td>
<td>78.5</td>
<td></td>
</tr>
<tr>
<td>$b_{RBHM}$</td>
<td></td>
<td>74.9</td>
<td>-5.3</td>
<td>1.1</td>
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<tr>
<td>$\sigma_{RBHM}$</td>
<td></td>
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<td>15.7</td>
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<tr>
<td>$m_D$</td>
<td></td>
<td>30.3</td>
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<td>27.9</td>
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<tr>
<td>$b_D$</td>
<td></td>
<td>1246.9</td>
<td>1265.3</td>
<td>1283.0</td>
<td></td>
</tr>
<tr>
<td>$\sigma_D$</td>
<td></td>
<td>2.7</td>
<td>3.9</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>$m_{2D}$</td>
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<td>57.7</td>
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<td>$b_{2D}$</td>
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<td>2531.5</td>
<td>2555.8</td>
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<tr>
<td>$\sigma_{2D}$</td>
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<td>3.9</td>
<td>2.6</td>
<td>3.7</td>
<td>3.5</td>
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Table B.3: Position and FWHM of the Lorentzian (LO) and Gaussian fits (GA) of the oxidized nanotubes for different excitation energies.

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<th>fit parameter</th>
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<tr>
<td>FWHM \text{LO}</td>
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<tr>
<td>Position \text{GA}</td>
<td>1316</td>
</tr>
<tr>
<td>FWHM \text{GA}</td>
<td>103</td>
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APPENDIX C

Supplementary measurements

\textbf{Figure C.1}: Raman spectra of the RBM of the sample enriched with (9,7) SWCNTs for excitation energies between 1.49 – 1.65 eV and for 1.85 and 2.05 eV, magnified 10 times (top to bottom). The spectra are plotted vertically offset.

\textbf{Figure C.2}: Raman spectra of the RBM of the sample enriched with (7,5) SWCNTs for excitation energies between 1.85 – 2.04 eV (top to bottom) and for 2.41 eV. Spectra were normalized to power and time; the spectra are plotted vertically offset.
Figure C.3: Raman spectra of the $D$ mode of the sample enriched with (7,5) SWCNTs for excitation energies between $1.85 - 2.04\text{ eV}$ and $2.41\text{ eV}$. Spectra were normalized to power and time; the spectra are plotted vertically offset.
Figure C.4: Raman spectra of the 2D mode of the sample enriched with (7,5) SWCNTs for excitation energies between 1.85 – 2.04 eV (top to bottom) and 2.41 eV. Amplitudes of the spectra were normalized to power and time; the spectra are plotted vertically offset.
Figure C.5: Raman spectra of the 2D mode of the sample enriched with (9,7) SWCNTs for excitation energies between 1.79 and 2.05 eV (top to bottom). Amplitudes of the spectra were normalized to one; the spectra are plotted vertically offset.

Figure C.6: Raman spectra of the RBM of oxidized nanotubes before (black) and after treatment with KOH (red) at 2.33 eV excitation energy. Amplitudes of the spectra were normalized to one.
Figure C.7: AFM picture of oxidized nanotubes drop casted on Si/SiO$_2$ before (left) and after the treatment with KOH (right).

\[ \text{Figure C.8: Amplitude profiles of the AFM recordings shown in Fig. C.7 before (black) and after the treatment with KOH (red).} \]

\[ \text{Figure C.9: Raman spectra of free-standing nanotube film in contact with air (black) and H}_2\text{O at 1.96 eV excitation energy. Shown are the RBM (a), D and G mode (b), and the 2D mode (c). Amplitudes of the spectra were normalized to one; the spectra are plotted vertically offset.} \]
Figure C.10: Raman spectra of free-standing nanotube film in contact with air (black) and H$_2$O at 2.33 eV excitation energy. Shown are the RBM (a), D and G mode (b), and the 2D mode (c). Amplitudes of the spectra were normalized to one; the spectra are plotted vertically offset.

Figure C.11: Raman spectra of the RBM at 2.18 eV excitation energy for reference (black), and functionalized nanotubes before (red) and after the separation in different fractions (green, blue) by DGU. Amplitudes of the spectra were normalized to one; the spectra are plotted vertically offset.
BIBLIOGRAPHY


[107] Absorption measurements were done by Olga Dyatlova using a NS1 NanoSpectalyzer from Applied NanoFluorescence.


