12 Carbon Nanotubes

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1 Preface

This experiment is part of the JARA-FIT nanoelectronic lab course since 2008. The experiences made in the first year lead to small changes of the experiment, its description and the data analysis. I thank Dr. Christian Spudat for the description of the CVD process.

Jülich, den 26.08.08

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2 Preliminary remarks

2.1 Laser safety

Attention! You are working with an instrument that contains a laser with a maximum output power of 1W. If the laser beam hits your eye with full intensity, it can be damaged permanently. Usually, the laser beam is fully covered during the experiment and is no imminent danger. Therefore, due to laser safety you are not allowed to make any changes at the apparatus which are not mentioned in the description of the experiment.

2.2 What you should learn

The aim of this experiment is to introduce a modern method of Raman spectroscopy. Using Fourier-transform spectroscopy, you will study carbon nanotubes (CNTs) and changes in their spectrum due to oxidation. You will learn to do chemical vapour deposition (CVD), an important process for the synthesis of carbon nanotubes.

2.3 Preparation

This and the following part shall help you to prepare the experiment. The points listed below are by no means complete, but should motivate you to study the relevant literature on your own. The references at the end of this section are given with the same intention. You will find that some terms in the text are underlined. These are essential for comprehension of the experiment and should be prepared in advance. With respect to the "Fortgeschrittenenpraktikum" the preparation of these terms is mandatory as they will be part of the interview prior to the experiment.

2.4 Compendium

- 1. Vibrational modes of molecules
- 2. Raman scattering and Raman spectroscopy
- 3. Fourier transformation
- 4. Michelson interferometer
- 5. Fourier-transform spectroscopy

2.5 Literature

Basics:

1. Kuzmany, Hans: Festkörperspektroskopie - Eine Einführung, Springer, 1989

English Title: Solid State Spectroscopy: An Introduction, Springer, 1998

2. Hecht, Eugene: Optik, Oldenburg, 2001

3. S.G. Lipson, H. Lipson and D.S. Tannhauser: Optical Physics, Cambridge University Press, 1995

For deeper understanding:

1. A. Jorio, M.S. Dresselhaus, G. Dresselhaus: Carbon Nanotubes, Springer, 2008

2. Schrader, Bernhard: Infrared and Raman Spectroscopy, VCH, 1995

3. Knorr, Fabian: Auswirkungen von Oxidation auf das Raman-Spektrum von Kohlenstoff Nanoröhren, Bachelorarbeit RWTH Aachen, Juli 2009 (you can download this thesis from http://www.fz-juelich.de/ibn/datapool/page/1025/V12_bachelor.pdf)

3 Raman spectroscopy of carbon nanotubes

3.1 Raman scattering

Light is scattered during its journey through a solid state sample or a molecule, if it encounters inhomogeneities in the order of magnitude of the wavelength. This process can be divided into two categories:

1. Elastic scattering, e.g., Mie- or Rayleigh scattering, if inhomogeneities occur only in space

2. <u>Inelastic scattering</u>, Raman- or Brillouin scattering, if the inhomogeneities are time dependent

For the elastic Rayleigh scattering the energy of the incident photon is the same as the energy of the scattered photon, $\hbar\omega_i = \hbar\omega_s$ (Fig. 1(a)). If a photon with energy $\hbar\omega_i$ is scattered inelastically, the molecule in state $|b\rangle$ absorbes the energy and is excited to an instable (virtual) intermediate state. Then a (scattered) photon with energy $\hbar\omega_s < \hbar\omega_i$ is emitted in a Stokes process. After this process the molecule exists in an excited vibrational state $|c\rangle$ with energy $\hbar\Omega_{cb} = \hbar\omega_i - \hbar\omega_s$ (Fig. 1(b)) due to conservation of energy.

The Anti-Stokes process becomes possible, if the initial state $|b\rangle$ already is a vibrational excited state. Here, the vibrational energy is transformed into radiation with $\hbar\omega_s > \hbar\omega_i$. The final state $|a\rangle$ lies below the initial state $|b\rangle$ and the difference in energy is $\hbar\Omega_{ba} = \hbar\omega_s - \hbar\omega_i$ (Fig. 1(c)).



Fig. 1: *Different scattering processes: (a) Elastic Rayleigh scattering (b) Raman Stokes process (c) Raman Anti-Stokes process*

Besides the conservation of energy also the momentum has to be preserved, $\hbar k_s = \hbar q \pm \hbar k_i$ (fig. 2). The maximum q-vector of the phonon is $q_{max} = k_i + k_s \approx 2k_i$ at 180°. Since k_i is of the order of magnitude $10^5 cm^{-1}$ for the visual spectrum, compared to size of the Brillouin zone only phonons close to the Γ point, i.e. $q \approx 0$, contribute to the scattering process. However, this holds only for one-phonon processes. Generally, the momentum needs to be preserved but for a reciprocal lattice vector G due to invariance of translation with $k_i - k_s + \sum_{l=1}^{N} q_l + G = 0$, with N number of phonons.

Not all vibrations are Raman-active. Only time dependent changes of the polarizability



Fig. 2: Conservation of momentum for Raman scattering.

$$\vec{P} = \alpha E(\omega) \tag{1}$$

lead to a Raman process. Periodic changes of the polarization \vec{P} cause the emission of a wave, the scattered wave. In classical approximation the scattered radiation can be understood as dipolar radiation from oscillating dipoles. The polarizability α is a function of the atomic coordinates. A vibration, i.e. a displacement in "x", can be treated as a small perturbation and the polarizability can be developed as

$$\alpha(x) = \alpha_0 + \frac{d\alpha}{dx}dx + O(\alpha^2).$$
(2)

If the displacement x can be described as $x = x_0 cos \Omega t$, the polarization is

$$\vec{P} = [\alpha_0 + \alpha_1 \cos(\Omega t)] E_0 \cos(\omega_i t) \tag{3}$$

$$= \alpha_0 \cos(\omega_i t) + (\alpha_1 \frac{E_0}{2}) \cos[(\omega + \Omega)t] + \cos[(\omega - \Omega)t]$$
(4)

with the ansatz for a plane monochromatic light wave $E = E_0 cos(\omega_i t)$. Infrared spectroscopy is often a complementary method to Raman spectroscopy. It reacts towards changes in the polarization measured by absorption of infrared (IR) light. Fig. 3 shows examples for Raman active and IR active modes.

3.2 Carbon Nanotubes

A <u>carbon nanotube</u> can be imagined as a single sheet of graphite, called graphene, rolled up to a seamless tube (fig. 4). The hexagonal lattice of graphene is rolled along the <u>chiral vector</u> $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$ with the unity vectors \vec{a}_1 and \vec{a}_2 of the graphene lattice. The indices n and m are used to describe the nanotubes. Nanotubes with n = m are also called "armchair"-tubes. The <u>chirality</u> is often given as angle ϕ or $\theta = 30^\circ - \phi$. For "armchair"-tubes $\phi = 0$ by definition. The indices allow to calculate the diameter of a nanotube with $d[nm] = 0.0783\sqrt{n^2 + m^2 + nm}$.

The electronic band structure of the nanotubes can be derived from graphene, in a process called zone folding approximation. Tight binding calculations show that the two-dimensional density



Fig. 3: *Change of polarizability and dipole moment. Raman and infrared activity for different molecules and vibrations. Taken from [1].*



Fig. 4: From a graphene sheet to a nanotube. Multiples of the unity vectors sum up to the chirality vector. The axis of the tube is perpendicular to the chirality vector.

of states of graphene is situated on six cone surfaces. If the graphene sheet is rolled up, the boundary condition for the electron wave functions is that they have to fit once (or in integer multiples) around the circumference of the tubes. This is resembled by cuts through the Fermi-surface of graphene along k_{\parallel} parallel to the tube axis. The distance between the cuts depends on the diameter of the tubes (fig. 5).

Carbon nanotubes can be divided roughly into two classes with respect to their electronic properties (see fig. 6):

1. Metallic nanotubes with finite density of states at $E_F = 0$ (cutting through the centre of a cone). This is true for indices (n, m) with mod[(n - m), 3] = 0.

2. Semiconducting nanotubes with zero density of states at $E_F = 0$ (cutting through a cone beside the centre). This holds for indices (n, m) with mod[(n - m), 3] = 1, 2.

Nanotubes are ideal one-dimensional conductors. The electronic transport is ballistic for several



Fig. 5: The dispersion relation of graphene (left) can be used to determine the one-dimensional band structure of the nanotubes by cutting along k_{μ} (see text). The band structure of the nanotubes depends on the indices (n,m).

micrometers. For metallic carbon nanotubes the Fermi-liquid theory breaks down. Instead, the Tomonaga-Luttinger-Liquid (TLL) theory for one-dimensional metals applies.



Fig. 6: Band structure for metallic nanotubes and semiconducting nanotubes, respectively.

3.3 Raman spectrum of carbon nanotubes

Fig. 7 shows a typical Raman spectrum of carbon nanotubes. The <u>radial breathing modes</u> (RBMs) have the smallest Raman shift. It is followed by the disorder induced <u>defect D-mode</u> and <u>the G-mode</u> (the latter also called high energy mode (HEM)). The ratio of their intensities is often used to determine the purity of a sample. The <u>D*-mode</u> is an overtone of the D-mode and reacts with a relative shift towards changes in the electronic structure caused by defects in the sidewall. The RBMs and the G-mode are <u>first order Raman effects</u>, while the defect modes are <u>second order Raman effects</u>.

All Raman modes have very small intensity and are visible only for resonant Raman scattering meaning that the intermediate state is not virtual but real: From 1st (2nd,3rd,...i-th) vanHove singularity (vHS) of the valance band the electrons are excited to the 1st (2nd,3rd,...i-th) vHS

of the conduction band. The energy difference between the vHS depends on the diameter of the tubes (see previous chapter). Therefore, at a fixed wavelength only tubes with a certain diameter are resonant (see figure in appendix A).



Fig. 7: *Typical FT-Raman spectrum of a carbon nanotube sample. The modes relevant for the experiments are labelled.*

3.3.1 The Radial Breathing Mode (RBM)

The vibration causing the RBM has radial symmetry with respect to the nanotube axis. All carbon atoms move outwards (or inwards) simultaneously (fig. 8). The resonance window of the RBM is particularly sharp with $Gamma_{RBM} = 8$ meV.



Fig. 8: Schematic drawing of the RBM.

The Raman shift of the RBM depends on the diameter, as well. As far as known today, it is:

$$\omega_{RBM}[cm^{-1}] = \frac{A}{d[nm]} + B \tag{5}$$

The parameters A and B depend on the environment. For isolated nanotubes on a silicon oxide surface they are $A = 248 cm^{-1}$ and B = 0. In the experiment of this lab course the tubes will form so-called "ropes" due to the high yield. Thus, the interaction between the tubes has to be taken into account and it is $A = 234 cm^{-1}$ und B = 10.

3.3.2 The G-Mode

Taking a closer look on the G-mode it becomes obvious that it consists of at least two peaks (fig. 9). The reason is that this mode has its origin in the vibrations of the carbon atoms against each other. One part is independent of the tube diameter and labelled G^+ . It is due to longitudinal optical (LO) phonons, vibrations along the axis of the tube. The second peak, G^- , correlates to transversal optical (TO) phonons, vibrations along the circumference of the nanotubes. It is clear that the position of this peak depends on the diameter of the tubes.

The resonance window of the G mode is much broader than the one of the RBM. Thus, the signals of tubes with different diameter overlap. As a result, the G^- peak is broadened in bulk samples and appears as shoulder of the G^+ peak.



Fig. 9: The two peaks of the G-mode and schemes for the corresponding vibrations.

3.3.3 The defect modes

The D-modes and the D*-mode have their origin in second order Raman scattering (higher order terms in equation 2). The D mode consists of one inelastic scattering process and one elastic scattering process at a defect (fig. 10 (b)). It is sensitive towards amorphous carbon in the surrounding of the tube as well as to chemical modifications. The overtone of the D-mode, the D*-mode, is a two-phonon process (fig. 10 (c)). It is sensitive towards changes in the electronic structure and changes its position due to, e.g., doping of the carbon nanotubes but also to the number of walls.

4 The Fourier-Transform spectrometer

Modern Raman- and infrared-spectrometers are often Fourier transform-spectrometer (FT- spectrometer). The core of such a spectrometer is not a monochromator (as in confocal Raman



Fig. 10: 2nd order Raman Stokes-processes for resonance with the incident light.

spectroscopy) but a <u>Michelson interferometer</u> (fig. 11). Semi-transparent mirrors separate the source into two interfering beams.

Compared to conventional Raman spectroscopy, FT-spectroscopy offers several advantages:

- A complete spectrum can be taken much faster saving a lot of time.
- Parallel measurement of all frequencies.
- Since the beam is not confined by slits, the light intensity on the sample is higher. The result is a better signal to noise ratio.
- The wavelength is determined with high accuracy, because the mirror position is controlled with a HeNe-laser.



Fig. 11: Michelson interferometer

4.1 The interference pattern

The spectrum of a sample is not taken directly in an FT-spectrometer. Instead, an <u>interference</u> pattern is measured, from which the spectrum is calculated using <u>Fourier transformation</u>. The

interference pattern is created by a Michelson-interferometer (fig. 11). It reflects the dependence of light intensity from the position of the mirror S2. A semi-transparent mirror P1 (the reflective layer S is on the backside) serves as beam splitter. The light is split in two components, beam I and beam II. The transmitted beam (I) passes a second plate P2 of identical thickness and is reflected back directly on the same path by mirror S1. A part of this reflected beam is directed towards the screen (detector) by the mirror layer S of the semi-transparent mirror.



Fig. 12: Optical diagram of a commercial Michelson interferometer for infrared and Raman spectroscopy (Bruker IFW66 with Raman Modul FRA 106). CE control electronics, D1/D2 IR detectors, BS beam splitter, MS mirror scanner, IP input port, S IR source, AC aperture changer, X1-X3 external beams, A aperture for Raman spectroscopy, D detector for Raman spectroscopy, FM Rayleigh filter module, SC sample space, L Nd:YAG laser, SP sample position

The second beam (II) is reflected by S vertically to its original direction; passing the glass plate P1 a second time, it is reflected back along the same path at the mirror S2. The part, which is then transmitted through S, reaches the screen (detector) and interferes with beam I. The optical retardation between the two beams can be varied moving the mirror S2 along the beam axis. The zero point setting, i.e. the setting where both paths are of exactly the same length can be determined best with white light: Using white light is an advantage, because the coherence length is extremely short and the zero point can be determined with high accuracy. The phase difference of π is caused by the fact that beam I is reflected at the outer part of the mirror, while beam II is reflected at the inner side of the mirror.

The compensation plate P2 is used within the Michelson interferometer in order to keep the beam paths identical for light of broad spectral range. Since both beams pass the glass plates

three times, their dispersion is the same. In case of monochromatic light, the interference pattern is a cosine function. Fig. 12 shows the schematic construction of a combined FT-infrared and FT-Raman spectrometer, similar to the one used in this lab course.

4.2 The Fourier transformation

The intensity I(x) at the detector as a function of the position x of the mirror (the interference pattern) and the intensity S(ν) as function of the wave number $\nu = \lambda^{-1}$ of the light are a Fourier transformation pair:

$$S(\nu) = \int_{-\infty}^{\infty} I(x)e^{i2\pi\nu x} dx$$
(6)

$$I(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} S(\nu) e^{-i2\pi\nu x} \, d\nu$$
(7)

Practically, a continuous interference pattern of infinite range cannot be measured. Instead, a finite number N of interference points with distance Δx is digitalized. The <u>discrete Fourier trans</u>formation (DFT) is created, if x is replaced by $n\Delta x$, ν by $k\Delta\nu$ and the integral by a sum:

$$S(k\Delta\nu) = \sum_{n=1}^{N-1} I(n\Delta x) e^{\frac{i2\pi k\Delta\nu n\Delta x}{N}} \Delta x$$
(8)

The points calculated in frequency space have the distance:

$$\Delta \nu = \frac{1}{N\Delta x} \tag{9}$$

The distance between the points $\Delta \nu$ determines the spectral resolution and is inversely proportional to the path of the mirror and the number of measurement points. Problems, which occur with the discrete Fourier transformation and their correction, are discussed in the next subsections.

4.2.1 Apodization

Due to the finite length of the measured interference pattern, the Fourier transformation can create artefacts. The interference pattern truncated at $x=x_{max}$ can be described as product of an infinit interference pattern and a rectangular function. The rectangular function is 1 for $0 \le x \le x_{max}$ und zero otherwise. As a consequence, additional minima and maxima arise next to the main peak. The amplitude of the largest minimum is as large as 22% of the main peak amplitude.

This interfering effect can be avoided multiplying the interference pattern with a function decaying towards zero more smoothly than the rectangular function. Such functions are called apodization functions. Information at the edges of the interference pattern is lost since the <u>apodization</u> causes line broadening, i.e. a decrease of resolution. The apodization functions are optimized with respect to small line broadening and strong suppression of additional maxima and minima. Different apodization functions can be chosen for measurements with the FT-spectrometer.

4.2.2 Zero filling

Very sharp modes might appear with smaller intensity due to the finite distance of sampling points. This error can be compensated by adding zeros at the end of the interference pattern (zero filling) corresponding to an approximation of an interference pattern measured with higher spectral resolution (i.e. longer mirror path). This reduces the distance of points in the Fourier transformed spectrum. However, this is only an interpolation between the sampling points of the spectrum. The spectral resolution is not increased. The zero filling parameter can be set within the measurement program.

5 Materials and Methods

5.1 Sample preparation with chemical vapour deposition (CVD)

While working in the chemical lab, it is necessary to ware gloves and saftey goggles!

- 1. Cleaning of the molybdenum substrates:
 - Sonication in 2-Propanol for about 2 minutes.
 - Blow dry substrate with nitrogen gun.
- 2. Preparation of the substrates:
 - Sonicate catalyst for about 10 minutes.
 - Use a pipette to drop the catalyst onto the substrate (3-4 drops) as demonstrated in fig.13 (left). The substrate should be covered with catalyst.
 - Place the substrate on a petri dish upon a heating plate. Heat up to 100 °C to evaporate the solvent of the catalyst. This will lead to a large amount of catalyst on the sample and therefore a high yield of nanotubes. Prepare two substrates in this way.



Fig. 13: Dropping the catalyst onto the substrate.

- 3. Growing carbon nanotubes with CVD:
 - Turn on the computer. Log in on the computer using a blank password and default user name.
 - Place the substrates into the quartz glass tube and put the tube in the furnace. The sample inside the tube has to be more or less in the centre of the furnace.
 - Connect the glass tube to the gas supply pipe on the right and the exhaust pipe on the left (fig.14, left). Check that all flexible tubes are without any kinks. Close the furnace and the transparent covers.



Fig. 14: Left: Connection of the glass tube. Right: Gas flow controller.

- Turn on the controller using the black switch (fig.14, right). Start the program "Flowsoft" from the desktop. This program is used to control the flow of the gases.
- The default values for the gases are not zero. Enter the values in three of the text boxes as zero. Notice that channel 1, 2, and 3 correspond to Argon, Methane and Hydrogen respectively. The fourth channel is not used.
- Turn on the main valves for the gas supply (see fig. 15, left) as well as the levers at the bottom of the CVD (fig. 15, right).
- Click on the "start" button to start monitoring the gas flow thought the tube.



Fig. 15: Left: Main gas supply. Right: Gas valves at the CVD machine.

Hydrogen can form an explosive mixture with oxygen and Methane is highly flammable!

Therefore, we first need to make sure that there is no oxygen left in the system. All gas pipes have to be flushed first and the system is heated up with Argon flow. This is done as follows:

- Turn on all gas channels for 2 minutes (1.52 l/min for Argon, 0.7 l/min for Hydrogen and 0.5 l/min for Methane) followed by 2 minutes flushing with Argon alone (enter zero for Hydrogen and Methane). If gas is flowing, you will see bubbles in the bubble counter on the left hand side of the CVD. This bubble counter also prevents oxygen drifting back into the system from the exhaust side.
- Keep the Argon flushing. Set the temperature of the furnace to 1150 °C and turn on the furnace. It takes usually about 25 minutes until the temperature is reached. If the current that heats the oven starts to drop to zero, the desired temperature is close.
- Wait until the temperature has stabilized. Enter the value for Hydrogen as 0.7 l/min. in the corresponding text box (channel 3).
- Enter the Argon flow as zero.
- Set the value for Methane flow to 0.52 l/min in the corresponding text box (channel 2).
- After 10 minutes, set the Methane flow back to zero.
- Turn off the furnace.
- Set the Argon flow to 1.52 l/min, then turn off the hydrogen flow by setting it to zero. Turn off the main supply and close the small valves for both Hydrogen and Methane.

Do not turn off the Argon supply, yet!



Fig. 16: Opening of the furnace for cool down.

- Open the furnace a little bit by using a piece of metal as support as shown in fig. 16. Use the thermo gloves.
- Cooling down takes about 30 minutes. Take out the quartz tube using thermo gloves. Avoid kinks in the flexible tubes. When the tube is cool enough to touch, stop the Argon flow in the software and close all valves. The bubbling in the test tube should stop.
- Take out your sample. Shut down the computer.

5.2 Operating the FT-Raman spectrometer

The FT-Raman measurements are done with a Bruker RAMII spectrometer. As shown in fig. 12, it is combined with an IR spectrometer and uses the same Michelson interferometer. For the lab-course, the spectrometer is prepared to operate in the Raman mode. Do not try to change this.

5.2.1 Switch on laser

- 1. The instrument is flushed with Argon. Check the Argon flow. It is okay if the black ball in the tube is not on the bottom.
- 2. Turn the key one step. The red diode "line" will light up as well as the orange "warm-up". After some time, "stand-by" will glow yellow. The output power will still show (and be) zero, though.

5.2.2 Load sample and start first measurement

1. Open the compartment. Be careful not to touch the big lens during the procedure. Optical elements are very sensitive towards even the smallest impurities (dust or oil from your

skin) and scratches. Pull back gently the small rod with the spring. Insert the sample and release the rod again gently. Close the compartment.

- 2. Open "Arbeitsplatz" (english "My computer"). Create a new folder in "C:\User\ Raman\Praktikum" which can be identified as yours.
- 3. Start the program "Opus" from the desktop of the computer. Use password "OPUS". Ignore the first error massage. At the lower right edge on the screen you will see a red dot. Click it left, close the opening window. The dot should be green now.
- 4. From the menu choose "Messen" and "Erweiterte Messung" in the scroll down menu. Select the tab "Grundeinstellungen" in the pop-up window.
- 5. Load default settings. Click on the "Laden" button next to "Experiment". Choose the file "Polystyrol.XPM" from the folder "C:\Programme\Opus_65 XPM_Raman".
- 6. Choose a sample name for the field "Probenname" and put a description for the type of sample in the field "Probenform".
- Choose the tab "Erweitert". "SNM" means, that your sample name will be inserted automatically. The path below should be "C:\User\Raman\Praktikum\ yourfoldername". Make sure that in the field "Zu speichernde Datenblöcke" the boxes of "Raman spectrum" and "Interferogramm" are checked. For now, do not change anything else.
- 8. Select the tab "Justiermodus". This will start the laser. The output power will rise. The diodes might blink between "warm-up" and "on". Wait until "on" lights up steady.
- 9. Click on the button "Anzeige skalieren". You should see a clear interference pattern. Click on "Peakposition speichern". Switch to "Spektrum". You should see the spectrum corresponding to the interference pattern.
- 10. Optimize the intensity of the signal. This is done by changing the sample position with the buttons "Forward" and "Backward" only. To check whether the signal is rising or falling, put the cursor on a peak maximum of medium intensity and move the cursor to the right side of the window. A dashed line appears on its level. If you do not move the cursor back into the window with the spectrum, the line stays. Now you can change the position of the sample with the buttons and follow the changes of the peaks.
- 11. Wait 10 minutes for the laser to stabilize. Start the measurement.

5.2.3 Change sample and settings

1. Open the compartment. The laser beam is automatically blocked with a shutter. Be careful not to touch the big lens during the procedure. Exchange the samples. Close the compartment.

- 2. Change the sample name in the sheet "Grundeinstellungen". You can change the laser power here, as well.
- 3. Select the tab "Justiermodus". Click on the button "Anzeige skalieren". You should see a clear interference pattern. Click on "Peakposition speichern". Switch to "Spektrum". Maximize the signal intensity as described above.
- 4. Settings of the Fourier transform (Apodization function etc.) can be changed in tab "FT". The number of phase interference pattern points ("Phasen-Interferogrammpunkte") needs to be at least 250.
- 5. In the tab "Erweitert" you can change the resolution and number of scans.
- 6. Settings of the acquisition as the measurement range can be changed in the tab "Akquisition".
- 7. Start the measurement.

5.2.4 Shut down after all measurements

After you finished all your measurements:

- 1. Click on the button "Laser ausschalten" in the sheet "Grundeinstellungen".
- 2. Watch the output power going down. When the output is zero, switch the key back to "off" position.
- 3. End "Opus" and get your data. Save them as ASCII file using "Opus viewer".

5.3 Preliminary tests

- 1. Start with the Polystyrene test sample.
 - Measure the spectrum and check the signal (peak at around 1000 cm⁻¹) to noise (between 2000 cm⁻¹ and 2100 cm⁻¹) ratio.
- 2. Change to the Naphtalene test sample. Use the parameters of the file "Naphtalen.XPM".
 - Take the spectrum and measure the deviation of the peaks at 513.8 cm⁻¹), 1382.2 cm⁻¹ and 3056.4 cm⁻¹). Determine the error for the peak position. Measure the half-width at half maximum of the peak at around 1382.2 cm⁻¹ to determine the spectral resolution.
 - Measure the spectrum with at least two other apodization functions, one of them "boxcar" meaning no apodization (rectangular function). Discuss the effects on the spectrum (use the peak between 500 cm⁻¹ and 520 cm⁻¹).
 - Change the aperture to a large value and measure the spectrum. Discuss the effect.

5.4 Measurements of carbon nanotubes

- 1. Insert the sample of carbon nanotubes you prepared in the first part of the experiment. Load the settings from "Raman-defocused.XPM". Optimize the parameters (apodization, zero-filling, aperture ...) with respect to accuracy in position and intensity of the lines. Note down these parameters.
- 2. Oxidize the nanotube sample by heating in the oven at 450 °C. Start with intervals of five minutes and take a spectrum each time. Observe position and intensity of the RBM, D and G-modes as well as of the D* mode.

6 Data analysis

During the experiment you can use the measurement program for preliminary data analysis, e.g. for peak position and widths use "Bandensuche" in the menu "Auswertung". For students from RWTH Aachen who do the experiment for the "Fortgeschrittenenpraktikum", an elaborate analysis using a suitable program (like Matlab, Gnuplot, Origin, Igor etc.) is compulsory for the lab report.

6.1 Preliminary tests

- Observe the interference pattern while the laser is stabilizing. Every now and then, you will see spikes. What is the origin?
- Determine the signal to noise ratio from the Polysterene sample measurements.
- Determine the accuracy of the peak position and the spectral resolution from the Naphtalene measurements.
- Discuss the effects of the different Apodization functions especially with respect to line shape (Gauss, Lorentz, Voigt) and width. Use the χ^2 test to determine the best fit.
- Discuss the effect of the aperture.

6.2 Carbon nanotubes

- Discuss your choice of parameters (apodization, zero-filling, aperture ...) for the nanotube measurements.
- Determine the diameter of the tubes in resonance with the laser excitation ($\lambda = 1063$ nm) using the RBMs and the figure in appendix A.

- Analyse the absolute and relative changes for the intensity of the RBM, the D- and Gmode and the G/D ratio with increasing oxidation time (You need to determine the signalto-noise ratio for the error discussion). Which parts of the spectrum do you use for the signal-to-noise analysis and why did you choose them?
- Normalize the spectra and discuss the development of the peaks in the RBM region with respect to each other. Explain the normalization you used.
- Analyse the changes of the peak position for D-, G- and D*-mode.
- Interpret the results including an error discussion.

7 Submission of the lab report

Relevant only for students who do the lab course within the "Fortgeschrittenen-Praktikum" of RWTH Aachen.

Please send the your report with the analysis to following address (written form or by email (use ps- or pdf-format)):

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APPENDIX

A



Fig. 17: *Diameter dependence of the energy difference of the vHS for semiconducting (circles) and metallic (stars) nanotubes (from M.S. Dresselhaus et al., Phys. Rep. 409, 47-99 (2005)).*