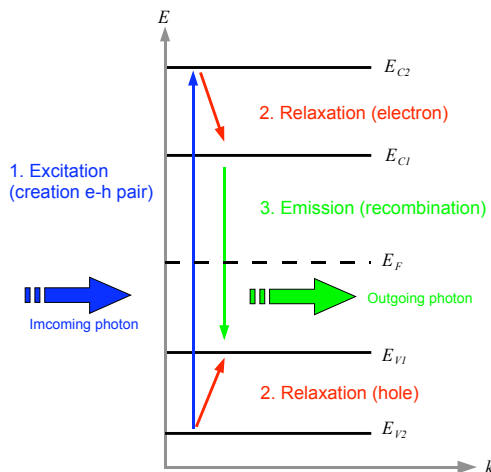


B13 - Photoluminescence on Carbon Nanotubes

1 Overview and goal of the experiment

Photoluminescence is a highly sensitive spectroscopic method to investigate optical transition energies of semiconductors. The term **photoluminescence** describes any process in which light is absorbed, generating an excited state, and then light of lower energy is re-emitted upon relaxation to a ground state. The process for an arbitrary semiconductor is schematically depicted in Fig. 1. An electron is excited from the second **valence band** E_{V2} to the second **conduction band** E_{C2} , creating an **electron-hole pair**. The electron (hole) then relaxes to the first conduction (valence) band E_{C1} (E_{V1}). The electron finally **recombines** radiatively with the hole by emitting light. The properties of the excitation and emission radiation depend on the properties of the material. Applied to low-dimensional materials like Carbon Nanotubes (CNTs), photoluminescence provides an insight into the physics of one-dimensional materials like CNTs.



In this experiment you will learn

- the basics of optical/photoluminescence spectroscopy
- electrical and optical properties of Carbon Nanotubes including the effects of reduced dimensionality
- to evaluate and interpret experimental photoluminescence data

Figure 1: Schematic PL process: 1. an electron-hole pair is created by a photon 2. the electron (hole) relaxes to the lowest conduction band (highest valence band) 3. the electron-hole pair recombines, emitting a photon of lower energy.

2 Carbon Nanotubes

2.1 Introduction

Single-walled carbon nanotubes are the one-dimensional form of carbon. They can exist in various sizes and structures, because graphene - a single layer of graphite - can be wrapped in various ways. One possibility is shown in Fig. 2. Thus, nanotubes properties can be deduced from those of graphene. Nanotubes are uniquely specified by a pair of two integers (n_1, n_2) called chiral index. Depending on the chiral index a tube is metallic, semi-metallic or semi-conducting. Nanotubes have many unique, extreme properties - a self-assembling molecule showing ballistic electron transport, the highest Young's modulus, and the highest thermal conductivity. Carbon nanotubes (CNTs) emit light. Their absorption and emission lines are strongly structured due to singularities in the density of states and exciton formation. Each (n_1, n_2) ¹ tube has a different set of singularities and transition energies. CNTs can have more than one shell: from double-walled (two shells) and triple-walled (three shells) to multi-walled (ten or more shells). Shells are coupled by weak van der Waals forces as for graphene layers in graphite. The properties of multi-shell tubes are determined by the distribution of diameters, chiral indices and the number of walls. As we do not deal with multi-walled tubes in this in experiment, the term carbon nanotube refers to single-walled carbon nanotubes only.

None of the current synthesis methods can produce just one type of tube. The growth product is a mixture of semi-conducting and metallic tubes with various diameters and structures. Nanotubes aggregate into bundles during growth. Bundles differ from single tubes, e.g. they do not emit light. Individual tubes can be obtained by breaking the bundles and dispersing the tubes in micelle-like suspension, where thousand of different tubes are all mixed. Currently, the key challenge for nanotube technology is to select or produce tubes with specific properties. Photoluminescence is a prime tool to reveal the presence of isolated CNTs and to determine which (n_1, n_2) type of semi-conducting CNTs is present in a suspension.

¹In literature the chiral index is sometimes expressed as (n,m) .

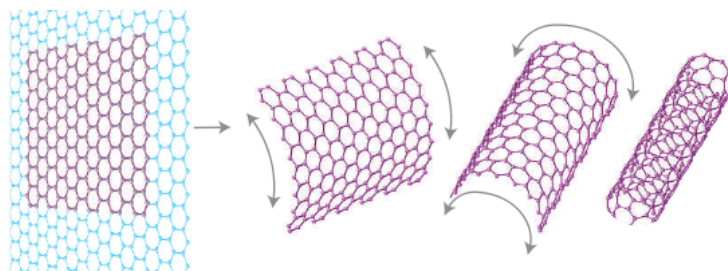


Figure 2: Rolling graphene sheet into a CNT. Graphene is rolled up in such a way that the height of the rectangle transfers into the circumference of the carbon nanotubes whereas its width transforms into the height of the unit cell. Taken from Ref. [1]

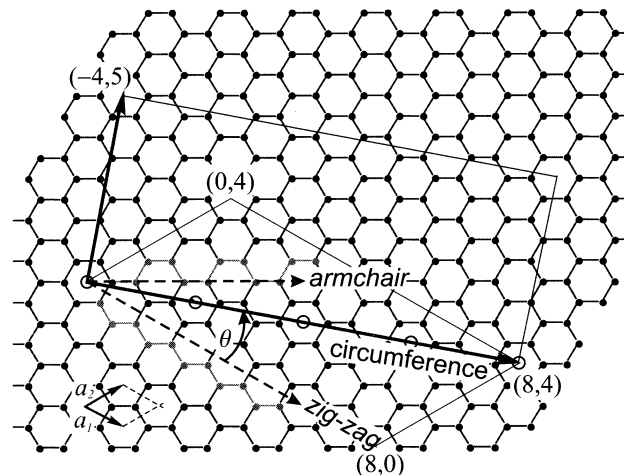


Figure 3: Circumference of an (8,4) nanotube given in term of the graphene lattice vectors \mathbf{a}_1 and \mathbf{a}_2 . Here the height a of the unitcell (\leftrightarrow translational period) is $(-4,5)$. Taken from Ref. [9].

2.2 Structure

The easiest way to describe the microscopic structure of a nanotube is to think about how we can wrap up a sheet of **graphene**. We can do it as it is depicted in Fig. 2. If we role up a different graphene rectangle, we will obtain a CNT with a different structure and different electrical and optical properties. Thus we obtain carbon nanotubes of different microscopic structure and diameter which we call different species. The different species of carbon nanotubes are characterised by their chiral index, a pair of two interger numbers (n_1, n_2) that uniquely defines every type of nanotube. In Fig. 3 a rectangle which defines the unit cell of an (8,4) nanotube is depicted. The circumference c of the CNT is given in terms of the graphene unit vectors \mathbf{a}_1 and \mathbf{a}_2 with the graphene lattice constant $a_0 = |\mathbf{a}_1| = |\mathbf{a}_2| = 2.461 \text{ \AA}$ as

$$\mathbf{c} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2. \quad (1)$$

The **chiral angle** Θ is defined as the angle between \mathbf{a}_1 and \mathbf{c} . CNT with $\Theta = 0$ or 30 are called **zig-zag** or **armchair** tubes, respectively. The diameter of a CNT is defined as

$$d = \frac{|\mathbf{c}|}{\pi} = \frac{a_0}{\pi} \sqrt{n_1^2 + n_1 n_2 + n_2^2}. \quad (2)$$

The height a of the unit cell depends on the circumference and is the shortest graphene lattice vector perpendicular to it. Here lattice vector implies that it starts and ends in the center of a graphene hexagon. For the (8,4) tube the height is given as $\mathbf{a} = -4\mathbf{a}_1 + 5\mathbf{a}_2$. In Fig. 4 the unit cells of three different nanotubes are given. Note that \mathbf{a} is also the **translational period** of the nanotube. The CNT unit cell can be composed of a few atoms (zig-zag, armchair) up to a couple of hundred atoms. For a more detailed description of the CNT structure see Chapter 1.1 of Ref. [2].

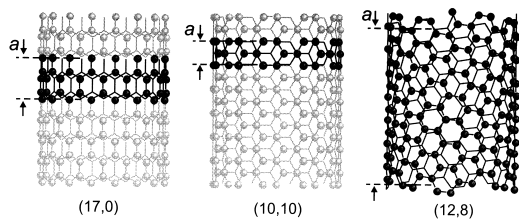


Figure 4: Unit cells of three different CNT. Note that the unit cells of armchair and zigzag tubes comprise significantly less atoms than other tubes. Taken from Ref. [9].

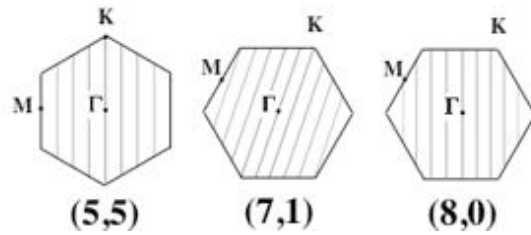


Figure 5: BZ of different tubes The (5,5) tube is metallic (K-point of graphene is allowed state), the other two are semi-conducting. Taken from Ref. [11].

2.3 Electronic properties

For the following we set the nanotube axis to coincide with z-axis ($\mathbf{a} \parallel \mathbf{z}$) and regard the nanotube to be of infinite length. The **reciprocal lattice vector** \mathbf{k}_z then corresponds to a as

$$k_z = \frac{2\pi}{a} \quad (3)$$

As we assumed the nanotube to be of infinite length, \mathbf{k}_z is continuous. The component of the wavevector which corresponds to c needs to satisfy the condition

$$m \cdot \lambda = |c| \quad (4)$$

where m is an integer and λ is the wavelength of the electron wave function along c . Hence m is quantized. Wavevectors that do not fulfill the condition of Eq. 4 vanish due to interference. The value of m is limited by the number of carbon atoms in the unit cell (see chapter 1.2 of Ref. [2] for detailed description). We can determine the allowed components of the wavevector with respect to c by projecting an arbitrary wavevector \mathbf{k} on the circumference using Eq. 4:

$$\mathbf{k}_m = \mathbf{k} \cdot \frac{\mathbf{c}}{|\mathbf{c}|} = \frac{2}{d} \cdot m \quad (5)$$

A wavevector of a CNT therefore consist of a continuous part \mathbf{k}_z as well as a quantized part \mathbf{k}_m (sometimes denoted as \mathbf{k}_\perp). Often the integer m is described as the quasi-angular momentum of the CNT.

Thus, the **Brillouin zone** (BZ) of a CNT consist of lines parallel to the z-axis of the nanotube as depicted in Fig. 5. According to Eq. 5 their distance is $2/d$. Every state \mathbf{k} on one of these lines represents an allowed electronic state of the nanotube. The position on the line is determined by \mathbf{k}_z . The allowed states of the CNT are projected on the electronic structure of graphene. So the energy of every allowed state of the nanotube is given by the position and orientation of the lines relative to the graphene BZ. The line itself is determined by \mathbf{k}_m . Every line belongs to another quasi-angular momentum. In Fig. 6 (b) the bandstructure of a (10, 10) nanotube is depicted. The x-axis refers to different values of \mathbf{k}_z along the lines, which belong to different values of m for the conduction as well as valence bands. The arrows in Fig. 6 indicate how the projection of the allowed states of a CNT on the electronic structure of graphene transforms into the CNT bandstructure. For a more detailed description of these topics read the chapter 1.2 and 1.3 of Ref. [2].

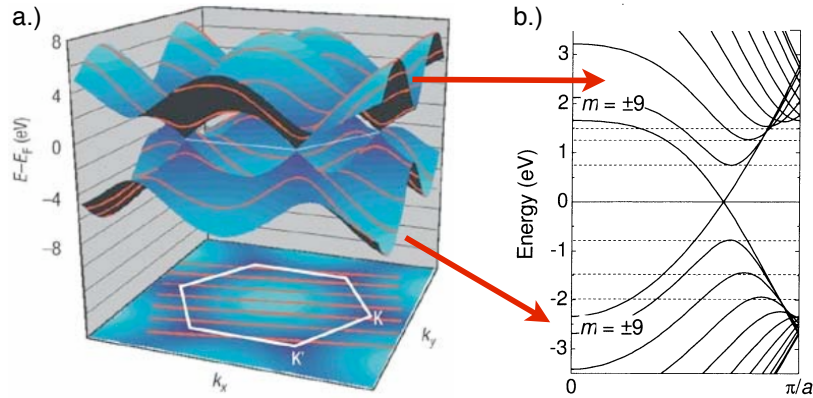


Figure 6: a.) Projection of the allowed states of a CNT (bottom) on the electronic structure of graphene (top). b.) bandstructure of a CNT. The red arrows indicate how the conduction band (upper arrow) and valence (lower arrow) each transform into m different conduction/valence bands of a CNT.

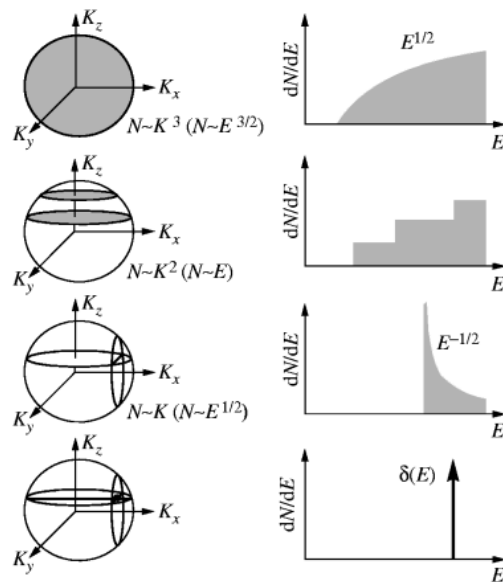


Figure 7: Density of states for an arbitrary three-, two-, one- and zero-dimensional system. On the left the allowed k -states are depicted.

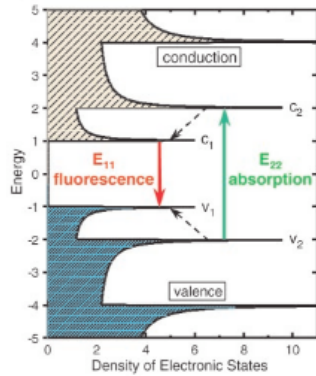


Figure 8: Schematic PL process for a 1D-system in the band-to-band-transition picture.

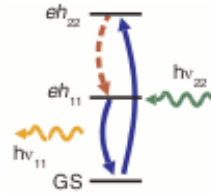


Figure 9: PL process in CNTs in the excitonic picture.

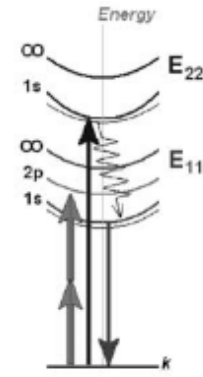


Figure 10: Excitonic subbands labeled according to angular momentum in the excitonic picture.

2.4 Density of states

The electronic density of states $n(E)$ is a measure for the number of states that can be occupied at each energy level. It depends crucially on the dimension of the physical system, as shown in Fig. 7. The density of states (DOS) is schematically depicted for different dimensions, from three dimension down to zero dimensions. Here N is the total number of occupied states. The DOS is given as $n(E) = dN/dE$. A derivation of the density of states can be found in any standard solid state textbook such as Ref. [3].

The DOS determines at which energies a photoluminescence (PL) process can take place. A higher DOS implies a higher probability of a PL process. In Fig. 8 the DOS and the PL transitions are depicted for a one dimensional system like carbon nanotubes. For a detailed description of the density of states in CNT read chapter 1.4 of Ref. [2].

2.5 Excitons

An electron and a hole in a crystal can form a bound state called **exciton**. It is mathematically equivalent to the hydrogen atom. Here the hole replaces the nucleus. The **binding energy** of an exciton in a three-dimensional system is given by

$$E_b = \frac{m^*}{2\epsilon_{cr}^2} Ry \quad (6)$$

where m^* is the **reduced effective mass** of the e-h-pair, ϵ_{cr} is the **dielectric constant** of the material and Ry is the ionization energy of an hydrogen atom ($1 Ry = 13.6 eV$). In a crystal E_b is much smaller than $1 Ry$ as the effective mass of the e-h-pair is low compared to an atom and the Coulomb interaction of the electron and the hole is **screened** by other particles. Typically exciton binding energies are of the order of $\approx 10 - 15 meV$. However, in a one-dimensional system like a carbon nanotube, E_b can have much higher values. This is mainly due to the fact that the screening of the coulomb interaction only applies along the tube axis. Excitonic binding energies up

to 0.4 eV have been reported.

The unbound exciton (= free e-h pair) state still exists in CNTs, but the **oscillator strength** shifts from the free e-h pair to the bound excitons. The process is schematically depicted in Fig. 9. Here $eh22$ denotes the exciton related to the $E_{V2} \rightarrow E_{C2}$ transition and $eh11$ denotes the exciton related to the $E_{V1} \rightarrow E_{C1}$ transition. The excitonic states in fact consist of subbands. Similar to the hydrogen atom, excitons have an angular momentum which effects the energy of the excitonic states. The labeling in Fig. 10 is similar the notation of the hydrogen atom. Here 2∞ refers to the unbound exciton (free e-h pair).

2.6 Selection Rules

According to Chapter 2.4 we expect absorption and emission transmissions to take place at the maxima/minima of the valence/conduction bands (see Fig. 8). The symmetry of the carbon nanotubes imply **optical selection rules** for the optical transitions. Two types of transitions are allowed:

- light polarized along the nanotube ($E \parallel z$) ; hereby the z-component of the angular momentum m is conserved ($\Delta m = 0$). This corresponds to the transitions depicted in Fig.8 as the notation E_{ij} refers to the transition from valence band with $m = j$ to the conduction band with $m = i$ (here $m = i = j$).
- light polarized perpendicular to the tube axis ($E \perp z$): hereby the light induces a change of the z-component of the angular momentum ($\Delta m = \pm 1$). Transitions like this are denoted e.g. E_{12} . Here i and j are restricted as $i = j \pm 1$.

In reality only the first type of transitions takes place. The second type is suppressed due to the antenna effect: the light polarized perpendicular to the tube axis induces charges on the nanotube wall which drastically reduce the external field, so that a second type transition hardly appears.

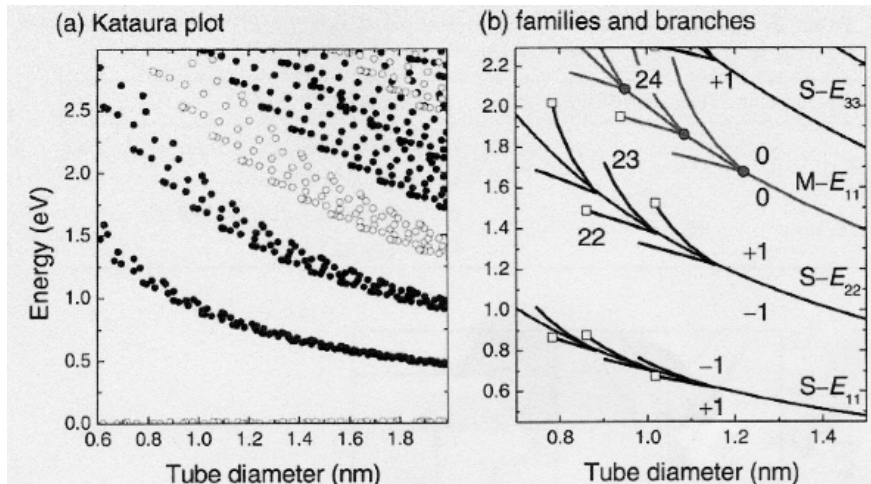


Figure 11: Calculated Kataura plots of the optical transition energies of single-walled carbon nanotubes. The notations in b.) refer **Metallic/Semiconducting** as well as to two types of grouping; if the chiral index (n_1, n_2) fulfills the condition $2n_1 + n_2 = const$, the tubes "sit" on one of the V-shaped branches. Whether they sit on the upper or lower part, depends on whether $n_1 - n_2 \pmod 3 = 1$ or -1 . The behaviour alternates for different optical transitions.

2.7 Kataura Plot

As showed in the previous chapters, structural, electronic and optical properties strongly depend on the chirality of the CNT. Figure 11 shows the dependence of the optical transitions on diameter and chirality. Here the optical transition E_{ii} are plotted versus the diameter of the nanotubes for every chirality (dots, a.) and as a theoretical trend (continuous, b.). These types of plots are called **Kataura plots**. Two features are observable: 1. the transition energies principally show a $1/d$ dependence on the radius. 2. every transition line splits into so-called V-branches. The splitting originates from the electronic structure of graphene. This effect is called the trigonal warping effect which will be briefly discussed in detail in the discussion before the experiment starts. For further details read chapter 2.3 of Ref. [2] or more detailed in Ref. [9, 10].

2.8 Photoluminescence Excitation

In photoluminescence excitation (PLE) a sample is scanned over a large range of excitation and emission wavelengths. As the absorption (E_{22}) and emission (E_{11}) strongly depends on the chirality, every CNT species has a specific combination of E_{22} and E_{11} as a fingerprint. Figure 12 shows a PLE map. High intensities are decoded in red color whereas low intensities are decoded in blue color. Thus, the bright spots each corresponds to CNT of specific chirality. CNT grow as a solid material. For PL measurements the CNTs are debundled, brought in solution and covered with surfactant, which prevents the CNT from rebundling. We use PLE to

- to measure ensembles of nanotubes

- to verify the presence of single-walled carbon nanotubes in a sample.
- to tell which species of semi-conducting single-walled carbon nanotubes are present in the sample (why not for metallic CNT?).
- to tell whether the CNTs occur isolated or in bundles (if they occur in bundles, they do not show photoluminescence due to quenching or shift in energy due to energy transfer processes).
- to investigate the effect of the solution, the surfactant itself or additives on the electrical and optical properties of the CNT.
- to verify the functionalization of nanotubes (e.g. attaching molecules that transfer energy to the tube)

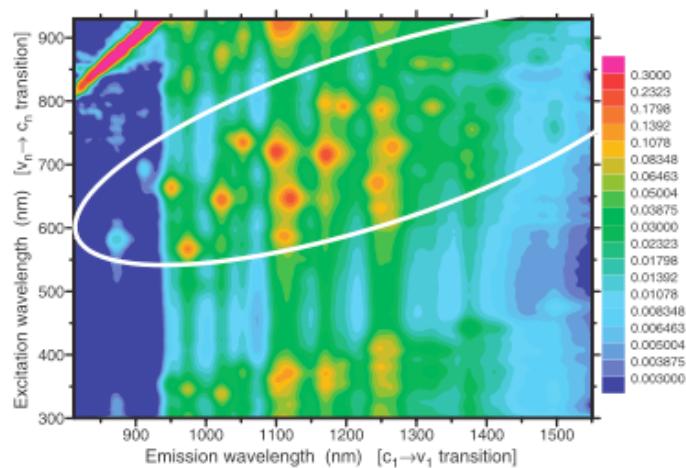


Figure 12: Photoluminescence excitation map. Every bright spot in the white oval corresponds with a specific CNT species. Picture taken from Ref. [4]

3 Photoluminescence spectrometer

3.1 General setup

The *Horiba Jobin Yvon Fluorolog-3 Spectrofluorometer* is a photoluminescence spectrometer that covers a large range of excitation and emission energies. A HgXe lamp produces a continuum of light from the ultraviolet to the near-infrared for sample excitation. Two different detectors are able to cover an emission range from 200nm to 1580nm. Within the excitation spectrometer a pivoted grating combined with two concave mirrors serves as a monochromator. It selects the desired excitation wavelength from the incoming polychromatic radiation produced by the HgXe-Lamp. Gratings with different groove-densities (300, 600 and 1200 grooves per mm) are available. By adjusting the slit-widths it is possible to control the intensity of the light that passes onto the sample. Together with the dispersion of the grating the slit-width also defines the bandpass using the formula: $\text{bandpass (nm)} = \text{slit-width (mm)} \times \text{dispersion (nm/mm)}$. In the sample compartment the excitation radiation hits the sample.

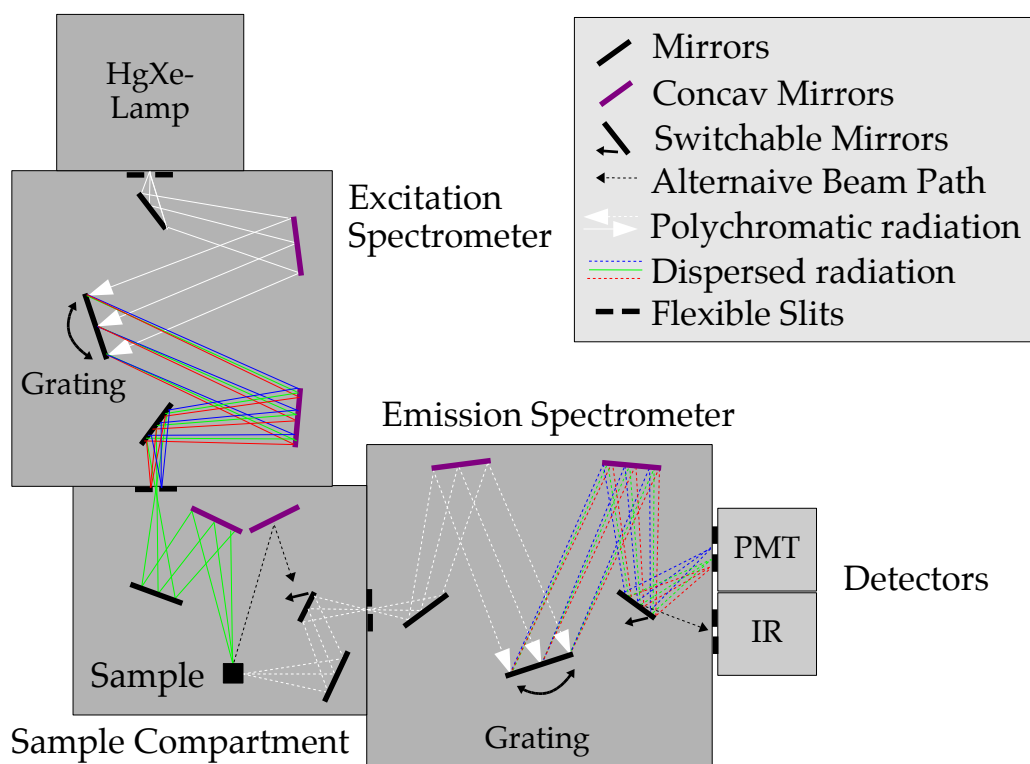


Figure 13: NanoLog. The excitation spectrometer select the excitation wavelength. The sample compartment is interchangeable in order to measure solid samples as well as liquids. Here the bandpass is set to transmit only green light. In the emission spectrometer a monochromator selects the wavelength which is transmitted to one of the detectors. The grating in the emission spectrometer is set to pass the blue part of the luminiscence to the PMT.

The emission from the sample can be collected in two different ways. Either perpendicular to the excitation radiation (see white dashed lines in Fig. 13) which is applied to liquid samples or almost parallel to it (see black dashed arrow). The latter is mainly used for solid samples. A switchable mirror selects the path of the emitted light into emission spectrometer.

Here we find the same configuration as in the excitation spectrometer. The dispersion of the grating and the slit-widths determine the amount of luminescence recorded by the detectors and its resolution. Only one detector can be activated at the time. A photomultiplier tube (PMT) detects luminescence between 200nm and 850nm. In liquid nitrogen cooled InGaAs detector covers the range from 860nm to 1580nm. In order to prevent second or higher order excitation signals, e.g. elastic scattering of a solid sample, different filters can be placed just before the entrance slit of the emission spectrometer.

In order to increase the accuracy of the monochromators, both the spectrometers contain in fact two gratings instead of one. Before exiting the radiation passes another similar set of concave mirrors and a grating. For simplicity those details have been left out of Fig.13.

4 Tasks

Switch on the instrument and fill the camera tank with liquid nitrogen. It takes the camera about 1.5 hours to cool down. The system is completely operated by the computer. The operation software is embedded in Origin software. Name the spectra properly and write down the parameters for each spectrum. **Bring a USB stick in order to store your data.**

There are a couple of experimental parameters to take into account:

- **Type of spectrum:** an *excitation spectrum* detects the signal of the excitation lamp using. An *emission spectrum* detects the emission from a sample at a fixed excitation wavelength. 3D takes several emission spectra at different excitation wavelengths. You can set the range of excitation wavelengths as well as the steps.
- **slidwidths** the slid in the excitation monochromator defines the bandpass and the intensity of the excitation light hitting the sample. The slid in the emission monochromator defines the bandpass of the emitted light and hence the resolution of the spectrometer.
- **time** sets the acquisition time of a spectrum
- **grating** the grating defines the resolution of the obtained spectrum. There are three gratings available for the emission spectrometer. The 150/1200 grating, for instance, has 150 grooves per millimeter and is blazed at 1200nm.
- **detector** there is one detector for excitation (*R*) and two for emission (*T* - visible, *S* - infrared).
- **detector options** *corrected* - the spectrum is corrected by the wavelength-dependent sensitivity of the corresponding detector. *dark offset* - the natural background/offset of the detector is removed.
- **detection angle:** **Front Face** - emission is detected in backscattering configuration; **Right Angle** - emission is detected perpendicular to excitation

Hint: If you are not sure which detector to use, check out the units.

4.1 Excitation spectrum

Take an excitation spectrum of the lamp with the parameters given in the documentation (which you will find next to the experiment) and check the position of the maximum (467 ± 1 nm). Compare the value to the signal intensity in the system log book. Recalibrate if necessary. Take an additional lamp spectrum but this time with a slidwidth of 10 nm (the other parameters stay the same).

4.2 Emission spectrum water

Take emission spectra of the Raman signal of water with parameters given in the documentation and compare the position/ value with the system log. Do this in FF and RA configuration and comment on the results/differences.

4.3 Calibration of grating

Check the calibration of the 150/1200 and 600/1000 gratings: Open the sample compartment (and leave it open) and place a piece of white paper onto the sample holder. Switch on the room lamp and take spectrum at 1014 nm in Real-time mode (RTC) at a slitwidth of 1 nm. Expect the mercury line at 1014 ± 1 nm. Recalibrate if necessary.

4.4 Emission spectra of CNT in solution

Now you are supposed to find the optimal parameters to measure the CNTs. Place the CNT sample in the sample holder. Take several spectra with different varying parameters (slitwidth excitation, slitwidth emission, grating, time, FF and RA configuration). At an excitation of 647nm and an emission range from 860 nm to 1560 nm. Enable the options "dark offset" and "corrected". Which grating is more suitable for further measurements and why? Use filters if necessary to block first order elastic scattering. Once you found the optimal parameters, go on to 4.7 and generate a PLE map. Discuss and justify the parameters you found.

4.5 Photoluminescence excitation map

Take a 3D spectrum in order to generate a photoluminescence excitation map as in [4]. Expect signals of CNTs to appear between 500nm and 850nm in excitation (see Fig 12). Take the emission range and the experimental parameters (step-size in acquisition, slitwidth, acquisition time, filters, etc.) you found in Sec. 4.4.

4.6 Data Evaluation

- Find the chiralities present in the sample by assigning peaks in the PLE map to the according chirality. Transform the values for excitation (E_{22}) and emission (E_{11}) from nanometers to eV and compare with the values given in Ref. [4]. Discuss possible deviations. Plot the PLE map (Origin: ContourPlot) in nanometers and mark the peaks you assigned.
- Plot E_{22} and E_{11} in eV versus the CNT diameter in one plot. Comment on the result.
- Plot PLE spectra (fixed emission versus excitation) and correct by the lamp intensity. Compare the corrected and uncorrected PLE spectra for an emission wavelength of 950 nm. Comment on the difference. Repeat the comparison for

emissions of 1120, 1200, 1260 nm. Discuss, which kind of information can be obtained from the data without lamp correction. For which kind of information is necessary to correct for the lamp?

- **Voluntarily:** correct the whole PLE map the the lamp intensity.

4.7 Density of states

The calculation of the electronic density of states of a free electron gas for 3D crystals can be found in several solid state text books. Calculate the electronic density of states for a free electron gas in three dimensions. Do the same for two and one dimension. Now explain the shape of the DOS in Fig. 7 as you adapt your calculation to real crystals (bands!).

4.8 PL on a isolated CNT

How would you would set up an experiment which has to detect the photoluminescence signal of a single, isolated carbon nanotubes? Imagine a single nanotube laying flat on a neutral surface. Here neutral means that the nanotube and its properties are not influenced by the substrate. Can you use the same source of light? If not, why? Can you use the same optical set up for excitation/emission? Draw the schematic setup of your experiment and explain the function of the components. Discuss the effect of selection rules (chapter 2.2 of [2]). Will a PL signal of an isolated CNT differ from the ensemble signal? **Do NOT include this in the experimental protocol. You will present your idea in the discussion of the protocol.**

5 How to do the analysis

In general it is recommended to use Origin software to do the analysis as the measured data are stored in an origin project, nevertheless your are free to use any appropriate software. In Origin an PLE map is a Contourplot, generated from a matrix. Thus you have to transform the spectral data into a matrix before generating the contour plot. A short introduction to Origin will be given during the experiment. The protocol should be written in Tex. In addition to the printed version, send a pdf with coloured plots/maps to the adviser of the experiment by email. Name it FP09_B13_GB99.pdf and replaces 99 by your group number.

6 Concepts to know and literature

You should know the terms printed in **bold** as well as the following terms:

diffraction, grating, blazed grating, monochromator, basid solid state physics.

Some standard solid-state textbooks such as *Kopitzki*, *Kittel* or *Ibach-Lüth* are good for refreshing solid state physics. A very good introduction into the experiment and

a more detailed description is the Bachelor thesis of B.Hatting [2]. A deeper analysis of Photoluminescence on CNTs is given in the article of J. Lefebvre [5]. An introduction to excitons in nanoscale systems is given in Ref. [6]. It comprises a general introduction as well as a paragraph on CNT. Further, there is a quite specific paper by S. Reich *et al.* that explains why some CNT species do not show luminescence [7]. The first discovery on CNTs has been published by Iijima in 1991 [8].

A copy of this manual, the documentation, the literature and the manual of the spectrometer will be next to the experiment.

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