12 Carbon Nanotubes - script

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1 How to use this script

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.

1.1 Compendium

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

1.2 Literature

Basics:

For deeper understanding:
2 Raman spectroscopy of carbon nanotubes

2.1 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. Inelastic scattering, 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 \(|b\rangle\) absorbs 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)).

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 \( 10^5 \text{cm}^{-1} \) for the visual spectrum, compared to size of the Brillouin zone only phonons close to the \( \Gamma \) 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
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 $\alpha$ 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

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

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

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

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

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.

### 2.2 Carbon Nanotubes

A carbon nanotube 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 chiral vector $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$ 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 chirality is often given as angle $\phi$ 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 \( k_n \) 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 \( \text{mod}[(n - m), 3] = 0 \).

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 \( \text{mod}[(n - m), 3] = 1, 2 \).

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 $k_{||}$ (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.

2.3 Raman spectrum of carbon nanotubes

Fig. 7 shows a typical Raman spectrum of carbon nanotubes. The radial breathing modes (RBMs) have the smallest Raman shift. It is followed by the disorder induced defect D-mode and the G-mode (the latter also called high energy mode (HEM)). The ratio of their intensities is often used to determine the purity of a sample. The $D^*$-mode 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 first order Raman effects, while the defect modes are second order Raman effects.

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 ??).

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

2.3.1 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 $\Gamma_{RBM} = 8 \text{ meV}$.

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:

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

(5)

The parameters $A$ and $B$ depend on the environment. For isolated nanotubes on a silicon oxide surface they are $A = 248 \text{ cm}^{-1}$ 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 $A = 234 \text{ cm}^{-1}$ and $B = 10$. 
2.3.2 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. It has its origin in longitudinal optical (LO) phonons, while the second peak, $G^-$, correlates to transversal optical (TO) phonons. The mode assignment is opposite for metallic tubes. The peak corresponding to the LO phonons is independent of the tube diameter, while the position of the peak assigned to the TO phonons 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.](image)

2.3.3 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.

3 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 Michelson interferometer (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

3.1 The interference pattern

The spectrum of a sample is not taken directly in an FT-spectrometer. Instead, an interference pattern is measured, from which the spectrum is calculated using Fourier transformation. 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 $\pi$ 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.

### 3.2 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 $S(\nu)$ as function of the wave number $\nu = \lambda^{-1}$ of the light are a Fourier transformation pair:

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

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

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

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

The points calculated in frequency space have the distance:

$$\Delta \nu = \frac{1}{N\Delta x} \quad (9)$$

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.

#### 3.2.1 Apodization

Due to the finite length of the measured interference pattern, the Fourier transformation can create artefacts. The interference pattern truncated at $x=x_{\text{max}}$ can be described as product of an infinit interference pattern and a rectangular function. The rectangular function is 1 for $0 \leq x \leq x_{\text{max}}$ 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 apodization 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.

### 3.2.2 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.
Fig. 13: 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)).