Physikalisches Fortgeschrittenenpraktikum
an der Universität Konstanz

Raman spectroscopy

1 Learning targets

After working on the Raman experiment you will be able to express the fundamentals of molecular vibrations and rotations, calibrate and use an USB spectrometer and deduce specific vibration patterns from the spectra you acquired.

2 Safety precautions

You are working with a **class 4 laser** which is dangerous for your eyes and your skin. It can ignite inflammable materials. The experiment is safe for you and your surroundings as long as you pay attention to the following rules:

- **Always** wear the appropriate <u>laser safety protection goggles</u> (532 nm blocked)
- Make sure **everyone else** is also protected from the beam and the stray light
- Switch on the <u>laser notification signal</u> outside the door to warn people entering the room
- Do not wear any reflective clothes, watches or jewelry
- Do not remove any blinds which screen the laser beam
- Do not insert anything into the laser beam
- Switch off the laser before changing the setup
- Switch off the laser if you do not need it for a longer period of time (e.g during a break)

You are also working with several liquids (listed later on) that are hazardous to health and/or flammable. Information, especially regarding toxicity on the different substances, can be found e.g. in the 'gestis substance database' (http://www.dguv.de/ifa/de/gestis/stoffdb/index.jsp). The liquids are well encapsulated in a glass tube. If – for any reason – a tube breaks:

- Make sure the ventilation is on, most substances vaporize easily
- Leave the room, if possible switch off the laser
- Make sure everyone else also leaves the room and no one enters
- Inform your supervising tutor what happened

Any violation of these rules may lead to an abortion of the experiment

If you are unsure at any point do not hesitate to ask your supervising tutor.

Please do not hesitate to advice anyone of these rules who contradicts them.

3 Applications of Raman spectroscopy: what is it good for?

- Structure determination of solids, liquids and gases in chemistry and biology
- Biomedical applications (skin and eye studies, cancer identification, dental examinations)
- Biotechnology and Pharmaceutics (Crystallization monitoring, high-throughput screening, fermentation)
- Forensics (identification of drugs, explosives, paints, inks, fibers)
- Nanotechnology (identification of carbon structures like fullerenes, nanotubes, graphene)
- Semiconductor industries (stress and defects in semiconductors)
- Polymers (reaction control, material identification)
- Ecology (plastics waste sorting, water pollution detection)
- Geology (identification of minerals by their crystalline structure)

4 Equipment

- Spectrometer Ocean Optics USB 4000, no entrance slit, fiber patch cable 25 µm, wavelength range 480 – 670 nm, Spectrasuite software (more information on the experiment's homepage)
- Semrock Notch filter 532 nm
- Nd:YAG Laser 532 nm, approx. 500 mW
- A helium gas and a mercury vapor discharge lamp as well as a thermal light source
- Glass tubes with different sample groups: Chloromethanes (CCl_4, $CHCl_3$ & $CDCl_3$, CH_2Cl_2), Carbon rings (C_6H_6 Benzene, C_6H_{12} Cyclohexane, $C_6H_5NO_2$ Nitrobenzene), Sulfur powder, ethanol

5 Preparation

After your successful preparation for the experiment you will be able to discuss the listed topics during the preexam. It is also recommended to have a closer look on the chemicals under investigation.

- Principles of Compton scattering (short), Rayleigh scattering and Raman scattering
- Rotational and vibrational Raman effect
- Differences to UV-Vis spectroscopy and IR spectroscopy
- Intensity ratio of Stokes and anti-Stokes lines
- Dipole moment and polarisability tensor
- Polarization of Raman lines
- Selection rules for Raman transitions
- Normal oscillation modes of molecules
- Vibrational energy and frequency of harmonic and anharmonic oscillators
- Diode pumped solid state (DPSS) Nd:YAG laser
- Czerny-Turner spectrometer
- Charge Coupled Devices (CCD)

6 Experiments

A good preparation for the actual experiment is a measurement schedule. Think in advance what are the important characteristics for the reconstruction of your measurements and what data do you need for the analysis of these measurements. The experiments proposed in the following section are suggestions but not necessarily complete! Feel free to explore the Raman spectroscopy on your own.

Part 1: Experimental setup

a. Dark signal
   o With no light input into the spectrometer there is already a non-zero signal. Where does it come from? (Note that different sources are present.)
   o What are its temporal and spectral characteristics? Does it average out?
   o How can you actually improve your signal quality for later measurements?
   o Are there any general improvements possible?

b. Calibration
   o Are you sure about the wavelength shown by the spectrometer?
   o Are there appropriate light sources in the lab which help you checking the calibration?
   o Describe the characteristics of the available light sources.
   o What functional relationship do you find between the wavelength and the pixel index?
   o Calibrate the spectrometer if necessary.

c. Resolution
   o What is the spectral width of the lines used for calibration?
   o What factors determine the line width, which limits it in this case?
   o Which wavelength difference is required so that two lines can be resolved?
   o What is the resolution of the used spectrometer?
   o Think about a way for changing (of course improving) the spectral resolution

d. Quantitative analysis
   o What about the linearity of the spectrometer? Doubled time = doubled signal?
   o How does the count rate depend on the integrated light intensity?
   o Why does the signal saturate? At which level? Have a look at the USB 4000's datasheet.
   o What happens if the signal exceeds the saturation and is this a problem?
   o Have a closer look at the line width in saturation. Is the broadening symmetric and why?

e. Polarization
   o Why is a polarization filter included in the beam path?
   o Does it have an influence on the calibration?
   o How is the 'Zero'-polarization defined?
   o Which error results, if the filter is misaligned by several degrees?

f. Notch filter
   o Why is a notch filter used in the experiment?
   o Which properties does it have?
   o How does the transmission curve look like? Is the transmittance flat?
   o Can you measure at least roughly a transmission curve?
   o What happens if the filter is tilted? Write down the changes, you might need them.

Part 2: Sample properties

a. Measure and compare the spectra of the chloromethanes CCl_4, $CHCl_3$, $CDCl_3$ and CH_2Cl_2.
   o Have you really found every observable line?
   o Can you find lines which are common in some of the spectra?
   o Which lines are moving or splitting?
   o Which lines are polarization-dependent? What kind of lines are totally polarized? Derive the polarization ratios for the individual lines!
   o Assign the lines to the different vibrational modes in the molecules, a graphical representation of the molecule may help.
   o Is the sequence of vibration types systematic?
   o Do calculations based on the harmonic oscillator model deliver the vibrational energies you measured? Have a closer look on the different chloroform samples.

b. Measure and compare the spectra of the carbon rings C_6H_6, C_6H_{12}, and $C_6H_5NO_2$
   o How do the molecules look like?
   o Do the spectra reflect the structure of the molecules? Discuss your results including the polarization ratio.
   o Which are the most prominent lines (polarization!) and how does the corresponding vibrational mode look like? A graphical representation of the molecule may help.
   o Are there basic similarities between the spectra, maybe shifted lines?
   o Which influence has the bonding character?
   o What is the most intense line and why is it that strong?

c. Measure a spectrum of sulfur
   o Can you extract the temperature of the sulfur sample from the spectrum using the Raman effect?
   o Which lines can be used? Which lines yield the best result?
   o Give an estimation of the accuracy and certainty of the measurement.
   o Normally the determined temperature is systematically too high. Can you think of an explanation for it?
   o (Do you see different temperatures with changing laser intensities (stay cool!)?)

d. Find out the concentration of ethanol in an unknown ethanol-water mixture. Pure ethanol and water are provided, as well as tools for mixing and a few empty glass tubes.
   o Measure pure ethanol and pure water to find a suitable line(s) for quantification.
   o Measure the sample with unknown concentration of a commercial alcoholic beverage.
   o Measure a dilution series of ethanol in water. Which range is suitable?
   o What is the minimal ethanol concentration you were able to detect? Try it out.
   o What concentration has the given sample?
   o What about the accuracy of this method? Discuss and quantify possible sources of error.

e. Identify an unknown liquid using its Raman spectrum
   o Measure the sample as detailed as possible; information about the polarization may help
   o Different chemical bonds and groups feature characteristic lines. Search for similarities. Narrow down the possible substances and – in the end – compare the spectra directly.

Part 3: Fundamental questions (after the experiment)

a. Which exact wavelength had the laser? Where can it be deduced from?

b. In practice, different lasers are used in Raman spectroscopy. Can you explain why and what differs in the results?

c. It is known that the perfectly covalent bonded hydrogen molecule has a vibrational frequency of about 4160 cm^{-1}. In a molecule consisting of heavier atoms (n protons) the core electrons (n-1) shield the core charge so that it appears as single charged hydrogen like core and the bond strength may be approximated by the H-H bond. Based on these assumptions, can you calculate the approximate frequencies of D-D, S-S and common organic bonds such as C-C, C-H, C-O, O-H? What about other compounds such as molecular oxygen or nitrogen? Compare your results to reference data. You could need them to identify the different lines occurring in the experiment. What causes the discrepancies between observed frequencies and the calculated frequencies?

d. Describe and discuss differences between UV-Vis spectroscopy, fluorescence spectroscopy, IR and Raman spectroscopy. Compare the excitation wavelengths, the excited processes, the type of the measured signal, etc. Name an application where Raman spectroscopy is superior to others.

7 Literature suggestions

- Extended spectra collections can be found under Signature che 308 in N library
- Ferraro, J.R. and Nakamoto, K.: Introductory Raman spectroscopy, Academic Press, 1994. UniKon signature: che 308/f27a
- Brandmüller, J. and Moser, H.: Einführung in die Ramanspektroskopie, Steinkopff, 1962. UniKon signature: che 308:n/b71, lbs 780/b70, phy 423/b71