Raman Spectroscopy

PC/AC Lab course, UNIST, 2018 -- Thomas Schultz

Course content

In this course, you will set up a spectroscopic experiment for the measurement of vibrational Raman spectra, you will measure spectra for an unknown compound, and you will identify the compound based on your measured spectra. Make sure you understand the practical and theoretical aspects of Raman spectroscopy before entering the lab.

The learning goals of this lab course are:

(1) Learn to build and use a spectroscopic instrument.
(2) Measure, analyze and interpret spectroscopic data.
(3) Present your knowledge, write a report.

Introduction

When electromagnetic radiation (light) interacts with matter, it may be absorbed, reflected, or scattered. Spectroscopic experiments investigate this interaction and almost all of our understanding about molecular properties and structure originated from spectroscopic experiments. Modern spectroscopy is an important tool to identify known compounds or analyze properties of unknown compounds.

Raman spectroscopy is based on the inelastic scattering of light in molecules (cf. Fig. 1). In a scattering process, light photons can change their direction and/or impulse. This is different from absorption spectroscopy, where a photon is either absorbed or not absorbed. In an inelastic scattering process, energy is exchanged between the scattered particles. Because molecules can only absorb or emit discrete (quantized) amounts of energy, the scattered *Raman light* is different for each molecular species and therefore helps to identify and characterize molecular samples. Raman spectroscopy was named after C. V. Raman, who discovered the Raman effect in 1928.

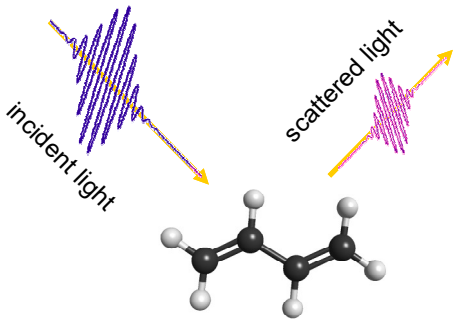

Fig 1: Inelastic scattering: The incident and scattered photons have different momenta and energy.

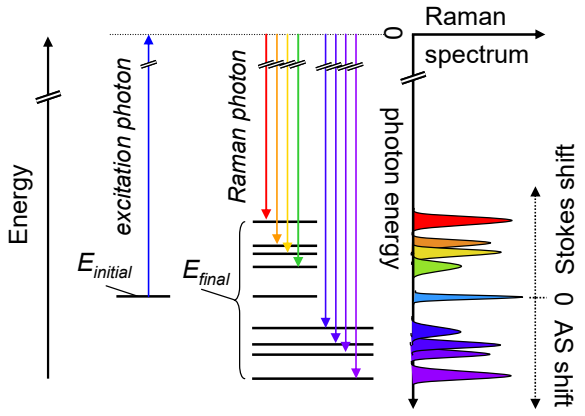

Fig 2: Energy scheme for Raman spectroscopy. An excitation photon (blue) is scattered and produces Stokes photons of lower energy (green-red) or anti-Stokes photons of higher energy (blue-purple).

The shift between the incoming and outgoing photon energy is called *Raman shift*. The Raman process may deposit energy in the molecule (Stokes transition, cf. Fig. 2) or remove energy from the molecule (anti-Stokes transition). The Raman shift (difference between incident and Raman photon energy) must be calculated after measuring the Raman light wavelength. This shift is often given in the pseudo-energy unit of wavenumbers $\Delta\omega$ (in units of cm^{-1}): $\Delta\omega = (1/\lambda_{incident} - 1/\lambda_{Raman})$. Measured Raman shifts directly correspond to relative molecular energy levels.

Raman spectroscopy relies on a second order interaction: the electromagnetic field first polarizes a molecule with polarizability α, and then interacts with the induced dipole D. The strength of a Raman transition S is therefore proportional to the second order of the light power P: $D \sim P \cdot \alpha$; $S = P \cdot D \sim P^2$. As a result, the intensity of Raman signal is very small as compared to the excitation light intensity and a very high excitation light intensity is required to generate any detectable Raman signal. Lasers can be focussed to very small spot sizes, greatly increasing the power of the light beam in a small spot. This greatly facilitates the experimental observation of Raman signals.

Vibrational Raman Spectroscopy

In vibrational Raman spectroscopy, the energy difference between incoming and outgoing photon corresponds to exactly one (or multiple) quantum of vibrational energy (cf. Fig. 3). Because vibrational modes are harmonic and have evenly spaced energy levels between neighbouring quantum numbers ν, the signals for all transitions $v \rightarrow v+1$ coincide. We therefore expect only one Raman band for each vibrational mode.

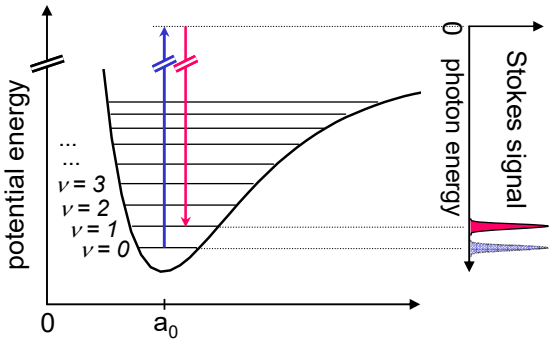

Fig. 3: Energy scheme for vibrational Raman spectroscopy: The photon energy difference corresponds to a vibrational energy quantum.

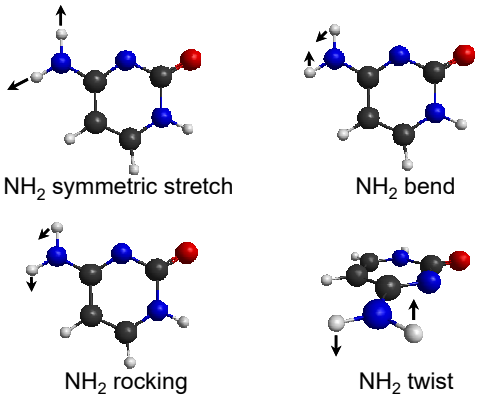

Fig. 4: Some vibrational modes of Cytosine

A non-linear molecule has *3N-6* vibrational degrees of freedom. Not all vibrational modes are Raman active and we cannot expect to see Raman signals for every molecular vibration. Only vibrations along molecular coordinates that affect the molecular polarizability α can be observed (Fig. 5). Raman spectroscopy and IR absorption spectroscopy are complementary: Raman spectroscopy allows to observe most IR inactive vibrational modes.

At room temperature, most molecules are in their vibrational ground state and the anti-Stokes process is very weak. The Stokes photons in the Stokes signal contain less energy than the incoming photons (cf. Fig. 2). This energy difference can be measured as a wavelength difference between excitation- and Stokes- light using a spectrometer. To avoid an overlap of the excitation and Raman wavelength, we require a very monochromatic source of excitation light.

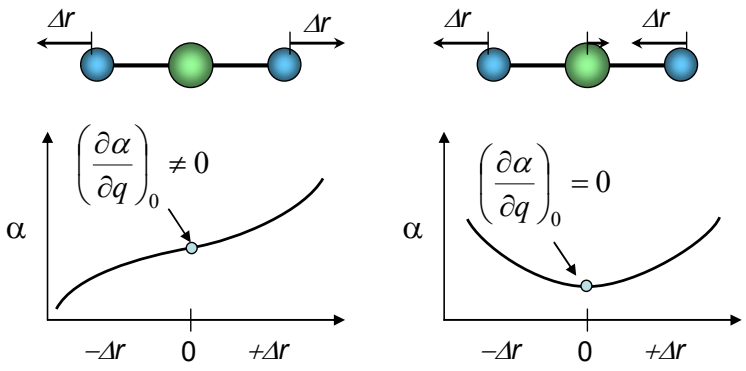

Fig. 5: Example for a Raman active vibration (left) that affects the molecular polarizability α, and a Raman inactive vibration (right).

Raman Spectroscopy Set-Up

To acquire Raman spectra, we need a light source for excitation light, an optical system to generate Raman signal in a sample, an optical system to collect the Raman light, and a spectrometer to analyze the Raman light.

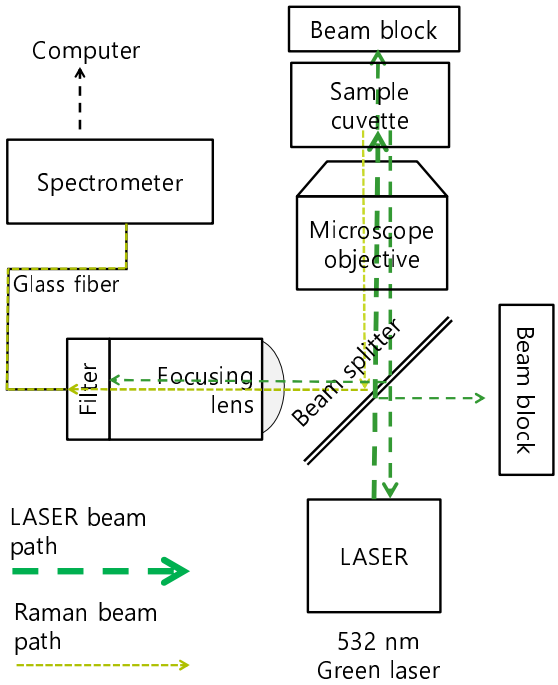

Fig. 6: Experimental set-up for Raman spectroscopy. Laser light is focussed into a sample with a microscope objective. The Raman signal is collimated by the objective and guided into a fiber spectrometer.

We use a laser modules with approx. 532 nm (green) and 638 nm (red) weavelength as excitation light sources. Lasers are monochromatic and can be focussed to very high intensities and are therefore best suited for this type of experiment.

In a first spectrometer set-up (Fig. 6), the laser is focussed by a microscope objective into a sample cuvette. The resulting focus is very small and has the required high intensity to generate detectable amounts of Raman signal.

The Raman signal is collected in a back-scattering geometry by the microscope objective mentioned above. A beam splitter (Semrock FF535-SDi01, reflectivity >95% at >539 nm, transmittivity >90% at 532 nm) reflects the Raman signal towards the spectrometer but transmits most of the scattered 532 nm laser light.

The Raman light is focussed with a lens onto the entrance of a fiber spectrometer. An additional cut-off filter (Omega Optical 538ALP) removes residual 532 nm laser light, but transmits the Raman signal with wavelengh >539 nm. The spectrometer (Brolight BIM-6 or Thorlabs CCS100) analyzes the wavelength-dependent spectrum and transmits the data onto a computer for further analysis.

A second Raman spectrometer set-up (Fig. 7) uses a red 538 nm laser module. The optical set-up is based on a different beamsplitter (Semrock FF649-Di01, reflectivity >98% at <642 nm, transmittivity >90% at >654 nm) and filter (Omega Optical 648 ALP), but is functionally equivalent to the spectrometer described above.

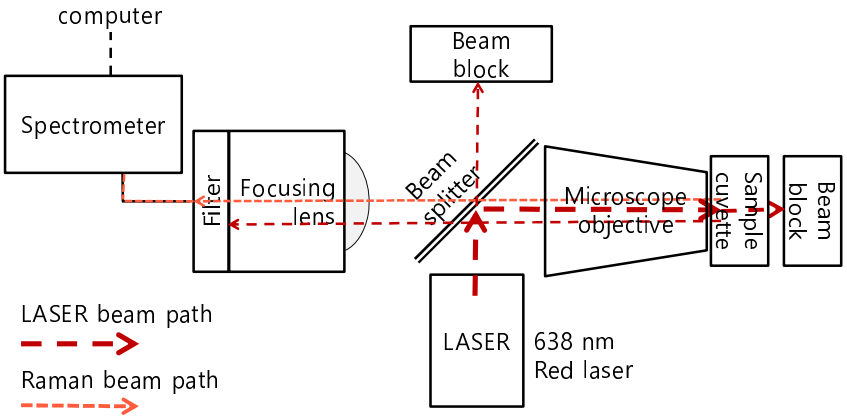

Fig. 7: Experimental set-up for Raman spectroscopy. Laser light is focussed into a sample with a microscope objective. The Raman signal is collimated by the objective and guided into a fiber spectrometer.

You will assemble one of these Raman spectrometers in the laboratory. To succeed, you must understand the measurement principle of Raman spectroscopy and you must understand the role of every optical element in the spectrometer set-up. Please ask questions in the presentation session if anything remains unclear.

Safety Considerations

In this lab course, you will work with class 3B laser modules that can cause lasting damage to your eyes. You need to follow several safety rules to protect yourselves and your colleagues:

(1) Never look directly into the laser beam.

(2) Keep all laser beams parallel to the laser table and at a height well-below eye-level. Keep the laser beam within the pre-defined alignment boundaries and ensure that every laser reflection is caught by a beam-block. Never bend down so that your eyes are at a height with the laser beam.

(3) Only adjust the laser direction if you and exposed colleagues wear laser goggles.

(4) Remove watches, jewelry, and other objects that could reflect the laser beam.

Spectroscopic Experiment

The Raman spectroscopy set-up will be used to measure Raman spectra of common organic chemicals. Each student will measure the spectrum of a different unknown compound and assign characteristic IR frequencies in the acquired spectrum. The compound should then be assigned based on identified chemical groups and by comparison to literature spectra or calculated data. To help your assignment, you can find an IR correlation table for common organic groups at the CRASY website: http://crasy.org/WP/archives/1080-08-2016-xk3.

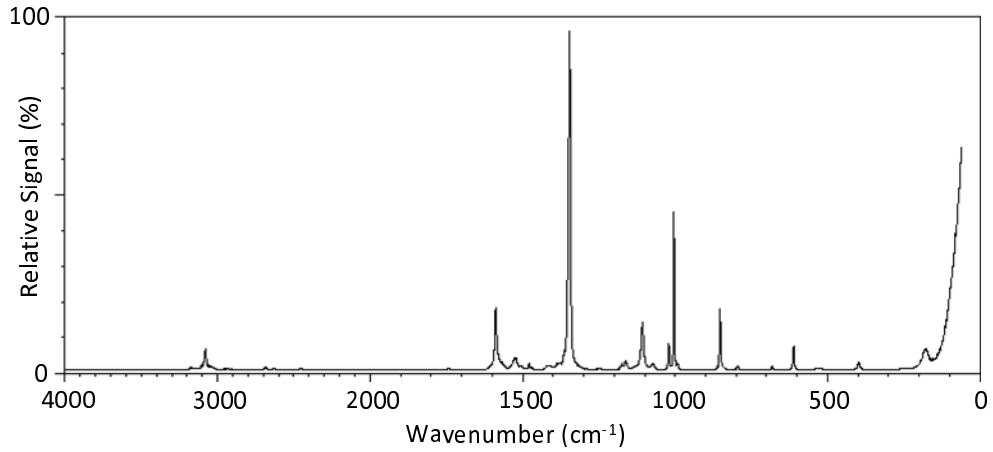

Fig. 8: Vibrational Raman spectrum for nitrobenzene. Note the characteristic aromatic C-H stretch (>3000 cm^{-1}) and N=O stretch (1500-1600 cm^{-1} and 1345-1385 cm^{-1}) frequencies. (Spectrum from SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 30-8-2016)

Writing a Report

You have to submit a report describing your experiment and the experimental results in <4 pages of English text and figures. I summarized some tips on writing and links to further information at: *http://crasy.org/WP/archives/1087-08-2016-xk3*. Please use the linked ACS article template for your report and set the line spacing to Double-Space. For style and structure, please follow the guidelines of the American Physical Society and maybe refer to the cheat sheet for writing a scientific manuscript.

Test your understanding about Raman spectroscopy with the following comprehension questions:

(1) Explain the difference between light scattering and light absorption.

(2) Why is the anti-Stokes transition much weaker than the Stokes transition?

(3) What is monochromatic light and why is it required for Raman spectroscopy?

(4) Give an example for a Raman-active and -inactive mode.

(5) What is the function of the beam splitter and the filter in the Raman set-up?

(6) Why is the wavenumber a pseudo-energy unit? How could you convert this unit into a true energy unit? Give an example.