

A56

Raman Spektroskopie

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1 Objectives

1. Take the Raman spectra of $\text{CO}_2(\text{s})$, $\text{CS}_2(\text{l})$, $\text{C}_6\text{H}_6(\text{l})$ and $\text{C}_6\text{D}_6(\text{l})$,
2. Determine Raman active vibrations and assign them to the respective modes,
3. Determine force constants of C=O- and C=S-bonds,
4. Comparison of C_6H_6 and C_6D_6 .

2 Hints for the risk assessment

Organize your risk assessment according to:

1. Handling of the laser of the Raman spectrometer (class 3A),
2. Handling of solid CO_2 (dry ice),
3. What has to be done if one of the cuvettes breaks that encloses CS_2 or benzene?

Distinguish according to:

1. Organisational and administrative protections,
2. Technical protections and
3. Personal protective equipment.

3 Theory and basics

Raman spectroscopy provides insight into vibrational and rotational states of molecules. It is complementary to infrared absorption spectroscopy (FTIR). Today, both methods are relatively inexpensive and they can be used as routine analytic method. Excitation of the sample, selection rules and physical basics are, however, different.

3.1 The Raman effect

If a molecule is irradiated with light of frequency ν_L ,¹ one can expect in principle three different processes:

1. *No interactions at all*: the major part of light runs through the sample without interaction if photons can not be absorbed resonantly.
2. *Elastic scattering, Rayleigh scattering*: a small portion of light is scattered in all spatial directions elastically: $\tilde{\nu}_{\text{Rayleigh}} = \tilde{\nu}_L$. Rayleigh scattering depends on the average molecular polarizability and is proportional to $\tilde{\nu}_L^4$! Blue light is scattered more strongly than red light ($\Rightarrow$ where is that important in daily life?). $\Leftarrow$
3. *Inelastic scattering, Raman scattering*: an even smaller portion of light is scattered inelastically. The frequency can be shifted to higher and/or lower values. This frequency shifted light is called *Raman scattering*, the subject of this experiment.

The molecular scattering of light can be envisaged in a simplified classical picture as follows: the incoming electromagnetic wave is an oscillating electrical field that interacts with the charges of the molecule. The electron cloud is displaced temporarily and spatially. Moving charges act as sources for electromagnetic waves which radiate nearly uniformly in all spatial directions. Why these waves are scattered elastically or inelastically can not be explained in this simple picture.

Hence, the scattering process has to be interpreted quantum-mechanically: the incoming photon excites the molecule to a virtual state. This *virtual* state is not a solution of the stationary Schrödinger equation of the molecule. Nevertheless, there is a final probability for the excitation of this state because it has a final life time ($\Rightarrow$ Why? How can you estimate this life time?). $\Leftarrow$

From this short-lived virtual state the molecule can relax in different ways (see therefore Fig. 1). Most often it relaxes elastically into the starting state (Rayleigh scattering). The emitted light is not shifted in frequency.

The process that is of interest here is inelastic scattering. One distinguishes between *Stokes* Raman scattering and *anti-Stokes* Raman scattering.

• Stokes-Raman scattering

The final state lies above the initial state (red arrows in Fig. 1). The scattered photon has a lower energy in comparison to the exciting one. The energy difference corresponds to the difference between two stationary quantum states of the molecule. These could be rotational states and/or vibrational states.

$$\frac{\Delta E_{\text{molecule}}}{hc} = \tilde{\nu}_L - \tilde{\nu}_{\text{Stokes}} \quad (1)$$

¹Instead of the frequency ν_L we use in the following the wave number $\tilde{\nu}_L$. Both quantities are proportional to the photon energy. With the vacuum speed of light c it holds: $\nu_0 = c \cdot \tilde{\nu}_0$

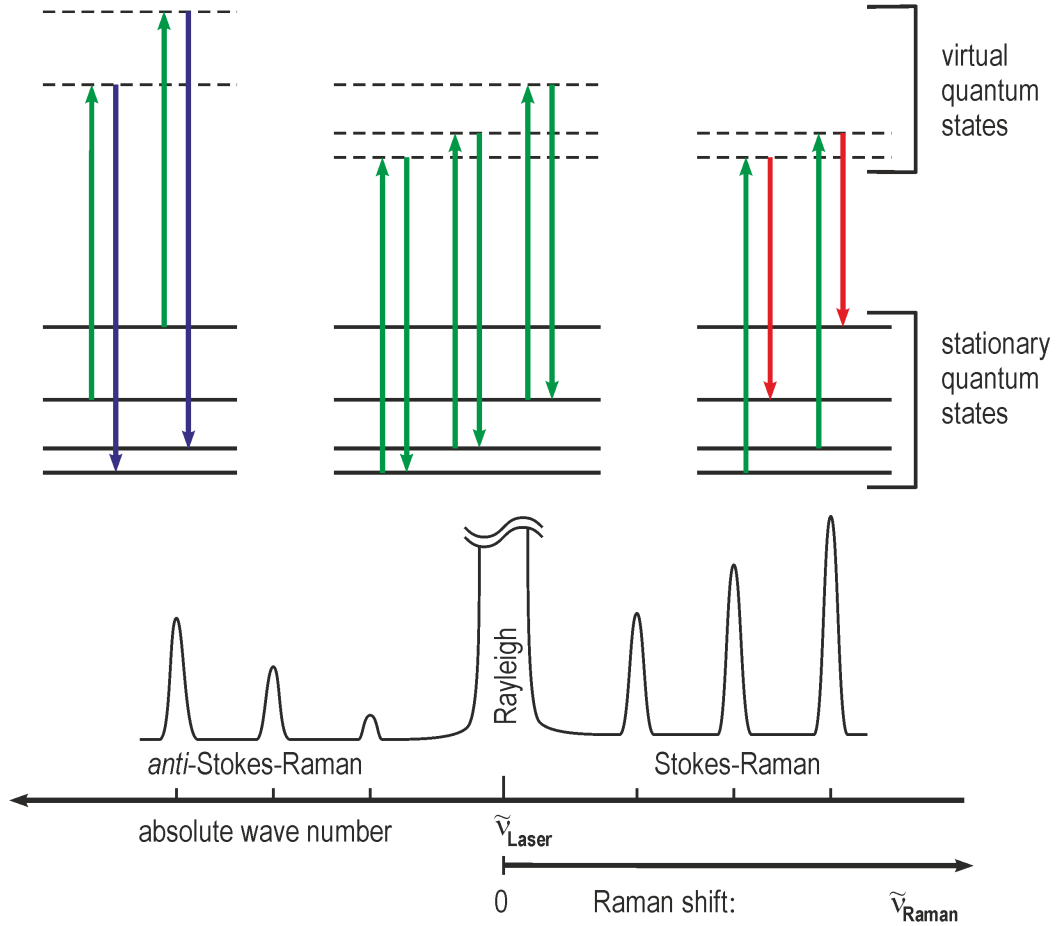


Fig. 1: Scheme of possible energy transitions and the corresponding Raman spectrum

- **anti-Stokes-Raman scattering**

The final state lies below the the initial state (blue arrows in Fig. 1). The scattered photon has a higher energy in comparison to the exciting one. Again, the photon energy difference corresponds to the difference between two stationary states of the molecule.

$$\frac{\Delta E_{\text{molecule}}}{hc} = \tilde{\nu}_{\text{anti-Stokes}} - \tilde{\nu}_L \quad (2)$$

Anti-Stokes scattering is possible if the molecule – prior to the scattering process – is in a thermally excited state. Since according to the Boltzmann distribution the majority of the molecules are in the ground state² Stokes scattering is in general more intense than anti-Stokes scattering. The routine spectrometer employed in this experiment is configured to exclusively record the Stokes part of the spectrum.

²This is true for vibrational states but not for rotational states.

In addition, only vibrational states are accessible. Pure rotational states can not be resolved.

3.2 Selection rules

Both Raman and IR spectra of a molecule are necessary for a complete vibrational spectroscopic characterization. Different selection rules decide if a vibrational mode is Raman- and/or IR-active.³ The general selection rule for IR-active vibration transitions reads:

The dipole moment of the molecule has to change during the vibration transition.

The dipole moment can be a permanent one or it can be temporarily build up during the vibrational motion. IR-inactive are vibrations that do not change the dipole moment (e.g. vibrations of homo-nuclear two atomic molecules).

The interaction of light with matter requires the existence of a temporarily changing dipole while the molecule rotates or vibrates. An electric field may induce a dipole moment $\vec{p}_i$ in a molecule without a permanent dipole moment.

$$\vec{p}_i = \alpha \vec{E} = \alpha \vec{E}_L \sin(2\pi\nu_L t) \quad (3)$$

with: α plarizability (in general a second rank tensor), ν_L laser frequency, $\vec{E}$ electric field with its maximum amplitude $\vec{E}_L$.

The meaning of the SI-unit of the polarizability in equation 3 is not clear at first sight: $[\alpha] = \frac{\text{C}\cdot\text{m}^2}{\text{V}}$. However, switching to the older CGS-system by dividing α by $4\pi\epsilon_0$ (vacuum permittivity ϵ_0) leads to a unit that is much more clear. $\Rightarrow$ Which one, and what does this unit tell about the molecule? $\Leftarrow$

In the following the vibrational selection rules for Raman spectroscopy will be derived. Starting point is the representation of the polarizability as function of elongation and contraction of the chemical bond employing a Taylor expansion. The relevant variable is the deviation x from the average bond length r_v in the quantum state v : $x = (r - r_v)$:

$$\alpha(x) = \alpha_v + \left(\frac{\partial\alpha}{\partial x} \right)_{x=0} x + \dots ; \quad (4)$$

α_v is the polarizability at $x = 0$. To approximate $\alpha(x)$ the Taylor series will be cut off after the linear term.

Assuming

$$x(t) = x_v \sin(2\pi\nu_v t) \quad (5)$$

for the molecular vibration in quantum state v and putting equations 5 and 4 into equation 3, one obtains:

$$\vec{p}_i(t) = \alpha \vec{E} = \left[\alpha_v + \left(\frac{\partial\alpha}{\partial x} \right)_{x=0} x_v \sin(2\pi\nu_v t) \right] \vec{E}_L \sin(2\pi\nu_L t) \quad (6)$$

³The term „IR-active“ or „infrared-active“ is used if one wants to express that a transition is visible in an *IR-absorption* spectrum.

Note, that the induced dipole moment $\vec{p}_i(t)$ is modulated by two different frequencies: (1) the frequency of the laser electric field ν_L that displaces the electron cloud with respect to the atomic cores and (2) the vibrational eigenfrequencies ν_v of the molecular framework. Remembering

$$\sin \phi \sin \theta = \frac{1}{2} [\cos(\phi - \theta) - \cos(\phi + \theta)]$$

it turns out for $\vec{p}_i(t)$:

$$\vec{p}_i(t) = \underbrace{\alpha_v \vec{E}_L \sin(2\pi\nu_L t)}_{\text{Rayleigh scattering}} + \underbrace{\frac{1}{2} \frac{d\alpha}{dx} x_v \vec{E}_L \left[\underbrace{\cos(2\pi(\nu_L - \nu_v)t)}_{\text{Stokes}} - \underbrace{\cos(2\pi(\nu_L + \nu_v)t)}_{\text{anti-Stokes}} \right]}_{\text{Raman scattering}} \quad (7)$$

One recognizes from equation 7, that the induced dipole moment emits electromagnetic radiation with three frequency components. That is the unchanged laser frequency ν_L (Rayleigh scattering) and $\nu_L \pm \nu_v$ which correspond to anti-Stokes and Stokes Raman scattering. In addition, one finds the general selection rule for Raman scattering. Equation 7 requires for a non zero Raman intensity that $(d\alpha/dx) \neq 0$. Or in other words:

The polarizability has to change during vibrational motion.

This condition is clearly fulfilled during a vibrational motion that increases and decreases the size of the molecule. See e.g. the vibrational motion of diatomic molecules (also the homonuclear ones) and the symmetric stretching mode of CO_2 (in contrast to the antisymmetric stretching mode).

All molecules in this experiment possess an inversion centre. For these molecules the exclusion principle holds. This means that a vibration mode is visible either in the infrared spectrum or in the Raman spectrum.

In harmonic approximation the **specific selection rule** in Raman vibration spectra is $\Delta v = \pm 1$ (same as in IR spectra).

3.3 The Raman spectrometer

The main components of a Raman spectrometer are the light source, the optical light guiding system, the monochromator and the detector. The light source has to fulfill the following conditions:

- high intensity since the Raman effect is a relatively weak effect (see the prefactor $\vec{E}_L$ in equation 7),
- high monochromacy,
- light wavelength should preferentially lie in the visible range to avoid absorption of the exciting light by vibrations or electronic transitions.

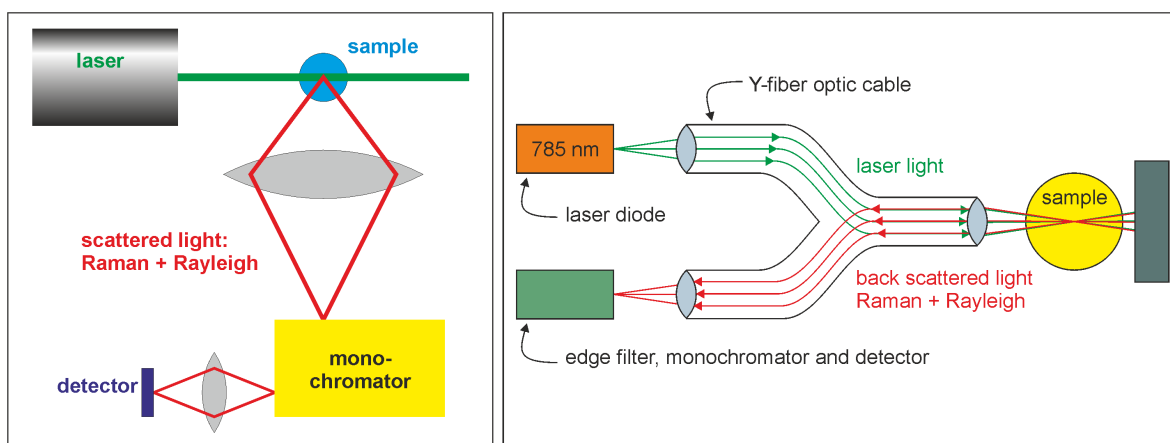


Fig. 2: Two Raman spectrometer architectures. Left: classical spectrometer in 90° -configuration with laser, sample, monochromator and detector. Right: spectrometer in back-scattering geometry with glass fibre optics (this is the building principle of the spectrometer in the practical course)

Therefore one uses monochromatic and intense lasers as light source. The laser beam is focused by a collecting lens into or onto the sample. The scattered light is focused onto the entrance slit of a monochromator. The monochromator may be oriented with respect to the exciting beam in an angle of 90° or 180° .

To separate the relatively weak Raman signal from the much stronger Rayleigh scattering the monochromator has to fulfil special conditions. In the classical setup (fig. 2 left) one uses double or triple monochromators to effectively suppress parasitic stray light. This construction principle is expensive and one can find it in some high end research instruments. The advantage is that one can measure in very close vicinity relative to the Rayleigh line. Thus, pure rotational Raman spectra are accessible.

The setup in our experiment is more simple and much less expensive (see fig. 2 right). The laser light (here: 785 nm) is focused with a Y-glass fibre optic into the sample. The scattered light runs through the same fibre back to the spectrometer. An effective edge filter suppresses the Rayleigh light. It follows a relatively simple monochromator and the line detector.

3.4 Applications

Raman and infrared spectroscopy are complementary methods to measure vibrational and rotational states of molecules. The characteristic sequence of absorption and/or scattering lines are the *fingerprint* of a molecule. Both methods can be used to uniquely identify molecules.

An infrared spectrum represents vibrations that modulate the molecular dipole moment. These are vibrations of polar groups and antisymmetric vibrations. A Raman spectrum represents vibrations that modulate the polarizability. These are vibrations of

unpolar groups and totally symmetric vibrations. IR and Raman spectra allow to identify the symmetry and the structure of molecules and their isomers. For the interpretation of the spectra one often uses theoretical chemical methods.

In addition, with the help of Lambert-Beer's law infrared absorption spectra can be used to measure concentrations and compositions quantitatively. This is much more difficult in Raman spectroscopy. The intensity of Raman lines depends on the exciting laser, on instrument specific parameters, and on the wavelength dependence of the detector. In the context of our present experiment this is evident for the example of the so called *breathing mode* of H₆-benzene and D₆-benzene, respectively. Raman spectra can supply quantitative information if one concentrates on small changes of the sample and if one uses every time the same spectrometer. An interesting example are food samples which can be studied during their shelf-time. The ageing of food (e.g. meat samples) is measurable by characteristic changes in the Raman spectrum, which can be recorded in the food store.

3.5 Raman spectra of Carbon dioxide and Carbon disulfide

Applying the harmonic oscillator approximation to a three-atomic linear molecule one expects one single Raman active mode and therefore one single line in the spectrum. However, in the spectra of CO₂ and CS₂ one observes two peaks, one of which is a combination vibration.

Real molecules can not be compressed or elongated infinitely. For a more precise description of molecular vibrations one has to apply the anharmonic oscillator model. The special selection rule $\Delta v = \pm 1$ has to be extended to $\Delta v = \pm 1; \pm 2; \pm 3 \dots$ for anharmonic oscillators. Hence, one observes higher harmonic oscillations – overtones with much less intensity – beside the fundamental. If such an overtone has coincidentally a similar frequency than a fundamental vibration, both modes start to interact: they shift a little bit and one mode gains intensity at the expense of the other. This effect is called *Fermi resonance*. In the case of CO₂ and CS₂ the first overtone of the bending mode couples to the symmetric stretching mode, and therefore, becomes visible.

4 Experimental procedure

1. Open the program BWSpec 4
2. For the dark scan open the shutter at the laser holder and cover the empty sample compartment with a cap. Switch the laser power to 100 and press *Dark Scan*
3. Set *Dark subtracted* in the menu *Display options*
4. Put the sample cuvette into the sample compartment (attention: the cuvette is breakable). Close the sample compartment with a suitable cap. Then start the measuring procedure: *Acquire one spectrum*

To measure solid CO₂ (−78 °C!) connect the black spacer to the laser head. Press the spacer onto the dry ice. Attention: this procedure should not take too much time since this could damage the lens in the laser head.

5. Variation of the integration time: the memory depth of the detector is two bytes, which represents an intensity scale from 0 to $2^{16} = 65536$. Record one spectrum where the strongest band does not exceed this value. If a molecule (e.g. C₆H₆ above 3000 cm^{−1}) shows strongly different band intensities one can enhance the exposure time to clearly identify the weakest bands.
6. Under *Tools* click *peak analysis*. Choose a suitable peak gate. Write down the selected peaks.
7. Store your data via *File ... save as* under „Eigene Dateien“, „A-Praktikum“, in your group directory.

5 Data Evaluation

1. Answer the questions in the text which are marked with an arrow ($\Leftarrow$).
2. How many vibrational degrees of freedom do the molecules have which are investigated in this experiment? Describe the vibrational modes of CO₂ and CS₂. Which are infrared active, which are Raman active?
3. Plot the spectra of the investigated molecules. Use the printed spectra or you may plot them using the stored spectra files (e.g. as *.txt or *.csv files).
4. Usually one can observe at approx. 0 cm^{−1} that the Rayleigh line leaks through the optical edge filter. This can be used to clearly identify the zero position of the Raman shift scale. Above approx. 100 cm^{−1} the edge filter becomes transparent and one recognizes the fading out of the foot of the Rayleigh band. Calculate the absolute wavelength λ_K of the filter edge (the edge filter has the following spectral characteristics: $T \approx 0$ für $\lambda \leq \lambda_K$ und $T \approx 1$ für $\lambda > \lambda_K$, with transmission T).
5. Identify the vibrational modes of CO₂ and CS₂ appearing in the Raman spectra. Discuss the result.
6. Calculate the force constant of the C=O and the C=S chemical bond.
7. Why and how much does the Raman line of the *breathing mode* of benzene shift when ¹H is exchanged by ²H (=D)? You find this line at the upper end of the spectra.

6 Data from literature

	ν_1	ν_2	ν_+	ν_-
CO ₂ : $\tilde{\nu}$ [cm ⁻¹]	1384,6	659,3	1384,6	1273,3
CS ₂ : $\tilde{\nu}$ [cm ⁻¹]	653,8	396,0	653,8	802,4

ν_1 : symmetric stretching vibration, ν_2 : bending vibration,
 ν_+ , ν_- : Raman modes observed in the spectra

C ₆ H ₆ : $\tilde{\nu}$ [cm ⁻¹]	606	849	992	1178	1584, 1606	3045	3061
C ₆ D ₆ : $\tilde{\nu}$ [cm ⁻¹]	577	661	867	945	1560	2264	2292

1. F. Bolduan, H. D. Hochheimer, H. J. Jodl; J. Chem. Phys. 84 (1986) 6997.
2. G. Allen, H. J. Bernstein; Can. J. Chem. 33 (1955) 1137.
3. See also: Food Raman spectroscopy

7 What you should know

- Operation of a laser
- General overview: spectroscopic methods
- Scattering processes
- Harmonic oscillator, Schrödinger equation
- Selection rules for IR absorption and Raman spectra
- Anharmonicity und overtones

