

# Physical chemistry advanced laboratory course

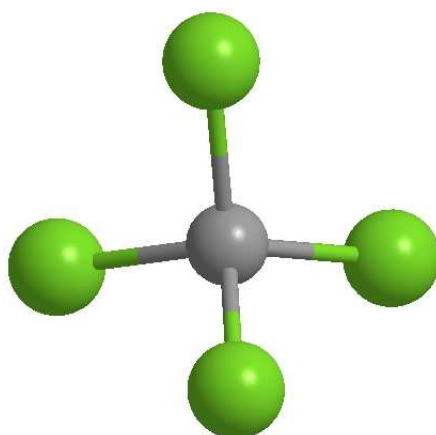
## Raman spectroscopy of the $\text{CCl}_4$ molecule

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### 1 Introduction

The object of this exercise is to familiarize you with the basics and practises of Raman spectroscopy and with using the symmetry properties of the normal mode vibrations as a tool in spectral analysis. In this study, the Stokes Raman spectrum and the depolarization information of carbon tetrachloride,  $\text{CCl}_4$ , is measured. The spectra are used to recognize vibrational transitions and the corresponding depolarization ratios. You will also study the fine structure of the Raman bands and sketch the corresponding anti-Stokes Raman spectrum.



## 2 Getting ready for the measurement

Before the measurement, it is good to get acquainted with the theory, to understand the measurement and to have a prediction for the expected results. So, *before* the measurements in the laboratory, go through the following things:

- The basic theory of vibrational Raman spectroscopy (mechanism, selection rules, measurement setup/requirements).
- Differences and similarities between IR- and Raman spectroscopy - which technique to choose in different situations and why?
- What does the depolarization ratio mean in Raman spectroscopy and what can you benefit from measuring it?
- Sketch out the normal mode vibrations for carbon tetrachloride, find out their symmetries and Raman and/or infrared activities (the character table for the  $T_d$  point group is attached below).

Table 1: The character table for the  $T_d$  point group

$T_d$	I	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
$A_1$	1	1	1	1	1	$\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$
$A_2$	1	1	1	-1	-1	
E	2	-1	2	0	0	$(\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz}, \alpha_{xx} - \alpha_{yy})$
$T_1$	3	0	-1	1	-1	$(R_x, R_y, R_z)$
$T_2$	3	0	-1	-1	1	$(T_x, T_y, T_z)$ $(\alpha_{xy}, \alpha_{xz}, \alpha_{yz})$

Use this outline to write the theoretical part of the report. In addition to stating the symmetries of the normal mode vibrations, you should show how they were determined.

### 3 The measurements

The measurements are carried out using the Raman setup in the Nanoscience Center laser laboratory. First you will get acquainted with the setup and with how it works. The sample, liquid  $\text{CCl}_4$ , is ready in a Raman cuvette and the assistant will help with the measurements. Remember to keep your own measurement log! The required measurements are the following:

- A lower resolution Stokes Raman spectrum: grating  $1200 \text{ mm}^{-1}$ , center wavelength  $550 \text{ nm}$ , slit  $100 \mu\text{m}$ . Accumulate 10 measurements with a 1 s exposure time per measurement. Only the calibration of the spectrograph is used.
- Depolarization spectra ( $\parallel$  and  $\perp$ ) with the previous settings. The polarizer is placed between the filter and the monochromator. First, the spectrum of the Raman scattering with polarization parallel to the excitation laser is measured by maximizing the intensity of the third band ( $\sim 460 \text{ nm}$ ). Then, turn the polarizer 90 degrees and measure the spectrum with perpendicular polarization.
- A higher resolution Stokes Raman spectrum: grating  $2400 \text{ mm}^{-1}$ , center wavelength  $545 \text{ nm}$ , slit  $50 \mu\text{m}$ , 10 accumulations with 1 s exposure.

You will get the measured spectra from the lab as ascii files for further analysis. In addition to the measurements, draw a diagram of the Raman setup, showing all the essential parts of the setup, and explain what each part in the setup is used for.

### 4 Analysis of the results

Determine the peak positions and intensities from the lower resolution spectrum. Assign the peaks to the normal mode vibrations of  $\text{CCl}_4$  and justify the assignments. As a help in assigning the peaks, you can use for example the IR and Raman activity of the

vibrations, the depolarization spectra, and, if you wish, IR spectra from the literature (attach the IR spectrum you used or a reference to it in the report). The most accurate values for the intensities are obtained by integrating the area under each peak (for example in Origin-program: plot the peak you wish to integrate, select Analysis → Calculus → Integrate. Note that the area is determined starting from the  $y = 0$  value, so a possible background should be removed before integrating). Compare the peak positions with literature values (from for example NIST) and comment on the accuracy of the calibration. How could you improve the calibration?

Use the depolarization spectra to calculate the depolarization ratios for the different transitions. Consider if removing the background from the spectra is necessary and compare the results with the theoretical predictions. Explain the differences if found.

Study the fine structure of the spectrum. Explain why there are two peaks in the  $\sim 780 \text{ cm}^{-1}$  region. Then examine the higher resolution spectrum of the  $\sim 459 \text{ cm}^{-1}$  band and explain the fine structure. Could you find any “hints” of the fine structure in the lower resolution spectrum?

Using the measured spectra, make a sketch of the anti-Stokes spectrum measured from the same sample (peak positions and intensities). What could you benefit in practise, if anything, from measuring the “both sides” of the Raman spectrum? If you could only measure either a Stokes- or an anti-Stokes spectrum, which one would you choose and why?

## References

- [1] P. W. Atkins ja R. S. Friedman. *Molecular Quantum Mechanics*, 3rd edition (1997) Oxford University Press, Oxford, UK, p. 320–322 and 341–353.
- [2] J. Michael Hollas. *Modern Spectroscopy*, 4th edition (2004) John Wiley & Sons, Ltd, England, chapters 4 and 6.

- [3] Dennis P. Strommen. “Specific Values of the Depolarization Ratio in Raman Spectroscopy – Their Origins and Significance”, *J. Chem. Educ.* **69** (1992) 803–807.
- [4] Monty L. Fetterolf ja Jack G. Goldsmith. “An Interactive Dry Lab Introduction to Vibrational Raman Spectroscopy Using Carbon Tetrachloride” *J. Chem. Educ.* **76** (1999) 1276–1277.