Examination of vibrational modes and concentration determination with Raman spectroscopy

(RAM)

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Abstract:

The following report deals with the analysis of different vibrational modes of dicholormethane and the determination of the concentration of ethanol in a vodka sample using Raman spectroscopy. The first goal was to familiarize ourselves with the different parts of the optics which were then optimized to get the best possible signal-to-noise ratio. The following vibrational modes of dicholormethylene were observed with backscattered light: CH_2 a-stretch and CH_2 s-stretch, CH_2 cis, CH_2 twist and CCl_2 s-stretch. With perpendicular scattering no peak could be evaluated due to insufficient signal-to-noise ratio. Using external calibration, the ethanol concentration of a vodka sample was determined to be approximately 32 vol%. The result differs from the concentration stated by the producer of the bottle, which is given by 40 vol%.

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1. Introduction

A typical technique to study organic compounds is IR spectroscopy. It is based on the interaction of electromagnetic radiation with a molecular system resulting in induced transitions between the specific vibrational energy levels of the molecule. However, there are cases where these transitions are forbidden or not IR active and IR spectroscopy can therefore not provide structural information about the molecule. In these situations, Raman spectroscopy can be used to replace or amend IR spectroscopy for the determination of structural properties of the examined molecule.

2. Theory [1]

Raman spectroscopy is based on the inelastic scattering of light by matter. The used monochromatic light can induce transitions to an excited vibrational state within the molecule. Three different types of scattering can occur (see Fig 1). Rayleigh scattering comes from a transition that starts and ends at the same vibrational energy level. Scattering which starts from a vibrational ground state level and ends at a higher vibrational level is called Stokes scattering. Anti-Stokes scattering arises from a transition from a higher to a lower vibrational energy level.

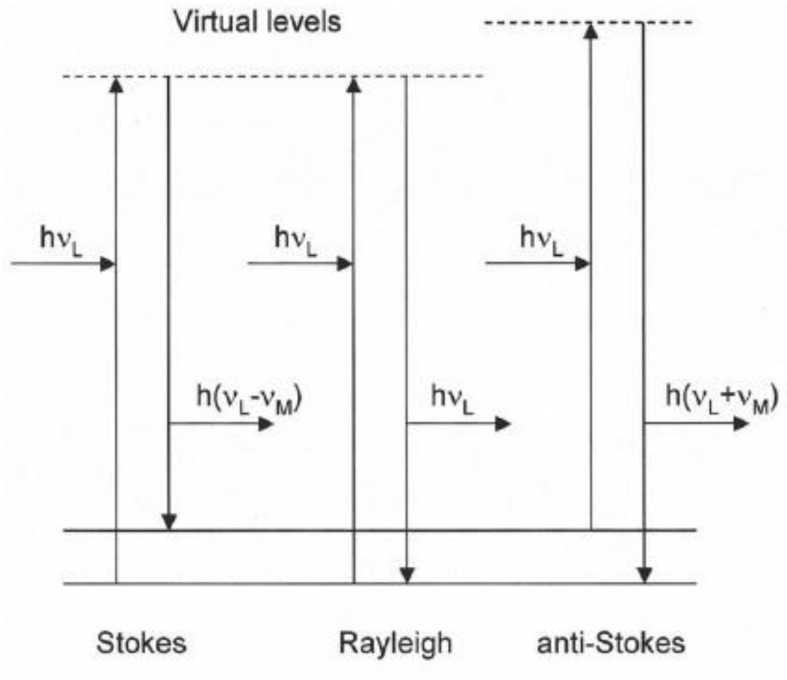


Figure 1: Schematic figure showing the basic transitions for Raman scattering. [2]

In contrast to IR spectroscopy where the change in the dipole moment is exploited, Raman spectroscopy relies on the change of molecular polarizability. In fact, Raman spectroscopy is a complementary technique to IR spectroscopy. For example in cases where the molecule has a centre of symmetry, certain normal vibrations will only be Raman active whereas other normal vibrations will only be IR active.

3. Experimental

3.1. Experimental setup

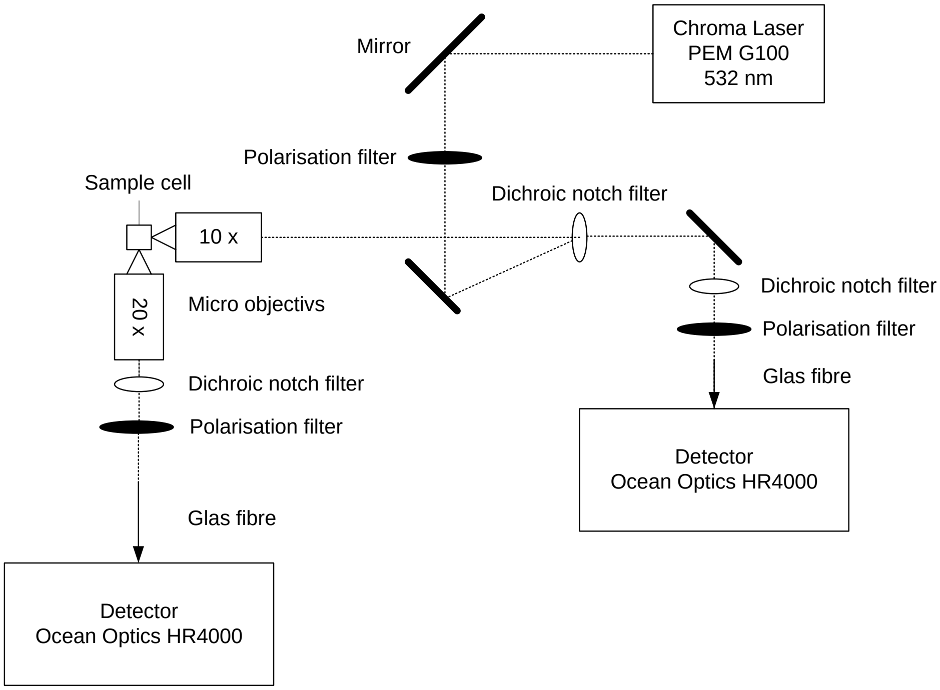


Figure 2: Schematic picture of the used experimental setup.

The polarization filters used in the experiment could be adjusted to horizontal or vertical orientation.

3.2. Execution of the experiment

3.2.1. Investigation of Raman spectrum

To obtain the maximum of the backscattered light the optical scheme was adjusted. The examined sample was a solution of the eye Rhodamine 6G in water. Furthermore the spectra of Dichlormethane of perpendicular-scattered light at different orientations of the polarizer were measured. For each measurement a background spectrum was measured. The integration time was set to 0.5 s and the number of scans to average was set to 60.

3.2.2. Investigation of compounds

In the second part of the experiment the concentration of ethanol in vodka was determined. For this, the spectra of pure ethanol, pure vodka and distilled water were measured. Additionally, the spectra of a 15.81, 32.95, 57.28 and 71.66 vol% solution of ethanol in water were measured. The integration time was set to 1 s and the number of scans to average was set to 37. The spectra were measured using backscattered light. Again, for every measurement the background was determined first.

4. Results

4.1. Vibrational analysis of Dichloromethane

4.1.1. Backscattered Spectrum of Dichloromethane

Wave number [cm^{-1}]	Interpretation
3016(4)	CH_2 a-stretch
2991.53(7)	CH_2 s-stretch
1426(1)	CH_2 scis
1161(7)	CH_2 twist
720(1)	CCl_2 s-stretch
705.1(3)	-

Table 1: Backscattered spectrum of dichloromethane

4.1.2. Perpendicular Spectrum of Dichloromethane

No peaks could be evaluated due to insufficient signal-to-noise ratio.

4.1.3. Determination of the ethanol concentration in vodka

For the determination of the ethanol concentration in vodka three different peaks were examined. Two peaks belong to the lines of ethanol, whereas the third is the water line.

Peak 1: Ethanol

Solution	Wave number [cm^{-1}]	Peak integration
pure vodka	2937.319	1093.66226
pure ethanol	2932.035	3044.94892
71.66 vol% of ethanol	2933.293	2397.97021
57.28 vol% of ethanol	2934.803	1994.59204
32.95 vol% of ethanol	2936.061	1173.97548
15.81 vol% of ethanol	2937.319	494.18814
Pure water	-	0

Table 2: Wave number and the integrated area for the first peak of ethanol in different solutions.

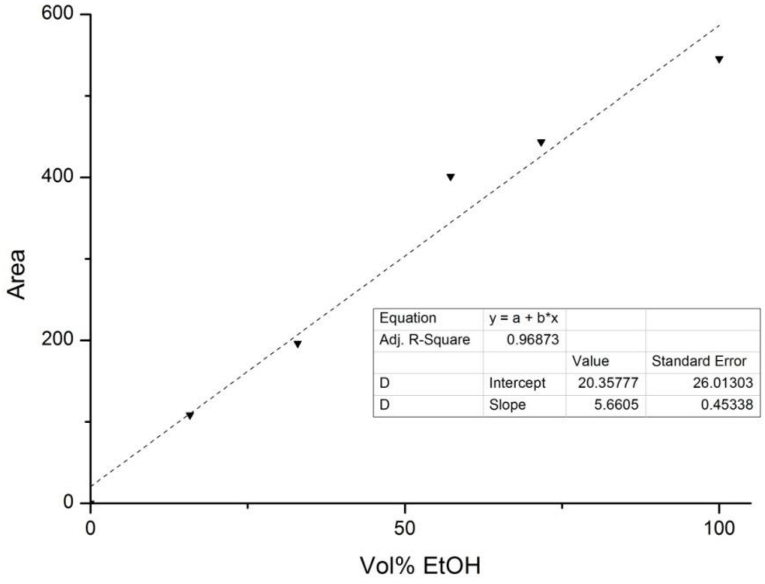


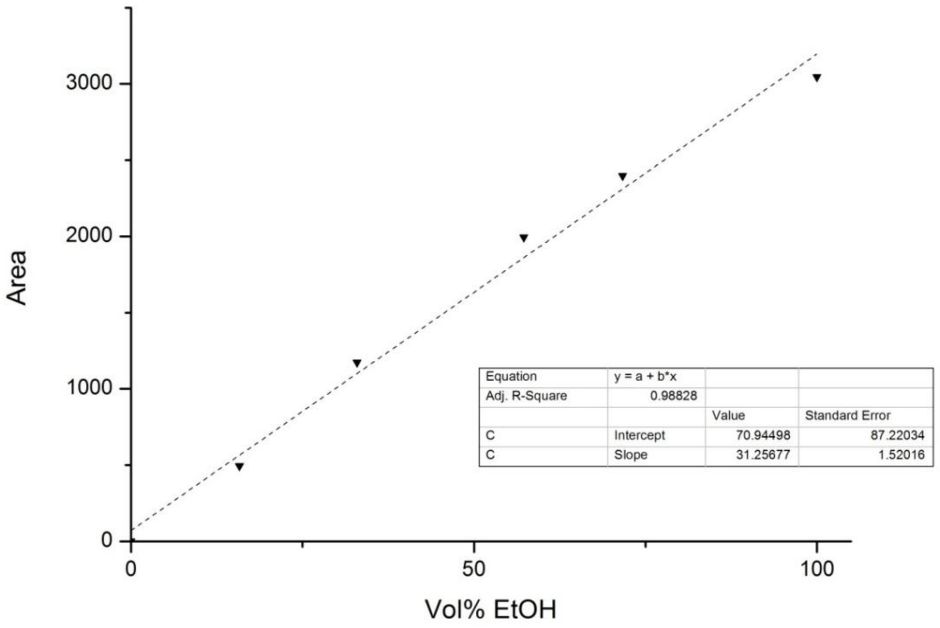
Figure 3: Plot of the area under the peak versus the vol% of ethanol and calculated regression line (dashed line).

The calculated concentration for ethanol is 32.72 vol%.

Peak 2: Ethanol

Solution	Wave number [cm^{-1}]	Peak integration
pure vodka	882.2666	198.60861
pure ethanol	885.7962	545.58744
71.66 vol% of ethanol	884.192	443.19232
57.28 vol% of ethanol	884.192	400.96397
32.95 vol% of ethanol	882.2666	196.14549
15.81 vol% of ethanol	882.2666	108.17691
Pure water	-	0

Table 3: Wave number and the integrated area for the second peak of ethanol in different solutions.



Equation	y = a + b*x		
Adj. R-Square	0.98828		
		Value	Standard Error
C	Intercept	70.94498	87.22034
C	Slope	31.25677	1.52016

Figure 4: Plot of the area under the peak versus the vol% of ethanol and calculated regression line (dashed line).

The calculated concentration for ethanol is 31.49 vol.%.

Peak 3: Water

Solution	Wave number [cm^{-1}]	Peak integration
pure vodka	3404.326	1298.5641
pure ethanol	3305.846	275.66648
71.66 vol% of ethanol	3376.792	477.56014
57.28 vol% of ethanol	3415.453	596.01724
32.95 vol% of ethanol	3461.451	1252.57535
15.81 vol% of ethanol	3408.116	1515.03719
Pure water	3401.719	2462.3125

Table 4: Wave number and the integrated area for the first peak of water in different solutions.

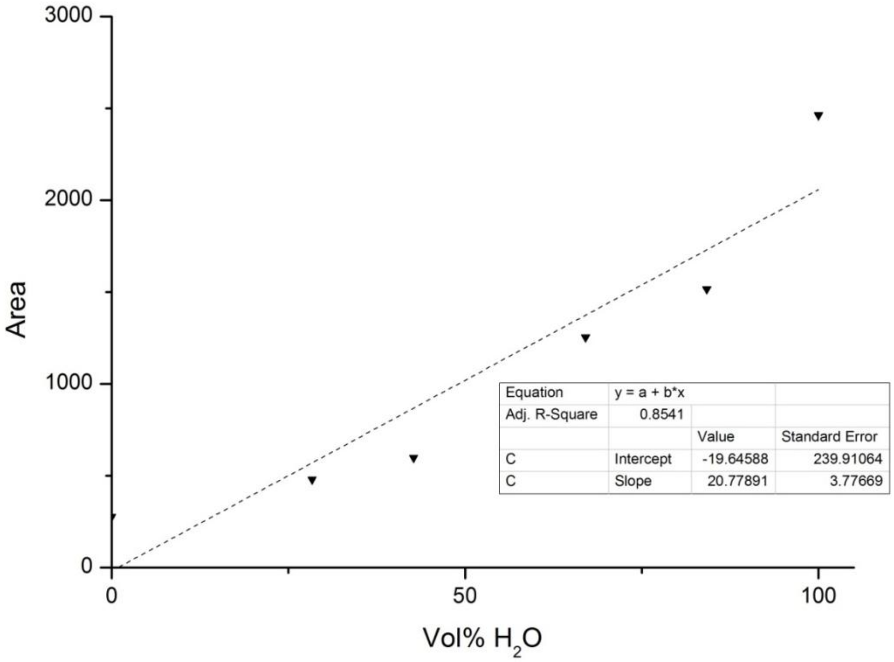


Figure 5: Plot of the area under the peak versus the vol% of water and calculated regression line (dashed line).

The calculated concentration for water is 63.44 vol%. This concentration is equivalent to an ethanol concentration of 36.56 vol%.

5. Discussion

The first task of analyzing yielded clear data only for a backscattered measuring using parallel orientation of the polarization filters. Already for crossed polarization, the signal to noise ratio and resolution impeded proper detection of the peaks. This came together with significantly worse peak-fitting parameters. For perpendicular scattering, the detection capabilities were insufficient. Even for parallel polarization filters, no clear signal was observed. This didn´t come as a big surprise, since the Raman activity of CH_2Cl_2 has to be considered low.

The second experiment was more challenging in terms of sample preparation. In some of the glassware used for preparation of the standard solution of ethanol and water were residues of a dye, which contaminated our solutions. A second problem was the forming of bubbles by mixing of the mixture.

Recording spectra was easily done by using backscattered light without any polarization filters which yielded properly resolved spectra for all mixtures. Data processing was done with Origin 8 and the results for three chosen peaks show different results for the ethanol concentration in the vodka sample.

The two ethanol peaks gave approximately the same result around 32 vol%, whereas the result acquired by integrating the water peak yielded a somewhat higher concentration. This is due to the fact, that there is significant overlap between an ethanol and the water peak. However, all three values are significantly lower than the 40vol% stated by the producer of the vodka. This can be explained by two effects. First, the vodka sample was already quite old and almost empty. It has to be assumed that some of the ethanol evaporated over the time, lowering the ethanol content of the sample. The second explanation is the fact that even our 100% ethanol standard still contains traces of water.

6. Appendix

6.1. Literature

[1] Instructions for spectroscopy lab course HS 2007: Raman Spectroscopy, Georg Seyfang

[2] IR and Raman Spectroscopy: Fundamental Processing, S. Wartewig, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

6.2. Investigation of Raman spectrum

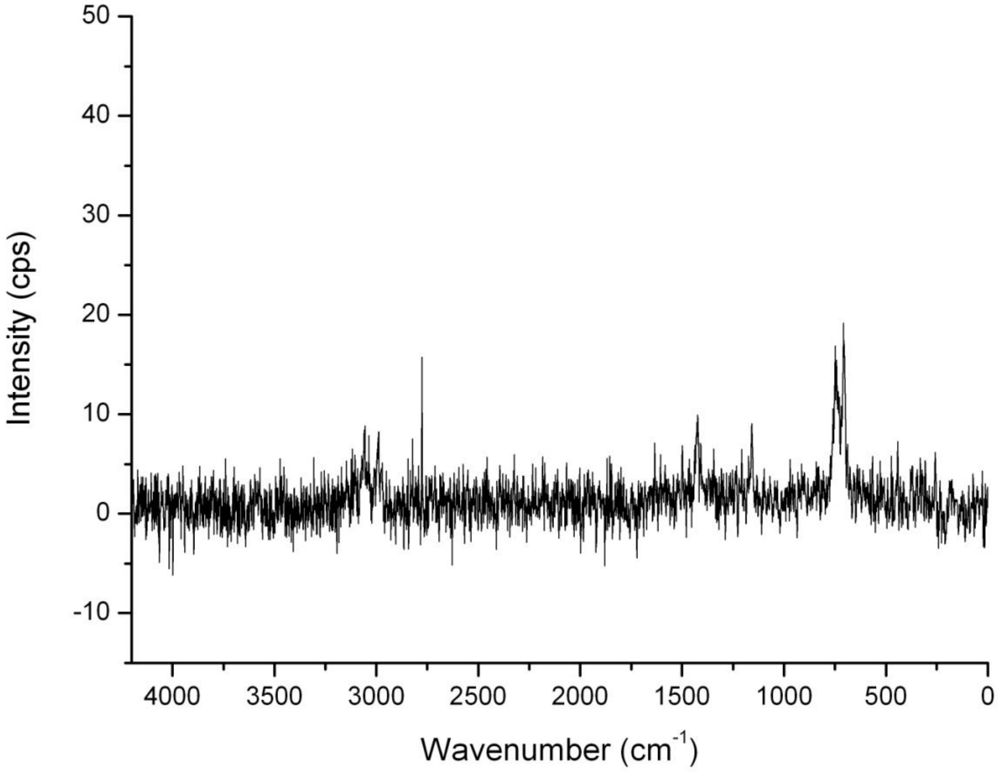


Figure 6: Spectrum of the backscattered light using crossed polarization filters.

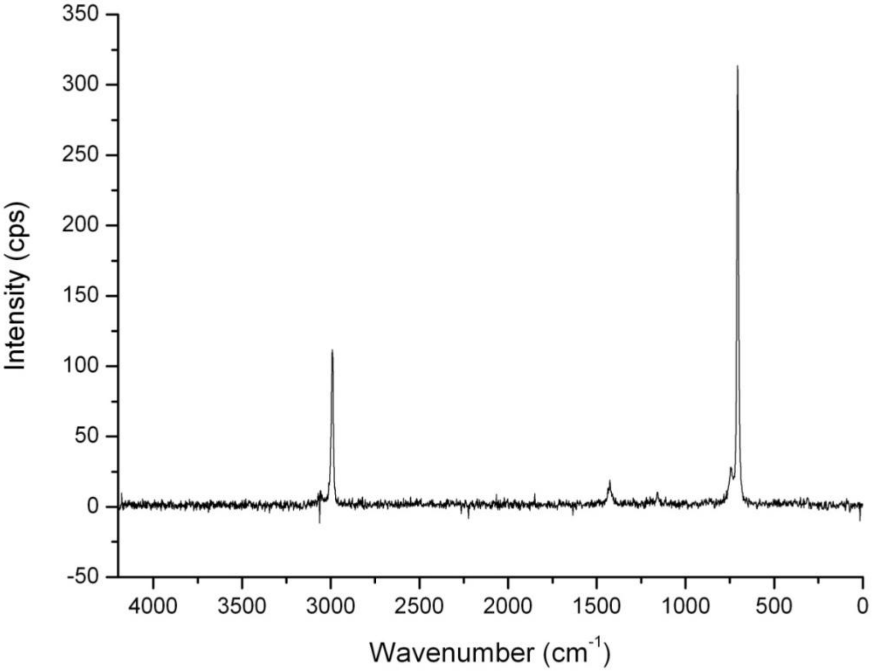


Figure 7: Spectrum of the backscattered light using parallel polarization filters.

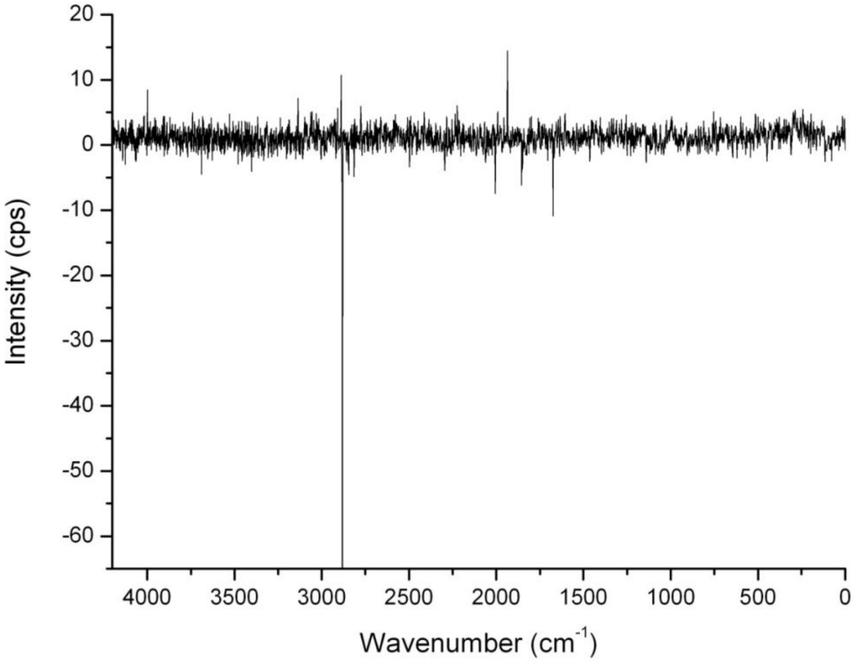


Figure 8: Spectrum of perpendicular scattered light using parallel polarization filters.

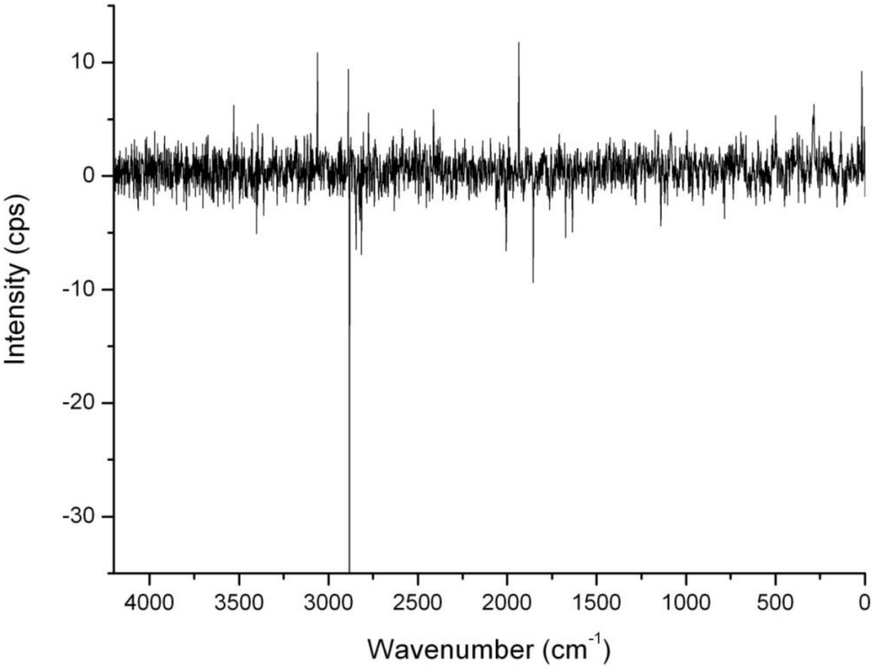


Figure 9: Spectrum of perpendicular scattered light using crossed polarization filters.

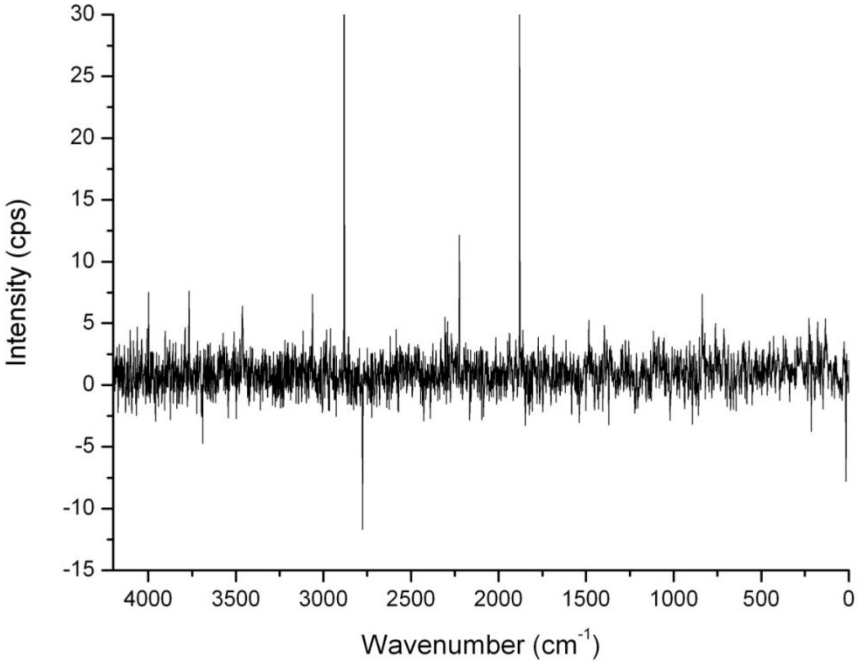


Figure 10: Spectrum of perpendicular scattered light using parallel (vertical) polarization filters.

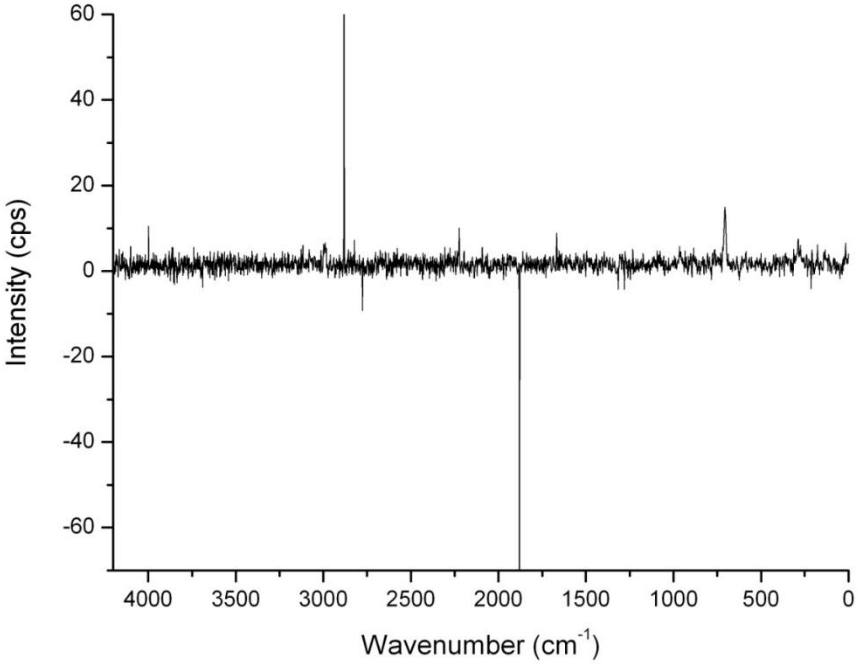


Figure 11: Spectrum of perpendicular scattered light using parallel (vertical) polarization filters.

6.3. Investigation of Compound

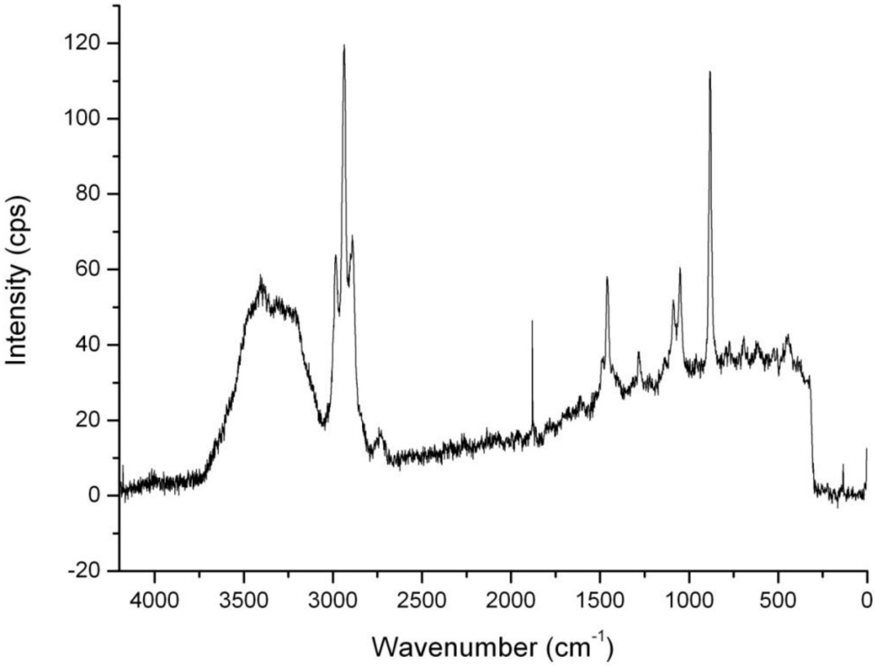


Figure 12: Spectrum of the standard solution with 15.81 vol% ethanol in water.

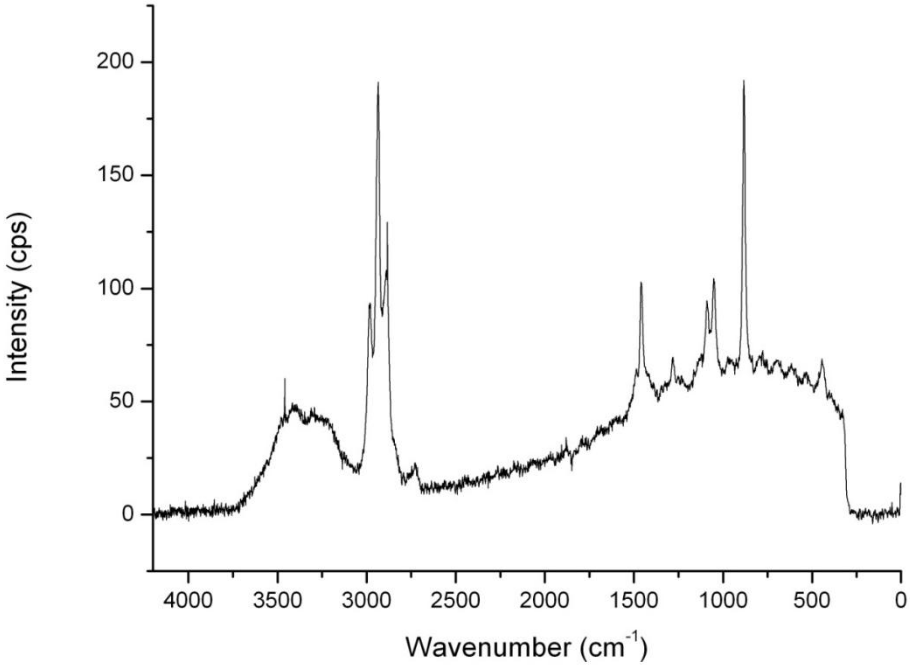


Figure 13: Spectrum of the standard solution with 32.95 vol% ethanol in water.

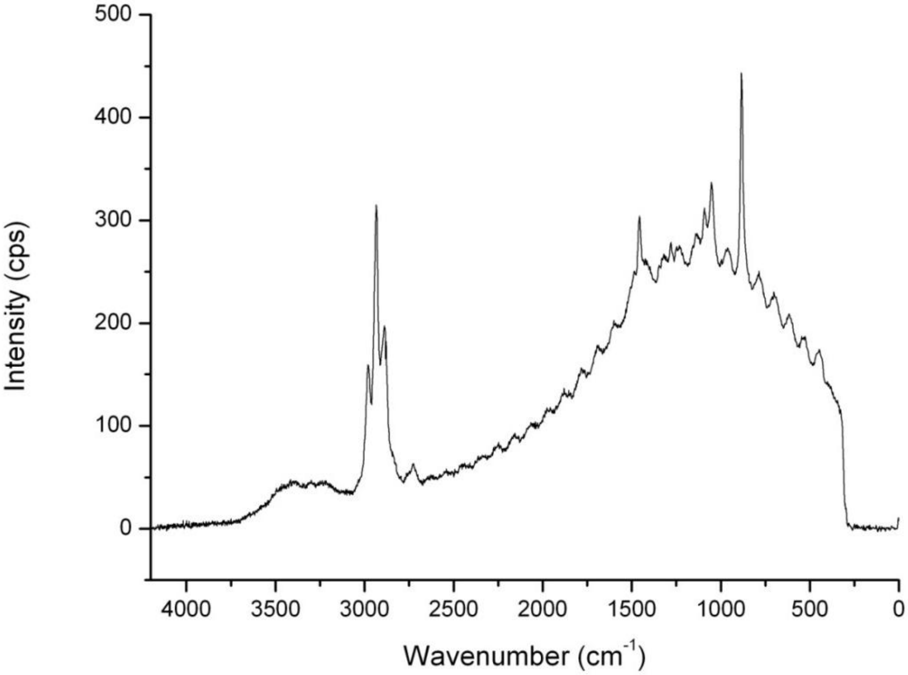


Figure 14: Spectrum of the standard solution with 57.28 vol% ethanol in water.

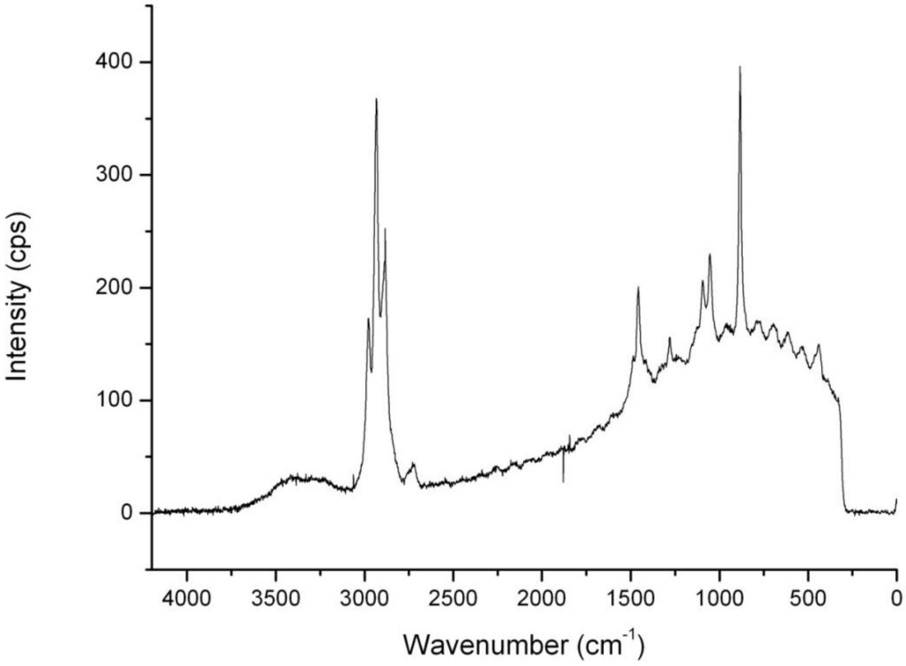


Figure 15: Spectrum of the standard solution with 71.66 vol% ethanol in water.

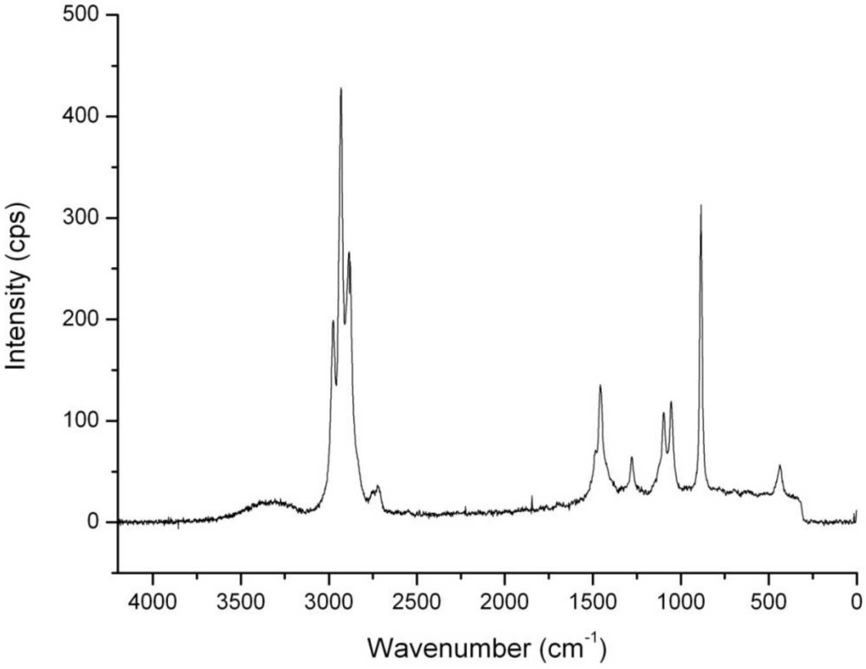


Figure 16: Spectrum of the standard solution of pure ethanol.

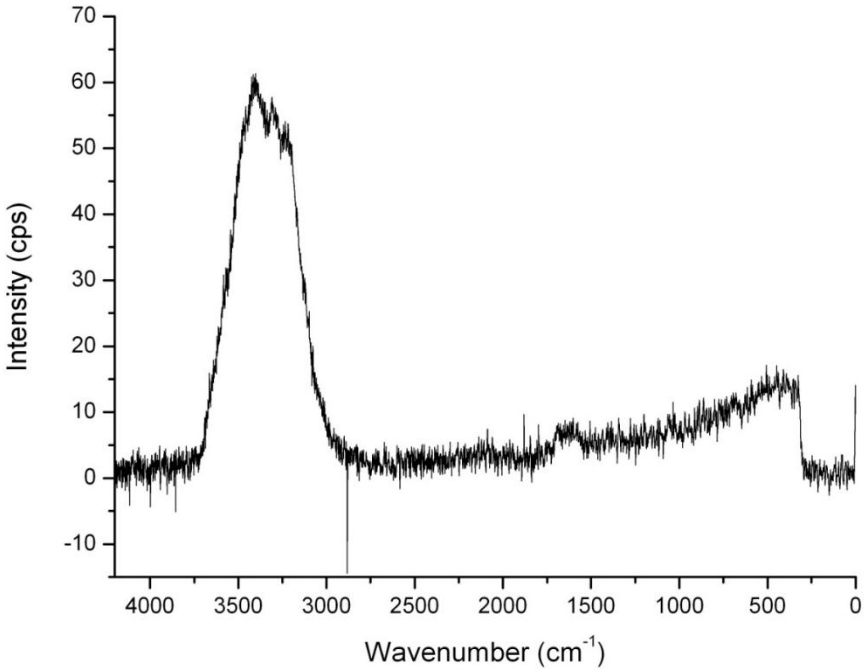


Figure 17: Spectrum of the standard solution of distilled water.

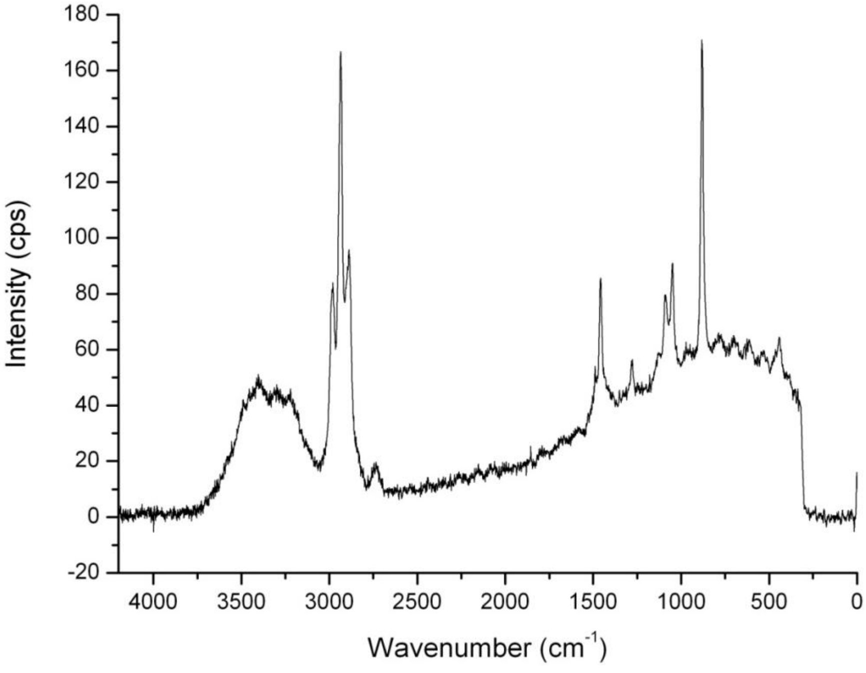


Figure 18: Spectrum of the standard solution of pure vodka.