

# FT-IR spectroscopy used for the analysis of isotopic effects in H<sub>2</sub>O, the rotational behaviour of HBr and the water absorption by DMSO, the identification of different polymers and the determination of ethanol contents of alcohol samples

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## Abstract

An IR spectrum using an FT-IR spectroscope from an liquid ethanol sample was taken to become more familiar with the measurement basics. The reproductibility of the measurements were approved to be more applicable for liquid than solid samples. The hygroscopic property of DMSO could be pointed out by measuring the increasing O-H absorption band with increasing ambient air exposition time. On the basis of the IR spectra from three unknown polymer samples their identity could be determined as nitrile, polyethylene terephthalate and polystyrene. The IR spectra of ethanol/water solutions, with known concentrations were used to asses the ethanol volume percentage of three alcohol samples. The determination resulted in  $16 \pm 1\%$  for white wine,  $36 \pm 1\%$  for rum and  $40.8 \pm 2.2\%$  for anise. The vibration wavenumber shift caused through isotopic substitution from H<sub>2</sub>O to D<sub>2</sub>O could be calculated as 0.728. The equilibrium bond length of HBr in the gaseous phase could be determined as 142 pm with the help of the transition wavenumbers within the measured IR spectrum.

## Introduction

Infrared spectroscopy (IR spectroscopy) has great value in the structure determination of molecules. Most molecules absorb infrared radiation and convert it into molecular oscillations. The absorption of the infrared radiation is characteristic for the different binding ratios in a certain molecule. Using a spectroscope the absorption is measured as a function of the wavenumber [ $\text{cm}^{-1}$ ]<sup>1</sup>. The resulting IR spectrum is specific to each molecule and depends on the masses involved, the bond distances and the bond strengths. Regarding the *Bouger-Lambert-Beer-law* the intensity of the absorbance is proportional to the thickness of the irradiated substance layer  $d$  and the concentration of the absorbing material  $c$ .

$$A(\tilde{\nu}) = \epsilon(\tilde{\nu})cd \quad (1)$$

$\epsilon$  is the proportionality constant and dependant on the wavenumber<sup>2</sup>.

These days it is common to use Fourier-transformation-infrared-spectroscopes (FT-IR spectroscopes) for measuring IR absorption spectra. The advantage is that the samples can be radiated permanently with the complete spectrum of light and therefore a lot of time can be saved<sup>2</sup>. A schematic scheme of a FT-IR spectroscope can be seen in Fig.1 and the functionality is further explained in the description of the figure. The radiation of the polychromatic light source reaches the detector after it passes through the interferometer. The detected signals are transferred to the computer where the Fourier transformation is carried out to obtain the IR absorbance spectrum<sup>3</sup>.

The FT-IR spectrometers can be equipped with an attenuated total reflection (ATR) module to generate better measurements with aqueous samples<sup>2</sup>. An IR beam with an intensity  $I_0$  is directed onto an optically dense crystal with a high refractive index  $n_1$  at a certain angle. At the interface between the crystal and the sample the light beam gets totally reflected. In the region, where the sample absorbs energy, the evanescent wave will be attenuated. The attenuated beam with intensity  $I_1$  is then directed to the detector, where the attenuated IR beam is recorded as an interferogram<sup>4</sup>.

In one of our experiments the reproducibility of measurements with a FT-IR spectroscope equipped with an ATR module were analyzed to assess the significance of the IR spectra from the other experiments, which were only measured once. Some of the other experiments had the aim to illustrate the hygroscopic property of dimethyl sulfoxide (DMSO), to identify the material of a plastic sample or to determine the ethanol content of an alcohol sample.

Using the model of an harmonic oscillator the stretching vibrations of two atoms, which are chemically bonded, can be approximately described. The behaviour of the two atoms is similar to two masses, which are connected by a spring. The resulting harmonic potential function is a parabola and symmetric regarding the stretching and compression of the bond. For the energy of the oscillating atom pair only discrete energy states are allowed, which are given by the vibration quantum numbers ( $\nu = 0, 1, 2, 3, \dots$ ). This leads to the fact that neighboring vibration levels always have the same energy difference. The wavenumber  $\nu_0$  for the harmonic oscillation can be described as

$$\nu_0 = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}, \quad (2)$$

whereas the reduced mass  $\mu$

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2} \quad (3)$$

can be calculated using the mass of the two atomic nuclei<sup>2</sup>. One of our experiment involved the verification of the wavenumber shift for the harmonic oscillation upon isotopic substitution.

Molecules can not only vibrate, but also rotate, which is also contributing to the total energy of the molecule. Equal to the changes in the state of vibration the changes in the state of rotation are quantized and therefore linked to discrete energy changes (the rotational level  $J = 0, 1, 2, 3, \dots$ ). In an IR spectrum the differences in energy between the vibration and rotation levels can be observed as absorption lines (transition wavenumber). Each of these lines correspond to a transition happening at the wavenumber position of the line. The fundamental band consists of a group of absorption lines with only vibration transitions from the basic vibration state ( $\nu = 0$ ) to the first excited vibration state ( $\nu = 1$ ). These lines are symmetrical and consist of a R- and a P-branch. The R branch consists of absorption lines with differences in rotational levels of  $\Delta J = +1$  and in the P-branch the differences are  $\Delta J = -1$ . The transition wavenumbers can be calculated as

$$\tilde{\nu} = \tilde{\nu}_0 - 2\tilde{\nu}_0 x_e + B_e[J'(J' + 1) - J''(J'' + 1)] - \frac{1}{2}\alpha_e[3J'(J' + 1) - J''(J'' + 1)]. \quad (4)$$

$J'$  stands for the rotational level at the basic vibration state and  $J''$  for the rotational level at the excited state.  $B_e$  is the rotational constant,  $\alpha_e$  a constant for the measure for the effect of vibration excitation on  $B_e$  and  $D_e$  is the centrifugal distortion constant<sup>2</sup>. The aim of our last experiment was to determine the equilibrium bond length of an diatomic molecule, which can be calculated with

$$R_e = \sqrt{\frac{\hbar}{8B_e\pi^2c\mu}}, \quad (5)$$

where  $\hbar$  is the Planck's constant and  $c$  the speed of light.

## Experimental

### Chemicals

For cleaning the measurement instrument and the verification of the reproducibility of the IR measurements ethanol,  $M_{\text{C}_2\text{H}_5\text{OH}} = 46.07 \text{ g mol}^{-1}$ <sup>5</sup>, not pure, provided from the HCl shop was used. For the ethanol/water solutions the ethanol purity was  $> 99.8\%$  and the water,  $M_{\text{H}_2\text{O}} = 18.02 \text{ g mol}^{-1}$ <sup>6</sup>, was deionized. Benzoic acid,  $M_{\text{C}_6\text{H}_5\text{COOH}} = 122.12 \text{ g mol}^{-1}$ <sup>7</sup>,  $> 99\%$  purity was used. The alcohol samples white wine, rum and anise were provided from the assistant. The same applies for the three polymer samples. DMSO,  $M_{(\text{CH}_3)_2\text{SO}} = 78.14 \text{ g mol}^{-1}$ <sup>8</sup>,  $< 0.03\%$   $\text{H}_2\text{O}$ , provided from VWR was used. For isotopic substitution analysis deuertium oxide,  $M_{\text{D}_2\text{O}} = 20.03 \text{ g mol}^{-1}$ <sup>9</sup>,  $99.9\%$  purity, provided from CIL was used.

### Sample preparation

Before the measurement benzoic acid was mortared using mortar and pestle. For the ethanol determination 13 solutions containing ethanol and distilled water were prepared. Each solution held a different ethanol concentration. Solutions with ethanol volume percentages of 0%, 9.1%, 16.7%, 18.6%, 37.5%, 44.4%, 47.4%, 50%, 60%, 66.7%, 75%, 80% and 100% were made.

## Measurements

All measurements are made with BRUKER Alpha FT-IR spectrometer using the ATR module unless otherwise specified. A simplified version of a Michelson interferometer, which is part of a FT-IR spectroscope, is shown in Fig.1. The sketch for the ATR module is shown in Fig.2. The data for the gaseous HBr sample was measured using the transmission module and provided by the assistant. For all measurements except for the gaseous HBr sample the following settings were used.

type	setting
resolution	$2\text{ cm}^{-1}$
sample scan time	16 scans (measurement time > 35 s)
save data from	4000 to $400\text{ cm}^{-1}$
result spectrum	absorbance
spectra extended ATR correction	standard

The spectroscope was connected with a laptop, which calculated the interferogram into an absorption spectrum. The used software was OPUS (version 7.5). Before the measurements a background sample was taken, which was deducted from all subsequent measurements. To get in touch with the measurement instrument an IR spectrum of ethanol was taken. For the verification of the reproducibility of IR measurements IR spectra of liquid ethanol and solid benzoic acid were measured each three consecutive times, replacing the samples after each measurement. From three different polymer samples an IR spectrum was taken for the identification of each sample. DMSO was placed at the measurement instrument and every three minutes an IR spectrum was taken, starting with time zero and ending at time 27 min. For the calibration function for the ethanol content determination from the 13 ethanol/water solutions, which were further described in the sample preparation, IR spectra were measured. In addition from three alcohols samples white wine, rum and anise an IR spectrum was taken. Last, an IR spectrum of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  was measured.

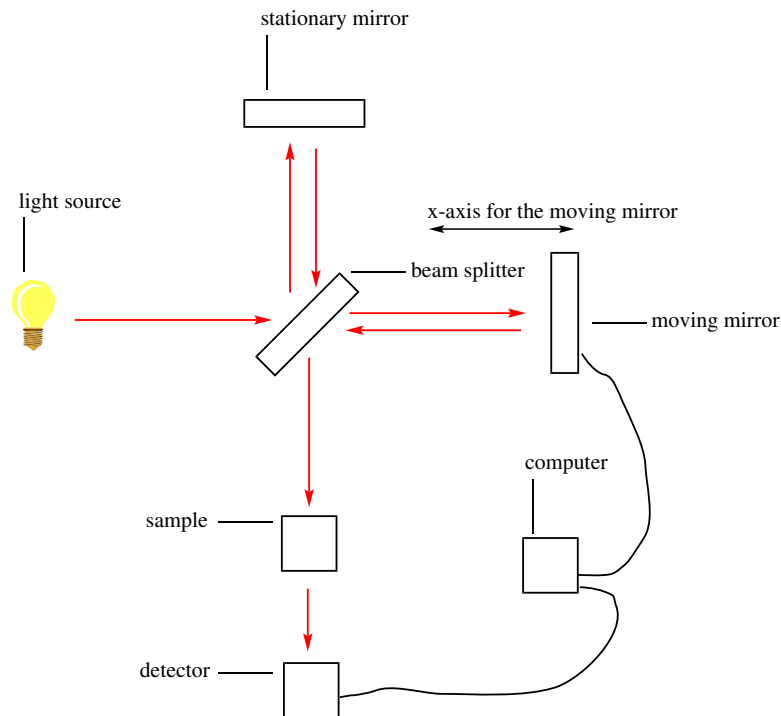


Figure 1: A simplified version of a Michelson interferometer in a FT-IR spectroscopy is illustrated. The polychromatic light of the light source is splitted at the beam splitter and reflected at the stationary and the moving mirror. The polychromatic light radiates through the sample and the not absorbed light will be recorded by the detector. For the interferogram, the detector signal is recorded as a function of the position of the moving mirror. For the calculation of the IR spectrum the computers uses some fourier transformation. All our experimental measurements were taken by a FT-IR spectroscopy.

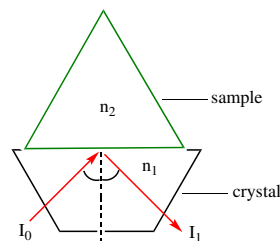


Figure 2: A schematic scheme of the ATR module. The entering light beam  $I_0$  gets totally reflected at the interface of the crystal and the sample on top of it. In the region, where the sample absorbs energy, the evanescent wave will be attenuated. The attenuated beam with intensity  $I_1$  is then directed to the detector, where the attenuated IR beam is recorded as an interferogram.

All measurements were plotted and the results calculated with Python (Version 3.8) as can be seen in the appendix.

## Results and Discussion

The measured IR absorption spectrum for ethanol as liquid with its prominent bands is shown in Fig.3. The peaks for the characteristic properties of ethanol from the measured IR spectrum compared with a reference IR spectrum are listed below.

measured wavenumber [ $\text{cm}^{-1}$ ]	reference wavenumber [ $\text{cm}^{-1}$ ]	assignment <sup>10</sup>
3340	3358 <sup>11</sup>	O-H stretch (hydroxyl group)
2974	2974 <sup>11</sup>	C-H stretch
1049	1050 <sup>11</sup>	C-O stretch (primary alcohol)

The measured IR spectrum shows the main significant peaks for the main functional group, the O-H and the C-O stretch of the primary alcohol. The absorption bands match those of the reference spectrum. Therefore a certain measuring accuracy of the measurement instrument can be assumed.

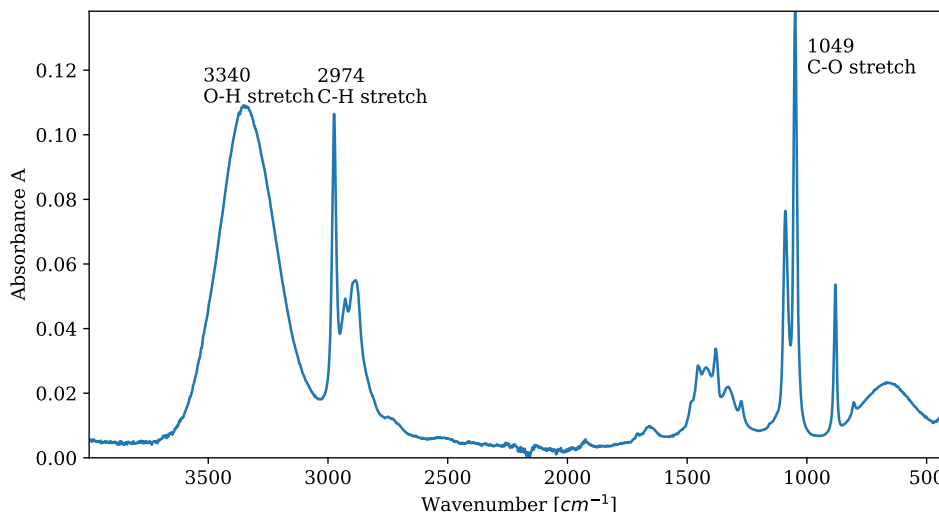


Figure 3: The IR spectrum of ethanol as liquid was measured using the ATR module. The characteristic bands for ethanol are labeled in black.

For the analysis of the reproducibility of FT-IR measurements from three samples of liquid ethanol and from three samples of solid benzoic acid an IR spectrum was taken. As can be seen in Fig.4 the reproducibility of the measurements of the liquid ethanol is better ensured than for the solid benzoic acid. The positions of the individual peaks remain constant for the liquid and the solid samples, but only for the liquid sample the intensity of the absorbance remain nearly consistent as well. The slight differences in the absorbance intensity of the ethanol samples can be neglected, because the cause is probably the fast evaporating of ethanol. The reproducibility for the measurements with liquid samples can be ensured, but with fast volatile substances, care must be taken that the substances are not exposed to air for too long before the measurement. Before the measurement the solid benzoic acid was mortared leading to different particle sizes, which

make the sample less homogeneous. In addition the layer thickness of the solid sample on the measurement instrument differentiated for each of the three measurements. So in conclusion the layer thickness and the concentration of the solid sample was different for the three measurements, which led with inclusion of the Bouguer-Lambert-Beer-law (Eq.1) to different absorbance intensities. In order to ensure the reproducibility of IR spectra with solid samples, the sample preparation and the sample thickness on the measuring plate has to be strictly equal for each measurement.

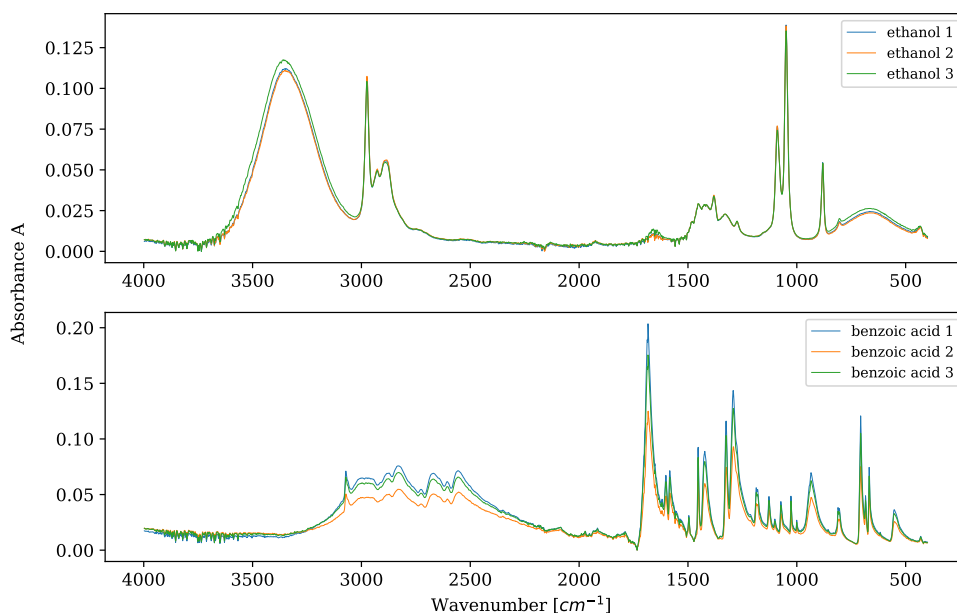


Figure 4: The IR spectrum of ethanol as liquid was measured using the ATR module for three times. The sample was replaced after each measurement. The same applies to the solid benzoic acid. For the liquid sample the measurement reproducibility is better ensured than for the solid.

The hydroxyl group has a characteristic peak between  $3670$  and  $2500\text{ cm}^{-1}$ <sup>10</sup>. For pure DMSO there is no band visible at this range, because the molecule has no hydroxyl group. As can be seen in Fig.5 the DMSO contained from the beginning some water as the first measurement at time zero shows a peak at the hydroxyl group region. The longer DMSO was exposed to ambient air, the more water it absorbed and the stronger the hydroxyl group peak is visible. This confirms the fact that DMSO is a highly hygroscopic substance<sup>12</sup>. At the wavenumber  $3442\text{ cm}^{-1}$  the absorbance and the exposition time of all ten measurement were plotted against each other, which is seen in Fig.6. The relation between absorption and time of ambient air exposition was fitted using a fourth degree polynomial function with a confident interval of  $0.0003$ , which confirms the accuracy of the fitted model.

$$A(t) = 12(5) \cdot 10^{-8}t^4 - 8(3) \cdot 10^{-6}t^3 + 12(5) \cdot 10^{-5}t^2 + 22(3) \cdot 10^{-4}t + 297(5) \cdot 10^{-4} \quad (6)$$

The fitted function can be seen as an orange graph in Fig.6. After 18 minutes of exposition time the function flattens and the ratio is not linear as in the beginning. DMSO forms hydrogen

bonds with water. Over the exposition time all DMSO molecules are saturated with water and no additional hydrogen bonds can be formed. The water absorption of DMSO has a capacity limit, which can be seen with the flattening of the function graph.

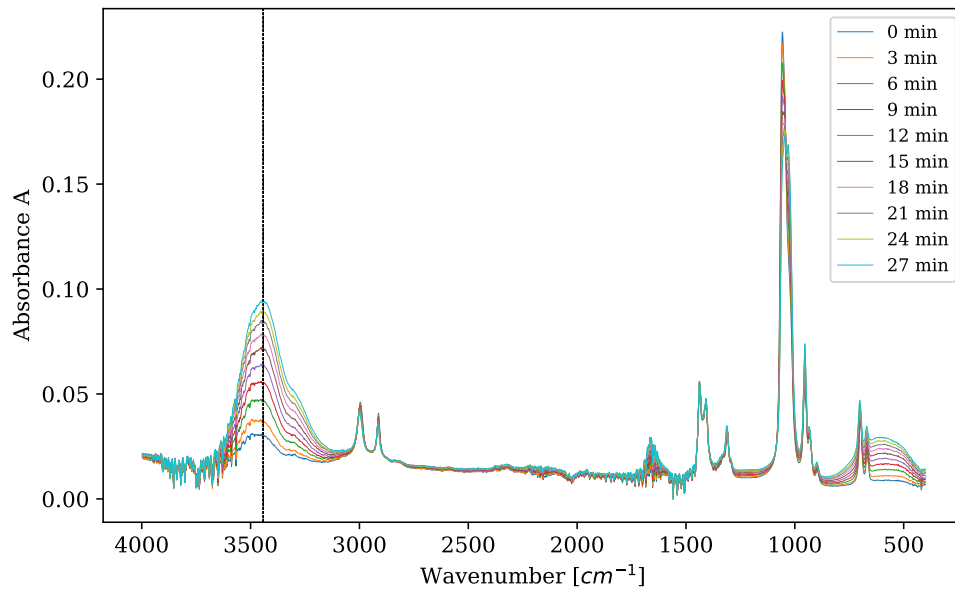


Figure 5: For 27 minutes after every three minutes an IR spectrum of DMSO, which was not replaced between the measurements, was taken. DMSO is highly hygroscopic and tends to absorb water by exposition to ambient air, which can be seen with the increasing intensity of the peak for the O-H stretch at wavenumber  $3442 \text{ cm}^{-1}$  marked by the dashed line.



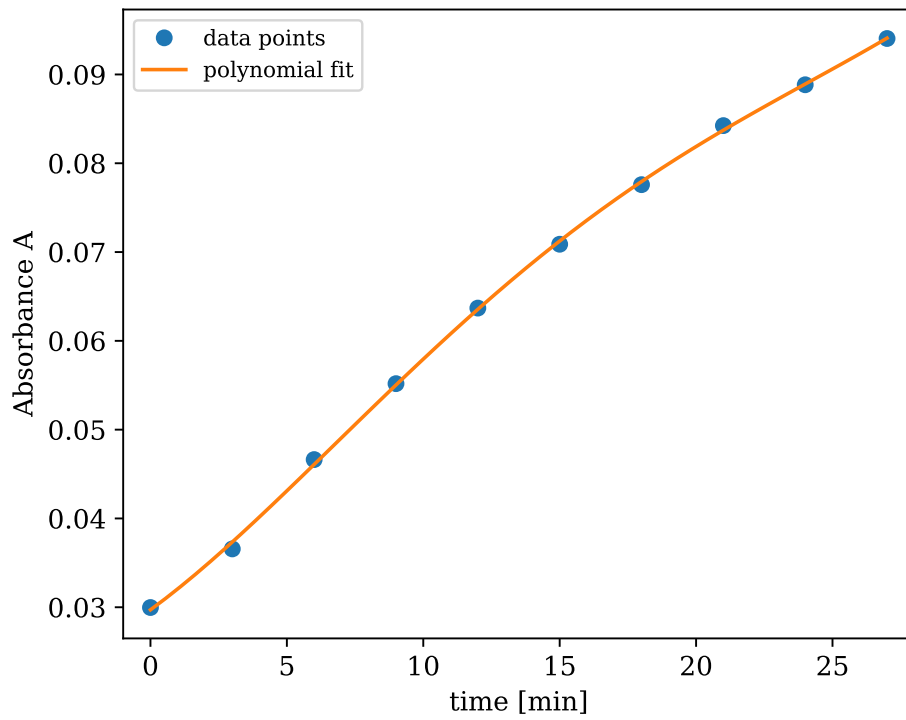


Figure 6: For all ten measurements of DMSO at different times the intensity of the absorbance at wavenumber  $3442\text{ cm}^{-1}$  was plotted against the time since DMSO was exposed to ambient air. The longer DMSO was exposed to ambient air, the more water was absorbed, but the relation is not linear. The beginning has a linear ratio, but towards longer exposition to ambient air, the function flattens.

The three IR spectra from the polymer samples were compared with spectra from the literature and thereby their identity was determined. The results can be seen in Tab.1. Since all samples could be assigned, IR spectroscopy is a suitable method for the identification of polymer samples.

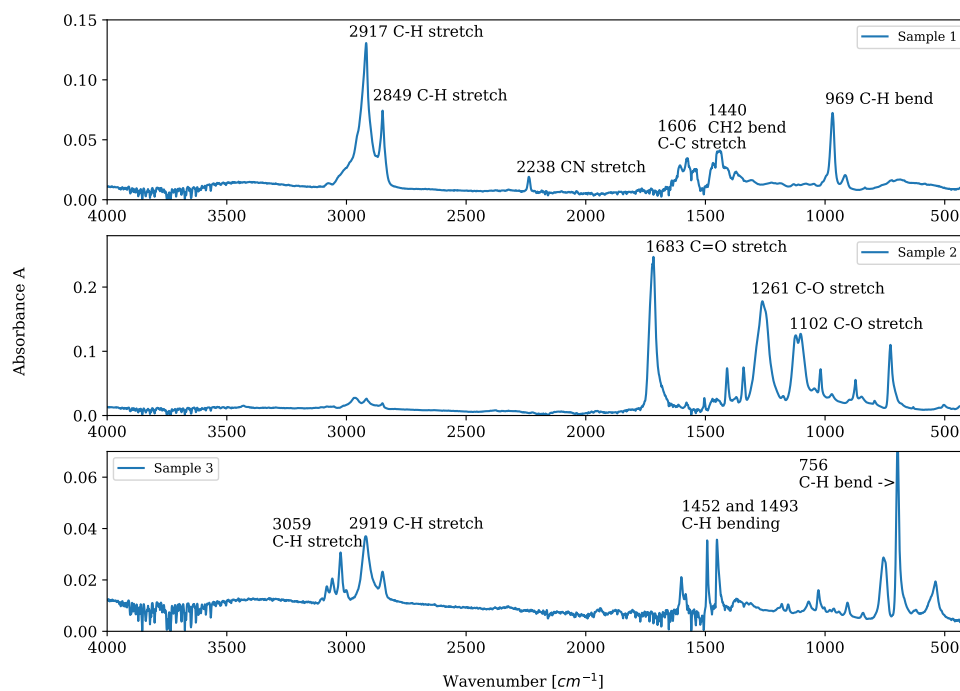


Figure 7: From three different polymer sample an IR spectrum was taken using ATR module. The characteristic bands for each sample are labeled in black and further explained in Tab.1.

sample	identification	measured wavenumber [ $\text{cm}^{-1}$ ]	reference wavenumber [ $\text{cm}^{-1}$ ]	assignment <sup>10</sup>
1	nitrile	2917 and 2849	2917 and 2849 <sup>13</sup>	C-H stretch
1	nitrile	2238	2237 <sup>13</sup>	CN stretch (nitrile)
1	nitrile	1606	1605 <sup>13</sup>	C-C stretch
1	nitrile	1440	1440 <sup>13</sup>	CH <sub>2</sub> bend
1	nitrile	969	967 <sup>13</sup>	C-H bend
2	polyethylene terephthalate	1683	1730 <sup>14</sup>	C=O stretch
2	polyethylene terephthalate	1261	1285 <sup>14</sup>	C-O stretch (carboxyl group)
2	polyethylene terephthalate	1102	1096 <sup>14</sup>	C-O stretch (ester group)
3	polystyrene	3059	3025 <sup>15</sup>	aromatic C-H stretch
3	polystyrene	2919	2921 <sup>15</sup>	C-H stretch
3	polystyrene	1452 and 1493	1451 and 1493 <sup>15</sup>	aromatic C-H stretch vibration
3	polystyrene	756	749 <sup>15</sup>	aromatic C-H deformation vibration

Table 1: The spectral bands from the three polymer samples assigned with their types of oscillation.

In Fig.8 different absorbance spectra from different ethanol/water solutions are presented. It is shown that the absorbance intensity of the O-H peak decreases with increasing ethanol content. The same pattern applies for the fingerprint region between 800 and 600  $\text{cm}^{-1}$ . The intensity of the O-H peak decreases with increasing ethanol content, because ethanol has only one O-H bond and therefore less hydrogen bonds and O-H bonds can cause oscillation in the region between 3550 and 2500  $\text{cm}^{-1}$  <sup>10</sup>. Unlike water, ethanol has C-H bonds in its molecule structure, which causes increasing peak intensities at 2975 and 2890 with rising ethanol content. The wavenumbers 3384, 2975 and 692  $\text{cm}^{-1}$  were selected to generate a function to calculate the ethanol content dependant on the absorbance intensity at these specific wavenumbers. Using the calibration points with the known ethanol contents a linear model was fitted using linear regression, which can be seen in Fig.9. The results of the ethanol content determination from three alcohol samples are shown in Tab.2.

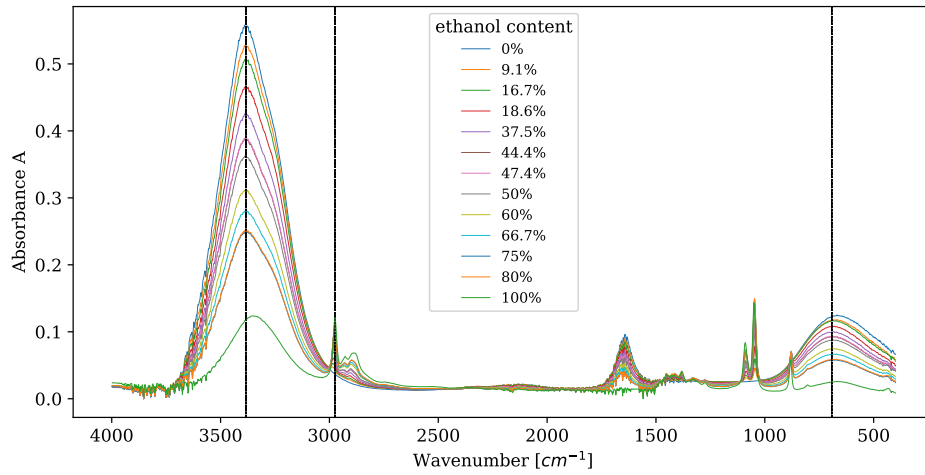


Figure 8: From known solutions with different ethanol and water contents IR spectra were measured. The higher the ethanol content of the solution the less the intensity of the O-H peak at wavenumber  $3384\text{ cm}^{-1}$  is visible. The same pattern applies in the fingerprint region at wavenumber  $692\text{ cm}^{-1}$ . In return the C-H peak at wavenumber  $2975\text{ cm}^{-1}$  increases with higher ethanol content. The changes in the band intensities at these three wavenumbers, which are marked with dashed lines, were used to determine the ethanol content of three different alcohol samples.

linear model	alcohol sample	calculated ethanol content [vol%]	reference ethanol content [vol%]
at O-H peak region	white wine	$16.2 \pm 1.8$	13.5
at O-H peak region	anise	$39.3 \pm 1.8$	35
at O-H peak region	rum	$36.4 \pm 1.8$	40
at C-H peak region	white wine	$18.1 \pm 2.4$	13.5
at C-H peak region	anise	$46.0 \pm 2.4$	35
at C-H peak region	rum	$36.9 \pm 2.4$	40
at fingerprint region	white wine	$14 \pm 3$	13.5
at fingerprint region	anise	$37 \pm 3$	35
at fingerprint region	rum	$34 \pm 3$	40

Table 2: In this table the results from the ethanol content determination of three alcohol samples is shown. The used linear model can be seen in Fig.9. The reference ethanol contents were provided from the assistant Luis Fábregas Ibáñez.

The calculated means and standard deviations for the three alcohol samples are for the white wine  $16 \pm 1\%$ , for the rum  $36 \pm 1\%$  and for the anise  $40.8 \pm 2.2\%$ . The calculations at the fingerprint region are the most truthful, because except for the rum the other two results fall within the confidence interval. It seems like the samples anise and rum interchanged, because rum should have the higher ethanol content than anise. Perhaps before the anise measurement the ethanol for cleaning the measurement instrument was not completely evaporated and therefore increased the ethanol content of the anise sample. The low percentage of the rum sample could

be explained as the measurement was not taken immediately after the sample was placed on the measurement instrument and some ethanol evaporated before the measurement. For the inaccurate results from all three samples has to be considered that the alcohol samples not only contain water and ethanol. Therefore the other ingredients can falsify the calculations, because the calibration function is based on water/ethanol solutions. In addition certain inaccuracies could be caused through the sample preparation of the water/ethanol samples and the measuring of the IR spectra from these samples. Ethanol is volatile and therefore by the sample preparation due to not fast enough closing of the sample containers some ethanol could have evaporated. After every ethanol/water sample measurement the measuring instrument was cleaned with ethanol. If not all of the ethanol evaporated it could have mixed up with the ethanol/water samples and increased their ethanol content.

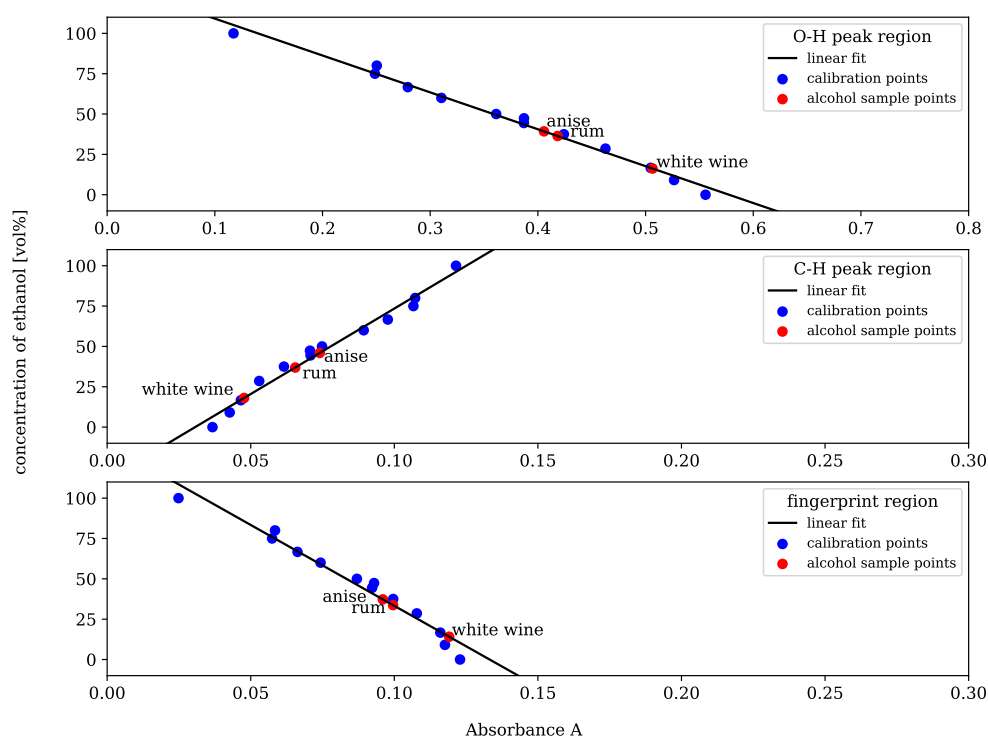


Figure 9: From the IR spectra from the ethanol and water solutions, which can be seen in Fig.8 at three specific wavenumbers, namely 3384, 29475 and  $692\text{ cm}^{-1}$ , the absorbance was plotted against the ethanol content. The ratios at all three wavenumbers were linear and therefore using linear regression a calibration function was determined. Using the calibration function the ethanol content of three samples was calculated.

The absorption spectra of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  are shown in Fig.10. The absorption spectra show the same absorption pattern, but their peaks positions are shifted. The shifts are caused upon isotopic substitution, since deuterium oxide has the higher reduced mass than water. The O-D peak is shifted to the right compared to the O-H peak. The O-H peak is at wavenumber  $3389\text{ cm}^{-1}$  and the O-D peak at wavenumber  $2496\text{ cm}^{-1}$ . Therefore the O-H peak is shifted by a value of 0.737. By transforming Eq.3 under the assumption that the spring constant for the O-H and O-D bond is equal the shift of the vibration wavenumber can be calculated as

$$\frac{\tilde{\nu}_{\text{O-D}}}{\tilde{\nu}_{\text{O-H}}} = \sqrt{\frac{16+2}{16 \cdot 2} \cdot \frac{16 \cdot 1}{16+1}} = 0.728. \quad (7)$$

Comparing the calculated shift number of 0.728 with the experimentally determined shift number of 0.737 it can be assumed that the measured absorption peaks of the O-H and the O-D band are accurate.

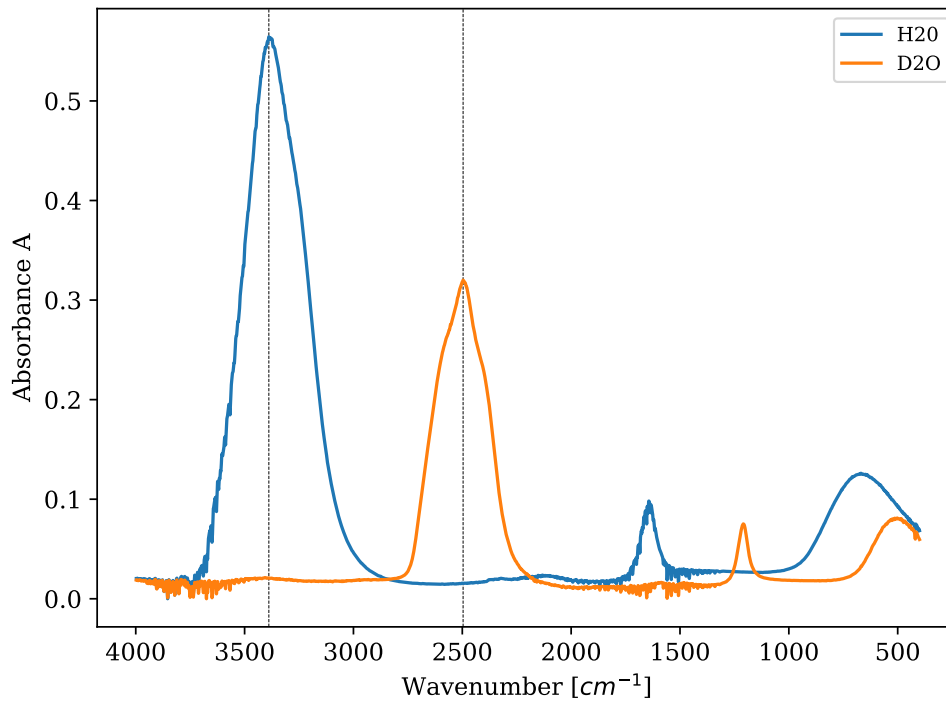


Figure 10: From distilled water and deuterium oxide IR spectra using ATR module were taken. The peak for the O-H stretch is at  $3389\text{ cm}^{-1}$  and the peak for the O-D stretch at  $2496\text{ cm}^{-1}$ , which is marked by the dashed lines. The peak for the O-D stretch is at a lower wavenumber, because deuterium oxide has the bigger reduced mass than distilled water.

An excerpt of the gaseous absorption spectrum of HBr, which can be seen in Fig.11, shows the fundamental band with its transition wavenumbers of the P- and R-branches. The transition wavenumbers of the P- and R-branches of the fundamental band are linear dependant on the coefficients q1, q2 and q3.

$$\tilde{\nu} = B_e q1 - \alpha q2 - D_e q3 + \tilde{\nu}_0 \quad (8)$$

The coefficients q1, q2 and q3 can be calculated from the vibration and rotation levels of the transition wavenumbers as

$$\begin{aligned} q1 &= J'(J' + 1) - J''(J'' + 1) \\ q2 &= (1(\nu = 1) + \frac{1}{2})J'(J' + 1) - \frac{1}{2}J''(J'' + 1) \\ q3 &= (J'(J' + 1))^2 - (J''(J'' + 1))^2, \end{aligned} \quad (9)$$

which comes from the Eq.4 and the results can be seen in Tab.3. Since only the fundamental band is analyzed the first two arguments in Eq.4 results in  $\tilde{\nu}_0$ , which is the intercept of Eq.8. A multiple linear regression was used to determine the rotational constant  $B_e$ , which resulted in  $8.463 \pm 0.016 \text{ cm}^{-1}$ . Using Eq.5 the bond length of HBr could be determined as  $142 \text{ pm}$ . In comparison with the value in literature of  $141 \text{ pm}$ <sup>16</sup> the calculations were accurate.

transition state	wavenumber [ $\text{cm}^{-1}$ ]	q1	q2	q3
R(0)	2575	2	3	4
R(1)	2591	4	8	32
R(2)	2606	6	15	108
P(1)	2542	-2	-1	-4
P(2)	2525	-4	0	-32
P(3)	2507	-6	3	-108

Table 3: The transition wavenumber of three R- and P-branches and the coefficients calculated from the vibration and rotation quantum numbers of the involved states are shown. The coefficients and the transition wavenumbers were used for the determination of the the rotation constant  $B_e$  of the molecule HBr.

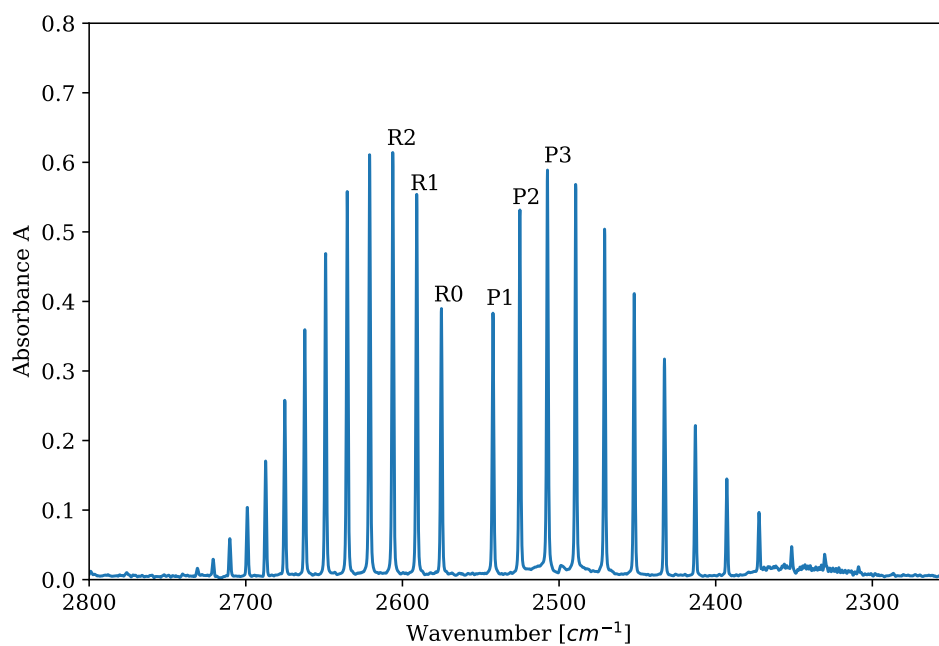


Figure 11: The for the calculation of the bond length relevant cutout of the gaseous HBr absorption spectrum, which was measured with the transmission method, is shown. The spectrum was provided from the assistant Luis Fábregas Ibáñez. The for the calculation used R- and P-branch transition states are labeled in black.



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## Appendix

A1 - Python Scripts  
A2 - Lab journal, dated March 30 2021.  
A3 - Task sheet  
A4 - Regression summaries

### A1 - Python Scripts

#### Python Code for part A

```
1 import numpy as np
2 from scipy import stats as stats
3 import matplotlib.pyplot as plt
4 from scipy.optimize import leastsq
5 from scipy.signal import find_peaks
6
7 filename = 'Ethanol.dpt'
8
9 font = {'family' : 'serif',
10         'weight' : 'normal',
11         'size' : 11}
12 plt.rc('font', **font)
13 Smallsize = 11
14 cm = 1/2.54
15
16 data = np.loadtxt(filename, delimiter=',', skiprows=1, dtype=float)
17 y = data[:,1]
18 x = data[:,0]
19 fig, ax = plt.subplots(figsize=(23*cm, 12*cm), dpi=600)
20 ax.text(3045,0.10985,'2974 \nC-H stretch')
21 ax.text(3521,0.11000,'3340 \nO-H stretch')
22 ax.text(1000,0.11900,'1049 \nC-O stretch')
23 plt.rc('font', size=Smallsize) # controls default text sizes
24 plt.rc('axes', labelsz=Smallsize) # fontsize of the x and y labels
25 plt.rc('legend', fontsize=9)
26 plt.ylabel(r'Absorbance A')
27 plt.xlabel('Wavenumber [ $\text{cm}^{-1}$ ]')
28 peaks, properties = find_peaks(y, height=0.1)
29 Peakpunkte = data[peaks]
30 plt.plot(x,y)
31 plt.axis([max(x),min(x),min(y),max(y)])
32 plt.savefig('TeilA.pdf')
33 plt.show()
```

#### Python Code for part B

```
1 import numpy as np
2 from scipy import stats as stats
3 import matplotlib.pyplot as plt
4 from scipy.optimize import leastsq
5 from scipy.signal import find_peaks
6
7 font = {'family' : 'serif',
8         'weight' : 'normal',
9         'size' : 11}
10 plt.rc('font', **font)
11 Smallsize = 11
12 plt.rc('font', size=Smallsize) # controls default text sizes
13 plt.rc('axes', labelsz=Smallsize) # fontsize of the x and y labels
14 plt.rc('legend', fontsize=9)
15 cm = 1/2.54
16
```

```

17 fig, ax = plt.subplots(2,1,figsize=(25*cm, 16*cm),dpi=600)
18 fig.text(0.5, 0.04, 'Wavenumber [cm-1]', ha='center')
19 fig.text(0.04, 0.5, 'Absorbance A', va='center', rotation='vertical')
20 filenamesEthanol = ['B1_Ethanol.dpt', 'B2_Ethanol.dpt', 'B3_Ethanol.dpt']
21 filenamesBenz = ['B1_Benzoesaure.dpt', 'B2_Benzoesaure.dpt', 'B3_Benzoesaure.dpt']
22 dataframesEthanol = []
23 labelse = ['ethanol 1', 'ethanol 2', 'ethanol 3']
24 labelsb = ['benzoic acid 1', 'benzoic acid 2', 'benzoic acid 3']
25 dataframesBenz = []
26 n = [0,1,2]
27 for i,f,k,l,m in zip(n,filenamesEthanol,filenamesBenz,labelsb,labelse):
28     dataframesEthanol.append(np.loadtxt(f, delimiter=',', skiprows=1, dtype=float))
29     dataframesBenz.append(np.loadtxt(k, delimiter=',', skiprows=1, dtype=float))
30     y = dataframesEthanol[i][:,1]
31     x = dataframesEthanol[i][:,0]
32     ax[0].plot(x,y,label = m,linewidth = 0.5)
33     ax[0].legend()
34     y = dataframesBenz[i][:,1]
35     x = dataframesBenz[i][:,0]
36     ax[1].plot(x,y,label = l,linewidth = 0.5)
37     ax[1].legend()
38
39 ax[0].invert_xaxis()
40 ax[1].invert_xaxis()
41 plt.show
42 plt.savefig('TeilB.pdf')

```

### Python Code for part C

```

1
2 import numpy as np
3 import statsmodels.formula.api as smf
4 import pandas as pd
5 from scipy import stats as stats
6 import matplotlib.pyplot as plt
7 from scipy.optimize import leastsq
8 from scipy.signal import find_peaks
9
10 font = {'family' : 'serif',
11         'weight' : 'normal',
12         'size' : 1}
13 plt.rc('font', **font)
14 Smallsize = 11
15 plt.rc('font', size=Smallsize) # controls default text sizes
16 plt.rc('axes', labelsz=Smallsize) # fontsize of the x and y labels
17 plt.rc('legend', fontsize=9)
18 cm = 1/2.54
19 fig, ax = plt.subplots(figsize=(20*cm, 12*cm),dpi=600)
20 filenames = ['C1_DMSO.dpt', 'C2_DMSO.dpt', 'C3_DMSO.dpt', 'C4_DMSO.dpt', 'C5_DMSO.dpt', 'C6_
DMSO.dpt', 'C7_DMSO.dpt', 'C8_DMSO.dpt', 'C9_DMSO.dpt', 'C10_DMSO.dpt']
21 labels = ['0 min', '3 min', '6 min', '9 min', '12 min', '15 min', '18 min', '21 min', '24
min', '27 min']
22 dataframes = []
23 n = [0,1,2,3,4,5,6,7,8,9]
24 for i,f,l in zip(n,filenames,labels):
25     dataframes.append(np.loadtxt(f, delimiter=',', skiprows=1, dtype=float))
26     y = dataframes[i][:,1]
27     x = dataframes[i][:,0]
28     x1 = dataframes[i][545,0]
29     ax.plot(x,y,label=l,linewidth = 0.5)
30     ax.vline(x1, color='k', linestyle='—',linewidth = 0.4)
31     ax.legend()
32     ax.set_ylabel('Absorbance A')
33     ax.set_xlabel('Wavenumber [cm-1]\n')
34
35 ax.invert_xaxis()
36 plt.savefig('TeilC1.pdf')
37

```

```

38 #Unterschied = 10 verschiedene Absorbanzen bei Wellenlänge 3441.65
39 Unterschied = np.zeros((10,2))
40 for i in range(0,10):
41     Unterschied[i] = dataframes[i][545]
42 fig, ax = plt.subplots(figsize=(15*cm, 12*cm), dpi=600)
43 fity = Unterschied[:,1]
44 fitx = np.array([0,3,6,9,12,15,18,21,24,27])
45 # Koeffizienten berechnen
46 coeffs, cov = np.polyfit(fitx, fity, 4, cov = True)
47 # macht Polynom fÄijr Plot
48 poly = np.poly1d(coeffs)
49 new_x = np.linspace(fitx[0], fitx[-1])
50 new_y = poly(new_x)
51 # gemessenen X-Werte in Polynomfunktion eingesetzt
52 y_val = poly(fitx)
53 plt.xlabel(r'time [min]')
54 plt.ylabel(r'Absorbance A')
55 plt.plot(fitx, fity, 'o', label='data points')
56 plt.plot(new_x, new_y, label='polynomial fit')
57 plt.xlim([fitx[0]-1, fitx[-1] + 1 ])
58 plt.rc('font', size=Smallsize) # controls default text sizes
59 plt.rc('axes', labelsz=Smallsize) # fontsize of the x and y labels
60 plt.rc('legend', fontsize=9)
61 plt.legend()
62 plt.savefig('TeilC2.pdf')
63 plt.show
64
65
66
67 Vertrauensintervall Berechnung
68
69 # Standardfehler Mittelwert
70 n = np.std(fity-y_val)/np.sqrt(10)
71 #t-taktil
72 ts = stats.t(df=9).ppf(0.975)
73 Verintervall = n*ts
74
75
76
77 Standardfehler fÄijr die einzelnen Coeffs
78
79 Standardfehlercoeffs = np.sqrt(np.diag(cov))
80 print('Standardfehler t^4, t^3, t^2, t und Steigung:\n', Standardfehlercoeffs)

```

## Python Code part D

```

1 import numpy as np
2
3 from scipy import stats as stats
4 import matplotlib.pyplot as plt
5 from scipy.optimize import leastsq
6 from scipy.signal import find_peaks
7
8 font = {'family' : 'serif',
9         'weight' : 'normal',
10        'size' : 1}
11 plt.rc('font', **font)
12 Smallsize = 11
13 plt.rc('font', size=Smallsize) # controls default text sizes
14 plt.rc('axes', labelsz=Smallsize) # fontsize of the x and y labels
15 plt.rc('legend', fontsize=9)
16 cm = 1/2.54
17
18 fig, ax = plt.subplots(3,1,figsize=(28*cm, 20*cm),dpi=600)
19 fig.text(0.5, 0.04, 'Wavenumber [Scm^-1]$ ', ha='center')
20 fig.text(0.04, 0.5, r'Absorbance A', va='center', rotation='vertical')
21
22 Handschuh = ['D1_Handschuh.dpt']
23 PET = ['D2_PET.dpt']

```

```

24 CD = ['D3_CD.dpt']
25 dataframesHandschuh = []
26 dataframesPET = []
27 dataframesCD = []
28 n = [0]
29 for i,f,k,m in zip(n,Handschuh,PET,CD):
30     dataframesHandschuh.append(np.loadtxt(f, delimiter=',', skiprows=1, dtype=float))
31     dataframesPET.append(np.loadtxt(k, delimiter=',', skiprows=1, dtype=float))
32     dataframesCD.append(np.loadtxt(m, delimiter=',', skiprows=1, dtype=float))
33     y = dataframesHandschuh[i][:,1]
34     x = dataframesHandschuh[i][:,0]
35     peaks, properties = find_peaks(y,height=None)
36     Peakpunkte = dataframesHandschuh[i][peaks]
37     ax[0].axis([400, 4000, 0, 0.15])
38     ax[0].plot(x,y,label = 'Sample 1')
39     ax[0].text(2990,0.13600,'2917 C-H stretch')
40     ax[0].text(2890,0.08285,'2849 C-H stretch')
41     ax[0].text(2290,0.02300,'2238 CN stretch')
42     ax[0].text(1700,0.04280,'1606 \nC-C stretch')
43     ax[0].text(1490,0.05600,'1440 \nCH2 bend')
44     ax[0].text(1000,0.08000,'969 C-H bend')
45     ax[0].legend()
46     y = dataframesPET[i][:,1]
47     x = dataframesPET[i][:,0]
48     #peaks, properties = find_peaks(y,height=0.02)
49     #Peakpunkte = dataframesPET[i][peaks]
50     ax[1].axis([400, 4000, 0, 0.28])
51     ax[1].plot(x,y,label = 'Sample 2')
52     ax[1].text(1750,0.255,'1683 C=O stretch')
53     ax[1].text(1310,0.19,'1261 C-O stretch')
54     ax[1].text(1150,0.135,'1102 C-O stretch')
55     ax[1].legend()
56     y = dataframesCD[i][:,1]
57     x = dataframesCD[i][:,0]
58     #peaks, properties = find_peaks(y,height=0.02)
59     #Peakpunkte = dataframesPET[i][peaks]
60     ax[2].axis([400, 4000, 0, 0.07])
61     ax[2].plot(x,y,label = 'Sample 3')
62     ax[2].text(3310,0.033,'3059 \nC-H stretch')
63     ax[2].text(2990,0.04,'2919 C-H stretch')
64     ax[2].text(1600,0.04,'1452 and 1493 \nC-H bending')
65     ax[2].text(1110,0.056,'756 \nC-H bend ->')
66     ax[2].legend()
67
68 ax[0].invert_xaxis()
69 ax[1].invert_xaxis()
70 ax[2].invert_xaxis()
71 plt.savefig('TeilD.pdf')
72 plt.show

```

## Python Code part E

```

1 import numpy as np
2 from scipy import stats as stats
3 import matplotlib.pyplot as plt
4 from scipy.optimize import leastsq
5 from scipy.signal import find_peaks
6
7 """
8 GrÃsseneinstellungen / Schrifteinstellungen
9 """
10 font = {'family' : 'serif',
11         'weight' : 'normal',
12         'size' : 11}
13 plt.rc('font', **font)
14 Smallsize = 11
15 cm = 1/2.54
16 """

```

```

17 Daten fÄijr die Kalibration mit den bekannten EthanolgehÄdltern
18 """
19 fig, ax = plt.subplots(figsize=(25*cm, 12*cm), dpi=600)
20 filenames = ['E1.dpt', 'E2.dpt', 'E3.dpt', 'E4.dpt', 'E5.dpt', 'E6.dpt', 'E7.dpt', 'E8.dpt', '
E9.dpt', 'E10.dpt', 'E11.dpt', 'E12.dpt', 'E13.dpt']
21 labels = ['0%', '9.1%', '16.7%', '18.6%', '37.5%', '44.4%', '47.4%', '50%', '60%', '66.7%', '75%',
'80%', '100%']
22 dataframes = []
23 n = [0,1,2,3,4,5,6,7,8,9,10,11,12]
24 for l,i,f in zip(labels,n,filenames):
25     dataframes.append(np.loadtxt(f, delimiter=',', skiprows=1, dtype=float))
26     y = dataframes[i][:,1]
27     x = dataframes[i][:,0]
28     plt.rc('font', size=Smallsize) # controls default text sizes
29     plt.rc('axes', labelsz=Smallsize) # fontsize of the x and y labels
30     plt.rc('legend', fontsize=9)
31     ax.plot(x,y, label = l, linewidth = 0.5)
32     x1 = dataframes[i][602,0]
33     x2 = dataframes[i][1003,0]
34     x3 = dataframes[i][3241,0]
35     ax.axvline(x1, color='k', linestyle='—', linewidth = 0.4)
36     ax.axvline(x2, color='k', linestyle='—', linewidth = 0.4)
37     ax.axvline(x3, color='k', linestyle='—', linewidth = 0.4)
38     plt.legend(title='ethanol content')
39     ax.set_ylabel(r'Absorbance A')
40     ax.set_xlabel('Wavenumber [Åm^{-1}]')
41 ax.invert_xaxis()
42 plt.savefig('TeilE1.pdf')
43
44 """
45 Daten der zu bestimmenden Substanzen
46 """
47 fig, ax = plt.subplots(figsize=(12, 4))
48 filenames2 = ['E_Rum.dpt', 'E_Weisswein.dpt', 'E_Anise.dpt']
49 dataframes2 = []
50 m = [0,1,2]
51 for i,f in zip(m,filenames2):
52     dataframes2.append(np.loadtxt(f, delimiter=',', skiprows=1, dtype=float))
53     y = dataframes2[i][:,1]
54     x = dataframes2[i][:,0]
55     ax.plot(x,y)
56     ax.set_ylabel(r'Absorbance')
57     ax.set_xlabel('Wavenumber [Åm^{-1}]')
58 ax.invert_xaxis()
59 plt.show
60 plt.figure()
61
62 Modellfunktionberechnung:
63 -bei WellenlÄdng 3383.52, bei Index 602 fÄijr OH stretch
64 -bei WellenlÄdng 2974.6, bei Index 1003 fÄijr CH stretch
65 -bei WellenlÄdng 692.409, bei Index 3241 in Fingerprint Region
66 """
67 Unterschied = np.zeros((13,2))
68 Unterschied1 = np.zeros((13,2))
69 Unterschied2 = np.zeros((13,2))
70 for i in range(0,13):
71     Unterschied[i] = dataframes[i][602]
72     Unterschied1[i] = dataframes[i][1003]
73     Unterschied2[i] = dataframes[i][3241]
74 Samples = np.zeros((3,2))
75 Samples1 = np.zeros((3,2))
76 Samples2 = np.zeros((3,2))
77 for i in range(0,3):
78     Samples[i] = dataframes2[i][602]
79     Samples1[i] = dataframes2[i][1003]
80     Samples2[i] = dataframes2[i][3241]
81
82 fig, ax = plt.subplots(3,1,figsize=(26*cm, 20*cm), dpi=600)
83 plt.rc('font', size=Smallsize) # controls default text sizes
84 plt.rc('axes', labelsz=Smallsize) # fontsize of the x and y labels
85 plt.rc('legend', fontsize=9)
86 fig.text(0.5, 0.04, r'Absorbance A', ha='center')

```

```

87 fig.text(0.04, 0.5, 'concentration of ethanol [vol%]', va='center', rotation='vertical'
88 )
89 # X Achse die verschiedenen Absorbanzen, Y Achse gibt den Ethanolgehalt
90 fitx1 = Unterschied1[:,1]
91 fitx2 = Unterschied2[:,1]
92 fitxSample = Samples[:,1]
93 fitxSample1 = Samples1[:,1]
94 fitxSample2 = Samples2[:,1]
95 fity = np.array([0,100/110*10,100/120*20,100/140*40,100/160*60,100/180*80,100/190*
96 90,50,100/250*150,100/300*200,100/400*300,100/500*400,100])
97 # Line fitting
98 model,cov = np.polyfit(fitx,fity,1,cov = True)
99 modell,covv = np.polyfit(fitx1,fity,1,cov = True)
100 model2,covvv = np.polyfit(fitx2,fity,1,cov = True)
101 predict = np.poly1d(model)
102 predict1 = np.poly1d(modell)
103 predict2 = np.poly1d(model2)
104 x_lin_reg = np.linspace(0, 1,1000)
105 y_lin_reg = predict(x_lin_reg)
106 y_lin_reg1 = predict1(x_lin_reg)
107 y_val = predict(fitx)
108 y_val1 = predict1(fitx1)
109 y_val2 = predict2(fitx2)
110 y_Samples = predict(fitxSample)
111 y_Samples1 = predict1(fitxSample1)
112 y_Samples2 = predict2(fitxSample2)
113 ax[0].axis([0, 0.8, -10, 110])
114 ax[0].scatter(fitx, fity, c = 'b', label = 'calibration points')
115 ax[0].scatter(fitxSample, y_Samples, c = 'r', label = 'alcohol sample points')
116 ax[0].plot(x_lin_reg, y_lin_reg, c = 'k', label = 'linear fit')
117 ax[0].annotate('white wine', (0.51, 17))
118 ax[0].annotate('rum', (0.43,36))
119 ax[0].annotate('anise', (0.408, 42.3))
120 ax[0].legend(title='O-H peak region')
121 ax[1].axis([0, 0.3, -10, 110])
122 ax[1].scatter(fitx1, fity, c = 'b', label = 'calibration points')
123 ax[1].scatter(fitxSample1, y_Samples1, c = 'r', label = 'alcohol sample points')
124 ax[1].plot(x_lin_reg, y_lin_reg1, c = 'k', label = 'linear fit')
125 ax[1].legend(title='C-H peak region')
126 ax[1].annotate('white wine', (0.012, 20.1))
127 ax[1].annotate('rum', (0.068,30.2))
128 ax[1].annotate('anise', (0.0755, 40.5))
129 ax[2].axis([0, 0.3, -10, 110])
130 ax[2].scatter(fitx2, fity, c = 'b', label = 'calibration points')
131 ax[2].scatter(fitxSample2, y_Samples2, c = 'r', label = 'alcohol sample points')
132 ax[2].plot(x_lin_reg, y_lin_reg2, c = 'k', label = 'linear fit')
133 ax[2].annotate('white wine', (0.12, 15))
134 ax[2].annotate('rum', (0.085,28.8))
135 ax[2].annotate('anise', (0.075, 35.7))
136 ax[2].legend(title='fingerprint region')
137 plt.savefig('TeilE2.pdf')
138 plt.show
139
140
141 Vertrauensintervall Berechnung
142
143 # Standardfehler Mittelwert
144 n = np.std(fity-y_val)/np.sqrt(13)
145 n1 = np.std(fity-y_val1)/np.sqrt(13)
146 n2 = np.std(fity-y_val2)/np.sqrt(13)
147 #t-taktil
148 ts = stats.t(df=12).ppf(0.975)
149 Verintervall = n*ts
150 Verintervall1 = n1*ts
151 Verintervall2 = n2*ts
152
153
154 Standardfehler des Koeffizienten und der Steigung
155
156 error1 = np.sqrt(np.diag(cov))
157 error2 = np.sqrt(np.diag(covv))

```

```
158 error3 = np.sqrt(np.diag(covvv))
159
160 print('Stdfehler fÄjr Funktion bei O-H peak:\nKoeffizient:', error1[0], '\n', 'Steigung:',
161       error1[1])
162 print('Stdfehler fÄjr Funktion bei C-H peak:\nKoeffizient:', error2[0], '\n', 'Steigung:',
163       error2[1])
164 print('Stdfehler fÄjr Funktion bei Fingerprint:\nKoeffizient:', error3[0], '\n', 'Steigung:',
165       error3[1])
166
167 """
168 Alkoholgehalt der Samples bestimmen
169 """
170 Referenzrum = np.array([40,40,40])
171 Referenzweisswein = np.array([13.5,13.5,13.5])
172 Referenzanise = np.array([35,35,35])
173 Rum = np.array([y_Samples[0], y_Samples1[0], y_Samples2[0]])
174 mRum = np.mean(Rum)
175 Weisswein = np.array([y_Samples[1], y_Samples1[1], y_Samples2[1]])
176 mWeisswein = np.mean(Weisswein)
177 Anise = np.array([y_Samples[2], y_Samples1[2], y_Samples2[2]])
178 mAnise = np.mean(Anise)
179 #Standardfehler Mittelwert
180 stdrum = np.std(Rum-Referenzrum)/np.sqrt(3)
181 stdweisswein = np.std(Weisswein-Referenzweisswein)/np.sqrt(3)
182 stdanise = np.std(Anise-Referenzanise)/np.sqrt(3)
```



## Python Code for part F

```

1 import numpy as np
2 from scipy import stats as stats
3 import matplotlib.pyplot as plt
4 from scipy.optimize import leastsq
5 from scipy.signal import find_peaks
6
7 """
8 import data
9 """
10 H2O = 'F_H2O.dpt'
11 D2O = 'F_D2O.dpt'
12 dataH = np.loadtxt(H2O, delimiter=',', skiprows=1, dtype=float)
13 dataD = np.loadtxt(D2O, delimiter=',', skiprows=1, dtype=float)
14 """
15 Schrift und GrÃsseneinstellungen fÃ¼r Plots
16 """
17 font = {'family' : 'serif',
18         'weight' : 'normal',
19         'size' : 11}
20 plt.rc('font', **font)
21 Smallsize = 11
22 plt.rc('font', size=Smallsize) # controls default text sizes
23 plt.rc('axes', labelsize=Smallsize) # fontsize of the x and y labels
24 plt.rc('legend', fontsize=9)
25 cm = 1/2.54
26 """
27 Plot H2O und D2O Spektrum
28 """
29 fig, ax = plt.subplots(figsize=(18*cm, 13*cm), dpi=600)
30 x = dataH[:,0]
31 y = dataH[:,1]
32 x1 = dataD[:,0]
33 y1 = dataD[:,1]
34 x2 = dataH[597,0]
35 x3 = dataH[1472,0]
36 peaks, properties = find_peaks(y1, height=0.3)
37 #peaks, properties = find_peaks(y, height=0.5)
38 PeakpunkteD = dataD[peaks]
39 #PeakpunkteH = dataH[peaks]
40 plt.ylabel(r'Absorbance A')
41 plt.xlabel(r'Wavenumber [cm-1 $]')
42 ax.axvline(x2, color='k', linestyle='--', linewidth = 0.4)
43 ax.axvline(x3, color='k', linestyle='--', linewidth = 0.4)
44 plt.plot(x,y, label = 'H2O')
45 plt.plot(x1,y1, label = 'D2O')
46 ax.invert_xaxis()
47 plt.legend()
48 plt.savefig('TeilF.pdf')
49 plt.show()
50
51 """
52 OH Peak bei H2O bei Wellenzahl 3389, Index 597
53 OH Peak bei D2O bei Wellenzahl 2496, Index 1472
54 """
55
56 Berechnungen fÃ¼r die reduzierte Masse
57 """
58 # Massen H, O und D in u
59 u = 2.65686*10**-23 # in gramm
60 mH = 1*u
61 mO = 16*u
62 mD = 2*u
63 c = 299792458*10**3 # Lichtgeschwindigkeit cm/s
64
65 muH = mH*mO/(mH+mO) # in Einheit u
66 muD = mD*mO/(mD+mO) # in Einheit u
67
68 """
69 Berechnung Federkonstante -> Annahme sind gleich
70 """
71 kH = ((3389*2*c)**2)*muH

```

```

72 | kD = ((2496*2*c)**2)*muD
73 |
74 | """
75 | Berechnung wavenumber shift von OH zu OD
76 | """
77 | shift = np.sqrt(muH*np.reciprocal(muD))
78 | waveshift = shift*3389

```

## Python Code for part G

```

1 |
2 | import numpy as np
3 | from sklearn import linear_model
4 | import statsmodels.api as sm
5 | from scipy import stats as stats
6 | import matplotlib.pyplot as plt
7 | from scipy.optimize import leastsq
8 | from scipy.signal import find_peaks
9 |
10 | """
11 | Schrift und GrÃusseneinstellungen fÃ¼r Plots
12 | """
13 | font = {'family' : 'serif',
14 |         'weight' : 'normal',
15 |         'size'   : 11}
16 | plt.rc('font', **font)
17 | Smallsize = 11
18 | plt.rc('font', size=Smallsize)           # controls default text sizes
19 | plt.rc('axes', labelsize=Smallsize)      # fontsize of the x and y labels
20 | plt.rc('legend', fontsize=9)
21 | cm = 1/2.54
22 |
23 | """
24 | import data and plot for spectrum
25 | """
26 | fig, ax = plt.subplots(figsize=(20*cm, 13*cm), dpi=600)
27 | HBr = 'G_HBr.txt'
28 | data = np.loadtxt(HBr, delimiter=',', skiprows=1, dtype=float)
29 | x = data[:,0]
30 | y = data[:,1]
31 | peaks, properties = find_peaks(y, height=0.3)
32 | Peakpunkte = data[peaks]
33 | plt.axis([2250, 2800, 0, 0.8])
34 | plt.annotate('R0', (2580, 0.4))
35 | plt.annotate('R1', (2595, 0.56))
36 | plt.annotate('R2', (2610, 0.625))
37 | plt.annotate('P1', (2546.5, 0.395))
38 | plt.annotate('P2', (2530, 0.54))
39 | plt.annotate('P3', (2509.7, 0.6))
40 | plt.ylabel(r'Absorbance A')
41 | plt.xlabel('Wavenumber [cm-1 $]')
42 | plt.plot(x,y)
43 | ax.invert_xaxis()
44 | plt.show()
45 | plt.savefig('TeilG.pdf')
46 |
47 | """
48 | Berechnung reduzierte Masse
49 | """
50 | u = 1.66054019999999*10**-24
51 | mH = 1*u
52 | mBr = 80*u
53 |
54 | muHBr = 1/((1/mH)+(1/mBr)) # Einheit gramm
55 |
56 | """
57 | bei WellenlÃngen 2800 bis 2400 / Zuordnung der WellenlÃngen
58 | """

```

```

59 | vR0 = 2575.08
60 | vR1 = 2590.88
61 | vR2 = 2606.18
62 | vP1 = 2542.19
63 | vP2 = 2524.99
64 | vP3 = 2507.40
65 | v = np.array([vR0, vR1, vR2, vP1, vP2, vP3])
66 | q0 = np.array([0, 0, 0, 0, 0, 0])
67 | q1 = np.array([1, 1, 1, 1, 1, 1])
68 | q2 = np.array([2, 2, 2, 2, 2, 2])
69 | q3 = np.array([2, 4, 6, -2, -4, -6])
70 | q4 = np.array([3, 8, 15, -1, 0, 3])
71 | q5 = np.array([4, 32, 108, -4, -32, -108])
72 |
73 | """
74 | multiple Linear Regression
75 | (wurde dann nicht verwendet fÄijr Bericht, da Fehler nicht gut ermittelbar sind)
76 | """
77 | X = np.array([q3, q4, q5]).transpose()
78 | y = v
79 |
80 | lm = linear_model.LinearRegression()
81 | lm.fit(X, y)
82 | coeffs = lm.coef_
83 | intercept = lm.intercept_
84 | y2 = lm.predict(X)
85 | print(coeffs)
86 |
87 | """
88 | multiple Linear Regression with OLS
89 | """
90 | X = sm.add_constant(X)
91 | model = sm.OLS(y, X).fit()
92 | ypred = model.predict(X)
93 | coef = model.params
94 | print(model.summary())
95 |
96 | """
97 | Berechnung Fehler
98 | """
99 | Differenz = y-ypred
100 | sterr = np.std(Differenz)/np.sqrt(6)
101 | ts = stats.t(df=5).ppf(0.975)
102 | Verintervall = sterr*ts
103 |
104 | """
105 | Berechnung BindungslÄänge im Gleichgewichtszustand
106 | """
107 | c = 299792458*10**2 # Lichtgeschwindigkeit cm/s
108 | h = 6.62607015*10**-27 # Plankkonstante in cm^2*g/s^3
109 | B = coef[1] # Einheit cm^-1
110 | R = np.sqrt(h/(8*B*np.pi**2*c*muHBr)) #Einheit cm

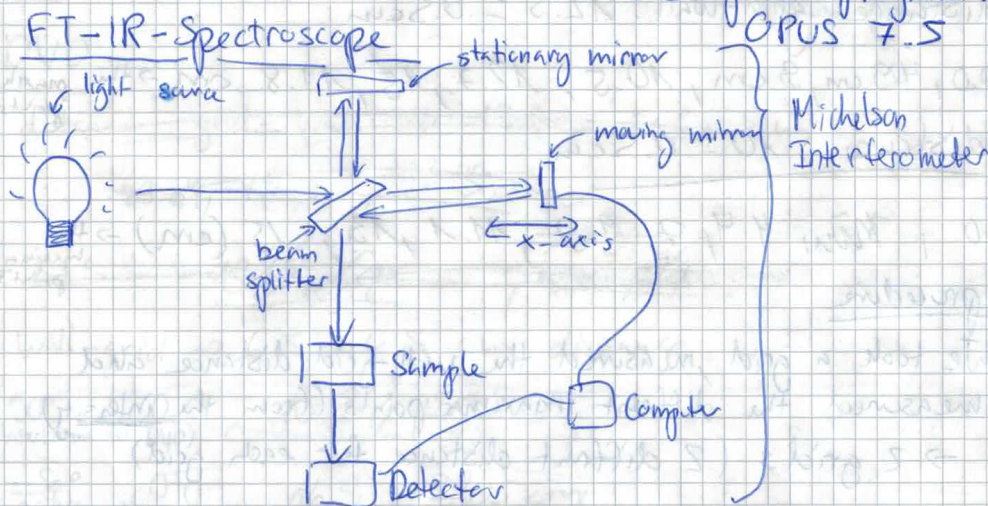
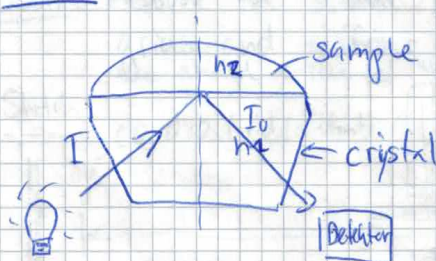
```

**A2 - Lab journal**

IRS, 30.3.21, Labpartner: Oasmin Schleiss  
Elin Sebesta

- IR spectroscopy has great value in chemistry. Molecules are excited to vibrations and rotations by absorption of photon energy. The vibrations and rotations are specific for certain molecule bonds and their environment. IR spectroscopy can be used for element identification by comparing the obtained spectra to literature references.

- all measurements are made with BRUKER Alpha FT-Spectrometers equipped with ATR and Transmission modules.  
→ computer program!

ATR - method



Settings

- Resolution:  $2 \text{ cm}^{-1}$
- Sample scan time: 16 scans (measurement time > 35 s)
- Background: " " " "
- Save data from  $4000 \text{ cm}^{-1}$  to:  $400 \text{ cm}^{-1}$
- Result spectrum: Absorbance
- Spectra extended ATR correction → standard

- ① Background was measured
- ② Ethanol sample with ATR technique was taken  
 ↳ Cas No.: 64-17-5 → saved as Ethanol
- ③ Benzoic acid was measured and then a IR spectrum was taken.  
 ↳ over 99% pure, 1243 g → saved as Benzoic acid

Test Reproducibility B

- 3 times with Ethanol an IR spectrum was taken  
 ↳ like ② → LHM from the HCl Shop (not pure)  
 → the sample was replaced after the measurements  
 ↳ (B1, B2, B3 - Ethanol.dpt)
- 3 times with the Benzoic acid (like from ③)  
 ↳ → saved as B1, B2, B3 - Benzoic acid.dpt.

Plastics D → 3 IR Spectra were taken from 3 unknown solid materials

- 1) Handschuh D1 - Handschuh sample was taken
- 2) D2 - sample PET " "
- 3) D3 - CD " "

### C DMSO exposed to ambient air

SO.3.21, Jasmin -  
Elia Seber

- A fresh sample of DMSO was prepared  
 $< 0.03\%$   $H_2O$   
 VWR 23500, 2.60
- 10 absorption spectra were measured by  
 waiting 3 min in between (without changing the sample)  
 → saved as C1...10-DMSO.dpt

### E → absolute, $> 99.8\%$

13  $H_2O$ /Ethanol solutions were prepared and an IR spectra was taken

- ① 100%  $H_2O$  (distilled) 100  $\mu l$   $H_2O$
- ② 100  $\mu l$   $H_2O$  10  $\mu l$  Ethanol
- ③ " 20  $\mu l$  E
- ④ " 40  $\mu l$  E
- ⑤ " 60  $\mu l$  E
- ⑥ " 80  $\mu l$  E
- ⑦ " 90  $\mu l$  E
- ⑧ " 100  $\mu l$  E
- ⑨ " 150  $\mu l$  E
- ⑩ " 200  $\mu l$  E
- ⑪ " 300  $\mu l$  E
- ⑫ " ~~350~~ 400  $\mu l$  E
- ⑬ 100  $\mu l$  Ethanol

→ saved as E1...E13.dpt



→ Samples E-Ram, E-Weisswein, E-Anise  
→ 40.0%, → 13.5%, → 35%  
→ IR Spectra were taken

Dr. J. C. S. S. S.  
D. S. S. S. S.  
S. S. S. S. S.  
E. S. S. S. S.

F → saved as F-H<sub>2</sub>O

1. an IR Spectra from H<sub>2</sub>O (deion.) was taken (100  $\mu$ l)

2. " " D<sub>2</sub>O, 99.9% pure (10  $\mu$ l)  
CIL, Inc  
DLM4-10

## A3 - Task sheet

**IRS****Infrared Spectroscopy Experiments**

Location:	HCI H290	Group: 25
Date:	March 30 2021, 13:00 Uhr	Assistant: <b>Luis Fábregas Ibáñez</b>
Report deadline:	April 23 2021	<i>luis.fabregas@phys.chem.ethz.ch</i>

**How to prepare to the introduction**

Read the document [1] as a good preparation to the IR experiment. Additional recommended references are listed at the end of this task list.

**Experiments**

*Note:* Spectrometer settings and sample details have to be recorded clearly. Each team works strictly independently to collect its own data (preparing solutions, measuring spectra) unless otherwise specified. Measurements are made with BRUKER Alpha FT-IR spectrometers, equipped with ATR and Transmission modules, respectively.

**A — Measurement basics**

With the ATR module measure the IR absorption spectrum of pure liquid or solid substance. Background and sample interferograms are measured and, with the spectrometer software, processed to obtain the single intensity spectra and finally the transmission and the absorption spectrum of the sample. With this example, explain and illustrate the route from the interferograms to the absorption spectrum. Compare the absorption spectrum with one taken from literature [2]. Assign prominent bands in the spectrum to the vibration of certain functional groups.

**B — Verification of measurement reproducibility**

Check, with liquid and solid samples, whether the ATR technique gives reproducible spectra (with respect to absorbance values and wavenumber positions of individual peaks). Take 3 measurements of each substance, replacing the sample between the measurements.

**C — Absorption spectrum of liquid DMSO exposed to ambient air**

DMSO is a highly hygroscopic substance and tends to absorb water by simple exposition to ambient air. IR allows us to monitor this phenomenon. Prepare a sample of fresh DMSO and measure 10 absorption spectra by waiting (e.g. 3 minutes) between measurements (without changing the sample). Plot all spectra, identify the water wavenumbers, and plot the absorbance values  $A$  against time  $t$ . Find an appropriate model function  $A(\phi_t)$  that fits the data.

**D — Absorption spectra and identification of plastics**

ATR-IR spectroscopy has a lot of industrial applications, one of them being quality control. Databases exist to identify e.g. polymers [3,4]. Measure absorption spectra of selected polymer samples. Draw the spectra in an overview for easy identification or differentiation. Assign prominent bands in the spectra to the vibration of certain functional groups.

**E — Absorption spectra of binary solutions of water and ethanol**

IR spectra of binary solutions of water (w) and ethanol (e) strongly depend on the composition. Prepare 12 binary solutions (including pure substances) with known volume fractions  $\phi_e = V_e/(V_e + V_w)$  and measure the absorption spectra of these samples with the ATR technique. Plot all spectra (full range and details) and discuss the spectral changes.

At a selected wavenumber determine absorbance values  $A$  and plot them against  $\phi_e$ . Find an appropriate model function  $A(\phi_e)$  that fits the data. Repeat the procedure with absorbance data taken at two other wavenumbers.

Measure the absorption spectrum of a sample of a liquor (e.g. wine, grappa, whisky, etc. feel free to bring a sample from home) and determine the alcohol content using the above calibration graphs.



**F — Vibrational spectra and transition energies of isotopomers**

Measure the IR absorption spectrum of a compound (*e.g.*  $\text{H}_2\text{O}$  or  $\text{CHCl}_3$ ) and of its deuterated analogon. Verify (by calculation of the reduced masses  $\mu$ ) the shift of the vibration wavenumber upon isotopic substitution [1].

**G — Rotational-vibrational spectra of diatomic molecules**

At high resolution, IR absorption spectra of small molecules may be observed with discrete rotational-vibrational transitions, see [1]. Aim of this experiment is to prepare several gaseous samples, to measure well-resolved spectra in a gas cell and to study and analyze the spectra of diatomic molecules to obtain specific molecular parameters such as bond lengths with high precision.

The discrete vibrational-rotational energy levels of a diatomic molecule can be described by

$$E_{\text{vib,rot}} = h\nu_0 \left(v + \frac{1}{2}\right) - h\nu_0 x_e \left(v + \frac{1}{2}\right)^2 + hc \left(B_e - \alpha \left(v + \frac{1}{2}\right)\right) J(J+1) \quad ,$$

$$B_e = \frac{h}{8\pi^2 \mu c R_e^2} \quad ,$$

$v$  and  $J$ : vibrational and rotational quantum number, respectively,  $\nu_0$ : frequency of the harmonic vibration,  $x_e$ : anharmonicity constant,  $B_e$ : equilibrium rotational constant,  $\alpha$ : rotation-vibration constant,  $R_e$ : equilibrium bond length.

Rotation-vibration absorption transitions  $(v=0, J'') \rightarrow (v=1, J')$  within the fundamental vibration transition occur at discrete transition wavenumbers

$$\tilde{\nu} = \frac{E_{v=1, J'} - E_{v=0, J''}}{hc} = \tilde{\nu}_0 - 2\tilde{\nu}_0 x_e + \left(B_e - \frac{3}{2}\alpha\right) J'(J'+1) - \left(B_e - \frac{1}{2}\alpha\right) J''(J''+1) \quad .$$

A simple method uses two differences of out of four transitions, *e.g.*

transition	$\Delta J$	change of $J$	transition	$\Delta J$	change of $J$
$R(0)$ transition	+1	$J'' = 0 \rightarrow J' = 1$	$P(1)$ transition	-1	$J'' = 1 \rightarrow J' = 0$
$R(1)$ transition	+1	$J'' = 1 \rightarrow J' = 2$	$P(1)$ transition	-1	$J'' = 2 \rightarrow J' = 1$

Explicit expressions of  $\tilde{\nu}$  for each of the four transitions are given in [1]. In the experiment you will determine the wavenumbers of these transitions from the absorption spectrum and further calculate the equilibrium bond length  $R_e$  of the molecule.

**Literature**

- [1] E. Meister, *Infrarotspektroskopie* (provisorische Versuchsanleitung), ETH Zürich (5.4.2020).
- [2] J. Coates, Interpretation of Infrared Spectra, A Practical Approach, in: R.A. Meyers, *Encyclopedia of Analytical Chemistry*, John Wiley & Sons, 2006.
- [3] SDBS Spectral Database for Organic Compounds, National Institute of Advanced Industrial Science and Technology (AIST), Japan.  
[sdb.sdb.aist.go.jp/sdb/](https://sdb.sdb.aist.go.jp/sdb/) (9.3.2020).
- [4] *Polymer Sample Identification Using Quest ATR*, Specac Application Note 42, [www.specac.com/en/documents/application-notes/polymer-identification-quest-application-note](http://www.specac.com/en/documents/application-notes/polymer-identification-quest-application-note) (9.3.2020).

**Lab report**

Consult the appendices B and C in the praktikum book and the document *Lab Report Correction Checklist* when preparing your report! The report should present quantitative as well as qualitative findings of your experiments, clearly described and with context to theory and literature references. Just consider your report a research paper!

Deadline to hand in the signed report (per email to [luis.fabregas@phys.chem.ethz.ch](mailto:luis.fabregas@phys.chem.ethz.ch) and C.C. to [erich.meister@phys.chem.ethz.ch](mailto:erich.meister@phys.chem.ethz.ch)) is **April 23 2021**.

Please add to your report:

- This task list
- copies of your lab journal
- program codes used
- all regression summaries

Please attach a ZIP file with all measured data, R files and report PDF to the email.

## A4 - Regression summaries

### for part C

The standard errors for the fourth degree polynomial function:

```
In [22]: runfile('C:/Users/sebes/OneDrive/ETH/4.Semester_2020_ETH/PC Praktikum/
2.Versuch_IRS/TeilC/C_DMSO.py', wdir='C:/Users/sebes/OneDrive/ETH/4.Semester_2020_ETH/
PC Praktikum/2.Versuch_IRS/TeilC')
Standardfehler t^4, t^3, t^2, t und Steigung:
[5.33479060e-08 2.90440032e-06 5.08218316e-05 3.10475243e-04
5.36884708e-04]
```

### for part E

The standard errors for the three linear regressions:

```
In [23]: runfile('C:/Users/sebes/OneDrive/ETH/4.Semester_2020_ETH/PC Praktikum/
2.Versuch_IRS/TeilE/E_Ethanolcontent.py', wdir='C:/Users/sebes/OneDrive/ETH/
4.Semester_2020_ETH/PC Praktikum/2.Versuch_IRS/TeilE')
Stdfehler für Funktion bei O-H peak:
Koeffizient: 7.390012199359168
Steigung: 2.882195820574911
Stdfehler für Funktion bei C-H peak:
Koeffizient: 46.17353509479053
Steigung: 3.682984870367805
Stdfehler für Funktion bei Fingerprint:
Koeffizient: 56.865354683960426
Steigung: 5.132956112610616
```

### for part G

The regression summary(OLS function used):

	coef	std err	t	P> t	[0.025	0.975]
const	2558.8621	0.019	1.38e+05	0.000	2558.782	2558.942
x1	8.4628	0.007	1131.278	0.000	8.431	8.495
x2	-0.2305	0.003	-70.847	0.000	-0.244	-0.216
x3	0	0.000	0	1.000	-0.002	0.002