

UNIVERSITY OF LEIPZIG

ADVANCED LABS

Lab report

Rotation-Vibration Spectra of Molecules

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Conducted on:

Contents

1	Introduction	1
2	Analysis	2
2.1	Task 1	2
2.2	Task 2	3
2.2.1	Calibration	3
2.2.2	Zerofilling	4
2.2.3	Apodization	5
2.2.4	Comparison	5
2.2.5	Step Size and Theoretical Spectral Resolution	6
2.3	Task 3	7
3	Conclusion	8
	Appendices	9
A	Task 1	9
A.1	Plots	9
A.2	Tables	9
B	Task 2	10
	Bibliography	11

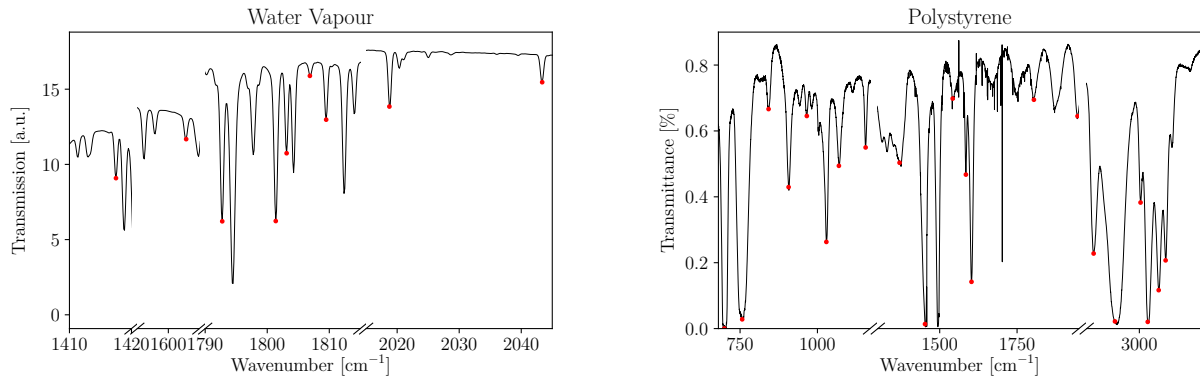
1 Introduction

2 Analysis

2.1 Task 1

Verify the calibration of the wavenumber scale of the infrared spectrometer Spectrum 100 using water vapor and polystyrene calibration bands. Plot the experimentally determined deviations and discuss them.

When measuring the spectrum of "water vapour", what we are actually measuring is the empty cuvette holder with air inside it, as a background spectrum that will prove useful later. The following plots show the spectra for water vapour and polystyrene:



(a) Water Vapour Spectrum, with the dips marked by red dots. Only the useful parts of the graph are shown; with ranges of $\bar{\nu} = 1410 - 1420$, $1595 - 1605$, $1790 - 1815$, $2015 - 2045 \text{ cm}^{-1}$.

(b) Polystyrene Spectrum, with the dips marked by red dots. Only the useful parts of the graph are shown; with ranges of $\bar{\nu} = 680 - 1170$, $1300 - 1950$, $2830 - 3200 \text{ cm}^{-1}$.

Figure 1: Useful parts of the water vapour and polystyrene spectra. Full plots found in Appendix A.1

The tables in Appendix A.2 show the comparison between the experimentally found dip wavenumbers and the ones provided in [1]. The following plot show the deviations from the theoretical values:

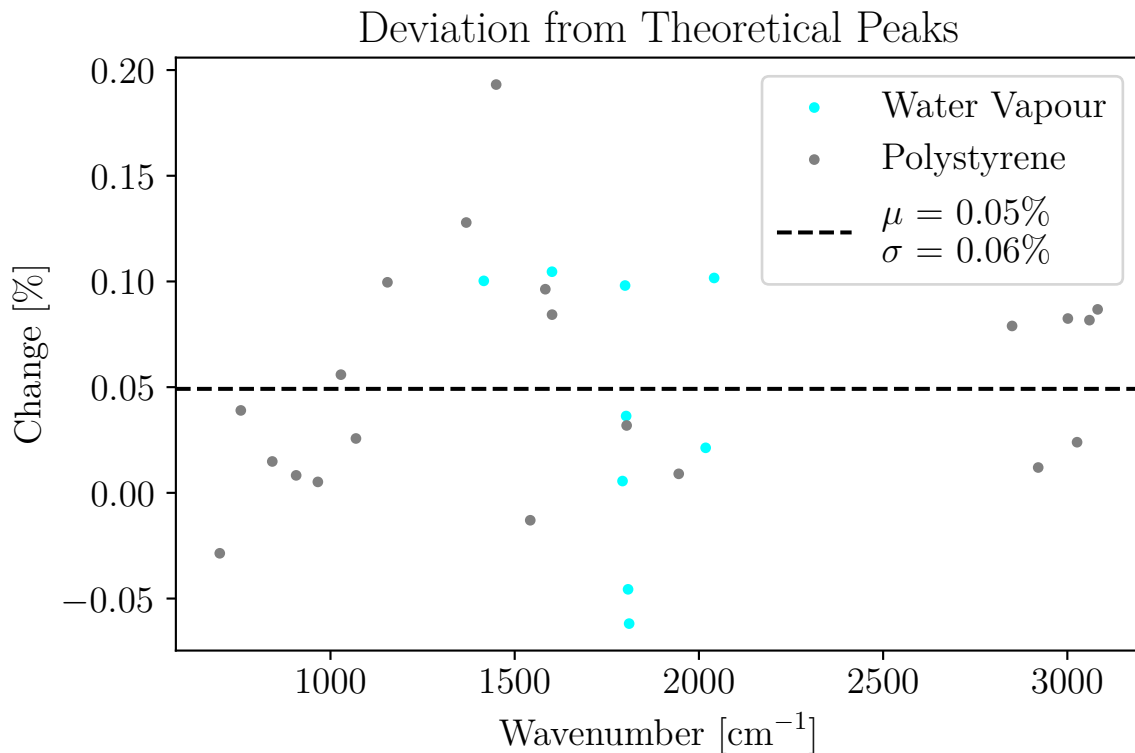


Figure 2: Deviations of the experimentally found wavenumbers from the theoretical ones for both water vapour and polystyrene.

Since the deviations should be device-dependent rather than sample-dependent, they can be plotted together for a better average. The average percentage change was around 0.05% with a standard deviation of 0.06%. In wavenumbers, this amounts to an average of 0.92 cm^{-1} and a standard deviation of 1.04 cm^{-1} . This shows that the device is well-calibrated as the deviations are well-within acceptable an acceptable range.

2.2 Task 2

Acquire interferograms of the water vapor spectrum using different mirror ranges of the interferometer. Obtain the spectra by applying a Fourier transformation to these interferograms. Calibrate the wavenumber scale of the thereby obtained spectra using the values for the water vapor bands. Determine step size of the optical path from the band width of the spectrum. Discuss the influence of the interferogram length and the applied zero-filling and apodisation on the spectral resolution based on the spectra. Based on the calculated step size, give the theoretical spectral resolution in dependence on the recorded data point count.

2.2.1 Calibration

When converting the raw interferograms to spectra, the x -axis needs to be calibrated. As the raw data has a scale of mirror position, and the Fourier transform is just a frequency of those, rather than a wavenumber. The following figure shows the raw and Fourier transformed data for the maximum mirror range:

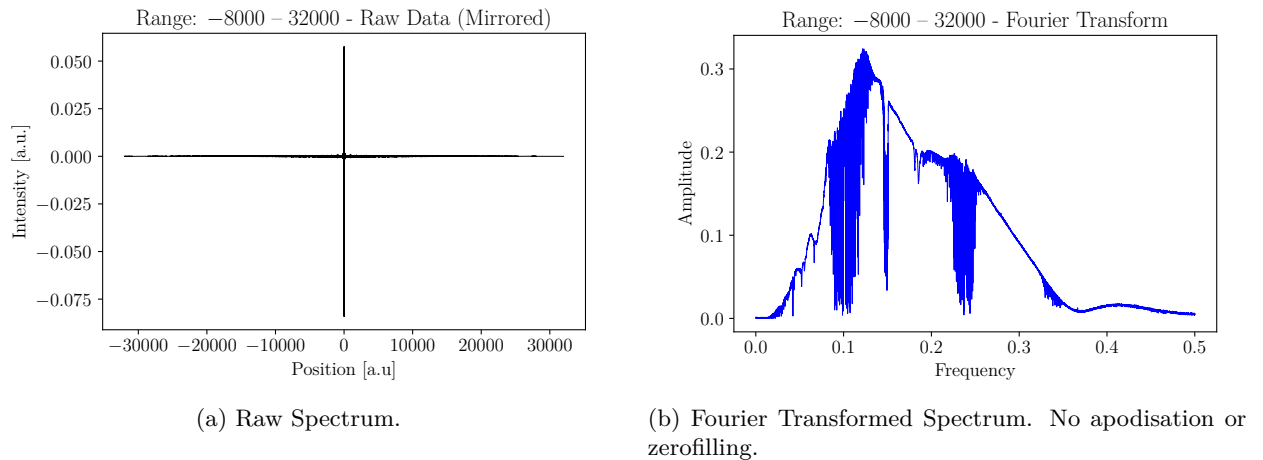


Figure 3: Raw and Fourier Transformed data

To calibrate the wavenumber scale, the wavenumbers of the water vapour bands are used, in a fashion similar to Figure 1a. The following figure shows the calibration of the wavenumber scale for the maximum mirror range:

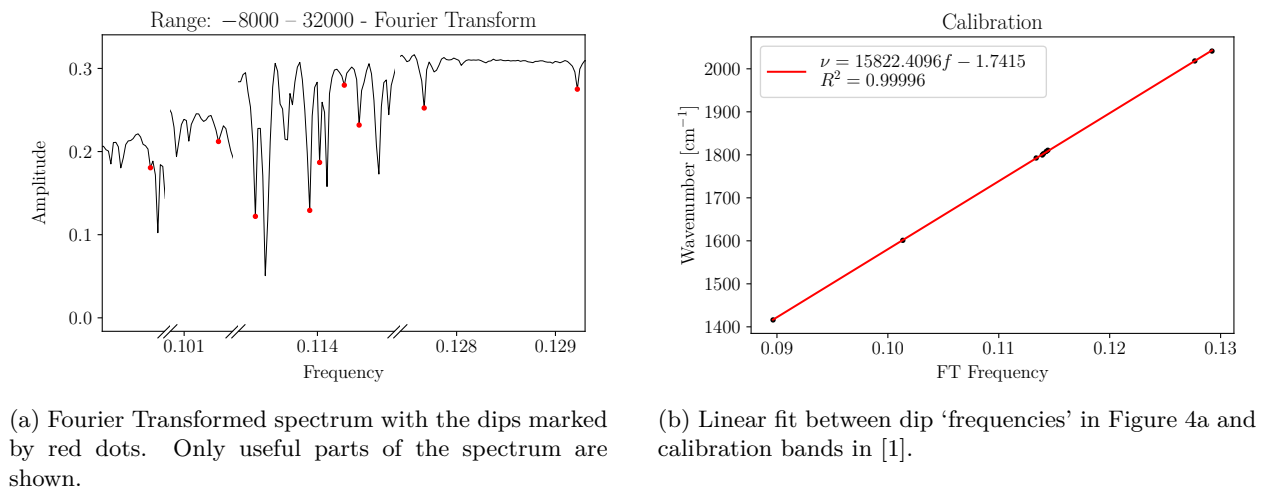


Figure 4: Calibration of the frequency scale

This linear function can now be used to convert from the frequency scale to the wavenumber scale. Since all known dips were used, and we have a high R^2 value, this equation is very reliable.

2.2.2 Zerofilling

Zerofilling is a technique used to increase the quality (but not resolution) of the spectrum by adding zeros to the end of the interferogram before fourier transforming, increasing the number of data points in the spectrum. The following figure shows the effect of zerofilling on a spectrum with a lower resolution:

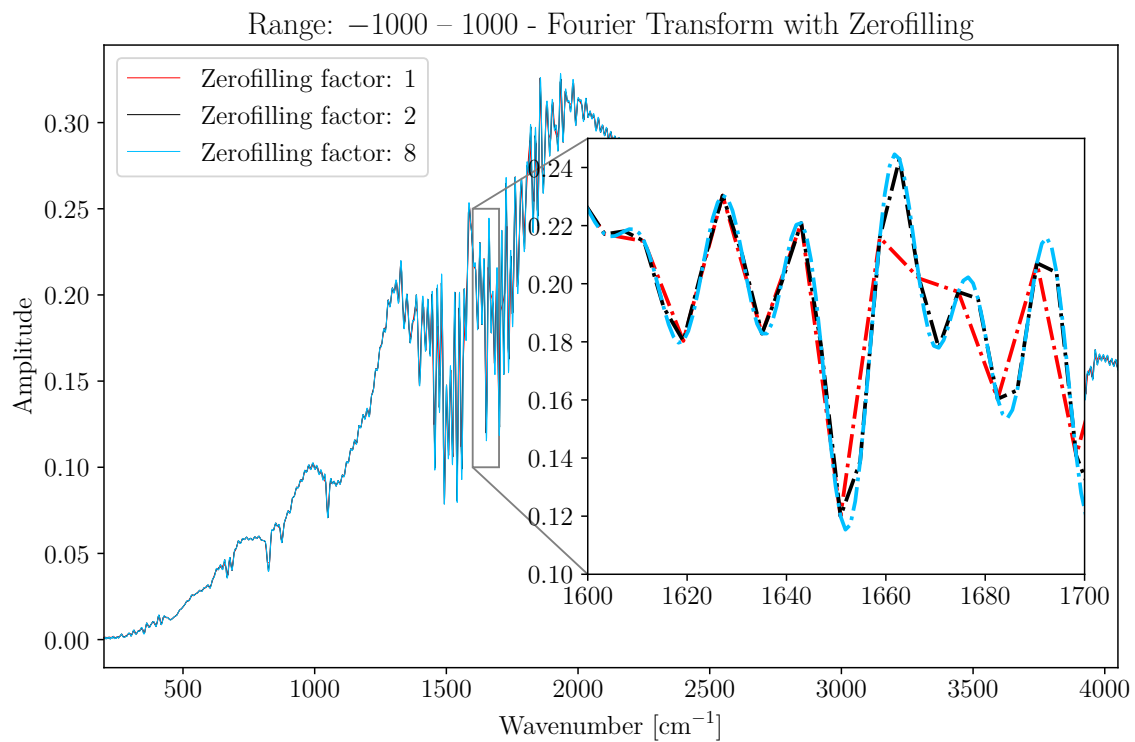


Figure 5: Spectrum with various factors of zerofilling. Inset axes show a zoomed in part of the spectrum where the effect is shown, and lines are dashed for better legibility.

Here the low resolution spectrum benefits from zerofilling, as the minima near 1670 cm^{-1} are more pronounced.

2.2.3 Apodization

Apodization is the process of applying a window function before the fourier transform is performed, reducing the “leakage effect” of a fourier transform. This happens due to the fact that fourier transforms need to be infinite, meaning you require a periodic signal to perform a fourier transform. If the signal is not periodic, there will be jumps in whatever is being transformed which can manifest as small amplitude modulations. A windowing/ apodization function will make the ends of what is being transformed close to zero such that the signal now looks periodic. The following figure shows the effect of apodization on a fourier transform:

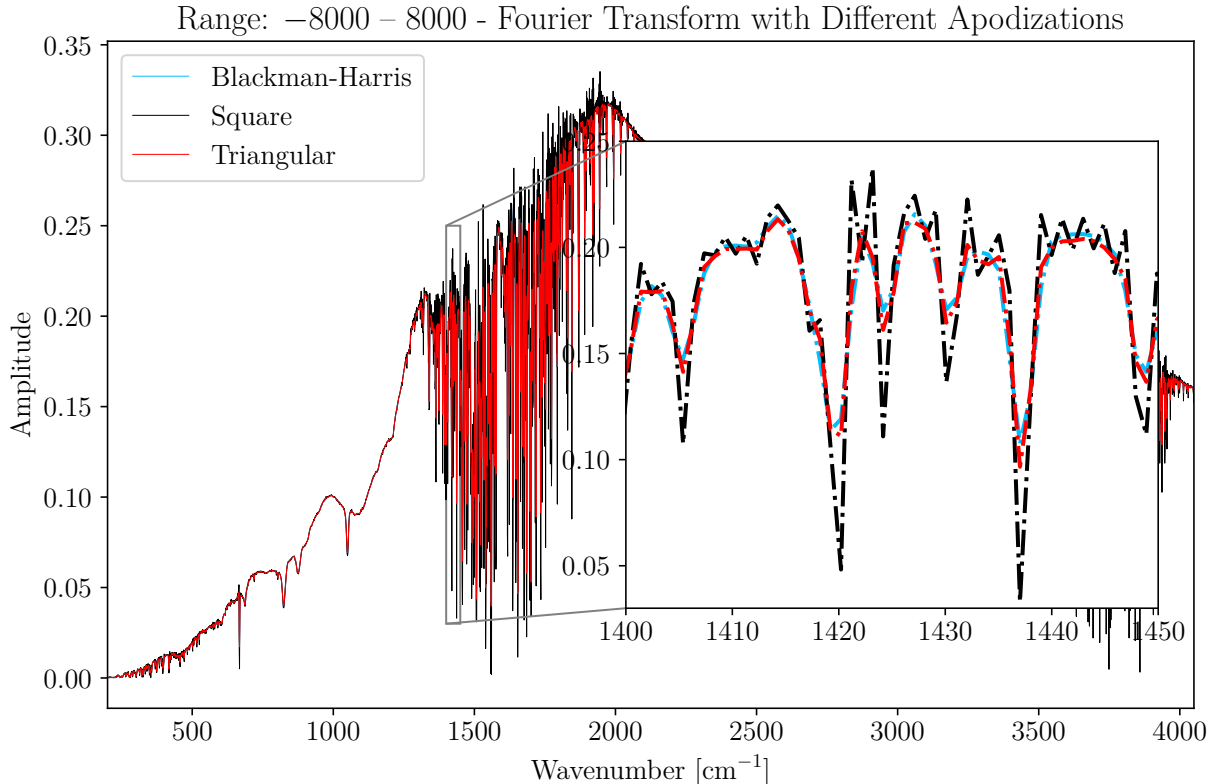
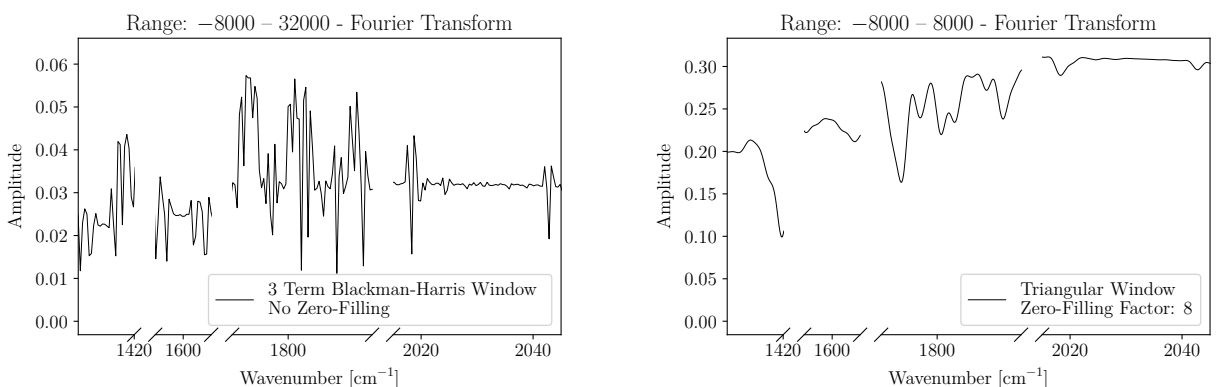


Figure 6: Spectrum with various apodization functions. Inset axes show a zoomed in part of the spectrum where the effect is shown, and lines are dashed for better legibility.

The square apodization function is just the default way an FFT is performed, so it is considered as “no apodization”. The 3 Term Blackman-Harris and Triangular apodization functions show a decrease in noise between the dips, but the dips themselves are less pronounced.

2.2.4 Comparison

Here, the difference between the spectrum at the maximum mirror range, with Blackman-Harris apodization and no zerofilling is compared to the spectrum with a lower mirror range, a zero-filling factor of 8 and no apodization. The following figure shows the two plots in the ranges used in Figure 1a:



(a) Maximum Mirror Range, no Zerofilling, Blackman-Harris Apodization.

(b) Lower Mirror Range, Zerofilling factor of 8, no Apodization.

Figure 7: Comparison of the two spectra

We chose this range as it is a good benchmark to compare to. Full figures are shown in Appendix B.

Figure 7a shows more pronounced dips compared to Figure 1a, but the noise is also more pronounced. Compared to Figure 7b, it shows more dips but this is only due to the higher resolution of the measurement. 7b shows less pronounced dips (and sometimes no dips due to the lower resolution), but they are much smoother and clearer to identify.

2.2.5 Step Size and Theoretical Spectral Resolution

The spectrometer operates in the mid-infrared range, so the wavelengths are between $2.5\mu\text{m}$ and $50\mu\text{m}$, meaning the maximum wavenumber is $\bar{\nu} = 4000 \text{ cm}^{-1}$. The step size is therefore

$$\Delta x = \frac{1}{2\bar{\nu}_{\text{max}}} = \frac{1}{2 \cdot 4000} = \boxed{1.25 \cdot 10^{-4} \text{ cm}}$$

So the theoretical spectral resolution given a number of measuring points n is

$$\Delta\nu = \frac{1}{n\Delta x} = \boxed{\frac{8000}{n} \text{ cm}^{-1}}$$

2.3 Task 3

Determine the detected signal strength in the blocking range of a glass and a NaCl blocking filter.

The following figure shows the spectra of the glass and NaCl blocking filters:

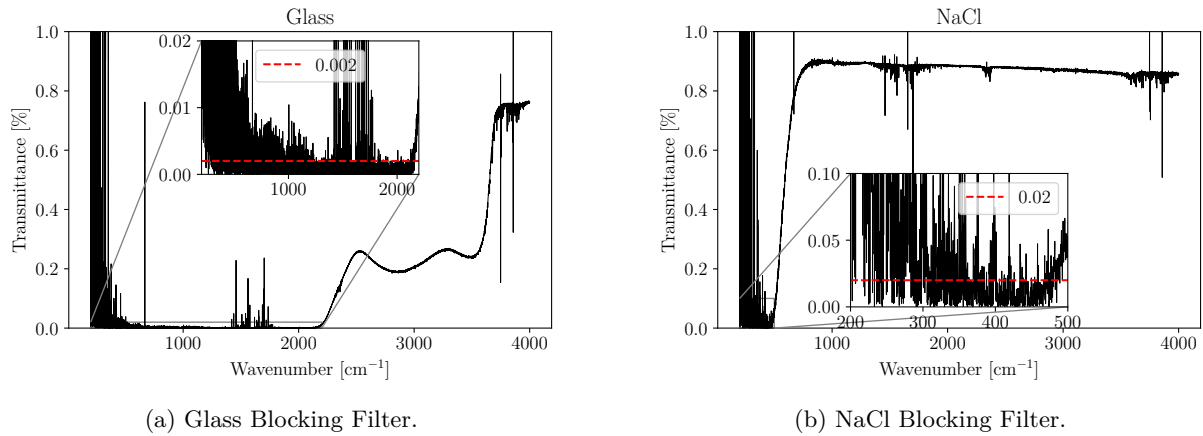


Figure 8: Spectra of the glass and NaCl blocking filters. Inset axes show a zoomed in part of the spectrum where the filter blocks the signal

It is clear that Glass blocks wavenumbers below $\approx 2100 \text{ cm}^{-1}$, while NaCl blocks wavenumbers below $\approx 500 \text{ cm}^{-1}$. However, the signal strength is not zero there, as the filters are not perfect. Moreover, our data for water vapour in Task 2 is oddly noisy in the lower wavenumbers, so the signal strength is not as clear as it should be.

It is still somewhat reasonable to assume that glass blocks the signal 10 times better than the NaCl filter, as seen by their signal strengths.

Further adding to the noise problem is that both spectra can have low values near low wavenumbers, and since we are normalizing with respect to the water vapour spectrum, small fluctuations cause large changes.

3 Conclusion

Appendices

A Task 1

A.1 Plots

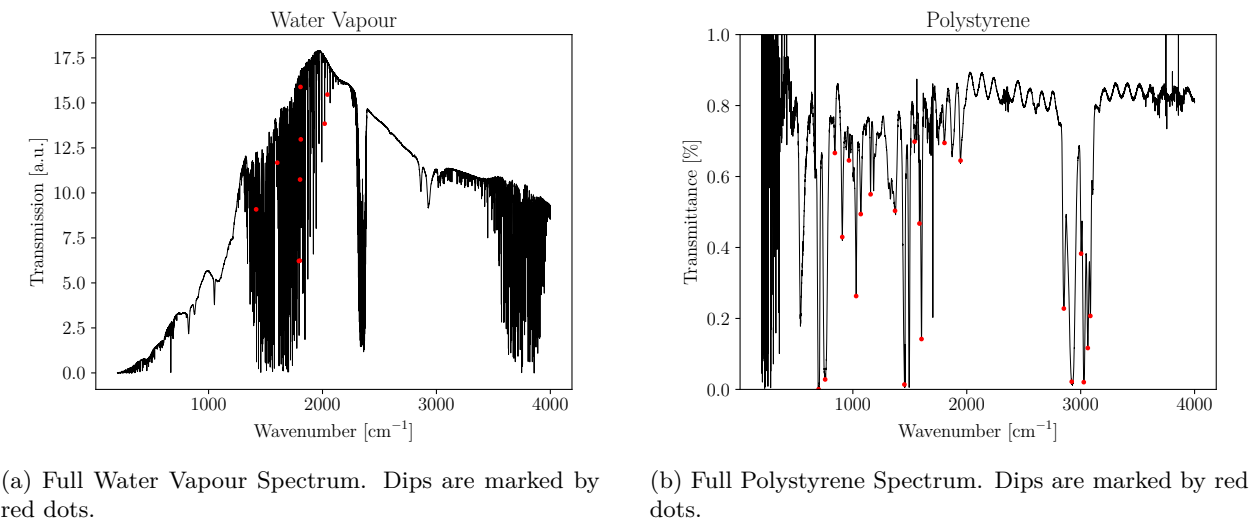


Figure 9

A.2 Tables

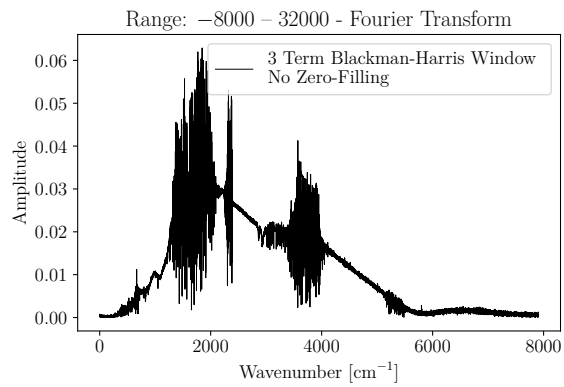
Polystyrene			
Theoretical [cm ⁻¹]	Experimental [cm ⁻¹]	$\Delta\bar{\nu}$ [cm ⁻¹]	% Error
699.450	699.250	-0.200	-0.029
756.580	756.875	0.295	0.039
842.000	842.125	0.125	0.015
906.800	906.875	0.075	0.008
965.700	965.750	0.050	0.005
1028.300	1028.875	0.575	0.056
1069.100	1069.375	0.275	0.026
1154.600	1155.750	1.150	0.100
1449.700	1452.500	2.800	0.193
1368.500	1370.250	1.750	0.128
1542.200	1542.000	-0.200	-0.013
1583.100	1584.625	1.525	0.096
1601.400	1602.750	1.350	0.084
1803.800	1804.375	0.575	0.032
1945.200	1945.375	0.175	0.009
2850.000	2852.250	2.250	0.079
2920.900	2921.250	0.350	0.012
3001.400	3003.875	2.475	0.082
3026.400	3027.125	0.725	0.024
3060.000	3062.500	2.500	0.082
3082.200	3084.875	2.675	0.087

Table 1

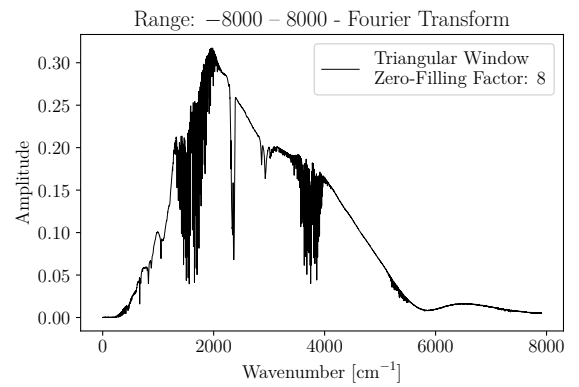
Water Vapour			
Theoretical [cm ⁻¹]	Experimental [cm ⁻¹]	$\Delta\bar{\nu}$ [cm ⁻¹]	% Error
1416.08	1417.50	1.420	0.100
1601.20	1602.88	1.675	0.105
1792.65	1792.75	0.100	0.006
1799.61	1801.38	1.765	0.098
1802.47	1803.13	0.655	0.036
1807.70	1806.88	-0.825	-0.046
1810.62	1809.50	-1.120	-0.062
2018.32	2018.75	0.430	0.021
2041.30	2043.38	2.075	0.102

Table 2

B Task 2



(a) Maximum Mirror Range, no Zerofilling, Blackman-Harris Apodization.



(b) Lower Mirror Range, Zerofilling factor of 8, no Apodization.

Figure 10: Comparison of the two full spectra

Bibliography

- [1] Volker Riede and Christian Kranert. Rotation-vibration spectra of molecules experiment for the advanced physics laboratory course. URL: http://www.uni-leipzig.de/%7Ephysfp/manuals/RotVib_englisch.pdf.