A new approach to EC-QCL-based mid-infrared dispersion spectroscopy

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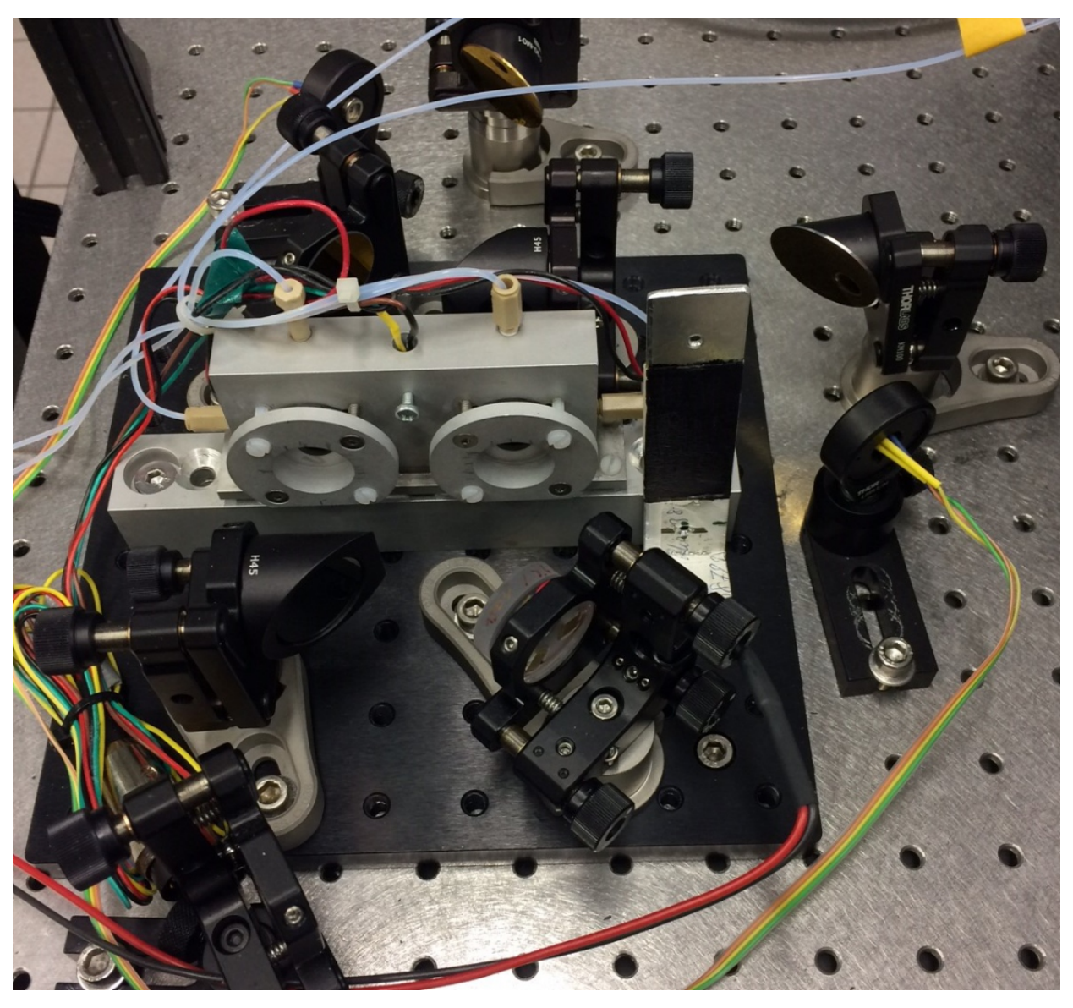
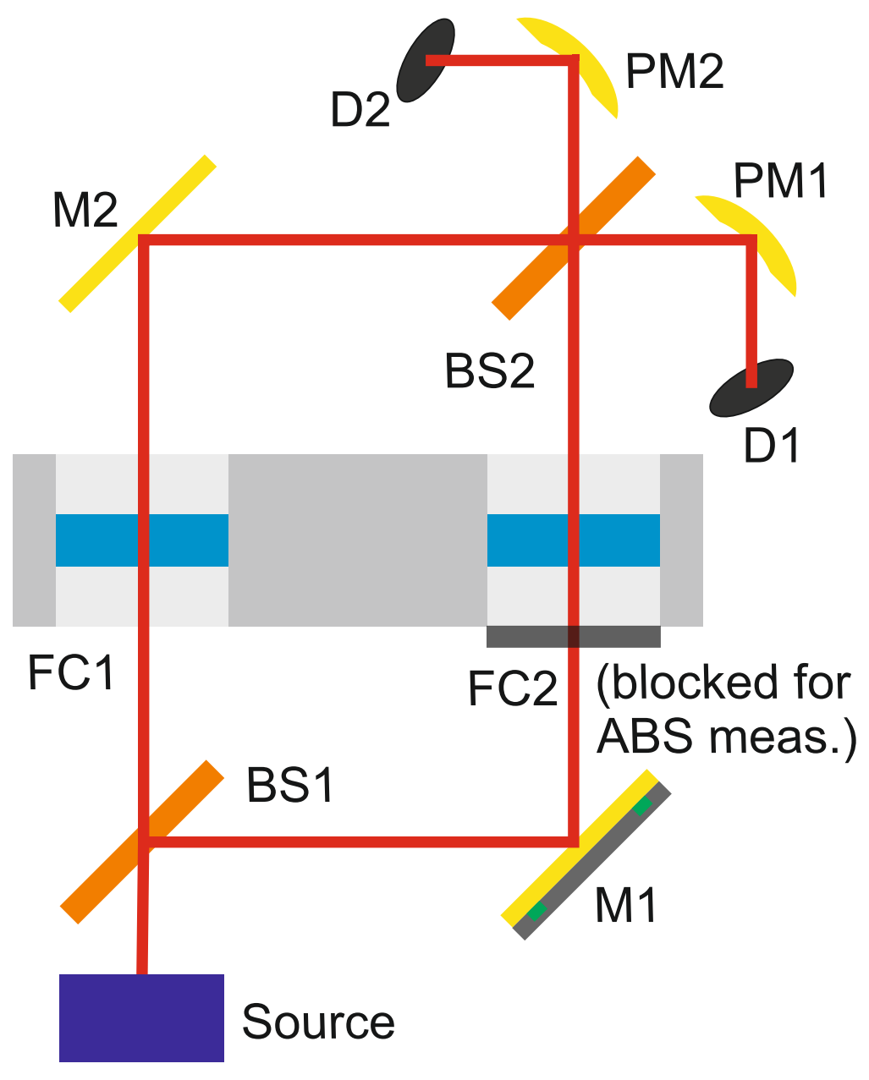
Introduction

Acquisition of classical absorption spectra of liquids in the mid IR-range with quantum cascade lasers (QCLs) is often limited in sensitivity by noise from the laser source. One approach to increase the robustness of measurements against excess intensity noise from the laser is to measure molecular dispersion, i.e. changes in refractive index, rather than absorption. While a number of studies on dispersion spectroscopy in the gas phase exist [1], applications to liquid phase spectroscopy are yet pending. We recently demonstrated the use of a Mach-Zehnder interferometer (MZI) for simultaneous recording of refractive index and absorption spectra [2], where the focus was on the investigation of absorption measurements. In this work, we focus on the refractive index spectra and discuss the principles and capabilities of a custom bulit setup for acquisition of dispersion spectra.

Experimental Setup

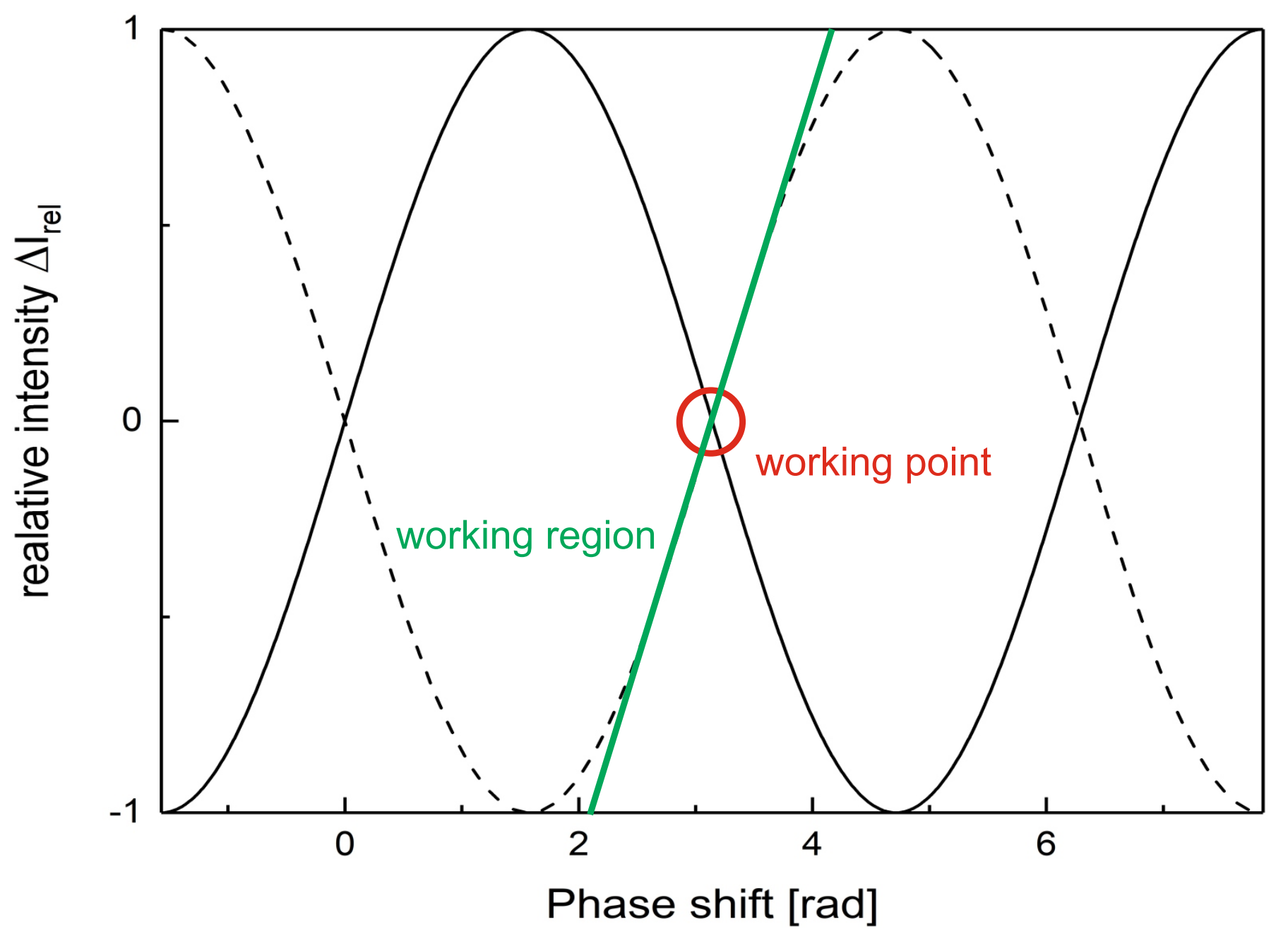
The main part of the experimental setup is a Mach-Zehnder type interferometer with a 50 µm-flow cell inserted in the two beam paths.





The laser beam is splitted in a 50:50 ratio by a ZnSe-beamsplitter (**BS1**). The reflected beam gets redirected by a gold mirror with attached piezo drive (**M1**), so that both beams go parallel through two 50 µm BaF_2 liquid flow cells (**FC1**, **FC2**), and are recombined with the same beamsplitter (**BS2**) and mirror (**M2**) before they are focused on two pyroelectric detectors (**D1**, **D2**) by two parabolic gold mirrors (**PM1**, **PM2**). For acquiring absorption spectra, **FC2** is blocked.

Dispersion Measurement



$$\Delta I_{rel} = \frac{I_1 - I_2}{I_1 + I_2}$$

Moving Piezo Method

- Relative intensity given to PID controller
- PID controlls piezo voltage
- Relative intensity held at zero
- Piezo voltages recorded, proportional to phase shift in sample beam path

Advantages

- Physical phase shift and out of that, absolute refractive index can be calculated out of measurement data

Disadvantages

- Measurement range naturally limited by maximum piezo displacement range
- Poor properties of piezo crystals like hysteresis effects have negative impacts on precisision

Fixed Piezo Method

- No PID Controller: PID input parameter used as primary signal
- Measured intensity needs to be corrected by replacing sine function by linear function
- For phase shifts farer away from zero (bigger than half wavelength) numerical fitting of sine curve necessary

Advantages

- No moving parts in the setup
- No limitation by piezo displacement
- Much wider measurement range
- Faster measurement
- No hysteresis effects

Disadvantages

- Loss of physical values for y-axis in spectra - unknown transfer function to get refractive index values

Absorbance Measurement

- Absorbance measurements possible with the same setup
- One beam path blocked
- Measured intensity of both detectors summed up
- Two seperate measurements: Reference spectrum of 1 % NaF in water (solvent) and sample spectrum
- Use of Beer's law for calculation of absorbance spectra

$$A = -\log\frac{I}{I_{ref}}$$

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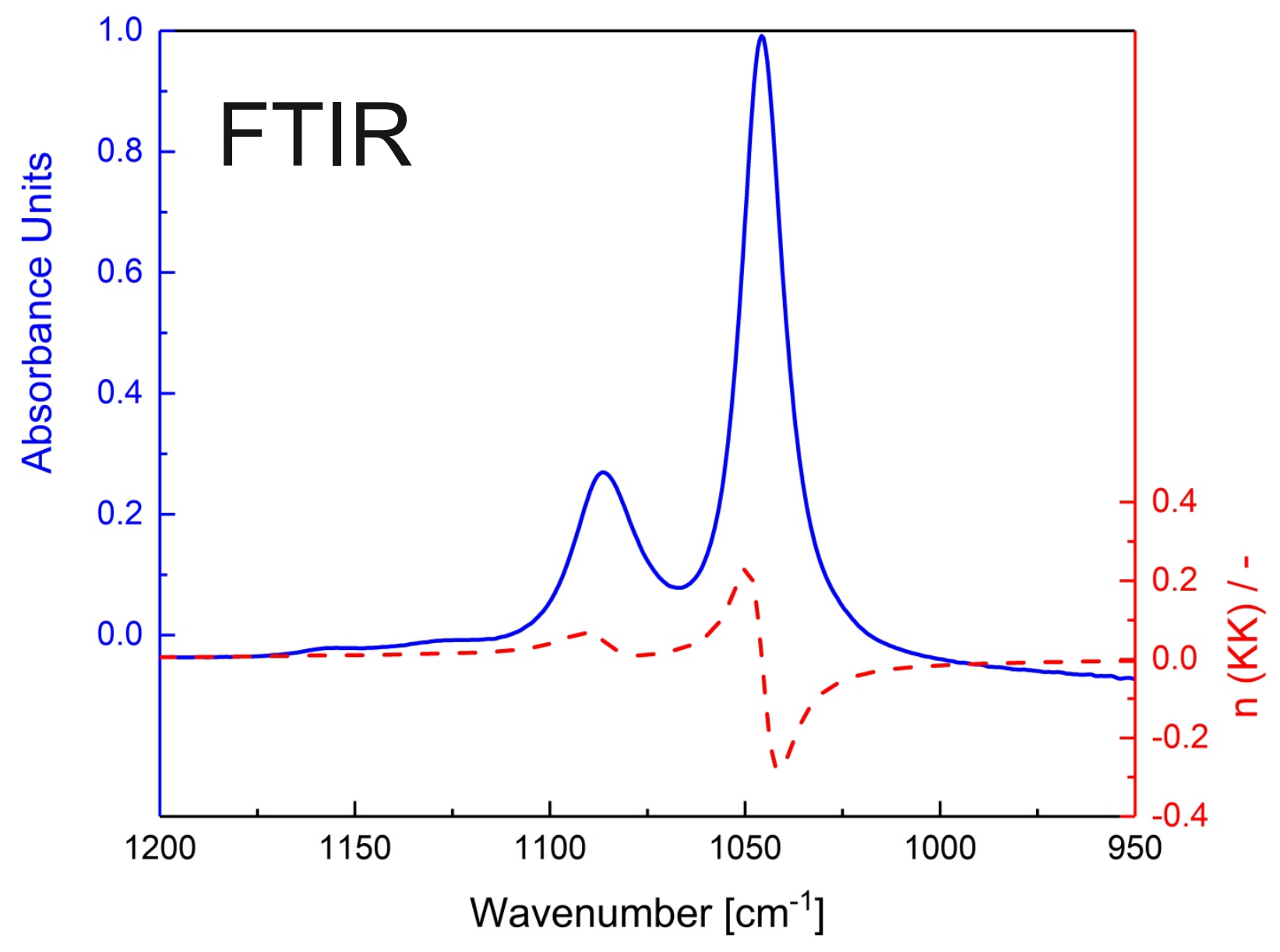
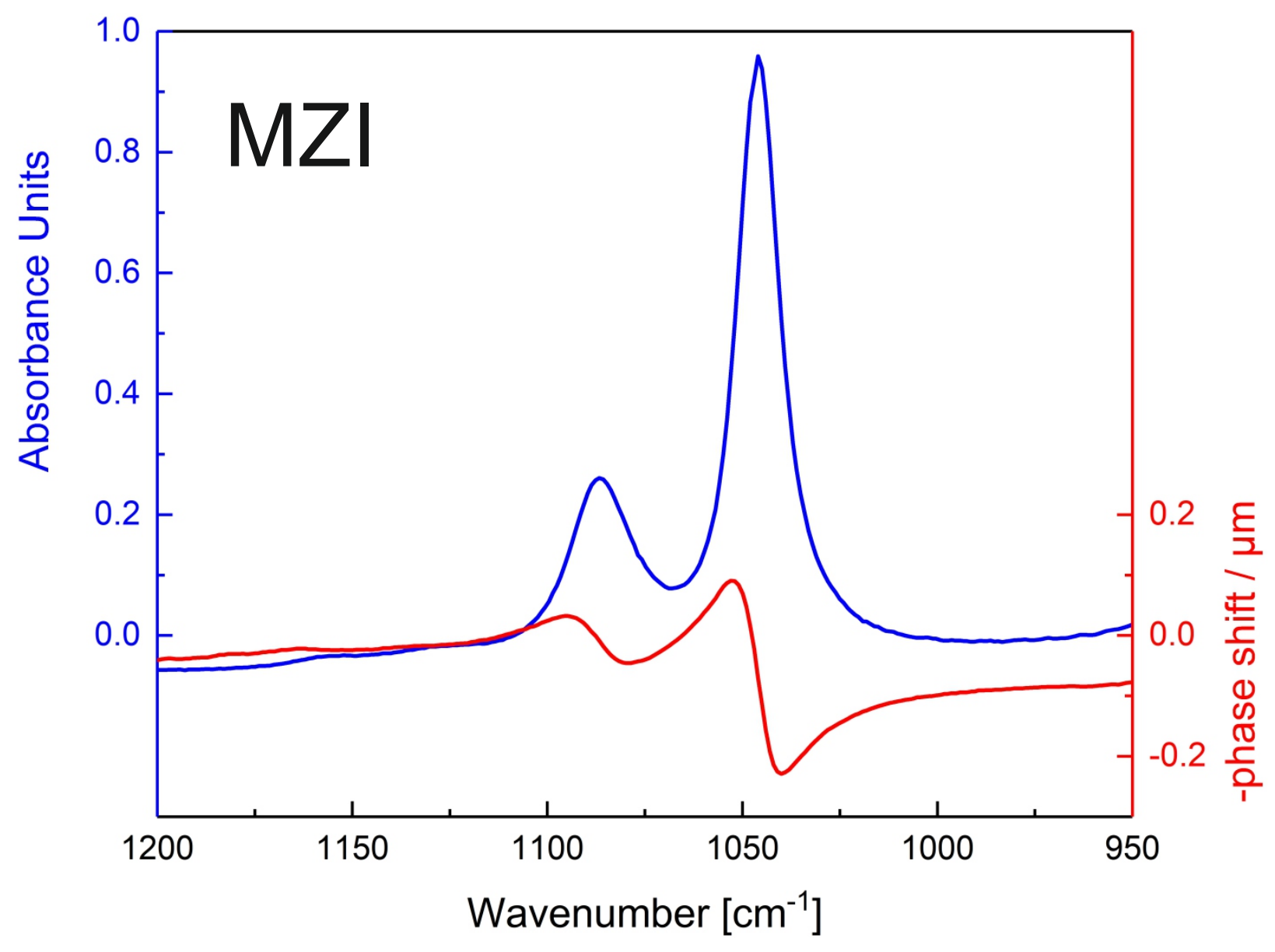
Kramers-Kronig Transformation

- Absorbance spectra acquired with commercial FTIR spectrometer
- Kramers-Kronig (KK) transformation applied to acquired FTIR spectra and resulting dispersion spectra compared to MZI-acquired dispersion spectra [4]

$$A(\omega_a) = -\frac{4\pi\log(e)}{\omega_0}\frac{2\omega_a}{\pi}P\int_0^\infty \frac{n(\omega) - n_\infty}{\omega^2 - \omega_a^2}d\omega$$

- Example spectra: 5 % ethanol in 1 % NaF solution

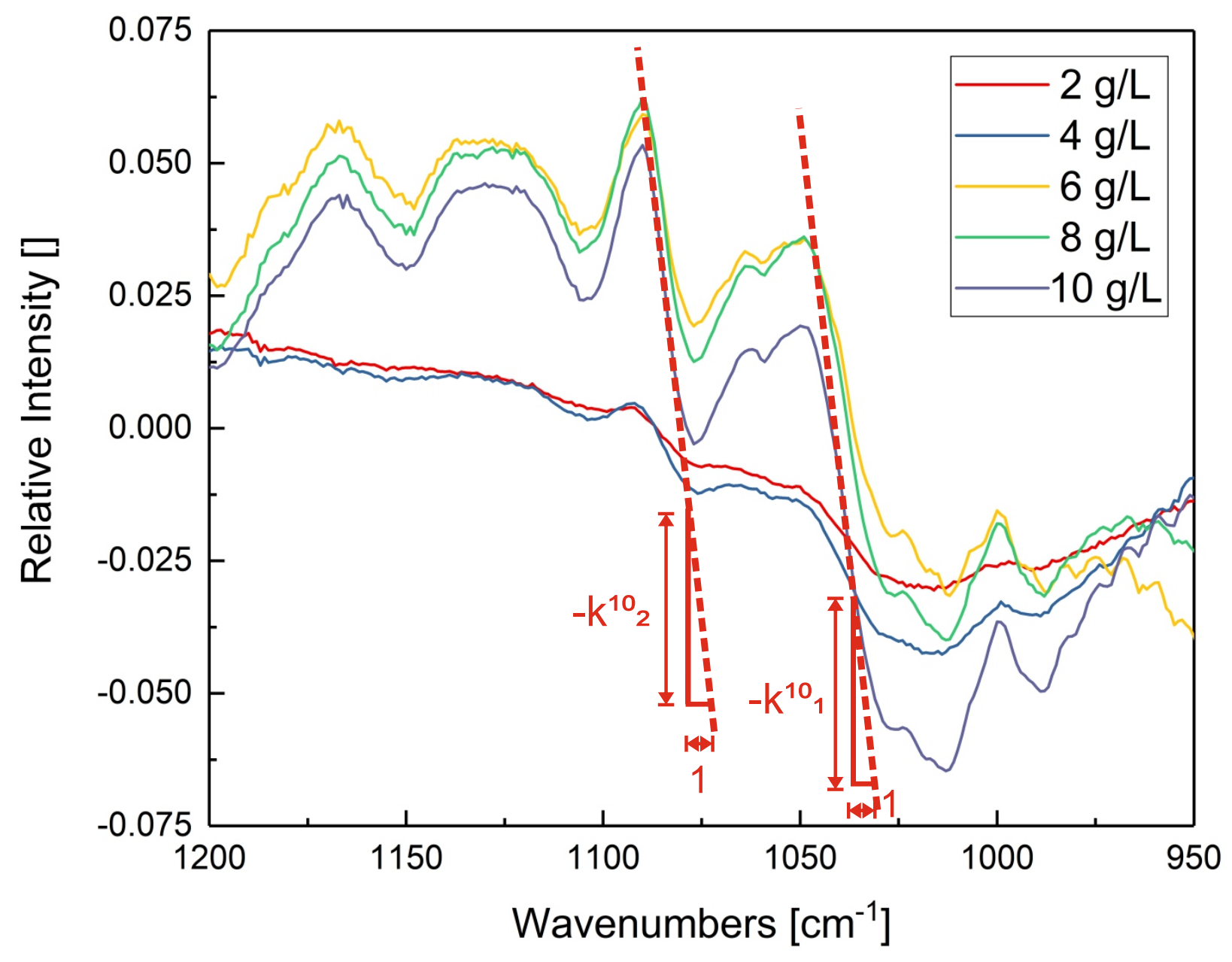


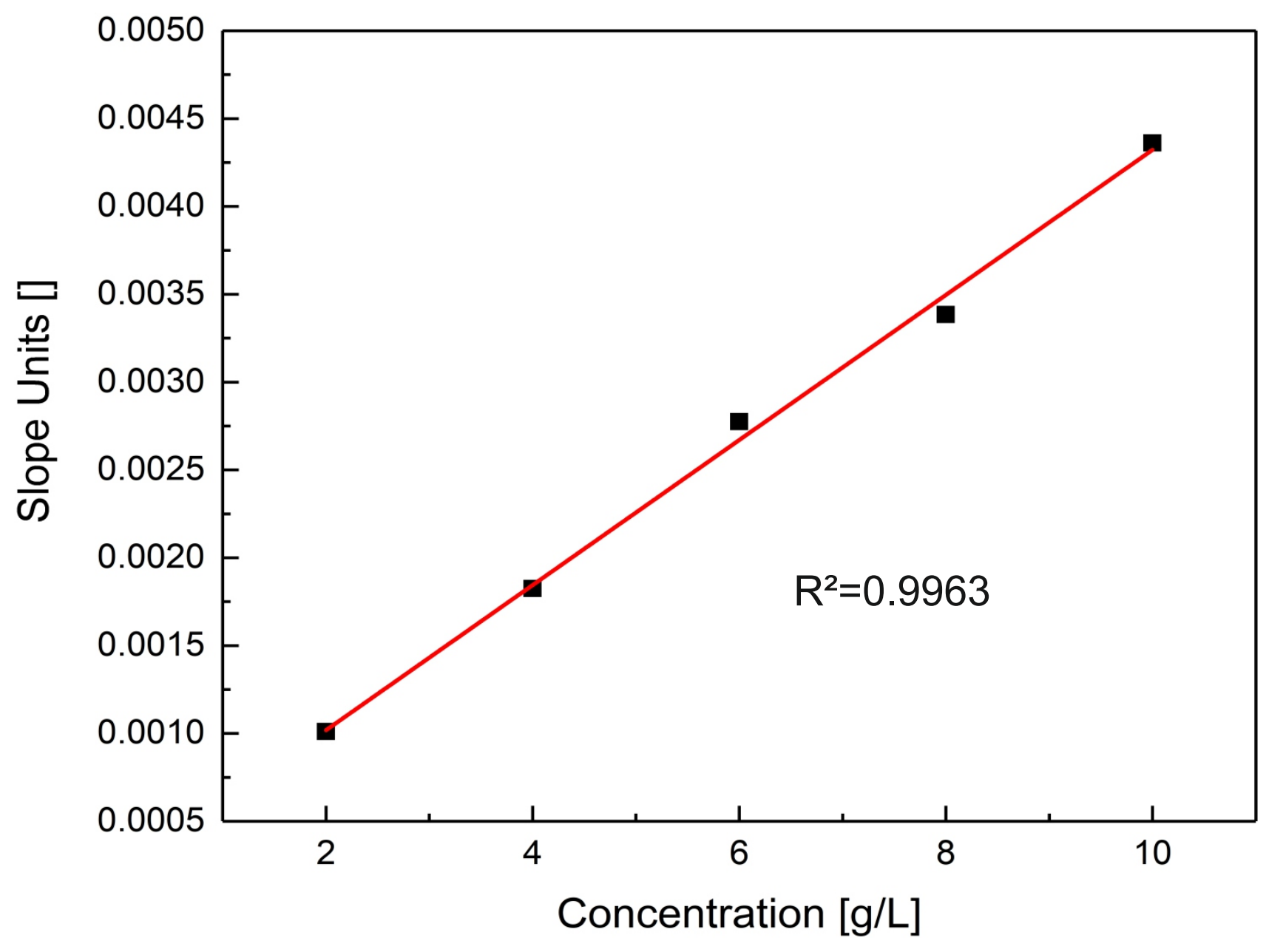


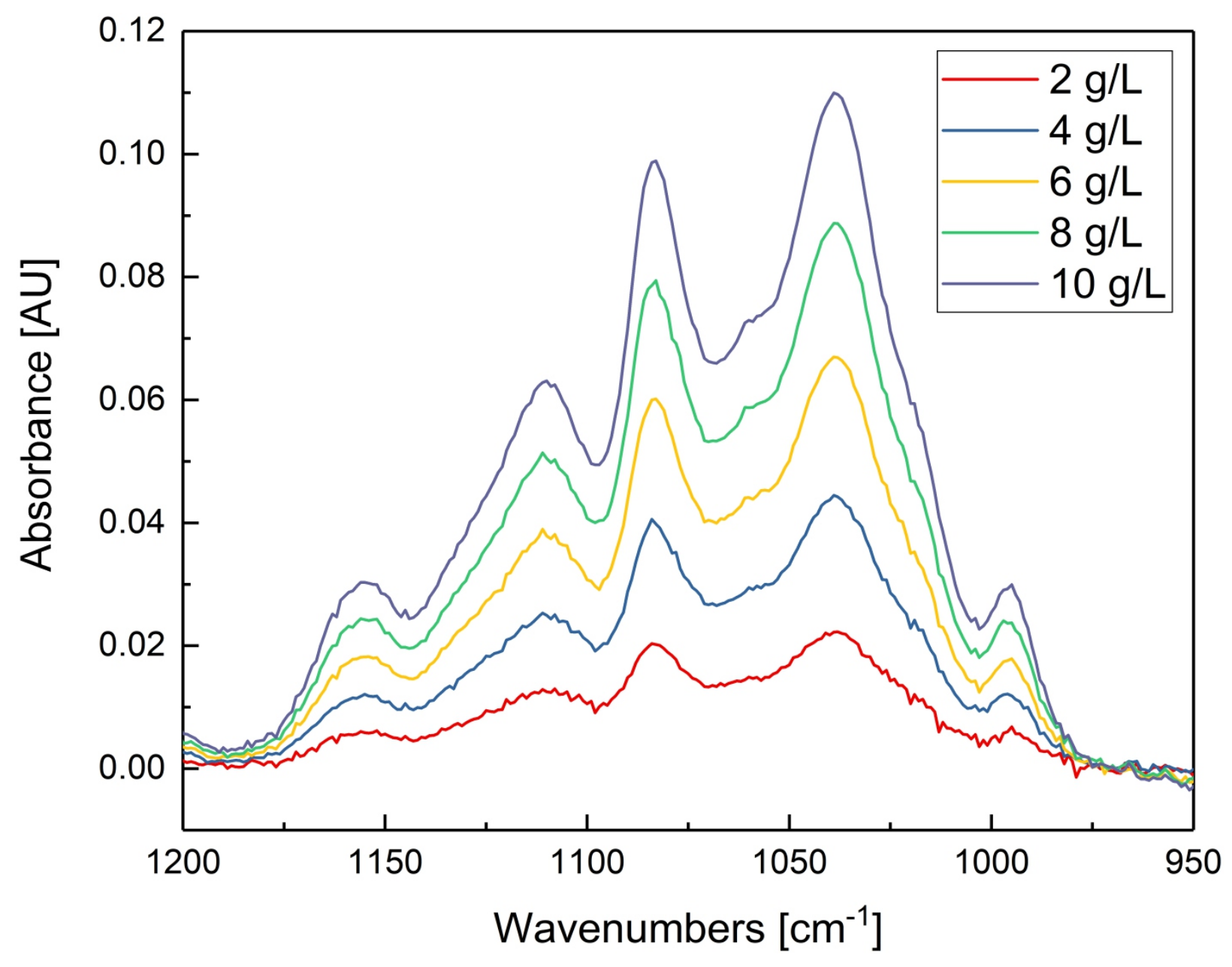
- **Left:** FTIR measured absorption spectrum (blue), KK-transformed dispersion spectrum (red)
- **Right:** MZI measured dispersion (red) and absorption spectra (blue)

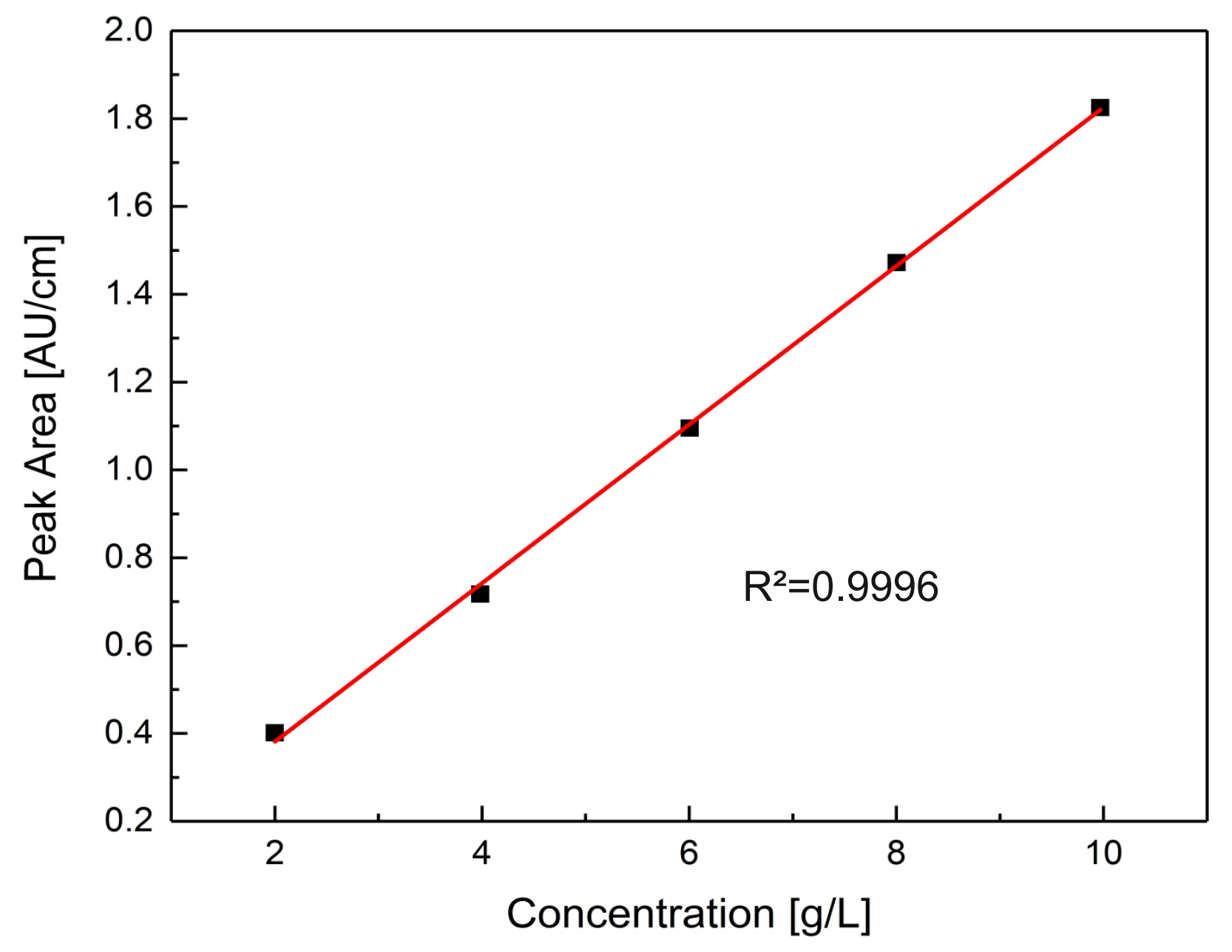
Quantitative Results - Carbohydrate Spectra

- Glucose used as test analyte to perform quantitative measurements
- Unstable offset values of dispersion spectra because of high sensitivity to temperature variations
- Offset-independent quantification method required
- Calibration with dispersion spectra: sum of slopes of the inflectional tangents at main characteristic dispersion spectral features









Conclusion and Outlook

- Absorption- and dispersion spectra acquireable in one instrument
- Good fit to Kramers-Kronig transformed FTIR absorbance spectra
- Sum of slopes of inflectional tangents of main characteristic dispersion spectral features useable as calibration value for quantification with dispersion spectra

- Application of different laser for analysis of the in amide I region of proteins planned
- Use of balanced detection system (VIGO) planned to improve signal to noise ratio

References

[1] P. Martín-Mateos, J. Hayden, P. Acedo, and B. Lendl: Heterodyne Phase-Sensitive Dispersion Spectroscopy in the Mid-Infrared with a Quantum Cascade Laser, *Anal. Chem.* 89, 5916–5922, **2017**
[2] J. Hayden, S. Hugger, F. Fuchs, B. Lendl: A quantum cascade laser-based Mach-Zehnder Interferometer for chemical sensing employing molecular absorption and dispersion, *Appl. Phys. B* 124:29, **2018**
[3] Wysocki, G., and D. Weidmann: Molecular dispersion spectroscopy for chemical sensing using chirped mid-infrared quantum cascade laser, *Opt. Express* 18, 26123–26140, **2010**
[4] G. Ramer, B. Lendl: Attenuated Total Reflection Fourier Transform Infrared Spectroscopy, *Encyclopedia of Analytical Chemistry*, DOI 10.1002/9780470027318.a9287, **2013**