Polarimetric Balanced Detection: Enhanced Attenuated Total Reflection Mid-IR Laser Spectroscopy for Sensing in Liquids

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Introduction

- In process analytical technologies, attenuated total reflection infrared (ATR-IR) spectroscopy is often used for probing liquids due to its robustness and ease of operation. Classic ATR Fourier-transform IR spectroscopy is however easily hampered by drifts over time [1].
- In this work, evanescent waves of different polarizations were used to exite unequal effective thicknesses (d_e) at the ATR element exploited for simultaneously recording reference and sample spectra.
- Polarimetric balanced detection posed to be a new interesting approach for ATR spectroscopy as it reduces long-term drifts, cancels out intensitiy noise of the employed quantum cascade laser and improves the limit of detection [2].

Theory

Classic ATR-Spectroscopy

Classic ATR-IR monitoring shemes use a background spectrum (I_0), recorded at a certain point in time, compared to continuously measured sample spectra ($I_{(t)}$). This mismatch in time often leads to artificats in the resulting absorprion spectra due to enviromental and instrumental drifts.

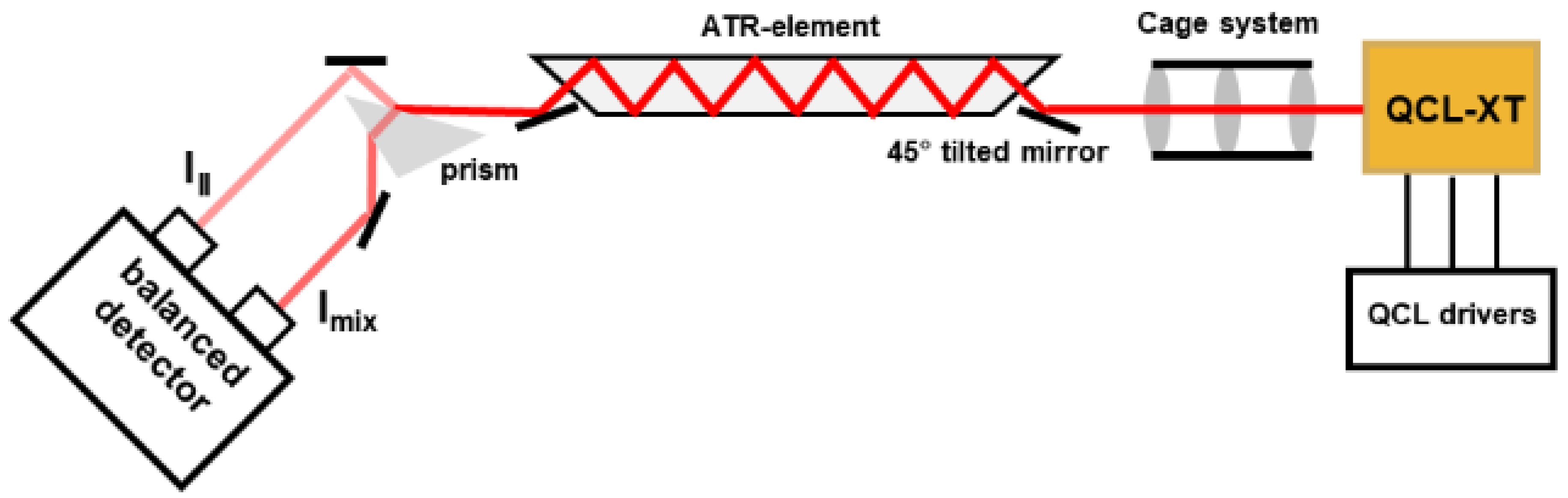
$$A = \log\left(\frac{I_0}{I_{(t)}}\right)$$

Polarimetric Balanced Detection

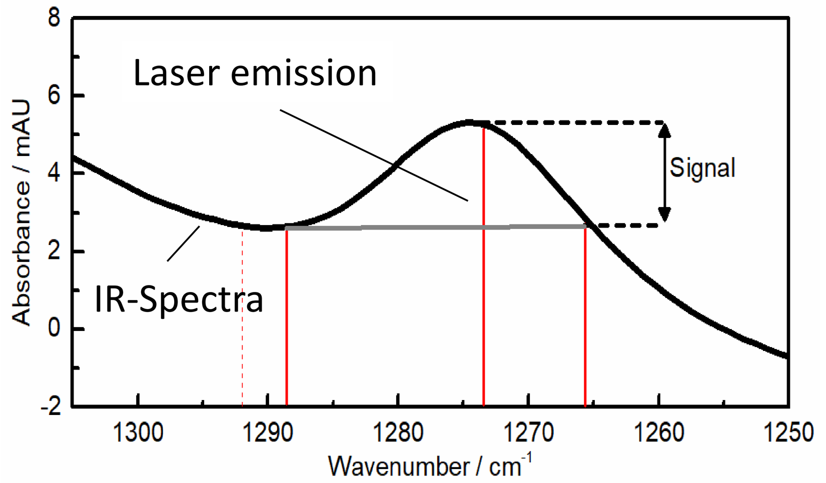
In contrast to classic ATR spectroscopy, reference and sample spectra are recorded at the same time. The mixed polarized channel serves as reference ($I_{mix\,(t)}$), whereas the parallel polarized channel, with the higher effective thickness, is used for sampling ($I_{\parallel\,(t)}$).This allows for common mode noise rejection, while performing absorbance measurments.

$$A_{pol.bal.} = \log\left(\frac{I_{mix\,(t)}}{I_{\parallel\,(t)}}\right)$$

Experimental



- The beam of an extendend tunable quantum cascade laser (QCL-XT), was guided into a multibounce (5 reflections) ATR setup.
- Via a mirror the linear polarized laser beam was tilted in an 45° angle in respect to the ATR surface to be equally parallel and perpendicular polarized, hence exciting different effective thicknesses ($d_{e,mix}$ = 14.65 µm, $d_{e,\parallel}$ = 26.30 µm).
- After the ATR element a zinc selenide prism mounted in the Brewster angle was used as polarizer. The beam fractions were directed towards a dedicated MCT TE cooled balanced detection module.
- The wide tunability of the laser was used to measure ethanol in water. Here, the QCL-XT posed to be a monolithic alternative to external cavity QCLs for sensing of liquids.



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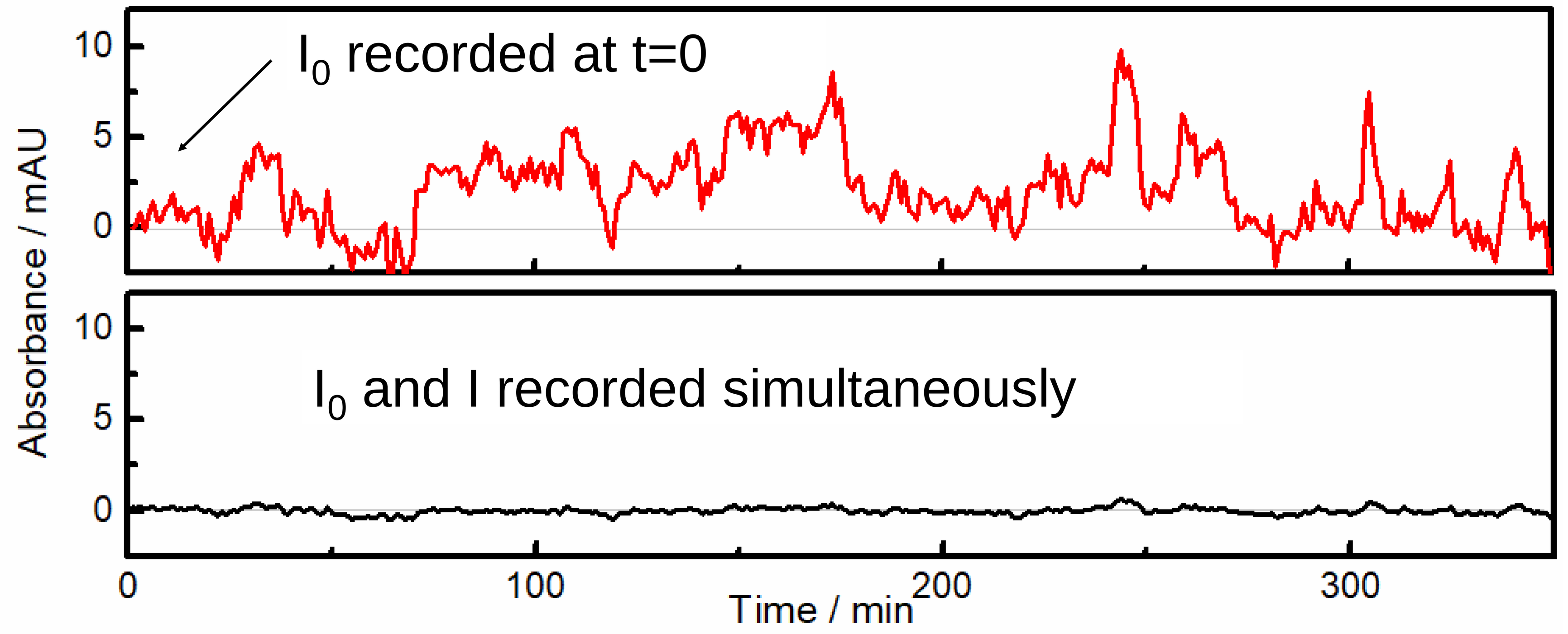
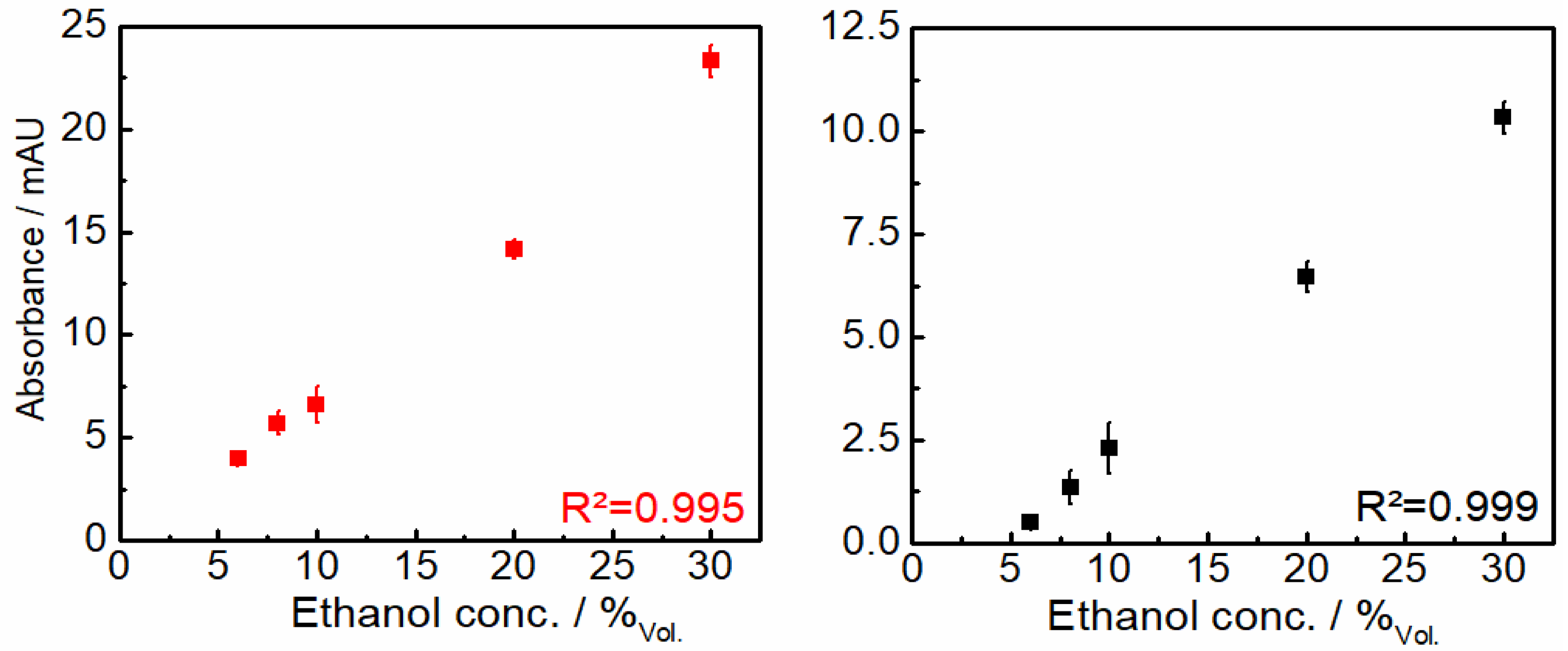
[1] Koch, C.; Posch, A. E.; Herwig, C.; Lendl, Appl. Spectrosc. 2016, 70, 1965-1973.
[2] Freitag S.; Baer M.; Buntzoll L.; Ramer G.; Schaighofer A.; Schmauss B.; Lendl. B. *Polarimetric Balanced Detection: Background Free Mid-IR Evanescent Field Laser Spectroscopy for Low Noise, Long-term Stable Chemical Sensing*; submitted to ACS Sensors, 2020

Results



Noise over time obtained via the parallel polarized beam using classic ATR spectroscopy (red line) and polarimetric balanced detection (black line).



Linear response of the setup using classic ATR spectroscopy (red) and polarimetric balanced detection (black).

Conclusion

- Compared to classic ATR spectroscopy the **long-term stabilty** of the device could be **improved by a factor of 10.**
- Polarimetric balanced detection yields a lower analytical signal compared to a purely parallel polarized beam. Due to common mode noise rejection, the **limit of detection is 2 fold better** than for classic ATR spectroscopy.