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Quantitative, time resolved detection of CH_4 in flows using IR absorption

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Abstract

The reduction of emissions from CO_2 and other greenhouse gases is an important driving force for the development of modern engines. Especially in the transport sector the use of alternative fuels like methane, the main component of compressed natural gas (CNG), is an applied measure to achieve this goal. This work describes the development of an optical measurement system for accurate quantification of CH_4 densities in gas flows based on broadband absorption of infrared light. We demonstrate the capability for a 3 µs time resolution and a high measurement precision. The optical setup of the system is designed for usage at an inlet manifold of a spark ignition engine fueled with CNG. It allows for detailed analysis of the mixture formation during an engine cycle. CH_4 density can be determined by monitoring the infrared light attenuation around 3.3 µm caused by the fundamental C-H-stretch vibration. We calculate the nonlinear relation between transmission and CH_4 density from absorption cross sections taken from HITRAN database. The theoretical transmission signals are corrected for spectral influences of the bandpass filter and the detector sensitivity. A linear calibration function corrects remaining differences between experimental and simulated values. We show that the sensor system is capable for determination of the air-fuel-ratio (lambda value) and demonstrate the dynamic quantification of a CH_4 injection into a flow channel under various flow conditions.

Keywords: optical measurement systems, infrared absorption, quantitative methane detection, time resolved measurement

Introduction

The worldwide climate change calls for changes and new developments in almost all areas of technology and society. One of the most important tasks is the emission reduction of greenhouse gases like CO_2. Transportation nowadays consumes a large part of primary energy resources and thus produces significant greenhouse emissions [1]. Therefore, sustainable mobility is one of the most important tasks of our time concerning technology and society. Electric cars struggle with short ranges and long charging times. Furthermore, their CO_2 balance only becomes favorable if the electricity originates from renewable sources. In conclusion combustion engines will stay the standard driving technology for many years. Consequently, the European Union set new limits for CO_2 and NO_x emissions of cars, which result in higher technological requirements for spark ignition (SI) engines. Increasing the efficiency and lowering the emissions need more and more effort, but is not the only way. The use of alternative fuels such as compressed natural gas (CNG) is an attractive opportunity for emission reduction [2-3]. CNG can serve as a bridging technology before electric mobility becomes competitive as well as blending with biogas allows for a striking CO_2 balance. To optimize engines using CNG detailed knowledge of the air/fuel mixture formation prior to the combustion is essential.

There are many different optical methods to analyze mixture formation. The best known method to achieve time resolved measurements of the mixture formation is gas sampling where the gas is analyzed by a flame-ionization-detector [3-5]. This method suffers from a time delay caused by the length of the sampling pipe which has been shown to be a disadvantage compared to the measurement system presented in this work [8].

We present the derivative of a measurement system developed previously for mixture formation analysis in conventional fuel engines [7-10]. Typically, the mixture formation in CNG engines already starts outside the combustion chamber by an injection into the inlet manifold. This work presents a method to determine the methane concentration under known temperature and pressure conditions based on

broadband infrared (IR) absorption. Furthermore, we show the development of a flexible optical measurement system for adaption to different inlet manifolds.

Experimental setup and measurement system

We used the flow channel depicted in Fig. 1 for all of our measurements. The channel serves as model geometry for an inlet manifold of a SI engine. Note that the time resolved quantification of CH_4 in an inlet manifold is the primary goal of the presented measurement technique. Nevertheless, a transfer to other environments and geometries is possible with only little effort.

The air drawn into the channel in Fig. 1 passes a flow meter and then enters a mixing module. The module enables addition of gas via a mass flow controller (MFC) to the stream of air and produces a homogenous mixture. After a certain distance which assures a laminar flow the gas / air mixture reaches the detection region.

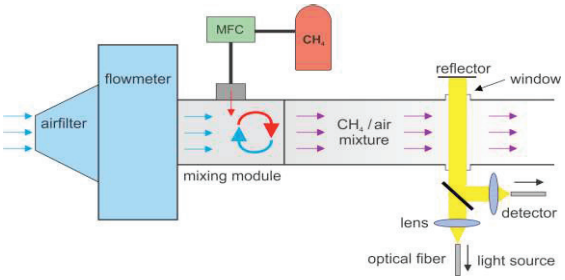

Fig. 1: Schematic drawing of the flow channel and the optical setup.

The optical measurement system consists of a quartz-tungsten-halogen (QTH) lamp as a broadband IR light source, an optical setup and a detection system. Light source and detection system are part of the ICOS system from LaVision GmbH. The optical setup consists of an optical fiber guiding the light of the source which is modulated by a chopper (max. 30 kHz) to the flow channel, where a lens collimates it to an 8 mm wide beam. After collimation the light passes a 50/50 beam splitter, enters and exits the flow channel through two quartz windows and is reflected back to the beam splitter passing the flow channel a second time. Another lens couples the light to a second optical fiber guiding it to the detection system. The geometry described here is chosen instead of a simple transmission setup, because it is more compact. Thus it is easier to adapt to an SI engine where free space around the inlet manifold is rather small.

The detection system was originally developed to measure the air-fuel-ratio inside the combustion chamber of a SI engine measuring simultaneously the exhaust gas recirculation (EGR) rate [8-10]. It consists of a cascade of four detectors covered by IR bandpass filters. The bandpass filters select a detection frequency range matched to the molecule of interest shown in Fig. 2. Two filters around the 2.7 µm region are used to determine the EGR rate. Another filter around 3 µm covers a region where no absorption of light by any of the present molecules occurs. This filter serves as a reference channel monitoring changes in the overall light intensity affecting all four detection channels. For further details see ref. [9].

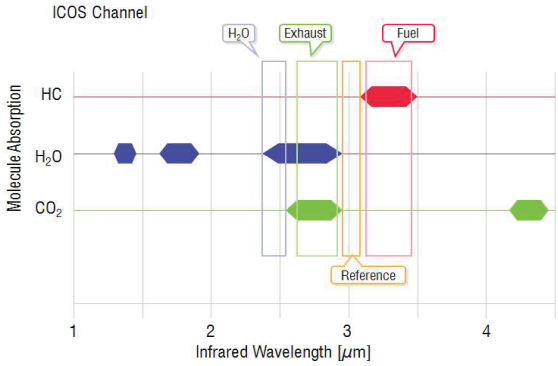

Fig. 2: Absorption bands with marked detection regions for H_2O, exhaust gas (H_2O+CO_2), reference and fuel (hydrocarbons, e.g. CH_4) of the sensor system used in this work.

In this work we focus on the broadband filter for fuel detection located around 3.3 µm for measuring absorption of the ν_3 vibration band of CH_4. The absorption in this region corresponds to the anti-symmetric C-H-stretch vibration and is present in all hydrocarbons. Consequently, the same bandpass filter may be used for the detection of different hydrocarbon molecules e.g. fluid hydrocarbon fuels. Nevertheless, the quantification procedure is different for CH_4 because of its small molecular structure revealing a strong influence of pressure and temperature on the transmission spectrum.

A mercury-cadmium-telluride (MCT) detector detects the transmitted light and gives an according voltage output. Dividing the signal of air/CH_4 mixture inside the channel by the signal with pure air gives a broadband transmission value for this mixture. The measurement technique presented in this work is then able to assign this transmission value to a CH_4 density depending on pressure and temperature during the measurement.

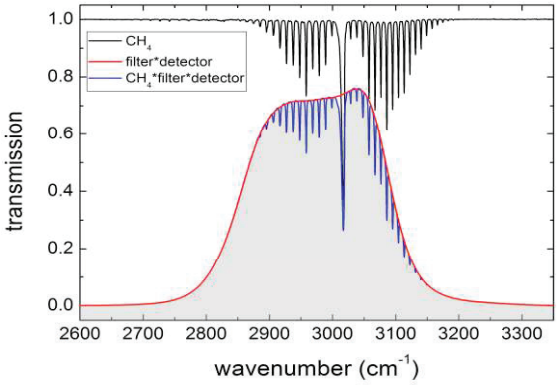

Fig. 3: Principle of broadband transmission measurements of a CH_4 spectrum: the area under the blue curve corresponds to the voltage output of the detector.

In Fig. 3 an infrared spectrum of methane as well as the product of filter transmission and detector sensitivity are shown. The detector's voltage output is proportional to the integrated spectral transmission of CH_4 multiplied with filter transmission and detector sensitivity. This product is shown as a grey area in Fig. 3. The area decreases with higher CH_4 density and constant temperature and pressure. Previous publications only considered the filter in the calculations [8]. We find that inclusion of the detector sensitivity significantly improves the quantitative agreement with the experimental data. We validate the theoretical simulation by comparison to experimental methane spectra acquired in a pressure cell by a Bruker Vector 33 FTIR spectrometer. The cell was filled with a CH_4/N_2 mixture, where N_2 is used as an IR inactive buffer gas to reach the desired pressure conditions.

Fig. 3 shows the transmission spectrum of methane around 3020 cm^{-1} with its C-H-stretch absorption band. The different peaks in the spectrum correspond to different rotational transitions. Especially in the case of methane, pressure and temperature have a severe influence on the spectrum. Higher pressure leads to broader but lower peaks whereas high temperature also broadens the whole spectrum. This is a result of the occupation of higher rotational energy states through thermal excitation. Due to the nature of broadband measurements using a filter changes in pressure and temperature can cause different signals for the same CH_4 density. This can be taken into account by measuring pressure and estimating temperature. Fortunately, the pressure and temperature inside the inlet manifold are rather low. They range around 20 - 250 kPa and 280 – 470 K depending on the location inside the inlet manifold. The highest temperatures are reached closest to the cylinder head. Typically the temperatures shouldn't exceed 390 K. The determination of fast changing pressure is possible with quartz pressure sensors and available at typical engine test stations. Facing the problem of dynamical changes of temperature conditions is subject to current research.

Calculation and calibration

Inside the flow channel the CH_4 molecules absorb parts of the infrared light according to Beer-Lambert's Law,

$$I = I_0 \exp\left[-\sigma(\nu, p, T)\rho(p, T)L\right] \quad (1)$$

where σ(ν) is the absorption cross section at a specific wavenumber ν, ρ is the density of the absorbing molecule, L is the length of the absorption path and p and T are pressure and Temperature respectively. The geometry of the flow channel defines the absorption path length while the density of methane can be calculated using the ideal gas law. Note that eq. (1) gives the transmission $\tau = I/I_0$ only at a fixed wavelength. To obtain broadband transmission values, one must integrate over the spectral range used for the measurements, considering filter transmission and detector sensitivity:

$$\tau = \frac{\int e^{-\sigma(\nu,p,T)\rho L}\tau_{filter}\tau_{detector}d\nu}{\int \tau_{filter}\tau_{detector}d\nu} \quad (2)$$

We assume here that the spectral intensity of the QTH lamp is constant within the frequency range of the filter transmission.

All experiments were performed under ambient conditions, so we use 298 K and 1 bar as temperature and pressure respectively to calculate the density. The channel has a profile area of 28 x 38 mm^2 and the light passes through the short side. Due to the optical setup with reflector and beam splitter the light passes the channel twice leading to an absorption path length of 56 mm. The maximum flow velocity in the channel is around 13 m/s and the pressure does not drop significantly below 100kPa.

To acquire calibration data we use MFCs for mixing a defined amount of CH_4 into the air flowing through the channel. In engine applications the air-fuel-ratio is typically stated as the λ-value. This value is defined as the mass ratio of air to fuel divided by the ratio in stoichiometric conditions. So for methane a stoichiometric mixture with an air to fuel ration of 9.5:1 has a value of $\lambda = 1$. The mass ratio is equivalent to the flow ratio of air and methane flowing through the channel. Therefore, we can adjust the lambda value of the mixture inside the channel by measuring the flow of air and adjusting the flow of CH_4 through the MFC accordingly.

We do the calibration measurements with a fixed air flow of 0.66 m/s and 1.1 m/s. Further experiments with higher air flows show no influence of flow velocity on the measured signal. The flow through the MFCs is adjusted equivalent to lambda values of 0.25 – 4. Before

each measurement we measure the pure air signal without CH_4 in the channel. Each pair of pure air and air/CH_4 mixture is measured three times. A repetition of the experiment minimizes the influence of small variations in the experimental conditions. This ensures a good quality of the measurements. All measurements are averaged and the 95% confidence interval is taken as uncertainty.

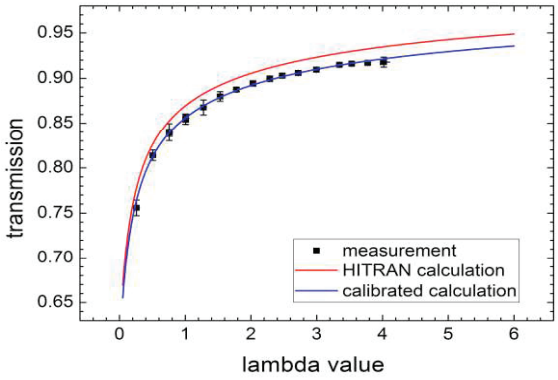

Fig. 4: Results of the calibration measurement (black dots) as well as calculated (red) and calibrated values (blue).

Fig. 4 shows the results of the calibration measurements as well as a calculated and a calibrated curve. The calculation uses absorption cross sections from the HITRAN database [11] and is carried out as numerical integration described by eq. (2). This procedure leads to the red curve in Fig. 4, which shows the same behavior as the measured values. There is still a significant quantitative difference so the calculation needs further calibration.

The calibration described here follows the procedure already used in ref. [8]. The differences between calculations and measurements may result from errors determining the path length, the filter transmission and the detector sensitivity. Furthermore, the absorption cross section extracted from the HITRAN database can differ from the real cross section resulting in another error. Additionally, we do not take all optical elements of the setup into account. There are many components, e.g. lenses, fibers and optical windows which could possibly influence the spectral transmission of the detection system. All these influences are considerably weak compared to filter transmission and detector sensitivity. Nevertheless, all the factors sum up and can explain the deviations of the simulation and experiment.

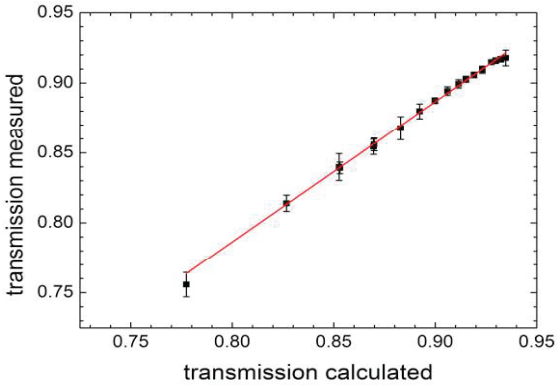

Fig. 5: Linear relation between measured and calculated broadband transmission for several methane densities.

To get a calibration function we plot measured over calculated transmission for all densities of the calibration experiment. Fig. 5 shows the plot and the linear relation between measured and calculated values. A slight deviation from the linear fit occurs at high transmission values but overall the linear fit matches the data well. From the fit we get a linear function:

$$\tau_{meas} = m * \tau_{calc} + b \qquad (3)$$

This relation works as a calibration function and adjusts the calculated transmission to the measured one. The parameters found with a linear fit are $m=1.00279$ and $b=0.0137$. The small deviations of m and b from 1 and 0, respectively, demonstrate an overall good agreement of simulation and experiment. Fig. 4 shows a very good quantitative agreement between measurements and calibrated calculations.

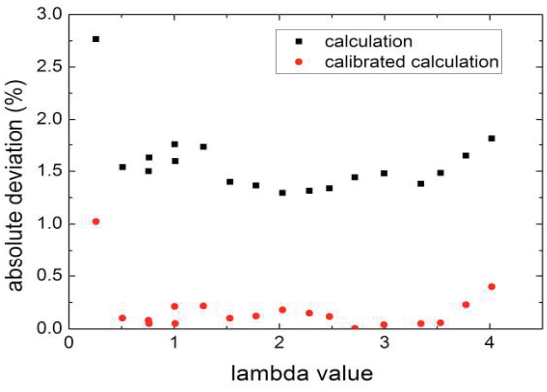

Fig. 6: Absolute deviation of calculated to measured transmission values before (black squares) and after (red dots) calibration.

Fig. 6 shows the absolute deviation between calculated and measured transmission values before and after calibration. Before calibration the deviation is below 2% illustrating the quality of the calculations. After calibration the deviation lies well below 0.5% with an average

deviation of 0.18%. The only exception to this result is the deviation at a λ = 0.25. For this value the absolute deviation is 2.8% and 1% before and after calibration respectively.

Quantification of CH_4 injection

The results presented in the previous section allow an accurate and time resolved quantification of a CH_4 injection into the flow channel. In the experimental setup described in Fig. 1 the mixing module and the MFC are replaced by a CNG injector from a standard SI engine. The time resolution of the experiment is ≈0.167 ms and the duration of a measurement cycle with one injection is 1200 ms. The injection starts 200 ms after the beginning of a cycle. This ensures, that the time between two injections is long enough two clean the measurement location of CH_4 even at low flow velocities. The injector is backed with a methane pressure of 700 kPa and opens for 7 ms in this experiment. Every measurement consists of 50 recorded cycles where the first 10 are without injection of CH_4. This procedure allows taking the first 10 cycles of every recording as background signal. The signal with CH_4 injection is divided by the averaged background signal resulting in a broadband transmission value. We average these values over the 40 cycles with injection, which minimizing the effect of small variations of single injections. Fig. 7 displays the different behavior of the transmission signal for different flow velocities. Independent of the flow velocity the transmission drops sharply directly after the injection at 200 ms followed by a flow velocity dependent increase in transmission due to transport of CH_4 away from the detection region. The curves in Fig. 7 show clearly, that the latter process becomes slower at lower flow velocities. At the slowest flow speeds a small amount of CH_4 remains in the measurement volume at the end of the recording cycle reflected by a transmission <1 in Fig. 7. The signal reaches 1 (no CH_4) right before the next injection. In conclusion, only tiny amounts of CH_4 stay at the measurement position until the next injection. This holds only for slow flows of air. Higher flows remove all CH_4 in less than 100 ms (green/blue curve in Fig. 7).

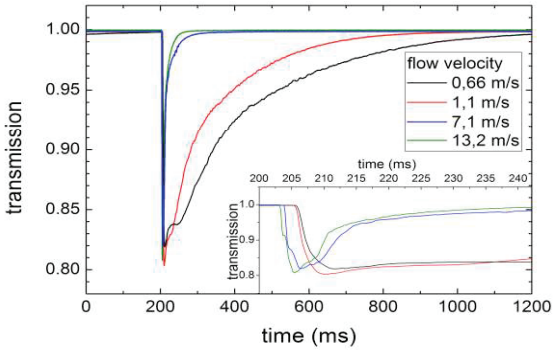

Fig. 7: Broadband transmission values for a CH_4 injection into the flow channel for different flow velocities.

We showed in the previous section that a broadband transmission value can be directly related to a CH_4 density or a λ value of the CH_4/air mixture using calculations based on the HITRAN database and a calibration function. Based on our calculations we created a look-up-table of λ value versus broadband transmission for λ=0.05 – 10. The maximum transmission is 95.3% corresponding to a mole fraction of ≈1% CH_4 in the mixture under ambient conditions (298 K, 100 kPa). Although the sensor is able to resolve higher transmissions this upper limit suits typical engine applications, because higher λ values are rarely of any interest. The quantification method compares every transmission value measured with the pairs of transmission and λ value of the look-up-table. After evaluation of the minimal deviation for transmission, the corresponding λ value is set.

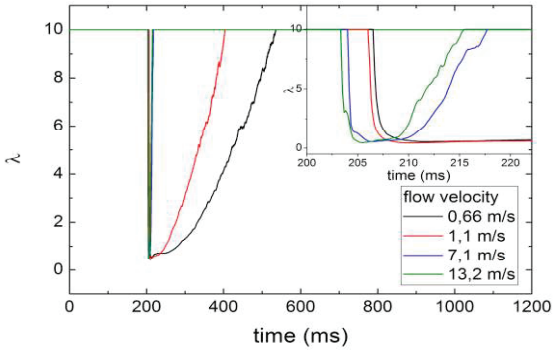

Fig. 8: Quantified results of the injection measurements for different flow velocities.

Due to the upper limit for λ the behavior in Fig. 8 is quite different from that in Fig. 7. The differences between high and low flow velocity are more pronounced. At highest velocity the injection appears only as a narrow 12 ms wide peak. For slow velocities of 0.66 m/s and 1.1 m/s the peak width is 320 ms and 200 ms, respectively. The initial drop reaches down to a lambda value around 0.5 independent of flow velocity.

Conclusion and outlook

In this work we presented the development of an optical sensor system for time resolved quantification of CH_4 densities in gas flows. The system defines a basis for mixture formation analysis in modern CNG SI engines and serves as a diagnostic tool for development of combustion engines. The design of the optical setup enables the use at the inlet manifold of a test station engine. Time resolved broadband transmission measurements of CH_4 inside a flow channel, which serves as a model for an inlet manifold, are presented. The time resolution is high enough to examine the behavior of a typical 7 ms injection into the flow channel. Simulations of expected broadband transmission values using the HITRAN database show very good quantitative agreement with measurements. Application of an empiric calibration yields further reduction of remaining deviations. The procedure allows for an accurate quantification of the lambda value during injection. It is important to note that the relation of detector signal and CH_4 density depends on the environmental conditions. Therefore, the maximum measurement accuracy requires the knowledge of pressure and temperature.

The next step is the adaption of the measurement system to a SI engine in order to validate the method under harsh, practically relevant conditions. In this environment dynamic pressures and temperatures changes must be considered for the quantification. Precise determination of pressure is no problem at engine test stations whereas temperature measurements are challenging. Estimations about the accuracy needed are subject of research in progress.

We emphasize, that the sensor system presented here is not limited to applications in automotive development. The basic concept is capable to measure CH_4 densities in any flows with high precision and time resolution. Moreover, a change of the bandpass filter enables the quantification of other IR-active molecular species like CO_2 and NO_x possible especially if they are part of the HITRAN database. Adjustment of the quantification method would be required accordingly.

Acknowledgements

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