Fiber Laser Intracavity Absorption Spectroscopy (FLICAS) for measurement of water, CO, and CO_2 during partial methane oxidation

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Introduction

Methane is a main component (80-99 % v/v) of natural gas and biogas. Natural gas is not a renewable source of energy, but contrary to oil, new remote natural gas deposits are being continually discovered at a significant rate around the globe. The direct use of methane as fuel for transportation faces several problems, the main of which is related to the fact that it cannot be converted into the liquid form at room temperature. Methane conversion to liquid fuels is essential as it makes transportation considerably safer and cheaper. Methane can be converted to a liquid hydrocarbon fuel using the Gas-to-Liquid (GTL) process. Usually, the first stage of GTL process is conversion of methane to H_2S and CO (syngas). The MILD combustion is characterized both by elevated temperature of reactants and low temperature increase in the combustion process. In our works, this type of combustion is used for partial methane oxidation to syngas. The highly diluted conditions characteristics of this combustion mode make the oxidation evolve in self ignition conditions, in absence of a flame propagation. Spectroscopic methods are very important for control of process in real time. We developed a method for concentration monitoring of the products based on Fiber Laser IntraCavity Spectroscopy (FLICAS). Experimental setup for experiments with MILD combustion is depicted in Fig.1)

Simultaneous measurements of CO and CO_2.

FLICAS uses an erbium-doped broadband laser capable of being tuned in the range 6350-6450 cm^{-1}. The range 6390 - 6410 cm^{-1}, which is emitted by the laser without tuning, allows for simultaneous observation of the CO, CO_2, and methane (CH_4) spectra. Truly simultaneous observation of these spectra is possible during one laser pulse with duration as short as 3.7 μs. The sensitivity of the CO measurement is about 20 times higher than that of CO_2, a feature which is advantageous for several applications. The concentration of CO can be measured with a sensitivity of 400 ppm at room temperature, and this sensitivity can be improved by increasing the generation time. The experiments were performed in a temperature and flow-controlled cell in order to evaluate the accuracy of the concentration and temperature measurements from 296 to 1200 K. The measured spectra of CO and CO2 are well described by the HITRAN database, allowing for accurate and simultaneous determination of CO, CO_2 and temperature. The temperature is evaluated using the CO2 spectrum, which includes many ”hot” transitions. The CH_4 HITRAN data are deficient at high temperatures, so this method only allows for the evaluation of methane concentrations at room temperature.

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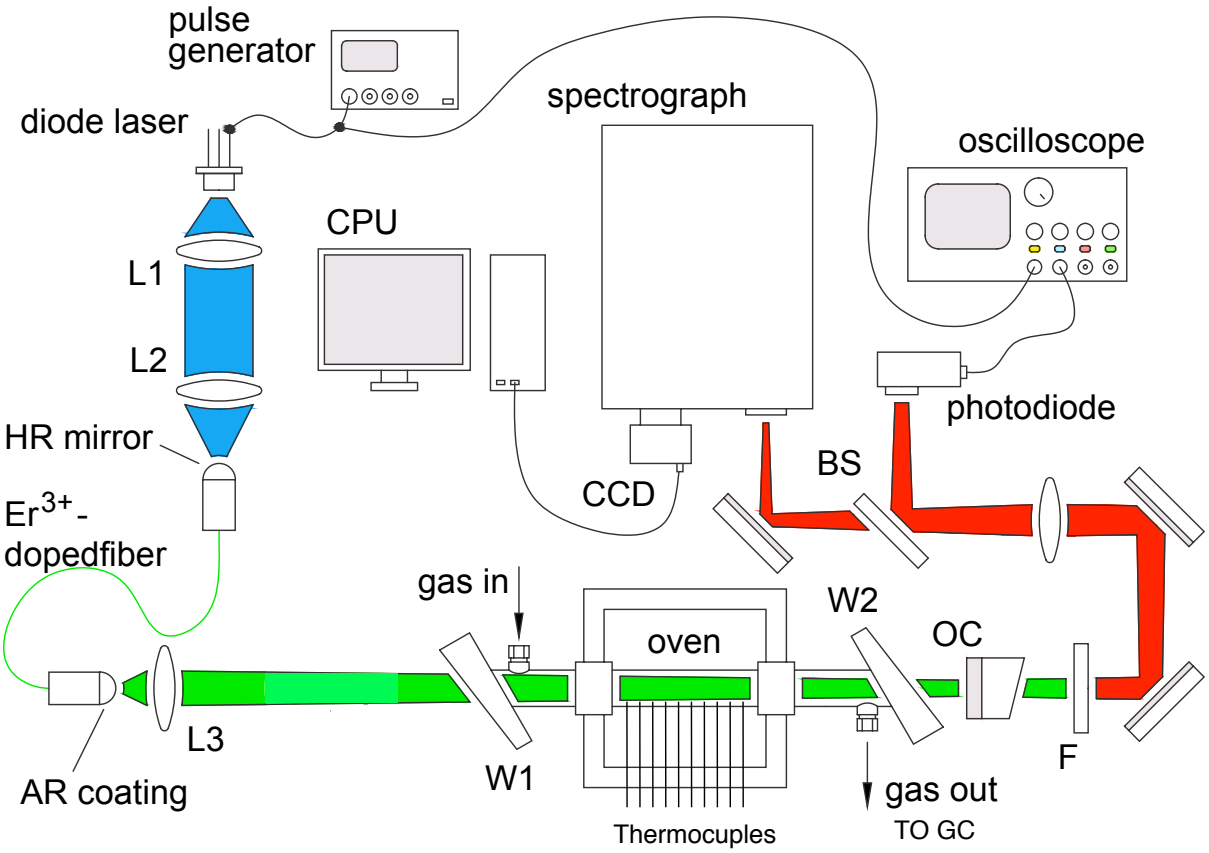

Figure 1. Schematic of the experimental setup. L1, L2, and L3 are aspherical lenses, OC is an output coupler, BS is a beamsplitter, PD is a photodiode, and F is a focusing lens.

High pressure measurements.

The feasibility of Fiber Laser Intracavity Absorption Spectroscopy (FLICAS) for measurement of concentration of CO and CO_2 and pressure at elevated pressures (up to 6.5 atm) was studied. FLICAS is a very sensitive absorption spectroscopy method which allows for simultaneous measurement of several species even in harsh environment, since it is not sensitive to broadband optical losses caused by particle scattering and absorption, optical window contamination, etc. However, the wings of spectral lines can overlap at elevated pressure resulting broad band absorption which is not monitored by FLICAS. The CO and CO2 spectra were studied under controlled conditions in the spectral range of 6350 - 6385 cm−1 and processed by custom LabVIEW code in order to take into account overlapping line effect. This procedure allows for accurate determination of pressure and the CO concentration at least up to 6.5 atm. Denser and line rich CO_2 spectrum allows correct pressure evaluation up to 6.5 atm, but with higher uncertainty. Accurate measurements of the CO_2 concentration is possible only up to 3.6 atm.

FLICAS in MILD combustion experiment.

The main challenge for the use FLICAS in the MILD combustion experiment related to the simultaneous presence spectra of several molecules including the hot water spectrum. The program for recovering spectral information was modified for this goal. The several variants of the recovering algorithm are analyzed.