

Optimizing OF-CEAS for the Detection of stable methane isotopes in the atmosphere

Cem Dinc¹, Ponkanok Nitzsche¹, Jens Goldschmidt¹, Katrin Schmitt^{1,2}, Jürgen Wöllenstein^{1,2}

¹ Laboratory for Gassensors, Department of Microsystems Engineering - IMTEK, University of Freiburg, Georges-Köhler-Allee 102, 79110 Freiburg, Germany

² Fraunhofer Institute for Physical Measurement Techniques IPM, Georges-Köhler-Allee 301, 79110 Freiburg, Germany
cem.dinc@imtek.uni-freiburg.de

Summary:

This work presents an approach to detect and measure the specific isotopic ratio of the stable methane isotopes $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ using a high-finesse cavity within an Optical Feedback CEAS system. The development of this approach is ongoing with the aim of precisely measuring the isotopic ratio under atmospheric conditions in the mid-infrared (MIR) spectral region around 3001.2 cm^{-1} , where the absorption lines of the two stable isotopologues are located and well separated under a pressure of 40 mbar enabling the simultaneous measurement of both within a spectral range of 1 cm^{-1} .

Keywords: Optical Feedback CEAS, Methane Isotopic Ratio, Absorption Spectroscopy, MIR Environmental Sensor, Greenhouse Gas

Motivation

To understand the impact of climate change, it is important to investigate greenhouse gases such as methane (CH_4) and carbon dioxide (CO_2). The current CH_4 concentration in the atmosphere is 1.9 ppm, which is still rising and has doubled over the last 200 years. In addition, it has a global warming potential that is almost 30 times higher than that of CO_2 , it is for this reason that CH_4 is the second most important greenhouse gas after CO_2 [1]. This is why it is of great importance to identify and monitor CH_4 sources and sinks and thus to study the CH_4 cycle and its influence on global warming. The identification is based on the isotopic ratio ($\delta^{13}\text{C}$) of the two stable isotopes $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ referenced to the Vienna Pee Dee Belemnite (VPDB) standard, which is a specific value for each source and every sink. For instance, one of the largest anthropogenic sources of CH_4 is natural gas, which has an isotopic ratio of $\delta^{13}\text{C} = -43\text{‰}$. A natural source of CH_4 is that of wetlands, which has a value of $\delta^{13}\text{C} = -60\text{‰}$ [2]. Precise measurement of the isotopic ratio can be achieved through established methods like isotope ratio mass spectrometry (IRMS) with the necessary sample preparation and cavity ring down spectroscopy (CRDS) [2]. We present an alternative to CRDS with a higher sensitivity: optical feedback cavity enhanced absorption spectroscopy (OF-CEAS). Based on the feedback of the resonant light into the laser that is transmitting from the cavity (OF),

the laser is self-locked to the resonance of the cavity. The effect of this process is the reduction of the laser line width, the improvement of the frequency stability and thus a higher signal-to-noise ratio (SNR) as well as a higher coupling efficiency [3].

The strongest absorption lines of CH_4 are in the MIR spectral region and to be able to determine the isotopic ratio of CH_4 within a single scan, a suitable region around 3001.2 cm^{-1} was selected. Both stable isotopologues are located here and well separated from each other under low pressure.

Experimental Setup

The cavity design allows to adjust crucial parameters, such as the effective absorption path length (L_{abs}) and the free spectral range (FSR).

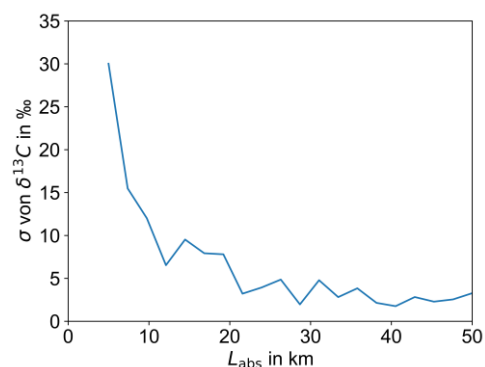


Fig. 1: Monte Carlo simulation to assess the uncertainty of the $\delta^{13}\text{C}$ value for different L_{abs} .

These parameters significantly influence the investigation of the spectral range and consequently the determination of the isotope ratio. Hence, a range of investigations and simulations were conducted utilizing the HITRAN database, comprising a Monte Carlo simulation to determine the L_{abs} necessary to optimize the precision of the $\delta^{13}\text{C}$ value [4]. The simulation parameters were a concentration of 1.9 ppm at a temperature of 298.15 K and a pressure of 40 mbar, with a noise level determined through measurements being introduced into the simulated spectrum. Using a fit of a Voigt profile-based physical model to the simulated signal including spectroscopic parameters from the HITRAN database, the isotope ratio could be determined for different L_{abs} . Ten simulations were run per L_{abs} to assess the uncertainty, which is shown in Figure 1. It is observable that the uncertainty reduces and stabilizes starting at a L_{abs} of 20 km. Therefore, the cavity was built in a V-shape with a planar mirror and two curved mirrors with a radius of curvature of 1000 mm. The reflectivity of the mirrors is 99.989 % and the arm lengths 905 mm. This results in a FSR of 82.8 MHz and a L_{abs} of 22.6 km. The advantage of the V-cavity is that it ensures that only the resonant light transmitted from the cavity is fed back to the laser and not the direct reflection. An interband cascade laser (ICL) with a central wavenumber of 2998.5 cm^{-1} was selected for operation within the specified spectral range. The beam is propagated through the cavity by passing a mirror, which is mounted on a piezo transmitter (PZT), enabling active control over the laser-cavity-distance to maintain the phase condition for the optical feedback [3]. To verify the ability of the system to detect atmospheric CH_4 the laser was tuned over a spectral range of approximately 1 cm^{-1} by applying a 1 Hz-sawtooth signal. The cavity which was housed with gas connections, pressure and temperature sensors, was flooded with ambient air under atmospheric condition. A measurement with a duration of 300 s was carried out for system characterization.

Results

As demonstrated in Figure 2, the system characterization results indicate a relatively stable methane concentration of 1 ppm in the ambient air over the measurement period. A deviation from the expected value of 1.9 ppm is clearly visible. The reason of this deviation includes cross-sensitivity to H_2O in this spectral range, which complicates baseline correction, and a deviation of the effective absorption path from the expected 22.6 km. The Allan deviation indicated an increasing precision with the integration time, which is not yet sufficient to precisely determine the stable isotopic ratio of CH_4 .

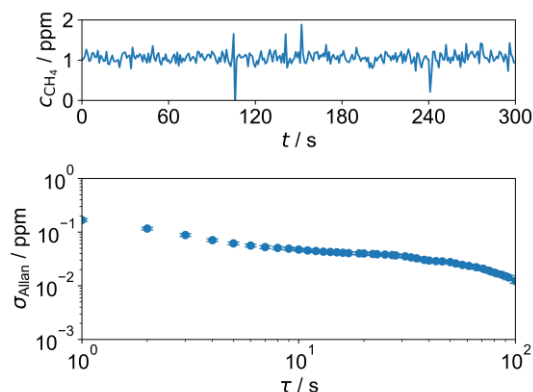


Fig. 2: Measured CH_4 concentration in ambient air under atmospheric conditions for 300 s and the corresponding Allan Deviation.

Conclusion

Here we have presented an OF-CEAS system capable of detecting CH_4 at atmospheric conditions in the selected spectral region, although still with a strong cross-sensitivity to H_2O . The system must be further optimized to be able to determine the isotopic ratio of CH_4 precisely. To enhance the accuracy of the baseline correction by reducing the cross-sensitivity, future measurements will be performed with dried air and low pressure. The application of a pressure of approximately 40 mbar permits the clear separation of the absorption lines of the stable isotopologues. Additional optimizations include the installation of the V-cavity within a custom-built Invar cell with active temperature control, which should enhance the stability of the cavity.

References

- [1] Masson-Delmotte, V., et al. IPCC, 2021: Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2391 pp.; doi:10.1017/9781009157896
- [2] Zhang, Z., et al. Novel Coalbed Methane (CBM) Origin Analysis and Source Apportionment Method Based on Carbon Isotope Ratio Using Infrared Dual-Wavelength Laser Absorption Spectroscopy, *Earth and Space Science*, 5.11, 721-735 (2018); doi: 10.1029/2018EA000437
- [3] Morville, J., et al. Fast, low-noise, mode-by-mode, cavity-enhanced absorption spectroscopy by diode-laser self-locking, *Applied Physics B* 80, 1027-1038 (2005); doi: 10.1007/s00340-005-1828-z
- [4] Gordon, Iouli E., et al. The HITRAN2020 molecular spectroscopic database, *Journal of quantitative spectroscopy and radiative transfer* 277, 107949 (2022); doi: 10.1016/j.jqsrt.2021.107949