

# CW EC-QCL Based Sensor for Simultaneous HOD/H<sub>2</sub>O, N<sub>2</sub>O and CH<sub>4</sub> Detection by Multi-pass Absorption Spectroscopy

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**Abstract:** A sensor system based on a CW EC-QCL was demonstrated for simultaneous atmospheric HOD/H<sub>2</sub>O, N<sub>2</sub>O and CH<sub>4</sub> detection. A 57.6m multi-pass absorption cell was employed. Wavelength modulation spectroscopy was implemented for data processing.

**OCIS codes:** (280.3420) laser sensors; (300.6340) spectroscopy, infrared; (140.5965) semiconductor lasers, quantum cascade;

## 1. Introduction

Atmospheric greenhouse gases, such as water vapor, nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>) play important roles in global warming and climate change [1]. Water vapor is a primary energy carrier in the atmosphere and the dominant absorber and emitter of radiation [1, 2]. Determination of the HDO/H<sub>2</sub>O isotope ratio in the atmosphere is relevant to trace the evolution and processes impacting water vapor concentrations at a specific location[3]. N<sub>2</sub>O, with atmospheric mixing ratios increasing at a rate of ~0.7 ppbv/year, has a global warming potential (GWP) of 298 (100-year horizon) and a longer lifetime than carbon dioxide and CH<sub>4</sub>[1]. CH<sub>4</sub> exhibits a GWP of 25 (100-year horizon) and constitutes a safety hazard in several industries, including natural gas storage, transportation and coal mining [1, 4]. Precise and sensitive detection of these relevant atmospheric trace gases is critical.

## 2. Methods

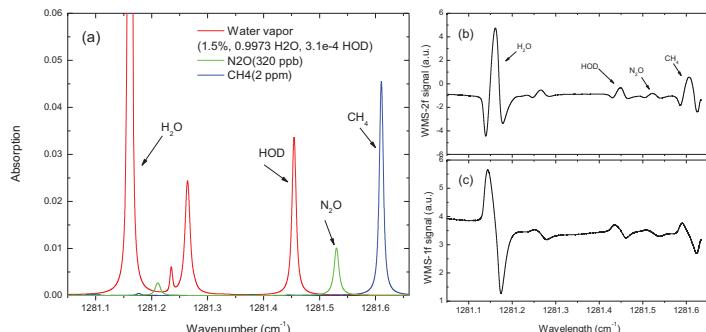


Fig. 1(a) HITRAN simulation of the absorption spectra of H<sub>2</sub>O, HOD, N<sub>2</sub>O and CH<sub>4</sub> at 296 K, 40 Torr and 57.6m path length in the 1281.05-1281.66 cm<sup>-1</sup> wavelength range; (b) 2f and (c) 1f signals from experimental measurements.

High-resolution absorption spectra of the targeted absorption lines at 296 K temperature, a pressure of 40 Torr and a 57.6m absorption path length are simulated by the HITRAN database for 1.5% water vapor (H<sub>2</sub>O and HOD in an abundance of 0.9973 and 3.1e-4, respectively), 320 ppb N<sub>2</sub>O and 2 ppm CH<sub>4</sub>, as depicted in Fig. 1(a). Four neighboring lines, a H<sub>2</sub>O line at 1281.161 cm<sup>-1</sup>, a HOD line at 1281.454 cm<sup>-1</sup>, a N<sub>2</sub>O line at 1281.53 cm<sup>-1</sup>, and a CH<sub>4</sub> line at 1281.61 cm<sup>-1</sup>, are well separated in a relatively narrow spectral range of 0.65 cm<sup>-1</sup>.

A sensor system was developed for the simultaneous monitoring of HOD/H<sub>2</sub>O, N<sub>2</sub>O and CH<sub>4</sub> by using a continuous wave external-cavity quantum cascade laser (CW EC-QCL) (Model 21080-MHF, Daylight Solutions, San Diego, CA) with a mode-hope-free spectral range of 1225-1285 cm<sup>-1</sup> and a compact dense-pattern multi-pass cell (MPC) with an effective path length of 57.6m. A combination of wavelength modulation spectroscopy (WMS) with second-harmonic (2f) and first-harmonic (1f) was implemented, which is immune to laser intensity fluctuation from non-absorption transmission losses[5]. Fig.1 (b) and (c) depict experimental measurements of WMS-2f and 1f signals, respectively.

## 3. Results

An Allan-Werle variance method was utilized to analyze the stability and precision of our sensor system. Minimum detection limits (MDLs) of 12.5 ppm for H<sub>2</sub>O, 26.5 ppb for HOD, 17.0 ppb for N<sub>2</sub>O and 24.0 ppb for CH<sub>4</sub> were achieved with a 1-s sampling time.

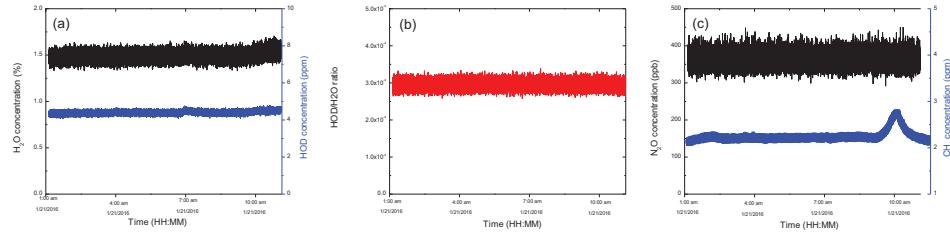


Fig. 2 Simultaneous measurements of (a) H<sub>2</sub>O, HOD (b) H<sub>2</sub>O/HOD ratio, (c) N<sub>2</sub>O and CH<sub>4</sub> in laboratory ambient air

The performance of our sensor system was evaluated for simultaneous atmospheric HOD/H<sub>2</sub>O, N<sub>2</sub>O and CH<sub>4</sub> detection in laboratory air. Continuous monitoring was conducted from 1:08 to 11:05 CDT on January 21, 2016. The H<sub>2</sub>O vapor concentration during this period was ~1.5%, shown in Fig. 2(a), slightly higher than the estimated value of ~1.22% based on the laboratory ambient conditions (T: 22.8 °C and RH: 44%). This observation is in agreement with Ref.[2]. Fig. 2(b) and (c) indicate that the HOD/H<sub>2</sub>O ratio and N<sub>2</sub>O mixing ratio are relatively constant during the sampling period, while CH<sub>4</sub> mixing ratio exhibited a peak in the later morning and subsequently returned to its original background level of ~2.1 ppm.

#### 4. Conclusions

We report the development and application of a sensitive sensor system for simultaneous monitoring of HOD/H<sub>2</sub>O, N<sub>2</sub>O and CH<sub>4</sub> by using a CW EC-QCL with wide mode-hope-free range and a compact MPC with a 57.6m optical path length. Four interference-free absorption lines in a narrow spectral range were selected at temperature of 296 K and pressure of 40 Torr. A 1f-normalized wavelength modulation spectroscopy with second-harmonic detection (WMS-2f/1f) strategy was employed. An initial experiment of sampling laboratory air was conducted to detect the gas species simultaneously. The MDLs at 1-s sampling time were 12.5 ppm, 26.5 ppb, 17.0 ppb and 24.0 ppb for H<sub>2</sub>O, HOD, N<sub>2</sub>O and CH<sub>4</sub>, respectively, based on an Allan-Werle variance analysis. Field deployment of the sensor system for real time detection of these trace gases in the atmosphere will be performed in the near future.

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