QCL Based Absorption Sensor for Simultaneous Trace-Gas Detection of CH_4 and N_2O

Wei Ren, Wenzhe Jiang, and Frank K. Tittel
Department of Electrical and Computer Engineering, Rice University, 6100 Main Street, Houston,TX 77005, USA
E-mail address:wr5@rice.edu

Abstract: A quantum cascade laser (QCL) absorption sensor system operating at 7.83 μm was developed for simultaneous dual-species monitoring of CH_4 and N_2O using a novel compact multipass gas absorption cell with a sampling volume of 225 mL.
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Methane (CH_4) and nitrous oxide (N_2O) are both significant greenhouse gases emitted from human activities [1]. CH_4 is emitted by natural sources such as wetlands and human activities such as leakage from natural gas systemsand the raising of livestock. Agriculture, fossil fuel combustion, wastewater management, and industrial processes increase the amount of N_2O in the atmosphere. The warming impact of CH_4 and N_2O is over 20 and 300 times, respectively, greater compared to the most prevalent greenhouse gas, carbon dioxide (CO_2) over a 100-year period. For these reasons, the detection of CH_4 and N_2O at low parts per billion (ppb) concentration levels is crucial in numerous environmental monitoring applications.

To perform quantitative and sensitive detection of atmospheric trace gases several highly sensitive spectroscopic techniques can be employed such as tunable diode laser absorption spectroscopy (TDLS) [2,3], cavity-enhanced absorption spectroscopy (CEAS) [4], and photoacoustic absorption spectroscopy (PAS) [5]. Recently we reported the sensitive detection of CH_4 and N_2O based on quartz-enhanced photoacoustic absorption spectroscopy (QEPAS) at 7.83 μm [6]. Atmospheric CH_4 and N_2O mixing ratios were measured at the BFI McCarty landfill, an urban solid waste disposal site in the Greater Houston area with the QEPAS sensor system [7]. In this work we report on the development of a compact sensor system for the sensitive real time field measurements of CH_4 and N_2O using a novel compact multipass gas absorption cell.

Quantum cascade lasers are widely used as convenient compact spectroscopic sources for sensitive trace gas monitoring in numerous applications [8]. In this work, the sensor system uses a thermoelectrically cooled (TEC) continuous wave (CW) distributed feedback (DFB) QCL operating at 7.83 μm and is wavelength scanned over two adjacent CH_4 (1275.38 cm^{-1}) and N_2O (1275.49 cm^{-1}) lines at a 1 Hz repetition rate. Figure 1 depicts the DFB-QCL wavelength characteristics as a function of injection current at different operating temperatures. Simulated absorption spectra for standard air using the HITRAN database [9] are depicted in Fig. 2 that are accessible within the QCL spectral tuning range. The two selected CH_4 and N_2O spectral lines have relatively strong absorption strengths at atmospheric concentrations and are close enough (with a line spacing of 0.1 cm^{-1}) to be accessible within a single laser scan. In addition, wavelength modulation spectroscopy (f = 10 kHz) with second harmonic ($2f$) detection is performed to enhance the detection sensitivity by more than a factor of 10.

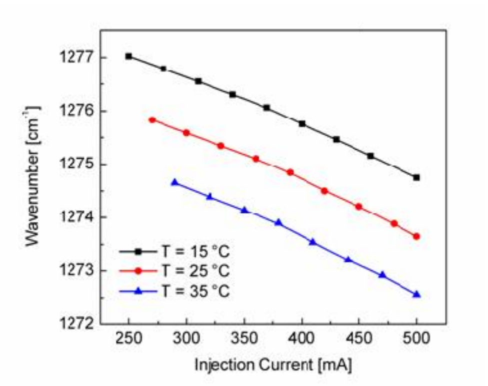

Fig. 1. DFB-QCL emission wavelengths as a function of injected current at three operating temperatures 15°C, 25°C and 35°C.

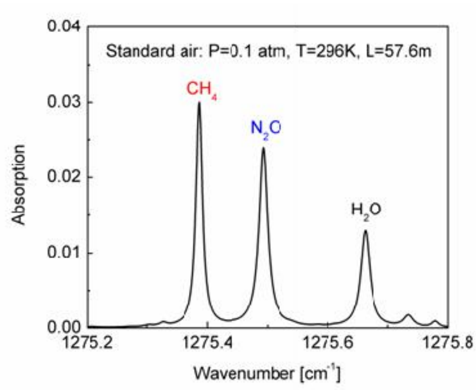

Fig. 2. Simulated CH4 and N2O absorption spectra in the 7.83 μm wavelength range (P=0.1, L=57.6 m) using the HITRAN database [9].

A visible diode laser beam (λ = 630 nm) was combined with the mid-IR QCL beam by means of a dichroic mirror (ISP Optics, model BSP-DI-25-3) to facilitate the optical alignment of the sensor system. Both laser beams are directed into a novel, ultra-compact multipass gas cell (Sentinel Photonics) to achieve an effective optical path length of 57.6 m. In this novel multipass cell, more than 450 beam passes occur in a resonator composed of two 40-mm-diameter spherical mirrors separated by 12.5 cm with optimized parameters that minimize spot overlap. The cell has a small sampling volume of only 225 mL which results in reduced gas-exchange times compared to traditional large multipass gas cells. This multipass gas cell is more than 10 times smaller than conventional multipass gas cell designs with equivalent sensitivity. The output beam is focused onto a TEC mercury–cadmium–telluride (MCT) detector (VIGO PVM-10.6-1x1-TO39) using a 10-cm focal length parabolic mirror.

With such a sensor configuration, ppb-level minimum detection limits for CH_4 and N_2O were achieved that are required for numerous environmental applications. The linearity and the stability of the reported absorption sensor were verified by monitoring continuously different calibrated CH_4 and N_2O concentrations. The main advantage of the reported CH_4 and N_2O sensor is its compact size and simultaneous dual-species detection, satisfying the requirements of a small in-situ sensor system. The sensor will be installed in a mobile monitoring van operated by the University of Houston Department of Earth and Atmospheric Science and deployed for further real-time field measurements of CH_4 and N_2O emissions in the Greater Houston area in 2014.

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