Single frequency quantum cascade-DFB laser based spectrometer for trace gas detection

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Abstract: Performance characteristics of a single frequency mid-infrared quantum cascade distributed feedback (QC-DFB) laser will be reported. Sensitive spectroscopic trace gas detection of CH_4, N_2O, H_2O and C_2H_5OH in the 7.9 μm spectral region was demonstrated using a 100-m Herriott multipass cell and a rapid "zero-air" background subtraction technique.

OCIS Codes: (140.5960) Semiconductor lasers; (300.6340) Spectroscopy, infrared; (010.1280) Atmospheric composition

Summary

Infrared laser absorption spectroscopy is an effective tool for monitoring atmospheric trace gas species. Applications of this method are limited mainly by the availability of convenient tunable sources in the spectroscopically important "fingerprint" region from 3 to 20 μm. Recently developed quantum-cascade lasers [1] have been demonstrated to be useful tunable single-frequency light sources for laser-based absorption spectroscopy [2-5]. In this work, we demonstrate the application of a cw single frequency QC-DFB laser operating at 7.9 μm to the sensitive detection of CH_4, N_2O and different isotopic species of H_2O in ambient air.

A schematic of the QC-DFB laser based gas sensor configuration is shown in Fig. 1. In these experiments, QC-DFB laser designed for continuous (cw) operation at cryogenic temperatures in the 7.9 μm spectral region was used. The laser was mounted in a liquid N_2 dewar equipped with a broadband AR coated ZnSe window. No active temperature stabilization was applied. Two off-axis aluminum gold-coated parabolic mirrors and an uncoated BaF_2 lens were used to shape the laser beam. To detect trace components of the ambient air, a commercial multipass cell aligned for a 100 m optical path was used. The air was continuously flowing through the cell, and the pressure in the cell was set to 20 to 40 Torr to minimize pressure broadening effects. After passing the cell, the laser radiation was collected onto a liquid nitrogen cooled photovoltaic MCT detector with a built-in 20 MHz preamplifier. The electrical signal was digitized using a 12 bit data acquisition card capable of a 50 MHz sampling rate.

The laser current was supplied by a low-noise driver. External modulation of current with this device has a 7 kHz bandwidth limitation. Therefore, when a rectangular pulse is applied to the external modulation input, the laser current grows exponentially from its minimum set value to the steady-state current. This technique was used for fast current scanning of the QC laser frequency using a pulse generator. The use of a pulse generator enabled the variation of the laser duty cycle and thus its average temperature and frequency. This method produces an essentially nonlinear frequency-time dependence, which however is not important when the transition frequencies of interest are known. All the absorption lines observed in these experiments were readily assigned. Typically, pulses of 120 μs to 235 μs duration were applied at a 800 Hz – 1000 Hz repetition rate and frequency scans were typically

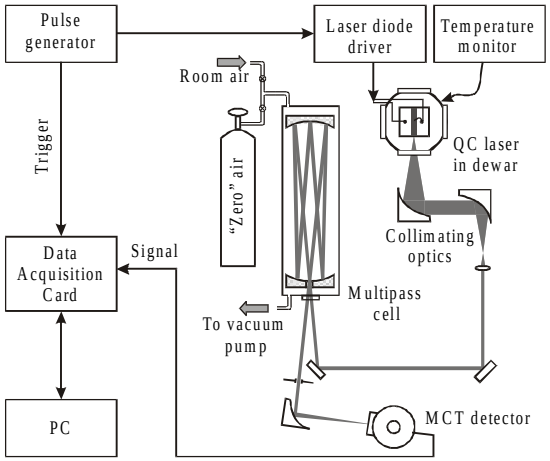

Fig. 1. Schematic of the QC-DFB based gas sensor.

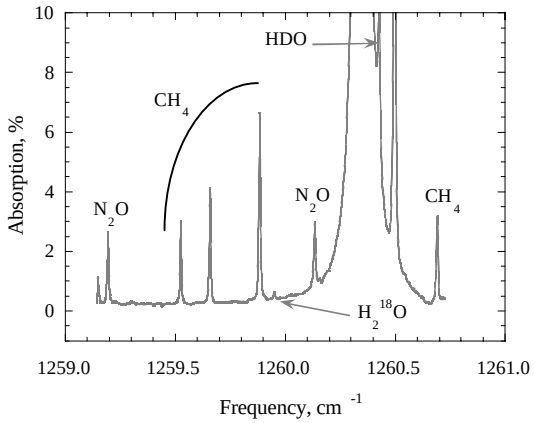

Fig. 2. An example of the ambient air absorption spectrum at 30 Torr, 100 m pathlength.

over 2 cm^{-1}.

The main sensitivity-limiting factors for detecting weak absorption lines were optical interference fringes and baseline inhomogeneities caused by optical diffraction and water absorption outside the cell. Higher-frequency fringes were washed out by applying a weak changing mechanical deformation to the multipass cell during the measurements. To suppress the influence of other interfering effects, a rapid "zero-air" background subtraction technique [6] was used. Spectra of ambient air and "zero air" were alternatively acquired. Replacing the air in the 3.3 l multipass cell took ~30 seconds. Subsequently, the zero-air signal (as a function of a datapoint number) was subtracted from the ambient air signal. The result was normalized to the zero-air signal, resulting in an absorption spectrum. In most of the measurements, pure air with an addition of 5% CO_2 was used as a zero gas. The resulting weak "negative absorption" CO_2 lines in the spectra aided in the spectral calibration of wavelength scans.

A typical absorption spectrum of ambient air obtained with the procedure described in the previous section is shown in Fig. 2. Four strong CH_4 lines, two strong N_2O lines and several H_2O lines corresponding to different isotopic species fall into the spectral range covered by this QC-DFB laser frequency scan. The spectrum depicted is the result of averaging over 6000 individual scans for both ambient air and zero-air. An acquisition and averaging of 6000 200 μs-long scans at 1 kHz repetition rate, 50 MS/s took ~30 seconds, because the software for this spectrometer has not yet been optimized for fast data acquisition. The minimum detectable absorption is estimated to be 10^{-4} (0.01%) for absorption lines with a linewidth of ~0.01 cm^{-1} characteristic for the pressure range from 20 to 40 Torr. The present sensitivity to weak absorption features is limited by an unstable baseline. This limitation can be minimized if a reproducible multipass cell deformation is applied as mentioned above. The current sensitivity achieved corresponds to a minimum detectable concentration of 3.5 ppb for CH_4 and 1.5 ppb for N_2O, based on intensities of the strongest absorption lines present in a given frequency scan.

Experiments were carried out to measure the $[^{13}CH_4]/[^{12}CH_4]$ ratio in ambient air. The natural abundance of $^{13}CH_4$ is close to 0.01 and can experience up to 10% variation depending on the methane source [7]. A $^{13}CH_4$ line centered at 1260.547 cm^{-1} was chosen for these measurements, because it experiences the least interference from

other absorption lines, though it is situated on the wing of a strong H_2O line. Isotopic abundances of $H_2{}^{18}O$ and $HD^{16}O$ could be measured as shown in Fig. 3. Isotopic composition measurements are of interest in determining sources and sinks of trace gas constituents in air [7].

The spectral range near 8 μm is also useful for detecting more complex organic molecules, such as ethanol (C_2H_5OH). The frequency of our laser falls close to the center of one of the absorption bands of this molecule. Unlike in the C-H and O-H stretch spectral region (~3 μm), this band has a reasonably well resolved ro-vibrational structure. This can be explained by a much smaller density of vibrational states at 1200 cm^{-1} compared to 3000 cm^{-1}, where the vibrational states already form a vibrational quasicontinuum [8]. The resolved spectral features makes it possible to distinguish the absorption of ethanol from other organic compounds. To calibrate the gas sensor for ethanol concentration measurements, absorption spectra of 1.1 Torr of ethanol vapor mixed with 30 Torr of air in a 0.43 m single-pass gas cell were recorded. For measurements with the multipass cell, a small amount of ethanol was spilled near the multipass cell air input, and the spectra were acquired at 5, 10 and 15 minutes later. The sensitivity to ethanol vapor concentration in ambient air was estimated to be 850 ppb.

This work demonstrates the successful application of a single-frequency QC-DFB laser to the analysis of trace gases in ambient air. A relatively simple technique was used to operate the QC laser, consisting of a liquid N_2 dewar with optical access, a laser current driver, and a pulse generator. To date this QC-laser based gas sensor has a demonstrated detection sensitivity of 3.5 ppb for CH_4, 1.5 ppb for N_2O and 850 ppb for C_2H_5OH for a ~60 sec data acquisition time. Measurements of the isotopic composition of H_2O and CH_4 in ambient air were also performed.

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