Quantum cascade laser-based spectrometer for high sensitive measurements of trace gases in air

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A quantum cascade (QC) laser-based spectrometer is developed to measure trace gases in air. The proposed spectrometer is tested for N_2O, and the results presented in this letter. This system takes advantage of recent technology in QC lasers by utilizing intra-pulse scan spectroscopy, which allows high sensitive measurement. Without calibration gases, the gas concentration can be calculated with scan integration and the corresponding values from the HITRAN04 database. By analyzing the Allan variance, a detection limit of 2 ppb is obtained. Continuous measurement of N_2O sampled from ambient air shows the applicability of the proposed system for the field measurements of gases of environmental concern.

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Laser spectroscopic techniques are ideally suited for a wide range of measurement and control applications that require *in situ*, chemically selective detection of molecular species in trace quantities. The availability of mid-infrared (MIR) sources has led to the evolution and utilization of MIR spectroscopic techniques for many technological and scientific fields because most gases of interest have fundamental absorption lines of inherent vibration–rotation level in the MIR region[1]. Recent developments in the applications of pulsed quantum cascade (QC) lasers[2,3] along with room temperature detectors promise better detection sensitivities in a cryogen-free environment. The characteristics of high optical power output, wide tuning range, and room temperature operation make QC lasers (QCLs) especially suitable for the remote sensing of environmental gases and pollutants in the atmosphere. One of the most important applications of QCL-based spectrometers is greenhouse gas detection, such as CO_2, CH_4, and N_2O. As these species have much stronger absorption lines in the MIR region, QCL-based spectrometers can provide reliable trace gas concentration with high sensitivity.

In this letter, a QCL-based spectrometer containing a QCL and a multipass cell for measuring N_2O was developed. The proposed spectrometer can satisfy the requirement for sensitivity and selectivity. The gas concentration can be calculated with scan integration and the corresponding values from HITRAN04 database by intra-pulse direct absorption technique without calibration. One may substitute a QCL operating at a different wavelengths to measure other gases.

The fundamental theoretical principle of absorption spectroscopy is the Beer–Lambert law. This law describes the relationship between transmitted and incident light intensities when the laser beam passes through a uniform gaseous medium[4]. For a single species and a particular transition, it can be approximated as

$$I = I_0 \exp[-PXS_0\Phi(\nu - \nu_0)l], \qquad (1)$$

where X is the mole fraction of the species, P is the total pressure; and S_0 and $\Phi(\nu - \nu_0)$ are the linestrength and lineshape, respectively. By dividing both sides by I_0 and taking their natural logarithm, Eq. (1) can be simplified as

$$\alpha_\nu = -\ln\left(\frac{I}{I_0}\right) = PXS_0\Phi(\nu - \nu_0)l, \qquad (2)$$

where α_ν represents the spectral absorbance.

A schematic of the QCL spectrometer is shown in Fig. 1. The key components of this spectrometer is a distributed feedback QCL (Cascade Technologies, Ltd.) centered at ~1274 cm^{-1} (or ~7.85 μm). The laser is mounted in an airtight housing supplied with a Peltier cooler, which can be used to set the laser heat-sink temperature. A homemade laser controller is used to control the laser pulse and the temperature. By changing the temperature from 10 to 35 °C, this laser sweeps across a wavenumber from 1 274.5 to 1 272.5 cm^{-1} which can access the absorption line of 1 273.7 cm^{-1} for N_2O. The laser is capable of providing single-frequency emission with max peak output power of up to 95 mW at 5% duty cycle and laser heat-sink temperature of 20 °C. As
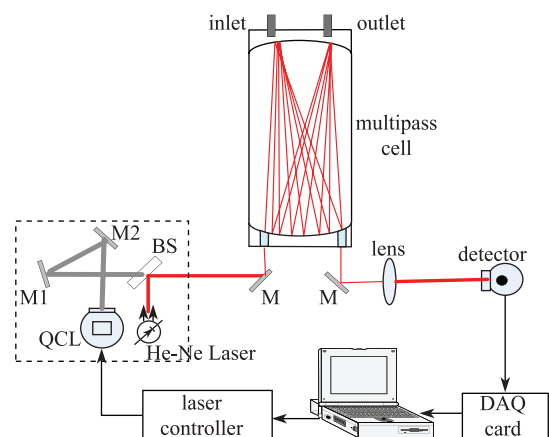

Fig. 1. Schematic diagram of the QCL-based spectrometer.

the MIR light is not visible to human eyes, the alignment of optical components was aided by a He–Ne laser adjusted to be coaxial with the infrared laser beam. The output laser beams were combined together using a set of steering mirrors, as shown in the inset of Fig. 1, and then passed into a multipass cell. The cell is of white type, with a base length of 1 m which produces an optical path length of 80 m. After traversing the multipass cell, the light was focused onto a high-speed photovoltaic mercury cadmium telluride detector (VigoSystems, Ltd.) incorporating an integrated immersion lens and a Peltier thermoelectric cooler. The detector output was sampled by a fast data acquisition (DAQ) system with a sample rate of 1 GHz, and then transferred to a personal computer via a Universal Serial Bus (USB) interface for further analysis.

The measurement is carried out using an intra-pulse scan method of the QCL. This technique relies on the frequency down-chirp that is induced when a current pulse is applied to a QCL as a result of local heating during the pulse. This down-chirp may cover a wide wavenumber range and can be used for sweeping across an absorption line to provide real-time display of the spectral feature[5]. Note that the extent of the frequency window depends on the duration of the applied current pulse. The fact that there is a linear correlation between the temporal and spectral profiles means that the temporal profile of a generated pulse can be recorded and the result is used to infer the spectral nature of the pulse[6]. In our previous studies[7,8], the best operation parameters for the laser were determined. Thus, by applying a top-hat pulse of 500 ns at repetition rate of 10 kHz with 13 V to the laser, the QCL emits light scanning across the full spectral transition. For all the measurements, the operation temperature of QCL was set at ∼15 °C. The outlet of the gas cell was connected to a vacuum pump, pumping the ambient air into the cell at a flow rate of 2
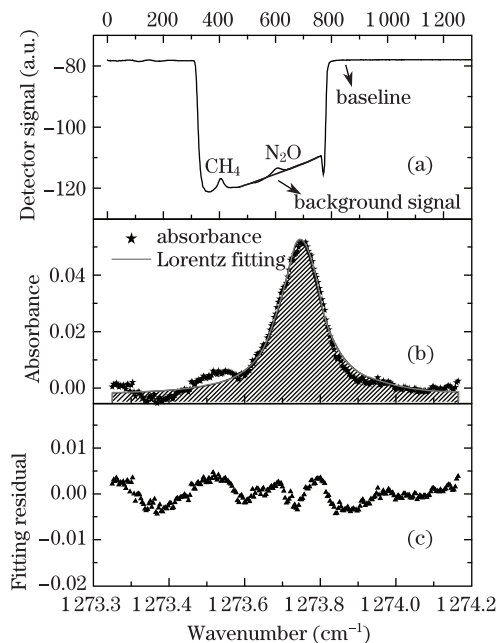

Fig. 2. (a) Raw detector signal during a single intra-pulse laser scan with polynomial fitting; (b) spectral absorbance and peak fitting; (c) fitting residual.
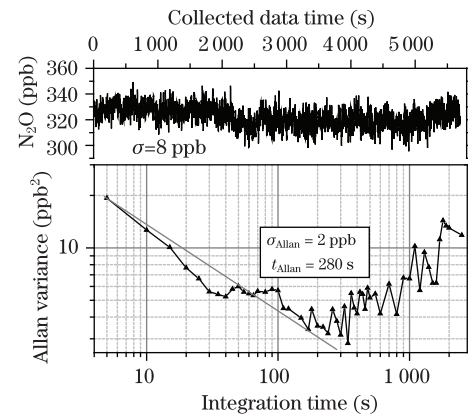

Fig. 3. Allan variance plot for N_2O during a 1.5-h period with 1-Hz sample rate of ambient air.

L/s, and then realizing the gas exchange. Two needle valves were used to regulate the sample flow through the inlet and outlet, such that the corresponding total pressure in the measurement cell could be maintained at 0.5 atm.

The initial processing of the raw data from the detector usually involves obtaining the background signal to retrieve the absorbance, as shown in Fig. 2(a). For direct absorption spectroscopy, the background signal is usually obtained by fitting the regions without absorption to a low-order polynomial. The fitting is normally done by first adjusting the baseline, which is introduced by detector response, to zero level, and then removing the data surrounding the absorption features and performing a linear least-squares fit to a polynomial. The absorption features are removed, so their effect is not incorporated into the baseline fit. The choice of the polynomial order is dependent on the behavior of the laser. Typical orders are 3th and 5th[9]. Next, the spectral absorbance, calculated as the natural logarithm of the ratio of the background signal versus the received signal, is derived from the experimental data. A peak fitting is given to the absorbance by Levenberg–Marquardt nonlinear least-squares method. This procedure is used to remove any remaining slope in the baseline and to fit a Lorentzian function to the peak, as shown in Fig. 2(b). Although the Voigt function is a more accurate description of the line shape, at the gas pressure used for the experiments, the dominant source of line broadening is due to collisions of the trace gas molecules, leading to a predominantly Lorentzian shape. The results demonstrate a good fit to the Lorentzian shape, as shown by the residual in Fig. 2(c). In the peakfitting program, according to the position of peak absorption and the width of the spectral line in time domain, along with the same spectral line information from HITRAN04, the linear relationship between time domain and frequency domain can be estimated. The area under the nonlinear fitting can then be integrated to calculate the concentration. We use C program and standard LabVIEW tools to calculate spectra, analyze these spectra to derive molecular concentrations, and archive the data.

Prior to performing the concentration retrieval, it is often desirable to average the spectra over many scans to improve signal-to-noise ratio. The major factor influencing high-sensitivity measurements is system stability.
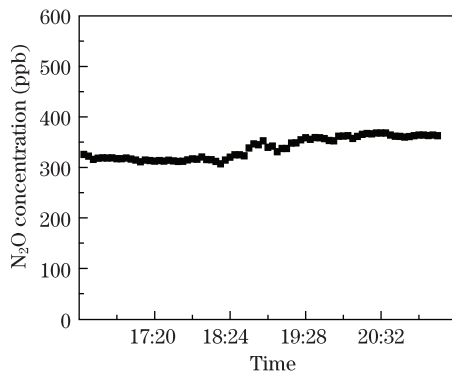
Fig. 4. Continuous measurement of N_2O sampled from ambient air during a 5-h period at optimum integration time.

The signal from a perfectly stable system could be averaged infinitely from a theoretical point of view. Unfortunuately, real systems are stable only for a limited time[10]. Therefore, Allan variance is used to seek the optimum averaging time for our system. For instrument characterization, the first step is to calculate the expected value for the Allan variance from a set of m′ independent measurements and thus obtain a precise estimate for the detection limit. If s denotes the sub-ensemble number, supposing the system is ergodic and practical measurements are sequential[11], then the time average Allan variance $\left\langle \sigma_A^2 \right\rangle_t$ is given by

$$\left\langle \sigma_A^2(k) \right\rangle_t = \frac{1}{2m} \sum_{s=1}^{m} [A_{s+1}(k) - A_s(k)]^2, \qquad (3)$$

$$A_s(k) = \frac{1}{k} \sum_{l=1}^{k} X_{(s-1)k+l}, s = 1, \cdots, m, m = m' - 1. \quad (4)$$

As all averages and variances are a function of the subgroup "binsize" k, the Allan variance $\left\langle \sigma_A^2(k) \right\rangle_t$ can be calculated using the formulas derived above and plotted against the averaging factor k on a log-log plot which gives the "Allan-plot"[12]. The data are assumed to be collected over a constant time interval Δt, and that the time $t = k\Delta t$ is equivalent to the averaging or integration time[10].

The Allan plot is generated by measuring the N_2O concentration during stable conditions while varying the integration times. The top trace of Fig. 3 shows the data collected over a 1.5 h period of relatively constant N_2O concentration. The figure shows a standard deviation of 8 ppb with 1-Hz sample rate. As each data point represents a value for 1 s of integration time, an Allan variance plot[10,13] was obtained by dividing all data points into different subsets. A minimum at 280 s integration time corresponding to σ_{Allan} of 2 ppb is shown, implying a detection limit of 2 ppb for the system. At a longer integration time, there was an increase in the Allan variance due to instrumental drift.

The spectrometer was then operated continuously in

our laboratory at the optimum averaging time obtained above. A representative 5-h segment is shown in Fig. 4. The measurement started from 17:00 to 22:00. Although N_2O is very constant in the free troposphere, it has a little variation within a day. The increase in concentration may be due to the accumulation of automobile and vegetation emission and weak turbulence at night. Furthermore, the system drift after a long operation time may also lead to the concentration increase.

In conclusion, the QCL-based spectrometer we developed realizes the sensitive measurement of trace gases in air. This system utilizes intra-pulse scan absorption spectroscopy, satisfying the requirements for high sensitivity without calibration gases. By analyzing the Allan variance, a detection limit of 2 ppb is obtained. This QCL-based spectrometer fulfills the measurement of N_2O in air and is suitable for the field measurement of gases of environmental concern.

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