

Monitoring of ethylene by a pulsed quantum cascade laser

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We report on the development and performance of a gas sensor based on a quantum cascade laser operating at a wavelength of $\sim 10 \mu\text{m}$ to measure ethylene (C_2H_4) concentrations by use of a rotational component of the fundamental ν_7 band. The laser is thermoelectrically cooled and operates in a pulsed mode. The influence of pulse-to-pulse fluctuations is minimized by use of a reference beam and a single detector with time discriminating electronics. Gas absorption is recorded in a 100-m optical path-length astigmatic Herriott cell. With a 10-kHz pulse repetition rate and an 80-s total acquisition time, a noise equivalent sensitivity of 30 parts per billion has been demonstrated. The sensor has been applied to monitor C_2H_4 in vehicle exhaust as well as in air collected in a high-traffic urban tunnel. © 2004 Optical Society of America

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1. Introduction

The detection of ethylene (C_2H_4) at trace levels is important in a number of gas sensing applications: atmospheric chemistry, medical diagnostics, and plant biology and agronomy. In atmospheric chemistry, anthropogenic emissions of C_2H_4 from sources such as motor vehicle exhaust and fugitive emissions from industrial sources promote the formation of tropospheric ozone in urban areas, in the presence of OH radicals and nitrogen oxides.¹ The mean concentration of C_2H_4 in the atmosphere is 20 parts per billion (ppb) but with an important spatial and temporal variability that requires concentration measurements with 1-ppb precision. Trace gas analysis of exhaled breath for medical applications is a promising tool for noninvasive diagnostics.² Specifically, C_2H_4 is a potential biomarker for destruction of cell membrane lipids by peroxide decomposition (oxidative stress), which produces trace amounts of C_2H_4 in concentration levels that range from 1 to 10 ppb (Ref.

3) among several other products including ethane and pentane.⁴ Ethylene is also an important hormone in plant biology; it diffuses from plant tissues to regulate growth and development. Thus analysis of the C_2H_4 level is key in the commercially important fruit ripening process.^{5,6} For fruit ripening control, ethylene concentrations range from 1 to 10 ppm, and for biological applications, such as individual plant and fruit studies, the required precision of concentration levels are in the range of 10 parts per trillion (ppt) to 1 ppb.

Laser spectroscopy is an effective optical technique for sensitive, selective, and fast-response trace gas monitoring. Laser based C_2H_4 concentration measurements were reported previously for the three applications mentioned above. Photoacoustic spectroscopy (PAS) was used to monitor C_2H_4 concentrations in an urban atmosphere.⁷ C_2H_4 produced by lipid peroxidation in human leukemic cells has been measured with a CO_2 -laser-based photoacoustic spectrometer.⁸ Binjen *et al.* used an intracavity CO_2 laser-based photoacoustic technique to monitor the instantaneous release of C_2H_4 from a tomato with a minimum detectable concentration of 6 ppt.⁹ Similarly, Martis *et al.* performed C_2H_4 measurements with a CO overtone laser and obtained a 2-ppb minimum detection level in physiological studies of plant damage and stress.¹⁰ In PAS, the detection sensitivity varies linearly with laser power, and, as a consequence, high optical power (hundreds of milliwatts) is required for low-ppb sensitivities to be obtained.

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This explains why gas lasers are an important spectroscopic source for PAS. In addition to PAS, Mürtz *et al.* used a mid-infrared gas laser source to perform cw cavity ring-down spectroscopy and reported a 1-ppb minimum detection sensitivity for C_2H_4 concentration measurements with a 100-s integration time.¹¹

The use of a gas laser as a spectroscopic source makes trace gas analyzers bulky and not practical for field deployment in some applications. Quantum cascade lasers (QCLs) are proving to be an effective tunable spectroscopic source in the mid infrared.¹² Pulsed QCLs provide quasi-room-temperature operation, high selectivity and sensitivity, real-time measurement capabilities, robustness, and compactness. Because pulsed QCLs do not require cryogenic cooling, the development of rather simple sensors that are suitable for field measurements can be achieved. Trace gas detection of C_2H_4 by use of quasi-room-temperature pulsed QC lasers with both direct absorption spectroscopy and PAS with a 60-ppm detection limit has been reported.¹³ Ethylene also was recently measured in cigarette smoke by QCL spectroscopy with a sensitivity of 150 ppb $Hz^{-1/2}$.¹⁴

In this paper we report on the development and performance of a 10- μm QCL-based direct absorption spectrometer and its application to C_2H_4 detection and monitoring in vehicular exhaust as well as in ambient air sampled from a high-traffic urban underground tunnel. By using an astigmatic Herriott multipass cell in conjunction with a pulse-to-pulse normalization technique we obtained a 30-ppb noise equivalent sensitivity with an 80-s total integration time and a 10-kHz pulse repetition rate, which corresponds to a normalized sensitivity of 270 ppb $Hz^{-1/2}$.

2. Spectral Line Selection for Optimum C_2H_4 Monitoring

Ethylene has two spectral regions with significant absorption in the mid infrared, according to the HITRAN 2000 database.¹⁵ The first region includes the range ~ 2100 – 3200 cm^{-1} (3.1–4.7 μm), which contains the ν_9 and ν_{11} fundamental bands, and the second region lies in the ~ 800 – 1100 cm^{-1} (9.1–12.5 μm) range and contains the ν_4 , ν_7 , and ν_{10} bands. The ν_7 band is the most intense and has been studied in detail.¹⁶

The ideal design for C_2H_4 monitoring for optimum sensitivity would target the strongest line ($8.41 \times 10^{-20}\text{ cm}^{-1}/\text{molecule cm}^{-2}$) at 949.65298 cm^{-1} , as shown in Fig. 1. Unfortunately, the QC laser available for this study had no access to this optimum absorption feature. The strongest C_2H_4 absorption line accessible with the available QC laser is at 993.45 cm^{-1} , as marked by an arrow in Fig. 1. The line strength is $2.2 \times 10^{-20}\text{ cm}^{-1}/\text{molecule cm}^{-2}$.

3. Experimental Details

The spectroscopic source is a thermoelectrically cooled pulsed distributed-feedback QCL. The QCL is operated at -21.5°C in vacuum tight housing to

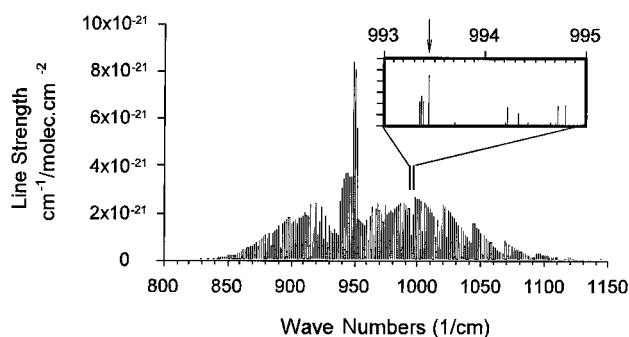


Fig. 1. Stick diagram of the ν_7 absorption band of ethylene. Inset, tuning range of the QCL used in this study.

prevent condensation of atmospheric water vapor on the laser chip and to minimize heat transfer. The QCL assembly was previously described in detail.¹⁷ The laser is excited by 15-ns duration pulses, with an amplitude of 3 A, close to the laser threshold (2.7 A for the QCL used in the study reported in this paper), which ensures a laser linewidth of $\sim 250\text{ MHz}$.¹⁸ The emitted peak power was estimated to be 1 mW, based on the HgCdTe detector sensitivity. The pulse repetition rate cannot be increased beyond 10 kHz because of the technical limitations of the gated integrators of the detection system (Stanford Research System, Model SR250). These characteristics are currently the main sensitivity limitation of the sensor. Hence development of an advanced QCL-based sensor platform that can operate with a 1-MHz repetition rate is in progress. In this case, the detection level is expected to be lowered by a factor of 10, assuming a white-noise limit. A linear subthreshold current ramp is added to the excitation pulse train for frequency tuning over the absorption line of interest. The rising part of a 6-Hz triangular waveform provided by a function generator is used as a ramp. The ramp amplitude is set to 42.5 mA. A typical frequency scan is $\sim 0.1\text{ cm}^{-1}$ as a result of the applied current ramp.

For frequency calibration of a laser scan, two 30' wedged ZnSe windows separated by 19.6 cm were temporarily inserted into the laser beam's path such that an etalon was created. The resultant fringe contrast was low, $\sim 2.5\%$, but sufficient for a frequency calibration to be performed. The typical signals that can be obtained are depicted in Fig. 2.

Figure 3 depicts the C_2H_4 analyzer system. The collimated beam at the output of the laser housing is split into a reference beam, which is directly focused on the mercury cadmium telluride (MCT) detector, and a signal beam that is coupled to a 100-m path-length Herriott multipass cell. The reference beam is used to normalize the signal to the energy of each laser pulse.

Two 45° -tilted ZnSe wedge windows are used as beam splitters to direct the reference beam. Only 8% of the available laser power reaches the detector in the reference optical arm. The signal beam passes through the first ZnSe beam splitter, and, by

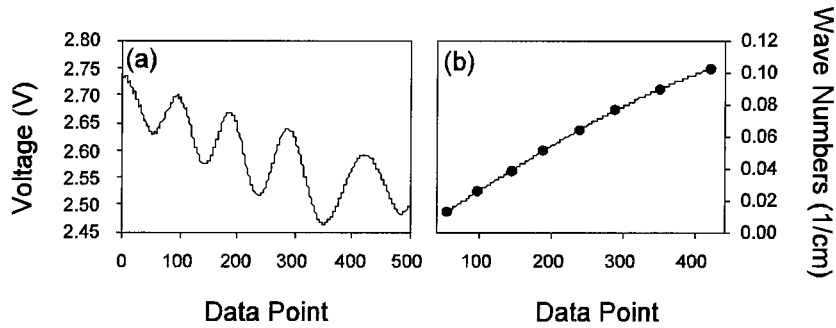


Fig. 2. Frequency calibration curves. (a) Etalon fringe signal obtained from two wedged ZnSe windows separated by 19.6 cm and (b) the resultant calibration when the solid curve is a third-order polynomial fit.

way of steering optics, is coupled to the multipass cell. A long-focal-length (500-mm) BaF₂ lens improves the coupling through the 3-mm-diameter entrance mirror hole. After 182 passes inside the multipass cell the effective optical path length reaches 100 m.¹⁹ The multipass absorption cell transmission is ~23%. Subsequently, the beam travels through a second ZnSe beam splitter. The overall transmission of the signal beam is ~4.6%. After the second beam splitter the two beams are recombined and focused onto the same MCT photovoltaic detector by a 1-in. (~25-mm-) diameter off-axis parabolic mirror with a 3-in. (~76-mm) focal length. The detector (Kolmar Model KMPV10-1-J1) has an active area of 1 mm² and a built-in impedance matched preamplifier with a bandwidth such that the detected pulse widths are ~40 ns. Signal and reference pulses can be discriminated in time because of the long transit time in the multipass cell (~300 ns),²⁰ as can be seen from the oscilloscope trace shown in Fig. 4. These pulses appear also to be useful in optimizing the sensor alignment procedure. Having two well-separated detected pulses confirms the correctness of the multipass cell alignment. The

delay between the two pulses indicates the actual path-length difference of the signal and reference beams.

The synchronization-acquisition system is depicted schematically in Fig. 3. A 10-kHz clock defines the pulse repetition rate and is connected to a laboratory-built pulse generator circuit, which provides a gate signal to the laser diode driver (Directed Energy, Inc., Model DLD-100B).

The output signal from the detector preamplifier is fed into two gated integrators with adjustable delays. These devices integrate the signal over a user-defined window. Typically we set the integration window width to be the full width at half-maximum of the detected pulse, as shown in the lower trace of Fig. 4. The integrated signals are then sampled by a National Instrument PCMCIA acquisition card (Model AI-16XE-50). An additional trigger from the ramp generator enables the acquisition sequence to be synchronized with the sweep. Both data acquisition and processing are managed by means of LabView-based software.

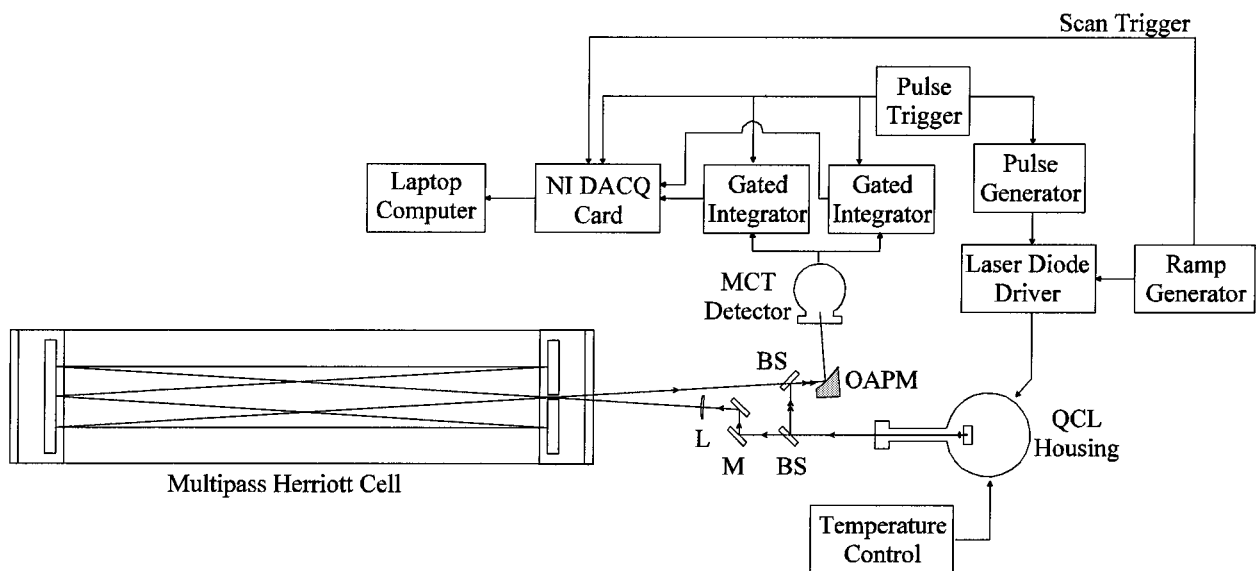


Fig. 3. QCL-based sensor architecture: BS's, beam splitters; M, mirror; L, lens; OAPM, off-axis parabolic mirror; NI DACQ Card, National Instruments data acquisition card.

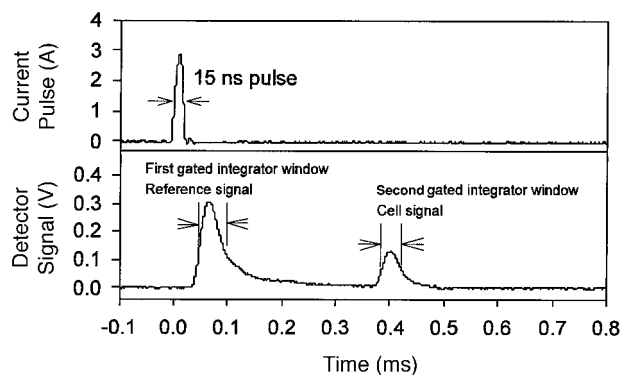


Fig. 4. Top, oscilloscope trace of the QCL drive current pulse. Bottom, the observed time discrimination of the reference and signal beams.

4. Gas Sensor Performance

The performance of the ethylene analyzer system was evaluated with a calibrated commercial gas mixture consisting of 1 ppm ($\pm 2\%$) of ethylene diluted with pure nitrogen (N_2). An initial estimate of the laser linewidth was made by comparison of theoretical and experimentally obtained line profiles of pure C_2H_4 at a gas pressure of 1 Torr. The linewidth was $\sim 0.008\text{ cm}^{-1}$, which we determined by taking the full width at half-maximum of the measured absorption feature. The Doppler width at this wavelength is 0.00193 cm^{-1} , so the observed linewidth of 0.008 cm^{-1} is dominated by the laser linewidth. The total pressure was adjusted such that the nitrogen pressure broadening matches the laser linewidth when the nitrogen broadening coefficient reported in Ref. 21 is used. This condition defines the minimum pressure that is possible without a major loss of the C_2H_4 absorption line intensity. The resultant pressure was 40 Torr. Adjustment of the pressure is a compromise between collisional broadening, which tends to decrease the maximum absorption value, and the increase of the total amount of absorbing molecules in the cell. With the chosen criteria, the observed spectral linewidth was close to two times the theoretical linewidth. At the same time the maximum absorption value was divided by a factor of 2. Pressures that are much higher should not be used, as they increase the collisional broadening and introduce the possibility of interference by overlapping transitions. As shown in Fig. 1, a doublet is close to the transition used in this study.

The calibrated mixture of C_2H_4 and N_2 at a pressure of 53.8 Torr was introduced into the Herriott cell. A set of 500 spectra was recorded and averaged with a total integration time of $\sim 80\text{ s}$. This procedure was repeated with the multipass cell evacuated to produce a baseline. As the detector response is not purely linear with respect to the laser power, the actual baseline is not flat and requires correction. Using the same detector for the two channels has the advantage of minimizing nonlinearity effects. However, as shown in Fig. 5, the effect of nonlinearity still remains because of the difference of optical power

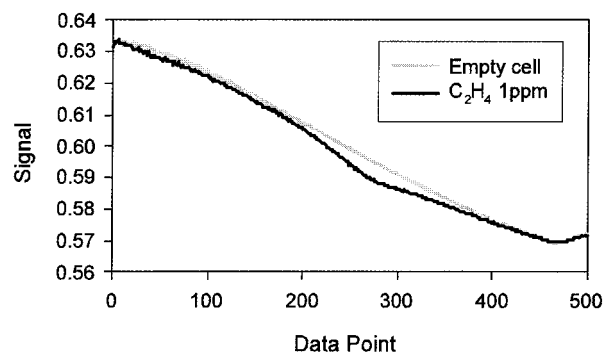


Fig. 5. Normalized signals for 1- and 0-ppm C_2H_4 recorded without baseline correction. The slight slope in the baseline or non-linearity between the normalized reference and sample beams is due to the gated integrators and the detector because the reference and sample signals possess different amplitudes.

between the two beams and the use of two gated integrators that are not identical, necessitating a baseline correction.

The minimum C_2H_4 detection sensitivity of the sensor was investigated next. The baseline was fitted with a fifth-order polynomial function. By subtracting the fit from the actual signal recorded with the evacuated cell, we obtained random signal fluctuations over a frequency scan as shown in Fig. 6. The 50 first and last data points were disregarded because they exhibited transient thermal effects from the beginning and the end of current ramp. Among the 400 remaining data points, only the 200 of these that encompass the entire C_2H_4 absorption window were retained. From this set of points, the standard deviation in terms of absorbance is $\sim 3 \times 10^{-4}$, to yield a noise-equivalent sensitivity of 30 ppb. This value could be improved to $\sim 6\text{ ppb}$ by use of the most intense absorption line of C_2H_4 in the ν_7 band at 949.65298 cm^{-1} .

To investigate the actual detection limit further, we recorded a C_2H_4 spectrum of a 100-ppb mixture at a cell pressure of 50 Torr and under the same conditions as stated above, i.e., 500 spectra were averaged during an 80-s total integration time. The C_2H_4 absorption line was obtained and is shown in Fig. 7. A second-order polynomial baseline was sufficient in

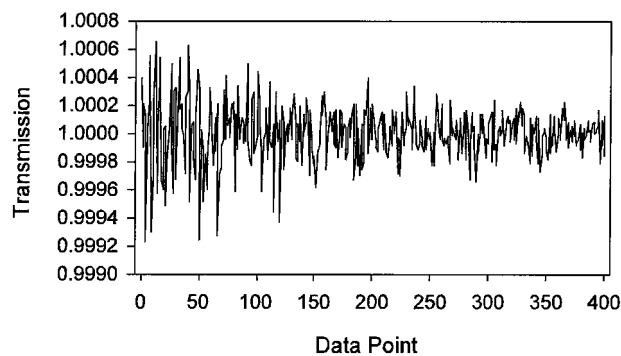


Fig. 6. Signal fluctuations in a frequency scan. An empty gas cell background spectrum was recorded and baseline corrected.

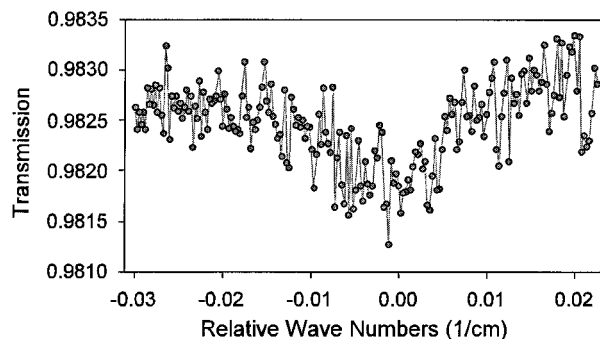


Fig. 7. Spectrum of 100 ppb of ethylene in a nitrogen mixture at a 50-Torr total pressure. Five hundred spectra were averaged during a total acquisition time of 80s.

that case because the frequency scan remained narrow. The absorption line is clearly visible. This result agrees well with the above estimated noise-equivalent detection limit of 30 ppb. The spectrum in Fig. 7 exhibits a baseline offset that is believed to be due to the gated integrators. Two different integrators are used for the reference and the sample channels. A slight difference in the integrators' sensitivity produces an offset between the reference and the sample spectra.

5. Applications

As was mentioned in Section 1, a significant contribution to atmospheric C_2H_4 originates from automotive gas exhaust, especially in urban environments with heavy traffic. C_2H_4 is by far one of the most reactive volatile organic compounds emitted by motor vehicles. The sensor was applied to monitor C_2H_4 emission from the exhaust pipe of a 1998 6-cylinder Ford Explorer SUV. During engine idling, we filled a Teflon bag with the exhaust from that vehicle, using a manual sampling pump approximately 30 cm downwind from the vehicle's, tail pipe. The multipass cell was filled to 53.8 Torr of the collected exhaust sample, and the absorption spectrum was recorded.

To determine the C_2H_4 concentration we compared the measured absorption spectrum and a calibrated absorption spectrum of C_2H_4 at a known concentration of 1 ppm. This measurement technique applied to pulsed QCLs is described in Ref. 17. With this technique we do not require an isolated line for performing concentration measurements and it is not necessary to know the characteristics of the QCL emission spectrum. In addition, frequency calibration is not required. Absorption of the calibrated $C_2H_4:N_2$ mixture was recorded under the same experimental conditions as absorption of the gas sample to be analyzed. Then the calibration absorbance was plotted as a function of the sample absorbance (i.e., the sample signal was plotted versus the recorded calibration reference signal), as shown in Fig. 8.

To retrieve the concentration, one has to determine the slope of the best fit linear function. At this low

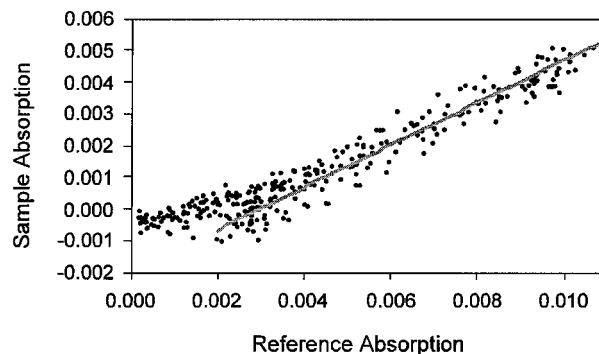


Fig. 8. Sample absorption versus the calibration mixture absorption. The slope of the best fitting linear function yields the ethylene sample concentration, i.e., 670 ppb.

C_2H_4 concentration, self-broadening remains insignificant and the slope gives directly the sample C_2H_4 concentration expressed in terms of calibration mixture units. In our case, as the calibration mixture was 1 ppm of ethylene and as the slope was 0.67, this yielded a C_2H_4 concentration of 670 ppb present in the measured car exhaust. The negative and close to zero absorbances that are visible in Fig. 8 are not significant and reflect baseline fluctuations.

In another evaluation test, the concentration of C_2H_4 inside a local roadway tunnel was measured. The Washburn Tunnel is a single bore-forced ventilation motor vehicle tunnel, with a length of ~ 900 m, which passes beneath the Houston ship channel in a highly industrialized area. Details of the tunnel and its use in measurement of the emission from motor vehicles can be found in Ref. 22. Rather than giving a detailed study of vehicle emissions as presented in Ref. 22, our aim here, was to demonstrate the feasibility of QCL-based C_2H_4 sensing. According to previous measurements,²² the C_2H_4 concentration in the tunnel can vary from 0 to 200 ppb, depending on tunnel ventilation and vehicle traffic volumes.

The Washburn Tunnel's air was sampled on two occasions by use of Teflon bags, which were then brought back to the laboratory for analysis. The first sample collection occurred on Friday, 26 June 2003, at ~ 1400 hours Central Standard Time (CST), and the second one on Tuesday, 1 July, at 1100 hours CST. Samples taken during the first pass did not exhibit any detectable ethylene concentration. The air sample collected in the second test traverse was determined to have an ethylene concentration of 51 ± 17 ppb.

6. Conclusion

A pulsed quantum cascade laser-based gas sensor was developed and has proved to be effective in monitoring C_2H_4 . The noise-equivalent detection limit for the reported gas analyzer is 30 ppb for a 10-kHz pulse repetition rate and an 80-s integration time. This limit can be improved to ~ 6 ppb by use of a more intense C_2H_4 absorption line at 949.65 cm^{-1} and to 2 ppb by use of an optimum detection system based on

a pulse track-and-hold approach. Such a system will allow us to increase the pulse repetition rate to 100 kHz–1 MHz and incorporate fast temporal gating of the single detector output for the reference and sample signals. To date, the C₂H₄ sensor has been evaluated in direct vehicle exhaust monitoring and with ambient air collected from a local roadway tunnel.

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