Cavity-enhanced quantum-cascade laser-based instrument for carbon monoxide measurements

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An autonomous instrument based on off-axis integrated cavity output spectroscopy has been developed and successfully deployed for measurements of carbon monoxide in the troposphere and tropopause onboard a NASA DC-8 aircraft. The instrument (Carbon Monoxide Gas Analyzer) consists of a measurement cell comprised of two high-reflectivity mirrors, a continuous-wave quantum-cascade laser, gas sampling system, control and data-acquisition electronics, and data-analysis software. CO measurements were determined from high-resolution CO absorption line shapes obtained by tuning the laser wavelength over the R(7) transition of the fundamental vibration band near 2172.8 cm^{-1}. The instrument reports CO mixing ratio (mole fraction) at a 1-Hz rate based on measured absorption, gas temperature, and pressure using Beer's Law. During several flights in May–June 2004 and January 2005 that reached altitudes of 41,000 ft (12.5 km), the instrument recorded CO values with a precision of 0.2 ppbv (1-s averaging time) and an accuracy limited by the reference CO gas cylinder (uncertainty $<$1.0%). Despite moderate turbulence and measurements of particulate-laden airflows, the instrument operated consistently and did not require any maintenance, mirror cleaning, or optical realignment during the flights.

OCIS codes: 120.4640, 120.6200.

1. Introduction

For almost 30 years, tunable diode laser absorption spectroscopy techniques have been developed by dozens of groups worldwide for applications that require fast, nonintrusive measurements of trace gases, including atmospheric and environmental monitoring,[1–15] combustion, propulsion, and other industrial processes.[16–28] Since Beer's Law is used to convert the measured absorption spectra to gas mixing ratio, increasing measurement sensitivity generally involves using longer optical paths, increasing the ability to detect small changes in transmitted laser intensity or cavity ringdown time, and probing absorption features with greater line strengths (typically in the mid-infrared or ultraviolet spectral regions). As a result, various strategies have been developed to achieve high sensitivity, including direct absorption spectroscopy using long-path multipass cells,[29] wavelength (and frequency) modulation spectroscopy,[30] cavity ringdown spectroscopy,[31] cavity-enhanced absorption spectroscopy,[32] integrated cavity output spectroscopy (ICOS),[33] and Off-Axis ICOS.[34,35]

In this work, we describe the development and operation of an autonomous instrument (Carbon Monoxide Gas Analyzer) based on Off-Axis ICOS that employs a continuous-wave quantum-cascade laser for measurements of CO onboard a DC-8 aircraft with sub-ppbv sensitivity and precision. Similar to its predecessor, the differential absorption CO monitor (DACOM), this instrument should prove useful in quantifying and tracking variations in CO, and characterizing the distribution of combustion products in the troposphere and tropopause. In the future, the instrument may be applied for sensitive measurements of other gases that absorb at other wavelengths by selecting an appropriate laser and cavity mirrors.

2. Technical Approach

The present measurements are based on Off-Axis ICOS whose methodology and governing equations have been presented previously.[34,35] Briefly, the laser intensity (I) transmitted through an empty cavity may be expressed as

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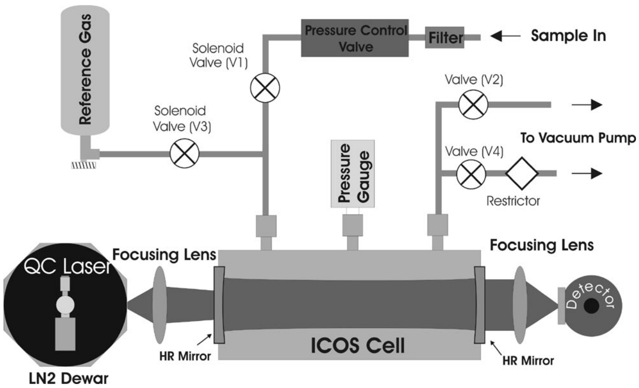

Fig. 1. Schematic drawing of the Carbon Monoxide Gas Analyzer optical layout.

$$I = \frac{I_L C_p T}{2(1-R)}(1-\exp(-t/\tau)), \qquad \tau = \frac{L/c}{1-R}, \quad (1)$$

where I_L is the incident (or reference) laser intensity, C_p is a cavity coupling parameter, R and T are the mirror intensity reflection and transmission coefficients, τ is the characteristic cavity (ringdown) decay time, L is the distance between the mirrors, and c is the speed of light. The coupling parameter C_p depends on geometric factors and has a value between 0 and 1.

After the laser beam enters the cavity, the intensity inside the cavity increases with the characteristic time constant τ. After sufficient laser power has accumulated in the cavity, the laser can be interrupted to observe a ringdown decay. Since the laser is continuously coupled into the cavity, the characteristic decay time τ may be periodically recorded with the laser tuned to a nonabsorbing wavelength i.e., 'off line', or in an empty cavity to monitor the effective optical path length in the cavity $L_{\mathrm{eff}} = L/(1-R)$.

With an absorbing gas between the mirrors, R is replaced by R', given by

$$R' = R\exp[-\alpha(\nu)], \quad (2)$$

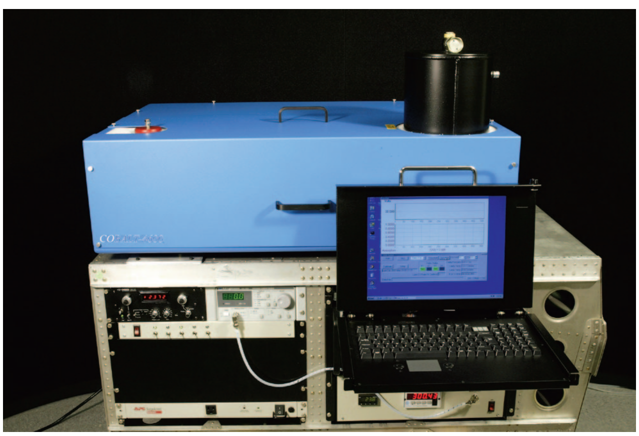

Fig. 2. (Color online) Photograph of the Carbon Monoxide Gas Analyzer designed to mount directly onto the NASA DC-8 flying laboratory.

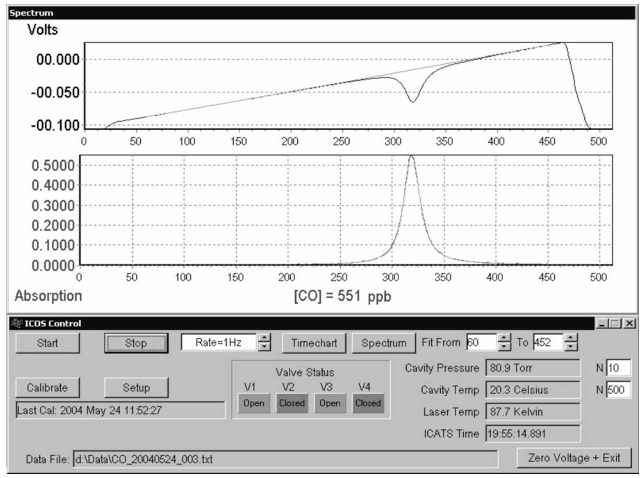

Fig. 3. Software spectrum display mode. The measured cavity-enhanced transmission intensity is shown in the top graph and is converted into an absorption spectrum in the bottom graph. The line shape in the bottom window is least-squares fit to a Voigt profile and combined with measured values of gas temperature and pressure in the cell to determine the CO mixing ratio.

where $\alpha(\nu)$ represents the optical depth (at frequency ν) of the gas over the cavity length. Comparing Eq. (2) with the Beer–Lambert absorption formula for a single pass $\{I/I_o = \exp[-\alpha(\nu)]\}$ through the cavity reveals that $I/I_o = R'/R$. Thus Eqs. (1) and (2) indicate that essential absorption information is contained in the steady-state cavity output intensity. From these equations, the change in steady-state cavity output ($\Delta I = I_L - I$) due to the presence of an absorbing species may be expressed

$$\frac{\Delta I}{I_o} = \frac{GA}{1+GA}, \quad (3)$$

where A is the single-pass absorption $\{A = 1 - \exp[-\alpha(\nu)]\}$ and $G = R/(1-R)$ is the cavity enhancement factor. The mole fraction of the probed species in natural air (i.e., uncorrected for dry air) may be determined from the measured spectra integrated over the entire absorption feature together with the measured temperature and total pressure in the cell, effective optical path length, and line strength of the target species.

3. Experimental

The Carbon Monoxide Gas Analyzer consists of a continuous-wave quantum-cascade distributed feedback (DFB) laser (QCL from Alpes Laser) mounted in a liquid-nitrogen dewar that is coupled into a high-finesse optical cavity in an off-axis trajectory using a 2-in diameter $F/1$ meniscus lens. Light transmitted through the cavity was focused onto a liquid-nitrogen-cooled InSb detector whose output signal was digitized, stored, and analyzed by an onboard computer. A schematic drawing of the instrument layout is shown in Fig. 1. A photograph of the instrument is shown in Fig. 2.

The quantum-cascade laser was mounted onto the cold head in the dewar using a custom mounting plate. The

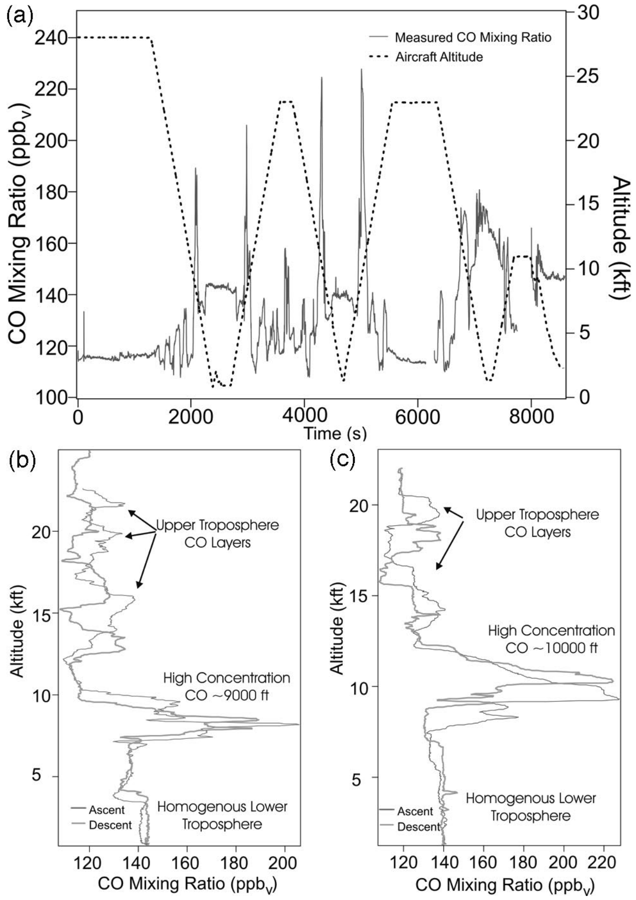

Fig. 4. (a) Measured CO mixing ratio (1-Hz sampling rate) as a function of time during second test flight. Note the high concentration of CO during Legs 1 and 2. (b) and (c) CO profiles for two legs of the test flight plan shown in Fig. 6. Note the pronounced higher concentration CO layer measured near 9000 ft in Leg 1 and 10,000 ft in Leg 2.

laser was held onto the plate by a mounting clamp that assures good thermal contact between the two. For the present application, the laser temperature was held to 94.0 K by adjusting the thickness of the mounting plate. A positive bias voltage was placed across the quantum-cascade laser by using a gold-coated spring clamp. The dewar was selected to have a hold time of greater than 24 h (no load), and an operating time of >8 h (with 10-W load). The bottom plate and feedthrough ports were customized to facilitate laser mounting, operation, and thermal measurement. The laser was driven by a low-noise laser current controller capable of 1-MHz bandwidth analog modulation with the compliance voltage (9 V) required by the laser. The single-mode laser wavelength was injection-current tuned at an 800-Hz rate about 0.5 cm^{-1} near 2172.8 cm^{-1} to record high-resolution measurements of the CO R(7) line of the fundamental vibration band.

The 40-cm-long (620 cm^3 volume) optical cavity was comprised of two highly reflective mirrors (1-m radius of curvature) with a total optical loss of 1000 ppm to yield an effective path length of 400 m.

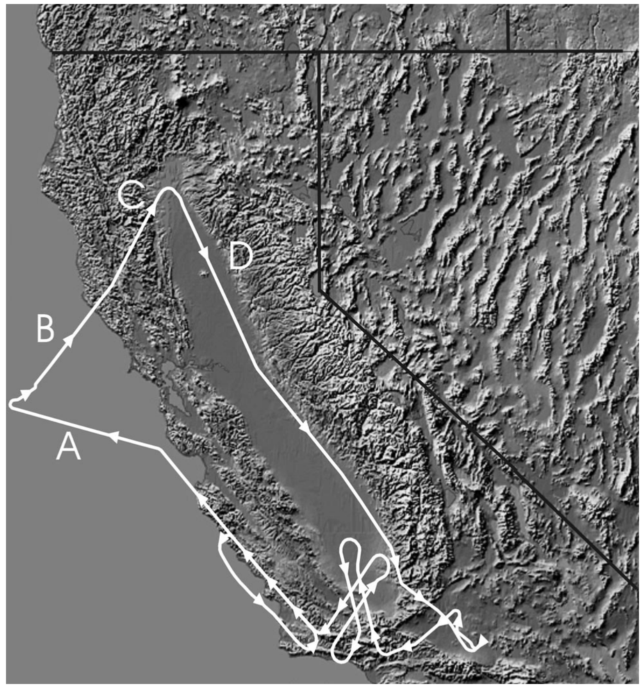

Fig. 5. Flight plan for the 12 May 2004 test flight (data shown in Fig. 4). Labels indicate the approximate plan position where an increased CO layer was measured.

While higher reflectivity mirrors are readily available (and would yield a longer effective path length), the given path length was sufficient for accurate measurements of CO levels typically present in the troposphere and tropopause (30–600 ppbv). The system may be easily modified to allow CO measurements in the stratosphere by replacing the present cavity mirrors with higher-reflectivity mirrors to increase the effective path length.

Sampled gas from the inlet was first routed through a particulate filter to minimize the particles that might otherwise accumulate on the mirrors. The gas was then directed into the ICOS cell through a pressure-control solenoid valve that works in conjunction with a capacitance manometer pressure gauge, mounted directly to the cell, and an external controller to maintain the desired pressure (80 torr) in the cell. The gas was then exhausted from the cell at a 2.8L/s flow rate via a dry vacuum pump. The ICOS cell can also be isolated from the inlet (using valves V1 and V3) and exhaust (using valves V2 and V4) system for static gas measurements via large orifice (1/4-in diameter) solenoid control valves. The gas temperature in the cell was monitored with a calibrated thermistor. In order to check mirror health during the flights, reference gas with known CO mixing ratio [(CO) = 550 ppbv in air] was directed into the cell at half-hour intervals. The entire instrument weighs 150 kg and consumes 180 W of electrical power, excluding the vacuum pump (0.8 kW).

Figure 3 shows a screenshot of the instrument user interface of the data analysis and control software. This software controls gas flow, displays and records transmission traces, analyzes the data, and stores the results to file in real time. For example, the measured raw data trace, representing cavity-enhanced transmission intensity, is shown in the top graph and is converted into an absorption spectrum in the bottom graph. The line shape in the bottom window was least-squares fit to a Voigt profile and combined with measured values (shown in the screenshot) of gas temperature and pressure in the cell to determine the CO mixing ratio.

4. Measurements: Data Analysis

The measured transmitted laser intensity, corrected for detector offset, was least-squares fit to multiple Voigt profiles that model the probed CO and smaller neighboring N_2O absorption features in the selected wavelength interval. The cavity enhancement factor (G) can be determined by measuring either the cavity ringdown or by the absorption of a known reference gas standard. The former method was not implemented in this instrument because the ringdown time was too short ($\sim 1\ \mu s$) to be accurately measured with the present detector amplifier bandwidth (30 kHz). Therefore the cavity-enhancement factor was determined by periodically measuring CO in a reference gas cylinder. Despite flying through clouds and smog, the instrument's cavity mirrors remained clean throughout the flight, and neither recalibration nor cleaning of the mirrors was necessary. Moreover, the particle filter did not clog or require cleaning.

5. Results

A. Flight Tests

The Carbon Monoxide Gas Analyzer was successfully tested in a series of research flights aboard NASA's DC-8 Airborne Research Laboratory in May and June 2004. The flights consisted of a combination of racetrack patterns, ascent and descent patterns, as well as level leg flight paths. In addition, the instrument was deployed on NASA's Polar Aura Validation Experiment (PAVE) in January 2005. All CO measurements were recorded with a 1-Hz sampling rate.

B. Troposphere Measurements

CO mixing ratios as a function of time from the test flight on 12 May 2004 are shown in Fig. 4(a). This flight pattern, shown in Fig. 5 to correlate with CO measurements, reached a maximum altitude of 27, 000 ft and included several racetrack patterns as well as ascents and descents. During this flight, the maximum CO mixing ratio was 227.8 ppbv; the minimum detected was 107.7 ppbv. CO profiles measured during the first two ascent and descent patterns (Leg 1 and Leg 2, respectively) are shown in Figs. 4(b) and 4(c). Leg 1 was performed over the Pacific Ocean and indicated a very distinct and narrow CO layer on descent (Fig. 5 waypoint A) near 8000 feet. The same layer was measured again on ascent over a different geographic location (Fig. 5 waypoint B) at almost the same altitude. This layer was detected again during Leg 2, over the northern part of the California Central Valley. During this leg, however, the layer was detected near 10,000 ft on descent (Fig. 5 waypoint C) and slightly higher on ascent (Fig. 5 waypoint D). It is interesting to note that the CO layers measured in the upper troposphere seem to descend, while the lower altitude layers seem to be increas in altitude. Lower troposphere CO also seems relatively homogeneous on these flights.

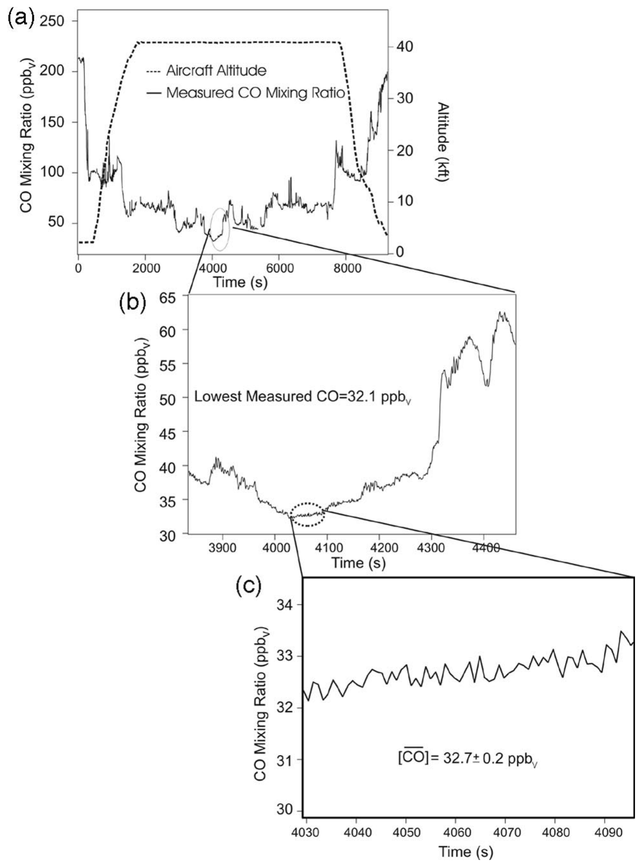

Fig. 6. (a) Measured CO values (1-Hz sampling rate) as a function of time for the 17 May test flight. (b) Expanded view of data in (a) demonstrating the instrument ability to distinguish small changes in CO. (c) Measurements recorded with a 1-Hz sampling rate over a 60-s interval in (b) demonstrate the high precision of the instrument.

C. Tropopause Measurements

CO mixing ratios measured during the 17 May 2004 test flight are shown in Fig. 6. This flight path remained mostly level at 41,000 ft. No distinct layers were detected, but extremely low mixing ratios consistent with stratospheric levels were measured. Figure 6(b) shows a 10-min section of data from this flight. The minimum measured CO mixing ratio was 32.1 ppbv. Figure 6(c) shows a 60-s segment of data (recorded at a 1-Hz data rate) where the CO mixing ratio was relatively constant. The average and standard deviation of the CO mixing ratio during this interval was 32.7 $\pm$ 0.2 ppbv.

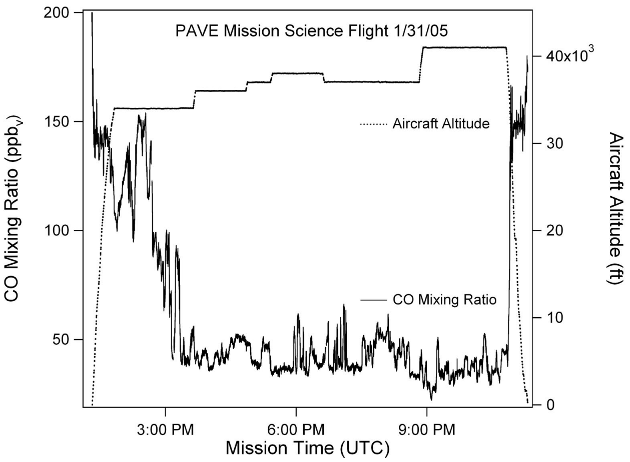

Fig. 7. Measured CO mixing ratios (1-Hz sampling rate) at corresponding aircraft altitude during PAVE Science Flight (31 January 2005).

D. Polar Aura Validation Experiment Science Flights

The Carbon Monoxide Gas Analyzer also participated in NASA Polar Aura Validation Experiment (PAVE) aboard the NASA DC-8 Airborne Research Laboratory in January 2005. This science mission was performed to validate data from NASA's Aura satellite, launched in July 2004. In addition, these missions were designed to help better understand the transport and transformation of gases and aerosols in the lower atmosphere (troposphere) and their exchange with those in the lower stratosphere.

Figure 7 shows the CO mixing ratio as a function of time during a 10-h science flight on 31 January 2005. During this flight, CO mixing ratios as low as 24 ppbv were recorded. To demonstrate instrument repeatability, accuracy, and mirror integrity, repeated measurements of CO from the known reference gas standard ([CO] = 550 ppbv) were recorded during the flight (at 30-min intervals) and are displayed in Fig. 8. The measured CO mixing ratios varied by less than 0.5% over the entire 10-h-long flight and indicated that regular system recalibration was not required.

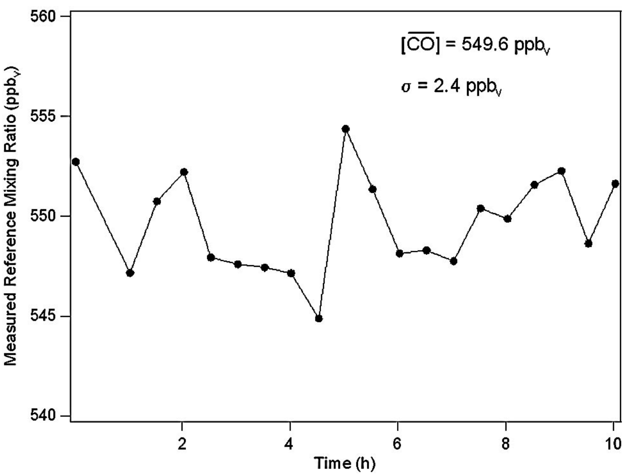

Fig. 8. Measured CO mixing ratios (1-Hz sampling rate) in the reference CO gas cylinder ([CO] = 550 ppbv in air) as a function of time during the PAVE science flight. Variation in measured [CO] of less than 0.5% over 10 h in flight demonstrates that the instrument was stable and yields reproducible results without regular external calibration and that the reflectivity of the cavity mirrors remains constant.

The goal in performing this work was to provide NASA with an autonomous instrument capable of quantitative CO measurements in the troposphere and tropopause based on Off-Axis ICOS measurements using a quantum-cascade laser near 4.6 μm. Further work is currently underway at Los Gatos Research to develop instruments for measurements of other important species from absorption line shapes recorded in different spectral regions using multiple laser sources.

6. Conclusions

Los Gatos Research has developed an autonomous field deployable instrument capable of measuring ambient CO with a precision of 0.2 ppbv that does not require regular calibration. The instrument recorded ambient CO values onboard a NASA DC-8 aircraft at altitudes that reached 41,000 feet (12.5 km) feet (12.5 km) in May–June 2004 and January 2005. The instrument operated consistently and did not require maintenance or optical realignment during or after the flights. The demonstrated performance suggests that the instrument may be useful for trace-gas measurements in atmospheric monitoring and other applications that require sensitive, precise, and accurate measurements without user intervention and regular external calibration. In the near future, we will investigate the use of cavity mirrors with higher reflectivity for increased effective optical path length and thus sensitivity for measurements of other interesting species.

References

1. G. W. Sachse, G. F. Hill, L. O. Wade, and E. P. Condon, "DACOM—A rapid, high sensitivity airborne carbon monoxide monitor," in *Proceedings of the Fourth Joint Conference on Sensing of Environmental Pollutants,* (American Chemical Society, Washington, D.C., 1978), pp. 590–593.
2. G. W. Sachse, G. F. Hill, L. O. Wade, and M. G. Perry, "Fast-response, high-precision carbon monoxide sensor using a tunable diode laser absorption technique," J. Geophys. Res. **92,** 2071–2081 (1987).
3. G. W. Sachse, J. E. Collins, Jr., G. F. Hill, L. O. Wade, L. G. Burney, and J. A. Ritter, "Airborne tunable diode laser sensor for high precision concentration and flux measurements of carbon monoxide and methane," Proc. SPIE **1433,** 157–166 (1991).
4. J. Podolske and M. Lowenstein, "Airborne tunable diode laser spectrometer for trace-gas measurement in the lower stratosphere," Appl. Opt. **32,** 5324–5333 (1993).
5. G. Durry, T. Danguy, and I. Pouchet, "Open multipass absorption cell for *in situ* monitoring of stratospheric trace gas with telecommunication laser diodes," Appl. Opt. **41,** 424–433 (2002).

6. A. C. Stanton, D. S. Bornse, J. A. Silver, D. C. Hovde, and D. B. Oh, "Measurement of atmospheric species by mid-infrared and near-infrared tunable diode laser absorption," in *Monitoring of Gaseous Pollutants by Tunable Diode Lasers, Proceedings of the International Symposium,* R. Grisar, H. Boettner, M. Tacke, and G. Restelli, eds. (Kluwer Academic, Dordrecht, The Netherlands, 1992), pp. 31–40.
7. D. C. Scott, R. L. Herman, C. R. Webster, R. D. May, G. J. Flesch, and E. J. Moyer, "Airborne Laser Infrared Absorption Spectrometer (ALIAS-II) for *in situ* atmospheric measurements of N_2O, CH_4, CO, HCl, and NO_2 from balloon or remotely pioloted aircraft platforms," Appl. Opt. **38,** 4609–4622 (1999).
8. F. G. C. Bijnen, F. J. M Harren, J. H. P. Hackstein, and J. Reuss, "Intracavity CO laser photoacoustic trace gas detection: cyclic CH_4, H_2O and CO_2 emission by cockroaches and scarab beetles," Appl. Opt. **35,** 5357–5368 (1996).
9. A. Fried, B. Henry, B. Wert, S. Sewell, and J. R. Drummond, "Laboratory, ground-based, and airborne tunable diode laser systems: performance characteristics and applications in atmospheric studies," Appl. Phys. B **67,** 317–330 (1998).
10. C. E. Kolb, J. C. Wormhoudt, and M. S. Zahniser, "Recent advances in spectroscopic instrumentation for measuring stable gases in the natural environment," in *Methods in Ecology: Biogenic Trace Gases: Measuring Emissions from Soil and Water,* P. A. Matson and R. C. Harris, eds. (Blackwell Scientific, 1995), pp. 259–290.
11. P. Werle, "Review of recent advances in laser based gas monitors," Spectrochim. Acta Part A **54,** 197–236 (1998).
12. P. Werle, "Diode-laser sensors for *in-situ* gas analysis," in *Lasers in Environmental and Life Sciences—Modern Analytical Methods,* P. Hering, P. Lay, and S. Stry, eds. (Springer Verlag, 2004), pp. 223–243.
13. M. S. Zahniser, D. D. Nelson, and C. E. Kolb, "Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS) sensors for combustion exhaust pollutant quantification," in *Applied Combustion Diagnostics,* K. K. Hoeinghaus and J. B. Jeffries, eds. (Taylor & Francis, 2002), pp. 648–668.
14. D. S. Baer, J. B. Paul, M. Gupta, and A. O'Keefe, "Sensitive absorption measurements in the near-infrared region using off-axis integrated-cavity-output spectroscopy," Appl. Phys. B **75,** 261–265 (2002).
15. J. B. Paul, J. J. Scherer, A. O'Keefe, L. Lapson, J. G. Anderson, C. Gmachl, F. Capasso, and A. Y. Cho, "Infrared cavity ringdown and integrated cavity output spectroscopy for trace species monitoring," Proc. SPIE **4577,** 1–11 (2001).
16. R. K. Hanson, P. A. Kuntz, and C. H. Kruger, "High-resolution spectroscopy of combustion gases using a tunable infrared diode laser," Appl. Opt. **16,** 2045–2048 (1977).
17. P. L. Varghese and R. K. Hanson, "Collision width measurements of CO in combustion gases using a tunable diode laser," J. Quant. Spectrosc. Radiat. Transfer **26,** 339–347 (1981).
18. S. M. Schoenung and R. K. Hanson, "CO and temperature measurements in a flat flame by laser absorption spectroscopy and probe techniques," Combust. Sci. Technol. **24,** 227–237 (1981).
19. P. L. Varghese and R. K. Hanson, "Room temperature measurements of collision widths of CO lines broadened by H2O," J. Mol. Spectrosc. **88,** 234–235 (1981).
20. S. M. Schoenung and R. K. Hanson, "Temporally and spatially resolved measurements of fuel mole fraction in a turbulent CO diffusion flame," in *Nineteenth Symposium on Combustion* (The Combustion Institute, 1982), pp. 449–458.
21. J. Wang, M. Maiorov, D. S. Baer, D. Z. Garbuzov, J. C. Connolly, and R. K. Hanson, "In situ measurements of CO using diode laser absorption near 2.3 μm," Appl. Opt. **39,** 5579–5589 (2000).
22. E. R. Furlong, D. S. Baer, and R. K. Hanson, "Combustion control and monitoring using a multiplexed diode-laser sensor system," in *Twenty-sixth Symposium on Combustion* (The Combustion Institute, 1996), pp. 2851–2858.
23. R. M. Mihalcea, D. S. Baer, and R. K. Hanson, "Diode-laser sensor for measurements of CO, CO_2 and CH_4 in combustion flows," Appl. Opt. **36,** 8745–8752 (1997).
24. R. M. Mihalcea, D. S. Baer, R. K. Janson, "Diode-laser absorption sensor system for measurements of combustion pollutants," Meas. Sci. Technol. **9,** 327–38 (1998).
25. E. R. Furlong, D. S. Baer, R. K. Hanson, "Real-time adaptive combustion control using diode-laser absorption sensors," in *Twenty-Seventh Symposium on Combustion* (The Combustion Institute, 1998).
26. S. I. Chou, D. S. Baer, R. K. Hanson, W. K. Collison, and T. Q. Ni, "HBr concentration and temperature measurements in a plasma etch reactor using diode laser absorption Spectroscopy," J. Vac. Sci. Technol. A **19,** 477–484 (2001).
27. M. Gupta, T. Owano, D. S. Baer, A. O'Keefe, and S. Williams, "Quantitative determination of singlet oxygen density and temperature for oxygen-iodine laser applications" Chem. Phys. Lett. **400,** 42–46 (2004).
28. S. Williams, M. Gupta, T. Owano, D. S. Baer, A. O'Keefe, D. R. Yarkony, and S. Matsika, "Quantitative detection of singlet O2 by cavity-enhanced absorption," Opt. Lett. **29,** 1066–1068 (2004).
29. J. B. McManus, P. L. Kebabian, and M. S. Zahniser, "Astigmatic mirror multipass absorption cells for long-path-length spectroscopy," Appl. Opt. **34,** 3336–3351 (1995).
30. J. A. Silver, "Frequency modulation spectroscopy for trace species detection: theory and comparison among experimental methods," Appl. Opt. **31,** 707–717 (1992).
31. A. O'Keefe and D. A. G. Deacon, "Cavity ring-down optical spectrometer for absorption measurements using pulsed laser sources," Rev. Sci. Instrum. **59,** 2544–2551 (1988).
32. R. Engeln, G. Berden, R. Peeters, and G. Meijer, "Cavity enhanced absorption and cavity enhanced magnetic rotation spectroscopy," Rev. Sci. Instrum. **69,** 3763–3769 (1998).
33. A. O'Keefe, "Integrated cavity output analysis of ultra weak absorptions", Chem. Phys. Lett. **293,** 331–336 (1998).
34. J. B. Paul, L. Lapson, and J. G. Anderson, "Ultrasensitive absorption spectroscopy with a high finesse optical cavity and off-axis alignment," Appl. Opt. **40,** 4904–4910 (2001).
35. D. S. Baer, J. B. Paul, M. Gupta, and A. O'Keefe, "Sensitive absorption measurements in the near-infrared region using off-axis integrated-cavity-output spectroscopy," Appl. Phys. B. **75,** 261–265 (2002).