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**Development of a Quantum Cascade Laser-Based Detector for
Ammonia and Nitric Acid**

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ABSTRACT

We have developed a compact, robust, atmospheric trace gas detector based on mid-infrared absorption spectroscopy using pulsed quantum cascade (QC) lasers. The spectrometer is suitable for airborne measurements of ammonia, nitric acid, formaldehyde, formic acid, methane, nitrous oxide, carbon monoxide, nitrogen dioxide and other gases that have line-resolved absorption spectra in the mid-infrared spectral region. The QC laser light source operates near room temperature with thermal electric cooling instead of liquid nitrogen which has been previously required for semiconductor lasers in the mid-infrared spectral region. The QC lasers have sufficient output power so that thermal electric cooled detectors may be used in many applications with lower precision requirements. The instrument developed in this program has been used in several field campaigns from both the Aerodyne Mobile Laboratory and from the NOAA WP3 aircraft. The Phase II program has resulted in more than 10 archival publications describing the technology and its applications. Over 12 instruments based on this design have been sold to research groups in Europe and the United States making the program both a commercial as well as a technological success.

Anticipated Benefits

The development of a sensitive, cryogen-free, mid-infrared absorption method for atmospheric trace gas detection will have wide benefits for atmospheric and environmental research and broader potential commercial applications in areas such as medical diagnostic and industrial process monitoring of gaseous compounds. Examples include air pollution monitoring, breath analysis, combustion exhaust diagnostics, and plasma diagnostics for semi-conductor fabrication. The substitution of near-room temperature QC lasers for cryogenic lead salt TDLs and the resulting simplifications in instrument design and operation will greatly expand the range of applications.

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Nelson, D. D., J. H. Shorter, J. B. McManus and M. S. Zahniser (2002). "Sub-part-per-billion detection of nitric oxide in air using a thermoelectrically cooled mid-infrared quantum cascade laser spectrometer." Applied Physics B-Lasers and Optics **75**(2-3): 343-350.

Jimenez, R., S. H. Herndon, J. H. Shorter, D. D. Nelson, J. B. McManus, M. S. Zahniser (2005). "Atmospheric trace gas measurements using a dual quantum cascade laser mid-infrared absorption spectrometer." Novel In-Plane Semiconductor Lasers IV. Bellingham, SPIE-INT SOCIETY OPTICAL ENGINEERING. Proc. SPIE **5738**: 318-331.

1. Problem Identification and Significance

Nitrogen oxides play an important role in determining the photochemistry of the troposphere by controlling the formation of tropospheric ozone, affecting the concentration of the hydroxyl radical, and contributing to acid precipitation [Logan, 1983]. Nitric acid (HNO_3) is often the most abundant of the nitrogen oxide species and provides the dominant sink for NO_x through surface deposition. Ammonia (NH_3) is an important tropospheric trace gas which can rapidly associate with acidic gases leading to fine particle aerosol formation. Determining the sources and sinks for ammonia and nitric acid is important for understanding the chemical mechanisms which affect regional air quality, atmospheric visibility, and global climate change.

Aircraft instrumentation platforms can provide measurements of trace gases over broad horizontal and vertical spatial scales and can be flexibly deployed for both survey studies and for focused research opportunities [Spicer et al., 1994]. There is a need for compact, light-weight, and power efficient instruments with rapid time response to measure ammonia and nitric acid from small and medium sized aircraft platforms where power and space limitations can be severe. Existing airborne instruments which are capable of measuring these gases using tunable diode laser (TDL) spectroscopy [Schiff et al., 1990] and mass spectroscopy (MS) [Spicer et al., 1994] are too large for many aircraft, although a new generation of smaller chemical ionization mass spectrometers (CIMS) is becoming available for HNO_3 measurements [Huey et al., 1998; Eisele et al., 1997; Miller et al., 2000; Fehsenfeld et al., 1998].

The goal of this Phase II project has been to develop an instrument to simultaneously measure both ammonia and nitric acid and other atmospheric trace gases with tunable infrared laser differential absorption spectroscopy (TILDAS) using newly developed quantum cascade (QC) lasers instead of conventional lead-salt diode lasers. In pulsed-mode, QC lasers operate near room temperature with Peltier cooling instead of liquid nitrogen, thus reducing the size of the instrument and complexity of operation. The excellent mode stability of QC lasers reduces operator expertise requirements and makes turn-key operation feasible. The increased output power can be used to maximize the sensitivity of the absorption technique while minimizing instrument size. These characteristics make QC-TILDAS an excellent candidate for trace gas detection from smaller aircraft.

Quantum cascade laser development background

Infrared laser spectroscopy using TDLs has been used for many years for atmospheric trace gas detection from both ground based and aircraft based instruments [Schiff et al., 1983; Sachse et al., 1987; Harris et al., 1992; Zahniser et al., 1995; Fried et al., 1997]. TILDAS methods offer high sensitivity, good specificity, and excellent time response for molecules with resolvable ro-vibrational structure in the mid-infrared spectral region. Wider applicability of the technique has been limited by the cryogenic cooling requirements of lead-salt TDLs which makes them difficult to characterize and often unstable with respect to crucial spectral characteristics such as their operating

wavelength and mode purity. A typical lead salt diode laser in a liquid nitrogen (LN2) dewar needs to be refilled every 12 hours, so that a source of LN2 generally must be co-located with the instrument. Lead salt lasers also are subject to long term drift of the operating wavelength, or perhaps sudden shifts in wavelength after a warm-up/cool-down cycle. These occasional wavelength shifts require either the presence of a trained operator or an extremely sophisticated computer control system which has yet to be demonstrated. Although these characteristics may be overcome with good optical engineering and careful diode selection, TDL techniques are generally considered to require a high level of expertise to operate successfully and are not readily amenable to turn-key operation which is an important characteristic for aircraft-based research.

QC lasers provide an alternative source of high resolution mid-infrared radiation and have overcome many of the difficulties associated with lead-salt TDLs. QC lasers offer the promises of long term device stability, near room temperature operation, the ability to tailor emission wavelength with high precision, broad and continuous tuning, and the use of mature material processing technology borrowed from telecommunications optoelectronics. These characteristics greatly expand the possibilities for nearly turn-key operation of a mid-infrared spectrometer for aircraft measurements. The freedom from cryogenic fluids in the laser source allows greater logistical freedom.

QC lasers are based on a new method of producing laser gain, using tailored layered structures and quantum effects of conduction electrons, rather than on the usual semiconductor bandgap transitions. Since QC lasers were first demonstrated [Faist et al., 1994], they have undergone rapid development [Capasso et al., 1999]. The lasers show high power output and narrow linewidth [Faist et al., 1998; Gmachl et al., 1998; Williams et al., 1999] making them ideal for spectroscopic measurements of trace gases [Sharpe et al., 1998; 1999; Webster et al., 2001]. Operation with non-cryogenic, Peltier, cooling in pulsed mode has been demonstrated in the mid-infrared [Sirtori et al., 1997; Faist et al., 1997]. Although laser line widths are considerably greater in pulsed mode than in cw mode, spectroscopic detection of trace gases is quite feasible [Namjou et al., 1998; Kosterev et al., 2000; McManus et al., 2002].

QC lasers are extremely stable with respect to wavelength drift, so that automatic computer control of the operating wavelength is much more practical. We have demonstrated that we can turn on a QC laser based system and have it reliably return to the correct operating point with no operator intervention. With the addition of commercially available thermoelectrically cooled infrared detectors, a mid-infrared QC laser system may be completely cryogen-free.

QC lasers have been commercially available since the year 2000 from Alpes Lasers (<http://www.alpeslasers.com>). Although most reported trace gas measurements have used these devices in continuous wave (CW) operation, which generally requires liquid nitrogen cooling, this Phase II program has demonstrated highly sensitive detection methods using using Peltier-cooled near-room temperature pulsed QC lasers.

2. Project Objectives

The overall objective has been to build, test, and demonstrate a prototype instrument that will be suitable for measurements of atmospheric ammonia and nitric acid from light aircraft platforms. The instrument development has been aimed at minimizing the size, weight, and complexity associated with conventional tunable diode laser instruments by incorporating the advantages of non-cryogenic QC lasers in both optical and electronic design. The instrument is capable of multiplexing two QC lasers into the same absorption cell for multiple species detection, initially NH_3 , HNO_3 , NO and NO_2 . Simultaneous measurements of these four gases will provide a clearer picture of nitrogen transformations in the troposphere.

During the Phase II project, a prototype instrument was extensively tested with ground based measurements from both fixed and mobile platforms. Thoroughly characterizing and validating the instrument in the laboratory and the field is essential prior to aircraft deployment. Inlet design considerations especially for “sticky” gases from aircraft were investigated during the Phase II project, to design a suitable sampling system to interface the instrument with the aircraft. Our primary goal by the end of Phase II was to have the instrument ready to be packaged for aircraft deployment.

Secondary goals for Phase II were to promote the commercialization of QC laser technology for atmospheric trace gas monitoring for researchers in the fields of environmental chemistry, urban air pollution, ecology, and agriculture emission studies. Ammonia emissions are strongly coupled to aerosols formation and there is a growing emphasis on the measurement of aerosol precursor gases. The prototype instruments from this program participated in several field measurement programs measuring ammonia in urban environments and in agricultural applications. The instrument designs developed in Phase II have resulted in a commercially available QC laser system which has been purchased by several research groups in the United States and in Europe.

The results of this program have been documented in several archival research papers which credit the DOE SBIR program listed in the following section. Several of the key publications are attached as an appendix to this report. Also listed are the customers and sales data for the commercial product resulting from this Phase II program.

3. Project Team

This research development effort has been conducted mainly at Aerodyne Research, Inc., under the direction of Dr. Mark Zahniser as Principal Investigator. Other participants at Aerodyne and their responsibilities include Dr. David Nelson -- electronic design, data acquisition and signal processing, Dr. J. Barry McManus -- optical design and assembly, Dr. Joanne Shorter -- laboratory testing of prototype instruments, and field testing in the ETV program, and Dr. Scott Herndon -- field measurement programs during Mexico City 2003 and ICART 2004.

Dr. Mathew Taubman at Pacific Northwest National Laboratory has participated in the design and evaluation of the high speed circuitry for pulsing the quantum cascade lasers. He has also provided general expertise in consulting on various aspects of the electronic design.

The project has benefited from the collaboration with the research group of Professor Steven Wofsy at Harvard University through related DOE-STTR and NSF-MRI programs to develop an airborne QCL instrument for measurements of CO₂, CO and CH₄. Dr. Rodrigo Jimenez has participated in extensive testing and improvements of the prototype instrument, and Mr. Bruce Daube has contributed to the instrument mechanical design for aircraft deployment.

4. Phase II Results

4.1 Instrument Description

The dual-QCL spectrometer (**Fig. 1**) combines commercially available QC lasers, an optical system, and a computer-controlled system that incorporates the electronics for driving the two QC lasers along with signal generation and data acquisition. The spectrometer is designed for simultaneous measurement of absorption (sample), pulse normalization (reference) and frequency-lock spectra from two QC lasers. A more detailed description of the instrument and operation principles may be found in Nelson et al., [2002] and Jimenez et al. [2005] which are attached in the Appendix.

We use commercially available distributed feedback (DFB) InGaAs-AlInAs/InP QC lasers designed for pulsed operation at near room temperature (Alpes Lasers, Neuchâtel - Switzerland). Molecular transition selection for a given laser is achieved by temperature tuning, typically within $-40\text{ }^{\circ}\text{C}$ to $+40\text{ }^{\circ}\text{C}$ using a two-stage Peltier element. The available spectral range observed (typically $\sim 6\text{--}14\text{ cm}^{-1}$ within $4\text{--}10\text{ }\mu\text{m}$) is about $\sim 0.6\%$ of the wavelength at $0\text{ }^{\circ}\text{C}$. This is in agreement with the reported temperature dependence of the waveguide refractive index ($\sim 7 \times 10^{-5}\text{ K}^{-1}$) and a temperature span of 80 K .

Figure 1. Left: 3D-CAD diagram of the dual QC laser spectrometer. Note the sample, reference, and frequency-lock beams. **Right:** Photograph of the spectrometer. The optical bench is 64 cm by 43 cm .

The primary function of the optical system is to collect light from the two QC lasers and to direct it through a multipass absorption cell onto a dual mid-IR photovoltaic detector. We use a reflecting microscope objectives (15 $\times$, NA 0.5) for collecting the highly divergent elliptical (typically $\sim 60^\circ$ vertical, $\sim 40^\circ$ horizontal) QC laser beams. We have found that microscope objectives, although comparable to aspheric lenses in terms of collection efficiency, are in most cases superior regarding beam quality. This is particularly important for spectroscopic applications requiring relatively long optical paths.

The collected beams from the two lasers (along with co-aligned visible trace beams from red diode lasers) initially converge at an intermediary focus coincident with a mechanically-indexed 200 μm pinhole is placed. The pinhole is used only for initial alignment of the optical system with the aid of the trace beams, and for alignment of the lasers mounted on translation stages. The beams from the two lasers are combined by focusing through the same pinhole, while closely sharing the field angle. After the pinhole, the co-aligned beams from the two QC lasers are directed to a wedged BaF₂ beam splitter. The beam resulting from the front reflection on the beam splitter ($\sim 8\%$ of the incoming light) is used for pulse normalization. Spectra measured from this beam define the wavelength dependence of the laser power, along with its temporal variability (both pulse to pulse and scan to scan). The pulse normalization beam is also used for determining the tuning rate by interposing a 25-mm Ge etalon into the beam before the detector. The optical pathlength of the pulse normalization beam is finely matched to the external pathlength of the absorption beam, i.e. the length of the path outside the multipass absorption cell. This insures that any significant interfering absorption at atmospheric pressure in the external path is cancelled out to less than $\sim 2\%$.

The beam reflected from the second surface of the beam splitter produces the frequency-lock beam. This beam is directed through a short (~ 5 cm), low pressure (~ 1 -20 torr) absorption cell onto the second photovoltaic detector. Absorption spectra derived from this beam serve initially to positively identifying the spectral region, and subsequently provide for active control of the laser wavelength (frequency lock) via laser temperature.

The beam transmitted through the beam splitter is re-imaged into the astigmatic Herriott multipass cell with a magnification of ~ 5 , resulting in a narrow beam ($f/\# \sim 70$ -100), which is well matched to the multipass cell. The cell mirrors have a reflectivity of $>99.2\%$ within 3-10 μm . The multipass cell used for the measurements reported below is 32-cm long, which provides sufficient optical absorption pathlength (55.7 m with 174 passes or 76.5 m with 238 passes) for high sensitivity measurement in a small volume of gas (0.5 liter). The multipass cell is typically operated at ~ 50 torr. At this pressure, the width of the laser line and the pressure-broaden transition are well matched. The cell has excellent flow characteristics. Its flow response time (i.e. the exponential fit time constant τ) is comparable to the plug flow residence time (V/Q). For instance with a sample flow rate of 3.6 SLPM at 45 torr (0.50 s residence time) the measured response time for CH₄,

N₂O and CO is 0.43 s. This implies a 90% recovery time (t_{90}) of 0.98 s, fully compatible with meaningful spectral measurements at 1 Hz. Higher flow rates and/or lower pressures may be used for applications requiring faster time response.

In most applications we use LN₂-cooled HgCdTe (MCT) detectors (Kolmar Technologies) operated at relatively high reverse bias voltages for improved linearity. We have also demonstrated high sensitivity with TE-cooled photovoltaic detectors (Vigo Systems). Both pulse normalization and absorption beams are imaged onto and detected by the same detector. This is possible due to the 190-250 ns (56-76 m) time lag between the two light pulses. The second MCT detector is used for detecting frequency-lock spectra.

The optical board is thermostated to better than ± 1 K in order to minimize thermal drift, which may cause dynamic variation of any optical interference fringes in the system. We have also improved the mechanical stability of the whole system, particularly of the QC laser translation stage in preparation for its use for airborne measurements.

Spectral scans are obtained by repetitively pulsing the laser while simultaneously applying a sub-threshold voltage ramp through a bias T. The laser is excited with ~ 10 -20 ns electrical pulses typically repeated at 1 MHz (~ 1 -2% laser duty cycle). The software-generated ramp modulates the laser temperature, and thus its spectral frequency across the target transitions. A fast (5 MHz) DAC/ADC board synchronously triggers the pulse electronics and integrates the resulting MCT signals. The signal integration gate (50 ns) is matched to the MCT detector response time (~ 60 ns rise time). The fast board also generates a TTL gate signal that defines the ramp duration, including a laser off period (~ 10 pulses) at the end of each sweep to measure the detector offset voltage. A typical spectral sweep consists of 100-400 light pulses (100-400 μ s at 1 MHz repetition rate), which implies a spectral sweeping rate of ~ 2.5 -10 kHz.

The operation of the spectrometer is fully automated and computer-controlled through *TDL Wintel*, a Windows-based proprietary software developed at ARI. Besides controlling the two lasers and the electronics, *TDL Wintel* controls two 3-way solenoid valves for user-scheduled background spectra (zero) measurement and span calibration. *TDL Wintel* retrieves, analyzes, and stores the spectra along with housekeeping data. Concentrations and laser linewidths are real-time determined from the spectra through a non-linear least-squares fitting algorithm (Levenberg-Marquardt) that uses spectral parameters from HITRAN and other databases. The data analysis procedure includes pulse normalization of the sample (multipass cell transmission) spectra, and simultaneous fitting of a low-order polynomial to the spectral baseline and of Gaussian-convolved Voigt profiles to the observed transitions.

4.2 Field Measurements and Applications

The prototype instrument has been extensively tested both in the laboratory and during several field measurements campaigns during a 3 year development period. These include measurements of ammonia from the Aerodyne Mobile Laboratory [Herndon et al., 2005a] during the Mexico City Metropolitan Area air quality study of 2003 [Molina and Molina, 2004]; measurements of ammonia from swine and cattle farms during the EPA-sponsored Environmental Technology Verification Program of 2003 [Cowan et al., 2004] http://www.epa.gov/etv/pdfs/vrvs/01_vr_aerodyne.pdf; and measurements of formaldehyde and ammonia from the NOAA WP3 aircraft during the New England Air Quality Study (NEAQS 2004) (Fig. 3.) The results of the NEAQS program have been presented at several workshops and meetings [Herndon et al., 2005b] and are currently being prepared for publication.

Figure 3. Quantum-cascade based formaldehyde system as integrated in the NOAA P3 aircraft for the NEAQS-2004 measurement campaign.

4.3 Publications and Presentations

This Phase II SBIR program has resulted in more than 10 publications and presentations which document the development of the technique and its application to laboratory and field measurement programs. Two of these [Nelson et al., 2002; Jimenez et al., 2005] are attached as Appendices to this report.

Zahniser, M. S., D. D. Nelson, J. S. Shorter and J. B. McManus (2001). Atmospheric Trace Gas Measurements Using Non-Cryogenic Pulsed Quantum Cascade Lasers: Sub-Part-per Billion Detection of Ammonia. Workshop on Quantum Cascade Lasers, Technology and Application, Freiburg, Germany

Nelson, D. D., J. H. Shorter, J. B. McManus and M. S. Zahniser (2002). "Sub-part-per-billion detection of nitric oxide in air using a thermoelectrically cooled mid-infrared quantum cascade laser spectrometer." Applied Physics B-Lasers and Optics **75**(2-3): 343-350.

McManus, J. B., David D. Nelson, Jr., Joanne Shorter, Mark Zahniser, Antoine Mueller, Yargo Bonetti, Mattias Beck, Daniel Hofstetter, Jerome Faist (2002). Quantum cascade lasers for open and closed path measurement of atmospheric trace gases. Diode Lasers and Applications in Atmospheric Sensing. Bellingham, SPIE-INT SOCIETY OPTICAL ENGINEERING. **4817**: 22-33

Shi, Q., D. D. Nelson, J. B. McManus, M. S. Zahniser, M. E. Parrish, R. E. Baren, K. H. Shafer, and C. N. Harward, (2003). "Quantum cascade infrared laser spectroscopy for real-time cigarette smoke analysis." Analytical Chemistry **75**(19): 5180-5190.

Nelson, D.D., J.B. McManus, J. Shorter, Q. Shi, M.S. Zahniser, and B. Wyslouzil (2004). "Environmental monitoring with pulsed quantum cascade lasers: Seeking sensitivity and stability." Laser Applications to Chemical and Environmental Analysis, February 9-11 2004.

Nelson, D. D., J. B. McManus, S. Urbanski, S. Herndon and M. S. Zahniser (2004). "High precision measurements of atmospheric nitrous oxide and methane using thermoelectrically cooled mid-infrared quantum cascade lasers and detectors." Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy **60**(14): 3325-3335.

Cowen, K., A. L. Sumner, A. Dindal, K. Riggs, Z. Willenberg, J. Hatfield, R. Pfeiffer, K. Scoggin (2004). "Environmental Technology Verification Report: Aerodyne Research, Inc. QC-TILDAS" U.S. Environmental Protection Agency ETV program report, July 2004. www.epa.gov/etv/pdfs/vrvs/01_vr_aerodyne.pdf

Jimenez, R., S. H. Herndon, J. H. Shorter, D. D. Nelson, J. B. McManus, M. S. Zahniser (2005). "Atmospheric trace gas measurements using a dual quantum cascade laser mid-

infrared absorption spectrometer.” Novel In-Plane Semiconductor Lasers IV. Bellingham, SPIE-INT SOCIETY OPTICAL ENGINEERING. Proc. SPIE **5738**: 318-331.

Herndon, S. C., J. T. Jayne, M. S. Zahniser, D. R. Worsnop, B. Knighton, E. Alwine, B. K. Lamb, M. Zavala, D. D. Nelson, J. B. McManus, J. H. Shorter, Manjula R. Canagaratna, T. B. Onasch and C. E. Kolb (2005). “Characterization of urban pollutant emission fluxes and ambient concentration distributions using a mobile laboratory with rapid response instrumentation.” Faraday Discuss. **130**: 327-339.

McManus, J. B., D. D. Nelson, J. H. Shorter, R. Jimenez, S. Herndon, S. Saleska, and M. S. Zahniser (2005). “A high precision pulsed quantum cascade laser spectrometer for measurements of stable isotopes of carbon dioxide.” J. Modern Optics **16**: 2309-2321.

Herndon, S. C., J. H. Shorter, D. D. Nelson, R. Jimenez, M. S. Zahniser (2005). “Formaldehyde and Formic Acid Measurements using Quantum Cascade Laser based Tunable IR Absorption Spectroscopy.” Eos Trans. AGU **86**(52): Fall Meet. Suppl., Abstract A51E-0128.

5. Commercialization and follow-on activities

We have developed a commercially available dual quantum cascade laser system based on the prototype units developed in this Phase II program. The instrument is listed on the Aerodyne Research, Inc. web site <http://www.aerodyne.com/> and has been advertised and demonstrated at several national and international meetings including TDLS2003 in Zermat, Switzerland, and TDLS2005 in Florence, Italy, for which Aerodyne was a sponsor. We have presented the results using these instruments at several SPIE meetings including Photonics West 2005, and we participated in the EPA Environmental Technology Verification program for agricultural ammonia monitors to gain further exposure for this technology.

The commercial sales and follow-on federal and non-federal funding credited to this program are shown in Table 1. This includes follow-on SBIR programs from DOE, DOC, NIH, and DOA. Funding for field measurement programs from federal agencies using the prototype instruments developed from this program are also identified in Table 1. Total revenue from follow-on activity amounts to \$3.9M through 2005.

Direct instrument sales to international research groups in the environmental and atmospheric monitoring area are included in this total. We have constructed and sold 12 instruments for customers in the United States and in Europe. These are highlighted in bold in Table 1. Instrument sales are important for disseminating the technology developed under this Phase II program, and for the commercial success of the SBIR program.

Table 1. Follow on activity credited to this Phase II program (DE-FG02-01ER83139). Deliverable instrument sales are highlighted in bold type.

<u>ARI #</u>	<u>Customer Name</u>	<u>Contract Title</u>	<u>Start Date</u>	<u>End Date</u>	<u>Funded Amt.</u>	<u>Funding Type</u>
10187	U. Manchester Inst. of Technology	UMIST QCL for NH3 and HNO3	04/24/02	02/28/03	\$262,000	Sales:Products
10198	DOE Headquarters	CO-CO2 QC Laser	07/22/02	04/21/03	\$100,000	Development:SBIR
10218	Inst. of Agricultural Sciences, Denmark	Danish QC Tildas for NH3, CH4, N2O	11/20/02	05/20/03	\$215,976	Sales:Products
05836	Institute Low Temp. Plasma Physics	QCL Workshop	03/14/03	03/31/03	\$5,000	Sales:Services
10238	Italian National Research Council	QCL for N2O	06/04/03	12/04/03	\$132,000	Sales:Products
10252	DOE Headquarters	Dvlpmnt of a High Precision, QCL-Based Detector for CO2	06/27/03	06/26/05	\$499,918	Development:SBIR
10250	U. of Missouri-Rolla	Aircraft Emissions (QC-TILDAS) (2 dual units)	07/01/03	06/30/05	\$299,810	Sales:Products
10105	UMIST	QCL Laser Housing	07/17/03	08/17/03	\$4,000	Sales:Products
10264	NSF Headquarters	Aircraft CO-CH4 QCL QC TILDAS for NO, NO2, and O3	08/01/03	07/31/05	\$250,141	Non-SBIR
10256	DOC-NIST		08/14/03	08/13/05	\$300,000	Development:SBIR
10259	UMIST	Nitric Acid Laser	09/01/03	09/30/05	\$14,000	Sales:Products
10275	UMIST	UMIST QCL Upgrade	02/13/04	03/13/04	\$15,500	Sales:Products
10285	NOAA	Aircraft Formaldehyde	05/01/04	12/31/04	\$135,000	Sales:Services
10320	Brookhaven, N.L.	QCL TILDAS for NH3	08/12/04	03/31/05	\$179,000	Sales:Products
10323	EPA Headquarters	QCL Feasibility Study	09/30/04	11/12/04	\$13,954	Non-SBIR
10337	NOAA	Global Change	10/01/04	09/30/05	\$126,624	Non-SBIR
10354	U. of Missouri-Rolla	Airport Lidar Study	10/01/04	06/30/06	\$37,500	Sales:Services
10331	Lawrence Berkeley National Lab.	QC TILDAS for NH3	11/29/04	05/28/05	\$126,500	Sales:Products
10322	Harvard University	HIAPER QCL Inst.	12/23/04	12/23/05	\$457,845	Sales:Products
10339	DOE Headquarters	Mexico City Field Meas. MCMA 2003	01/01/05	12/31/07	\$49,317	Sales:Services
10338	ECN/Netherlands	QCL TILDAS for NH3, CH4, N2O	01/25/05	06/30/05	\$216,580	Sales:Products
10275	EMPA Duebendorf	Consulting Services	03/16/05	03/18/05	\$7,000	Sales:Services
10349	USDA Fire Service	QCL TILDAS CH4, CO	06/21/05	10/31/05	\$170,050	Sales:Products
10359	DOC Headquarters	Aircraft HCHO - H2HO	07/15/05	01/15/06	\$74,741	Development:SBIR
10368	NSF Headquarters	Mexico City Measurements	09/01/05	08/31/06	\$53,732	Sales:Services
10370	National Institute of Health	Breath Analysis	09/15/05	03/15/06	\$99,924	Development:SBIR
10376	DOA Headquarters	Ammonia Monitor	09/15/05	05/14/06	\$80,000	Development:SBIR
10375	INP Greifswald	TILDAS Software	10/07/05	11/04/05	\$4,000	Sales:Products
10275	INP Greifswald	PCB Connector	10/21/05	10/30/05	\$800	Sales:Products
TOTAL:					\$3,930,912	

SUMMARY

We have developed a compact, robust, atmospheric trace gas detector based on mid-infrared absorption spectroscopy using pulsed quantum cascade (QC) lasers. The spectrometer is suitable for airborne measurements of ammonia, nitric acid, formaldehyde, formic acid, methane, nitrous oxide, carbon monoxide, nitrogen dioxide and other gases that have line-resolved absorption spectra in the mid-infrared spectral region. The QC laser light source operates near room temperature with thermal electric cooling instead of liquid nitrogen which has been previously required for semiconductor lasers in the mid-infrared spectral region. The QC lasers have sufficient output power so that thermal electric cooled detectors may be used in many applications with lower precision requirements. A list of trace gases and detection limits using this technology is shown in Table 2.

Table 2. Trace gas detection limits using the 76 m multiple path absorption cell in the Aerodyne QC-Tunable Infrared Laser Differential Absorption Spectrometer.

Trace gas ^(a)	Wavenumber [cm ⁻¹]	Precision [ppb·Hz ^{-1/2}] ^(b)	LOD (100 s) [ppb] ^(c)
NH ₃	967	0.2	0.06
C ₂ H ₄	960	1	0.5
O ₃	1050	1.5	0.6
CH ₄	1271	0.8	0.4
N ₂ O	1271	0.3	0.1
<i>H₂O₂</i>	<i>1267</i>	<i>3</i>	<i>1</i>
<i>SO₂</i>	<i>1370</i>	<i>1</i>	<i>0.5</i>
NO ₂	1600	0.2	0.1
HONO	1700	0.6	0.3
HNO ₃	1723	0.6	0.3
HCHO	1765	0.3	0.15
HCOOH	1765	0.3	0.15
NO	1900	0.6	0.3
<i>OCS</i>	<i>2071</i>	<i>0.06</i>	<i>0.03</i>
CO	2180	0.5	0.2
N ₂ O	2240	0.2	0.1
¹³ CO ₂ / ¹² CO ₂	2311	0.5 ‰	0.1 ‰

(a) Entries in black come from laboratory and field measurements. Values in red (*italic*) are projections based on HITRAN simulations, and laser linewidths extrapolated from adjacent wavelengths.

(b) 1-s RMS precision [ppb] (1-sigma)

(c) Limit of detection (LOD) is 2-sigma at 100-s averaging time

The instrument developed in this program has been used in several field campaigns from both the Aerodyne Mobile Laboratory and from the NOAA WP3 aircraft. The Phase II program has resulted in more than 10 archival publications describing the technology and its applications. Over 12 instruments based on this design have been sold to research groups in Europe and the United States making the program both a commercial as well as a technological success.

The development of a sensitive, cryogen-free, mid-infrared absorption method for atmospheric trace gas detection will have wide benefits for atmospheric and environmental research and broader potential commercial applications in areas such as medical diagnostic and industrial process monitoring of gaseous compounds. Examples include air pollution monitoring, breath analysis, combustion exhaust diagnostics, and plasma diagnostics for semi-conductor fabrication. The substitution of near-room temperature QC lasers for cryogenic lead salt TDLs and the resulting simplifications in instrument design and operation will greatly expand the range of applications.

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APPENDICES

Nelson, D. D., J. H. Shorter, J. B. McManus and M. S. Zahniser (2002). "Sub-part-per-billion detection of nitric oxide in air using a thermoelectrically cooled mid-infrared quantum cascade laser spectrometer." Applied Physics B-Lasers and Optics **75**(2-3): 343-350.

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Sub-part-per-billion detection of nitric oxide in air using a thermoelectrically cooled mid-infrared quantum cascade laser spectrometer

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ABSTRACT Non-cryogenic, laser-absorption spectroscopy in the mid-infrared has wide applications for practical detection of trace gases in the atmosphere. We report measurements of nitric oxide in air with a detection limit less than 1 nmole/mole (< 1 ppbv) using a thermoelectrically cooled quantum cascade laser operated in pulsed mode at $5.26\ \mu\text{m}$ and coupled to a 210-m path length multiple-pass absorption cell at reduced pressure (50 Torr). The sensitivity of the system is enhanced by operating under pulsing conditions which reduce the laser line width to $0.010\ \text{cm}^{-1}$ (300 MHz) HWHM, and by normalizing pulse-to-pulse intensity variations with temporal gating on a single HgCdTe detector. The system is demonstrated by detecting nitric oxide in outside air and comparing results to a conventional tunable diode laser spectrometer sampling from a common inlet. A detection precision of $0.12\ \text{ppb Hz}^{-1/2}$ is achieved with a liquid-nitrogen-cooled detector. This detection precision corresponds to an absorbance precision of $1 \times 10^{-5}\ \text{Hz}^{-1/2}$ or an absorbance precision per unit path length of $5 \times 10^{-10}\ \text{cm}^{-1}\text{Hz}^{-1/2}$. A precision of $0.3\ \text{ppb Hz}^{-1/2}$ is obtained using a thermoelectrically cooled detector, which allows continuous unattended operation over extended time periods with a totally cryogen-free instrument.

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1 Introduction

Tunable infrared laser differential absorption spectroscopy (TILDAS) has been widely used for atmospheric trace-gas detection due to its high sensitivity, good specificity, and fast time response for molecules with resolvable ro-vibrational structure especially in the mid-infrared spectral region containing the stronger fundamental vibrational bands. Wider applicability of the technique has been limited by the cryogenic cooling requirements of lead-salt tunable diode lasers (TDLs), which make them difficult to characterize and less stable with respect to spectral characteristics such as wavelength reproducibility and mode purity. Quantum cascade (QC) or unipolar lasers provide an alternative source

of high-resolution mid-infrared radiation that has overcome some of the difficulties associated with lead-salt diode lasers by providing near-room-temperature operation, single-mode continuous tuning over several wavenumbers, and increased power output. Since QC lasers were first demonstrated [1], they have undergone rapid development [2–4] and been used for a number of applications for atmospheric trace-gas detection in both continuous-wave operation with liquid-nitrogen cooling [5–7] and in pulsed mode with thermoelectric (TE) cooling [8–12]. QC lasers are extremely stable with respect to wavelength drift so that automatic computer control is quite practical. The output power is sufficient to allow the use of thermoelectrically cooled detectors even when coupled into multiple-pass absorption cells with a large number of reflections.

In this paper we demonstrate measurements of nitric oxide in air with a detection limit of less than 1 nmole/mole (< 1 ppbv) using a totally thermoelectrically cooled QC-TILDAS instrument. The method is widely applicable to other trace gases of interest in studies of atmospheric and environmental chemistry, global climate change, as well as industrial process monitoring.

2 Experimental

The experimental system employed for this study combined a commercially available unipolar laser and associated drive electronics, a laser control and signal processing system adapted from our infrared tunable diode laser instruments, and an optical system constructed at Aerodyne for use with tunable diode lasers, including a 210-m path length absorption cell. We have tested the system with both a liquid-nitrogen-cooled detector (Kolmar Technologies, Inc.) and with a thermoelectrically cooled detector (Vigo Systems, Ltd.). A schematic of the experimental system is shown in Fig. 1. The unipolar (quantum cascade) laser as well as the laser pulser and bias circuit were obtained from Alpes Laser (Neuchatel, Switzerland). The laser was of the same design as described by Hofstetter et al. [13]. The laser is grown using the InGaAs material system and includes a distributed-feedback grating. The laser operates between 1880 and $1900\ \text{cm}^{-1}$, in pulsed mode, at a temperature set by a Peltier cooler of between $+10$ and -40° .

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FIGURE 1 Schematic of QC laser spectrometer

2.1 Optical system

The optical system used in this study was adapted from earlier mid-infrared TDL designs [14, 15] with the thermoelectrically cooled unipolar laser housing becoming a drop-in replacement for the liquid-nitrogen laser dewar. The most notable single element of the optical system was a multiple-pass absorption cell with a path length of 210 m and a volume of 5 l, which allows high-sensitivity measurements to be made with sub-second flow response times [16]. The cell is described in more detail below. The laser output, in the form of a broad ($\sim F\# 1$) cone, is collected and transformed into a $F\# 15$ beam by a $15\times$ (Schwarzschild) reflecting objective. The beam is brought to an intermediate focus, which serves as a fixed alignment point for the rest of the optical system, and as a point to observe the laser position using a microscope eyepiece. We also coalign a visible trace beam for alignment purposes, using the first focus as an indexing location. After the first focus, the laser beam is re-imaged into the middle of the absorption cell, with the appropriate magnification to give the very narrow beam ($\sim F\# 50\text{--}100$) that matches the cell recirculation mode. Matching the input beam to the cell mode ensures a minimal beam size within the cell and gives low levels of interference fringes [16].

The optical system also includes a reference path, derived from the portion of the laser beam that reflects from a BaF_2 beam splitter. The reference path is used primarily for pulse normalization, as described below. The reference path is also used to measure the laser tuning rate, by inserting a 25.4-mm germanium etalon, or for absorption-line identification, by inserting a short reference cell containing a low-pressure high-concentration sample of the gas of interest. Both the main (long absorption path) and reference-path beams are directed at a single detector. The TE-cooled detector is a HgCdZnTe photodiode. The liquid-nitrogen-cooled detector is a HgCdTe photodiode. The signals from the two beam paths can be separated temporally. The laser pulses are on the order of 5–10 ns long, the multi-pass absorption cell provides a delay of ~ 700 ns, and both detectors are sufficiently fast (< 70 ns FWHM) to recover between the reference and main signal pulses.

The multi-pass absorption cell is of the astigmatic Herriott type, which offers very long path lengths in a small volume, in a simple and rugged design [16]. The cell used in this study is a variation on the design reported in 1995, with a longer base length (0.88 m) but using mirrors with the same radii of curvature as in the shorter (0.55-m base length) cell. The longer base length requires the selection of a different recirculation pattern, which is quite feasible since there are a great number of available patterns with good optical properties that cover a range of pass numbers from 100 to 300. For a given entrance and exit beam geometry, a unique recirculation pattern can be selected with small adjustments of the cell mirror spacing and the rotation angle of their astigmatic axes.

The uncertainty in the path for a given pattern and set of mirrors with known radii of curvature is less than 1% of the calculated length. Confidence in our calculated length is based in part on comparisons of predicted and observed patterns of the visible trace beam spots on the mirrors, which can be counted for low pass numbers and compared with calculated patterns for higher pass numbers. For high pass number recirculation we observe cell transmission, both intensity and position, consistent with the predicted pass number at the calculated settings of mirror spacing and rotation. Further verification of the path length is provided by the observed absorption due to an added quantity of a gas with known line strength.

The advent of mid-IR lasers with short pulse lengths offers an independent method for validating the calculated path length in the astigmatic cell. We can now directly measure the time delay between light entering and exiting the cell. In Fig. 2 we show an oscilloscope trace of the signal from the single detector with both reference and main pulses. The time delay between the pulses is 708 ± 2 ns, corresponding to a total path length of 212 m. This agrees, within the uncertainty of the timing measurement, to the path length calculated from the identified recirculation pattern (238 passes), the separation between the mirrors of 0.883 m calculated from the mirror radii of curvature for this particular pattern, and the measured

FIGURE 2 Time delay of laser pulse with 210 m multiple pass absorption cell

external path length difference of 1.9 m between the paths of the reference beam and the main beam on the optical table. The flat baseline between the pulses in Fig. 2 confirms that greater than 99.5% of the light emerging from the cell has traveled the specified path length. No light exiting the cell for path lengths other than the specified one is observable.

2.2 Laser control and signal processing system

The data-acquisition system drives the QC lasers, monitors the infrared detector, calculates infrared spectra, analyzes these spectra to derive molecular concentrations, and archives the data. The data-acquisition procedures are implemented using the software package 'TDLWintel', originally developed at Aerodyne for cw tunable diode lasers [14, 15] and recently adapted to pulsed QC lasers. The TDLWintel data-acquisition program operates within Microsoft Windows and is designed to frequency scan one or two tunable lasers (pulsed or cw), acquire the resulting absorption spectra, and analyze them by performing an advanced type of sweep integration. In this method, we sweep the laser frequency across the full spectral transition or group of transitions, and then integrate the area under the transitions using non-linear least-squares fitting to the known spectral line shapes and positions. We do not use frequency-modulation (FM) techniques.

For pulsed lasers, each scan is created by repetitively pulsing the laser while simultaneously sweeping its frequency across the desired transition frequency using a software-generated voltage ramp to heat the QC laser. A commercial pulser (Laser Diode Driver, LDD 100, with TTL Pulse Generator TPG 128, both supplied by Alpes Lasers) provided the drive pulses to the laser. The voltage ramp is applied to the QC laser using a bias T. The light pulses are triggered and detected synchronously using a fast (5 MHz) DAC/ADC board which integrates the detector outputs for each pulse. At the end of the scan several laser current pulses are suppressed to determine the detector voltage corresponding to the absence of laser light. Typically, we use a laser pulse rate of 1 MHz, which produces a spectral sweep rate of 10 kHz for a 100-point spectrum. This sweep rate is fast enough to strongly suppress the effects of $1/f$ noise, thus obviating the need for FM detection. Spectra are averaged in a background process while analysis and display are performed in the foreground maintaining a 100% data acquisition duty cycle. The resultant spectrum is fitted in real time to a set of Voigt line shape functions whose line widths and line strengths are derived from the HITRAN spectral database [17] in conjunction with measurements of the pressure and temperature of the sample and the observed laser line width.

By operating the QC laser in pulsed mode, we are able to avoid the use of cryogenic fluids or closed-cycle refrigerators. However, pulsed operation of the lasers does bring two new challenges – broader laser line widths due to the transient heating during the laser pulse and pulse-to-pulse amplitude variation.

The pulse-to-pulse amplitude variation is typically 1 to 2 percent. This can be greatly reduced with signal averaging but is still the largest source of spectral noise if it is left uncorrected. We have therefore implemented a pulse-normalization scheme to reduce the effects of amplitude fluctuation. A refer-

ence laser beam is created using a BaF₂ beam splitter (Fig. 1). This reference beam is sent to the same detector as the signal beam but without traversing the optical multi-pass cell. The signal pulse and the reference pulse arrive at the detector at different times (due to their 212-m path-length difference). Thus a reference spectrum and a signal spectrum are acquired virtually simultaneously. After signal averaging, a normalized spectrum is created by dividing the signal spectrum by the reference spectrum. This procedure can reduce the spectral noise and improve the detectivity by as much as a factor of 10.

The second difficulty associated with pulsing the laser is that it broadens the laser line width. These broader line widths (approximately 4–5 times the Doppler width) reduce spectral resolution and detectivity slightly, but can be tolerated especially at higher sampling pressures. Our efforts to minimize the line width are discussed below. Our present data-processing routines account for the excess line width by approximating the laser line shape as Gaussian. As we will discuss in Sect. 3.1, this approximation is only valid if the laser is operated at a drive voltage just above threshold in order to minimize asymmetrical line broadening due to thermal 'chirp'. The use of a Gaussian approximation for the laser line shape is computationally convenient since the laser line-shape function may be added in quadrature to the Doppler line-shape function (which is also Gaussian) to produce a combined low-pressure line-shape function. At intermediate pressures, this line-shape function is then convolved with a Lorentzian line-shape function (calculated from the sample pressure and temperature and the HITRAN pressure-broadening coefficients) to produce a Voigt line-shape function, which is an adequate representation of the observed line shape in the optically thin limit.

A typical normalized spectrum during ambient monitoring is shown in Fig. 3. This is a 1-s spectrum of the nitric oxide unresolved doublet at 1897 cm⁻¹ in room air. In this case the laser is pulsed at a rate of 900 kHz, yielding a sweep rate for a 100-point spectrum of 9 kHz. A laser line width of 0.010 cm⁻¹ (HWHM) is determined from a separate, low-pressure spectrum (< 5 Torr), as described in Sect. 3.1.2 below. The laser tuning rate is determined from a germanium etalon. The sampling pressure for ambient monitoring of 48 Torr was chosen to approximately match the pressure-broadened line width to the laser line width. The NO mixing

FIGURE 3 Nitric oxide transmission spectrum with 1-s averaging time using TE-cooled laser and detector. The fit is obtained with a laser line width of 0.010 cm⁻¹ HWHM. The simulation without laser broadening for the NO doublet is shown by the dashed line

ratio determined from the spectrum is 10 ppb and the corresponding peak absorption is $\sim 1.3 \times 10^{-3}$.

3 Results

3.1 Laser line width studies

The spectral width and shape of the laser pulse are crucial parameters that determine the applicability and the sensitivity of pulsed quantum cascade lasers for trace-gas detection. Ideally the laser line width should be narrow compared to the absorption line width, resulting in the maximum absorption depth and minimum dependence of the absorbance on the shape of the laser line. This is difficult to achieve with pulsed QC lasers, however, since their output frequency sweeps rapidly during the laser pulse due to the heating by the current pulse. Line widths of 0.005 to 0.05 cm^{-1} (HWHM) have been reported in the literature [8–12] for spectra acquired with pulsed QC lasers. These line widths are significantly larger than typical Doppler widths for small molecules. For instance, the room-temperature Doppler width for NO at 1900 cm^{-1} is 0.002 cm^{-1} (HWHM). We have investigated this problem both empirically and theoretically. On the theoretical side, we have modeled the heat flow in the laser junction to better understand the frequency broadening during a laser pulse. On the empirical side we have varied the current pulses driving the laser in an attempt to reduce the line width.

3.1.1 Thermal modeling of QC lasers. We have modeled the thermal properties of QC lasers in order to better understand the line width under pulsed operation, as well as other thermal tuning issues. The mechanism for generating a finite line width for relatively long pulses is primarily heating during the pulse. The heat changes the refractive index of the laser-active region and causes expansion of the waveguide and overlying grating, causing the laser frequency to sweep, or ‘chirp’. For extremely short pulses ($< 5 \text{ ns}$) there is an additional mechanism for generating a finite line width, which is the broad spectral bandwidth of the pulse itself, referred to as ‘uncertainty broadening’.

Heat-flow calculations in the QC lasers have been performed in one and two dimensions, with both steady-state and time-dependent heat inputs [18, 19]. The steady-state heat calculations yield thermal resistances, the characteristic equilibrium temperature rise per unit heat input. The total thermal resistance of the laser structure is the sum of the thermal resistances for the deposited (active) layers, the InP substrate, and the Cu heat sink. Our result for the total thermal resistance of 3.8 K/W is similar to values reported in the technical literature [20]. Time-dependent heat-flow calculations were used to model the temperature history of the laser over the range of relevant time scales: the duration of the short laser pulse ($\sim 15 \text{ ns}$), the cooling time between pulses ($\sim 2 \mu\text{s}$), and the cycle time of the tuning ramp ($\sim 250 \text{ ms}$).

A numerical model (in one dimension) using the actual QC laser structure [13] was used to study the thermal history of the active region on the time scale of the laser pulses. The model results were in line with expectations from the literature, that very little heat leaves the active region on the time scale of our drive pulses ($\sim 15 \text{ ns}$). On short time scales, the temperature rise of the active region

is well described by the integral of the heat deposited by the drive pulse. The rate of heat deposition in the active region is the input electrical power ($P = I^2 R(I)$) and the rate of temperature rise is also proportional to the power. With a linear tuning rate, the frequency chirp is proportional to the change in active-region temperature during the time that the laser is above threshold. A simple estimate of the thermal chirp line width can be made as follows. With the laser near threshold, we have $V \approx 14$, $I \approx 3.3$, and $\sim 46.2 \text{ W}$ deposited primarily in the active region, with volume $1.9 \times 10^{-7} \text{ cm}^3$ ($1.43 \mu\text{m} \times 44 \mu\text{m} \times 3 \text{ mm}$). The active region is modeled with the thermal properties of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$, which has a heat capacity of 0.343 J/g K (at 250 K) and a density of 5.5 g cm^{-3} [21], so the rate of temperature rise is $1.3 \times 10^8 \text{ K/s}$. The laser emission frequency (ν) is set primarily by the DFB grating period (Λ) and the waveguide refractive index (n_g), $\nu = c/(2n_g\Lambda)$. Temperature rise produces a change in the refractive index and hence the emission frequency, with a sensitivity $\nu^{-1} d\nu/dT = -7.6 \times 10^{-5} \text{ K}^{-1}$ (for a laser structure very similar to ours [13]). Thus, for our laser operating near threshold at 1900 cm^{-1} , the chirp rate is $-1.9 \times 10^7 \text{ cm}^{-1}/\text{s}$, or $-0.019 \text{ cm}^{-1}/\text{ns}$. For a pulse that is above threshold for 10 ns , the total chirp would be $\sim 0.19 \text{ cm}^{-1}$. If we assume a parabolic shape for the laser output above threshold as a function of time, we estimate the HWHM line width as $1/2\sqrt{2} \times$ the full chirp. The HWHM line width corresponding to a total chirp of 0.19 cm^{-1} would therefore be $\sim 0.067 \text{ cm}^{-1}$. This simple estimate may be modified by considering electrical power deposition outside the active region and by including explicit time dependence of the electrical pulse, non-linear resistance, and laser output power.

3.1.2 Laser line width measurements. The effect of electrical pulse shape on the laser line width was studied experimentally by collecting a series of absorption spectra while recording the current pulse shape on a digital oscilloscope. Laser instrumental line shapes are determined by recording spectra from a low-pressure (4 Torr) isolated molecular absorption, which is narrow (0.002 cm^{-1} HWHM) compared to the laser line width. A closely spaced multiplet of NO lines at 1894.1 cm^{-1} , which is unresolvable at Doppler resolution, was used in these studies. The linear bias current used to tune the laser results in a quadratic dependence of laser frequency with current since the temperature of the laser junction varies with the change in electrical power. Figure 4 shows a typical NO spectrum and a germanium etalon spectrum recorded simultaneously. The spectral baseline is well approximated with a smooth low-order polynomial function, since most of the variation of laser power with bias current has been removed by normalizing the sample spectrum by the unabsorbed reference spectrum. The etalon spectrum is used to quantify the laser tuning rate function. Knowledge of the tuning rate and the spectral baseline allows us to transform the experimental spectrum to a transmission spectrum as a function of frequency. The laser line shape is obtained by deconvolving the observed transmission spectrum and a synthetic NO transmission spectrum calculated using the HITRAN database parameters at the appropriate pressure and temperature. The deconvolution must be done on the transmission spectrum to conserve the area under

FIGURE 4 Normalized detector signal versus bias current ramp showing absorption by nitric oxide in air at a total pressure of 4 Torr. The output of the current ramp decreased linearly by 0.1 Amp during the sweep. The lower trace shows the fringe pattern obtained with a germanium etalon with a free spectral range of 0.0483 cm^{-1}

the transmission curve. Example spectra for the same NO concentration using two sets of laser drive conditions are shown in Fig. 5. The fits to the data are the result of re-convolving the laser line shapes with the synthetic spectrum.

When the laser line width is much broader than the molecular line width, a good approximation to the laser line width may be obtained simply from the observed spectrum without the deconvolution procedure. Several spectra taken with different pulse energies are displayed in Fig. 6 as absorbances. Each spectrum was signal-averaged for approxi-

FIGURE 5 Nitric oxide transmission spectra for two laser pulser conditions. The calculated spectrum uses the NO line parameters from HITRAN at the experimental pressure (4 Torr) and temperature (296 K) with the NO column density adjusted to match the area of the experimental transmission spectrum

FIGURE 6 Spectra of NO in air ($P = 4 \text{ Torr}$) with a pulse width of 13 ns and pulse driver voltages between 14.0 and 15.6 V. The minimum line width is 0.010 cm^{-1} (HWHM)

mately 20 s. These spectra were obtained with a fixed pulse width of 13 ns and supply voltage settings to the pulser unit that varied from 14.0 V to 15.6 V. In all cases the observed line width significantly exceeds the spectral line width by at least a factor of four, so that the instrumental line width is essentially equal to the observed line width. The corresponding electrical pulse shapes were collected using a fast storage oscilloscope with no signal averaging.

The electrical pulse waveforms are shown in Fig. 7. Each of these pulses has a width of $\sim 13 \text{ ns}$ (FWHM). The pulses have the same basic shape at all voltages in the range and vary only in amplitude. Each pulse has a rise time on the order of 8 ns, with a slower fall time. The corresponding absorption spectra, however, vary significantly in both width and shape. At higher drive voltages, the spectrum is asymmetric with an overall half-width of 0.020 cm^{-1} (HWHM) but a sharper low-frequency edge with a half-width of only 0.01 cm^{-1} . The narrowest spectrum in Fig. 6, collected at the lowest drive voltage of the series (14.0 V), which is just above threshold, has a half-width of 0.010 cm^{-1} (HWHM). As the drive voltage is increased, the width of the line increases rapidly.

The rapid increase of line width with drive voltage is associated with a sharp increase in the lasing duration. The laser is above threshold for a longer time and is therefore swept further in frequency. We estimate that the lowest-voltage pulse (with line width 0.01 cm^{-1} HWHM) is only above threshold for approximately 4–5 ns, whereas the highest-voltage (15.6 V) pulse (with line width 0.022 cm^{-1} HWHM) is above threshold for 7–8 ns. The spectra acquired with higher drive voltages are also asymmetric with broad tailing to the high-frequency side. This implies that the laser frequency distribution is also asymmetric with tailing to the low-frequency side. The observed current pulses do not readily explain this asymmetry – that is, they do not show marked asymmetry. We

FIGURE 7 Electrical pulse shapes applied to the laser corresponding to spectra in Fig. 6. The actual voltages to the laser are 10 times greater than the voltage observed on the oscilloscope

are continuing to investigate this phenomenon. An important unanswered question is whether this frequency distribution is a property of an individual pulse or whether it is due to pulse-to-pulse frequency jitter – which could result in an apparent asymmetric shape after averaging of several thousand spectra. The measured line widths are smaller by a factor of 1/2 than the simple chirp estimate given in Sect. 3.1.1. If the laser were above threshold for 7.5 ns (15.6-V pulse), the estimated chirp is 0.05 cm^{-1} HWHM, while the measured value is 0.022. The discrepancy could be due in part to the assumption that all of the electrical power is deposited in the active layer, as well as uncertainties in the thermal constants in the model.

Our observed line widths are among the sharpest reported in the literature to date, especially when expressed as a fraction of the laser frequency. This is a sensible way to report the line width since a given amount of thermal expansion will chirp the laser by an amount proportional to its lasing frequency. In these terms, the 0.010-cm^{-1} line width reported above corresponds to a fractional line width of 5×10^{-6} (HWHM). Literature values for the fractional line width range from 4×10^{-6} to 25×10^{-6} [8–12] with the best previous results reported by Kosterev et al. [9] using ~ 5 -ns pulses. The line widths observed here are narrow due to the fact that we are operating close to threshold and therefore with minimum power output from the laser and a lasing duration which is brief compared to the pulse duration. There is a strong trade-off between high output powers and narrow line widths for optimizing sensitivity for a given optical system and detection approach. This is shown in Figs. 5 and 6 where the peak absorbance decreases proportionally to laser line width while the laser power (not shown) increases substantially for the higher pulse voltages. The pulse energy collected by the signal detector using the 14-V drive voltage was only $\sim 0.3 \text{ pJ}$, which corresponded to an average power of $\sim 300 \text{ nW}$. We estimate, from the optical collection effi-

ciency (~ 0.1) and the multi-pass cell transmission efficiency (~ 0.1), that the average output power of the laser was no more than $30 \mu\text{W}$ for the narrowest line widths. By increasing the drive voltage, we can easily collect 10 times more power at the expense of the instrumental line width.

We are continuing to investigate methods for generating short ($< 5 \text{ ns}$) pulses at high repetition rate and with excellent stability in order to further improve our detection sensitivity and spectral resolution. However, we do not expect dramatic further improvements in line width with these lasers, since we are clearly close to the transform limit for spectral resolution with 4–5 ns pulses. By approximating the part of the pulse above threshold as a Gaussian with 2.5-ns width (FWHM), we estimate that the uncertainty broadening associated with these pulses is 0.003 cm^{-1} . If we assume that the laser chirp is linear with time and that the two broadening mechanisms can be added in quadrature, then a minimum line width of 0.007 cm^{-1} might be achievable with a 1.4-ns Gaussian drive pulse (FWHM) for lasers operating near 1900 cm^{-1} . This would correspond to a fractional spectral resolution of 4×10^{-6} (HWHM) for operation just above threshold. In fact, we have observed narrower line widths (0.007 cm^{-1} HWHM) with a prototype faster pulse driver from Alpes Laser but we did not achieve an improved detection limit with this driver. This may be due to increased amplitude variability in the pulse train. Thus, the NO ambient monitoring results reported in Sect. 3.2 used the original Alpes Laser pulse driver and its associated spectral resolution of 0.010 cm^{-1} .

An ideal pulse driver circuit would operate with an electrical pulse width which matches thermal broadening and uncertainty broadening. It should have a fast rise and fall time to maximize the operating voltage while minimizing the lasing duration. This would allow increased laser output power while maintaining better overlap between the instrumental width and the molecular line width to maximize sensitivity. Alternative pulse driver circuits are presently being investigated which could provide substantial increases in laser power output while maintaining narrow line widths.

3.2 Ambient monitoring of NO

We have employed the QC system for ambient monitoring of nitric oxide. The unresolved doublets at either 1900.08 cm^{-1} or 1896.98 cm^{-1} were used with similar results. A sampling pressure of 48 Torr was chosen to approximately match the pressure-broadened line width to the laser line width. Each spectrum is similar to the one shown in Fig. 3. A time series of the results of successive fits of 1-s spectra is shown in Fig. 8. The figure shows only two small portions of an extended one-month period of continuous sampling of ambient air from the Aerodyne rooftop. The time series on the left-hand side of Fig. 8 highlights a region with low NO mixing ratios, while the data on the right-hand side has high NO events. The time series in Fig. 8 shows the influence of vehicular traffic from a nearby highway and a local delivery truck on ambient NO mixing ratios. The QCL and TDL instruments concurrently measure NO in the outside air using separate but collocated sampling tubes. Zero air from a cylinder of compressed nitrogen was introduced into the sampling system at 15-min intervals. The measurement precision of

FIGURE 8 Nitric oxide from local vehicle traffic sampled from Aerodyne rooftop comparing results for QCL and TDL spectrometers at low concentrations (*left*) and high concentrations (*right*). The *inset* shows the precision for the QCL system during 'zero' gas addition to the inlet

the QCL system may be obtained during these zero additions and is $0.12 \text{ ppb Hz}^{-1/2}$ (1σ) when using the liquid-nitrogen-cooled HgCdTe detector. This corresponds to an absorbance precision of $1 \times 10^{-5} \text{ Hz}^{-1/2}$ based on the correspondence between mixing ratio and peak absorbance determined from the simulation in Fig. 3 with a laser line width of 0.01 cm^{-1} . The corresponding absorbance per path length with the 210-m multiple-pass cell is $5 \times 10^{-10} \text{ cm}^{-1} \text{ Hz}^{-1/2}$.

During a portion of the measurement period, the data could be compared directly with a dual tunable diode laser system [15] operating with a lead-salt tunable diode in cw mode. The optical layouts for the two systems are similar. The TDL system used a multiple-pass cell set for 150-m path length, and used the NO transitions at 1896.98 cm^{-1} with a lower sampling pressure of 25 Torr. The TDL system used continuous peak locking to a reference cell, periodic background subtraction with 'zero' air addition (e.g. the gap in the TDL data at $\sim 08:47$ in Fig. 8), and a heated and thermostated optical table to minimize baseline drifts due to changes in optical interference fringes. The QCL system operated on a laboratory cart without thermal stabilization of the optical system. The optical fringes in the pulsed QCL system appeared to be substantially reduced compared to the TDL system. Instrumental zero drift was $\pm 2 \text{ ppb}$ with a typical drift rate of $< 1 \text{ ppb/h}$. The two instruments compare very well over a wide range of ambient mixing ratios from 1 to 2000 ppb. The mixing ratios reported by the TDL and the QCL over the time period plotted in Fig. 8 are compared in Fig. 9 by plotting the NO concentration determined by the QCL system against that determined by the TDL system. There is good correlation over more than three orders of magnitude in mixing ratios with no apparent deviation from linearity even at relatively high absorbance. A linear regression slope of 0.931 ± 0.002 is obtained, which is in reasonable agreement considering that the calibration of both systems is based totally upon the spectroscopic constants and the fitting procedures as described in Sect. 2. Since the spectroscopic constants both come from the HITRAN database [17], the greatest relative errors in this comparison are due to the uncertainties in the determination of the QC laser line width and approximations used in the fitting program for the QC line shape and tuning rate function.

The majority of the ambient measurements were conducted using a thermoelectrically cooled HgCdZnTe detec-

tor, since it permitted totally cryogen-free operation, which is especially convenient for extended monitoring. The detector noise was a factor of two to four greater for this detector compared to the liquid-nitrogen-cooled detector. The bandwidth for the TE-cooled detector was also sufficiently fast to perform pulse normalization with a single detector, as is shown in the oscilloscope trace in Fig. 2. (Both Figs. 2 and 3 were recorded using the TE-cooled detector.) A time-series trace is shown in Fig. 10 for an 18-h period. A precision of $0.3 \text{ ppb Hz}^{-1/2}$ (1σ) is obtained from the variations observed during short periods of relative stability in the ambient NO or while sampling laboratory room air. The CO_2 trace shown in Fig. 10 was recorded with a non-dispersive infrared analyzer and shows a strong correlation between NO and CO_2 , which indicates combustion as the local source of NO. The totally cryogen-free mid-IR system will greatly simplify the opera-

FIGURE 9 Comparison of NO concentrations from QCL and TDL instruments for the data shown in Fig. 8

FIGURE 10 NO mixing ratios obtained with TE-cooled QCL spectrometer and detector. The lower trace shows CO₂ data obtained with a non-dispersive infrared monitor

tion logistics of using mid-IR absorption for urban emission monitoring compared to using lead-salt TDLs [22].

4 Abstract and conclusions

Detection of nitric oxide in the atmosphere with a mixing ratio less than 1 nmole/mole (ppb) has been demonstrated using mid-infrared absorption with a unipolar (quantum cascade) laser operating in the pulsed mode with thermoelectric cooling of laser and detector. High sensitivity is obtained in the pulsed mode by (i) coupling the laser to a long path length (210 m) multiple-pass absorption cell, (ii) operating the laser near threshold to minimize laser line width, and (iii) reducing the effects of pulse-to-pulse amplitude variations by normalizing each spectrum to a reference spectrum recorded simultaneously on the same detector element. A precision of $0.3 \text{ ppb Hz}^{-1/2}$ (1σ) is obtained using a TE-cooled detector, limited mainly by detector noise. With a more sensitive liquid-nitrogen-cooled detector, a precision of $0.12 \text{ ppb Hz}^{-1/2}$ is obtained, limited by a combination of detector noise and residual pulse-to-pulse amplitude variations. This corresponds to an absorbance precision of $1 \times 10^{-5} \text{ Hz}^{-1/2}$ or an absorbance per path length of $5 \times 10^{-10} \text{ cm}^{-1} \text{ Hz}^{-1/2}$.

The ability to operate a mid-infrared laser spectrometer continuously without cryogenic cooling opens up numer-

ous possibilities for long-term environmental measurements. Other trace gases detectable with this technique include nitrogen dioxide, ozone, carbon monoxide, formaldehyde, methane, nitrous oxide, sulphur dioxide, ammonia, and nitric acid as unipolar or quantum cascade lasers become more widely available at the requisite wavelengths.

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Atmospheric trace gas measurements using a dual quantum-cascade laser mid-infrared absorption spectrometer

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ABSTRACT

We present an overview of the dual QC laser spectrometer developed at Aerodyne Research and various examples of its application for atmospheric trace gas detection. The instrument incorporates two pulsed QC lasers, a compact 76-m (or 56-m) multipass absorption cell, a dual HgCdTe detector, and a sophisticated signal generation, data acquisition and processing system. Recent findings and hardware innovations are highlighted. Our results show that the precision and minimal detectable absorbance obtainable with pulsed QC lasers are comparable to those achieved with cryogenically cooled CW Pb-salt lasers in spite of the broader laser linewidths inherent to pulsed operation. This is demonstrated through *in situ* measurements of several trace gases, including methane, nitrous oxide, carbon monoxide, formaldehyde, formic acid, nitrous acid and ethylene. Recent measurements of HCHO and HCOOH on board a NOAA aircraft are presented. The precision, stability and intrinsic accuracy of the instrument were assessed through inter-comparisons measuring CH₄ and CO. These measurements were made either comparing two QC lasers sweeping over different transitions or comparing the dual QCL spectrometer and a standard instrument (NDIR CO). The absorbance precision achieved is typically $2 \times 10^{-5} \text{ Hz}^{-1/2}$. For long-lived species, such as CH₄ and N₂O, this implies 1-Hz fractional precisions of 0.1% or better, which fulfill the requirement for meaningful measurements from aircraft platforms. Spectroscopically derived mixing ratios are accurate within 5% or better. The spectrometer is equipped to perform automatic, periodic calibrations with zero and span gases whenever higher accuracy is required.

1. INTRODUCTION

Tunable infrared laser differential absorption spectroscopy (TILDAS) is a widely used technique for atmospheric trace gas detection due to its high sensitivity, excellent specificity, and fast time response for molecules with resolvable rovibrational structure. The method has its highest sensitivity in the mid-infrared spectral region where a large number of molecules display their strong fundamental vibrational bands compared to near infrared (IR) overtone bands. Wider applicability of the technique has been limited by the cryogenic cooling requirements of lead-salt tunable diode lasers and their lack of stability in frequency and mode purity. Quantum cascade lasers (QCL) provide alternative sources of high resolution mid-infrared radiation that have overcome some of the difficulties associated with Pb-salt diode lasers by providing near room temperature operation, single-mode continuous tuning over several wavenumbers, and increased power output. Since QC lasers were first demonstrated [1], they have undergone rapid development [2-5] and been used for a number of applications for atmospheric trace gas detection in both continuous wave (CW) operation with liquid nitrogen (LN₂) cooling [6, 7] and in pulsed mode with thermoelectric (TE) cooling [8-11]. QC lasers are extremely stable with respect to wavelength drift so that automatic computer control is quite practical. The output power is often sufficient to allow the use of TE-cooled detectors even when coupled into multiple pass absorption cells with a large number of reflections. Many applications of tunable infrared laser spectroscopy will benefit from more stable lasers that do not require cryogenic cooling. Research areas that benefit from more convenient spectroscopic instruments include air quality, global geochemical cycles, ecology, and geology. Other areas with potentially wider application of spectroscopic instrumentation include routine environmental monitoring, medical and biological tests (e.g. respiration and breath analysis), and industrial process monitoring.

In previous papers [10, 11], we reported high precision measurements of NO, N₂O and CH₄ using a single QC laser spectrometer. Here we specifically describe a new dual QC laser spectrometer and its application for simultaneous measurements of methane, nitrous oxide, carbon monoxide, formaldehyde, formic acid, nitrous acid and ethylene. The lasers are operated in pulsed-mode which allows for thermoelectric cooling near room temperature. When coupled with a multiple pass absorption cell, a sensitive infrared detector, and a sophisticated data processing system, the precision and minimal detectable absorbance obtainable with pulsed QC lasers is comparable to that achieved with cryogenically cooled CW Pb-salt lead lasers in spite of the broader laser linewidths inherent to pulsed operation.

2. THE DUAL QC LASER SPECTROMETER

The dual-QCL spectrometer (**Fig. 1**) combines commercially available QC lasers, an optical system, and a computer-controlled system that incorporates the electronics for driving the two QC lasers along with signal generation and data acquisition. The spectrometer is designed for simultaneous measurement of absorption (sample), pulse normalization (reference) and frequency-lock spectra from two QC lasers.

We use commercially available distributed feedback (DFB) InGaAs-AlInAs/InP QC lasers designed for pulsed operation at near room temperature (Alpes Lasers, Neuchâtel - Switzerland). All the QC lasers that we use are single mode. We have only rarely observed multimode behavior, usually when operating high above threshold. Molecular transition selection for a given laser is achieved by temperature tuning, typically within $-40\text{ }^{\circ}\text{C}$ to $+40\text{ }^{\circ}\text{C}$ using a two-stage Peltier element. The available spectral range observed (typically $\sim 6\text{--}14\text{ cm}^{-1}$ within $4\text{--}10\text{ }\mu\text{m}$) is about $\sim 0.6\%$ of the wavelength at $0\text{ }^{\circ}\text{C}$. This is in agreement with the reported [12, 13] temperature dependence of the waveguide refractive index ($\sim 7 \times 10^{-5}\text{ K}^{-1}$) and a temperature span of 80 K.

Figure 1. Left: 3D-CAD diagram of the dual QC laser spectrometer. Note the sample, reference, and frequency-lock beams. **Right:** Photograph of the spectrometer. The optical bench is 64 cm by 43 cm.

The primary function of the optical system is to collect light from the two QC lasers and to direct it through a multipass absorption cell onto a dual mid-IR photovoltaic detector. We use a reflecting microscope objectives (15 $\times$, NA 0.5) for collecting the highly divergent elliptical (typically $\sim 60^\circ$ vertical, $\sim 40^\circ$ horizontal) QC laser beams. We have found that microscope objectives, although comparable to aspheric lenses in terms of collection efficiency, are in most cases superior regarding beam quality. This is particularly important for spectroscopic applications requiring relatively long optical paths.

The collected beams from the two lasers (along with co-aligned visible trace beams from red diode lasers) initially converge at an intermediary focus coincident with a mechanically-indexed 200 μm pinhole is placed. The pinhole is used only for initial alignment of the optical system with the aid of the trace beams, and for alignment of the lasers mounted on translation stages. The beams from the two lasers are combined by focusing through the same pinhole, while closely sharing the field angle. After the pinhole, the co-aligned beams from the two QC lasers are directed to a wedged BaF₂ beam splitter. The beam resulting from the front reflection on the beam splitter ($\sim 8\%$ of the incoming light) is used for pulse normalization. Spectra measured from this beam define the wavelength dependence of the laser power, along with its temporal variability (both pulse to pulse and scan to scan). The pulse normalization beam is also used for determining the tuning rate by interposing a 25-mm Ge etalon into the beam before the detector. The optical pathlength of the pulse normalization beam is finely matched to the external pathlength of the absorption beam, i.e. the length of the path outside the multipass absorption cell. This insures that any significant interfering absorption at atmospheric pressure in the external path is cancelled out to less than $\sim 2\%$.

The beam reflected from the second surface of the beam splitter produces the frequency-lock beam. This beam is directed through a short (~ 5 cm), low pressure (~ 1 -20 torr) absorption cell onto the second photovoltaic detector. Absorption spectra derived from this beam serve initially to positively identifying the spectral region, and subsequently provide for active control of the laser wavelength (frequency lock) via laser temperature.

The beam transmitted through the beam splitter is re-imaged into the astigmatic Herriott multipass cell [14] with a magnification of ~ 5 , resulting in a narrow beam ($f/\# \sim 70$ -100), which is well matched to the multipass cell. The cell mirrors have a reflectivity of $>99.2\%$ within 3-10 μm . The multipass cell used for the measurements reported below is 32-cm long, which provides sufficient optical absorption pathlength (55.7 m with 174 passes or 76.5 m with 238 passes) for high sensitivity measurement in a small volume of gas (0.5 liter). The multipass cell is typically operated at ~ 50 torr. At this pressure, the width of the laser line and the pressure-broaden transition are well matched. The cell has excellent flow characteristics [10, 11, 14]. Its flow response time (i.e. the exponential fit time constant τ) is comparable to the plug flow residence time (V/Q). For instance with a sample flow rate of 3.6 SLPM at 45 torr (0.50 s residence time) the measured response time for CH₄, N₂O and CO is 0.43 s. This implies a 90% recovery time (t_{90}) of 0.98 s, fully compatible with meaningful spectral measurements at 1 Hz. Higher flow rates and/or lower pressures may be used for applications requiring faster time response.

In most applications we use LN₂-cooled HgCdTe (MCT) detectors (Kolmar Technologies) operated at relatively high reverse bias voltages for improved linearity. We have also demonstrated high sensitivity with TE-cooled photovoltaic detectors (Vigo Systems) [11]. Both pulse normalization and absorption beams are imaged onto and detected by the same detector. This is possible due to the 190-250 ns (56-76 m) time lag between the two light pulses. The second MCT detector is used for detecting frequency-lock spectra.

The optical board is thermostated to better than ± 1 K in order to minimize thermal drift, which may cause dynamic variation of any optical interference fringes in the system. We have also improved the mechanical stability of the whole system, particularly of the QC laser translation stage in preparation for its use for airborne measurements.

Spectral scans are obtained by repetitively pulsing the laser while simultaneously applying a sub-threshold voltage ramp through a bias T. The laser is excited with ~ 10 -20 ns electrical pulses typically repeated at 1 MHz (~ 1 -2% laser duty cycle). The software-generated ramp modulates the laser temperature, and thus its spectral frequency across the target transitions. A fast (5 MHz) DAC/ADC board synchronously triggers the pulse electronics and integrates the resulting MCT signals. The signal integration gate (50 ns) is matched to the MCT detector response time (~ 60 ns rise time). The fast board also generates a TTL gate signal that defines the ramp duration, including a laser off period (~ 10 pulses) at the end of each sweep to measure the detector offset voltage. A typical spectral sweep consists of 100-400 light pulses (100-400 μ s at 1 MHz repetition rate), which implies a spectral sweeping rate of ~ 2.5 -10 kHz. An example spectrum is shown in **Fig. 2**.

We have recently developed and tested a more compact and efficient QC laser pulse electronics module. In our previous design [11], we thermostated the pulse electronics to ± 0.1 K using a closed-circuit water cooling system to insure optimal performance. The new module is co-located with the laser. This allows heat-sinking the temperature sensitive components of the electronics directly to the laser housing without direct water cooling. Additionally, the electrical signal path is shorter, which results in sharper, highly reproducible electrical pulses. Measured short- and mid-term light intensity variations are a factor ~ 2 smaller with the new module compared with the previous design [11]. Moreover, as a result of sharper pulses, the new module also reduces by a factor ~ 2 the amplitude of the monotonic variation of the light intensity within a spectral scan. This should reduce the impact of detector non-linearity on the concentration retrieval accuracy.

The operation of the spectrometer is fully automated and computer-controlled through *TDL Wintel* [10, 11], a Windows-based proprietary software developed at ARI. Besides controlling the two lasers and the electronics, *TDL Wintel* controls two 3-way solenoid valves for user-scheduled background spectra (zero) measurement and span calibration. *TDL Wintel* retrieves, analyzes, and stores the spectra along with housekeeping data. Concentrations and laser linewidths are real-time determined from the spectra through a non-linear least-squares fitting algorithm (Levenberg-Marquardt) that uses spectral parameters from HITRAN [15] and other databases. The data analysis procedure includes pulse normalization of the sample (multipass cell transmission) spectra, and simultaneous fitting of a low-order polynomial to the spectral baseline and of Gaussian-convolved Voigt [16] profiles to the observed transitions.

Figure 2. Typical 1-Hz CH_4 , N_2O and CO transmission spectrum (8th July 2004 3:00 AM) at 40 torr (56 m absorption pathlength) as displayed by *TDL Wintel*. The first portion of the spectrum shows CH_4 and N_2O target transitions at ~ 1271 cm^{-1} (note the weak water vapor transition in between – not included in the fit). The second portion shows the CO transition at ~ 2180 cm^{-1} . The spectrum is assembled from 350 laser pulses (plus 10 pulses off).

3. ATMOSPHERIC TRACE GAS MEASUREMENTS

We have extensively tested the dual QCL spectrometer both in the laboratory and in the field. In Section 3.1 we first discuss laboratory examples demonstrating high precision measurements of CH₄, N₂O and CO, trace gases with relatively high atmospheric mixing ratios. In Sections 3.2 and 3.3 we present field measurement examples demonstrating high sensitivity for gases such as HCHO and HONO, which are present at comparatively lower atmospheric mixing ratios, closer to the detection limit of the instrument.

3.1. Methane, nitrous oxide and carbon monoxide

Methane and nitrous oxide are infrared active gases that play a major role in the radiative balance of the Earth. Carbon monoxide is a hydrocarbon oxidation byproduct, also an infrared-active gas, which affects the oxidative capacity of the atmosphere. Simultaneous measurements of these species allow characterization of the emission sources (e.g. biomass burning, fossil fuel combustion) and estimation of their source strengths using inverse modeling techniques. As these species are long lived (CH₄, N₂O) or moderately long lived (CO), their concentrations in the upper atmosphere show only small variations, typically a few percent or less. Fractional precisions on the order of ~0.1% or better are thus required for meaningful measurements. This is particularly true for airborne measurements in the upper troposphere/lower stratosphere. High resolution IR spectroscopy systems based on Pb-salt tunable diode lasers [17-20], LN₂-cooled CW QC lasers [6, 9, 21], and TE-cooled pulsed QC lasers [8-11] have been developed during the last years for rapid and sensitive detection of CH₄, N₂O and CO with sufficient time response for eddy covariance flux measurements [22].

We have previously demonstrated precisions with TE-cooled pulsed QC lasers of 1.5 and 4 ppb-Hz^{-1/2} for methane and of 0.4 and 3 ppb-Hz^{-1/2} for nitrous oxide using LN₂- and TE-cooled detectors, respectively [11]. More recently we have achieved precisions with a LN₂-cooled MCT and a 56-m multipass cell of 0.8, 0.3 and 0.5 ppb-Hz^{-1/2} for CH₄, N₂O and CO, respectively. This corresponds to 1-s fractional precisions of ~5×10⁻⁴, ~8×10⁻⁴ and ~4×10⁻³ for CH₄, N₂O and CO at typical tropospheric mixing ratios of 1800, 340, and 140 ppb, respectively.

Fig. 2 shows a typical dual QCL transmission spectrum for the simultaneous detection of three species. The first QC laser scan across CH₄ and N₂O transitions at 1271 cm⁻¹. The second one subsequently scans across the R(20) transition of CO centered at 2180 cm⁻¹. Both lasers are driven with 12-ns electrical pulses repeated at 1 MHz. The overall sweep rate is 2.8 kHz. This sweep rate strongly suppresses the effects of the 1/f noise. The CH₄ QC lasers at ~7.9 μm display very little chirping leading to relatively narrow linewidths (~5×10⁻³ cm⁻¹ HWHM) at quite high power levels. These are among the best pulsed QC lasers that we have used. On the contrary, our CO lasers at ~4.6 μm display lineshape asymmetry even at current levels of only ~5% above threshold. Symmetric laser lineshapes of ~10⁻² cm⁻¹ HWHM are nevertheless obtained near threshold at the cost of lower power compared to the CH₄ lasers. The penalty is a lower absorbance precision for CO (5×10⁻⁵ Hz^{-1/2}) compared to CH₄ and N₂O (2×10⁻⁵ and 1×10⁻⁵ Hz^{-1/2}, respectively). High-frequency noise and interference fringes at 1 Hz are typically on the order 10⁻⁵-10⁻⁴ (peak-to-peak) optical depth.

A valuable test to determine the robustness, comparability and drift of the system consists in measuring the same species with two lasers exploiting either the same or different transitions. **Fig. 3** (above) shows simultaneous measurements of ambient air methane at the ARI site using two side-to-side pulsed QC lasers operating at 1271 cm⁻¹ (CH₄ singlet) and 1348 cm⁻¹ (CH₄ doublet) over a period of ~15 h. The two lasers sense the same air sample using a 56-m astigmatic multipass cell. The 1348 cm⁻¹ laser displays a larger pulse-to-pulse variability, and is less powerful at a slightly broader linewidth (~6×10⁻³ cm⁻¹ HWHM) compared to the 1271 cm⁻¹ laser. This results in a precision degraded by a factor ~3 for the 1348 cm⁻¹ laser compared with the 1271 cm⁻¹ laser. Concentrations directly derived from the measured spectra without periodic calibration are typically accurate within ~5% or better. The time series in Fig. 3A shows calibrated concentrations. Background (dry N₂) and calibration spectra were measured every 100 s and 500 s, respectively. Upon calibration, the mixing ratios agree within ±20 ppb, approximately ±1% of the ambient level. The major source of low-frequency variation between calibrations is probably laser wavelength drift. The thermal drift of the optics contributes to a minor extent. This may have an impact on the retrieval due to the slight non-linearity of the

detector. **Fig. 3** (below) also shows the scatter plot and orthogonal linear regression of the simultaneous CH₄ measurements over a period of ~3 h. Residuals during this period are lower than ± 10 ppb and reflect span variations and the lower short-term precision achieved with the 1348 cm⁻¹ laser.

Figure 3. Above: Calibrated concentration time series of methane measured at ARI using two pulsed QC lasers operating side-to-side on the same spectrometer. **Below:** Scatter plot, orthogonal linear regression and regression residuals.

A similar test was made by comparing two CO lasers sweeping over different transitions of the same branch (R) (see **Fig. 4**). In this case no calibration was made. The mixing ratios derived only from the measured spectra agree within better than $\pm 2\%$. Correlation residuals are within $\sim 1\%$ of the retrieved mixing ratios. Residuals result from drift and mid-term random variations. The short-term precision is ~ 0.5 ppb-Hz^{-1/2}.

The QCL CO measurements were also inter-compared with a tightly calibrated (zero and span) standard NDIR instrument (Thermo Environmental Instruments, 48C). **Fig. 5** shows co-located measurements of ambient air CO at ARI. The instruments were calibrated with different periodicity and using different tanks. The excellent agreement between the QCL and the NDIR CO measurements over a ~3-day period confirms the stability and linearity of the QCL system. Moreover, the QCL instrument captures atmospheric events that take place on the 1-Hz time scale not seen by the NDIR instrument, which requires ~ 1 -min integration time for a ~ 20 ppb precision (see inset).

The methane and carbon monoxide concentration time series show low and high frequency variations. The low frequency component is indicative of the mixed layer height. The high frequency component results from road traffic emissions. Outgassing from nearby swamps is also an important methane source.

Figure 4. Above: Spectroscopically derived CO concentrations from two QC lasers operating side to side on a dual QC laser spectrometer. **Below:** Scatter plot and residuals. The discrepancy between the two instruments is due to thermal drift.

Figure 5. CO concentration time series as measured at ARI with a QC laser operating at 2180 cm⁻¹ and standard NDIR CO instrument. Both series are calibrated values. The calibrated QCL time series were boxcar convolved to the time resolution of the NDIR monitor.

3.2. Airborne measurements of formaldehyde and formic acid

The use of TILDAS to measure formaldehyde (HCHO) in flight has been demonstrated by the pioneering studies of Alan Fried and colleagues [23-25] using a lead salt diode laser spectrometer accessing spectral transitions in the 2800 cm^{-1} (ν_1 and ν_5) band. ARI also has performed spectroscopic studies and field measurements of HCHO in this spectral region [26]. The 1745 cm^{-1} (ν_2) band also provides specific “fingerprint” detection of HCHO and the absorption line strengths in this band have been well quantified [27]. These line lists allows the use of newly available QC lasers, which operate pulsed at near room temperature in this spectral region.

In July 2004, an ARI pulsed QC laser system was deployed aboard NOAA’s P3 aircraft as part of the New England Air Quality Study (NEAQS). Tropospheric concentrations of HCHO and formic acid (HCOOH) were measured with this instrument. Formaldehyde and formic acid have excellent line strengths in the vicinity of 1765 cm^{-1} . A single quantum-cascade laser with sufficiently narrow linewidth ($\sim 9 \times 10^{-3} \text{ cm}^{-1}$) was able to cover transitions of both species in a single sweep. The instrument installed in the aircraft is shown in **Fig. 6**.

This campaign represented one of the first flight-based measurement of any species using a TE-cooled pulsed QCL for mid-IR absorption spectroscopy. The formaldehyde instrument had been previously tested in the laboratory and in Aerodyne’s mobile laboratory applications. The aircraft instrument used a heated PTFE inlet system and a formaldehyde-free zero air generator based on the design of the NCAR HCHO instrument of Fried and co-workers to obtain background spectra [24, 28].

Results from the flight measurement are shown in **Fig. 7**. Each of the panels in this figure shows a portion of the northeastern United States and eastern Canada, with the respective measurements along the flight track. During this flight, a forest fire plume originating at ground level in western Canada was intercepted at 3500 meters over Hudson’s Bay, Canada. The location where the concentration of formic acid increases dramatically near 52 °N, -68 °W marks this fire plume (see **Fig. 8**).

Also observed in **Fig. 7**, is the city outflow emanating from Boston. The high concentrations of formaldehyde begin at the city and extend eastward over the Atlantic. One of the major goals of the NEAQS campaign was to characterize the evolving city outflow and sharpen our understanding of middle term smog chemistry as air masses are diluted into the free troposphere. Further analysis of over 50 hours of flight data is in progress.

Figure 6. Quantum-cascade based formaldehyde system as integrated in the NOAA P3 aircraft for the NEAQS-2004 measurement campaign. The visible components are labeled; a more thorough description of the instrument is given in Section 3.2.

Figure 7. Formic Acid and Formaldehyde above the Northeastern United States and Canada. Data collected aboard the NOAA P3 NEAQS flight on July 9th, 2004 using QCL laser spectroscopy.

Figure 8. Fire Plume Intercept from NOAA P3. The top panel shows the altitude of the aircraft determined from the onboard GPS system. The middle and lowest panels show the formaldehyde and formic acid concentrations measured with QCL. The shaded region indicates the fire plume intercepts

3.3. Application of QCL measurements to aircraft exhaust characterization: Nitrous acid, ethylene and other species measured at APEX

Commercial aircraft exhaust emissions have been characterized in the context of the International Civil Aircraft Organization (ICAO) guidelines since the 1970's. During the last 40 years, the atmospheric science community has an improved understanding of the important processes in the atmosphere. Advances in measurement technology have improved gaseous and particulate aircraft engine quantification in both engine test cells that can simulate operation at altitude [29-35] and at cruise altitudes, utilizing instrumentation on "chase" aircraft [36-38]. Much of this effort has focused on quantifying NO_x (NO + NO₂) emissions because of their critical role in ozone chemistry, sulfur oxide emissions because of their role in triggering sulfate aerosol formation, and direct fine particulate emissions because of their role in contrail and cloud formation.

In April of 2004, the Aerodyne Mobile Laboratory [39] participated in the Aircraft Particle Emissions Experiment or APEX, where the engines of the NASA-DC8 research airplane were characterized using state-of-the-art particle instrumentation. Several gas phase instruments were also deployed, including two dual QCL systems and a Pb-salt diode laser based instrument. Figure 9 shows some of the gas phase results from this study. In the top panel, two hydrocarbons, formaldehyde (HCHO) and ethylene (C₂H₄) are seen to decrease logarithmically as the temperature of the combustor is increased at greater throttle settings. In the lower panel, the NO_x species data is presented, including one of the first measurements of nitrous acid (HONO) by QCL spectroscopy. The NO_x species agree well with the ICAO reference points shown in black. The NO data shown in Figure 9 was provided by Changlie Wey (NASA Glenn), and is included for comparison.

The use of quantum cascade laser based TILDAS has only begun to uncover many important findings related to aircraft exhaust and its impact on the atmosphere.

Figure 9. Results from TILDAS measurements at APEX. The measurements, expressed as Emission Index (EI) are shown as a function of the throttle position. The top panel shows a decrease in two hydrocarbons, HCHO and C₂H₄ while the lower panel shows the speciation of NO_x emissions.

4. CONCLUSIONS AND PERSPECTIVES

Our measurements demonstrate that QC lasers can attain the absorbance precision levels obtained with cryogenically-cooled CW Pb-salt lead lasers despite the broader laser linewidths inherent to pulsed operation. Absorbance precisions achieved with a 56-76 m multipass absorption cell are typically on the order of $2 \times 10^{-5} \text{ Hz}^{-1/2}$.

We have demonstrated high precision measurements of several atmospheric key species using a dual QC laser spectrometer. The dual QCL spectrometer allows for simultaneous measurements of two or more species. A carefully selected set of species may provide valuable information to the understanding of complex atmospheric phenomena, as demonstrated with HCHO and HCOOH as indicators of photochemistry and biomass burning. **Table 1** summarizes our current detection capabilities with pulsed QC lasers for various atmospheric species. The detection limits are given for a dual QCL spectrometer with a pathlength of 76 m, and reflect an absorbance precision of $2 \times 10^{-5} \text{ Hz}^{-1/2}$.

Our measurements show that the current intrinsic accuracy of spectroscopically derived concentrations can be 5% or better. We are currently addressing what we believe are the two the most important sources of error: detector non-linearity and pulsed QC laser lineshape.

Current advances in detector manufacturing allow us to expect significant improvements in responsivity, detectivity and linearity, particularly for TE-cooled detectors. An even more important breakthrough is the demonstration of near-room temperature operated CW QC lasers [40-42]. This rapid development, both in laser and detector technology should lead to completely cryogenic-free spectrometers with precisions at least as good as those currently achieved with LN_2 -cooled detectors and pulsed QC lasers.

Table 1. Species detected with pulsed QC lasers using a 76-m multipass absorption cell

Trace gas ^(a)	Wavenumber [cm ⁻¹]	Precision [ppb·Hz ^{-1/2}] ^(b)	LOD (100 s) [ppb] ^(c)
NH ₃	967	0.2	0.06
C ₂ H ₄	960	1	0.5
O ₃	1050	1.5	0.6
CH ₄	1271	0.8	0.4
N ₂ O	1271	0.3	0.1
<i>H₂O₂</i>	<i>1267</i>	<i>3</i>	<i>1</i>
<i>SO₂</i>	<i>1370</i>	<i>1</i>	<i>0.5</i>
NO ₂	1600	0.2	0.1
HONO	1700	0.6	0.3
HNO ₃	1723	0.6	0.3
HCHO	1765	0.3	0.15
HCOOH	1765	0.3	0.15
NO	1900	0.6	0.3
<i>OCS</i>	<i>2071</i>	<i>0.06</i>	<i>0.03</i>
CO	2180	0.5	0.2
N ₂ O	2240	0.2	0.1
¹³ CO ₂ / ¹² CO ₂	2311	0.5 ‰	0.1 ‰

(a) Entries in black come from laboratory and field measurements. Values in red (*italic*) are projections based on HITRAN simulations, and laser linewidths extrapolated from adjacent wavelengths.

(b) 1-s RMS precision [ppb] (1-sigma)

(c) Limit of detection (LOD) is 2-sigma at 100-s averaging time

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