Abstract: We have demonstrated a mid-IR semiconductor laser-based absorption spectrometer for field measurements of ambient CH$_4$. The field sensor uses a Type II Quantum Cascade Laser (or Interband Cascade Laser, ICL) operating near 3.3 μm to monitor a well-isolated line in the $\nu_3$ fundamental band of CH$_4$. The ICL operates in cw mode at cryogenic temperature. The sensor uses a multipass cell that provides an optical path of ~7 meters with an 0.25 m base path. Thermoelectrically-cooled InAs detectors are used along with Balanced Ratiometric Detection to achieve a precision of 15 ppbv for a 60 sec integration time. Several successful field demonstrations were carried out at sites maintained by the University of New Hampshire (UNH).

Keywords: interband cascade laser, methane, climate change, mid-infrared
1. Introduction

Methane is a significant greenhouse gas, with a current global radiative forcing second only to CO$_2$.\textsuperscript{1} Methane has been increasing in concentration since the beginning of the industrial era but its rate of increase has slowed during the 1990s. Recent research is focusing on quantifying sources, both anthropogenic and natural and their response to climate forcings.\textsuperscript{2,3} Global warming and climate change are two current issues of direct concern to scientific research, governmental bodies, and society at large. Important policy decisions are currently being made or planned in order to minimize human-induced climate change. In order to better understand the sources and sinks of CO$_2$, CH$_4$, and other greenhouse gases, and how they change under various climatically related forcings, the North American Carbon Program (NACP) was initiated to foster research in understanding several important questions in carbon cycle science.\textsuperscript{4} The NACP has identified, as one of its highest priorities, the development of high accuracy \textit{in situ} sensors for measurements of CO$_2$, CO, and CH$_4$.

Our prototype sensor for measurements of ambient CH$_4$ uses a Type II Quantum Cascade Laser (or Interband Cascade Laser, ICL) operating near 3.3 $\mu$m to monitor a well-isolated line in the $v_3$ fundamental band of CH$_4$. The sensor also utilizes a compact optical multipass cell having 6.8 m optical path. The sensor's precision is 15 ppbv for a 60 sec acquisition. We demonstrated the sensor at two field sites in collaboration with the University of New Hampshire Climate Change Research Center.
2. Methane Field Sensor

The primary goal for the methane field sensor was to design and fabricate a sensor that could make measurements of ambient CH$_4$ with good precision and accuracy in a package that is man-portable. Our approach was to create a sensor that uses new ICLs in combination with a high sensitivity detection technique. ICLs operate in the mid-IR, allowing us to access transitions in the fundamental bands that have large linestrengths in order to generate useful absorptions (i.e. 1 to 10%). In combination with a high sensitivity detection technique like Physical Sciences Inc.’s (PSI) Balanced Ratiometric Detection, use of an ICL permits the shortest possible optical pathlength and smallest sensor footprint without resorting to a cavity enhanced technique. Target precision was 0.5% of ambient, which is ~9 ppbv out of 1.7 ppmv. This level of precision in experimental data is of direct use to modelers. The CH$_4$ field sensor consists of two major assemblies, the optical breadboard containing the laser, transfer optics, sample cell, and detectors, and the instrumentation module containing the power supplies and system control computer.

2.1 Optical Breadboard

2.1.1 Interband Cascade Laser

The CH$_4$ field sensor utilizes an ICL operating in cw mode at cryogenic temperature and near 3 $\mu$m to monitor CH$_4$ on an isolated absorption line in the $v_3$ fundamental band. The device was provided by Maxion (identification number M14E-5). Characterization data for this device are presented in Figures 1-3. Figure 1 shows the I-V-L curves. The compliance voltage is relatively
high, near 7 V, compared to near-IR TDL devices. Threshold current is very low, at 2 mA at 80 K. Output power is in the 6 mW range near maximum recommended operating current.

The output spectrum of the device was characterized using an FTIR spectrometer with resolution of 0.5 cm\(^{-1}\), or 15. GHz. Emission intensity (around the main operating mode) vs. injection current is shown in Figure 2. Figure 3 shows the output spectrum over a wider frequency range and reveals that the device is not single mode. The side mode suppression is relatively poor at \(\sim -11\) dB. In fact, only approximately half the output power is in the primary mode. This fact impacted the measurement algorithm and calibration and we discuss this further below.

Fortunately, the output spectrum was stable with time. Current state-of-the-art single mode ICLs are now available that operate near room temperature, with high output power, and improved side mode suppression. Meyer and coworkers have recently reported a single-mode ICL operating at 3.6 \(\mu\)m that produces cw output power of 12 mW at room temperature with a side mode suppression ratio of -30 dB.\(^5\) These characteristics are sufficient for most in situ trace gas sensing applications.

We measured the static tuning of the device as a function of temperature and injection current. Figure 4 shows the output frequency as a function of temperature at a fixed injection current of 30.7 mA DC. The measured temperature tuning rate was -0.150 cm\(^{-1}\)/deg K. We also measured the output frequency as a function of injection current at a fixed temperature of 79 K. The measured current tuning rate was -0.051 cm\(^{-1}\)/mA.
The laser was mounted in a custom dewar manufactured by Kadel. The dewar was designed to have a small form factor and measures 3.5 inch in diameter by 7 inch tall. The laser carrier is mounted on a fixture which is itself attached to the side-looking cold finger. The mounting fixture is thermally insulated from the cold finger using a sheet of 0.01 in thick Berquist Sil-pad A2010 material, allowing heat to be applied to the mounting fixture by a small Kapton heater (25 ohm). The temperature of the mounting plate was monitoring using a silicon diode mounted under the laser carrier. A commercial controller from LakeShore Cryogenics (Model 321) monitored the temperature of the Si diode (DT670) and controlled the heater through a feedback loop (1A, 25 W max). This arrangement allowed the temperature of the device to be raised to 91 K at the maximum output of the heater. An important feature of the dewar design is the inclusion of a fiberglass support for the dewar itself. This piece supports the bottom of the cryogen bottle and prevents significant motion in the vertical dimension during cooling. The laser is housed behind a 38 mm diameter x 5 mm thick, uncoated CaF₂ window having a wedge angle of 30 min.

Injection current control for the laser was accomplished using a current controller from Wavelength Electronics (model MPL-250). In addition to its small form factor, another advantage of the unit is that it provides up to 250 mA of current with a compliance voltage of >6 V.
2.1.2 Breadboard and Transfer Optics

The optical breadboard contains the laser and dewar, transfer optics, sample cell, and detectors. A schematic diagram of the optical breadboard is presented in Figure 5. All optical elements are reflective except for the dewar and cell windows and the beamsplitter. The optical elements are 1 in diameter. All optics are mounted on 1 in diameter posts in mounts having precision, lockable adjustment screws. After exiting the dewar, light from the laser is collimated using a reflective microscope objective (15 x, 0.4 NA). The device is 38 mm long by 49 mm in diameter. The working distance is 24 mm and the exit beam diameter is 9.7 mm. The optic was held in a 3 axis precision mount. The obscuration from the secondary mirror support was 27 %. After collimation, the beam is transported to the multipass cell via a simple optics train. A beamsplitter creates a reference beam that is directed onto a detector and signal beam that is injected into the absorption cell. The reference beam is focused onto its detector using an f/4 spherical mirror. An f/4 spherical mirror focuses the signal beam into the absorption cell. The beam exciting the cell is refocused onto its detector using another f/4 spherical mirror.

2.1.3 Multipass Optical Absorption Cell

The multipass cell is a spherical Herriott configuration with a re-entrant design. The optical path is 6.8 meters for a mirror separation of 0.264 m and 26 passes. It is fabricated of aluminum and has an internal volume of ~1 liter. The mirrors are Au-coated stainless steel substrates with HfO₂ coating for hardness and durability. The front, or launch mirror is fixed directly to the cell flange. The back, or return, mirror is held at the correct separation by 4 rods. This creates a
mirror assembly independent of the outer can. The back mirror is adjustable. The cell window is CaF$_2$ and is 1 in diameter with a 30 min wedge. It is not antireflection coated.

The mirror separation and radius of curvature were chosen based on several considerations. The first was that an optical pathlength of 5-8 m was found necessary to generate absorptions of 1-5% on typical lines that might be accessed by the ICL. The second was the desire to keep the physical length of the cell to 0.25 m or less. The third was to use a reentrant design so that the entrance and exit beams were on the same side of the cell. Lastly, we wanted to keep neighboring spots on the spot pattern well separated. The transmission through the cell, including the spot patterns on the mirrors, was modeled with the raytracing program, “TracePro”. This modeling verified that neighboring spots were not overlapping (which can lead to interference effects) and to vary cell parameters to achieve the reentrant condition. Figure 6 shows the calculated spot pattern on the launch mirror assuming a collimated, 3 mm diameter input beam. The mirrors are 1.4 in diameter with a 15 cm focal length and a separation of 26.4 cm. The left plot shows the result of a simple raytrace defined by launching 5 rays, 1 paraxial and 4 at the half width half maximum power radius. The right plot shows the results acquired from TracePro launching 29,000 rays in a Gaussian beam pattern. The exit spot (#26) and the launch spot (#0) are almost exactly overlapped to achieve the reentrant condition.

The cell is thermally stabilized. Thermal modeling calculations indicated that ~ 8 W are required to increase the cell temperature from ambient to 35 C. The heaters require ~ 2 A at start up. Equilibrium at 35 C is reached from startup at 15 C in ~ 60 seconds. The ALGOR computational model was used to validate initial estimates and to ascertain that temperature
uniformity is better than 0.7 C over the length of cell. Conformal heaters were used on the outer surface of the cell. The heaters are controlled with a simple, compact p-i-d controller (Omega).

Pressure in the absorption cell is stabilized at 130 mB. This operating pressure was chosen after a consideration of the spectral environment of the operating line. We desired to maximize the spectral contrast, or differential absorption of the operating line and to minimize the spectral interference from neighboring lines. Spectral modeling revealed that, for operating at ~100 mB, the peak absorption remains close to its maximum while the collisional broadening is significantly reduced.

2.1.4 Gas Handling System

Figure 7 illustrates the gas handling system. A 100 µm precision orifice placed on the inlet to the cell sets the mass flow through the cell. Pressure in the cell is monitored with a compact capacitance manometer and regulated by a controller and an internal p-i-d control loop through action of a proportioning valve. The system is driven by a 1.4 m³/h (23 lpm) diaphragm pump (model MD1 Vacuubrand). Manual shut off valves are used to direct either calibration gas into the cell or ambient air that has passed through a Nafion counterflow drier. A drier is used so that the sensor reports dry air mixing ratios. We used a 24 in long model PD-50 which is capable of drying incoming air having a dew point of 20 C to -22 C, or the dew point of the drying gas, whichever is higher. We used a flow of 1 lpm for the counterflow gas.
The desired mass flow through the sample cell, which is determined by the temperature, pressure, and volumetric flow through the cell, is one of the two primary factors used in sizing the sampling orifice. The desired pressure in the cell is the second primary factor. The pressure differential across the orifice, in combination with the desired mass flow, determines the orifice size. To determine the mass flow through the orifice as a function of orifice size, we evaluated the standard compressible flow expansion equation:

\[
\dot{m} = P_0 A^* \left[ \frac{\gamma W}{R T_0} \left( \frac{2}{\gamma + 1} \right)^{(\gamma+1)/(\gamma-1)} \right]^{1/2}
\]

where \( P_0 \) = source (upstream) pressure, \( A^* \) = orifice area, \( \gamma \) = heat capacity ratio (the ratio of the specific heat capacities for constant temperature and volume, \( c_p/c_v \)), \( W \) = molecular weight, \( R \) = gas constant and \( T_0 \) = source (upstream) temperature. From these calculations, we found, for an orifice size of 0.15 mm (150 \( \mu \)m), the flow rate is 0.25 gm/min at an upstream pressure of 1 atm.

We calculated the volumetric flow rate (at temperature and pressure) that would occur in our gas handling system as a function of mass flow rate and desired cell operating pressure. We found that for a mass flow rate of 0.25 gm/min, the volumetric flow rate in the cell is \(~2\) lpm at 100 mB. The flow rate into the cell from atmospheric pressure is 180 sccm. We then sized our pump to handle these requirements. We measured the residence time of the cell (41 sec, 1/e) by monitoring internal pressure vs. time.
2.1.5 InAs Detectors

The spectrometer uses two matched, TE-cooled InAs detectors. The detectors are Judson model J12TE2-66D-R01M. They are 1 mm diameter and have an NEP = 2.2 pW Hz$^{1/2}$. Each detector is mounted on a two stage TE cooler so that the detectors operate at -40 C. This guarantees that the radial responsivity profile is constant across the detector surface. Operation at reduced temperature does decrease the responsivity at the red end. The responsivity at 3.3 µm = 93 % of peak, at 3.4 µm = 62 % of peak. The detector and coolers are housed in a TO-66 package with a sapphire window. The TECs are operated by dedicated controllers that are mounted in close proximity to the detectors on the breadboard.

The sensor uses our Balanced Ratiometric Detection (BRD) technology. In this dual beam technique, photocurrent from the sample detector is electronically balanced against that from the reference detector so that common mode laser amplitude noise is removed. This technique typically enables measuring absorbances as small as $1 \times 10^{-5}$ in field spectrometers. The beam paths external to the cell are not purged. Instead, we equalized the length of the external reference and signal beam paths after the beamsplitter so as to null out the residual methane absorption. The external path after the beamsplitter is $\sim 1$ m vs 6.8 m of path internal to the cell.

2.2 Instrumentation Module

A system diagram for the CH$_4$ field sensor is presented in Figure 8. The general dimensions of the instrumentation module are: 27 x 22 x 28.5 width x depth x height [in]. The unit weighs
137.5 lbs. The unit draws 150 W of 110 VAC when operating; 75 W of that is used by the computer. A small format desktop computer controls the sensor. Data acquisition is implemented with PCI format boards from National Instruments. Current control for the laser is provided by a Wavelength Electronics controller (MPL-250). The laser is modulated with a negative going ramp produced by the NIDAQ boards. Detector signals are processed by the BRD and acquired by the NIDAQ boards. Cell and air sample temperatures are transduced by thermistors and acquired by the NIDAQ boards. As mentioned before, the cell pressure is controlled by a separate controller based on the output of the pressure transducer. The cell temperature is controlled by a separate controller.

2.3 Sensor Characterization

Several methane absorption lines are within the tuning range of the ICL. Figure 9 shows a HITRAN modeled spectrum near 2938 cm\(^{-1}\) showing several lines in the \(v_3\) fundamental band. The spectrum was calculated for conditions of 1.7 ppmv CH\(_4\) in air at 50 mB, 296 K and for a pathlength of 20 m. With the laser off, the indicated temperature of the laser was routinely 78.2 K. With the heater off, we were able to sweep the laser across the triplet at 2938.2 cm\(^{-1}\). We did this with a current ramp of 21.5 to 28 mA. Initial lab characterization data and some of the initial field demonstration data was obtained using this triplet as the absorption feature. Later, as the laser aged during operation, we found that we could no longer scan over the entire triplet feature. To do so would have required a base temperature less than 77 K. We then switched operation to the single line at 2937.767 cm\(^{-1}\). We did this by increasing the current ramp to scan between 29.5 to 33 mA.
Not all the output power of the laser lies in the primary mode, as shown in Figure 3. Since the detectors respond to all incident power within their spectral bandwidth, we needed to measure the ratio of power in the primary mode to that out of the primary mode. We integrated the emission spectrum of Figure 3 and found that ~50% of the power lies in the primary mode and 50% lies in all the other minor modes combined. We corrected all measured transmission spectra for this factor, since without correction, we measure less absorption than expected. By looking at the long term precision of the measured absorption over the course of a day, we found this number to be stable. We did observe a slow drift in this ratio on the time scale of days to weeks. This effect is corrected for by periodically measuring known calibration gas as part of the measurement protocol.

We characterized the spectral bandwidth of the laser by comparing the observed triplet feature with a HITRAN model of the same spectrum. We convolved a Gaussian lineshape representing the laser with the HITRAN model and varied the width of the Gaussian until the experimental spectrum was matched. Our results are presented in Figure 10. We found the spectral bandwidth of the laser to be 0.012 cm\(^{-1}\) or 360 MHz fwhm. This is in general agreement with data from the manufacturer (100-200 MHz). The results show a disagreement between the observed and modeled strength of the line at 2938.25 cm\(^{-1}\).

We characterized the precision of the sensor by flowing a high precision 2 ppmv CH\(_4\)/air mixture that had been calibrated by National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostic Laboratory (NOAA CMDL) and recording the measured concentration for periods of 1000 sec at a 10 Hz sweep rate. We then performed an Allan
variance analysis of the data. The square root of the Allan variance is plotted vs. averaging time in Figure 11. The Allan variance shows the classic behavior for averaging times shorter than 100 sec. The minimum in the variance yields a precision of 15 ppbv for a 60 sec integration period. The peak absorption for a 2 ppmv CH₄ concentration, 7 m path at 296 K and 0.13 atm pressure is 0.7%. The precision of 15 ppbv represents a noise equivalent absorption (NEA) of 5.3 x 10⁻⁵. A similar analysis for the pressure measurement in the cell showed the precision in the pressure measurement to be 0.0015 mB for a 60 sec integration period.

Our precision compares favorably with results achieved by other researchers. There are only a few ICL absorption spectrometers reported to date. Miller and coworkers combined an ICL with an off-axis Integrated Cavity Output Spectroscopy (ICOS) cell to create a sensor for HCHO. The reported sensitivity is 150 pptv for a 3 sec measurement. Wysocki and coworkers created a dual ICL spectrometer with a 100 m astigmatic Herriott multipass cell that monitors both HCHO and ethane. The sensitivities are 3 ppbv and 150 pptv respectively for a 1 second measurement. Webster and coworkers have flown an ICL-based sensor for CH₄ for upper atmospheric measurements. There have been several QCL-based spectrometers developed for methane sensing. McManus and coworkers report a QC laser sensor operating near 7.9 μm in combination with a 76 m multipass optical cell with sensitivity of 2 ppbv for a 1 second acquisition. Table 1 compares our results in terms of NEA normalized to bandwidth (Hz⁻¹/²) and NEA normalized to both optical pathlength and bandwidth (cm⁻¹ Hz⁻¹/²) with the results of other groups.
Sensors for ambient methane have been developed based on other laser sources as well. Petrov and coworkers have developed a spectrometer for CH\textsubscript{4} using difference frequency generation in periodically poled lithium niobate and report measuring CH\textsubscript{4} to < 1 ppbv.\textsuperscript{11} Richard and coworkers have developed an airborne tunable diode laser sensor for CH\textsubscript{4} that uses a near-IR tunable diode laser operating at 1.67 \mu m in combination with a multipass optical cell providing 250 m of optical path to achieve a sensitivity of 20 ppbv in the upper troposphere/lower stratosphere.\textsuperscript{12} Baer and coworkers also have developed a near-IR tunable diode laser sensor for CH\textsubscript{4} operating at 1.67 \mu m in combination with ICOS, which provides ~2100 m of optical path, to achieve a sensitivity of 1 ppbv for 1 sec acquisition.\textsuperscript{13} There are several current efforts to develop spectrometers to measure the $^{12}$CH\textsubscript{4}/$^{13}$CH\textsubscript{4} ratio.\textsuperscript{14,15}

3. Sensor Field Demonstrations

We demonstrated the sensor at two field sites maintained by the University of New Hampshire Climate Change Research Center. The first site was the Thompson Farm Atmospheric Observatory near Durham, NH.\textsuperscript{16} The laser sensor was collocated with a UNH-maintained GC instrument. The GC and laser instruments shared the same ambient air sampling line. The GC processes an ambient sample and a reference gas sample once every 5 min. The reference calibration gas had a measured mixing ratio of 2.305 ppmv CH\textsubscript{4}/N\textsubscript{2} and was cross calibrated against a primary standard obtained from NOAA ESRL Global Monitoring Division. The primary standard had a mixing ratio of 1.8133 ppmv CH\textsubscript{4}/N\textsubscript{2} ± 0.0006 ppmv CH\textsubscript{4}/N\textsubscript{2}. We implemented the following measurement protocol for the laser sensor. The laser sensor measured ambient sample continuously for 50 min of every hour and measured the same
reference gas as the GC for 10 min. Typical results from 5/11/06 19:17:28 UTC are presented in Figure 12. Excellent agreement was obtained with the GC.

Typically, the ambient methane concentrations measured at the site during the day are near 1.8 ppmv. However, certain conditions can result in excursions from this average. If local winds are calm from dusk to dawn, no mixing occurs, with the result that CO$_2$ from plant respiration and other species such as CH$_4$, build up in the lower layers of the atmosphere. We captured one such thermal inversion event over the night of 6/21 to 6/22/06. During the event, the CO$_2$ concentration increased from the nominal 380 ppmv to almost 550 ppmv. Figure 13 presents data showing the CH$_4$ concentration increasing from 1.8 ppmv to over 2 ppmv during this event. At the start of this measurement, the laser sensor was changed from operation on the multiplet feature at 2938.2 cm$^{-1}$ to operation on the singlet at 2937.767 cm$^{-1}$. Excellent agreement was obtained with the GC instrument.

The second field demonstration site was the Sallie’s Fen Environmental Station (SFES) maintained by the University of New Hampshire and located near Barrington, NH. Emissions of both CO$_2$ and CH$_4$ have been measured at the site from 1990 to the present. Emissions have been measured using a static chamber technique either manually or, since 2001, automatically. Emissions are monitored using a network of 10 automatic chambers and an associated control system.$^{17}$ A measurement cycle consists of sequential periods during which a chamber lid is closed and opened. When closed, emissions of CO$_2$ and CH$_4$ build up inside the chamber. The concentration-time profile is recorded and fluxes calculated from that data. The lid is then opened to refresh the volume with ambient air. Air from each chamber is pulled continuously by
a diaphragm pump to the central measurement location and through a CO₂ NDIR analyzer (Model 6252, LiCor, Inc.). The flow through the system is controlled by a mass flow controller at 5 lpm. A muffin fan is used to mix the chamber head space during lid closure. At the central measurement location, a system computer opens and closes each of the 10 chambers every 3 hours. Air from an individual chamber is selected every 18 min using a switching manifold. The first 8 min flushes the tubing, clearing the sample line of previous air artifacts. At 10 min the lid closes, CO₂ concentration is sampled every 3 s and averaged every 30 s.

A port from which syringe samples were drawn by hand for measurement of CH₄ by GC off site was installed on the exhaust line from the NDIR sensor. The laser sensor also sampled the exhaust line of the NDIR sensor. The air stream was processed through the Nafion dryer before entering the laser sensor. The laser sensor was housed in a temperature-controlled enclosure next to the NDIR sensor and was operated remotely. As before, the laser sensor measured the air sample and periodically switched to the 1.8 ppmv primary reference standard for span calibration. Figure 14 presents data measured by the laser sensor and by the GC. The numbers in the boxes above each peak in the CH₄ concentration represent the particular chamber from which the sample originated. At ~ 13:30 the laser sensor integration period was changed from 60 sec to 3 sec. Breaks in the laser data trace represent the times during which the sensor was sampling the reference gas. Excellent agreement was again obtained with the GC sensor.
4. Conclusions

We have developed and demonstrated an Interband Cascade Laser-based absorption spectrometer for ambient methane. The sensor has a precision of 15 ppbv for a 60 sec integration time. The sensor was demonstrated at Sallie’s Fen Environmental Station of the University of New Hampshire.

5. Acknowledgements

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6. References


4. For background information on the NACP, see www.esig.ucar.edu/nacp.


Biographies

David Sonnenfroh received his Ph.D. in Chemistry from the University of Rochester in 1985 after working with James M. Farrar in the field of chemical reaction dynamics. He held a National Research Council Postdoctoral Research Fellowship with Stephen Leone at the Joint Institute for Laboratory Astrophysics at the University of Colorado and was the first Enrico Fermi Scholar in the Chemistry Division at Argonne National Laboratory. Dr. Sonnenfroh joined PSI in 1990 as a Principal Scientist and became Group Leader for Atmospheric Sciences in 2001. A primary focus of his current research involves the development semiconductor laser-based sensors for use in tropospheric and stratospheric studies of trace gas chemistry and transport. These sensors are based on both near-IR diode laser and mid-IR quantum cascade laser sources. He has developed sensors for NASA and DOE research aircraft, including unmanned aerial vehicles. He is also developing sensors for high precision trace gas measurements in the boundary layer. He currently leads several efforts to develop small automated LIDARs for both aerosol and wind measurements. Additional research interests include the optical properties, microphysics and heterogeneous chemical processes of importance on aerosols.

Richard Wainner received his B.S. with honors in Mechanical Engineering from the University of Florida in 1992. He received his Ph.D. in Aerospace Engineering in 1999 under Jerry M. Seitzman at the Georgia Institute of Technology. His initial focus was on combustion/gas dynamics, fluid mechanics, shear flow and research aimed at improving air/fuel mixing. Dr. Wainner’s later studies concentrated on the application of laser diagnostics in combustion environments. Dr. Wainner then joined the Ignition and Combustion Branch at the Army
Research Laboratory in Aberdeen Proving Ground, MD under an ASEE post-doctoral fellowship. There, he studied the detection of lead in soil and paint via laser-induced breakdown spectroscopy, and gas species monitoring via tunable diode laser absorption spectroscopy.

Dr. Wainner joined Physical Sciences Inc. in January 2001. He has been involved in several programs aimed at miniaturization and commercialization of tunable diode laser sensors using wavelength modulation spectroscopy. Dr. Wainner has also been involved in the development of portable sensors using spark-induced breakdown spectroscopy (SIBS) for the detection of heavy metals in soils and aerosols and for airborne bioagent threats.

Mark Allen received his B.S. with honors in Mechanical Engineering in 1981 from the University of Kentucky. He received M.S. (1982) and Ph.D. degrees (1987) in Mechanical Engineering from Stanford University under the guidance of Prof. Ronald K. Hanson. His research included development of techniques and instrumentation for laser-based probes of species concentration fields in reacting flows. Since joining Physical Sciences Inc. in 1987, Dr. Allen has continued his research in the development of laser and optical devices, sensor systems, and measurement techniques. He is currently Vice-President of Photonics at PSI, where he directs research and development of advanced sensor and optical components for medical, industrial, aerospace, environmental, and security applications. He is an author of over 230 papers and presentations in laser-based sensors, spectroscopy, and combustion. These include 30 invited presentations in the U.S. and abroad, as well as several book chapters.

Ruth K. Varner received her BS in Geology from Hartwick College in 1991 and her M.S. in Hydrology from the University of New Hampshire (UNH) in 1993. Her PhD, awarded in 2000,
is in Earth Sciences - Geochemical Systems also from UNH. Dr. Varner is currently a Research Associate Professor in the Complex Systems Research Center in UNH’s Institute for the Study of Earth, Oceans, and Space and in the Department of Earth Sciences. Her research is focused on using varied field techniques to understand the cycling of radiatively important trace gases in terrestrial and marine ecosystems. Most recently, her work has focused on using a combination of long term measurement of fluxes in conjunction with field manipulations and isotopic methods to understand the cycling of carbon dioxide and methane in wetland ecosystems.
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<th>Group</th>
<th>Species</th>
<th>NEA (Hz$^{1/2}$)</th>
<th>NEA (cm$^{-1}$ Hz$^{1/2}$)</th>
<th>Notes</th>
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<td>CH$_4$</td>
<td>$3.5 \times 10^{-4}$</td>
<td>$5.0 \times 10^{-7}$</td>
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<td>$1.5 \times 10^{-10}$</td>
<td>TDL (1.6 μm), 2100 m path</td>
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Figure 1. V-I and L-I curves for cryogenic ICL M14E operating at 80 K.

Figure 2. Output spectrum of device M14E-5 at 80 K measured with FTIR spectrometer.
Figure 3. Output spectrum of device M14E-5 at 80 K measured with FTIR spectrometer.

Figure 4. Output frequency as a function of temperature for device M14E-5 at a fixed injection current of 30.7 mA.
Figure 5. Schematic diagram of the optical breadboard.

Figure 6. Simple calculation of spot pattern on launch (front) mirror (left).

Raytrace calculation of spot pattern using TracePro (right).
Figure 7. Gas handling schematic.

Figure 8. System level schematic.
Figure 9. HITRAN model spectrum near 2938 cm\(^{-1}\) of 1.7 ppmv CH\(_4\) in air at 296 K and 50 mB for a 20 m path.

Figure 10. HITRAN model spectrum near 2938.2 cm\(^{-1}\) of 1.7 ppmv CH\(_4\) in air at 296 K and 130 mB for a 7 m path.
Figure 11. Allan variance analysis showing precision of 15 ppbv for a 60 sec integration period.

Figure 12. Ambient methane measured at Thompson Farm AirMap site by the GC and the laser sensors. Data from 5/11/06 19:17:28 UTC.
Figure 13. Ambient methane measured at Thompson Farm AirMap site by the GC and the laser sensors. Data from 6/21/06 20:24 EDT.
Figure 14. Ambient methane measured at Sallies Fen site by the GC and the laser sensors.

Data from 7/20/06 12:00 EDT.