Chemical sensors based on quantum cascade lasers

Frank K. Tittel[*a], Anatoliy A. Kosterev[a], Michel Rochat[b], Mattias Beck[b], and Jerome Faist[**b]
[a]Rice University; [b]University of Neuchatel

ABSTRACT

There is an increasing need in many chemical sensing applications ranging from industrial process control to environmental science and medical diagnostics for fast, sensitive, and selective gas detection based on laser spectroscopy. The recent availability of novel pulsed and cw quantum cascade distributed feedback (QC-DFB) lasers as mid-infrared spectroscopic sources address this need. A number of spectroscopic techniques have been demonstrated. For example, the authors have employed QC-DFB lasers for the monitoring and quantification of several trace gases and isotopic species in ambient air at ppmv and ppbv levels by means of direct absorption, wavelength modulation, cavity enhanced and cavity ringdown spectroscopy. In this work, pulsed thermoelectrically cooled QC-DFB lasers operating at ~15.6 μm were characterized for spectroscopic gas sensing applications. A new method for wavelength scanning based on the repetition rate modulation was developed. A non-wavelength-selective pyroelectric detector was incorporated in the gas sensor giving an advantage of room-temperature operation and low cost. Absorption lines of CO_2 and H_2O were observed in ambient air providing information about the concentration of these species.

1. INTRODUCTION

Quantum cascade (QC) laser technology has made significant advances since its first introduction by Capasso et al in 1994[1,2]. One aspect of this progress is the extension of the available wavelength coverage in the mid-infrared spectral range. Presently, type-I QC laser can be engineered to emit at any wavelength from 4.5 to 24 μm. Most recently a QC laser operating at λ=66 μm was reported [3,4], which represents the availability of semiconductor quantum emitters in the terahertz region. This extended spectral coverage opens increased opportunities for chemical sensing applications for QC lasers. For example, benzene can be detected most efficiently at a wavelength of ~14.8 μm (674 cm^{-1}), where there is a strong narrow Q-branch of its ν_4 vibrational mode[5]

One of the most attractive features of QC lasers is their ability to be operated within the temperature range of thermoelectric coolers (TECs)[2,6-7]. Such devices are especially attractive for portable spectroscopic gas sensors[8]. However, most thermoelectrically cooled QC lasers require high current and must be driven in a low-duty cycle pulsed mode to prevent overheating of the active region. This mode of operation sets specific challenges for spectroscopic applications. Laser line broadening must be minimized and a method for laser frequency tuning must be developed .

At longer wavelengths photodetectors that do not require cooling below liquid nitrogen temperatures are limited. Although HgCdTe photovoltaic detectors have their long cut-off wavelength at 11.5 μm, photoconductive detectors based on the same material can be used up to 22 μm, but require cryogenic cooling, which should be preferably avoided in a portable gas sensor design. Therefore a thermal (pyroelectric) detector, which requires no cooling and has a flat response over the wide spectral range was employed in this work.

Spectroscopic measurements of CO_2 and H_2O concentrations present in ambient air were performed to evaluate the new signal detection and wavelength scanning techniques developed in this work for two pulsed QC-DFB lasers operating at ~15.6 μm. The methodology developed in this work can be readily transferred and applied to volatile organic compounds (VOCs), in particular benzene detection with the availability of a 14.8 μm pulsed QC-DFB laser[5].

---

*fkt@rice.edu; phone 1 713 348-4833; fax 1 713 348-5686; http://www.ece.rice.edu/lasersci/; Rice University, MS 366, 6100 Main St., Houston, TX, USA 77005; **jerome.faist@iph.unine.ch; University of Neuchatel, Neuchatel, Switzerland

2. EXPERIMENTAL DETAILS

The experimental setup for the acquisition of spectroscopic data with a λ=15.6 μm QC-DFB laser is shown in (Fig. 1). The laser chip was mounted on a three-stage TEC inside an evacuated housing[8,9]. The output window of the laser housing was tilted 5° to suppress optical interference fringes caused by reflections from its surfaces. The pulsed laser driver (Directed Energy, Inc. DLD-100B) produced current pulses with the same duration as the TTL gate pulses with a minimum pulse duration of 14 ns. The gate pulses were generated by a custom-built pulse generator. The pulse repetition rate was controlled by an external voltage. Two PCMCIA cards (National Instruments) were used with a laptop computer for both laser temperature control and data acquisition. A DAQCard™-1200 was used exclusively for laser temperature control through a Proportional-Integral-Derivative (PID) algorithm, while a DAQCard™-AI-16XE-50 card was used for data acquisition. A 45 cm long single-pass gas cell equipped with ZnSe Brewster windows was employed in the spectroscopic measurements.

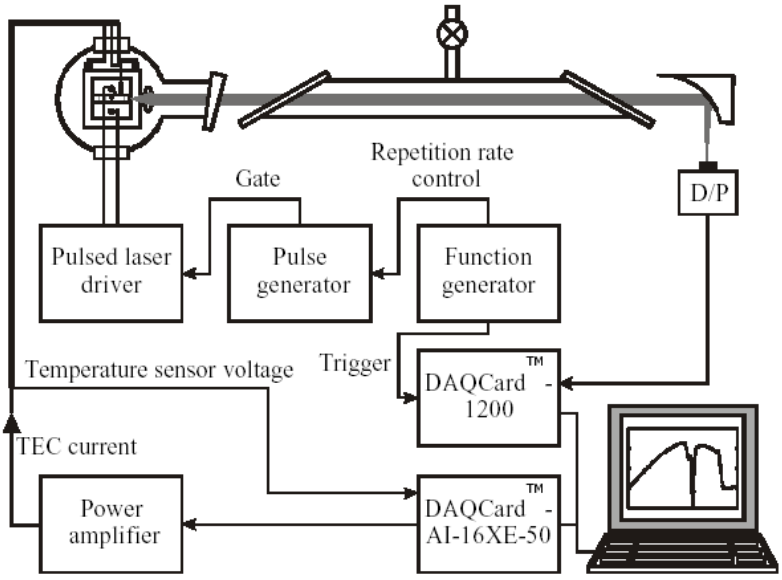

Fig. 1: Long wavelength mid-infrared QC-DFB laser based gas sensor

We used a pyroelectric detector (LIE 311f, InfraTec®) in a current mode with a Rice-developed preamplifier to detect the laser radiation. The responsivity of this detector varies <2% in the spectral range from 1 to 17 μm and exhibits useful sensitivity up to 25 μm. Our tests show that the active area of the detector is circular with an almost flat sensitivity profile of 1.2 mm diameter. The detector/ transimpedence preamplifier bandwidth was measured to extend from 8 to 1,150 Hz. At higher modulation frequencies the response dropped at a rate of 4.25 dB/octave. When the QC laser radiation was applied, a number of peaks at various harmonics of the power line frequency (60 Hz) appeared. This noise can be avoided by the appropriate choice of the modulation frequency. At 200 Hz the D/P noise is 10^{-5} V in a 1 Hz band. The D/P sensitivity was calibrated using a 1.66 μm diode laser and power meter and found to be 3.84 V/mW. Thus if the laser power is 0.1 mW and the modulation frequency is 200 Hz, the SNR in a 1 Hz band exceeds 38,000 , which means that the detectable absorption is $<3\times10^{-5}$. Such a performance is adequate for most gas-sensing applications.

A QC-DFB laser chip designed for near-room temperature operation in a low duty cycle mode was provided by the University of Neuchatel[10]. The chip originally contained two single-frequency lasers. Both devices were electrically similar to a 3Ω resistor. Their tuning characteristics were initially obtained at the University of Neuchatel using an FTIR spectrometer, and subsequently verified at Rice University by comparing the acquired absorption spectra of CO_2 with HITRAN-based simulations[13]. The first laser (*Laser I*) operated at ~646 cm^{-1} with a temperature tuning coefficient of -0.053 cm^{-1}/K, and the second laser (*Laser II*) at ~637 cm^{-1} with a temperature tuning coefficient of -0.048 cm^{-1}/K. The lasing threshold for both devices was ~7A (10 kA/cm^2) at -40°C , for current pulses of 50 ns duration at a 267 kHz pulse

repetition rate. Both QC lasers operated up to +30°C. A peak current of up to 18 A was applied to the lasers, which resulted in an average power of > 1 mW for the pulse durations and repetition rates reported above. However, for spectroscopic measurements the pulse duration and peak current was restricted to lower values in order to maintain a sufficiently narrow laser linewidth . In most of the experiments the pulse duration was set to τ=20 ns and the peak current to $I \approx 10$A. For such conditions and a laser temperature of T= -20°C the maximum laser power detected after the absorption cell was 0.18 mW. It should be noted that both the collimating lens and the laser housing window were ZnSe optics, AR coated for 8 to 12 μm and therefore introduced power losses at 15.5 μm.

The aspherical collimating lens inside the laser housing with a focal length of 3 mm was aligned so as to provide the narrowest beam cross-section at a distance of 40 cm from the laser housing window. This distance corresponds to ~55 cm from the lens. We performed a series of experiments with *Laser I* to establish the minimum laser linewidth. A 45 cm long gas cell was filled with 1.3 Torr of CO_2. The laser was excited by a sequence of pulses with the constant amplitude I, duration τ, and repetition rate f, while the laser temperature was continuously varied from ~-20°C to 0°C to provide frequency tuning. The laser beam was mechanically chopped at 637 Hz. The observed CO_2 absorption lines were readily assigned and provided absolute frequency calibration. The laser frequency depended linearly on temperature, in agreement with the earlier published results[11,12] The observed width of the CO_2 absorption line at 645.9407 cm^{-1} was compared for different values of I and τ. The best linewidth with a FWHM $\Delta\nu_{exp}$=0.007 cm^{-1} (210 MHz) was obtained with τ=17 ns, I=9A (~5% above threshold) and a 1 MHz pulse repetition rate. The average laser power reaching the detector was 17 μW. The theoretical FWHM of this partially saturated absorption line is $\Delta\nu_{th}$=0.002 cm^{-1} (60 MHz). Both experimental and simulated lineshapes can be reasonably well fitted with a Gaussian function. Therefore, the QC laser linewidth can be estimated to be $\Delta\nu_l=[(\Delta\nu_{exp})^2-(\Delta\nu_{th})^2]^{1/2} \approx 200$ MHz. An integration of the area under each curve shows a good agreement between the theoretical and experimental data, confirming that the laser radiation is concentrated in a single laser mode. Spectral properties of *Laser II* were similar to those of *Laser I*. After completion of the linewidth optimization experiments *Laser I* was accidentally damaged, and all subsequent measurements described below were performed with *LaserII*.

A pyroelectric detector requires modulated signals, since it does not detect CW radiation. A mechanical optical chopper is convenient in laboratory operation, but not desirable in portable gas analyzers. Therefore, we investigated the feasibility of electronic laser beam chopping (e-chopping): a train of nanosecond current pulses applied to the laser is switched ON and OFF at a certain frequency Ω. This scheme has the added advantage of reduced power consumption by both the laser and the TEC. We also found that the average laser power during ON periods was about 1.7 times higher compared to the mechanical chopping mode at the same peak pump current and laser wavelength. The laser wavelength was tuned, as previously, by changing the laser substrate temperature.

3. CO_2 AND H_2O CONCENTRATION MEASUREMENTS IN AMBIENT AIR

For many applications it is preferable to scan the laser temperature electronically (i.e by some kind of the laser current manipulation) rather than by changing the substrate temperature[7]. Temperature scans are intrinsically slow, and there is always some lag between the temperature sensor readings and the actual temperature of the laser active region complicating the processing of spectral data. A common technique for fast-scanning of the pulsed QC-DFB laser wavelength is to apply a modulated (usually as a triangular ramp) sub-threshold current in addition to short intense pulses[14]. This technique works well if the average power dissipation resulting from the train of nanosecond pulses is small. However, this is not the case for the 15.5 μm laser used in this work and operated with a ~1 MHz pulse repetition rate. With I~10A and a resistivity R~3-4 ohms, the peak power dissipation exceeds 300 W which results in 3W or more of average dissipation at a 1% duty cycle. This generates a significant load to the TEC, and it is not desirable to further increase this load by adding a sub-threshold QC laser current. Furthermore, the laser exhibits a low temperature tuning coefficient. We have observed that an ON-OFF modulated sub-threshold current of up to 280 mA (~1W of additional power dissipation) does not result in noticeable laser line split.

A possible scheme to address this issue is to modulate the peak current of the short pulses analogous to the way the wavelength of a CW QC-DFB or diode lasers is normally scanned. However, this approach has a significant shortcoming. The linewidth and spectral shape of the pulsed QC-DFB laser emission strongly depends on the pump current unlike the case for CW operation.

Therefore, we developed a technique for fast scanning of the pulsed laser wavelength by modulating the repetition rate f of the laser pulses. In this case the thermal dissipation in the laser is directly proportional to the control voltage V_f applied to the voltage-to-frequency converter. The repetition rate was linearly swept from 100 kHz to 1,000 kHz in ~11 ms, followed by an OFF period of the same duration to allow the pyroelectric detector to relax. In this mode the average laser power rises up to 810 kHz of the repetition rate followed by a roll-off because of the laser heating. The peak detector signal corresponds to a laser power of 130 μW. In this case, the pulse duration and current were set to τ=20 ns and I=9.5A, respectively. These values were chosen to satisfy a compromise between the span of the wavelength scan and the laser linewidth (both grow with a per pulse dissipation of $W \sim \tau I^2$).

An absolute calibration of the laser frequency for fast wavelength scans was performed using CO_2 absorption lines in the same way as is possible for temperature scans. For a detailed relative frequency calibration we used interference fringes created by two air-separated uncoated ZnSe surfaces.

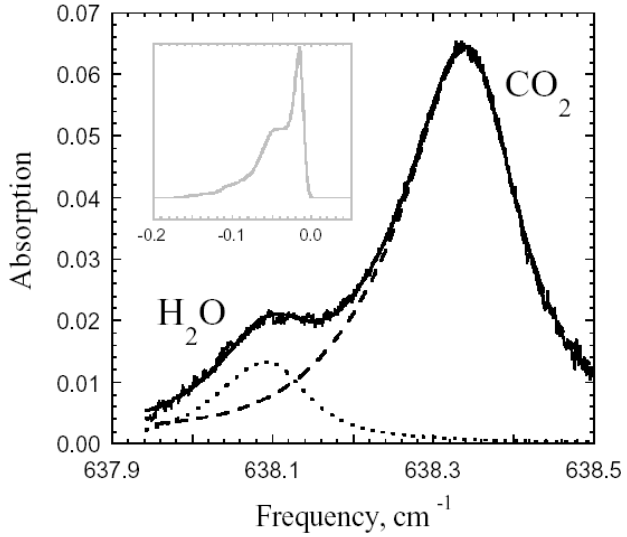

Fig. 2 : Water and carbon dioxide absorption lines in laboratory air. Data was acquired using the fast scan technique. The line exhibiting noise is the experimental absorption. The bold solid line is a fit of the absorption with two adjustable parameters: the peak intensities of the two lines, and the dashed curves are contributions to the absorption from each line. An insert shows the spectral line shape of the laser, horizontal scale in cm^{-1}.

In order to measure atmospheric concentrations of H_2O and CO_2 , a 45 cm long gas cell placed in the QC-DFB laser beam path was initially evacuated and then filled with air at atmospheric pressure. These two data sets were used to obtain the absorption spectrum of ambient air shown in Fig 2. This spectrum was fitted by the function

$$A(\nu) = k_1 h_1(\nu) + k_2 h_2(\nu)$$

where the functions $h_i(\nu)$, i=1,2 represent absorption by CO_2 and H_2O, respectively, simulated using HITRAN-PC and then convolved with an instrument function. The instrument function is shown as an insert in Fig.2 and was obtained by acquiring a CO_2 absorption spectrum at low pressure with a subsequent smoothing. The dashed and dotted curves in Fig 2 show the functions with the best fit coefficients, which correspond to a CO_2 concentration of 465 ppmv and H_2O partial pressure of 5.1 Torr (25% humidity at +22°C).

In order to estimate an input of the pyroelectric detector noise into the data shown in Fig. 2 we used the data acquisition card bandwidth of 66 kHz from its specifications at a gain of 10. Since each of the two data sets used to obtain the absorption spectrum is a result of averaging of 100 scans, the bandwidth is reduced to 660 Hz. The D/P noise

density at this frequency is 13 μV/Hz^{½}. Substraction of the two data sets increases the noise $\sqrt{2}$ times. So, the expected noise is $13\frac{\mu V}{\sqrt{Hz}} \times \sqrt{660\,Hz} \times \sqrt{2} = 470\,\mu V$. Taking into account that the maximum D/P signal was ~470 mV, we obtain a SNR=1,000. In other words, the D/P related point-to-point noise in the absorption spectrum should be ~10^{-3}. This value is in a good agreement with what is observed in Fig 2.

The CO_2 concentration values obtained are reasonable for, but the calculated humidity appears to be too low. Typical hygrometer readings in the laboratory are in the 60% to 70% range. We checked the data by acquiring absorption spectra at 240 Torr of air in the cell, when the absorption lines of CO_2 and H_2O were almost completely separated. The area under H_2O line was calculated from the experimental data and then compared to HITRAN based simulations. This procedure resulted in a 4.9 Torr of H_2O partial pressure, in a good agreement with the 5.1 Torr found previously. We believe that this discrepancy with the hygrometer readings indicates an inaccuracy in the HITRAN'96 data with respect to this particular rotational H_2O band.

4. CONCLUSIONS

We have demonstrated that a pulsed QC-DFB laser operating in the spectral region beyond 10 μm can be used in combination with a low cost pyroelectric detector for sensitive absorption spectroscopy. This detector can achieve a <0.003% absorption detectivity in a 1 Hz bandwidth with 0.1 mW of laser power. A novel scanning technique of the optical laser frequency by varying the repetition rate of the QC laser current pulses was demonstrated and provides a convenient means to perform fast wavelength scans. This method can potentially be used to modulate laser wavelengths at up to several kHz frequencies. CO_2 and H_2O concentration measurements in ambient air were performed. Water vapor concentrations were monitored by a rotational absorption line. To the best of our knowledge, this represents the first observation of a pure rotational line obtained with a QC laser.

ACKNOWLEDGEMENTS

Financial support of the work performed by the Rice group was provided by the National Aeronautics and Space Administration (NASA), Institute for Space Systems Operations (ISSO), the Texas Advanced Technology Program, the National Science Foundation, and the Welch Foundation. The work performed at the University of Neuchatel, Switzerland was partially supported by the Swiss National Science Foundation.

REFERENCES

1. J. Faist, F. Capasso, D. L. Sivco, C. Sirtori, A. L. Hutchinson, A. Y. Cho, "Quantum Cascade Lasers", Science **264**, pp. 553-556, 1994.
2. F. Capasso, C. Gmachl, R. Paiella, A. Tredicucci, A. L. Hutchinson, D. L. Sivco, J. N. Baillargeon, A. Y. Cho, "New frontiers in quantum cascade lasers and applications", IEEE Selected Topics in Quantum Electronics **6**, pp. 931-947, 2000.
3. M.Rochat, L.Ajili, H.Willenberg, J.Faist, H.Beere, G.Davies, E.Linfield, D.Ritchie, submitted to Applied Physics Letters, May 2002.
4. R. Köhler, A. Tredicucci, F. Beltram, H. E. Beere, E. H. Linfield, A. G. Davies, D. A. Ritchie, Rita C. Lott, "Terahertz Semiconductor-Heterostructure Laser", Nature **417**, pp. 156-159, 2002.
5. W.Chen, F.Cazier, F.K.Tittel and D. Boucher, "Benzene concentration measurements using difference frequency laser absorption spectroscopy", Applied Optics **39**, 6238-6242, 2000.
6. D.Hofstetter, M.Beck, T.Aellen, J.Faist, U. Oesterle, M. Ilegems, E. Gini, H. Melchior "Continuous wave operation of a 9.3 micron quantum cascade laser on a Peltier cooler", Appl. Phys.Lett **78**, pp. 1964-1966 ,2001.
7. A.A Kosterev and F.K.Tittel, "Chemical sensors based on quantum cascade lasers", IEEE Journal of Quantum Electronics **38**, pp. 582-591, 2002.

8. A. A. Kosterev, R. F. Curl, F. K. Tittel, R. Köhler,C. Gmachl, F. Capasso, D. L. Sivco, A. Y. Cho, "Transportable automated ammonia sensor based on a pulsed thermoelectrically cooled QC-DFB laser", Applied Optics **41**, pp. 573-578, 2002.

9. A. A. Kosterev, R. F. Curl, F. K. Tittel, R. Köhler, C. Gmachl, F. Capasso, D. L. Sivco, A. Y. Cho, S. Wehe, M. Allen, "Room temperature quantum cascade laser based gas sensor for continuous monitoring of atmospheric CO", Applied Optics **41**, pp. 1169-1173, 2002.

10. M.Rochat,M.Beck and J.Faist, "Long-wavelength λ = 16 microns, room-temperature, single-frequency quantum-cascade lasers based on a bound-to-continuum transition" Appl. Phys. Lett **79**, pp. 4271-4273, 2001.

11. R. Köhler, C. Gmachl, F. Capasso, A. Tredicucci, D. L. Sivco, A. Y. Cho, **"**Single-mode tunable quantum cascade lasers in the spectral range of the CO2 laser at lambda=9.5-10.5 microns" IEEE Photonics Technology Lett. **12**, pp. 474-476, 2000.

12. A. A. Kosterev, F. K. Tittel, C. Gmachl, F. Capasso, D. L. Sivco, J. N. Baillargeon, A. L. Hutchinson, A. Y. Cho, "Trace gas detection in ambient air with thermoelectrically cooled QC-DFB laser", Applied. Optics. **39**, pp. 6866-6872, 2000.

13. L.S. Rothman, C.P. Rinsland, A. Goldman, S.T. Massie, D.P. Edwards, J.-M. Flaud,A. Perrin, C. Camy-Peyret, V. Dana, J.-Y. Mandin, J. Schroeder, A. McCann, R.R. Gamache, R.B. Wattson, K. Yoshino, K.V. Chance, K.W. Jucks, L.R. Brown,V. Nemtchinov, P. Varanasi: J. Quant. Spectrosc. Radiat. Transfer 60, 665, 1998.

14. S.W. Sharpe, J.F. Kelly, J.S. Hartman, C. Gmachl, F. Capasso, D.L. Sivco, J.N. Baillargeon, and A.Y. Cho, "High-resolution (Doppler-limited) spectroscopy using quantum-cascade distributed-feedback lasers" Opt. Lett. **23**, pp. 1396-1398, 1998.