Intracavity widely-tunable quantum cascade laser spectrometer

Richard A. Brownsword and Damien Weidmann*

Space Science & Technology Department, STFC Rutherford Appleton Laboratory, Harwell Oxford Campus, Didcot, Oxfordshire, OX11 0QX, UK

*damien.weidmann@stfc.ac.uk

Abstract: A grating-tuned extended-cavity quantum cascade laser (EC-QCL) operating around 7.6 µm was assembled to provide a tuning range of ~80 cm$^{-1}$ with output power of up to 30 mW. The EC-QCL output power was shown to be sensitive to the presence of a broadband absorbing gas mixture contained in a 2-cm cell introduced inside the extended laser cavity. In this arrangement, enhanced absorption relative to single path linear absorption was observed. To describe observations, in the QCL rate-equation model was included the effect of intracavity absorption. The model qualitatively reproduced the absorption behavior observed. In addition, it allowed quantitative measurements of mixing ratio of dimethyl carbonate, which was used as a test broadband absorber. As the intracavity absorber modifies the laser threshold current, phase-sensitive detection of the laser threshold current was found to be the most attractive way to determine the mixing ratio of the absorber. The dimethyl carbonate detection limit was estimated to be 1.4 ppmv for 10 second integration. Limitations and possible ways of improvements were also identified.

©2013 Optical Society of America

OCIS codes: (140.5965) Semiconductor lasers, quantum cascade; (300.6360) Spectroscopy, laser; (280.3420) Laser sensors.

References and links

1. A. A. Kosterev and F. K. Tittel, “Chemical sensors based on quantum cascade lasers,” IEEE J. Quantum Electron. 38(6), 582–591 (2002).
2. R. F. Curl, F. Capasso, C. Gmachl, A. A. Kosterev, B. McManus, R. Lewicki, M. Pusharsky, G. Wysocki, and F. K. Tittel, “Quantum cascade lasers in chemical physics,” Chem. Phys. Lett. 487(1-3), 1–18 (2010).
3. R. Maulini, M. Beck, J. Faist, and E. Gini, “Broadband tuning of external cavity bound-to-continuum quantum-cascade lasers,” Appl. Phys. Lett. 84(10), 1659–1661 (2004).
4. G. Wysocki, R. F. Curl, F. K. Tittel, R. Maulini, J. M. Bulliard, and J. Faist, “Widely tunable mode-hop free external cavity quantum cascade laser for high resolution spectroscopic applications,” Appl. Phys. B 81(6), 769–777 (2005).
5. T. Tsai and G. Wysocki, “External-cavity quantum cascade lasers with fast wavelength scanning,” Appl. Phys. B 100(2), 243–251 (2010).
6. B. Mroziewicz, “External cavity wavelength tunable semiconductor lasers – a review,” Opto-Electron. Rev. 16(4), 347–366 (2008).
7. M. C. Phillips, M. S. Taubman, B. E. Bernacki, B. D. Cannon, J. T. Schiffer, and T. L. Myers, “Design and performance of a sensor system for detection of multiple chemicals using an external cavity quantum cascade laser,” Proc. SPIE 7608, 76080D, 76080D-11 (2010).
8. S. Welzel, G. Lombardi, P. B. Davies, R. Engeln, D. C. Schram, and J. Röpcke, “Trace gas measurements using optically resonant cavities and quantum cascade lasers operating at room temperature,” J. Appl. Phys. 104(9), 093115 (2008).
9. D. J. Hamilton and A. J. Orr-Ewing, “A quantum cascade laser based optical feedback cavity-enhanced absorption spectrometer for the simultaneous measurement of CH$_4$ and N$_2$O in air,” Appl. Phys. B 102(4), 879–890 (2011).
10. M. C. Phillips and M. S. Taubman, “Intracavity sensing via compliance voltage in an external cavity quantum cascade laser,” Opt. Lett. 37(13), 2664–2666 (2012).
11. G. Medhi, A. V. Muravyov, H. Saxena, C. J. Fredrickson, T. Brusentsova, R. E. Peale, and O. Edwards, “Intracavity laser absorption spectroscopy using mid-IR quantum cascade laser,” Proc. SPIE 8032, 80320E, 80320E-7 (2011).
1. Introduction

Quantum cascade lasers (QCLs) possess a number of characteristics which make them attractive sources for the development of gas-phase chemical sensors. The ability to produce high optical power (tens of mW) in the mid-IR region allows sensitive detection of a wide range of gas-phase molecules via infrared absorption spectroscopy on their intense fundamental transitions. Besides, the compact nature and the ability of QCLs to operate at ambient temperatures facilitates their development as practical field-deployable devices [1, 2]. When operated in external cavity (EC) configuration [3–5] that includes a suitable frequency-selective element, the broad gain profile of a Fabry-Perot QCL (typically >100 cm⁻¹) becomes accessible. This offers the additional advantage of wide spectral coverage with a single device, allowing spectral features from different species to be sampled, or the entire broadband absorption typical of large molecules such as volatile organic compounds (VOCs) to be recorded [2, 6]. Broadband, sensitive, laser spectroscopy of large molecules with unresolved rotational structure would offer a compact alternate solution to gas chromatography, mass spectrometry analysis techniques, in a compact package, and with greater temporal resolution for analysis.

Despite their advantages, EC-QCL devices suffer from the sensitivity limitations inherent to tunable infrared absorption spectroscopy. Multipass absorption or resonant cavity cells, in conjunction with phase-sensitive methods, can be used to increase the sensitivity of EC-QCL device to the ppb detection level [7–9], at the expense of increased size, complexity, and cost. Intracavity absorption (ICA) could offer an alternative or additional means of sensitivity enhancement. In this arrangement, the absorbing sample is introduced into the laser cavity [10, 11], hence potentially offering a way to implement compact and broadband spectroscopic sensors. Sensitivity of ICA spectroscopy depends on the properties of the laser employed but also, crucially, on whether the laser operates single- or multi-mode [12]. Effective absorption length demonstrated for multi-mode ICA devices, are in the range 10–10000 km, corresponding to sensitivity enhancements over single path absorption spectroscopy of up to ~10⁷. Such devices, however, require spectral analysis, which implies an additional, potentially bulky, external spectrometer. Furthermore, extraction of quantitative data from the ICA spectra is not straightforward [12]. In contrast, intracavity absorption performed with a single-mode laser does not require an external spectrometer, but provides less absorption enhancement than multimode ICA. A sensitivity enhancement of ~100 has been demonstrated using near infrared diode lasers [13] and simulations have suggested that enhancements from 10⁴ to 10⁷ [12, 14] are achievable, though these values are likely to be limited by practical considerations such as injection current stability and the sensitivity of infrared detectors.

In this work, the implementation of a grating-tuned EC-QCL and its application to quantitative ICA measurements is reported. In the first section, the experimental layout is described as well as the first empirical ICA signals observed, which demonstrated an ICA enhancement. In a second section, a physical model based on QCL rate equations is
developed so that quantitative concentration measurements can be made. In the last section before conclusion, results obtained on diluted mixtures of a broadband absorber such as dimethyl carbonate are presented.

2. Experiment

2.1 Optical layout

The EC-QCL system was built upon a Fabry-Perot QCL chip exhibiting a maximum gain at 7.63 μm (Maxion technologies, type FQ7-M738) [15]. The QCL facet receiving the external cavity feedback was treated with an anti-reflection (AR) coating with reflectivity of ~0.2% at 7.8 μm. The other QCL facet was left uncoated. The QCL was mounted on a TE-cooled cold plate in a custom housing. This housing was attached to a three-axis translation stage to allow optimization of feedback from the external cavity. Temperature and current control of the QCL chip was provided by linear PID controllers (ILX Lightwave LDT-5545B and LDX-3232 respectively). The laser operating temperature was 17 °C.

The overall experimental layout of the ICA EC-QCL is depicted in Fig. 1. Emission from the facet internal to the EC was collimated by an AR-coated germanium aspheric lens (25 mm focal length, f number of 1) and directed onto a reflection grating (150 lines/mm, blaze 10.6 μm) mounted in first-order Littrow configuration such as to receive S-polarized light. The grating was mounted on a combined rotation-translation piezo-actuated stage (Newport AG-PR100 and AG-LS25-27) to allow simultaneous tuning of the grating angle and the cavity length. A microswitch with 1 μm sensitivity, configured to generate a logic transition when activated, was used to provide a reference point for the grating angle. A 2-cm long gas cell is introduced inside the extended laser cavity, between the germanium lens and the grating. This cell was fitted with 38 mm diameter wedged ZnSe windows, coated with a broadband AR coating centered at 7.6 μm. Gas handling of the intracavity cell was controlled by miniature solenoid valve inlets allowing easy flushing and sample mixture selection. The EC-QCL output was monitored by collimating emission from the external facet and directing it to a Peltier cooled photodiode (Vigo Systems PV-2TE-10.6). Alternatively, a flip mirror could direct the radiation to a Bristol 721 wavemeter for wavelength calibration. The signal acquisition, piezo actuator control, and valve control was performed via a DaqCard (NI USB-6284) and LabView software from National Instruments.

![Fig. 1. Schematic and photograph of the ICA EC-QCL device.](image)

2.2 EC-QCL characteristics

Once the alignment of the external cavity had been carried out, operation of the EC-QCL was characterized in term of laser threshold current and output power. Figure 2(a) shows the optical power vs. injection current for three cases: 1) the bare QCL chip without feedback, 2) the QCL chip integrated into the EC, and 3) reference data from the manufacturer of a similar chip with one facet coated for high reflection. The third case can be assumed as the strong feedback limit, which exhibits ~50% decrease in threshold current. With the EC, the reduction is only of ~20%. Indeed, in this case, back-coupling is affected by losses and imperfect coupling of the field into the QCL waveguide. An analysis performed using the Zeemax software has shown that owing to the diffraction limit of the germanium lens, only 23 ± 8% of the light could get back into the 13 μm by 1.8 μm QCL waveguide.
Subsequently, the output power, representative of the gain, and the frequency emitted by the EC-QCL were measured as a function of the grating angle. These measurements are shown in Fig. 2(b). The abscissa in the plots refers to the number of grating rotational steps from the microswitch reference point. The grating tuning is discrete. The mean wavelength increment over the tuning range of \(~75\) cm\(^{-1}\) is \(~0.055\) cm\(^{-1}\) per step, estimated from the slope of a linear function fit of the tuning curve. However, the tuning is not entirely driven by the grating angle. Histogram analysis of the frequency increments reveals large occurrence of spectral increments multiples of \(~0.5\) cm\(^{-1}\), which are interpreted as hops between successive modes of the QCL itself. The reproducibility of successive full scans of the grating angle was found to give a frequency calibration accurate within \(0.20 \pm 0.16\) cm\(^{-1}\), which as far as broadband absorbers at atmospheric pressure are concerned does not introduce significant spectral calibration issues.

### 2.3 Intracavity absorption observations

One of the particular benefits inherent to the wide tunability of EC-QCLs relates to their potential in broadband absorber spectroscopy. As a first empirical test to observe ICA signals with the EC-QCL, dimethyl carbonate (DMC) was chosen as a test broadband absorber. DMC possesses a broad unstructured absorption in the interval 1250-1320 cm\(^{-1}\) [16], due to the \(\nu_{20}\) O-C-O stretch [17]. DMC is in the liquid phase at 25 °C but exhibits a vapor pressure of 52 Torr. To prepare calibrated vapor mixtures, a PTFE tube containing DMC was made and the permeation of DMC through this tube was gravimetrically measured to be 64.3 ± 0.08 μg/min at 70° C. An Owlstone gas generator (OVG-4) was used to produce a 349 ± 7 ppmv mixture in dry nitrogen, which was used as sample mixture at atmospheric pressure.

The EC-QCL output power was recorded as the wavelength was tuned through grating rotation. Dry nitrogen and the 349 ppmv DMC mixture were alternately admitted to the intracavity cell. Figure 3(a) shows traces recorded with an injection current of 1100 mA into the QCL chip. For comparison, the plot also shows the expected linear absorption from a 2 cm long absorption cell. The Beer-Lambert law was used for the calculation. There is a clear, significant, absorption enhancement from the intracavity configuration. The asymmetry of the DMC absorption band is perceptible and yields laser extinction below 1280 cm\(^{-1}\). The large variability of the output power around 1310-1320 cm\(^{-1}\) is believed to be related to the laser gain profile.

More interestingly, these records were repeated at different injection currents, as shown in Fig. 3(b). The observed magnitude of absorption appears to be dependent on the injection current and therefore on the laser characteristics. In other words, the DMC absorption at lower QCL chip current (1000 mA) provokes full laser extinction and therefore affects the laser threshold. In order to understand and exploit these effects a physical model has been developed and is presented in the next section.
Fig. 3. (a) Output power from the EC-QCL as a function of wavenumber, for a background of dry nitrogen (red line) and a mixture of 349 ppmv of DMC in dry nitrogen (green line) at a QCL injection current of 1100 mA. The black line is the calculated expectation of DMC absorption when linear absorption with a 2-cm path is used. (b) Similar traces recorded for three different QCL chip injection currents.

3. QCL intracavity absorption model

The QCL three-level rate-equation model [18, 19] was used as the framework for interpreting the effect of intracavity absorption on the EC-QCL. The system is considered as single cavity with one of the facet characterized by an effective reflectivity taking into consideration the grating reflectivity and the coupling losses. The notation used in this work follows that of Ref [18]. The steady-state solution of the rate equations for the photon number \( P \) in the cavity is expressed by Eq. (1), as the root of a quadratic equation, whose polynomial coefficients are given by Eqs. (2), (3) and (4).

\[
P = \frac{-B + \sqrt{B^2 - 4 \cdot A \cdot C}}{2A}\tag{1}
\]

\[
A = \frac{g}{\tau_p} \left( \frac{1}{\tau_{21}} + \frac{1}{\tau_{31}} \right)\tag{2}
\]

\[
B = \frac{1}{\tau_p \tau_{21}} \left( \frac{1}{\tau_{32}} + \frac{1}{\tau_{31}} \right) + \frac{I_{in} \cdot Z \cdot g}{q} \left( \frac{1}{\tau_{32}} - \frac{1}{\tau_p \tau_{21}} - \frac{\beta}{\tau_e} \right)\tag{3}
\]

\[
C = \frac{Z \cdot \beta \cdot I_{in}}{q \cdot \tau_e \cdot \tau_{21}}\tag{4}
\]

\( I_{in} \) is the injection current and \( q \) the charge on the electron. Other parameters appearing in Eqs. (2), (3) and (4) are listed in Table 1, together with values adapted from Gensty & Elsäßer [18]. These values were used in subsequent simulations.

The effect of intracavity absorption is modeled by adding a term to the rate equation to account for additional photon loss introduced by absorbing molecules. This term, given by Eq. (5), needs to be added to the photon population rate equation. \( N \) is the molecular number density and \( \epsilon \) the molecular absorption cross section of the intracavity absorber.

\[
\frac{dP}{dt}_{\text{ICA}} = -P \cdot \epsilon \cdot N \cdot c \cdot \frac{l}{L}\tag{5}
\]

In other words, this additional absorption loss leads to a reduction of photon lifetime compared to the case where no intracavity molecular absorption occurs. With a molecular
absorber, the photon lifetime $\tau_{P'}$ is given by Eq. (6), in which $\tau_{P''}$ accounts for the photon lifetime without intracavity absorber.

$$\frac{1}{\tau_{P'}} = \frac{1}{\tau_{P''}} + \frac{\varepsilon \cdot N \cdot c \cdot l}{L}$$  \hspace{1cm} (6)

| Symbol | Parameter | Value     |
|-------|-----------|-----------|
| $\tau_{32}$ | Phonon scattering time (3 $\rightarrow$ 2) | 2.1 ps     |
| $\tau_{31}$ | Phonon scattering time (3 $\rightarrow$ 1) | 2.6 ps     |
| $\tau_{21}$ | Phonon scattering time (2 $\rightarrow$ 1) | 0.3 ps     |
| $\tau_e$ | Electron lifetime | 1.16 ps    |
| G | Differential gain coefficient | 140 s$^{-1}$ |
| Z | No. of gain stages | 25                         |
| B | Spontaneous emission factor | $10^{-6}$ |
| $\tau_{P''}$ | Intrinsic photon lifetime | 250 ps     |
| L | Total cavity length | 20 cm       |
| l | Length of intracavity cell | 2.5 cm     |

Table 1. Parameters used in the three-level rate-equation model.

Figure 4(a) illustrates the effect of additional intracavity absorber on the evolution of the photon population as a function of injection current. In the simulation, the intracavity absorber was a mixture of 300 ppmv of DMC. At 1300 cm$^{-1}$, the absorption coefficient is $\varepsilon \cdot N = 0.013$ cm$^{-1}$ which would produce an absorption of $\sim 6\%$ if linear absorption is assumed, using a cell length of 2.5 cm. Data are plotted as a function of the reduced current $\eta = I/I_{thr,0}$, where $I_{thr,0}$ is the threshold current in the absence of intracavity absorption. Figure 4(a) shows several noticeable effects induced by the introduction of DMC: 1) the threshold current is increased, 2) the power efficiency (slope) is decreased, and 3) at a given injection current, the absorption induced is in the range of $\sim 75\%$, about 12 times more than expectations calculated from the Beer-Lambert equation. These three effects depend on the sample absorption coefficient and therefore provide leverage to deduce concentrations of intracavity absorbers.

In order to quantify the absorption “enhancement” induced by the intracavity operating mode, a factor is defined by taking the ratio of absorption observed in the ICA mode to that given by the Beer-Lambert law using the intracavity cell length. Calculations of the enhancement factor are shown in Fig. 4(b). These calculations were carried out for several absorption coefficients $\varepsilon \cdot N$, on which the enhancement factor also depends.

The enhancement factor plot spans both sides of the threshold current ($\eta = 1$ in absence of ICA sample). Before laser threshold, it relates to luminescence. As mentioned previously, the ICA provokes an increase of the current threshold. For each absorption coefficient of ICA sample in Fig. 4(b), a dashed vertical line indicates the new value for the laser threshold. In any case, greatest enhancement relative to linear absorption is achieved at currents only just above threshold, in contrast to previously observed behavior for a near infrared EC diode laser [12]. In the next section a series of experimental studies are conducted to validate the ICA model and its outcomes.
4. Experimental results on EC-QCL intracavity absorption

4.1 Transmission measurements

The first experimental approach was motivated by the theoretical expectation that the ICA enhancement factor increases as the operating injection current gets closer to the threshold current. Measurements of the EC-QCL output power were made at fixed wavelength of 1295 cm\(^{-1}\) (DMC cross section of 3.9 \(\times\) 10\(^{-18}\) cm\(^2\)). DMC concentrations in the intracavity cell were varied, and so was the injection current. In all cases the intracavity cell pressure was 1 atm. From output powers measured with and without DMC, for each concentration and injection current, the transmission was calculated. The results are shown in Fig. 5(a) as a function of reduced current \(\eta\).

The ICA model from section 3 was used to interpret data. The transmission is defined as the ratio of the photon number \(P'\) (with ICA) to \(P\) (without ICA). To simplify and produce readable analytical expressions, only current at least \(\sim\)1% above the laser threshold was considered. This assumption translates into a simplification as in this case \(B^2 \gg 4AC\), and the transmission can be expressed by Eq. (7), which includes parameters given by Eq. (8).

\[
\frac{P'}{P} = \frac{K + R \cdot \gamma \cdot \tau_{p} \cdot I}{K + \gamma \cdot \tau_{p} \cdot I_{in}} \quad (7)
\]

\[
K = \frac{\tau_{31} + \tau_{31}^{-1}}{\tau_{21} \cdot g}, \quad \gamma = \frac{Z \cdot (\tau_{31}^{-1} - \tau_{21}^{-1} - \beta \cdot \tau_{e}^{-1})}{q}, \quad \text{and} \quad \tau_{p}' = R \cdot \tau_{p} \quad (8)
\]

Equation (9) gives the expression of the parameter \(R\). This is the parameter of interest as it contains the information about the absorber concentration.

\[
\frac{1}{R} = 1 + \frac{\varepsilon \cdot N \cdot C \cdot l}{L} \cdot \tau_{p} \quad (9)
\]

Equation (7) was implemented as a fitting function with \(K\), \(R\) and \(\gamma \tau p\) as fit parameters, initialized where appropriate using the physical parameters of Table 1. The resulting least-squares fits are shown as solid lines overlaid to the experimental plots in Fig. 5(a). The agreement between the experimental points and the modeled curve is good. The experimental points exhibit an increased scattering as the DMC concentration decreases because temporal fluctuations in the QCL output power caused by current and opto-mechanical instabilities become more significant relative to the absolute signal attenuation induced by the intracavity absorber.
To further check the ICA model, the inverse of the fit parameter $R$ was plot against DMC number density as shown in Fig. 5(b). The model predicts a linear relationship corresponding to Eq. (9) that was used to fit the solid line appearing in Fig. 5(b). The data points and the model agree well: the intercept is one, as expected, and the slope is $(9.76 \pm 0.61) \times 10^{-18}$ cm$^{-3}$, implying a photon lifetime of $1.04 \pm 0.06$ ns in the absence of ICA. From the reflectivity of the QCL facets and grating, the coupling loss, and by assuming internal losses to be negligible in comparison, a photon lifetime of $\sim 0.7$ ns would be expected. This is consistent with the measurements. In principle, transmission measurements and the use of Eq. (9) offers a way to infer absolute molecular concentration of ICA absorbers. However, this requires knowledge of the photon lifetime in absence of ICA. Therefore a prior form of calibration is needed.

The validity domain of the approximations made to allow for simple analytical equations to be produced has been further checked for the relevant experimental conditions. The parameters $A$, $B$, and $C$ (Eqs. (2)-(4)) were estimated. Considering the two extremes in concentration values, the approximation was calculated to be valid for $\eta > 0.0004$ for 11 ppmv of DMC and for $\eta > 0.014$ for 300 ppmv, which is well within the experimental conditions.

4.2 Threshold current measurements

In a second experimental approach, the laser threshold change with the ICA was investigated. From the model, the threshold current can be calculated by applying the condition $B = 0$ in Eq. (3) with no intracavity absorber ($I_{\text{thr},0}$) and with an intracavity absorber ($I_{\text{thr}}$). The ratio of the two then gives a direct measurement of the $R$ parameter as given by Eq. (10). Therefore, the shift in threshold current offers a way to measure the concentration of intracavity absorber, which is an extremely appealing feature as concentration information can be derived solely from laser operating parameters, and laser threshold is typically an abrupt power variation.

$$\frac{I_{\text{thr}}}{I_{\text{thr},0}} = 1 + \frac{\varepsilon \cdot N \cdot c \cdot L}{\tau_p}$$

Similarly to the transmission approach described in section 4.1, the knowledge of the photon lifetime in absence of ICA is required for quantitative concentration measurement. To do so experimentally, threshold current shifts were measured by sweeping the QCL current over the threshold at 1 Hz, with a 20 mA peak-peak injection current modulation. The resulting output power evolution was fitted with the functional described by Eq. (1), using a non-linear least-squares routine. The fitting parameters were the threshold current without
ICA, $I_{thr,b}$ and the factor by which the threshold current is increased when ICA occurs, as defined by Eq. (10). For a particular frequency of 1301 cm$^{-1}$ (DMC cross section of 3.78 x 10$^{-18}$ cm$^2$), three traces were recorded corresponding to an intracavity sample of air, 58 ppmv of DMC, and 116 ppmv of DMC, respectively. The first two traces allow calibration of the photon lifetime, from which the concentration of the third record is retrieved. Figure 6(a) shows the three experimental records and their corresponding least-squares fit. The mixture of 58 ± 1 ppmv of DMC in dry nitrogen was used as the calibrant. The retrieved concentration for the sample was then 123 ± 1.6 ppmv when the true concentration was of 116 ± 1.7 ppmv.

So far, measurements have been made using fixed laser frequency. However, as the molecular cross section $\varepsilon$ depends on the laser frequency, the EC-QCL can record profile information, which is useful when complex mixtures are considered for carrying out spectral unmixing. With the current bench-top demonstrator prototype, repetition of the calibration process at each wavelength is necessary, owing to wavelength-dependence of threshold current and photon lifetime. Figure 6(b) shows spectrally-resolved measurements of a test DMC sample at 116 ± 1.7 ppmv on which is overlaid the expected absorption coefficient according to the PNNL database [16]. The error bars indicated in the plot in Fig. 6(b) are derived from the random noise affecting the detector signal and represent detector noise limited operation. Although the overall agreement is fair, the deviation of most of the points from the database value lies outside the error bars. Clearly, other processes are impeding the measurements. These will be discussed in Section 5.

Lastly, the rate equation model also predicts that the gradient $dP/dI_{in}$ in the post-threshold region is proportional to the photon lifetime $\tau_P$ as well as to parameters intrinsic to the QCL chip. A change in gradient induced by intracavity absorption could therefore be used to infer the absorber concentration. However, the post-threshold power was frequently seen to be modulated as a result of residual standing waves that restricted the accuracy with which the gradient could be determined.

4.3 Phase-sensitive methods (PSD)

The initial results shown in the previous section demonstrate the utility of threshold current measurements in determining the concentration of an intracavity sample. In order to get more accurate and straightforward measurements of the threshold current, a phase sensitive approach was developed. The QCL chip injection current was ramped over the laser threshold whilst simultaneously being modulated by a small (~1 mA) sinusoidal signal at 2 kHz. The output from the detector was fed into a lock-in amplifier to produce the second and third harmonic demodulated signals. As a first approximation, the second harmonic signal provides a peak trace whose maximum coincides with the laser threshold. The threshold current can thus be accurately measured through a peak detection routine. Furthermore, the third
harmonic signal exhibits a zero crossing waveform that can be used as error signal to lock the current source to the threshold current value. Figure 7(a) shows the 1f, 2f, and 3f demodulated signals recorded at 1295 cm$^{-1}$. The bottom trace represents the raw power signal as the injection current is scanned over the threshold. The middle panel shows the demodulated signal at the second harmonic, and the top one the demodulated signal at the third one. The integration time on the lock-in amplifier was set to 5 ms, and the slow sawtooth ramping signal was set at a frequency of 1 Hz.

With the 2f signal, the threshold evolution can be followed in time in a convenient way. The intracavity cell is equipped with miniature automatic valves controlled by software. They allow to swap gas samples quickly without touching the cell. While continuously measuring at 1295 cm$^{-1}$ (DMC cross section of 3.9 x 10$^{-18}$ cm$^2$), the sample contained in the cell was switched from air to 116 ± 2 ppmv of DMC, and then switched back to air again. The temporal evolution of the 2f signal is shown in Fig. 7(b). The change of threshold current induced by the DMC mixture is clearly visible. The few tens of seconds of interrupted signal either side of the DMC episode is related to the cell being evacuated, and the presumed slight window deformation or shift, altering the EC coupling efficiency. This exemplifies the sensitivity of the system to mechanical perturbation.

The trace starting after 230s elapsed time, when an air sample is reintroduced to the cell, has been used for a stability analysis. The stability time was found to be ~10 s, at which time the Allan deviation is 0.012 mA. In contrast, the threshold measurements using the power evolution as described in section 4.2, were giving a one sigma, one second, precision of 0.24 mA. Clearly the 2f phase-sensitive threshold detection method enhanced the precision of the measurement. The 10 s one sigma precision on the threshold current measurement corresponds to a minimum detection of 1.14 ppmv of DMC, corresponding to an absorption coefficient of 1.1 x 10$^{-4}$ cm$^{-1}$.

5. Insights on sensitivity and limitations

Of those described in Section 4, the phase-sensitive method with 2f detection appears the most attractive, allowing for a more precise threshold current determination and benefiting from the signal to noise enhancement inherent to PSD techniques. As mentioned above, a calibration with a known sample is necessary to account for the lack of knowledge of the cavity photon lifetime in the absence of ICA. At a single frequency point (corresponding to a peak absorption of the sample for instance), the error propagation analysis down to the absorption coefficient can be expressed by Eq. (11), where $\epsilon N_{CAL}$ is the absorption coefficient of the calibration mixture, and $I_{thr,CAL}$ the corresponding threshold current measurement.
Assuming a calibration mixture is determined well enough not to introduce additional uncertainty, the relative error on the absorption coefficient determination is driven by the precision of the threshold measurement weighted by the threshold current difference between an empty cell and one filled with the calibration mixture. For example, in the experimental cases shown in the previous section, in 10 seconds the Allan deviation on the current threshold is 12 µA while a 116 ppmv DMC calibration mixture produces a threshold change of ~2 mA. This yields a relative error on the absorption coefficient of ~0.012.

However, this development is ideal and only accounts for a random noise limited system. If ideally the system is highly sensitive to ICA losses introduced by a sample, it is similarly so to any other potential losses within the EC-QCL affecting the photon lifetime. In practice drifts primarily caused by changes of EC back-coupling efficiency, like those induced by slight movement of the ICA cell windows as shown in Fig. 7(b), are limiting the first demonstrator prototype system hereby described. Other limiting effects have been observed, like mode hops induced by temperature fluctuations as small as ~0.1 K, mechanical instabilities (vibrations and expansion), and current noise. All these aspects can certainly be improved, and along with the study of noise sources, will be in scope for further developments.

Owing to the sensitivity of the threshold current to intracavity losses, measurements are also impeded by a limited dynamic range. Indeed, if ICA is too large, the laser emission stops and no measurements can be made. This can however be mitigated by an increase in injection current to increase the laser pump rate, in which case the dynamic range is limited only by the QCL’s intrinsic threshold current and maximum operating current.

6. Prospects and conclusion

An ICA EC-QCL system has been developed as well as the corresponding physical model describing well the experimental results observed using DMC as a sample broadband absorber, and allowing quantitative measurements to be made directly from laser threshold current changes. It appears that ICA alters the intracavity photon lifetime and can show an enhanced absorption compared to single path linear absorption. Using the tuning capability of the EC-QCL, absorption coefficient profiles can be recorded, provided that calibration is made with a known absorber.

The optimum approach to measuring variation of the laser threshold current was found to be through current induced power modulation and subsequent phase sensitive detection at the second harmonic. Theoretical error propagation analysis indicates the spectrometer could measure absorption coefficients with a relative uncertainty as low as 0.012, which in the case of a 116 ppmv DMC mixture, at the band maximum, would correspond to 1.4 ppmv or 1.3 × 10^{-4} cm^{-1}. However, in practice, the high sensitivity of the ICA EC-QCL to internal losses was limited by drifts affecting the early bench-top demonstrator.

This early work opens the path to many prospects in developing the ICA EC-QCL further as this kind of spectrometer would offer sensitivity in the measurement of mixing ratio of broadband absorbers in a very compact and simple package, not to mention the long term potential of integration into monolithic devices. Further work will include the implementation of the active threshold locking (through 3f signal), reduction of the system footprint, overall thermal stabilization, fast power modulation, and quieter current source integration.

Improvements can also be made by enhancing the photon lifetime to increase the magnitude of the threshold change as indicated by Eq. (11). Through integration of a partially reflective coating on the external QCL chip facet, and improvement of the 1st order grating back-coupling into the chip, a gain of ~20 could be achieved on the photon lifetime.

Finally, more practical calibration methods will be investigated such as, for example, the use of attenuating foils of well known absorption.
Acknowledgments

The authors wish to acknowledge the valuable assistance of Mr. Wayne Robins from the RAL Space Science & Technology Department Precision Development Facility, and Dr. Marc Ferlet of the Optical Design Group.

This project was supported through a UK Natural Environment Research Council proof of concept grant NE/H002014/1.