

Highly Sensitive Detection of Trace Gases Using Pulsed Quantum Cascade Lasers

Geoffrey Duxbury^a, Erwan L. Normand, Nigel Langford,
Michael T. McCulloch and Stephen Walker

Department of Physics and Applied Physics, University of Strathclyde, John Anderson Building, 107 Rottenrow,
Glasgow, G4 0NG, UK.

ABSTRACT

We show that by using a high resolution Fourier transform infrared spectrometer we can map the temporal characteristics of a pulsed quantum cascade laser into the wavenumber domain, and hence show that when a square current pulse is applied to a distributed feedback laser a linear sub-microsecond frequency chirp is developed. We describe a mid infrared spectrometer, that is based upon the use of this linear chirp, which can provide a real-time display of the spectral fingerprint of molecular gases. The sensitivity of the spectrometer is based upon the use of long pathlength White or Herriot cells, and the multiplex advantage associated with recording the entire spectral window during each electrical pulse. For a cell with a path length of 9.6 m, dilution measurements made on the ν_9 band transitions of 1,1 difluoroethylene indicate a sensitivity of 30 parts per billion.

Keywords: Laser Physics; Laser sources; Atomic and molecular spectroscopy; Gas sensing

1. INTRODUCTION

Recent advances in the fabrication of pulsed quantum cascade (QC) lasers have allowed the development of lasers that work at or close to room temperature whilst producing pulses with peak powers that are in excess of 1 Watt with duty cycles approaching 100 %. The operating wavelength associated with QC lasers falls typically in the 3 – 15 μm window and so makes the QC laser an ideal light source for probing the spectral features associated with the fundamental vibration-rotation rotational absorption bands of gaseous molecules.

Most of the present generation of QC laser based spectrometers^{1,2} operate in a manner similar to that initiated by Namjou et al [3]. In these systems a short duration current pulse (~ 3 to 10 ns) is applied to the QC laser and this results in the generation of a pulse in the spectral domain, which covers a given wavenumber range. This spectral pulse is then tuned through the absorption feature of interest by applying a slowly varying sub-threshold current ramp to the pulse train. As a result the observed frequency tuning is a quadratic function of the applied current ramp. Using this technique, spectral scans over the range of 0.23 cm^{-1} to 0.74 cm^{-1} have been achieved. Once the gas of interest has been probed the recorded spectral data must then be corrected to take into account the effects of the quadratic frequency chirp. Further more, to achieve trace level sensitivity a modulation of several kiloHertz is applied to the current ramp to allow phase sensitive detection and as a result the rate at which data is collected is limited. Another severe restriction of the approach developed by Namjou et al.³ is that the applied current pulse defines the effective linewidth of the spectrum of the emitted radiation from the quantum cascade laser and this in turn restricts the spectral resolution of the spectrometer. Namjou et al.³ have shown that a 10 ns duration current pulse results in an effective line width of 0.023 cm^{-1} . This restricts the use of QC laser based spectrometers for molecular fingerprinting.

Our approach to measuring the spectral fingerprint of a given molecular gas differs significantly to the approach taken by Namjou et al.³, and is based upon our characterisation of the spectral behaviour of pulsed quantum cascade lasers using high resolution continuously scanning Fourier transform spectrometers. By using this method we have shown that when a top-hat current pulse is applied to a QC laser a linear frequency down-chirp is produced which may be used to scan the oscillating frequency through the molecular transitions of interest⁴. In the present paper we describe aspects of the characterization process, and the ways in which they may be applied to spectrometer design, concluding by the description of our current spectrometer system.

^a corresponding author, E-mail G.Duxbury@strath.ac.uk, Telephone 0044-141-548-3271

2. CHARACTERISATION OF PULSED QUANTUM CASCADE LASERS

2.1 EXPERIMENTAL

The experimental configuration for laser characterization is shown in Figure 1a⁴. For the results described here QC laser (QCL), fabricated by Alpes Lasers, had a DFB structure and was designed to oscillate at a wavelength of 10.2 μm . The laser was housed in airtight chamber, and the light was coupled from the chamber through an anti-reflection coated ZnSe window. The QC laser substrate was mounted on a Peltier cooler, which allowed the substrate temperature to be varied between -40°C and $+40^\circ\text{C}$. The temperature of the substrate was stabilised to a level of $\pm 0.01^\circ\text{C}$. The laser was excited using a pulsed current source designed within our group⁵. This generated top-hat shaped current pulses with durations ranging from 40 ns to 200 ns, at repetition rates of up to 8.3 MHz (using a maximum duty cycle of 2.5%), and with peak currents of up to 20 A. Previous measurements that we have made on this laser⁴ indicate that by varying the temperature of the QC laser substrate, the oscillating wave number can be tuned at a rate of $-7.6 \times 10^{-2} \text{ cm}^{-1}/\text{K}$, which corresponds to a frequency down-chirp of 2.3 GHz/K.

The amplitude and shape of the current pulse applied to the QC laser were monitored using a Rogowski coil⁶ placed between the current source and the QC laser. The threshold current of the QC laser was 3.2 A at a substrate temperature of 0°C . The spectral profile of radiation produced by the QC laser was studied by use of two Fourier transform spectrometers, a Bomem DA-3 FTS which had a maximum effective resolution of 0.005 cm^{-1} , (150 MHz), and a Bruker IFS 120HR with a maximum resolution of 0.0015 cm^{-1} , (45 MHz). Once a numerical filter is applied to the interferogram, the maximum sampling frequency of these spectrometers is very much less than than the repetition frequency of the current pulses applied to the QC laser (20 – 100 kHz), hence the QC laser appears as a quasi-continuous-wave light source when viewed by the FT spectrometers.

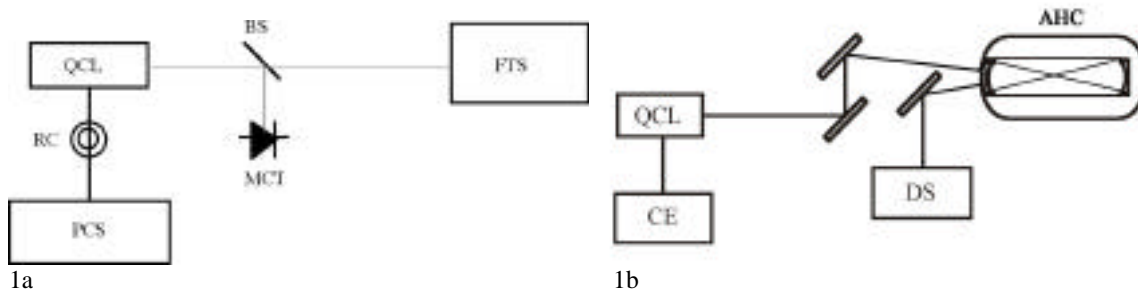


Figure 1 Experimental configurations (a) for pulse diagnostics, (b): Real-time spectrometer: QCL, QC laser; PCS, pulse control system; RC, Rogowski coil; BS beam splitter; MCT, mercury cadmium telluride photovoltaic detector; FTS, Fourier transform spectrometer; CE, control electronics; AHC, astigmatic Herriot cell; DS, detection system

2.2 RESULTS

In a previous paper⁴, for which Bomem DA-3 FT spectrometer (FTS) was used, we showed that the wavenumber/ cm^{-1} down chirp was almost linear, and that regular etalon fringes could be observed when a solid Ge etalon was inserted in the beam path. An example of these fringes recorded via the FTS is shown in Figure 2.

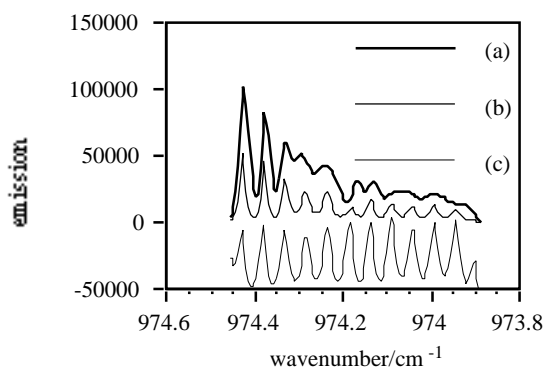


Figure 2: Wavenumber tuning produced by a 100 ns current pulse observed via the 0.05 cm^{-1} fringe pattern of a solid Ge etalon. The resolution of the FTS was 0.005 cm^{-1} : (a) without etalon, (b) with etalon, (c) etalon fringes obtained by the ratio of (b)/(a).

By using the higher resolution Bruker spectrometer in the NERC Molecular Spectroscopy Facility (MSF) at Rutherford Appleton Laboratory (RAL) we have been able to further characterize the pulse structure, and to examine the structure of molecular fingerprint absorption lines which lie within the tuning range of the present laser. In Figures 3 and 4 examples are shown of the high resolution absorption spectrum of 1,1 difluoroethylene, CF_2CH_2 recorded using the QCL and a globar. Since the linewidth of these two spectra is identical, and determined by the instrument function, it can be seen that the effective linewidth of the wavenumber swept QCL must be less than 45 MHz. From this figure it may also be seen that the effects of the switch on of the current pulse are to produce a very fast transient oscillation of the output power which damps rapidly, so that over most of the current pulse the envelope of the laser output has an approximately trapezoidal shape with a low amplitude slow oscillation superimposed. It is this part of the output pulse that we use to provide the basis of our QCL spectrometer.

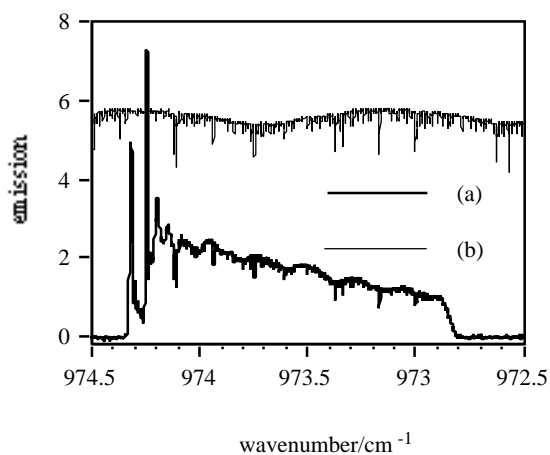


Figure 3 :

The high resolution absorption spectrum of 1,1 difluoroethylene, CF_2CH_2 is shown in Figure 3, and in expanded form in Figure 4. The spectrum was recorded using the Bruker IFS 120HR spectrometer at the NERC MSF using a resolution of 0.0015 cm^{-1} . The absorption cell had a path length of 26 cm and the gas pressure was 0.9 Torr. (a) QCL 20 scans, 200 ns pulse length, 20 kHz repetition rate 240 V drive voltage, temperature 271.66 K. (b) globar, 100 scans.

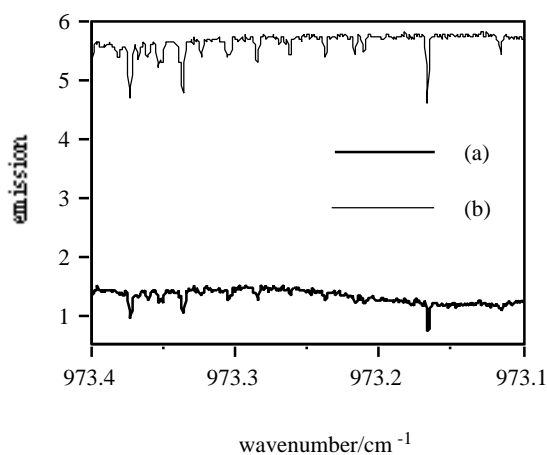


Figure 4

In Figure 5 a comparison is made of the comparatively sparse absorption spectrum of 1,1, difluoroethylene and the complex many line spectrum of 1,1,1 trifluoroethane which lie within the chirp range of the laser.

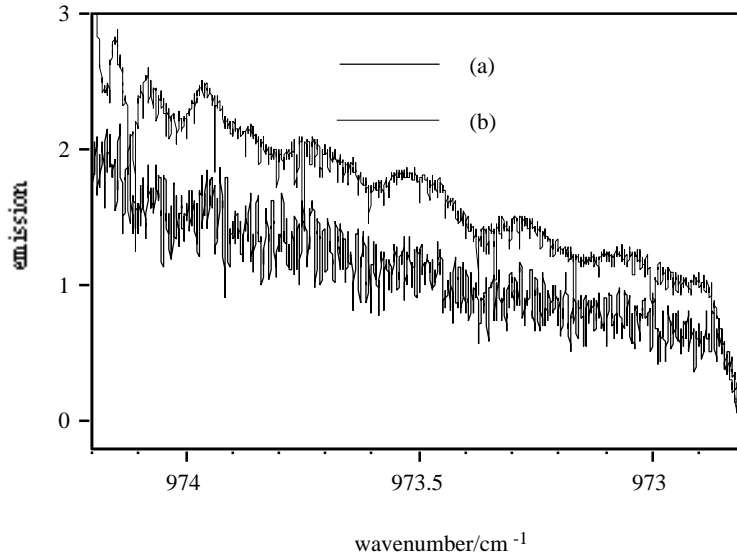


Figure 5: The spectra of (a) CF_2CH_2 and (b) 1,1,1 trifluoroethane, CF_3CH_3 , recorded using the same QCL settings as in Figures 3(a) and 4(a). The gas pressure of CF_3CH_3 was 0.9 Torr.

3. IMPLEMENTATION OF A FAST REAL-TIME SPECTROMETER

3.1 EXPERIMENTAL DESIGN

The experimental arrangement of our spectrometer is shown in Figure 1b^{5,7}. The output from a distributed feedback QC laser, described in section 1.1, was collected and collimated by an off-axis parabolic mirror-germanium telescope arrangement to produce a beam of diameter 3 mm which was subsequently passed into either a White Cell⁷ or an astigmatic Herriot Cell⁸. In the first experiments using the White cell, the mirrors in the cell were separated by 0.6 m and configured to give 16 passes, corresponding to an effective path length of 9.6 m. After traversing the White cell the light was then focussed onto a high-speed photovoltaic mercury-cadmium-telluride (MCT) detector and the output from this detector was then amplified and coupled to a digital oscilloscope. The temporal resolution of MCT detector, amplifier and oscilloscope combination was estimated to be 6.2 ns, corresponding to a wavenumber resolution of 0.046 cm^{-1} . In the second set of experiments described in the present paper, the White cell was replaced by an astigmatic Herriot cell whose mirrors were designed by Howieson⁹. The Herriot cell mirrors were also separated by approximately 0.6 m, and were used with 36 passes, leading to an effective path length of approximately 21.5 m. This may be increased by using the maximum effective number of passes of 202. The ray tracing software used to model the behaviour of this cell has been developed within our group, and is based the model of McManus et al.⁸. The original detector amplifier was also replaced by one having 1 GHz bandwidth, allowing the temporal resolution to be improved to less than 2 ns, a wavenumber resolution of less than 0.0014 cm^{-1} .

We have already seen in Figures 3, 4 and 5 that, once the ringing associated with the switching transient is passed, the remainder of the output pulse of the QC laser has an approximately trapezoidal shape with a low amplitude slow oscillation superimposed. It is this part of the output pulse that we use to provide the basis of our QCL spectrometer. The linear correspondence between the pulse duration and wavelength-up-chirp is further verified by reference to Figures 2 and 6. When the temporal position of the fringes is plotted as a function of fringe number the tuning may be shown to be almost linear (see Figure 6). By using the fringe spacings of the two germanium etalons, (a) nominally 0.02 cm^{-1} and (b) nominally 0.05 cm^{-1} , the rate of change of wavenumber, as a function of pulse duration, using a pulse repetition frequency of 500 Hz, was determined to be $5.95 \times 10^{-3} \text{ cm}^{-1}/\text{ns}$ (178 MHz/ns). This may be compared with our previous value of $6.1 \times 10^{-3} \text{ cm}^{-1}/\text{ns}$ (181 MHz/ns) which we derived from variation of the widths/(wavenumber/ cm^{-1}) of pulses measured using the Bomem FT spectrometer as the time duration of the pulse widths was varied.⁴ The quality of the temporal resolution of the detection system may be inferred from the observation of etalon fringes having a spacing of 0.02 cm^{-1} .

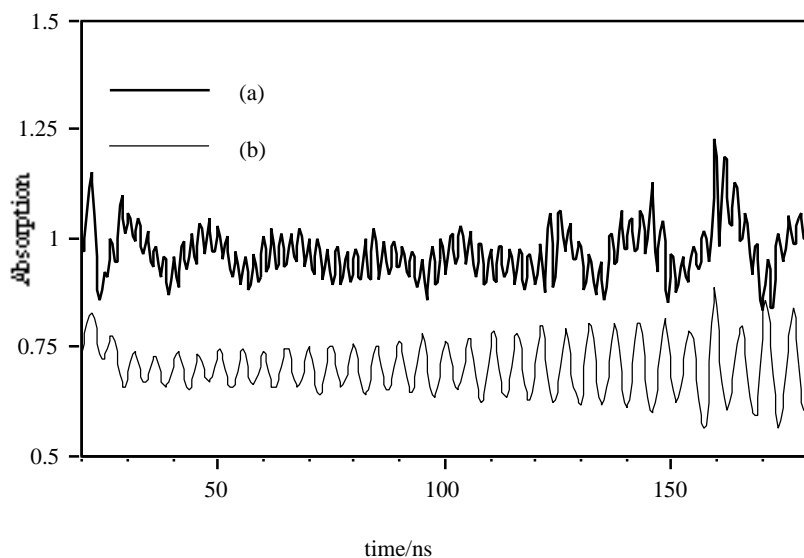


Figure 6 Ge etalon fringes recorded using the real-time spectrometer of Figure 1b, (a) 0.02 cm^{-1} etalon ($0.01995 \text{ cm}^{-1} 10$), (b) 0.05 cm^{-1} etalon (0.0481 cm^{-1}). The QCL had a 200 ns pulse length, 500 Hz repetition rate 240 V drive voltage and an operating temperature 271.66 K.

$$y = 5.154x + 19.589$$

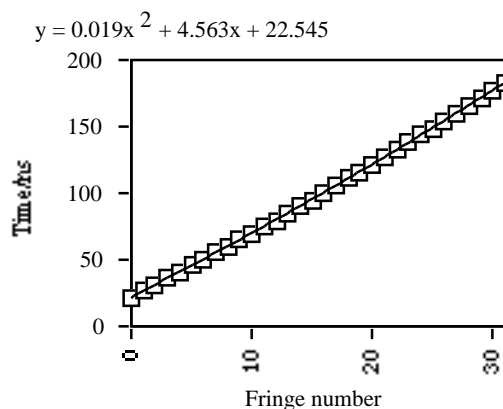
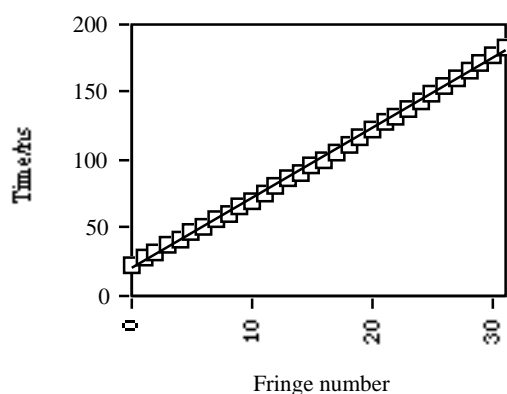


Figure 7 Analysis of the linearity of the 0.05 cm^{-1} etalon fringes shown in Figure 6. (a) linear fit, (b) quadratic fit. Note that the observed tuning is almost linear.

As we have noted, our approach to measuring the spectral fingerprint of a given molecular gas differs significantly from that adopted previously³, since we rely on the linear frequency down-chirp, that is induced when a top-hat current pulse is applied to a QC laser, to scan the oscillating frequency through the transitions of interest. This down shift is independent of the temperature of the QC laser substrate but depends of the current applied to the laser⁵ [5]. The fact that there is an almost linear correlation between the temporal and spectral profiles means that we can record the temporal profile of a generated pulse and use this to infer the spectral nature of the pulse. This means that we can observe and record the spectral profiles of molecular gases in real time at very high repetition rates (say for example up to 1 MHz using 100ns duration pulses and a 10% duty cycle). This feature enables the rapid collection of data and the subsequent averaging of this data, thereby bringing about improvements in the signal to noise ratio of the collected data by a factor of n , where n is the number of scans recorded. Furthermore, the resolution of our spectrometer is not

limited by the effective line width induced by the current pulse but by the temporal resolution of the detection system. In the case of a detection system with an infinite bandwidth, the resolution is actually determined by the instantaneous linewidth of the laser radiation⁶. As a result our spectrometer opens up the potential for the simultaneous measurement and identification of several molecular gases as well as the potential to observe the temporal/spectral evolution of short-lived chemical reactions.

3.2 RESULTS

As we have shown above, provided the pulse current amplitude is fixed, for a given sub-microsecond pulse duration the frequency down chirp is almost linear across this window and, within the spectral resolution of our detection system, the achievable spectral resolution is determined by the instantaneous line width of the QC laser⁶. These two features mean that we should be able to make a direct measurement of the absorption bands of any molecular gas that absorbs within the wave number region covered by our QC laser without having to step tune the QC laser through the absorption band.

To demonstrate the effectiveness of our proposed spectrometer the substrate temperature of the laser was set to be 271.64 K and the laser was driven with a pulse of duration 200 ns with a driver voltage of 250 V at a repetition frequency of 500 Hz., corresponding to a rate of change of wave number of $-5.9_5 \times 10^{-3} \text{ cm}^{-1}/\text{ns}$. The resulting spectral output from the laser covered the wave number window of $972.8 - 974.3 \text{ cm}^{-1}$. The Herriot cell was filled to a pressure of 0.183 Torr of CF_2CH_2 and the signal transmitted through the cell was ratioed against a stored background signal and a rolling average of 500 scans was displayed on the high speed digital oscilloscope, as shown in Figure 8a.. This may be compared with the higher resolution spectra shown in Figures 3 and 4. 1,1 difluoroethylene is a near-oblate asymmetric rotor molecule, and its spectral signature consists of almost equally spaced clumps of lines as seen in Figure 8a. In order to demonstrate the specificity of the spectrometer the cell was filled with 0.137 Torr of carbonyl fluoride, COF_2 , which is also a near-oblate asymmetric rotor, but has slightly different rotation constants. The resultant spectrum is shown in Figure 8b and also consists of almost equally spaced groups of lines. However in this case the sub-structure of these groups is more regular, and some similarities of the partially resolved sub-structure may be seen in successive groups. Etalon fringes measured using the 0.05 cm^{-1} Ge etalon are provided in Figure 8c to provide a calibration scale for the scans.

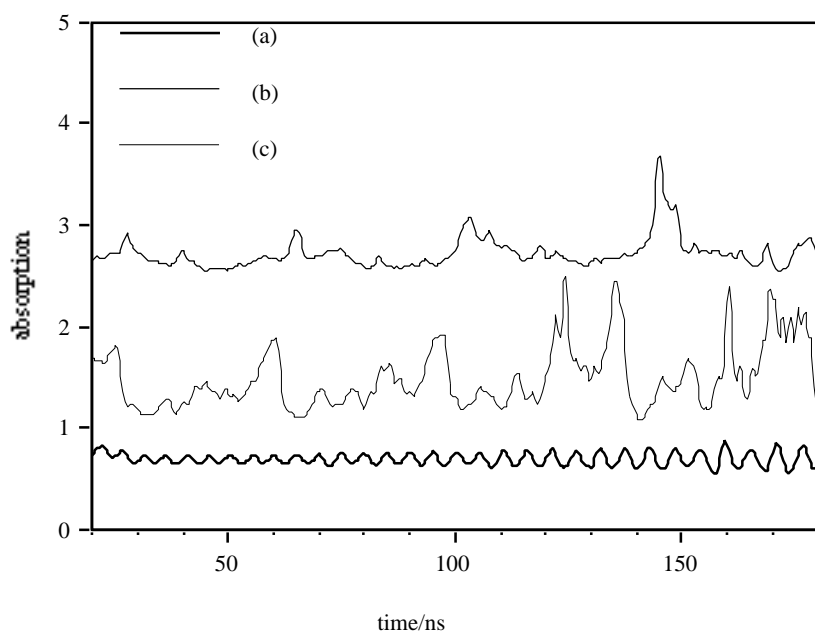


Figure 8 Spectra recorded using the same laser conditions as Figure 6, using 36 passes through the astigmatic Herriot cell. (a) CF_2CH_2 0.182 Torr, (b) COF_2 , 0.137 Torr (c) 0.05 cm^{-1} Ge etalon fringes

In Figure 9 spectra of COF_2 , recorded at three different pressures, are displayed. At the lowest pressure of 0.048 Torr the rotational fingerprint pattern may still be clearly seen. To determine the sensitivity of our spectrometer we performed a simple dilution experiment in which the spectrum of the gas was recorded whilst concentration of the gas was reduced. For the gas under investigation we were able to determine the sensitivity to be 32 parts per billion.

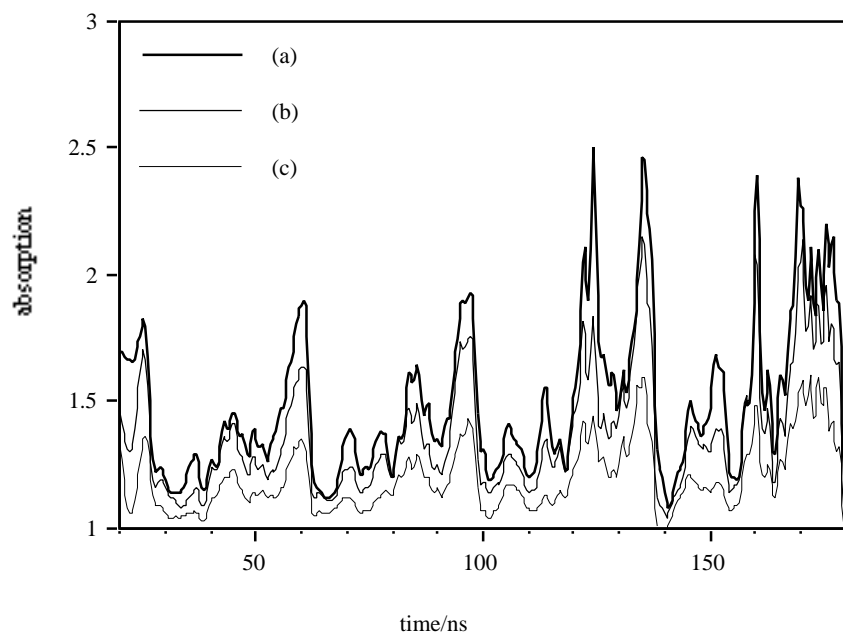


Figure 9 Spectra of COF_2 recorded using the same laser conditions as Figure 6, using 36 passes through the astigmatic Herriot cell (a) 0.137 Torr, (b) 0.101 Torr, (c) 0.048 Torr.

4. CONCLUSION

In conclusion we have demonstrated a simple real time mid infrared spectrometer that is capable of making sensitive measurements of the concentration of molecular vapours as well as providing a display of the molecular fingerprint associated with a particular gas. We are currently identifying those factors that limit the resolution of our system and these will be reported on at a later date. We believe that our system has the potential to operate in many different environments and with the recent advances in quantum cascade laser technology provide sub parts per billion sensitivities.

ACKNOWLEDGEMENTS:

The authors would like to thank the United Kingdom Engineering and Physical Sciences Research Council for the funding of this work through the research grant GST/M69111 1999. We would also like to thank David Newnham and the staff at the NERC molecular spectroscopy Facility at the Rutherford Appleton Laboratory for their support of the first part of this project.

REFERENCES

1. C. R. Webster, G. J. Flesch, D. C. Scott, J. E. Swanson, R. D. May, W. S. Woodward, C. Gmachl, F. Capasso, D. L. Sivco, J. N. Baillargeon, A. L. Hutchinson and A. Y. Cho, *Applied Optics-LP* 40, 321 (2001).
2. A. A. Kosterev, R. F. Curl, F. K. Tittel, C. Gmachl, F. Capasso, D. L. Sivco, J. N. Baillargeon, A. L. Hutchinson and A. Y. Cho, *Applied Optics* 39, 6866 (2000)., and references therein.
3. K. Namjou, S. Cai, E. A. Whittaker, J. Faist, C. Gmachl, F. Capasso, D. L. Sivco and A. Y. Cho, *Optics Letters* 23, 219 (1998).
4. E. Normand, G. Duxbury and N. Langford, *Optics, Comm.* 197, 115 (2001).
5. E. Normand, M. McCulloch G. Duxbury and N. Langford to be submitted to *Review of Scientific Instruments*.
6. A. Cross, private communication
7. E. Normand, M. McCulloch, G. Duxbury and N. Langford to be submitted to *Optics Communications*.
8. J.B McManus, P.L. Kebabian and M.S. Zahniser, *Appl. Opt.* 34, 3336 (1995)
9. I.F. Howieson, "Near Infrared Tunable Diode Laser Absorption Spectrometer for Trace Gas Detection", PhD Thesis, (1997), University of Strathclyde.
10. Yu Gang, "High Resolution Infrared Molecular Spectroscopy", PhD Thesis, (1992), University of Strathclyde.