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Quantum cascade lasers bring sensitivity and speed to infrared gas sensing

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Introduction

Some of the earliest uses of tunable diode lasers were for molecular spectroscopy and gas sensing. The first lasers used were lead salt devices, or IV–VI lasers, designed and developed by the group of Calawa and Harman¹ in the Lincoln Laboratory of Massachusetts Institute of Technology (MIT) starting in 1966. These lasers were direct band gap diodes whose energy gap corresponded to infrared (IR) wavelengths in the region from 12 to 5 μm. The progress from the development of the first devices to deployment in IR spectrometers was very rapid, so that by 1972 the technology was becoming mature,² leading to the development of a spin-off company, Laser Analytics Inc. Although lead salt laser-based spectrometers have been very widely used in the intervening period, they have only been developed for a limited range of applications, principally spectroscopy. One of the main reasons for this is that all of these IV–VI laser diodes need cryogenic cooling, initially to temperatures in the region from 4 to 30 K and latterly to liquid nitrogen temperatures, 77 K. This requires the use of either closed cycle coolers or bulky cryostats.

In parallel with the development of the lead salt lasers, the family of GaAs, or InP based, III–V lasers, which emit in the visible to near infrared (NIR) region proved to be more useful for telecommunications and for data storage applications. As a result there were a series of major technological advances in materials growth and device fabrication, particularly epitax-

ial growth, leading to the development of a wide range of compact lasers operating near or at room temperature. Some of these lasers in the telecommunications band from 1.3 to 1.8 μm have proved to be very useful for gas sensing applications, as discussed recently by Martin and Holdsworth.³ However for many spectroscopic measurements it is preferable to work in the mid IR rather than the NIR region. The quantum cascade laser relies upon developments made in growth technology, particularly of III–V materials, to be used to fabricate lasers, which can emit in the mid IR region.

The reason why lasers based upon wide band gap semiconductors can be made to emit at long wavelengths is due to the novel way in which they are used. Quantum cascade (QC) lasers are based upon the manufacture of a type of artificial semiconductor in which the wavelength of the emitted light depends on the way the semiconductors from which it is constructed are laid down in thin layers, like a set of miniature sandwiches. The original idea for creating this type of device was first described by Kazarinov and Suris in 1971⁴ but it was not until 1994⁵ that a group led by Federico Capasso, at Bell Telephone Laboratories of Lucent Technologies, fabricated the first quantum cascade laser. The basic design structure of this laser is shown in Figure 1. By using alternating layers of semiconductor of different levels of doping, it is possible to create a structure known as a mini-band in which three energy levels are created. Electrons are fed into the top level via an injector. When the

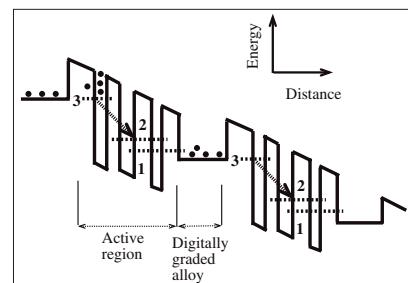


Figure 1. A schematic conduction band energy diagram of part of a section of a quantum cascade laser. Electrons are injected through a barrier into the $n=3$ energy level of the active region. The laser transition then takes place between levels 3 and 2. The lower state population is then depleted by coupling to level 1 of the adjacent cell. They are then transferred to the next injection region of the cascaded structure and the process is repeated (after Faist *et al.*, Reference 5).

electron falls to the second highest level, light is emitted; the electron then falls into the lowest level by processes which do not involve light emission. As there is an electric field within the device, the mini-bands form a staircase or "cascade". The slope of this staircase is chosen so that the electrons from the lowest energy level of the first system in the cascade may be injected into the highest level of the next mini-band, and so on, for the number of mini-bands in the cascade system. As the electrons jump at every step of the cascade structure, one electron may give rise to a large number of photons, one from each step.

In parallel with the earlier development of practical lead salt lasers, a rapid

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period of technological development has taken place since the first laser action was obtained in 1994. This has involved both the development of more efficient structures owing to major design efforts in a number of laboratories, as well as improvements in the methods of heat extraction from the QC laser devices themselves. As a result, most IR QC lasers may be operated at or near room temperature in pulsed mode. The first continuously operating lasers had to be operated at cryogenic temperatures, often in liquid nitrogen cooled housings. However, since the operation of the first room temperature laser in 2002, major design improvements have led to room temperature devices being commercially available in 2006.⁶ Thus, the QC laser can be housed in a compact, electrically-cooled housing, with similar convenience to the use of room temperature NIR lasers. As suitable electrically-cooled IR detectors are also becoming available, QC spectrometers now hold the possibility for being deployed in situations where unattended operation is possible. From this we can see that, in the 12 years since the demonstration of the first QC laser, the technology has advanced to the point where it is a competitive alternative to lead salt and NIR lasers in many areas of chemical sensing.⁷

At present, most of the applications of QC lasers, where room temperature operation is favoured, have used pulsed lasers since, until recently, they were the only lasers available commercially. Although with the recent availability of continuously-operating room temperature lasers this is now beginning to change, for many purposes pulsed lasers still have some advantages for trace gas detection, not least of which is the relative cost of the devices.

The spectrometers using pulsed lasers fall into two categories, the inter-pulse and intra-pulse approaches.⁷ In the inter-pulse method, a short current pulse is used to produce quasi-monochromatic output. The frequency tuning is then produced by using a sub-threshold current ramp. This is often called the inter-pulse method and has been widely used, particularly by the group of Tittel and Kosterev at Rice University (Houston,

TX, USA) and that of Zahniser and McManus at the Aerodyne Corporation. As this method has been described in detail in several recent reviews and papers,⁸ we will concentrate in this article on the less commonly described intra-pulse method, since it produces a spectrum which can cover a much wider frequency tuning range and also allows this complete range to be recorded for each current pulse.

Intra-pulse QC laser spectrometers

In an intra-pulse instrument,⁷ a long current pulse is used so that the laser frequency sweeps in frequency during the pulse. A complete spectrum of a frequency micro-window is then recorded during each pulse. This method requires a very fast, wide frequency bandwidth IR detector–amplifier combination and also a fast and efficient digitiser. In Figure 2, we show a schematic diagram of the intra-pulse spectrometer developed at the University of Strathclyde and, in Figure 3, a sample spectrum. The resolution of the intra-pulse spectrometer is neither determined by the pulse shape, nor by the instantaneous line-width of the laser, but by the chirp rate and the Fourier transform, time-frequency limitation.⁷ The other advantage of the use of pulsed lasers is that it minimises the effects of interference fringes, which occur when multiple pass cells are used for absorption spectroscopy. For the sample spectrum, we have chosen to use the ν_3 band of 111 trifluoroethane, CF_3CH_3 . In Figure 3(a) we show the almost trape-

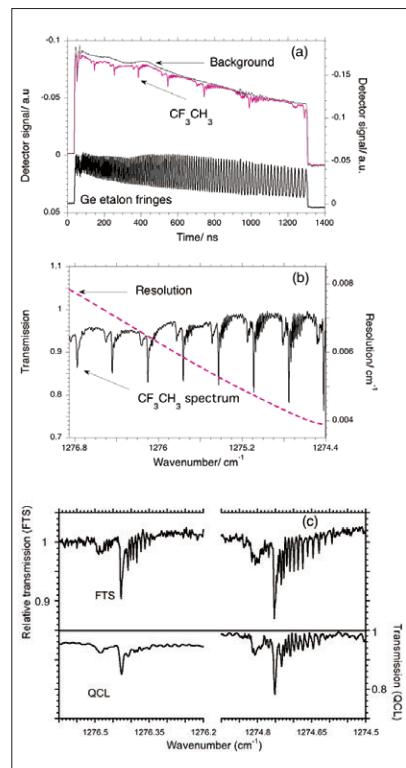


Figure 3. (a) Time dependence of a QC laser pulse of $1.3\mu\text{s}$ duration passing through a 100 m pathlength astigmatic Herriott cell. Black line empty cell, red line c. 5 mTorr CF_3CH_3 . The fringes produced using a Ge etalon of 0.002cm^{-1} free spectral range are displaced for clarity. (b) Non-linear rate of wavenumber sweep during the current pulse. Transmission spectrum, black; calculated resolution, dashed red line. The calculated full width at half height (cm^{-1}) of the Gaussian instrument function, $\Delta\tilde{\nu}$ is related to the chirp rate $d\nu/dt$ by the relationship $\Delta\tilde{\nu}=1/c(\text{adv}/dt)$. For a Gaussian function $a=0.442$. For more details see Reference 7. (c) A comparison of the resolution of the QC laser spectrometer (QCL) with that of a high resolution Bruker interferometer at the NERC Molecular Spectroscopy Laboratory (FTS).

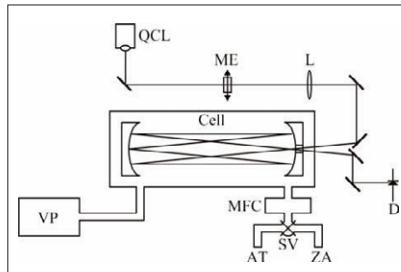


Figure 2. Schematic diagram of the experimental arrangement for trace molecule detection. QCL, QC laser; ME, motorised etalon; L, lens; D, detector; MFC, mass flow controller; AT, atmospheric gas; SV, solenoid valve; ZA, zero air; VP, vacuum pump.

zoidal shape of the laser output during a 1300 ns ($1.3\mu\text{s}$) current pulse, without and with a low pressure sample of CF_3CH_3 in a long path-length absorption cell. The change in the rate of the rapid frequency sweep from high to low frequency (a frequency down-chirp) may be seen from the increasing separation of the fringes from the Ge etalon as a function of time. In Figure 3(b), we show a transmission spectrum of CF_3CH_3 and the calculated resolution assuming a Gaussian window function. The



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resolution changes from approximately 0.008 cm^{-1} , at the beginning of the scan, to 0.004 cm^{-1} at the end.

The increased resolution at longer scan times may also been seen in this spectrum. In Figure 3(c), The spectrum of CF_3CH_3 measured with the QC laser spectrometer is compared with one recorded using a high-resolution Fourier transform spectrometer (FTS) with a resolution of 0.00177 cm^{-1} . Although the resolution of the QCL system is much worse than that of the FTS at the beginning of the scan, shown on the left-hand side, at the end (right-hand side) it becomes comparable with that of the FTS. The time taken to record the QC spectrum was 1s, whereas the FT spectrum required several hours. The unusual line shape of the QC spectrum is due to the rapid passage of the laser through the molecular absorption line, which has been discussed in detail recently⁷ and is similar in origin to the "wiggles" seen in old swept frequency nuclear magnetic resonance (NMR) spectrometers.

Applications

We have chosen two examples of practical applications of the long pulse approach, the first being the detection of ambient concentrations of methane, nitrous oxide and water in the earth's atmosphere⁹ and the second being the probing of the variation of the methane:acetylene ratio in the chemical vapour deposition (CVD) reactor in Ashfold's diamond group at Bristol University¹⁰ in the UK.

In Figure 4, we show the transmission spectrum of atmospheric samples recorded close to the physics department at Strathclyde University (a) and in a low altitude flight using the NERC ARSF (Natural Environment Research Council Airborne Research and Survey Facility) Dornier aircraft (b).

It can be seen that four lines belonging to the v_3 band of nitrous oxide and four of the v_4 vibration of methane may be easily identified. In addition, there are two lines belonging to the v_2 band of water vapour. One of these at 1276.8 cm^{-1} is anomalously narrow, it is the P branch analogue of the R branch transition showing this anomalous pressure-induced narrowing,

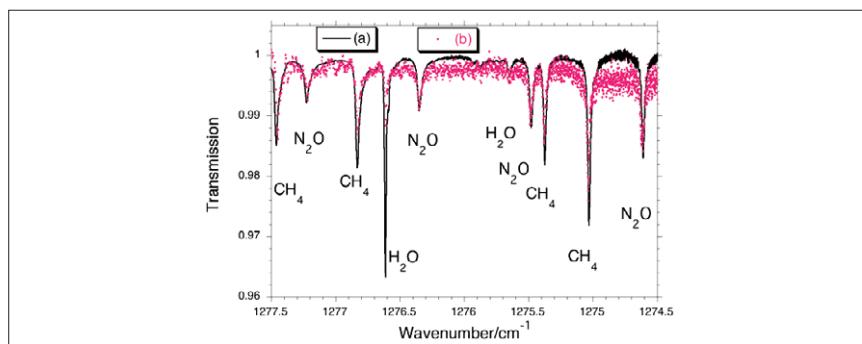


Figure 4. Transmission spectra of the atmosphere using a pressure of 100Torr within a multi-pass astigmatic Herriott cell having a path-length of 27.7m. (a) air sampled adjacent to the Physics Department at Strathclyde University in October 2005 (b) air sampled at approximately 400 m during the flight of the NERC ARSF Dornier aircraft near Oxford in September 2005. The concentrations of the trace gases, from (a), are N_2O 319 ppbv, CH_4 , 2463 (20) ppbv and H_2O c 8000 ppmv. In (b) our estimated value of the methane concentration is c. 2000 ppbv.

Dicke narrowing, first measured by the Lincoln Laboratory group at MIT in 1972. By comparing these spectra, we can see that there is far more methane in the spectrum recorded in central Glasgow and, also, that there is far more water vapour in the city centre site.

The final example is of some recent measurements of the interchange between methane and acetylene in microwave plasma-enhanced chemical vapour deposition of diamond. These

experiments took place using the Element 6 plasma reactor in Professor Michael Ashfold's group at Bristol University.¹⁰ The ability to record high quality spectra every half second allowed the Bristol group to examine the interchange between acetylene and methane, which occurs on the way to the establishment of equilibrium conditions within the reactor. In Figure 5, the appearance of methane with acetylene feed gas, or acetylene with methane feed gas is shown.

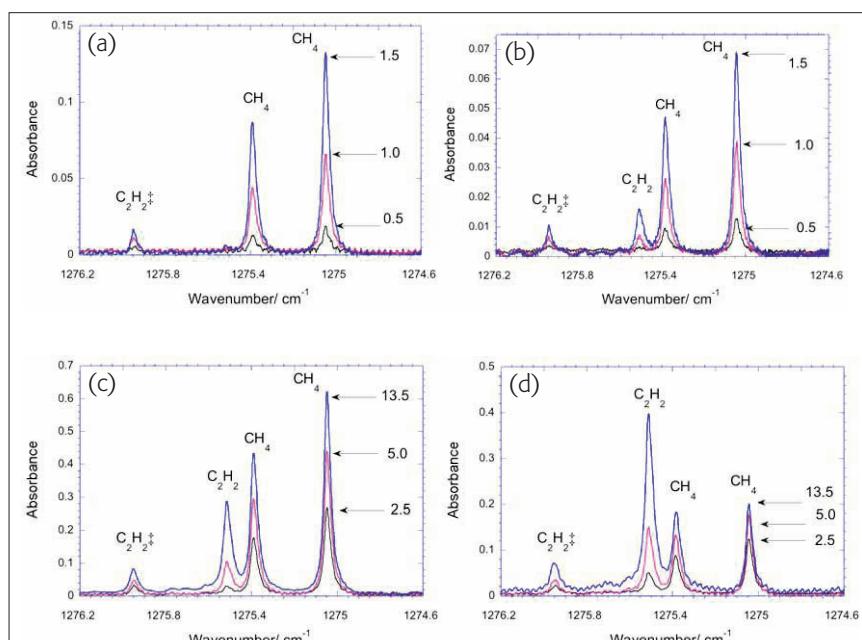


Figure 5. Absorption spectra measured in the range $1276.2\text{--}1274.6\text{ cm}^{-1}$, as a function of time in s, indicated on the right-hand side of each trace. The time sequence is first black, second red and third blue. (a) and (c) are following the addition of 8.8% CH_4 and (b) and (d) following the addition of 4.4% C_2H_2 .

One interesting point is the appearance of vibrationally hot acetylene before that of cold acetylene. The hot acetylene is denoted by the double dagger (\ddagger) symbol. These experiments show that QC laser spectrometers may prove to be a useful tool for exploring a range of industrial processes.

In addition to these examples, it is possible to examine vehicle exhausts and cigarette smoke. As with the diamond reactor example, the ability to record the time history of some of the reactive species in a chemical reaction may allow some interesting aspects of the chemistry to be understood. Finally, since it is possible to record a complete section of an IR spectrum in from 0.2 to 2 μ s, a future use may be to examine the chemistry of short-lived species, such as the hydroperoxy radical (HO_2), which are formed in many atmos-

pheric reactions and also in combustion systems.

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