

# QUANTUM CASCADE LASERS FOR BIOSENSING APPLICATIONS

Pietro Regoliosi

*Lehrstuhl für Nanoelektronik, Technische Universität München, Arcistrasse 21, 80333 Munich, Germany  
INFN – Sezione di Trieste, Via A.Valerio 2, 34127 Trieste, Italy*

Andrea Vacchi

*INFN – Sezione di Trieste, Via A.Valerio 2, 34127 Trieste, Italy*

Giuseppe Scarpa, Paolo Lugli

*Lehrstuhl für Nanoelektronik, Technische Universität München, Arcistrasse 21, 80333 Munich, Germany*

**Keywords:** Nanotechnology, optical biosensors, infrared spectroscopy, quantum cascade lasers.

**Abstract:** Quantum cascade lasers represent nowadays a mature technology to obtain laser sources in the medium and far infrared region (up to THz). Several advantages with respect to other coherent sources make this kind of lasers particularly attractive: the emission frequency can be selected by properly designing the growth structure, the emission wavelength is tunable with a very good precision and a high optical power in the IR range can be emitted in a spot of small size. These properties make them suitable for several applications, including gas spectroscopy in the IR range. In this work we introduce different types of quantum cascade lasers and we provide a description of their performances and properties, showing that they are suitable candidates for biosensing applications.

## 1 INTRODUCTION

In recent years, the first realization and the further development of quantum cascade lasers (QCL) (Faist, 1994; Hofstetter, 2001; Pfügl, 2003; Faugeras, 2005) have provided reliable, powerful and tunable sources for the IR region, whose wavelength emission can be selected along a wide range by properly designing the constituting layered structure. Therefore, possible applications of such a source have been already explored in different fields of IR spectroscopy, like environmental monitoring (McManus, 2005), medical diagnostics (Roller, 2002), atomic spectroscopy (Vacchi, 2006), plasma diagnostics (Röpcke, 2006). QCL look quite profitable, since they could provide a compact and unique source also in the IR region, avoiding the requirement to use sophisticated and complicate laser systems.

In the present work, we present the development and testing of QCL sources designed to be used in

atomic spectroscopy, with the aim to describe the characteristics which make them usable also for other applications. In Section 2 we describe the peculiar structure of quantum cascade lasers and we introduce the lasers tested in order to define the achievable performances.

In Section 3 it is presented the experimental setup which allowed us to perform the measurements aimed to define the lasers characteristics: the results are shown in Section 4. Finally, in Section 5 a discussion of the possible applications of QCL in the field of biosensing is provided taking into account the obtained results and presenting some of the worldwide already running activities.

## 2 DEVICES UNDER TEST

In conventional semiconductor lasers light is generated by stimulated emission across band-gap

(inter-band emission); in the case of QCL radiation is generated by intersubband transitions across designed energy gap inside the same band (intra-band emission). Thus the emission transition can be designed by mean of band-structure engineering, i.e. by choosing the thickness of the different layers of the device. A scheme of the basic principle is shown in Figure 1.

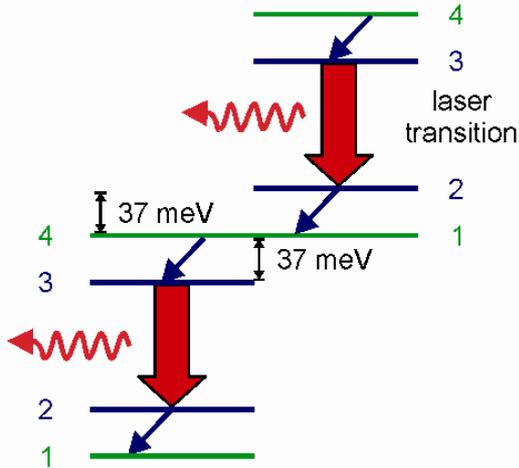


Figure 1: Scheme of the principle of an injectorless QCL.

The QCL structures we designed have been thought for high power and reduced instability in the laser pulse. The scheme is called bound-to-continuum (Pfügl, 2003): the upper laser state is a bound one as in the basic case of QCL structure, while the lower state is spread on a continuum of state, which helps the laser emission, the fast injection of the following active layer and thus inversion of the population. The optimal structure as derived by simulations is presented in Figure 2.

Three different groups of lasers have been designed and fabricated with a lattice matched technique in order to avoid strain problems (morphological defects). The different designs aimed to check the possibility to span the emission over a wider range around  $7\mu\text{m}$ .

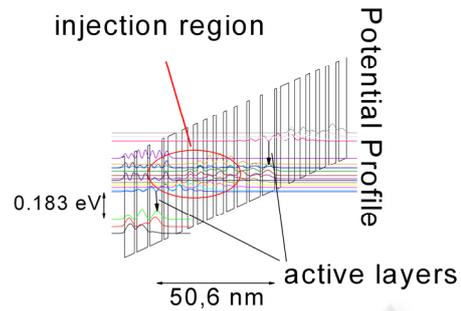


Figure 2: Bound-to-continuum scheme for a QCL with injection region.

Such kind of lasers are basically Fabry-Perot structures, thus expected to have multimode emission (i.e., to emit with several different near peaks). For spectroscopy purposes, single-mode, narrow linewidth lasers with well-defined, precise tunability can be required. In order to achieve these goals, QCL are fabricated with a periodic structure built in the cavity (Figure 3). This periodic variation of the refractive index or of the gain leads to a certain amount of coupling between the back- and forth-travelling waves. The coupling becomes strongest if the periodicity is an integer multiple of half the laser wavelength in the cavity. Because feedback occurs along the whole cavity and not only on the mirrors, these devices are called distributed feedback lasers (DFB). They show usually an excellent single-mode behaviour, can be precisely tuned with temperature or current, and deliver a reasonable amount of output power. In order to test the DFB monomode behaviour, we commissioned such a structure from Alpes Lasers SA, Switzerland, with specification able to match our structures.

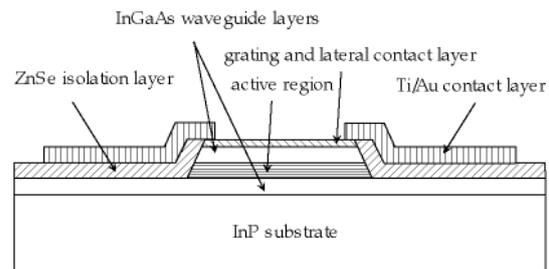


Figure 3: Scheme of the distributed feedback structure, with the grating superimposed to the active region (from University of Neuchatel).

### 3 EXPERIMENTAL SETUP

The lasers are fixed on the cold finger of a cryostat, whose chamber can be evacuated and cooled down to a temperature as low as liquid nitrogen temperature (77K). The emitted light is coupled out of the cryostat through a CaF window (more than 90% transmission in the 2-9  $\mu\text{m}$  range), then collimated and focused on a IR detector by two parabolic reflectors (equivalent  $f/\# \sim 3.9$ ). The measurements are performed by applying a pulsed voltage on the QCL, and reading out the optical power on the detector by mean of an oscilloscope.

In case of spectral measurements, the focused beam has been coupled to the input of a monochromator, and the detector has been positioned at the output of the monochromator itself. We performed both power and spectral measurements at different temperature, in order to define the achievable power and the possible tuning of the laser emission. A scheme of the whole setup is depicted in Figure 4.

In order to perform both the kind of measurements in the same time, it has been explored another possible setup, by mean of inserting a ZnSe beam splitter in the optical path. The beam splitter divides the emitted light in two parts: one is focused directly on a photo detector to measure the optical power, the other is coupled with the monochromator for a contemporaneous spectral measurement. The configuration is also able to provide an online feedback on the drifting of the emission wavelength, which shows to be useful in case of spectroscopy measurements.

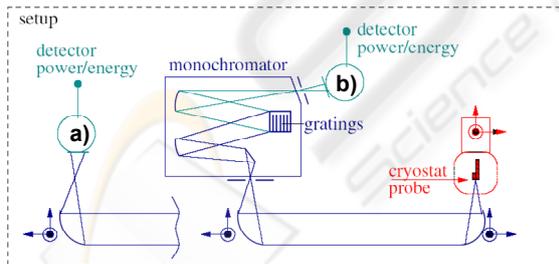


Figure 4: Setup for the optical power measurements: (a for power estimation, b for spectral measurements).

### 4 RESULTS

In Figure 5 an example of the I-V characteristics of our set of lasers is shown as a function of the temperature together with the corresponding emission peak powers. The measurements gave the

idea of the achievable power: more than 1W at cryogenic temperatures; about half of such power is still present at room temperature. The laser could be operated up to 400K. Considering that the laser facet has an area of about 60-100  $\mu\text{m}^2$ , it corresponds to a power density of  $10^6 \text{ W/cm}^2$  if the whole power is perfectly focused. The amount of power allows the lasers to be exploited in spectroscopy of gas, for example by mean of absorption measurements.

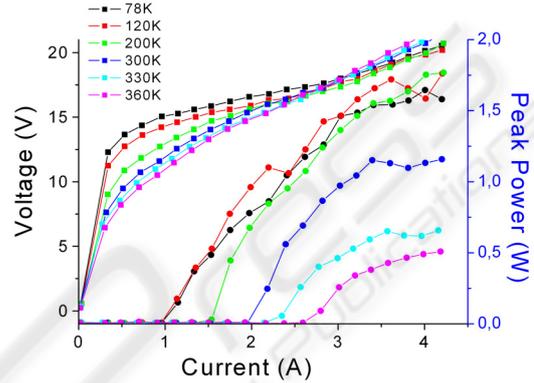


Figure 5: I-V curves and peak power of QCL of our set of laser in the range between 77K and 360K.

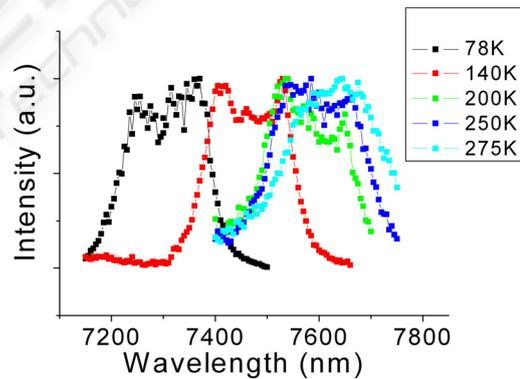


Figure 6: QCL Spectra between 78K and 275K.

The corresponding spectra for one of the three groups of lasers are shown in Figure 6 as a function of the temperature. Due to the high emitted power, it is possible to observe fine structures: none of the spectra could be optimally fit with a simple Gaussian curve, due to the expected multimode emission. The convoluted spectra have widths spanning from 70 nm to about 150 nm. Taking into account all the three groups, the overall range that is possible to span with such lasers is very wide, from 6900 nm up to 7800 nm, demonstrating the possibility to tailor the structure in order to span a desired wavelength range. This feature is another important one in terms of spectroscopy application,

since it could allow to scan wide spectral ranges with a limited number of different devices.

In order to define the achievable tunability, we performed studies on the DFB structure: since it emits in monomode behaviour, its tunability is more well defined. The power achievable with the DFB structure is lower than the one emitted by our structures (even if still about 1W at cryogenic temperatures). However the emission is clearly monomode in a certain range of temperatures as it is possible to estimate from the measurements shown in Figure 7 and it is tuneable with very nice precision by mean of changing the voltage applied by the pulser. Figure 8 reports the study of the tunability, performed at 90K: the peak wavelength increases with increasing voltage (due to the increase of the temperature of the active region), and the behaviour is linear. The achievable tunability is as low as  $(30 \pm 1)$  pm/V around the emission, and the estimation is limited by the resolution of the spectrometer (the actual width of the laser line should be as narrow as 5 pm).

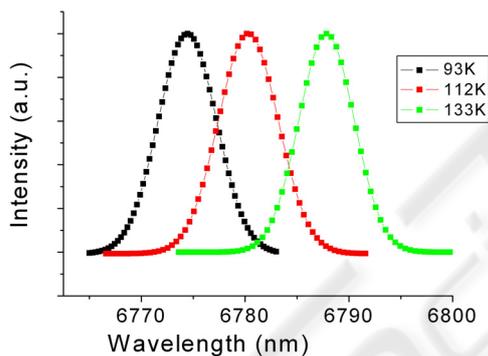


Figure 7: Monomode emission of DFB structure and its shift with the temperature.

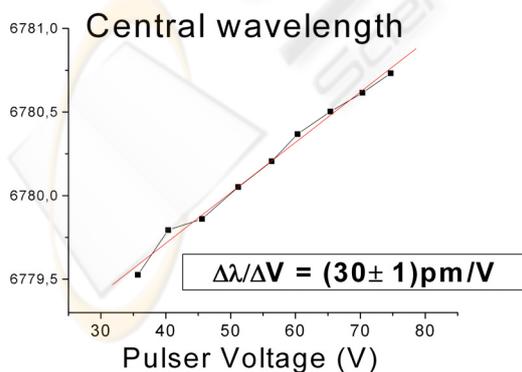


Figure 8: Linear fit of the variation of the central emission wavelength as a function of the pulser voltage.

The very nice achievable precision is a feature strictly required for atomic spectroscopy, where the fine definition of the transition energies is quite important, but it can be also exploited in general spectroscopy.

## 5 QCL FOR BIOSENSING

The presented results describe the achievable performances with a QCL source: high IR power localized in the space, spanning on a very wide range of wavelengths or with monomode emission depending on the chosen structure, providing the availability of fine tuning by mean of very precise temperature changes. All these properties look profitable for spectroscopy in the IR region, and they can be applied as well to biosensing applications.

Indeed, most of the chemical species have distinctive absorption lines in the range between 3 and 20  $\mu\text{m}$  ( $500 - 4000 \text{ cm}^{-1}$ ), due to the vibration modes of the most important organic bonds (see the panel in Figure 9). For example, the QCL structures presented so far emit around 7  $\mu\text{m}$  which means about  $1425 \text{ cm}^{-1}$  (they have been designed in order to provide sources for atomic applications), thus they could be used to detect the C-H bending in the alkanes. Moreover as mentioned above it is possible to choose the emission wavelength only by changing or using different materials without modifying the achievable performances.

Therefore, molecular detection in terms of vibrational spectroscopy is possible, and it is currently under development. Most of the activities is oriented on the utilisation of DFB structures, since spectroscopic applications usually require single mode operation. The laser emission is collimated and focused in a gas cell (usually a tube terminated with antireflection coated windows), which provides both the volume where the absorption takes place and a way to increase the optical path of the radiation and thus to increase the sensitivity of the system. The method has been explored with different kinds of laser to detect different gases, like  $\text{CO}_2$  and  $\text{H}_2\text{O}$  ( $640 \text{ cm}^{-1}$ , Kosterev, 2002),  $\text{C}_2\text{H}_4$  and  $\text{NH}_3$  ( $1000 \text{ cm}^{-1}$ , Weidmann, 2004),  $\text{NO}$  ( $1920 \text{ cm}^{-1}$ , Weber, 2002), providing detection limit down to  $< 1 \text{ ppbv}$ , which could be already exploited in medical diagnostics. Recently, more sophisticated approaches as the off-axis integrated cavity output spectroscopy (OA-ICOS) have been applied to deeply investigate the achievable sensitivity (Bakhtirkin, 2006). Another explored way to realize QCL-based gas sensors has made use of photonic bandgap fibers, which are able to transmit radiation in the IR range. The QCL emission is coupled into

the fiber using a coupling cell: a sensor able to detect C-H stretch band of ethyl chloride gas has been realized in this way ( $975\text{ cm}^{-1}$ , Charlton, 2005). THz lasers, which have higher wavelengths, have been used for gas phase spectroscopy (Hübers, 2006).

For laser spectroscopy of larger molecules with broad absorption features narrow linewidth is not required, but it is more important to be able to tune the emission over a wide wavelength range. In this case, the bound-to-continuum structures we presented provide the required broad spectrum (the lower state of the transition is a relatively broad continuum). The fine tuning is achieved by mean of the utilization of an external cavity configuration: the emission of the laser is collimated and reflected off a diffraction grating so to create a resonant cavity. The first order diffraction from the grating provides the laser feedback, while the output of the

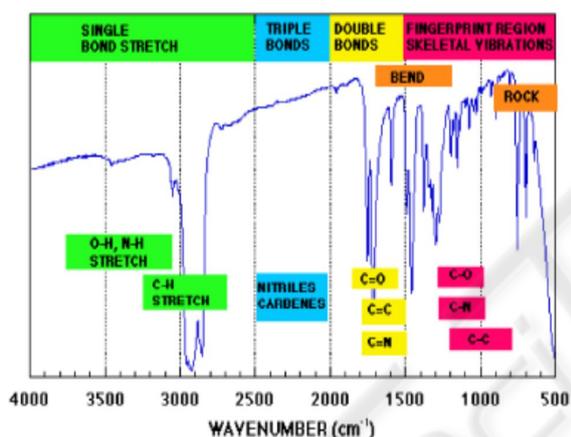


Figure 9: Absorption regions in the infrared.

external cavity is obtained by the zeroth order. The tunability is provided by moving and rotating the grating with piezo actuated positioners. The method has been proved to be fruitful (Wysocki, 2005) and it is currently exploited for measuring absorption spectra of large molecules, like Freon (around  $1150\text{ cm}^{-1}$ , Phillips, 2007).

Another idea which can be exploited comes from the realization of surface-emitting quantum cascade micro cavity lasers: the active region of the laser is covered with a patterned surface, like a photonic crystal. The presence of the crystal provides both feedback for the laser action and a selection of the polarization of the emitted light (Colombelli, 2003). This structure could allow also the possibility to allocate defects on the photonic crystal which can absorb chemical species: the change in emission due to the absorption of molecules can be monitored as a change of the laser emission and the whole would

perform as a compact and sensitive biosensing device.

## 6 CONCLUSIONS

QCL present themselves as reliable sources for IR range: they provide high optical IR power, their emission can be tailored to span a selected range and by mean of a superimposed grating it could be made monomode. The emission is also tuneable with very fine precision, either intrinsically by changing the laser temperature or externally by using a coupled diffraction grating. Their performances make them suitable for a series of application, since most of the molecular species present distinctive absorption lines in the medium infrared.

Different methods to realize QCL-based biosensor have been already tested or are currently in development, principally in the field of the gas sensing for medical diagnostics applications or environmental control: several substances have been already proved to be detectable through the utilization of QCL based sensing devices, which start to provide significant and interesting results.

Such a development is a very interesting field which looks to be double faced. From one side a new class of biosensors could profit of the unique properties of QCL in the IR range: the versatility of such structures could allow a very wide range of design and applications. On the other hand the study of such sensors could provide a further push to the design and development of even more efficient QCL structures properly aimed to better match the requirements of biosensor field.

## ACKNOWLEDGEMENTS

The present work has been performed in cooperation with the SISTER project of the AREA Science Park of Trieste, Italy.

## REFERENCES

- Faist J. (1994) 'Mid-infrared field-tunable intersubband electroluminescence at room temperature by phonon-assisted tunneling in coupled-quantum wells', *Applied Physics Letters*, vol. 64 no. 9, February, pp. 1144-1146.
- Hofstetter D. (2001) 'High temperature operation of distributed feedback quantum-cascade lasers at  $5.3\ \mu\text{m}$ ', *Applied Physics Letters*, vol. 78 no. 4, January, pp. 396-398.

- Pflügl C. (2003) 'High-temperature performance of GaAs-based bound-to-continuum quantum-cascade lasers', *Applied Physics Letters*, vol. 83 no. 23, December, pp. 4698-4700.
- Faugeras C. (2005) 'High-power room temperature emission quantum cascade lasers at  $\lambda=9 \mu\text{m}$ ', *IEEE Journal of Quantum Electronics*, vol. 41, no. 12, December, pp. 1430-1438.
- McManus J.B. (2005) 'A high precision pulsed quantum cascade laser spectrometer for measurements of stable isotopes of carbon dioxide', *Journal of Modern Optics*, vol. 52 no 16, November, pp. 2309-2321.
- Roller C. (2002) 'Simultaneous NO and CO<sub>2</sub> measurements in human breath with a single IV-VI mid-infrared laser', *Optics Letters*, vol. 27 no.2, January, pp. 107-109.
- Vacchi A. (2006) 'Steps towards the development of a QCL laser for muH experiments', *Book of Abstracts*, International Conference on Precision Physics of Simple Atomic Systems, Venice, Italy, p. 33.
- Röpcke J. (2006) 'Application of mid infrared tuneable diode laser absorption spectroscopy to plasma diagnostics: a review', *Plasma Sources Science and Technology*, vol.15, October, pp. S148-S168.
- Kosterev A. (2002) 'Chemical sensing with pulsed QC-DFB lasers operating at  $15.6 \mu\text{m}$ ', *Applied Physics B*, vol. 75, August, pp. 351-357.
- Weidmann D. (2004) 'Monitoring of ethylene by a pulsed quantum cascade laser', *Applied Optics*, vol. 43, June, pp. 3329-3334.
- Weber W. (2002) 'Using a wavelength-modulated quantum cascade laser to measure NO concentrations in the parts-per-billion range for vehicle emissions certification', *Applied Spectroscopy*, Vol. 56, June, pp. 706-714.
- Bakhirkin Y. (2006) 'Sub-ppbv nitric oxide concentration measurements using cw thermoelectrically cooled quantum cascade laser-based integrated cavity output spectroscopy', *Applied Physics B*, vol. 82, November, pp. 149-154.
- Charlton C. (2005) 'Midinfrared sensors meet nanotechnology: Trace gas sensing with quantum cascade lasers inside photonic band-gap hollow waveguide', *Applied Physics Letters*, vol. 86, May, 194102.
- Hübers H.-W. (2006) 'High-resolution gas phase spectroscopy with a distributed feedback terahertz quantum cascade laser', *Applied Physics Letters*, vol. 89, August, pp. 061115.
- Wysocki G. (2005) 'Widely tunable mode-hop free external cavity quantum cascade laser for high resolution spectroscopic applications', *Applied Physics B*, vol. 81, September, pp. 769-777.
- Phillips M. (2007) 'External cavity quantum cascade laser for quartz tuning fork photoacoustic spectroscopy of broad absorption features', *Optics Letters*, vol. 32, May, pp. 1177-1179.
- Colombelli R. (2003) 'Quantum cascade surface-emitting photonic crystal laser', *Science*, November, pp. 1374-1377.