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High-precision molecular spectroscopy in the mid-infrared using quantum cascade lasers

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Abstract Quantum cascade lasers (QCLs) are becoming a key tool in several advanced experiments in the field of precision molecular spectroscopy and absolute frequency metrology. In view of this, a thorough control of their emission properties must be achieved, including a narrow linewidth as well as a high frequency stability combined with referencing to a primary standard. Here, we give a review on recent developments and next perspectives in this scope, with particular regard to the use of QCLs in fundamental Physics spectroscopic searches.

1 Introduction

The Standard Model (SM) has accurately predicted the existence of every particle detected over the past decades in the particle accelerators worldwide [1]. However, this theory is flawed by its failure to predict the imbalance of matter and antimatter, and the origin of dark matter and dark energy, among other things. Thus, it is expected that other particles and forces remain to be discovered. Complementary to the conventional approach of high-energy physics, this frontier research is now tackled also in advanced tabletop-scale experiments. These use precision measurement techniques and devices from the atomic/molecular, quantum, and condensed-matter world to detect tiny signals due to new Physics at the eV energy scale [2,3]. Examples range from precision tests of QED (proton radius puzzle) to time-reversal violation (electron's electric dipole moment), from light dark

matter detection (axions) to General Relativity studies (Einstein's equivalence principle).

Particularly, infrared (IR) precision laser spectroscopy of molecular gas samples, maybe in the cold temperature regime, is playing a significant role in the assessment of the time constancy of the proton-to-electron mass ratio [4], in the search for hypothetical long-range fifth forces between hadrons [5], and in the detection of parity violation [6]. These and other challenges can be tackled with compact and high-performance quantum cascade lasers (QCLs), now competing at least on a par with more conventional but cumbersome coherent radiation sources based on nonlinear down-conversion processes (difference frequency generators and optical parametric oscillators).

The review is organized as follows: section 2 deals with state-of-the-art narrow-linewidth QCLs whose application in absolute frequency metrology is discussed in section 3. Section 4 reports on the related achievements in the field of mid-IR precision spectroscopy. In Section 5, conclusions and perspectives are drawn.

2 Narrow-linewidth QCLs

2.1 QCLs: technology, properties and availability

The mid-IR spectral region is particularly suitable for precision molecular spectroscopy due to the occurrence of ro-vibrational transitions characterized by very intense line strengths and Hz-level natural linewidths. These can be effectively addressed with QCLs which, thanks to

their peculiar structure, can be engineered for emitting over an extremely broad wavelength range. QCLs are unipolar devices exploiting optical transitions between electronic states (conduction subbands) realized by spatial confinement in semiconductor multi-quantum-wells. Thanks to a cascade mechanism through tens of lasing stages, QCLs are able to operate at power exceeding the W level. Threshold currents range between a few hundreds of mA to 1 A, with typical compliance voltage above 10 V. Control and tuning of the emitted frequency and power is achieved by acting on their temperature and bias current, with typical tuning coefficients of ~ 2 GHz/K and ~ 500 MHz/mA for room-temperature mid-IR devices.

In principle, QCLs may be realized using almost any semiconductor material system. To date, the best QCL performance has been obtained by using four semiconductor material systems: GaInAs/AlInAs grown on InP substrates, GaAs/AlGaAs grown on GaAs substrates, AlSb/InAs grown on InAs, InGaAs/AlInAsSb, InGaAs/GaAsSb or InGaAs/AlInGaAs grown on InP substrates [7]. After two decades from their invention in 1994 [8], QCLs operating in the mid-IR have reached impressive performance levels. Multi-watt output power [9], continuous wave (CW), room-temperature devices have been realized with wall-plug efficiencies of up to 21%. Spectral coverage has been achieved at wavelengths from ~ 3 – 25 μm with the potential for large tunability. Furthermore, in 2002 the first QCL emitting in the THz region was demonstrated [10], although limited to operating temperatures of few-to-tens Kelvin. Research is going on the improvement of THz QCLs performance and on the application of THz QCLs for spectroscopy.

Most of these systems are now commercially available from a number of companies, including Alpes Lasers, Hamamatsu Photonics, AdTech Optics, Daylight Solutions, MirSense. Commercial devices include single-mode DFB lasers with >100 mW output power and typical tunability of few tens of wavenumbers, extended-cavity (EC) devices with tens-to-hundred mW output power and tuning up to 200 cm^{-1} , frequency-comb QCLs and broadband high-resolution dual-comb spectrometers based on QCL combs. Research on QCLs is now mostly involved in new promising material systems allowing to cover the first atmospheric window (3 – $5\text{ }\mu\text{m}$) [11], in the development and full control of QCL combs [12, 13], and in the design and realization of devices emitting in the THz region with temperatures approaching the ambient one [14, 15] and in a comb configuration [16, 17].

2.2 QCLs frequency stabilization

From the spectroscopic perspective, since the first demonstration in 1994, many efforts have been devoted to make QCLs useful tools for high-resolution applications. Indeed, by virtue of their intersubband operation and short

level lifetimes, QCLs were immediately expected to have a small intrinsic linewidth. This prompted several groups to study the frequency noise features of QCLs, together with novel stabilization techniques aimed at reducing their emission linewidth [18, 19]. Initial predictions were finally confirmed fifteen years later with the first direct measurement of the intrinsic linewidth of a QCL [20–22] and subsequent theoretical and experimental studies [23–27]. These works demonstrated an intrinsic linewidth as low as few hundreds of Hz, both for cryogenically-cooled and room-temperature mid-IR devices. In parallel, several experimental studies shed light on the frequency dynamics of QCLs and on the influence of the driving current noise to their linewidth broadening [25, 28–30, 7], triggering a series of improvements in the power supply of the QCL chip as well as in the stabilization of its temperature. Over the years, several frequency locking techniques have been employed to reduce the free-running linewidth of QCLs. Among them, we mention: all-electronic locking [31, 32], locking to a spectroscopic sub-Doppler profile [33, 34], to the resonance of a mid-IR Fabry-Perot cavity [35, 36], to a crystalline whispering-gallery-mode (WGM) resonator [37, 38], to an OsO_4 -stabilized CO_2 laser [39], to a near-IR ultra-low-expansion (ULE) reference cavity after up-conversion by sum frequency generation [40]. With such techniques, linewidths in the 10-Hz range were demonstrated [39, 40], with a relative stability down to the 10^{-14} range at 1 s, and an accuracy down to 3×10^{-12} .

As detailed in the next section, among the different stabilization techniques so far demonstrated to control the emission frequency of QCLs [18, 34–36, 39, 41, 42], coherent phase lock to an optical frequency comb (OFC) is an invaluable solution. Indeed, while allowing for tuning the QCL frequency with absolute precision, it is also able to narrow the laser emission linewidth [43–45].

3 Absolute frequency metrology with QCLs

The advent of visible and near-IR optical frequency combs (OFCs) in 1999 [46–48] had a tremendous impact on high-precision spectroscopy, as it offered the opportunity of down-linking the domain of optical frequencies to that of radiofrequency (RF), paving the way for absolute optical-frequency measurements with the accuracy and reproducibility of atomic clocks [49–51]. As QCLs became more reliable and mid-IR spectroscopic measurements with these sources grew in number and quality, the problem of absolute frequency calibration of a QCL against an OFC was soon recognized as a compelling, yet challenging task, due to the need to establish a coherent link with the visible/near-IR, the only available region for commercial comb synthesizers [52].

The frequency gap between near-IR combs and mid-IR QCLs can be filled by second-order nonlinear optical processes based either on sum-frequency-generation

(SFG) or on difference-frequency-generation (DFG). Fig. 1 summarizes a variety of approaches that have been pursued. A first family—(a) and (b) panels—makes use of two additional continuous-wave (CW), near-IR lasers whose frequencies ν_1 and ν_2 are separated by the QCL frequency ($\nu_{QCL} \simeq \nu_2 - \nu_1$) and are locked to comb modes of different order with some offset frequency Δf (here assumed equal for the two lasers), i.e. $\nu_1 \simeq f_{ceo} + n_1 f_{rep} + \Delta f$ and $\nu_2 \simeq f_{ceo} + n_2 f_{rep} + \Delta f$, where f_{rep} and f_{ceo} are the comb repetition rate and the carrier-envelope offset, respectively. In this configuration, a RF beat note is detected either by mixing ν_2 with the SFG signal $\nu_{SFG} = \nu_{QCL} + \nu_1$, i.e. $f_{beat} = |\nu_{SFG} - \nu_2| = |\nu_{QCL} + \nu_1 - \nu_2|$, or by mixing ν_{QCL} with the DFG signal $\nu_{DFG} = \nu_2 - \nu_1$, i.e. $f_{beat} = |\nu_{QCL} - \nu_{DFG}| = |\nu_{QCL} - \nu_2 + \nu_1|$. Both approaches lead to $f_{beat} = |\nu_{QCL} - (n_2 - n_1)f_{rep}|$, which allows calibrating the QCL frequency against the comb repetition frequency and, in principle, against any primary RF reference through the simple formula:

$$\nu_{QCL} = (n_2 - n_1)f_{rep} \pm f_{beat} \quad (1)$$

The beat note f_{beat} can be counted or even stabilized against a RF local oscillator by a feedback loop that acts on the QCL current: if the loop bandwidth is sufficiently large to cover most of the frequency noise spectrum of the QCL, not only the average emission frequency but also the phase of the QCL is actively stabilized to the $(n_2 - n_1)$ -th harmonic of f_{rep} , leading to the so-called phase-locking regime. This leads to a significant narrowing of the QCL linewidth with a positive impact on the spectral resolution of the measurement.

Panels (c) and (d) of Fig. 1 highlight two alternative approaches, again based on SFG and DFG respectively, which allow direct referencing of the QCL to the comb without the need for additional lasers. In the SFG case, ν_{QCL} is summed to a given spectral portion of a near-IR comb, described by $\nu_1 = f_{ceo} + n_1 f_{rep}$, to generate a frequency-shifted comb $\nu_{SFG} = f_{ceo} + n_1 f_{rep} + \nu_{QCL}$: the superposition of ν_{SFG} with the high frequency part $\nu_2 = f_{ceo} + n_2 f_{rep}$ of the original comb leads to a beat note $f_{beat} = |\nu_{SFG} - \nu_2| = |\nu_{QCL} - (n_2 - n_1)f_{rep}|$ and thus to the same f_{ceo} -free referencing formula given by Eq. 1. Alternatively, the difference between the spectral portions ν_2 and ν_1 of a broadband near-IR comb produces an offset-free mid-IR comb spectrally overlapped to the QCL, whose frequency can then be determined by measuring the beating signal with the nearest comb mode and again using Eq. 1. Both configurations necessitate a delay line (not required in cases (a) and (b)), in the SFG case to synchronize on the detector the pulses obtained by SFG with those from the comb, in the DFG case to synchronize, on the nonlinear crystal, pump and signal pulses.

DFG and SFG approaches lead to similar optical power levels of the beat note signal. SFG, anyway, has the advantage of producing a beat note in the near-IR,

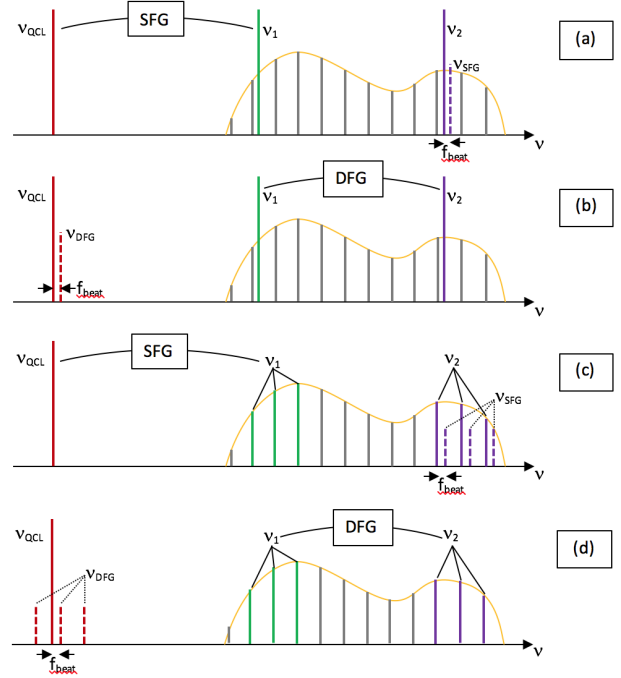


Fig. 1 Referencing of a mid-IR QCL to a near-IR comb: SFG mediated by CW optical oscillators (a); DFG mediated by CW optical oscillators (b); direct link to the comb by SFG (c); direct link to the comb by DFG (d).

where the spatial matching and alignment of the interacting beams is easier and may be further facilitated by optical fibers. Moreover, cost-effective, low-noise detectors with high bandwidths are readily available, also in balanced schemes, that provide a 3-dB enhancement of the signal-to-noise ratio (SNR). Use of intermediate CW lasers suffers from the drawback of additional costs and complexity, as well as from the need for a higher number of servos. However, a powerful CW laser allows for high SNRs and enables offset frequency locking schemes where the QCL frequency can be scanned back and forth over GHz-wide ranges simply by tuning the RF local oscillator. The DFG approach allows for the use of the comb as a transfer oscillator (original concept from Telle and coworkers [53]). This virtually eliminates any noise contribution from the comb and the QCL linewidth can be shrunk down to the level of the narrowest of the two CW lasers used for DFG [54].

The first referencing of a QCL to a near-IR comb, specifically a liquid-nitrogen cooled DFB-QCL at $4.3 \mu\text{m}$ to a Ti:Sa comb, was achieved in 2007 through the (a) scheme [43], ν_1 being provided by a powerful 1.2-W Nd:YAG laser and ν_2 by a diode laser. This system was successfully exploited to measure the absolute frequency of the QCL when locked to a sub-Doppler feature of a CO_2 transition, with a kHz level precision and an overall uncertainty of 75 kHz [55]. A few years later, the same type of QCL at $4.3 \mu\text{m}$ was directly locked to an Er:fibre comb through the (c) scheme [56] and exploited to infer

line centers [57], pressure broadening and shifting coefficients [58], molecular densities [59] from Doppler broadened CO₂ spectra acquired by f_{rep} tuning. In all these demonstrations, no phase locking was achieved, because of the large amount of QCL frequency noise (linewidth of ~ 2.5 MHz). Very recently, frequency locking of an EC-QCL emitting around $7.8 \mu\text{m}$ to a Tm-comb via the same (c) scheme [60]. Locking of EC-QCLs is not trivial because of their much larger free-running jitter induced by the external cavity (~ 20 MHz at the ms timescale [61, 60]), and only a reduction of a factor 8 (2.5 MHz FWHM over few ms) was achieved with a locking bandwidth of about 30 kHz.

Phase-locking was demonstrated only in 2012 using a much narrower room-temperature DFB-QCL at $9.1 \mu\text{m}$, a Tm:fibre frequency comb and an SFG scheme in an AgGaSe₂ crystal [62]. Interestingly, a bandwidth of 100 kHz was enough for phase locking, thanks to the very low quantum noise pedestal of DFB-QCLs [20–22] and to their peculiar frequency noise spectrum that is largely dominated by a $1/f$ behavior till about 100 kHz [29]. Almost in parallel, phase-locking of a room-temperature DFB-QCL at $4.3 \mu\text{m}$ was demonstrated against an ultra-narrow comb-referenced DFG source [63] and exploited for saturated spectroscopy of some CO₂ lines with sub-kHz resolution and kHz accuracy [64]. The locking bandwidth was later pushed up to 500 kHz, with a residual integrated phase noise down to 0.78 rad, using the (d) referencing scheme, with DFG performed in GaSe and a beat-note detection at $8.6 \mu\text{m}$ with a DFB-QCL driven by a low noise current driver [65]. Such a comb source has been successfully applied to precision spectroscopy of CHF₃ in both a Doppler [65] and a sub-Doppler regime [66]. In 2015, the coherence of an ultra-stable Hz-linewidth $1.55 \mu\text{m}$ laser was transferred to a $10.3 \mu\text{m}$ QCL through interposition of an Er:fibre comb, with state-of-the art frequency stability of 2×10^{-15} [67].

Some recent works have benefited from a novel, high-performing technology for disseminating the primary frequency standard with accuracy levels far beyond the GPS technology. It is based on dissemination of an ultra-stable optical reference, linked to a Cs fountain, via fiber links managed by national institutes for metrological research (including the PTB in Germany, the LNE-SYRTE in France, the INRIM in Italy, the AGH in Poland, and the NPL in the UK), connecting to different laboratories tens to hundreds of km far away. Impressive results in QCL stabilization were recently reported by the NPL group which achieved 10-Hz linewidth and sub-Hz relative stability by locking a $10.3\text{-}\mu\text{m}$ QCL to an OFC stabilised against a remote near-IR ultra-stable frequency reference via an optical fibre from LNE-SYRTE [67]. A little later, at CNR-INO in Firenze a QCL emitting around $6 \mu\text{m}$ was stabilized to a near-IR optical reference distributed via fiber link from INRIM, making the QCL to reliably reflect the long-term stability and accuracy levels of the Cs fountain and allowing for absolute

frequency measurements of molecular transitions with a relative uncertainty at the 10^{-11} level [68].

In parallel, an effort was spent to reduce the QCL linewidth while increasing the frequency stability, not necessarily in conjunction with OFCs, either to improve the spectral resolution of a given spectroscopic apparatus or for the synthesis of an optical standard in the mid-IR. A variety of approaches have been exploited: locking of a QCL to the side of a ro-vibrational resonance of nitrous oxide at $8.5 \mu\text{m}$ [18] or to the resonance of an optical cavity through a Pound-Drever-Hall technique [35], optical injection of a QCL with a comb-referenced DFG source at $4.7 \mu\text{m}$ [69], stabilization of a QCL against the Lamb-dip feature of a CO₂ transition at $4.3 \mu\text{m}$ [34], optical-feedback locking of an $8.6\text{-}\mu\text{m}$ QCL to a stable V-shaped optical cavity [36], and stabilization of a $4.3\text{-}\mu\text{m}$ QCL to a monolithic whispering-gallery-mode microresonator with high Q factor ($10^7 \div 10^8$) [37]. In the best cases, the resulting linewidth and stability was found to be at the sub-kHz level.

4 High-resolution spectroscopic applications with QCLs

Whenever high-precision measurements of either weak ro-vibrational molecular bands or extremely rare isotopologues are needed, any spectroscopic setup/technique eligible for this task must be highly performing both in terms of resolution and in terms of sensitivity. Regarding the technique, its detection limit must be low enough to detect a measurable absorption at the experimental thermodynamic conditions of the gas sample. Regarding the laser source, its emission linewidth must be narrower than the spectral feature to be measured. As already pointed out, QCLs have proven to be well suitable tools for precision spectroscopy in the mid IR thanks to the possibility to narrow their linewidth and refer them to the primary frequency standard.

4.1 Sub-Doppler saturated-absorption spectroscopy

As already mentioned, in 2007 the first absolute measurements of a molecular transition with a comb-referenced QCL could be performed [43]. A cryogenically-cooled DFB QCL emitting around $4.4 \mu\text{m}$ was tuned onto a Doppler-broadened CO₂ transition. Its frequency was absolutely referenced to a comb operating between 500 and 1100 nm by means of an up-conversion process in a periodically-poled lithium niobate (PPLN) crystal. The achieved precision of $3 \cdot 10^{-8}$ for the absolute frequency measurement of CO₂ transitions was limited by the free-running QCL jitter. The system was improved one year later by moving to a sub-Doppler set up, with the same laser and comb-referencing scheme. In that experiment, the QCL was frequency-stabilized to the CO₂ Lamb-dip center with a locking bandwidth of a few hundreds Hz,

allowing for the correction of temperature drifts and for averaging over time. The final precision in the absolute frequency measurements was improved by about 2 orders of magnitude, with an overall precision over repeated scans of 75 kHz [55].

In 2013, a QCL that was phase-locked to a metrological-grade DFG source yielded sub-Doppler saturated-absorption measurements of several CO₂ lines around 4.3 μm [63]. The saturated-absorption setup, depicted schematically in Fig.2 (lower part), used less than 10 mW power from the QCL in a classical configuration of counter-propagating pump-probe beams. Within the tuning range of the QCL,

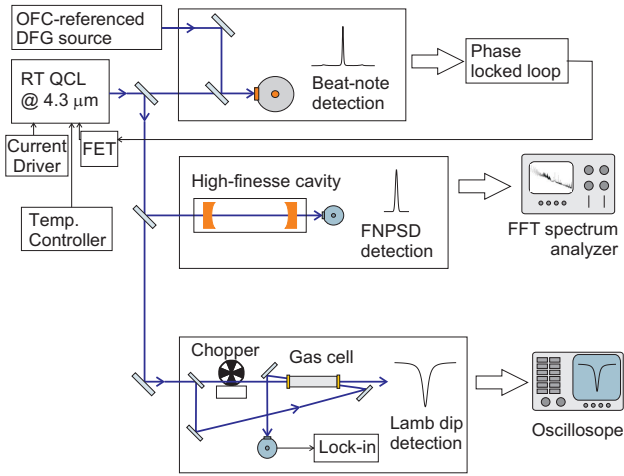


Fig. 2 Schematic of the experimental setup. We see three main parts: the beat-note detection between QCL and DFG for phase-locking, the high-finesse cavity for frequency-noise power spectral density (FNPSP) analysis, and the saturation spectroscopy signal detection for the absolute frequency measurement of the CO₂ transitions. Reprinted with permission from [63], copyright 2013.

the absolute center frequency of six CO₂ transitions belonging to the *P* branch of the (01¹1–01¹0) ro-vibrational band could be measured. An optical chopper on the pump beam, combined with a lock-in detection, allowed for the cancellation of the Doppler background due to the probe radiation. Moreover, it allowed to retrieve the Lorentzian Lamb-dip profile with an optimal signal-to-noise ratio, when the absolute frequency of the phase-locked QCL was scanned across the Lamb dip by a step-wise tuning of the DFG source. As an example, the recorded Lamb-dip spectrum of the P(34)f line is shown in Fig.3. Each data point represents the average of 10 samples, acquired by the lock-in amplifier with a chopping frequency of 2.49 kHz and a time constant of 10 ms. The 20-MHz scan across the Lamb-dip feature takes two minutes and is performed over both directions with 50 kHz steps. Any frequency shift caused by pulling effects of the lock-in integration is compensated in this way. In Fig.3 the Lorentzian fit curve and the correspond-

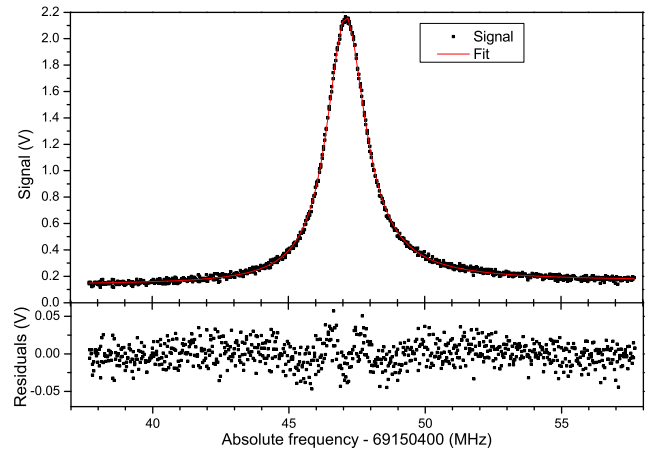


Fig. 3 Lamb-dip recording of the P(34)f line at 2306.6108 cm⁻¹ at 12 Pa and 295 K. The fit is a Lorentzian function corrected both for a linear amplitude modulation (as the QCL frequency is scanned by ramping its driving current) and a background signal of the lock-in amplifier. Reprinted with permission from [64], copyright 2013.

ing residuals are also plotted. Thanks to the high precision/accuracy achieved by our setup, we were able to perform a series of acquisitions by varying the pressure of the CO₂ gas in a very small range (1–26 Pa), thus allowing for precise measurement of the self pressure shift. With this setup, a \sim 1-kHz precision on the absolute frequency of the transitions, corrected by systematic pressure shift, was achieved.

4.2 Saturated-absorption cavity ring-down spectroscopy

In 2010, Saturated-Absorption Cavity Ring-down Spectroscopy (SCAR) was invented [70,71] and successfully exploited for sub-Doppler measurements of the ¹⁶O¹²C¹⁷O isotopologue of carbon dioxide at low pressure, resolving the hyperfine structure of its (00⁰1 – 00⁰0) R(0) ro-vibrational transition [72]. The earlier experimental SCAR setup was based on a low-power (< 100 μW) DFG coherent source with both narrow linewidth and absolute frequency traceability, provided by the phase locking of pump and signal sources to a near-IR frequency comb and by a GPS-disciplined Rb clock, respectively [52,54]. This apparatus, with an improved DFG source [73], allowed for the first ever optical detection of the ultra-rare ¹⁴C¹⁶O₂ isotopologue of carbon dioxide at natural abundance (\sim 1.2 ppt) [74]. In addition, the absolute frequency traceability allowed to observe tens of transitions belonging to the (00⁰1 – 00⁰0) ro-vibrational band of ¹⁴C¹⁶O₂, measuring their absolute frequencies with MHz (or even sub-MHz, in the best cases) uncertainty [75].

In the latest SCAR apparatus, the comb-assisted DFG source has been replaced with a couple of DFB QCLs, one of which (QCL1) probes the molecular transition, the second one (QCL2) being locked to the (02⁰1 – 02⁰0)

R(16)e line of $^{14}\text{N}_2^{16}\text{O}$ and used as a frequency reference [76]. The new setup has been calibrated by measuring for a long averaging time a CO_2 gas sample produced by burning the ^{14}C standard (oxalic acid, NIST Standard Reference Material 4990C) in an elemental analyzer. Fig. 4 shows both the experimental results and the data fit. As many as 121 absorption spectra were ac-

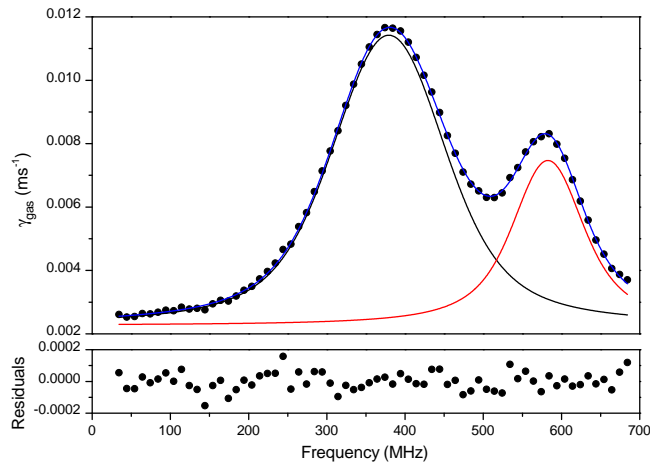


Fig. 4 Calibration of the SCAR setup. Black dots are experimental data points of light decay rate due to gas absorption from both the $(00^0_1 - 00^0_0)$ P(20) line of $^{14}\text{C}^{16}\text{O}_2$ (left peak) and the $(01^1_1 - 01^1_0)$ Q(12)e interfering line of $^{14}\text{N}_2^{16}\text{O}$ (right peak). Black and red curves are Voigt profiles best fitting the 2 peaks, and the blue curve is their sum. Fit residuals are plotted below. A constant value of 66 227 000 MHz was subtracted to the frequency scale.

quired for an overall averaging time longer than 20 hours (split in different days), with thermodynamic conditions of the gas sample of 12 mbar pressure and 170 K temperature. This setup not only allowed for improved sensitivity in radiocarbon detection, but proved to be effective also for precision spectroscopic measurements. As a first result, by combining the more accurate measurement of the $(00^0_1 - 00^0_0)$ P(20) line center of $^{14}\text{C}^{16}\text{O}_2$ reported in [75] with the value retrieved by the present fit, the value of the N_2O line center frequency was measured with an improved uncertainty with respect to the HITRAN database, i.e. 66 226 711.22(91) MHz. More importantly, this setup has demonstrated sub-MHz precision for line center measurements, even in Voigt regime, which is an impressive result when considering the extremely low concentration of the $^{14}\text{C}^{16}\text{O}_2$ isotopologue.

4.3 Spectroscopy on molecular beams

Molecular beams are particularly attracting because they are a relatively simple sources of cold, non-colliding molecules where Doppler broadening is strongly reduced. To save on pumping capacity, molecular beams are often operated in pulsed mode, which matches nicely the repetition

rate of Q-switched lasers (commonly 10–100 Hz). Typical number densities in molecular beams are of the order of 10^{11}cm^{-3} , which corresponds to intermediate UHV conditions [77]. Therefore, CW QCLs are not a natural choice for spectroscopy on molecular beams. However, QCLs are rather unique in their coverage of the mid-IR range and the most recent devices yield tens of mW, which corresponds to Rabi frequencies at the MHz level, for transition dipole moments in the range 0.01–0.1 debye, typical for vibrational transitions.

Recently, a vibrational transition in metastable CO was measured with 11 digits of precision in a triple-resonance experiment on a pulsed molecular beam [68]. The metastable state was produced with a pulsed laser from the ground state. The QCL drove the vibrational transition $v = 1 \leftarrow 0$. From $v = 1$ the molecules were detected by multiphoton resonance-enhanced ionization (REMPI), thus allowing for a background-free measurement. The vibrational transition was saturated with a few mW of power. This setup yields a Doppler-broadened absorption profile with a FWHM of 900 kHz and final uncertainty on the center of the transition of 3 kHz, improving the results available in the literature by more than 4 orders of magnitude over ref. [78]. Key to this result is a phase-locking scheme that requires only a tiny amount of QCL power, whereas the rest is used for the spectroscopic transition. A 640-km-long optical fibre from the national metrological institute carries a frequency reference close to 1550 nm to the laboratory; an optical frequency comb keeps the frequency difference between two CW lasers constant, so that they can be mixed in an orientation-patterned GaP crystal to generate mid-IR radiation. The mid-IR QCL is eventually locked to this radiation.

A drawback of QCLs is their extreme sensitivity to back reflections. This, together with the lack of efficient optical isolators in the mid-IR over $5\text{ }\mu\text{m}$, prevents the use of perfectly overlapped, back-propagating beams, thus strongly limiting the possibility of using high-finesse optical cavities. Therefore, alternative approaches are required to avoid systematic Doppler shifts. Moreover, no straightforward solution has yet been proposed for two-photon, sub-Doppler measurements on a molecular beam. A further problem for high resolution spectroscopy on molecular beams arises from the lack of a proper cavity in QCLs. This typically yields beam profiles of a very poor quality. Spatially coherent laser beams can be produced for Rabi or Ramsey schemes by filtering the QCL beam with hollow fibres or pinholes, at the cost of a reduction in power.

In another pulsed experiment, Tokunaga [79] et al. measured the Re=O antisymmetric stretch in methyltrioxorhenium (MTO) around $10.2\text{ }\mu\text{m}$. The measurement was performed on a 4-Kelvin sample produced via buffer gas cooling (BGC), yielding a resolution of 8 MHz.

5 Conclusion and perspectives

Precision spectroscopy with QCLs has been so far carried out only with DFB sources, which are the most interesting option because of their relatively narrow linewidth, their free-running stability and their straightforward tunability, even at high frequencies, by current modulation. On the other hand, even acting on the temperature of the chip, their overall tuning range remains limited to about 10 cm^{-1} , which makes them inadequate to tackle the investigation of entire absorption bands, that would require a 100 cm^{-1} spectral coverage. For such large ranges an alternative solution is represented by external cavity quantum cascade lasers (EC-QCLs). Actually, due to their large amount of frequency noise, their use in combination with frequency combs has been poorly exploited, the only examples being the open-loop comb-based calibration of a frequency swept EC-QCL source at $4.6\text{ }\mu\text{m}$ [61] and the frequency locking of a $7.8\text{-}\mu\text{m}$ EC-QCL to a Tm:comb via SFG [80,60]. The former was applied to the investigation of the ν_3 band of N_2O with an 800 kHz accuracy [60], the latter to the ν_1 band of N_2O with an accuracy improved to 60 kHz [81], yet limited by the extremely large linewidth of the EC-QCL (about 20 MHz over the ms timescale, reduced to 2.5 MHz in frequency-locking conditions [60]). In a future, however, a reduction of the frequency noise via better coating quality and higher mechanical stability of the laser cavity could result in EC-QCLs with sub-MHz linewidths, mode-hop-free tuning ranges up to 100-cm^{-1} and optical power of a few hundreds mW. This would pave the way to precision line surveys over broad bands, at wavelengths from 4 to $12\text{ }\mu\text{m}$, even in a sub-Doppler regime, in some way replicating in the mid-IR what is currently achieved in the near-IR with extended-cavity diode lasers.

Further progress in the performance of QCLs, either DFB or EC, would mark the birth of a new class of mid-IR laser sources with a unique mix of spectral features. Then, combination with state-of-the-art optical frequency standards, as delivered by actively stabilized fiber links, as well as with more sophisticated interrogation techniques, like two-photon excitation in the optical domain, would push the precision of ro-vibrational molecular spectroscopy to extreme levels. Ultimately, application of such a spectroscopic instrumentation to cold molecular samples, as produced by modern BGC machines, would effectively overcome the transit-time broadening limit in sub-Doppler spectra, thus producing new sets of ultra-precise frequency measurements in the mid-IR spectral region.

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