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Comb-calibrated sub-Doppler spectroscopy with an external-cavity quantum cascade laser at 7.7 μm

BIDOOR ALSAIF,[1] DAVIDE GATTI,[2] MARCO LAMPERTI,[2] PAOLO LAPORTA,[2] AAMIR FAROOQ,[1] AND MARCO MARANGONI[2,*]

[1] *King Abdullah University of Science and Technology (KAUST), Clean Combustion Research Center (CCRC), Physical Sciences and Engineering Division, Thuwal 23955, Saudi Arabia*
[2] *Physics Department of Politecnico di Milano and IFN-CNR, Via G. Previati 1/C, 23900 Lecco, Italy*
**marco.marangoni@polimi.it*

Abstract: We study the frequency noise and the referencing to a near-infrared frequency comb of a widely tunable external-cavity quantum-cascade-laser that shows a relatively narrow free-running emission linewidth of 1.7 MHz. The frequency locking of the laser to the comb further narrows its linewidth to 690 kHz and enables sub-Doppler spectroscopy on an N_2O transition of the ν_1 band near 7.7 μm with sub-MHz resolution and absolute frequency calibration. The combined uncertainty on the measured transition center is estimated to be less than 50 kHz.

1. Introduction

The invention of quantum-cascade-lasers (QCLs) has made many commercial laser solutions available over a large part of the so-called fingerprint region, from 4 to 13.6 μm, which is of major relevance for trace gas detection at high chemical selectivity. QCLs are now deployed for several applications [1], such as industrial process control, monitoring of pipeline leaks, emission control of pollutants and green-house gases, safety in workplaces and so on. In parallel, QCLs have been largely used in the research arena for breath analysis [2], study of gas kinetics in combustion processes [3], investigation of plasma [4] or supersonic expansion of gases [5] and precision spectroscopy [6]. In the latter respect QCLs were recognized early as excellent candidates for high-resolution applications because of a quantum noise limit of few hundred hertz [7]. However, their emission linewidth remained at a level of a few MHz for several years even for the narrower distributed-feedback versions [8, 9], mostly due to the impact of current noise from power supplies [10]. Besides improving the noise level of current drivers, a variety of locking techniques have emerged to shrink their emission linewidth. Among these (see review given in [6] and references therein), the coherent phase lock to an optical frequency comb (OFC) turned out to be highly powerful [11–14], as it allows precise tuning, absolute frequency calibration and line narrowing, all at once. By this approach a variety of molecules have been studied in the mid-infrared even with sub-Doppler resolution, such as CO_2 [12], OsO_4 [14], CF_3H [15]. However, phase locking to an OFC has been demonstrated so far only with distributed-feedback QCLs, which offer narrower emission linewidth as compared to their external-cavity (EC) counterparts [16–18].

On the other hand, EC-QCLs stand out because of their typically higher output power in a single longitudinal mode (up to 200 mW and beyond) and of their much larger tuning range (up to 100 cm^{-1}), which is highly beneficial for multi-species gas sensing and for quantitative detection of complex molecules with unresolved rotational structure at environmental pressure and temperature. Their large free-running emission linewidth, often found at the 10-20 MHz level, kept them away from precision spectroscopic studies. Only in a few cases EC-QCLs have been exploited in conjunction with an OFC, either in an open loop configuration,

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where their beat-note with the comb was tracked in real time while sweeping their frequency, or more recently in a regime of frequency locking [18], yet without solving the problem of an effective linewidth in excess of 10 MHz. In parallel, it was shown that an improved design of external cavities may result in a significant line narrowing and enables sub-Doppler spectroscopy [19]: specifically, an emission linewidth down to 2.5 MHz was inferred from the instrumental broadening of the observed Lamb dips. However neither any measurement of the frequency noise spectrum of these lasers, nor any attempt to get them locked to an OFC for longer-term stability and absolute frequency calibration has been reported so far.

In this work, we fill this gap by measuring the frequency noise spectrum of a commercial EC-QCL emitting at around 7.7 μm with improved linewidth performance. The characterization is performed both in free-running conditions and laser locking to a near-infrared Tm:fiber OFC. The noise spectrum is found to be consistent with a free-running linewidth of 1.7 MHz at 10 ms, which shrinks to 690 kHz under OFC locking. This is indirectly proven by saturated spectroscopy of the R16 line in the ν_1 band of N_2O at variable pressures. At about 1 mTorr the full-width-at-half-maximum of the dip amounts to ~850 kHz without any deconvolution with the laser line. To the best of our knowledge these are the narrowest features ever observed with an EC-QCL. Additionally, we exploit the absolute frequency scale of the OFC to infer the line center and compare it against the metrological data provided by Ting et al. [20]. The overall agreement is within 50 kHz.

2. Methods

The experimental setup is sketched in Fig. 1 and is based on a commercial EC-QCL from Daylight solutions (41078 MHF, model year 2015) that offers tunability from 7.25 to 8.00 μm with a maximum optical power of 120 mW. Frequency-locking to a Tm:fiber comb emitting at 1.9 μm [21] is achieved through the nonlinear-referencing scheme described in detail in [18], which is insensitive to the carrier-envelope-offset frequency of the comb. Synthetically, the optical frequency of the EC-QCL is summed up to the frequency comb in a zinc-germanium-phosphide (ZGP) crystal to generate a frequency-shifted comb near 1.54 μm: when this is superimposed in a balanced photodetector (BD in the figure) with a supercontinuum at 1.54 μm generated from the comb itself, a beat-note signal is produced which provides the instantaneous frequency difference between the EC-QCL and an integer number of the repetition rate of the comb. As the rep rate is in turn stabilized against a primary clock via a GPS-disciplined Rb oscillator, the beat-note measurement allows for an absolute calibration of the EC-QCL frequency. Additionally, the beat-note may be stabilized with respect to a radiofrequency local oscillator by feedback to the EC-QCL current and piezo actuators, which enables highly reproducible and absolutely-calibrated frequency scans by tuning of the comb rep rate. It is worth pointing out that in such a referencing scheme no contribution is provided by the comb offset-frequency [6].

A part of the EC-QCL light, after being diffracted by an acousto-optic modulator (AOM), is used for the spectroscopic measurements. The AOM serves two purposes: firstly, it reduces the laser instabilities that arise because of optical feedback from the counter-propagating geometry imposed by the saturated absorption measurements; secondly, in combination with a servo loop and an MCT photodetector that monitors the output power before the gas cell, it provides a way to actively stabilize the optical power sent to the cell itself, which is beneficial to suppress the laser intensity noise and to flatten the spectral baseline. The laser beam crosses a 66 cm stainless steel gas cell equipped with AR-coated Zn-Se windows that transmits a power up to 10 mW. At the cell output the beam is back-reflected along the same optical path to read out the absorption saturation imprinted by the incoming beam. A lens with a long focal length (1 m) helps in compensating the divergence of the laser due to diffraction while guaranteeing a good spatial overlap between the two beams. The spectroscopic signal is collected by a liquid nitrogen-cooled MCT detector with a bandwidth of 2 MHz.

The absorption lines are unambiguously identified against the HITRAN database [22] by taking advantage of the broad laser tunability and thus of the chance to measure several adjacent N_2O lines. Moreover, as the line center frequencies of the fundamental ν_1 band of N_2O are given in the HITRAN database with an uncertainty (3-30 MHz) well below the comb mode spacing (100 MHz), the assignment of the comb mode order is straightforward.

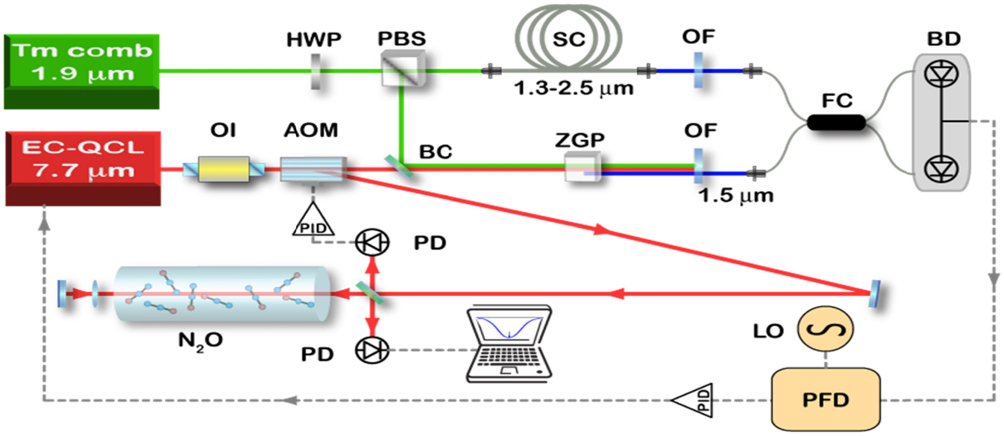

Fig. 1. Experimental setup. HWP: half-wave plate; PBS: polarizing beam splitter; SC: supercontinuum fiber; OF: optical filter; FC: frequency coupler; BD: balanced detector; OI: optical isolator; AOM: acousto-optic modulator; BC: beam combiner; ZGP: Zinc Germanium Phosphide crystal for sum-frequency generation; PD: photodetector; LO: local oscillator, PID: proportional-integral-derivative servo; PFD: phase frequency detector.

3. Results and discussion

To characterize the frequency noise of the EC-QCL we firstly measured the electrical spectrum of the beat-note signal between the comb and the EC-QCL in free-running conditions over a measurement time of 10 ms, i.e. before the onset of evident laser drifts. Since comb modes are stable and narrow (below 100 kHz linewidth) this spectrum traces the EC-QCL emission line. The inset of Fig. 2(a) (blue line) shows a nearly Gaussian profile for the beat-note spectrum due to the prevailing 1/f noise contribution, with a full width at half-maximum of 1.7 MHz, the smallest ever observed so far for a free-running EC-QCL to the best of our knowledge. Using two servo loops, the first providing feedback to the EC-QCL piezo over a few tens of hertz, the second acting on the EC-QCL current at > 100 Hz, we managed to lock the EC-QCL to the comb. The beat-note spectrum is modified according to the red line in Fig. 2(a), with the appearance of a coherent peak. This is the signature of a robust frequency locking yet not of a phase locking because of the small contrast of the peak.

To have a deeper insight into the laser noise under free-running and locked conditions, we exploited the edge of an intense N_2O absorption line as a frequency discriminator to infer the frequency noise power spectral density of the laser. The calibration of the frequency-to-amplitude conversion coefficient was readily obtained by a controlled scan of the comb repetition rate while keeping the EC-QCL locked to the comb. The resulting frequency noise spectrum is shown in Fig. 2(b). In free-running conditions the noise behavior differs from that of EC-QCLs from the same manufacturer with older cavity designs [16,18] because of the absence of any $1/f^2$ dependence and of the reduction of 1/f contribution by nearly two orders of magnitude, thus representing a significant advancement. The locking loop provides noise reduction till a frequency of 100 kHz but with a rather small depth due to the difficulty to quench the rather large mechanically-induced noise in the 100 Hz range while preserving the stability of the feedback loop. This translated also into an impossibility to achieve phase locking. By integrating the frequency noise spectrum down to 100 Hz we infer an EC-QCL linewidth of 1.7 MHz and 690 kHz in free-running and locking conditions, respectively, thus in good agreement with the beat-note spectra at 10 ms. These values are almost one decade above the comb mode limit [11] and constitute the first demonstration of an EC-QCL suitable for measurements with sub-MHz spectral resolution.

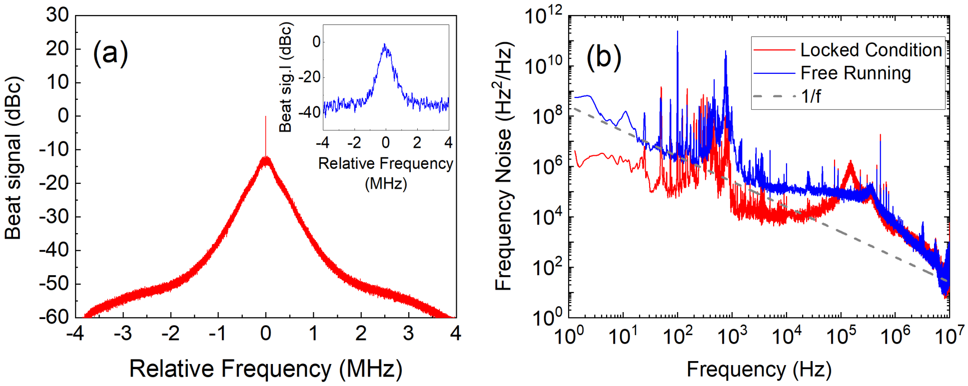

Fig. 2. (a) Electrical spectrum of the beat-note signal in free-running (inset) and locking conditions. (b) Power spectral density of the laser frequency noise in the two conditions together with 1/f asymptote.

We applied the comb-locked laser source to the sub-Doppler study of the R16 line in the ν_1 band of N_2O. Figure 3(a) shows a zoomed view of Doppler spectra acquired at different pressures by tuning the rep rate of the comb over 880 Hz with steps of 1 Hz, corresponding to spectral points separated by 380 kHz: Lamb dips are clearly evident even with a such coarse spacing, with a contrast up to 20% of the linear absorption. Further acquisitions were performed over a narrower spectral range and with closer spectral points, at different pressures and at different power levels. An example of those spectra, at a pressure of 10 mTorr and with a total measurement time of 1.5 minutes, is reported in Fig. 3(b). The solid line represents a Voigt fit with a Lorentzian width fixed at the 80 kHz value given by pressure broadening [22]. The fit returns a Gaussian width that varies from 850 to 1150 kHz depending on the optical power, as it is shown in the inset. Interestingly, the minimum width closely approaches the laser linewidth of 700 kHz previously measured: on one hand, this is the signature of a relevant instrumental broadening given by the laser, on the other hand this attests the feasibility, for the first time, of sub-MHz resolution with an EC-QCL.

The comparison between line centers obtained from repeated measurements of the same dip returns a statistical uncertainty of 4.5 kHz for the single measurement, which is consistent with a dip signal to noise ratio of about 200 and a sub-MHz dip. The retrieved line center frequency calculated as a weighted mean of the line positions obtained at different power values (38931326476.0(3.5) kHz) differs by 48 kHz from the calculations reported in [20, 23], which are declared accurate to within 2.4 kHz, and by 57 kHz from a recent model based on Doppler broadened comb-calibrated spectra [24]. In a worst-case scenario, we estimate at the 50 kHz level the accuracy of our determinations, mainly limited by a residual few-percent asymmetry of the spectral baseline that emerges from the residuals (Fig. 3(c)). The fitting of dip spectra with advanced profiles accounting for speed-dependent collisional effects might lead to flatter residuals and eventually to a reduction of the systematic uncertainty. However, as the choice of the profile and the tuning of profile parameters is far from trivial in a sub-Doppler regime, this type of analysis extends beyond the scope of the work and will be the object of future investigations.

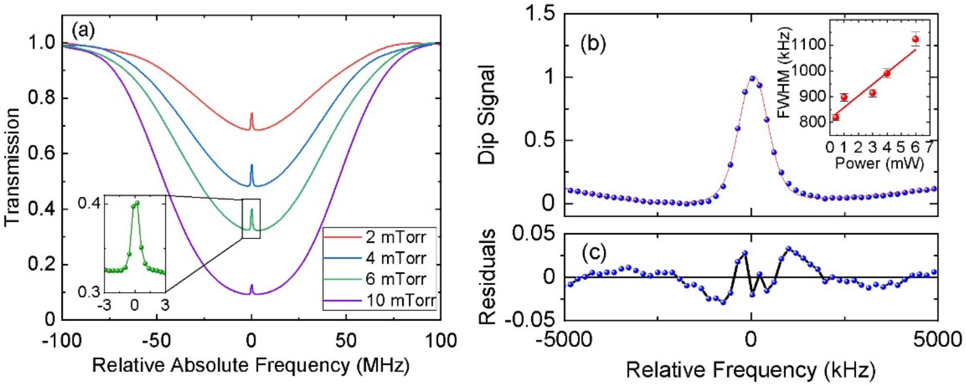

Fig. 3. (a) Measured spectra of the R16e N_2O line at a wavelength of 7.70 µm at different pressures. Inset: zoomed in view of the Lamb dip. (b) Lamb dip measured with a denser spectral grid at a pressure of 10 mTorr and at a power of 1 mW. Measurement time: 1.5 minutes. A fitting procedure with a Voigt profile at fixed Lorentzian collisional contribution returns a total linewidth that linearly increases with the optical power as displayed in the inset. (c) Fit residuals reveal a distortion around 2% and a signal-to-noise ratio in excess of 200.

4. Conclusions

In this paper we study the frequency noise behavior and the applicability to precision spectroscopy of a new family of commercial external-cavity quantum-cascade-lasers. Thanks to the large optical power and to a free-running linewidth of 1.7 MHz they are a powerful solution for sub-Doppler spectroscopy over spectral ranges as large as 100 cm^{-1} in the mid-infrared, i.e. in the region where optical absorption lines are particularly intense and easier to be saturated. Their use in conjunction with a near-infrared optical frequency comb turns out to be a powerful solution for Doppler-free precision spectroscopy thanks to a highly repeatable and absolutely calibrated frequency axis.

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