A widely tunable 10-µm quantum cascade laser phase-locked to a state-of-the-art mid-infrared reference for precision molecular spectroscopy

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We report the coherent phase-locking of a quantum cascade laser (QCL) at 10-µm to the secondary frequency standard of this spectral region, a CO2 laser stabilized on a saturated absorption line of OsO4. The stability and accuracy of the standard are transferred to the QCL resulting in a line width of the order of 10 Hz, and leading to our knowledge to the narrowest QCL to date. The locked QCL is then used to perform absorption spectroscopy spanning 6 GHz of NH3 and methyltrioxorhenium, two species of interest for applications in precision measurements.

With their rich internal structure, molecules can play a decisive role in precision tests of fundamental physics. They are being used to test fundamental symmetries such as parity4,13 or parity and time reversal5,6 to measure absolute values of fundamental constants5,7 and their possible temporal variation5,10. Many of these experiments can be cast as measurements of resonance frequencies of molecular transitions, for which ultra-stable and accurate sources in the mid-infrared (mid-IR) are highly desirable, since most rovibrational transitions are to be found in that region.

Our group has a long-standing interest in performing spectroscopic precision measurements on molecules at extreme resolutions around 10 µm10,11. We are currently working on two such measurements: the determination of the Boltzmann constant, k_B, by Doppler spectroscopy of ammonia5,12 and the first observation of parity violation by Ramsey interferometry of a beam of chiral molecules3,13. For these experiments, we currently use spectrometers based on custom built ultra-stable CO2 lasers. We obtain the required metrological frequency stability and accuracy — 10 Hz line width, 1 Hz stability at 1 s, accuracy of a few tens of hertz4,13,15 — by stabilizing these lasers to saturated absorption lines of molecules such as OsO4. CO2 lasers have a major shortcoming: a lack of tunability. They emit at CO2 molecular resonances. An emission line is found every 30 to 50 GHz in the 9-11 µm wavelength range, and each line is tunable over about 100 MHz. Although, as in our spectrometers, this range can be extended a few gigahertz using electro-optical modulators (EOMs), this is done at the expense of power (EOMs at these wavelengths have an efficiency of 10^-4) and necessitates subsequent spectral filtering. Overcoming these difficulties without the loss of stability is key to enabling precision measurements in the mid-IR.

One solution would be to use frequency comb-referenced continuous-wave (cw)16,18 or femtosecond19 mid-IR sources. These are based on frequency mixing in nonlinear crystals and provide absolute-frequency referencing, reasonable line widths and tunability, but are very complex and often exhibit limited power. By comparison, cw quantum cascade lasers (QCLs) are a new mature and robust technology that offer broad and continuous tuning over several hundred gigahertz at 100 mW-level powers. Several can be combined giving access to the whole mid-IR region. Recent studies of the emission spectrum of cw free-running distributed-feedback (DFB) QCL20–24 confirm their suitability for high resolution spectroscopy and frequency metrology. Furthermore, narrow-emission, absolutely referenced mid-IR QCLs have been demonstrated, either by phase-locking to a CO2 laser25–26, frequency locking to a sub-Doppler molecular transition27, optical injection locking28 or phase-locking29,30 to narrow optical frequency comb-based sources. Sub-kHz emission line widths, corresponding to relative stabilities in the high 10^-12, and accuracies of a few 10^-12 have been shown23,26. Note however that most of this work has been done using QCLs emitting around 4-5 µm. Work at longer wavelengths (including most of the molecular fingerprint region) has remained scarce (see refs.23,25 around 9 µm).

We extended this range to 10 µm. A 10 µm QCL exhibiting remarkably low free-running frequency noise is coherently phase-locked to the OsO4-stabilized CO2 laser. This allows both line width narrowing, by about 4 orders of magnitude down to an unprecedented 10 Hz level, and absolute frequency referencing at the 10^-12 level. In order to preserve some of its tunability, the QCL is in fact locked to one of two optical sidebands (tunable over 10 GHz) generated by coupling the CO2 laser light through an EOM. Once locked, we use this QCL to demonstrate high-resolution spectroscopy of both NH3 and methyltrioxorhenium (MTO) over a range of over 6 GHz. These species are of interest for the two precision measurements under progress in our group. The former is our molecule of choice for measuring k_B, while the latter, MTO is an achiral test organometallic complex whose chiral derivatives are considered for a parity violation test3,13,14.

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The QCL is a cw-mode near-room-temperature (near-RT) single-mode DFB laser (from Alpes Lasers) tunable between 10.34 and 10.42 \( \mu \text{m} \) (28.76 to 29.00 THz). For the experiments described in this paper, it is typically operated at a temperature of 243 K (at which the threshold current is 710 mA) and a current ranging from 0.96 to 1.02 A, delivering 40 to 60 mW around 28.95 THz. At the QCL output, the laser beam is collimated with a spherical ZnSe lens \( (f = 25 \text{ mm}) \). First, we measure the frequency noise of the free-running QCL. This allows us to estimate the feedback bandwidth required to narrow its line width. As illustrated in Fig. 1(a), we use the side of an ammonia linear absorption line as frequency discriminator. The absorption signal from a 5 cm path length cell containing 250 Pa of \( \text{NH}_3 \) is recorded with a liquid nitrogen-cooled HgCdTe detector (with a bandwidth of a few megahertz) and processed by a Fast Fourier Transform (FFT) spectrum analyzer. The frequency-to-amplitude conversion coefficient is measured by recording the same rovibrational line using our stabilized \( \text{CO}_2 \) laser spectrometer. Fig. 2 shows the resulting frequency noise power spectral density (PSD) of the QCL. It has a \( 1/f \) trend at low frequency, followed by a steeper slope above \( \sim 300 \text{ kHz} \), as observed in different experiments. Note however that the measured frequency noise PSD is roughly one order of magnitude lower than previously published characterizations of free-running cw-mode near-RT DFB QCLs.

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The measured beat signal between the QCL and the sideband of a \( \sim 1 \text{ kHz} \) wide free-running \( \text{CO}_2 \) laser recorded with a RF spectrum analyzer (1 kHz resolution bandwidth). The dashed line is the QCL line shape calculated from the measured frequency noise PSD. For these measurements the QCL was conveniently locked to the side of the \( saQ(6, 3) \) \( \text{NH}_3 \) line with a \( \sim 1.5 \text{ Hz} \) bandwidth.

Fig. 2 also shows the contribution from the laser intensity noise, obtained with the laser tuned far off resonance, as well as the contribution from a home-made low-noise current source. The latter is obtained by multiplying the driver’s current noise spectrum \( (< 300 \text{ pA}/\sqrt{\text{Hz}} \text{ above } 10 \text{ kHz}) \) by the laser DC current-to-frequency response \( (230 \text{ MHz}/\text{mA}) \). The drivers current noise was accurately measured by balancing two identical home-made sources of opposite polarity and detecting the residual AC-currents.

Fig. 2 also shows that the expected white noise level \( N_w \) corresponding to the Schawlow-Townes limit does not seem to be reached at 1 MHz. Thus, only an upper limit of \( N_w \sim 50 \text{ Hz}^2/\text{Hz} \) (and an upper limit of the corresponding intrinsic laser line width of \( \Delta \nu = \pi N_w \sim 160 \text{ Hz} \) can be inferred). This is 1.7 times lower than measured for a cw mode near-RT DFB QCL at 4.3 \( \mu \text{m} \).

The real laser line width is broadened by flicker noise and depends on the observation time. The inset in Fig. 2 shows a beat signal between the free-running QCL and a free-running \( \text{CO}_2 \) laser which exhibits a record \( \sim 60 \text{ kHz} \) full width at half maximum after 1 ms of integration time \( (i.e. 1 \text{ kHz resolution bandwidth}) \). The line width of the free-running \( \text{CO}_2 \) laser was measured to be \( \sim 1 \text{ kHz} \) making its contribution negligible in the observed width. The measured beat signal agrees well with a theoretical estimation of the QCL emission line shape based on the measured frequency noise PSD (following and accounting for the 1 ms observation time), as indicated by the dashed line in the inset of Fig. 2.

The experimental setup used to coherently phase-lock the QCL to a \( \text{CO}_2 \) laser stabilized on a saturated absorption line of \( \text{OsO}_4 \) is shown on Fig. 1(b). In this work, the \( R(6) \) \( \text{CO}_2 \) laser carrier is frequency-locked to the...
that chops the beam at 2 kHz, and a lock-in detection are of the excellent transfer of the locked CO$_2$ laser. This results in a record QCL line width of the order of 10 Hz, a relative stability $\sim 10^{-12}$, and a relative accuracy $\sim 5.5\%$ absorption and $\sim 100$ MHz wide $\sim 2\%$ deviations as expected from the dense anti-symmetric Re=O stretching mode of the molecule.$^{31,33,39}$

Both spectra were normalized by numerically correcting for the baseline.

In conclusion we characterized the frequency noise of a free-running cw near-RT DFB 10.3 $\mu$m QCL. The laser is then phase-locked to a frequency-stabilized CO$_2$ laser, and we observe that the spectral properties of the latter are successfully copied to the QCL. This results in a record line width of the order of 10 Hz, a relative stability at 1 s in the $10^{-14}$ range and a relative accuracy of $3 \times 10^{-12}$. Spectra of ammonia and MTO over several GHz using our QCL source were presented, thereby demonstrating the potential of QCLs for precision measurements devoted to metrological applications or tests of fundamental laws of nature.

The use of QCLs will eventually allow the study of any species showing absorption between 3 and 25 $\mu$m, with much broader continuous tuning range and with

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**FIG. 3.** (a) Beat signal spectrum between the frequency-stabilized CO$_2$ laser sideband and the phase-locked QCL taken with a RF spectrum analyzer (30 kHz resolution bandwidth). (b) Phase-noise power spectral density of the beat signal between the QCL and the frequency-stabilized CO$_2$ laser carrier.
FIG. 4. Linear absorption spectra of NH$_3$ (red curve (a)) and MTO (blue curve (b)) recorded over more than 6 GHz with a $\sim$ 10 Hz line width QCL phase-locked to a frequency-stabilized CO$_2$ laser. From left to right, the ammonia spectrum exhibit the three isolated rovibrational lines $saQ(6, 3)$ (probed in our experiment dedicated to the determination of $k_2$), $saQ(6, 2)$ and $saQ(6, 1)$ of the $v_2$ vibrational mode of $^{14}$NH$_3$. The inset shows a zoom on the MTO spectrum. Experimental conditions: chopper frequency 2 kHz, lock-in amplifier time constant 30 ms, 500 kHz steps, power 1 $\mu$W, absorption length 60 cm, $\sim$ 10 Pa of NH$_3$ or $\sim$ 4 Pa of MTO.

reasonable powers. It will broaden the scope of our spectroscopic precision measurement experiments using molecules. We eventually plan to reach the $3 \times 10^{-16}$ accuracy of the Cs fountain, the $10^{-15}$ stability of the best near-IR oscillators, and take full advantage of the QCL’s tunability by locking it to a frequency comb stabilized via on optical fiber to an ultra-stable near-IR reference monitored against atomic fountain clocks. This was recently demonstrated in our group with a CO$_2$ laser. Stabilizing the laser this way provides the ultimate frequency accuracy and stability, and frees us from having to lock the QCL to any particular reference (another laser or a molecular transition), which would constrain the laser’s operating frequency. Finally, narrow line width light sources such as QCLs would benefit the entire spectroscopy community, beyond our scope of interest. Commercial QCLs are available at wavelengths spanning the entire mid-IR, the molecular fingerprint region, which hosts many spectral signatures of molecules of interest for atmospheric, planetary or interstellar physics, chemistry, biology, medical or industrial diagnostics.

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