SUPPLEMENTARY MATERIAL

Optical frequency metrology in the bending modes region

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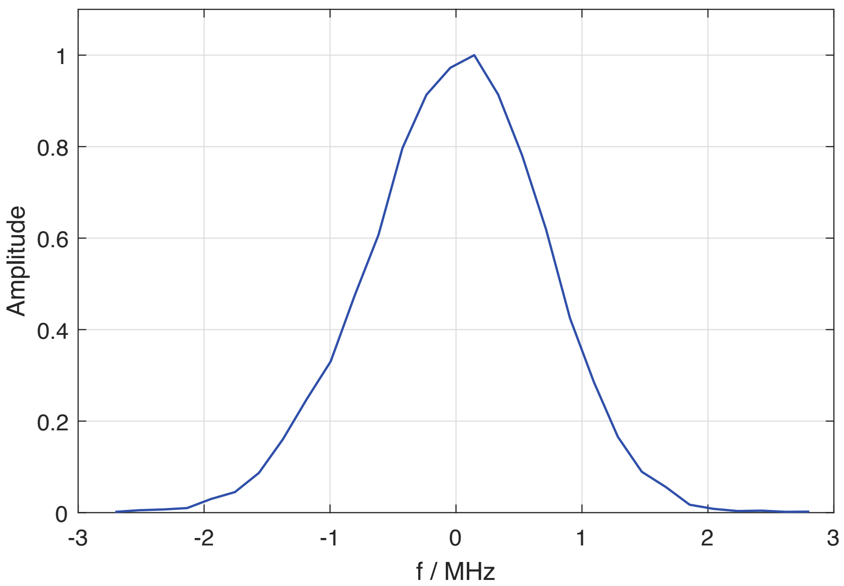
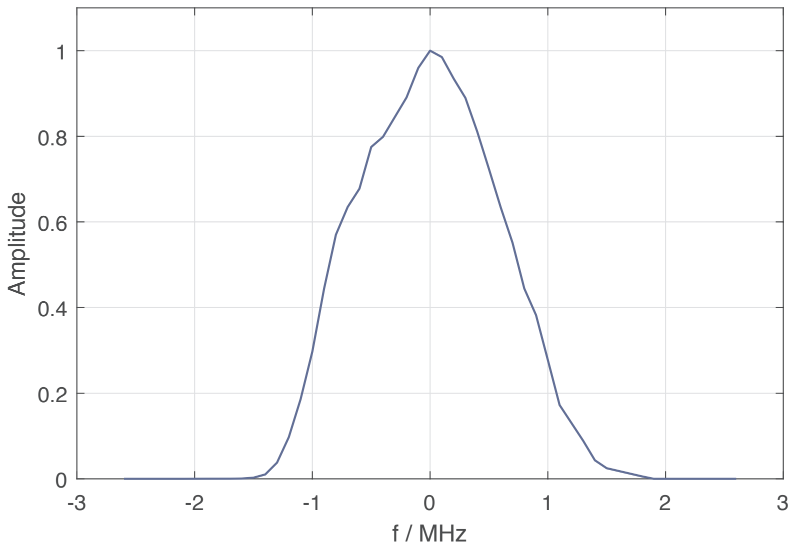
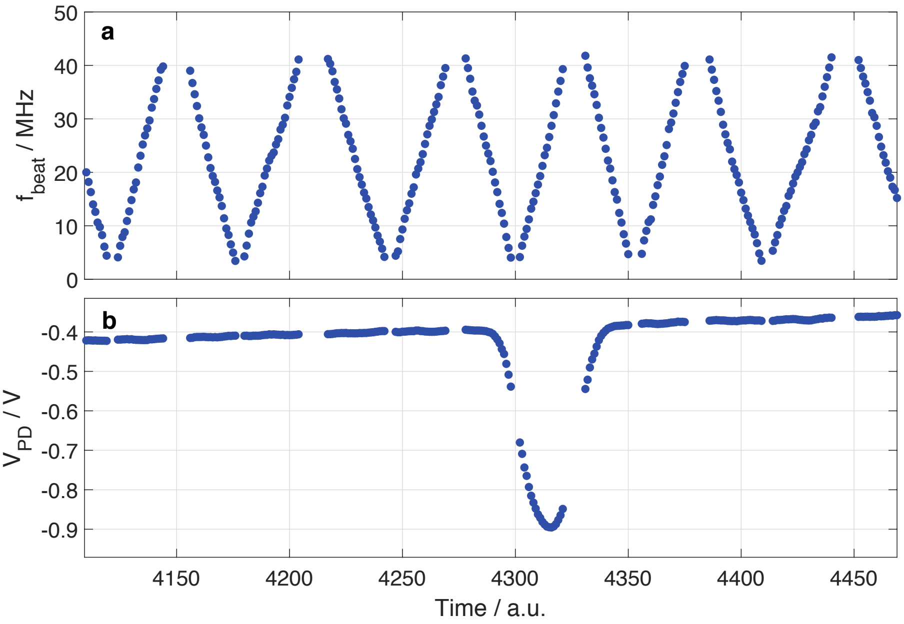
Supplementary Figures



Supplementary Figure 1 | Beat note spectrum between quantum cascade laser and comb. Obtained as a histogram of the beat note barycentre frequencies measured by the acquisition board over subsequent time windows of 10 μs. The relatively large width of 1.6 MHz could be shrunk to the sub-MHz level by the use of a less noisy current driver[1,2]



Supplementary Figure 2 | Beat note spectrum between CO_2 laser and comb. Obtained as a histogram of the beat-note barycentres measured by the acquisition board over subsequent time windows of 10 μs. The slight asymmetry derives from the pulsed operation of the laser. A significant decrease of the linewidth, down to below 100 kHz, could be obtained by recurring to a cw emission regime.



Supplementary Figure 3 | Raw measurement data for a single CO_2 line. a Time behaviour of the beat note frequency between quantum cascade laser and comb and **b** of the photodetector signal.

Supplementary tables

Band	Line	Obs / cm^{-1}	HITRAN/ cm^{-1}	Obs-HITRAN / 10^{-6} cm^{-1}	N
ν_2	R(10)	676.01943603(66)	676.019431	5.0	25
ν_2	R(12)	677.6008247(13)	677.600821	3.8	6
ν_2	R(14)	679.18538721(70)	679.185387	0.2	27
ν_2	R(16)	680.7731066(15)	680.773099	7.6	2
ν_2	R(18)	682.3639287(18)	682.363927	1.7	2
ν_2	R(20)	683.9578497(10)	683.957836	13.8	25
ν_2	R(22)	685.5548060(34)	685.554794	12.0	5
ν_2	R(24)	687.1547798(30)	687.154767	12.9	2
ν_2	R(26)	688.7577330(62)	688.757719	14.1	1
$\nu_1 \leftarrow \nu_2$	Q(36)	719.4226506(45)	719.422625	25.7	2
$\nu_1 \leftarrow \nu_2$	Q(34)	719.5662865(32)	719.566271	15.5	2
$\nu_1 \leftarrow \nu_2$	Q(32)	719.7026444(29)	719.702628	16.5	2
$\nu_1 \leftarrow \nu_2$	Q(30)	719.8315747(41)	719.831557	17.7	2
$\nu_1 \leftarrow \nu_2$	Q(28)	719.9529553(39)	719.952922	33.4	2
$\nu_1 \leftarrow \nu_2$	Q(26)	720.0666311(55)	720.066601	30.2	2
$\nu_1 \leftarrow \nu_2$	Q(24)	720.1724819(58)	720.172478	3.9	2
$\nu_1 \leftarrow \nu_2$	Q(22)	720.2704506(72)	720.270446	4.6	2
$\nu_1 \leftarrow \nu_2$	Q(18)	720.4422813(75)	720.442276	5.3	2
$\nu_1 \leftarrow \nu_2$	Q(14)	720.5814236(50)	720.581411	12.6	2
$\nu_1 \leftarrow \nu_2$	Q(12)	720.6385565(71)	720.638544	12.6	2
$\nu_1 \leftarrow \nu_2$	Q(8)	720.7276548(51)	720.727664	-9.2	2
$\nu_1 \leftarrow \nu_2$	Q(6)	720.7595686(35)	720.759565	3.7	2
$\nu_1 \leftarrow \nu_2$	Q(4)	720.7829825(26)	720.782984	-1.5	2
$\nu_1 \leftarrow \nu_2$	Q(2)	720.7979103(34)	720.797897	13.4	2

Supplementary Table 1 | Carbon dioxide line list. Observed and calculated wavenumbers of the transitions assigned to ν_2 and $\nu_1 \leftarrow \nu_2$ for CO_2, ordered for increasing energy. The heading N indicates the number of independent spectral measurements used to infer the observed line centre frequency.

Supplementary Notes

Supplementary Note 1 | Characterization of the difference frequency generation linewidth

The linewidth of the difference frequency generation (DFG) laser source has been estimated from the measured beat notes of quantum cascade laser (QCL) and CO_2 laser with the comb (Supplementary Fig. 1 and 2, respectively). These have an almost Gaussian-like shape, which justifies a quadrature sum of their widths to have a reliable estimation of the DFG linewidth. The contribution of the comb linewidth (~ 100 kHz) to the beat notes (~ 1.5 MHz) is negligible.

For both lasers, the beat note has been measured via the 100 MS s^{-1} digital acquisition board (DAQ) used for spectral acquisition, by subdividing the beat note samples in groups of 1024 points and calculating the barycentre of the electrical spectrum for each group via fast Fourier transform (FFT). This is equivalent to repeatedly measuring the average laser frequency (as compared to the comb) over a measurement time of 10 μs (1024 points at every 10 ns). The distribution of these frequencies is shown in Supplementary Fig. 1 and 2 for QCL and CO_2 laser, respectively. The full widths at half maximum (FWHM) of these distributions, 1.6 and 1.5 MHz, respectively, provide an estimated value of their linewidths. As both distributions have a Gaussian line-shape, we applied the quadrature sum of their widths to infer the width of their convolution, which gives the DFG linewidth and thus the resolution of the spectrometer.

Supplementary References

1. Tombez, L. *et al.* Frequency noise of free-running 4.6 µm distributed feedback quantum cascade lasers near room temperature. *Opt. Lett.* **36**, 3109-3111 (2011).

2. Mills, A. A. *et al.* Coherent phase lock of a 9 µm quantum cascade laser to a 2 µm thulium optical frequency comb. *Opt. Lett.* **37**, 4083-4085 (2012).