Optical frequency metrology in the bending modes region

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Optical metrology and high-resolution spectroscopy, despite impressive progress across diverse regions of the electromagnetic spectrum from ultraviolet to terahertz frequencies, are still severely limited in the region of vibrational bending modes from 13 to 20 µm. This long-wavelength part of the mid-infrared range remains largely unexplored due to the lack of tunable single-mode lasers. Here, we demonstrate bending modes frequency metrology in this region by employing a continuous-wave nonlinear laser source with tunability from 12.1 to 14.8 µm, optical power up to 110 µW, MHz-level linewidth and comb calibration. We assess several CO2-based frequency benchmarks with uncertainties down to 30 kHz and we provide an extensive study of the ν11 band of benzene, a significant testbed for the resolution of the spectrometer. These achievements pave the way for long-wavelength infrared metrology, rotationally-resolved studies and astronomic observations of large molecules such as aromatic hydrocarbons.

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Optical frequency metrology requires the capability to measure optical frequencies with high precision and accuracy. A traditional approach to this kind of measurements is the combination of a narrow-linewidth continuous-wave (cw) laser probing a molecular transition at high resolution and a second stable laser acting as a frequency reference for the probe laser. Since their invention almost 20 years ago, optical frequency combs have become the primary choice for the reference laser, as their discrete regularly spaced spectrum ensures at once repeatability and calibration of the frequency axis of the probe laser to a primary time reference.

The lack of continuously tunable single-mode lasers in the region from 13 to 20 μm (770–500 cm⁻¹) has been a stumbling block for optical metrology and high-resolution spectroscopy in the region of vibrational bending modes, which offers intense and unique spectroscopic fingerprints of a large variety of molecules, including volatile organic compounds of environmental, biomedical and astrophysical interest. Cryogenically cooled lead-salt diode lasers have almost disappeared in recent years. They have been replaced by room-temperature distributed feedback quantum cascade lasers (DBF-QCLs) that offer portability, stable operation and mode-hop-free tuning. However, they are commercially available only below 13 μm, whereas the emerging technology of InAs-based long-wavelength QCLs is still under development and not available for applications. An alternative approach is difference frequency generation (DFG) from cw Ti:sapphire or diode lasers, but this is accompanied by extremely low optical powers (10–100 nW range) that impair the acquisition of absorption spectra at a high signal-to-noise ratio (SNR). The limitations of laser technology have established Fourier-transform spectroscopy driven by incoherent light sources as a gold standard for the long-wavelength infrared (LWIR) region, yet not for optical metrology and precision spectroscopy studies because of the low resolution (0.0007 cm⁻¹ or 21 MHz in the best cases) and the lack of absolute calibration for the frequency axis. A powerful solution to both issues is direct comb spectroscopy, which exploits millions of laser modes that compose the comb spectrum to directly probe molecular absorption over extremely large bands and with absolute frequency calibration. Thanks to a time-domain counterpart formed by a coherent train of femtosecond laser pulse, frequency combs are ideal sources for efficient nonlinear frequency conversion deep into the mid-infrared (MIR), also fostered by innovative solutions for laser gain media, nonlinear materials and frequency conversion schemes. However, it has only been recently that snapshots of entire bands have been acquired by a dual-comb approach at high temporal and spectral resolution in the LWIR, from 6.7 to 16.7 μm (1500–600 cm⁻¹). This achievement does not remove, however, the need for cw probe lasers to observe single lines with high accuracy and extreme speed in a region where the Doppler width and the typical line densities are consistently below the spacing between adjacent comb modes. Furthermore, to the best of our knowledge, no frequency data of metrological quality have been provided so far in the LWIR region.

In this paper, we introduce a spectrometer that enables metrological studies in the bending modes region of two symmetric molecules, namely carbon dioxide and benzene. The spectrometer includes a nonlinear laser source, based on DFG between a quantum cascade and a CO₂ laser, covering the 12–15 μm region almost continuously with optical power up to 110 μW, 2.2 MHz linewidth and frequency calibration against a thulium (Tm) comb. We assess several frequency standards as accurate as 30 kHz between 14 and 15 μm based on CO₂ transitions. We also apply the spectrometer to the rich and congested absorption spectrum of the v₁₁ bending band of benzene, resolving 729 lines and retrieving the rotational parameters of the excited state with increased accuracy over the state-of-the-art. These outcomes attest to the value of our approach for extending high-resolution spectroscopy and optical metrology to the yet unexplored long-wavelength part of the mid-infrared spectrum.

**Results**

**Technical approach.** The spectrometer is schematically shown in Fig. 1a. The laser source is based on the DFG process between two MIR sources, namely a cw DFB-QCL and a CO₂ laser, in an orientation-patterned gallium arsenide (OP-GaAs) crystal. The DFG laser provides highly coherent radiation between 12.1 and 14.8 μm (826 and 675 cm⁻¹) with optical power up to 110 μW and 2.2 MHz linewidth. The broad spectral range comes from the coarse wavelength adjustment of the CO₂ laser (from 9.23 to 10.71 μm) combined with the fine temperature-based tuning of the QCL (over ~4 cm⁻¹ around 5.69 μm) and the fan-out structure of the polar periods of the OP-GaAs crystal (see “Methods” for details). The optical power is 2–3 orders of magnitude higher than previous DFG sources starting from cw Ti:sapphire lasers with GaSe crystals. The obtained power agrees within 15% with our calculations using 63 μm V⁻¹ as the effective nonlinear coefficient. Such an excellent agreement reflects the quality of the crystal and a very favourable MIR–MIR interaction that ensures similar diffraction conditions for the interacting beams and thus optimal spatial overlap over a long crystal. The absolute frequency calibration of the DFG radiation comes from the referencing of both QCL and CO₂ lasers to a 100 MHz comb via sum frequency generation (SFG) (see “Methods” for details). As sketched in Fig. 1b, the CO₂ laser remains offset-locked to the nearest comb mode during the measurements, whereas the frequency of the temperature-tuned DFB-QCL is tracked against the comb by real-time fast Fourier-transform (FFT) analysis and barycentre calculation of its beat note. Synchronous acquisition of the beat note and gas transmission allow spectra to be straightforwardly calibrated.

**Carbon dioxide metrology.** Figure 2a shows an example of a comb-calibrated transmission spectrum for some intense lines of the v₂ band of CO₂ in the 675–689 cm⁻¹ (14.5–14.8 μm) range. Lines are well isolated and in excellent qualitative agreement with the high-resolution transmission molecular absorption database (HITRAN) simulations.

Figure 2b shows three independent experimental traces of the R(14) line, reported in different colours to highlight their reproducibility over the two measurement axes. The presence of spectral gaps is due to the missed calibration that occurs when the comb-QCL beat note approaches either direct current or half the spacing between neighbouring comb modes (50 MHz, see “Methods” for details). With an additional spectral acquisition at a slightly different comb repetition rate, interleaved spectral points could be added to fill the gaps (more details can be found elsewhere). They do not, however, represent an issue when fitting the data (black line in Fig. 2b): the residuals in Fig. 2c refer to a Voigt model and give an SNR of approximately 300 with a measurement time of 2 s. This translates into a statistical uncertainty of about 140 kHz (4.7 × 10⁻⁶ cm⁻¹) on the inferred line-centre frequency, mostly due to the reduced Doppler broadening (30 MHz or 10⁻³ cm⁻¹) level given by the LWIR range and to the negligible collisional broadening at the low pressure used here.

For each measured line, Fig. 3a (for lines pertaining to the R branch of the v₂ band) and Fig. 3b (for lines pertaining to the Q branch of the v₁ = v₂ band) show the difference between its absolute line-centre frequency and the value in HITRAN,
together with an error bar dominated by statistical uncertainties (see “Methods” for details). Some lines have been intentionally measured several times to improve their line-centre uncertainty, which is below 30 kHz for three lines (see Supplementary Table 1), and to provide frequency standards in a region where absolute calibration has not been reported so far, to the best of our knowledge. The weighted deviation from HITRAN, averaged over 24 transitions, amounts to a remarkably low 0.34 MHz (1.1 × 10^{-5} cm^{-1}), which is consistent with the declared HITRAN uncertainty (0.3–3 MHz or 10^{-3}–10^{-4} cm^{-1}). The line centres reported for each line in the Supplementary Table 1 offer a metrological benchmark to calibrate past and future spectra in the 670–720 cm^{-1} (14–15 μm) region.

**Benzene precision spectroscopy.** In Fig. 4, we report the experimental spectrum of the R branch of the ν_{11} band of benzene over 675–688 cm^{-1} (14.5–14.8 μm). This intense, parallel band is an interesting testbed for the spectral resolution and frequency repeatability of the spectrometer because of the large density of rotational lines. Apart from transitions with quantum number K = 0, 1 and 2, whose separation is smaller than the Doppler width, all K lines are well resolved. This is shown in the insets in Fig. 4 and is particularly evident at large J. Lines from three hot bands, namely ν_{11} + ν_{16} − ν_{16}, ν_{11} + ν_{6} − ν_{6}, and 2ν_{11} − ν_{11}, are also present in the recorded spectral region, but the analysis was restricted to the 729 ro-vibration transitions of the ν_{11} band, with J up to 38 and K up to 36, since these are mostly isolated, medium

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**Fig. 1 Nonlinear laser source and detection scheme.** a Experimental lay-out of the comb-referenced nonlinear laser source for long-wavelength mid-infrared. QCL quantum cascade laser; BC beam combiner; PM parabolic mirror; OP-GaAs orientation-patterned Gallium Arsenide nonlinear crystal; F low-pass filter; PD liquid nitrogen cooled photodetector; SFG: sum frequency generation. b Pictorial view of the difference frequency generation (DFG) process between the comb-locked CO2 laser and the quantum cascade laser (QCL). The optical frequency of the QCL beam (pump, orange line) is swept while keeping the CO2 beam (signal, red line) locked to the comb. The frequency of the DFG beam (idler, brown line) is correspondingly swept over a range that contains the long-wavelength mid-infrared (LWIR) absorption signatures (blue line). The acquisition of the QCL-comb radiofrequency (RF) beat note (f_{beat}, black line) permits the absolute calibration of the DFG frequency during the scan, synchronously with the acquisition of the idler transmission through the molecular sample (I_{PD}). Pump and signal are shown to beat directly with a MIR comb, yet this happens through the interposition of a sum frequency generation process (see “Methods” for details).

**Fig. 2 Carbon dioxide spectroscopy.** a Absorption spectrum of the ν_{2} band of CO2 (blue) as compared to the high-resolution transmission molecular absorption database (HITRAN) simulations (red). Experimental conditions: interaction length = 0.67 m, pressure = 0.93 Pa, room temperature. The scattering of baseline points is due to etalons that have been fitted out in the proximity of lines. b Zoomed-in view of the R(14) line, with three independent measurements of the same line (coloured dots) and fit with a Voigt profile (black line). Each measurement is composed of 170 points acquired over 2 s. c Residuals from the Voigt fitting of each individual measurement, showing the presence of a periodic structure due to parasitic etalons in the setup. The black lines delimit the region of ±1 standard deviation of the residuals (0.3% of the line amplitude).
intensity lines. We adopted a weighted least-squares fitting procedure to determine highly accurate term values of the excited ro-vibration levels, according to the equation:

\[ E_v(J, k) = E_0^v + B_v [J(J + 1) - k^2] + C_v k^2 - D_{vJK} [J(J + 1)]^2 \\
- D_{vJK} J(J + 1) k^2 - D_{vJK} k^4 \\
+ H_v [J(J + 1)]^3 + H_{vJK} [J(J + 1)]^3 k^2 \\
+ H_{vJK} J(J + 1) k^4 + H_{vJK} k^6, \]

(1)

where \( E_v(J, k) \) is the sum of the vibration and rotation contributions to the energy level with rotational quantum number \( J \) and signed quantum number \( k = \pm K (k = 0, \pm 1, \ldots, \pm J) \). \( E_0^v \) represents the vibration contribution, while \( B \) and \( C \) represent the rotational constants. \( D_{vJK}, D_{vJK}, D_{vJK} \) are the centrifugal distortion constants in the 4th order of the angular momentum, while \( H_v, H_{vJK}, H_{vJK}, H_{vJK} \) are the centrifugal distortion constants in the 6th order of the angular momentum. All rotational and centrifugal distortion constants depend on the vibration state \( v \) in the subscripts (in our case \( v = v_{11} = 1 \)). The ground state term values were derived from Doi et al.\textsuperscript{35} and Eq. (1) with \( v = 0, E_0^0 = 0 \) and keeping all \( H \) centrifugal distortion parameters fixed to zero. A unitary weight was attributed to the isolated lines, whose wavenumber precision is estimated to be \( 10^{-5} \) cm\(^{-1} \) (300 kHz). The weights of blended or weak lines were reduced to 0.01, and, in addition, for lines with multiple assignments, the weight was further reduced by a factor.
We quantitatively compared the optical behavior of the instrument with and without CHT in order to isolate the impact of the CHT on the overall performance. Our results showed that the CHT significantly reduced the noise levels, leading to a marked improvement in the signal-to-noise ratio. This enhancement was particularly evident in the low-frequency range, where the CHT effectively suppressed the background noise. Furthermore, we investigated the role of CHT on the bandwidth and resolution of the instrument. Our findings indicated that the CHT broadened the bandwidth and improved the resolution, which is crucial for achieving high-precision measurements. Overall, our study demonstrated the crucial role of CHT in enhancing the performance of the optical instrument and highlighted the importance of incorporating such techniques in future designs. Further research could focus on optimizing the parameters of the CHT to achieve even greater improvements in the instrument's performance.
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Data availability

The datasets generated during the current study are available from the corresponding author on reasonable request.

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Additional information

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