

Bending modes metrology in the 12-15 μm region

M. Lamperti¹, R. Gotti¹, D. Gatti¹, M. K. Shakfa², E. Cané³, F. Tamassia³, P. Schunemann⁴, P. Laporta¹, A. Farooq², and M. Marangoni¹

¹Dipartimento di Fisica - Politecnico di Milano and IFN-CNR, Via Gaetano Prevati 1/C, 23900 Lecco, Italy

²King Abdullah University for Science and Technology, Clean Combustion Research Center, Thuwal 23955, Saudi Arabia

³Università di Bologna, Dipartimento di Chimica Industriale, Viale del Risorgimento 4, 40136 Bologna, Italy

⁴BAE Systems, Inc., MER15-1813, P.O. Box 868, Nashua, New Hampshire 03061-0868, USA

Author e-mail address: marco.marangoni@polimi.it

Abstract: Bending modes metrology through a comb-referenced widely tunable nonlinear laser source is demonstrated. We report center frequencies of CO₂ lines determined with 30 kHz uncertainty and an extensive study of the ν_{11} band of benzene. © 2020 The Author(s)

The long wavelength mid infrared (LWIR) region has always attracted spectroscopists' interest due to the presence of fundamental transitions of molecules with a strong relevance in the environmental, astrophysical and biomedical fields. The lack of single-mode quantum cascade lasers (DFB-QCL) emitting above 13 μm has severely limited spectroscopic investigations in the LWIR [1]. Fourier Transform spectroscopy based on incoherent sources has been the standard approach to probe molecular features in this region but the low resolution (at best 21 MHz [2]) makes it inadequate for precision spectroscopy and optical metrology. In this framework direct frequency comb techniques represent valuable alternatives thanks to the intrinsic absolute frequency calibration and to the ultrashort pulsed nature which turns out to be very effective to shift the comb spectrum in the LWIR through nonlinear interactions [3]. A recent demonstration has been obtained by a dual-comb approach, with entire bands measured till 16.7 μm . [4]. This achievement does not remove the interest for cw-laser-based spectroscopy tools to study single absorption lines with ultimate accuracy and speed, in a region where the comb tooth spacing is considerably larger than the Doppler broadening of a single line.

In this contribution we demonstrate a LWIR spectrometer based on a widely tunable (12.1-14.8 μm) cw single-mode laser (2.2 MHz linewidth) obtained through difference frequency generation (DFG) between a DFB-QCL and a CO₂ laser and fully referenced to a 1.9 μm thulium frequency comb. We characterize several transitions of CO₂ with 30 kHz total uncertainty and we resolve the complex spectrum of the ν_{11} band of benzene increasing the state-of-the-art accuracy in the assessment of the rotational parameters. The experimental setup is depicted in Fig. 1.a. A distributed-feedback quantum-cascade-laser (DFB-QCL) emitting around 5.69 μm is collinearly combined with a CO₂ laser operating in a pulse modulation mode (duty cycle of 20%, modulation frequency of 10 kHz) in an orientation patterned gallium arsenide (OP-GaAs) crystal. The nonlinear process generates a radiation tunable in the range 12.1–14.8 μm (675–826 cm^{-1}) as a combined result of the temperature tuning of DFB-QCL and the selected lasing line of the CO₂ laser (9.23 μm -10.71 μm).

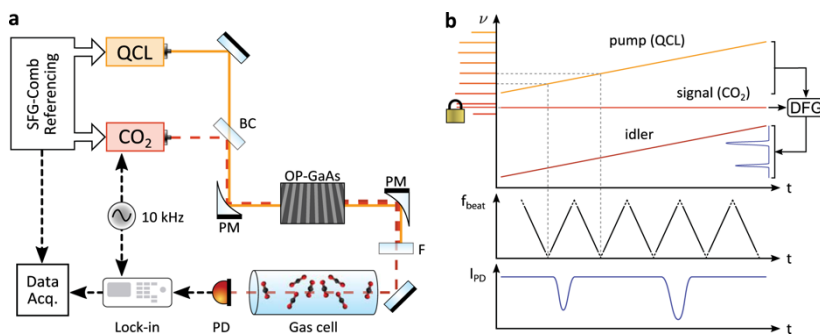


Fig. 1. a) Experimental setup, b) detection scheme.

The power emission of the DFB-QCL ranges from 17 to 48 mW depending on the temperature whereas the CO₂ laser emits up to 27 W depending on the selected laser line. The generated power remains between 20

and 110 μW in the overall LWIR range. Two independent sum frequency generation (SFG) processes in AgGaSe₂ and ZnGeP₂ (ZGP) crystals are employed for the referencing of DFB-QCL and CO₂ laser, respectively, against a Tm: fiber comb [5]. In particular two beatnote frequencies are generated when the two SFG combs centered at 1.4 μm and 1.6 μm are superimposed with the coherent continuum generated from the thulium comb. One beatnote is used to tightly lock the CO₂ frequency against the comb whereas the second one is acquired in real-time by an FPGA-based 100 MS/s acquisition board during the wavelength scan of the DFB-QCL (Fig 1.b.). The synchronous acquisition of the gas absorption signal allows to straightforwardly calibrate the frequency axis of the acquired spectrum.

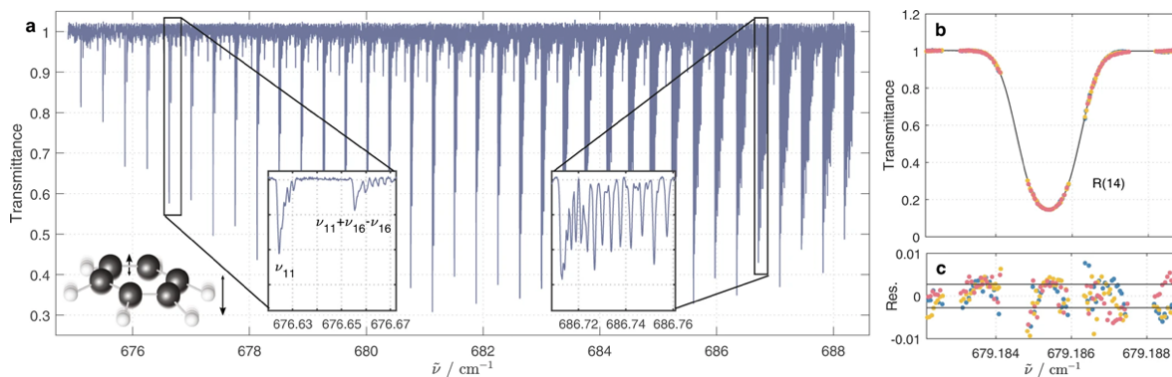


Fig. 2.a. Absorption spectrum of the R branch of the ν_{11} band of benzene. b. Three independent measurements of the $R(14)$ line belonging to the ν_2 band of CO₂ and fit with a Voigt profile (black line). c. Residuals from the Voigt fitting.

Figure 2.a. displays the R branch of the ν_{11} band of benzene between 675 and 688 cm^{-1} (14.5–14.8 μm) at a pressure of 13.3 Pa. The complexity of such a spectrum constitutes an important testbed for the system, which is capable to resolve all lines except those characterized by the $K=0,1,2$ quantum numbers, whose distance is smaller than the Doppler width. Rotational parameters have been retrieved with a standard deviation of 1.5 MHz from the analysis of 723 transitions, with an uncertainty improved by one order of magnitude with respect to the state-of-the-art [6].

We have also characterized the ν_2 band of CO₂ in the 675–689 cm^{-1} region, which is an ideal candidate for frequency metrology due to the presence of well isolated lines. In Fig. 2.b,c three independent measurements of the $R(14)$ line are reported together with the residuals of a Voigt fit. We achieve a signal-to-noise ratio (SNR) of the order of 300 over an observation time of 2 s that translates into a statistical uncertainty of about 140 kHz ($4.7 \times 10^{-6} \text{ cm}^{-1}$) on the inferred line centre frequency. Averaging over more than 20 acquisitions reduces the uncertainty to 30 kHz. The weighted deviation from the HITRAN line list is 0.34 MHz and fully consistent with the declared uncertainty [7].

An innovative spectrometer based on a comb-referred nonlinear laser source is demonstrated for high resolution molecular spectroscopy in the LWIR. The spectrometer enables the study of complex spectra of large molecules such as BTEX species (benzene, toluene, ethylbenzene, xylenes) that are of high interest for atmospheric modelling and combustion studies. Infrared bands such as the ν_{11} of benzene investigated here may help the detection of hydrocarbon in remote spatial environments, such as exoplanetary atmospheres. The survey of the ν_2 band of CO₂ demonstrates the metrological quality of the system and allows a straightforward calibration of spectra in the 670–720 cm^{-1} (14–15 μm) region where frequency standards are currently missing.

References

- [1] Consolino, L., Cappelli, F., De Cumis, M. S. & De Natale, P. “QCL-based frequency metrology from the mid-infrared to the THz range: A review, “. *Nanophotonics* **8**, 181–204 (2018).
- [2] Albert, S., Keppler, K., Lerch, P., Quack, M. & Wokaun, A. “Synchrotron-based highest resolution FTIR spectroscopy of chlorobenzene,“ *J. Mol. Spectrosc.* **315**, 92–101 (2015).
- [3] Schliesser, A., Picqué, N. & Hänsch, T. W. “Mid-infrared frequency combs“, *Nat. Photon.* **6**, 440–449 (2012).
- [4] Kowligy, A. S. et al. “Infrared electric field sampled frequency comb spectroscopy,“. *Sci. Adv.* **5**, eaaw8794 (2019).
- [5] Gambetta, A. et al. “Mid-infrared quantitative spectroscopy by comb-referencing of a quantum-cascade-laser: Application to the CO₂ spectrum at 4.3 μm ,“ *Appl. Phys. Lett.* **99**, 251107 (2011).
- [6] Hollenstein, H., Piccirillo, S., Quack, M. & Snels, M. “High-resolution infrared spectrum and analysis of the ν_{11} , A_{2u}(B₂) fundamental band of ¹²C₆H₆ and ¹³C¹²C₅H₆,“ *Mol. Phys.* **71**, 759–768 (1990).
- [7] M. Lamperti, R. Gotti, D. Gatti, M. K. Shakfa, E. Cané, *et al.* “Optical frequency metrology in the bending modes region,“ *Commun. Phys* **3**, 175 (2020).