

# Comb-calibrated Spectroscopy in the 12–15 $\mu\text{m}$ Region

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**Abstract:** We present a comb-calibrated, widely tunable laser spectrometer in the bending mode region applied for metrology-grade measurements on the  $\nu_2$  and  $\nu_{11}$  bands of  $\text{CO}_2$  and benzene, respectively. © 2021 The Author(s)

## Introduction

Optical sensing through laser absorption spectroscopy is a powerful and effective method to identify and quantify different species in a gas sample. The spectral region of long wavelength mid infrared (LWIR) is of particular interest due to the presence of fundamental transitions of molecules with a strong relevance in the environmental, astrophysical and biomedical fields. Yet, the lack of single-mode quantum cascade lasers (QCL) emitting above 13  $\mu\text{m}$  has severely limited spectroscopic investigations in this region [1]. Incoherent sources can be used in Fourier Transform spectrometers (FTS) to probe molecular features in LWIR, but the low resolution (at best 21 MHz [2]) prevents their adoption for precision spectroscopy and optical metrology. Frequency comb-based spectrometers could represent a valuable alternative, thanks to absolute frequency calibration and the chance to shift the comb spectrum (usually in the near infrared) to the mid infrared through nonlinear interactions [3]. Recently a broadband spectrum between 6.7 and 16.7  $\mu\text{m}$  has been demonstrated via dual comb spectroscopy [4]. Yet, for the study of single absorption lines with ultimate accuracy and speed, in a region where the comb tooth spacing is considerably larger than the Doppler broadening, other methods are preferable.

We present an LWIR spectrometer based on a cw nonlinear laser source with 2.2-MHz linewidth and wide tunability between 12.1 and 14.8  $\mu\text{m}$ . The source is based on a difference frequency generation (DFG) interaction between a DFB-QCL and a  $\text{CO}_2$  gas laser, and is referenced to a 1.9  $\mu\text{m}$  Thulium frequency comb. The comb-calibrated source is used to realize a spectrometer with absolute frequency calibration. We applied the spectrometer to measure transition frequencies of several transitions of carbon dioxide with 30 kHz total uncertainty and to resolve the complex spectrum of the  $\nu_{11}$  band of benzene, increasing the state-of-the-art accuracy in the assessment of the rotational parameters.

## Experiment

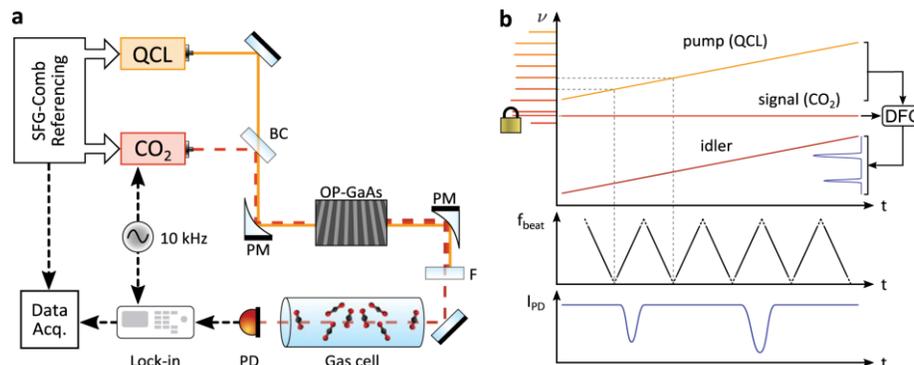


Fig. 1. (a) Experimental setup, (b) detection scheme. Adapted from [7] under [CC 4.0 license](https://creativecommons.org/licenses/by/4.0/). © the authors.

The spectrometer, depicted in Fig. 1(a), is constituted of a DFB-QCL (pump source) emitting around 5.69  $\mu\text{m}$ , collinearly combined with a  $\text{CO}_2$  gas laser (signal source) 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 an idler beam tunable in the range 12.1–14.8  $\mu\text{m}$  ( $675\text{--}826\text{ cm}^{-1}$ ), resulting from temperature tuning of the DFB-QCL over  $4\text{ cm}^{-1}$  and from lasing line stepping of the  $\text{CO}_2$  laser from 9.23 to 10.71  $\mu\text{m}$ .

Two beat note frequencies are generated when the two SFG combs centered at 1.4  $\mu\text{m}$  and 1.6  $\mu\text{m}$  are superimposed with the coherent continuum generated from the thulium comb [5]. Exploiting these beat notes, the  $\text{CO}_2$  laser is locked against the comb whereas the frequency of the DFB-QCL tracked 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.

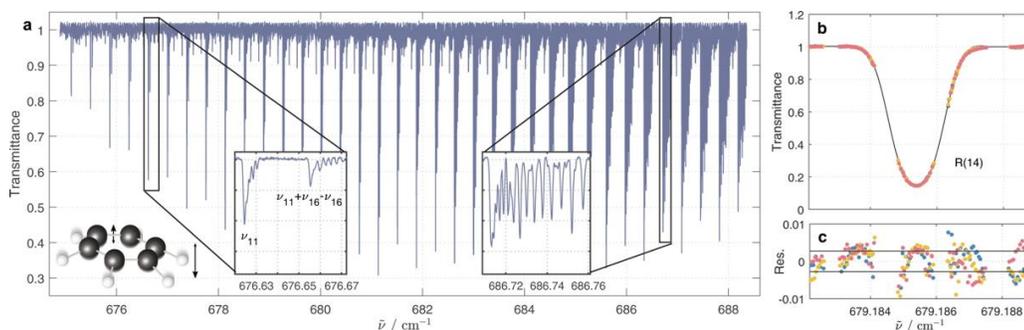


Fig. 2(a) Absorption spectrum of the  $R$  branch of the  $\nu_{11}$  band of benzene. (b) Three independent measurements of the  $R(14)$  line belonging to the  $\nu_2$  band of  $\text{CO}_2$  and fit with a Voigt profile (black line). (c) Residuals from the Voigt fitting. Adapted from [7] under [CC 4.0 license](#), © the authors.

The experimental spectrum of the  $R$  branch of the  $\nu_{11}$  band of benzene, between 675 and 688  $\text{cm}^{-1}$  (14.5–14.8  $\mu\text{m}$ ), is shown in Fig. 2(a) at a pressure of 13.3 Pa. Its complexity shows the ability of the spectrometer to resolve all lines except those separated less than the Doppler width. By fitting line frequencies, we retrieved rotational parameters with a standard deviation over the residuals of 1.5 MHz from the analysis of 723 transitions, one order of magnitude better than the best reported values [6].

We also performed frequency metrology on the  $\nu_2$  band of  $\text{CO}_2$  in the 675–689  $\text{cm}^{-1}$  region, which offers many isolated lines that can be used as frequency standards in the LWIR. Repeated measurements over the same lines allow to shrink the errors on the transition frequencies from 140 kHz (single measurement over 2 s with a signal to noise ratio of 300) to below 30 kHz [7]. An exemplary spectrum, on the  $R(14)$  line, is shown in Fig. 2(b) together with a Voigt fit and fit residuals in Fig. 2(c) that are consistent with the above signal-to-noise ratio.

We have recently substituted the DFB-QCL with an EC-QCL providing internal frequency calibration and broadband mode-hop-free tuning range. The reduction of complexity by removal of the frequency comb and the extended tuning capability enabled by the ECQCL make the spectrometer appealing for laser gas sensing and molecular fingerprinting in the LWIR, at the price of a reduced calibration of the frequency axis. This work will be presented in a future publication.

## Conclusions

We have presented an innovative laser spectrometer based on difference frequency generation and demonstrated its capabilities for high-resolution molecular spectroscopy and metrology. Its characteristics make it ideal for the study of complex spectra of large molecules such as BTEX species (benzene, toluene, ethylbenzene, xylenes), which are of high interest for atmospheric modelling and combustion studies. Application of the system to study simpler molecules, such as  $\text{CO}_2$ , allows for accurate determination of spectroscopic parameters of transitions to be used to populate spectroscopic databases.

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