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Field deployment of a 4320-nm quantum cascade laser-based TDLS system to compare the background CO₂ levels in Mt. Abu with foreground measurements in Gandhinagar, India

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Abstract. We report on the design, development, and field deployment of a 10-mW, 4320-nm distributed-feedback quantum cascade laser-based tunable diode laser spectroscopy (TDLS) system in India for *in situ* measurement of atmospheric CO₂. The portable system was deployed at Mount Abu (24.5926° N, 72.7156° E), a hill station in western India, to carry out week-long measurements of background atmospheric CO₂ using direct detection. The mean mole fraction was estimated to be 396 ± 8 ppm. The system was then deployed in Gandhinagar (23.2156° N, 72.6369° E), the capital of the state of Gujarat, to make foreground measurements over the next week. The mean mole fraction at this location was 503 ± 27 ppm. The difference between the background levels in Mount Abu and foreground levels in Gandhinagar is evident. The detection limit of the system, as measured from an Allan variance analysis, was determined to be 260 ppb for an integration time of 58 s and a path length of 20 cm, which is sufficient for such measurements. Another compact and light-weight TDLS system was also deployed for water vapor measurement. It consisted of a 1392.54-nm distributed feedback laser driven by custom electronics and a digital signal processor to carry out waveform generation, data acquisition, and postprocessing tasks. © The Authors. Published by SPIE under a Creative Commons Attribution 4.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI. [DOI: [10.1117/1.OE.59.2.024110](https://doi.org/10.1117/1.OE.59.2.024110)]

Keywords: tunable diode laser spectroscopy; quantum cascade laser; greenhouse gas monitoring; background carbon dioxide; direct detection.

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1 Introduction

Accurate *in situ* measurement of greenhouse gases (GHGs) is a key requirement in modern climate science research. Reliable measurements are required to build accurate models that help to understand the sink and source patterns of GHGs and also to assess the effectiveness of the international agreements that aim to reduce GHG emissions. Although India is the fourth highest contributor¹ to the global GHG emissions after China, United States, and European Union, the need for GHG monitoring did not receive much attention till the early 1990s. In 1993, an air sampling station was established at Cape Rama (a coastal site in western India) through the collaborative efforts of the Australian Commonwealth Scientific and Industrial Research Organisation (CSIRO), Physical Research Laboratory (PRL), Ahmedabad, and National Institute of Oceanography, Goa. From February 1993 to October 2002, Bhattacharya et al.² collected air samples at this station and sent them to the Global Atmospheric Sampling Laboratory (GASLAB), Australia, for measurement of carbon dioxide and other trace species using gas chromatography (GC). The air samples (collected in 500-ml glass flasks) were analyzed after storage times that ranged between 6 and 25 months. According to the authors, this long storage time led to permeation of air through the O-rings, thereby changing the mixing ratios of the constituent gases in the flasks. Moreover, GC-based instruments are bulky and need periodic calibration with high-purity gas samples. This restricts their use in long-term field

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measurements. From March to June 2003, Latha and Murthy³ carried out carbon dioxide (CO₂) measurements at Goa using a nondispersive infrared (NDIR) gas analyzer (LI-COR, LI-7500). They noticed a systematic reduction in CO₂ levels during the premonsoon months (March to May). Sarma et al.⁴ quantified the magnitude and variability of CO₂ fluxes over the Indian Ocean for the period 1990 to 2009 using various simulation models and compared them with available data. However, owing to insufficient CO₂ measurements available for that region, none of the models represented the measured data accurately. Lin et al.⁵ carried out measurements of CO₂ and other trace gases from 2007 to 2011 at three locations in India. These are: Hanle (high-altitude site located in south-western Ladakh in the Himalayas), Pondicherry (located on the south-east coast of India), and Port Blair (located in the Andaman and Nicobar Islands in the Bay of Bengal). The air samples were collected in glass flasks and analyzed (about 150 days after the sampling date) at the Laboratoire des Sciences du Climat et de l'Environnement, France, using GC. The authors also pointed out the need to develop a comprehensive GHG monitoring network in India with adequate spatial and temporal coverage. Ravi Kumar et al.⁶ made ship-based observations of CO₂ over the Bay of Bengal from July 17 to August 17, 2009. Air samples were collected in glass flasks and later analyzed at the Indian Institute of Tropical Meteorology (IITM), Pune, using GC. They observed higher values of CO₂ with large variability near the coastal regions and relatively low values with less variability over the ocean. Nalini et al.⁷ studied the seasonal and spatial variability of CO₂ over the Indian region from 2009 to 2012 using satellite retrievals, ground-based measurements (at Sinhagad and Cape Rama), and simulation models. The disagreement between satellite-based and ground-based observations indicates the need of a well-distributed ground-based network of monitoring stations. Sharma et al.⁸ made CO₂ measurements at Dehradun and Gadanki from October 2010 to September 2011 using an NDIR analyzer (Vaisala, GMP-343). The mole fraction values at Gadanki were found to be lower than that at Dehradun. Mahesh et al.⁹ monitored CO₂ levels at Sriharikota from October 2011 to January 2012 using an NDIR analyzer (Vaisala, GMP-343). Since Sriharikota is a coastal station, the land and sea breezes were found to control the CO₂ mixing ratios at that location. Chanda et al.¹⁰ investigated the spatial and seasonal variability of CO₂ and water vapor from April 2011 to March 2012 at three selected locations situated at the northern, middle, and southern parts of the Sundarbans, the world's largest mangrove forest region, using an NDIR analyzer (LI-COR, LI-840A). Chandra et al.¹¹ studied the seasonal variability of CO₂ and carbon monoxide (CO) at Ahmedabad from November 2013 to May 2015 (with a gap from March to June 2014), using cavity ring-down spectroscopy. The average annual mole fraction of CO₂ and CO was found to be 413 and 0.5 ppm, respectively. However, these measurements were done at a single location (campus of the PRL, Ahmedabad) and do not therefore capture the scenario in the city's congested areas.

The Central Pollution Control Board¹² is a statutory organization under the Ministry of Environment, Forest and Climate Change, Government of India, and is the apex organization in the country in the field of pollution control. As part of the National Air Quality Monitoring Program, it monitors the ambient air quality at multiple locations in India by measuring CO (using NDIR spectroscopy technique), SO₂ (using ultraviolet fluorescence), NO, NO₂ (using gas phase chemiluminescence), and particulate matter (PM_{2.5}, PM₁₀). The Ministry of Earth Sciences (MoES), Government of India, has recently launched an initiative named System of Air Quality and Weather Forecasting and Research (SAFAR)¹³ to provide location-specific information on air quality on an almost real-time basis through web-based and mobile application-based platforms. The system has been developed by the IITM, Pune, in collaboration with the India Meteorological Department and National Centre for Medium Range Weather Forecasting. However, no records for the GHGs exist. Currently, SAFAR reports the air quality indices only for four cities, namely, Delhi, Pune, Mumbai, and Ahmedabad. Therefore, it is unable to capture accurately the air pollution scenario of the entire country. According to a report¹⁴ released by the Netherlands Environmental Assessment Agency in December 2017, India's GHG emissions rose by an alarming 4.7% in 2016 while United States and China reduced their emissions by 2% and 0.3%, respectively, in the same year. Although there have been several efforts by various researchers toward atmospheric CO₂ monitoring in India, they have been done on a campaign basis instead of on a continuous basis. In addition, *in situ* measurements have not been widely reported because such campaigns are difficult to plan, fund,

and involve development of rugged and portable systems. Therefore, data are not available over long time intervals and over large geographical regions. This makes it difficult to understand the variations of carbon dioxide over the Indian subcontinent.¹⁵ Thus, there is a pressing need to develop robust portable sensors for continuous monitoring of GHGs over India.

In this paper, we report the design and field deployment of a compact, rugged, and portable midinfrared tunable diode laser spectroscopy (TDLS) system in India for *in situ* high-sensitivity and continuous measurement of atmospheric CO₂. This is the first instance of such a system being deployed anywhere in India. The high sensitivity and excellent selectivity of TDLS-based systems make them ideally suited for such applications in which spectral interference from various atmospheric constituents is unavoidable. Conventional gas sensing instruments such as the GC require periodic recalibration to maintain accuracy of measurements. This requires human intervention to flow high-purity calibration gas mixtures through the system. This adds to the infrastructural and power requirements and limits portability. The development of several successful calibration-free TDLS approaches^{16–20} in the last decade makes it possible to totally avoid the tedious recalibration steps. This is especially desirable for in-field measurements. As a result of these developments, TDLS is a widely used technique in atmospheric gas measurement applications. This work uses the direct detection TDLS approach in which the gas line shape itself is faithfully recovered by normalizing the absorption signal by the baseline signal. A simulated gas absorption line is then fitted to the data in a least squares sense and the mole fraction (and pressure) is extracted. The main advantage of this approach is that it is an inherently absolute measurement technique, and it is easy to extract information from the measured signals.

The expedition to Mount Abu was aimed at obtaining the background CO₂ levels. It is necessary to do these background measurements at a remote location far away from cities to minimize the effect of automobile and industrial emissions. We therefore chose Mount Abu, which is a hill-station 1220 m above mean sea level, as the nearest practical location for the expedition because it is far away from busy cities and industrial hubs. A measurement campaign of 2 weeks was planned comprising week-long measurements in Mount Abu followed by week-long foreground measurements in Gandhinagar. Here, “foreground” refers to measurements done in an urban area. The aim was to compare the background and foreground CO₂ levels under similar climatic conditions at that time of the year. This study also aims to demonstrate that robust TDLS systems can be built to fill the measurement gaps that currently exist.

2 Measurement Technique

TDLS is a mature and robust gas-sensing technique that can be used to detect several gases simultaneously. Gas parameters such as mole fraction, pressure, and temperature can be extracted very accurately in real time. TDLS is widely used in a variety of applications, such as atmospheric studies,^{21,22} combustion monitoring,^{23,24} breath analysis,²⁵ and fire detection.²⁶ In the basic form of TDLS known as direct detection, a narrow-linewidth (typically few MHz) tunable diode laser is initially temperature-tuned close to the target gas absorption line by applying a current to the built-in thermo-electric cooler (TEC). A low-frequency ramp signal (typically tens of Hz) is applied to the injection current of the laser to precisely tune the emission wavelength across the target absorption line. The spectral distribution of the transmitted light intensity is recorded to extract the gas parameters. A polynomial fit to the nonabsorbing spectral regions of the recorded gas absorption signal yields an accurate estimate of the laser intensity. The relative transmission is then obtained by normalizing the absorption signal by the laser intensity. Note that the normalization process removes the dependency of the absorption signal on the laser intensity and yields the absolute lineshape. The relative transmission is given by the Beer–Lambert law

$$I(\nu)/I_0(\nu) = \exp[-\alpha(\nu)], \quad (1)$$

where $I_0(\nu)$ is the incident laser intensity, $I(\nu)$ is the transmitted laser intensity, ν is the emission frequency, and $\alpha(\nu)$ is the absorbance, given by

$$\alpha(\nu) = \sum_j S_j(T) P X \phi_j(\nu) L, \quad (2)$$

where $S_j(T)$ ($\text{cm}^{-2} \text{atm}^{-1}$) is the line strength of the j 'th transition at temperature T , X is the mole fraction of the target species, P (atm) is the total pressure, $\phi_j(\nu)$ (cm) is the transition line shape, and L (cm) is the optical path length. The line-strength of a transition has a temperature dependence, given as

$$S(T) = S(T_0) \frac{Q(T_0)}{Q(T)} \left(\frac{T_0}{T} \right) \exp \left[-\frac{hcE''}{k} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \left[1 - \exp \left(-\frac{hc\nu_0}{kT} \right) \right] \left[1 - \exp \left(-\frac{hc\nu_0}{kT_0} \right) \right]^{-1}, \quad (3)$$

where $S(T_0)$ is the line strength at reference temperature T_0 (296 K), $Q(T)$ is the partition function²⁷ of the absorbing molecule, E'' (cm^{-1}) is the lower state energy of the transition, h (J s) is the Planck's constant, c (cm s^{-1}) is the speed of light, k (J K^{-1}) is the Boltzmann's constant, T (K) is the gas temperature, and ν_0 (cm^{-1}) is the line center frequency of the transition.

The shape of a gas absorption line is dictated by the thermodynamic condition of the gas molecules. The two dominant broadening mechanisms that determine the line shape of a particular transition are Doppler broadening and collision broadening. Doppler broadening refers to the apparent shift in frequency of the radiation absorbed during a transition due to the motion of the gas molecules relative to the light source. Doppler broadening is a nonhomogeneous process and is characterized by a Gaussian line shape

$$\phi_D(\nu) = \frac{2}{\Delta\nu_D} \sqrt{\frac{\ln 2}{\pi}} \exp \left[-4 \ln 2 \left(\frac{\nu - \nu_0}{\Delta\nu_D} \right)^2 \right], \quad (4)$$

where $\Delta\nu_D$ (cm^{-1}) is the full-width at half-maximum (FWHM) of the Gaussian profile and is given as

$$\Delta\nu_D = \nu_0 \sqrt{\frac{8 k T \ln 2}{m c^2}} \approx 7.1623 \times 10^{-7} \nu_0 \sqrt{\frac{T}{M}}, \quad (5)$$

where M (g mol^{-1}) is the molar mass of the absorbing species. Collision broadening and pressure-induced shifting of spectral lines are caused by perturbation of the energy levels due to molecular collisions. Collision broadening is a homogeneous process and is characterized by a Lorentzian line shape

$$\phi_C(\nu) = \frac{1}{\pi} \frac{\Delta\nu_C/2}{(\nu - \nu_0 - \Delta\nu_S)^2 + (\Delta\nu_C/2)^2}, \quad (6)$$

where $\Delta\nu_C$ (cm^{-1}) is the FWHM of the Lorentzian profile and $\Delta\nu_S$ (cm^{-1}) is the pressure-induced shift of the line center frequency of the transition. These are proportional to the pressure (P) and are given as

$$\Delta\nu_C(\nu) = P \sum_j X_j 2\gamma_j, \quad (7)$$

$$\Delta\nu_S(\nu) = P \sum_j X_j \delta_j, \quad (8)$$

where γ_j ($\text{cm}^{-1} \text{atm}^{-1}$) is the collision broadening coefficient and δ_j ($\text{cm}^{-1} \text{atm}^{-1}$) is the pressure-induced frequency shift coefficient.

The collective effect of Doppler broadening and collision broadening leads to a Voigt line shape, which is essentially a convolution of the Gaussian and Lorentzian line shapes:

$$\phi_{\text{Voigt}}(\nu) = \phi_D(\nu) * \phi_C(\nu). \quad (9)$$

The spectral absorbance is simulated using spectroscopic parameters available in the high resolution transmission (HITRAN) database²⁸ and a Voigt line shape function. The mole fraction and pressure of the target gas are conveniently extracted by least-squares fit of the simulated line shape to the experimentally recovered gas absorption line.

3 System Design

3.1 Selection of the Absorption Line

The midinfrared region is very attractive for high-sensitivity detection of trace atmospheric species since most gases have their strong fundamental rotational–vibrational transitions in this spectral region. Figure 1(a) shows the simulated absorption spectra of 400 ppm CO₂ and 1% water vapor from 4170 to 4380 nm at a pressure of 0.45 bar. The mole fraction values for the simulation are chosen in accordance with their typical atmospheric abundance, and the pressure value is chosen to represent the pressure at which the measurements would be made. The simulation is carried out using spectroscopic parameters available in the HITRAN database. The interference due to water vapor is negligible in this wavelength range; and therefore, it is easier to choose a well-isolated CO₂ absorption line. The dashed box marks the CO₂ transitions that can be accessed with the quantum cascade laser (QCL) (Alpes Lasers, HHL-513) used for the CO₂ measurements. These transitions are shown in Fig. 1(b). Among these, the transition at 4319.30 nm (in the dashed box) is selected for the CO₂ measurements. This transition is shown in Fig. 1(c). The line strength of this transition is $7.945 \times 10^{-19} \text{ cm}^{-1}/(\text{mol cm}^{-2})$ at 296 K. Equation (3) is used by the postprocessing algorithm to convert this line strength value to the line strength value at the ambient temperature during the field measurements.

A 1392.54-nm distributed feedback (DFB) edge-emitting laser (Eblana Photonics, EP1392-DM-B) was also used for water vapor measurements. The simulated absorption spectra of 400 ppm CO₂ and 1% water vapor for the temperature tuning range (1390.5 to 1394.5 nm) of the DFB laser is shown in Fig. 2. Spectral interference due to CO₂ is negligible. The water vapor transition at 1391.672 nm (7185.597 cm^{-1}) is chosen because sufficient nonabsorbing regions are available on both sides of the transition. These are necessary for baseline fitting

Fig. 1 (a) Simulated absorption spectra of 400 ppm CO₂ and 1% water vapor from 4170 to 4380 nm for path length of 20 cm at pressure of 0.45 bar and temperature of 296 K. The dashed box marks the CO₂ transitions that are accessible using the HHL-513 QCL, (b) absorption lines of CO₂ accessible with the HHL-513. The dashed box marks the line used during the measurements, (c) line selected for atmospheric CO₂ measurement.

Fig. 2 Simulated absorption spectra of 400 ppm CO₂ and 1% water vapor for the tunable range of the 1392.54-nm DFB laser. The selected line at 1391.672 nm is marked with a dashed box.

during direct absorption spectroscopy. At 296 K, the line strength of this transition is $5.984 \times 10^{-22} \text{ cm}^{-1}/(\text{mol cm}^{-2})$.

3.2 Experimental Arrangement for CO₂ and Water Vapor Measurements

A schematic of the experimental set-up for CO₂ measurements is shown in Fig. 3(a). A 10-mW, 4320-nm QCL (Alpes Lasers, HHL-513) driven by a laser diode controller (Thorlabs, ITC4002QCL) is used to interrogate the target CO₂ transition at a scan rate of 10 Hz. The laser

Fig. 3 (a) Block diagram of the TDLS setup used for CO₂ measurements, (b) the QCL and HgCdTe PD in the acrylate enclosure with a path length of 20 cm between them. The dimensions of the acrylate enclosure are 42.5 cm × 20 cm × 25 cm.

diode controller can supply up to 2 A of laser current and can be modulated up to 130 kHz. The QCL is encapsulated in a high heat load (HHL) package for superior heat dissipation. In addition, it is mounted on an aluminum heat sink that is fitted with a 5-V DC fan to circulate the air and keep the base-plate of the QCL cool. Light from the QCL traverses a free space path length of 20 cm and is detected by a thermoelectrically cooled HgCdTe photodetector (PD) (Vigo, PVI-4TE-6). The QCL-detector assembly shown in Fig. 3(b) is housed in an acrylic enclosure to protect it from dust. The dimensions of the enclosure are 42.5 cm $\times$ 20 cm $\times$ 25 cm. The enclosure is provided with an inlet and an outlet. A fresh volume of air is drawn inside the pre-evacuated enclosure through the inlet before each measurement. A vacuum pump (Tarsons, Rockyvac 300) with flow rate 20 l/min is then used to reduce the pressure to around 0.45 bar by drawing air through the outlet. It is necessary to reduce the pressure because the nonabsorbing regions adjacent to the CO₂ absorption line broaden out significantly at ambient pressure, thereby leading to baseline fitting errors. The (PD) output is digitized by a 500-MHz digital storage oscilloscope (Tektronix, TDS3054C) and acquired by a LabVIEW application. The mapping of time-indexed values obtained from the oscilloscope to wavelength-indexed values is known as wavelength referencing¹⁶ and is a standard and well-known step in the field of gas sensing using tunable laser diodes. In this procedure, the gas line is used as an absolute wavelength marker and an etalon's output (whose free spectral range is precharacterized and therefore known) is used as a frequency scale to map the time-indexed values to corresponding wavelength-indexed values. A MATLAB program extracts the mole fraction and pressure of carbon dioxide simultaneously in real-time by fitting a simulated Voigt profile to the wavelength-indexed gas absorption line.

The water vapor detection system consists of a 10-mW, 1392.54-nm DFB tunable diode laser (Eblana Photonics, EP1392-DM-B) that is mounted on a butterfly mount (Thorlabs, LM14S2) and is driven by custom electronics. The custom driver circuit consists of a miniature temperature controller IC (Thorlabs, MTD415TE) that is compatible with 10 k Ω thermistor and can supply up to 1.5 A of TEC current, and a miniature current controller IC (Thorlabs, MLD203CHB) that can supply up to 200 mA of laser current and can be modulated up to 100 kHz. The laser temperature is set by the internal digital proportional-integral-derivative loop. The system is driven by a digital signal processor (DSP) (Texas Instruments, TMS320F28377D) that has a clock speed of 200 MHz, 1 MB flash memory, and 204 kB random access memory. The DSP controls all aspects of signal generation, data acquisition, and postprocessing to extract the mole fraction of water vapor. The DFB laser and the compact laser driver are assembled inside a small box (16 cm $\times$ 10.5 cm $\times$ 4 cm) as shown in Fig. 4. The laser beam passes through a fiber-optic

Fig. 4 The 1392.54-nm DFB edge-emitting laser along with the custom driver electronics assembled inside a small box (16 cm $\times$ 10.5 cm $\times$ 4 cm). The driver electronics consists of a temperature controller IC (Thorlabs, MTD415TE), a current controller IC (Thorlabs, MLD203CHB), and an Arduino Nano.

collimator (Thorlabs, 50-1550A-APC) and on to a variable-gain thermo-electrically cooled InGaAs PD (Thorlabs, PDA-10DT-EC). The path length for this open-path configuration is 69 cm.

A comparison between a bench-top laser controller (Stanford Research Systems, LDC502) and the compact laser driver is presented in Table 1. The 183-fold reduction in weight, 114-fold reduction in volume, and 46-fold reduction in cost of the system are important attributes. The power requirement is reduced from 220 V (AC) to 5.5 V (DC). These aspects are very important from the point of view of field deployment of these sensor systems and building large GHG monitoring networks.

The block diagram of the direct detection algorithm implemented on the DSP is shown in Fig. 5. A 12-bit digital-to-analog converter generates the current ramp to interrogate the target water vapor transition at a scan rate of 10 Hz. The PD signal is acquired by a 12-bit analog-to-digital converter (ADC) at a sampling rate of 10 kSps. It acquires 1000 sample points for a ramp period. An eight-point moving average filter reduces the noise in the acquired signal and a polynomial fit of second order is then used to normalize the acquired gas line. A two-parameter Voigt line shape fit to the normalized gas line is done to extract the mole fraction and pressure of water vapor. Programming a convolution operation to simulate the Voigt line shape on a DSP board requires significant computational resources. Researchers have proposed various ways to approximate the Voigt line shape to reduce the computational complexity.^{29–31} Liu et al.²⁹ proposed a weighted sum of Lorentzian and Gaussian line shapes as an analytical approximation for the Voigt line shape. We have used Liu’s approach to simulate the Voigt line shape during the measurements. The iterative fitting process on the DSP uses a variable step-size least-mean-square (VS-LMS) algorithm.³²

Table 1 Comparison between a bench-top laser controller and the compact laser driver.

Parameter	Stanford Research Systems, LDC502	Compact laser driver
Weight	6800 g	37 g
Dimensions	12.7 cm × 38.1 cm × 17.78 cm	5.3 cm × 9.5 cm × 1.5 cm
Price	INR 2,11,000	INR 4500
Power requirement	220 V (AC)	4.5 to 5.5 V (DC)

Fig. 5 Block diagram of the direct detection algorithm implemented on the DSP board for water vapor measurements. The fitting process uses a VS-LMS approach.

Fig. 6 (a) Experimental and simulated direct detection signals for a calibrated gas sample of 515 ppm CO₂ (balance N₂). The mole fraction extracted by the algorithm is 507.78 ppm. (b) Plot of Allan deviation as a function of integration time, showing a detection limit of 260 ppb CO₂ for an averaging time of 58 s.

3.3 Validation of the System and Estimation of Detection Limit

Before deploying the system for in-field measurements, the TDLS system was validated by laboratory-based measurements of mole fraction of calibrated CO₂ samples. A calibrated sample of 515 ppm CO₂ (balance N₂) was introduced into the acrylate enclosure (described in Sec. 3.2). The path length between the QCL and PD was 20 cm. The PD output was normalized and fitted for extraction of mole fraction and pressure. Figure 6(a) shows the excellent agreement between experimental and simulated direct detection signals for the calibrated CO₂ sample. The mole fraction extracted by the algorithm was found to be 507.78 ppm, which is sufficiently close to the mole fraction value certified by the manufacturer (Jay Path Industrial Gases, Ahmedabad, Gujarat, India). The accuracy of mole fraction extraction is 98.6%. The difference between the extracted mole fraction value and the certified value is attributable to a combination of baseline fitting error and etalon fringes.

Interference from etalon fringes and $1/f$ noise are the primary factors that determine the limit of detection of a TDLS sensor. Therefore, an Allan variance analysis³³ was carried out to estimate the detection limit of the measurement system. A calibrated sample of 515 ppm CO₂ (balance N₂) was introduced into the acrylate enclosure, and then the direct absorption signal was monitored for 500 s with a time resolution of 1 s. The peak value of the direct absorption signal (acquired repeatedly over the duration of 500 s) was used as the data for generating the Allan plot for CO₂. The Allan deviation plot [shown in Fig. 6(b)] obtained from this data showed a single-pass detection limit of 260 ppb carbon dioxide for an integration time of 58 s and path length of 20 cm. This corresponds to a sensitivity of 52 ppb-m when normalized to a path length of 1 m. This sensitivity is clearly sufficient for atmospheric CO₂ measurements.

4 Field Measurements at Mount Abu and Gandhinagar

4.1 Measurement Locations

Figures 7(a) and 7(b) help to form an idea about the measurement locations. These are: (i) guest house of the Mount Abu Infrared Observatory (MIRO) in Rajasthan, (ii) campus of the Indian Institute of Technology Gandhinagar (IITGN) in Gujarat. The distance between the two measurement locations is around 240 km. Mount Abu (24.5926° N, 72.7156° E) is a hill station in the state of Rajasthan in western India. It is situated in the Aravalli Range at an altitude of 1220 m above mean sea level. The week-long measurements were made at the guest house of the MIRO, PRL. The expedition to Mount Abu was aimed at obtaining the background CO₂ levels. The second measurement location is the campus of the IITGN in Gujarat. Gandhinagar (23.2156° N, 72.6369° E) is the capital of Gujarat and has a population of over 200,000. The IITGN campus is located on the outskirts of the city. Figures 7(c) and 7(d) show the TDLS system deployed at Mount Abu and IITGN, respectively, for measurement of atmospheric CO₂ and water vapor.

Fig. 7 (a) Map of India with the western part of the country marked by a dashed box, (b) zoomed-in view of western India showing the measurement locations: (1) guest house of the IITGN in Gujarat, (2) campus of the IITGN in Rajasthan, and (c) the TDLS system deployed at Mount Abu for measurement of atmospheric CO_2 and water vapor. The site is at an altitude of 1220 m above mean sea level. (d) The same system deployed at IITGN campus, which is at an altitude is 81 m above mean sea level.

4.2 Carbon Dioxide Measurements

The measurements at Mount Abu (from June 10 to 16, 2018) and IITGN (from June 18 to 24, 2018) were made just before the monsoon set in. Data were acquired at 15 min intervals during 00:00 to 06:00 h. Figures 8(a)–8(d) show the excellent agreement between experimental and

Fig. 8 Experimental and simulated direct detection signals of CO_2 for the measurements made on (a) June 10, 2018, at 01:45 h, (b) June 11, 2018, at 04:00 h, (c) June 23, 2018, at 03:30 h, and (d) June 24, 2018, at 00:45 h, showing excellent agreement between simulation and experiments.

Fig. 9 Variation in CO₂ mole fraction at (a) Mount Abu from June 10 to 16, 2018, and (b) IIT Gandhinagar from June 18 to 24, 2018, during 00:00 to 06:00 h. The average for the observations at Mount Abu and IITGN are 396 ± 8 and 503 ± 27 ppm, respectively.

simulated direct detection signals of CO₂ for the measurements made on June 10, 2018, at 01:45 h, June 11, 2018, at 04:00 h, June 23, 2018, at 03:30 h, and June 24, 2018, at 00:45 h, respectively. The maximum error along the scan range is $\sim 2\%$.

Carbon dioxide variations at Mount Abu and IITGN are shown in Figs. 9(a) and 9(b), respectively. The maximum and minimum mole fraction values were 419 and 365 ppm, respectively, and the mean for the week-long observation was 396 ± 8 ppm. These values agree well with background CO₂ levels recorded by monitoring stations around the world. The weekly average at the Mauna Loa Observatory³⁴ in Hawaii for the week beginning on July 1, 2018, was 409.38 ppm. Measurements at IITGN campus showed maximum and minimum mole fraction values of 652 and 420 ppm, respectively, with an average of 503 ± 27 ppm. The large difference between the background levels in Mount Abu and foreground levels in Gandhinagar is evident.

4.3 Water Vapor Measurements

The mole fraction and pressure of water vapor were extracted by an algorithm on the DSP board. Figures 10(a) and 10(b) show the excellent agreement between experimental and simulated direct detection signals for the measurements made at IITGN on June 18, 2018, at 02:00 h and June 21, 2018, at 04:00 h, respectively. The maximum error along the scan range is $\sim 1.5\%$.

Fig. 10 Experimental and simulated direct detection signals of water vapor for the measurements made at IITGN on June 18, 2018, at 02:00 h and June 21, 2018, at 04:00 h, respectively, showing excellent agreement between simulation and experiments.

Fig. 11 Variation in water vapor mole fraction at (a) Mount Abu from June 10 to 16, 2018, and (b) IITGN from June 18 to 24, 2018, obtained using the compact TDLS system. The mean mole fraction values for the observations at Mount Abu and IITGN are $2.619 \pm 0.09\%$ and $3.051 \pm 0.12\%$, respectively.

The water vapor measurements at Mount Abu and IITGN are shown in Figs. 11(a) and 11(b), respectively. The mean mole fraction values for the week-long observations at Mount Abu and IITGN are $2.619 \pm 0.09\%$ and $3.051 \pm 0.12\%$, respectively. The measurements were carried out just before the monsoon set in and therefore the mole fraction values are significantly higher than our previous measurements²¹ made at IITGN during summer of 2017 (2.161% on May 28 and 2.248% on May 29).

5 Conclusion

This paper reports the first midinfrared TDLS-based comparison of foreground and background atmospheric CO₂ levels in India. The measurements show that while the foreground levels (as measured in Gandhinagar) are much higher than the global average, the background CO₂ levels measured in Mount Abu are closer to the global average. The direct detection TDLS technique used in this work to extract the mole fraction of the gases is an inherently absolute measurement technique. Therefore, there was no need to calibrate the system when it was taken to a different location. This is extremely important for in-field measurements in which the signal levels vary not necessarily due to changes in the mole fraction of the gas but due to unavoidable systematic issues such as laser intensity variations and variable optical coupling due to mechanical vibrations or dust. The portability of the instrument is another important aspect. Some Indian cities have very high levels of GHGs, and it is important to develop systems that could be deployed on vehicles and mounted on drones. That is the only way a spatially resolved map of urban built-up areas could be obtained. The next phase of measurements will focus on developing a multi-component QCL-based system to carry out vehicle-mounted on-road measurements of GHGs to develop a map of the Ahmedabad–Gandhinagar region with high spatial resolution. A smartphone-based data logging system has been developed that can be interfaced to the DSP over a wireless connection. We also aim to carry out measurements in heavily polluted areas such as New Delhi, where the air pollution scenario is one of the worst in the world. In summary, these results clearly demonstrate that TDLS-based instruments are very well suited to strengthen nation-wide efforts in air quality monitoring and climate change research.

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