Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-177, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 13 June 2016

Atmospheric CO_2 retrieval from ground based FTIR spectrometer over Shadnagar, India.

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Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-177, 2016
Manuscript under review for journal Atmos. Meas. Tech.
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Abstract

The column-averaged volume mixing ratio (vmr) of carbon dioxide (XCO_2) has been retrieved over Shadnagar (Latitude=17.03° N, Longitude=78.21° E), India at Near Infrared (NIR) spectra using ground based high resolution ($\Delta\nu$=0.01 cm^{-1}) Fourier Transform InfraRed (FTIR; model IFS125M) spectrometer. It is first of its kind in India for measuring columnar and vertical mixing ratios of atmospheric trace gases and other greenhouse gases (GHGs). In the present study, retrieval of XCO_2 could be performed for a week at near Sun's nadir view (solar zenith angle-SZA, ±75.0°) using line-by-line radiative transfer algorithm (LBLRTA). Vertical profiles of CO_2 have been retrieved at NIR and middle IR (MIR) spectra using a version of the Fast Atmospheric Signature Code 3 (FASCODE3) model which is for the retrieval of atmospheric trace gas profiles. Error residuals between measured and fitted atmospheric transmission lie with in ±1.0% for CO_2 (6180-6380 cm^{-1}) and O_2 (7800-7940 cm^{-1}) respectively. During analysis period mean (standard deviation, 1σ) XCO_2 was observed to be 385.24 ppm (4.22 ppm) with 1.0 % of daily variation. Minimum and maximum averaged molecular column densities of CO_2 (O_2) are 6.15×10^{21} (3.3×10^{24}) molecules/cm^2 and 8.06×10^{21} (4.72×10^{24}) molecules/cm^2 respectively. Obtained an average high signal to noise ratio (SNR) of 833 and 625 for NIR and MIR spectra, respectively.

Keywords: Column CO_2, Vertical profile, FTIR, FASCODE3, Trace gases

1. Introduction

Greenhouse and other trace gases such as carbon dioxide (CO_2), methane (CH_4), ozone (O_3) and nitrous oxide (N_2O) play a vital role in controlling the climate system of the lower atmosphere (Stocker et al., 2013; Smedley et al., 2015; Sreenivas et al., 2016). CO_2 in the atmosphere is the most important contributor to positive radiative forcing that increases the greenhouse effect (Forster et al., 2007). It has increased about 40% from the year 1750 to 2011 with the level of atmospheric abundance of CO_2 was 390.5 ppm (390.3 to 390.7) in the year 2011 (Stocker et al., 2013). To understand better and manage CO_2 emissions, estimates of source and sink strengths are required by the integrated approach of in-situ, remote sensing and model simulation. Currently the information about atmospheric CO_2 is mainly inferred from in situ (Warneke et al., 2005; Petri et al., 2012) and remote sensing technology.

Rayner and O'Brien (2001) have shown that space-based column CO_2 can substantially improve understanding of surface fluxes only if they have accuracy and precision of 1-2 ppm with good spatial and temporal coverage. National Aeronautics and Space Administration (NASA) launched a dedicated Orbiting Carbon Observatory-2 (OCO-2) satellite in 2014 to measure column CO_2 (http://oco.jpl.nasa.gov/). The OCO-2 instrument aimed to measure XCO_2 with a precision better than 0.3 % on spatial scales (<100 km). Air-borne and satellite based measurements of such parameters are subjected to uncertainties associated with the constraints related to the retrieval techniques and limitations inherent to the sensor (A.P. Cracknell & C.A. Varotsos 2014). Thus, direct measured column measurements are potentially a decisive input for atmospheric CO_2 inversion because of lower impact from errors in modeled vertical convection (Warneke et al., 2005; Kobayashi et al., 2010). Column measurements are especially important in the tropics, as convection is consistently strong and as a result flux signals are only weakly seen in surface measurements (Gloor et al., 2000).

National Remote Sensing Center (NRSC) of Indian Space Research Organization (ISRO) has established a dedicated Atmospheric Sciences Lab (ASL) to record, monitor and analyzes the greenhouse and other trace gases along with radiation measurements towards understanding the impact of atmospheric processes and assess the air quality. A high resolution (maximum $\Delta\nu$=0.0035 cm^{-1}; optical path depth (OPD) of 257 cm) FTIR spectrometer for measuring atmospheric trace gases and GHGs has been installed and currently operational on clear sky days at ASL, Shadnagar since March 2014. We hope these measurements provide highly reliable and accurate standard data sets over a long period. Additionally, they provide complementary information to the satellite measurements such as diurnal variations.

In the present study, NIR and MIR spectra have been utilized to retrieve column averaged and vertical profile of CO_2 using LBLRTA and radiative inverse model (FASCODE3).

2. Data measurement and analysis

High resolution ($\Delta\nu$=0.01 cm^{-1}; OPD=90 cm) Sun spectra have been obtained using ground based FTIR spectrometer over Shadnagar region (Latitude=17.03° N, Longitude=78.21° E) of India have been evaluated for a week. An IFS 125M FTIR housed at ASL is equipped with set of beam splitters and detectors such as Potassium Bromide (KBr) and Calcium fluoride (CaF_2) beam splitters and Mercury Cadmium Telluride (MCT) and Indium antimonide (InSb) detectors cooled with liquid nitrogen (LN_2). Details are summarized in table 1. In the present study, the measured spectra using InSb detector to understand the typical columnar concentrations of CO_2 by implementing the basic LBLRTA at 6100 cm^{-1}-6400 cm^{-1} spectral range. Also attempted to retrieve CO_2 vertical profile information in NIR and MIR spectral range using FASCODE3 model (Notholt 1994). The FASCODE3 (Smith et al., 1978; Wang et al., 1996) coupled with an inversion module is based on the optimal estimation method of Rodgers (1976), provides error analysis tools necessary to determine the information content of the retrievals. The reader is referred to detailed retrieval methods and their error analysis explained in Miller et al. (1999). Observations covering the spectral range from 6000 cm^{-1} to 8000 cm^{-1} were used to retrieve the column averaged dry mole fraction (DMF) of CO_2 and vmr of O_2 (Wallace and Livingston, 1990 and Yang et al., 2002).

Implemented LBLRTA for the analysis of solar spectra absorption features to retrieve the columnar abundance of CO_2 in the atmosphere. In the present study, the absorption bands for CO_2 at 6100 cm^{-1}-6400 cm^{-1} and for O_2 at 7800 cm^{-1}-7960 cm^{-1} have been used. Retrieval includes various options such as scaling of *a priori* profiles of pressure (P), temperature (T) and volume mixing ratios (vmr). In this study, we have used *a priori* profiles (vmr) simulated over Izana (Tenerife, 28.3° N, 16.5° W) by National Center for Atmospheric Research/Whole Atmosphere Community Climate Model (NCAR/WACCM). Typical climatological profile of CO_2 and (P, T) obtained for 44 levels (~120 km) from NCAR/WACCM and analysis provided by NASA Goddard Space Flight Center (GSFC, science@hyperion.gsfc.nasa.gov). The CO_2 and O_2 spectral parameters were obtained from High Resolution Transmission (HITRAN) 2012 database

(Rothman et al., 2013). Figure 1 provides atmospheric signal measured over Shadnagar with different combination of detectors and beam splitters.

Spectra were recorded at 0.01 cm^{-1} resolution. It is possible to derive zenith column densities of CO_2, CH_4, N_2O, CO, O_3, C_2H_6 and HF. The present study reports retrievals of CO_2 and O_2 gases for one week during 08th, 10th, 15th, 16th, 21st and 23rd March 2016.

3. Results and discussion

The measured spectra were analyzed at various times throughout the day particularly solar zenith angle (SZA) at around nadir view (±75.0°) to obtain the atmospheric signal over the study region. The spectra are analyzed are generally co-additions of 2-4 individual spectra, each taking 5 minutes to acquire. In our analysis, an average SZA taken to be 75°.0. Figure 2 shows a sample (21st March 2016) spectral analysis in which two spectral bands of CO_2 and O_2 were fitted against measured. FASCODE3 model has been used to fit the CO_2 and O_2 spectra against measured transmittance spectra. It computes spectral transmittance, radiance and optical depth for a given spectral range. The spectral line parameters are based on the latest HITRAN line list (Rothman et al., 2013). Heart of the FASCODE3 is a line-by-line calculation which computes atmospheric transmittance at very high spectral resolution. Summary of the retrievals and model inputs with SNRs of spectral windows provided in table 2.

In our analysis, we used central wave numbers (ν_c) for CO_2 and O_2 are 6348 cm^{-1} and 7808 cm^{-1} respectively. It has an advantage of being collected using the same detector and the ratio of CO_2/O_2 will mostly cancel out the systematic effects such as instrument line shape (ILS). In figure 2b and 2d residual (measured-calculated) errors were shown for CO_2 and O_2 that lie within ±1.0% respectively. The time series column-averaged concentration of CO_2 were shown in figure 3. These limited spectra particularly selected to obtain vertical column abundance at near nadir view over Shadnagar region. Thus, these spectra were obtained during 11:30 LT to 12:30 LT for 5 min interval where SZA is 75.0°. The ratio of CO_2 and O_2 column amounts, scaled by the standard atmospheric O_2 fraction have been computed as

$$\mathrm{XCO2_{DMF}(ppm)} = 0.2095 \times \left[\frac{\mathrm{Column\ of\ X_{CO2}}}{\mathrm{Column\ O_2}}\right] - - - (1)$$

Time series observations were averaged within the selected time interval which may probably reduce the thin clouds impact on absorption features and instrumental effects such as line shape. The column-averaged CO_2 was observed to be minimum (maximum) of 381.0 ppm (390.0 ppm). Minimum and maximum averaged molecular column densities of CO_2 (O_2) are 6.15×10^{21} (3.3×10^{24}) molecules/cm^2 and 8.06×10^{21} (4.72×10^{24}) molecules/cm^2 respectively. Daily means of the standard deviations (1σ) are 3.04 ppm, 3.58 ppm, 3.40 ppm, 0.74 ppm, 0.84 ppm and 3.12 ppm respectively.

In the present study, using FASCODE3 we retrieved CO_2 concentration in the vertical profile for one day (21st April 2015 and 23rd March 2016) in two consecutive years as shown in figure 4. These retrievals are critically dependent on atmospheric pressure and temperature profiles. Present study used NIR (6100-6400 cm^{-1}) and MIR (660-700 cm^{-1}) spectral windows for sensitivity comparison for two different days in different years. Both the profiles are likely to be same with the varied temperature input. The mean standard deviations (1 σ) for NIR and MIR are 0.07 ppm and 0.08 ppm respectively. Since the temperature and pressure profiles are essential to the retrieval, a priori profile information of (P, T) obtained from reanalysis data provided by NASA-GSFC (science@hyperion.gsfc.nasa.gov). The criteria for choosing these bands also include the relative spectral line intensities, the number of lines and minimization of molecular species interferences on main species. FASCODE3 also computes the strength of line intensities in the retrieval window and the total number of lines (shown in table 3).

For the spectral band in the NIR region (6100-6400 cm^{-1}), spectral line lists are 14,247 which are less compared to that of this band in the MIR region (660-670 cm^{-1}) of 44,065 lines. Fortunately, these two spectral regions are less influenced by other molecular species as shown in table 3.

4. Conclusion

This work presents the column-averaged concentration and an attempt made to retrieve vertical profile of CO_2 concentration using a line-by-line radiative transfer algorithm and FASCODE3 over Shadnagar region of India. Six day direct solar radiation spectra were utilized with high spectral resolution of 0.01 cm^{-1} recorded by ground-based FTIR spectrometer. Measured transmittance spectra compared against model computed transmittance spectra and found to be good agreement with high SNR. The mean residual lie within ± 1.0% for CO_2 and O_2 spectral windows. During the analysis period mean (standard deviation, 1σ) XCO_2 was observed to be 385.24 ppm (4.22 ppm) with 1.0 % of variation in selected SZA period. This precision has to be improved by using near real time meteorological information acquired by INSAT-3D. Present study used NIR (6100-6400 cm^{-1}) and MIR (660-700 cm^{-1}) spectral windows to compare retrieved vertical profile of CO_2 during two different days. The mean standard deviations of retrieved CO_2 (1 σ) for NIR and MIR bands are 0.07 ppm and 0.08 ppm respectively. To understand the spectral dependencies and resolution for trace gas retrievals, further analysis required using FASCODE3 and that would form the future work. In addition, attempts would be made to use near real time temperature and pressure profiles from satellite data to improve the retrieval accuracy.

Acknowledgement

The authors sincerely thank colleagues of Atmospheric and Climate Sciences Group (ACSG) of Earth and Climate Science Area (ECSA) for their immense support in collecting the data. We would like to acknowledge Dr. J. Hannigan, NCAR, Boulder, CO and Dr. Frank Hase, project manager Collaborative Carbon Column Observing Network (COCCON) for sharing a priori climatology data and their valuable suggestions. The authors specially thank our colleague Mr. Biswadip Gharai for his valuable suggestions and support during this work.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-177, 2016
Manuscript under review for journal Atmos. Meas. Tech.
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Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-177, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 13 June 2016

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Tables

Table 1 Measurement details using FTIR 125M (Bruker make)

Detector	**Beam Splitter**	**Spectral Range (cm^{-1})**	**Resolution ($\Delta\nu$) cm^{-1}**	**OPD (cm)**	**SNR**	**Noise (rms)**
MCT	KBr	600-4800	0.01	90	625	0.16
InSb	CaF_2	1000-11000	0.01	90	833	0.12

Table 2 Model inputs and retrieved column averaged CO_2/O_2 windows

<table>
<tr><td>Detector</td><td>Beam splitter</td><td>Retrieval window (cm^{-1})</td><td>Central wavenumber (ν_c, cm^{-1})</td><td>Species</td><td>SNR</td><td>Noise(rms)</td></tr>
<tr><td>MCT</td><td>KBr</td><td>660-700</td><td>668</td><td>CO_2 profile</td><td>1111</td><td>0.09</td></tr>
<tr><td>InSb</td><td>CaF_2</td><td>6100-6400/7800-7960</td><td>6348/7808</td><td>XCO_2/O_2</td><td>2941/2564</td><td>0.03/0.04</td></tr>
<tr><td colspan="7">Inputs-FASCODE3</td></tr>
<tr><td>Spectra library (HITRAN2012)</td><td>SZA</td><td>Observed height from mean sea level (km)</td><td>Modified Atmospheric (tropical) model</td><td>Retrieval height (km)</td><td colspan="2">Mean mixing ratio of CO_2 (assumed 390 ppm, Stocker et al. 2013)</td></tr>
</table>

Table 3 FASCODE3 computed line strength in NIR (6100 cm^{-1}-6400 cm^{-1}) and MIR (660 cm^{-1}-700 cm^{-1} spectral region

Molecule	**No.of Lines (NIR/MIR)**	**Line Strengths (sum) (NIR/MIR)**
H_2O	1543/937	2.61E-27/2.97E-23
CO_2	14247/44065	1.55E-25/1.377E-20
N_2O	236/1257	3.90E-26/4.405E-22
CO	677/0	6.84E-26/0.0
O_2	91/0	5.04E-33/0.0

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Manuscript under review for journal Atmos. Meas. Tech.
Published: 13 June 2016

Figures

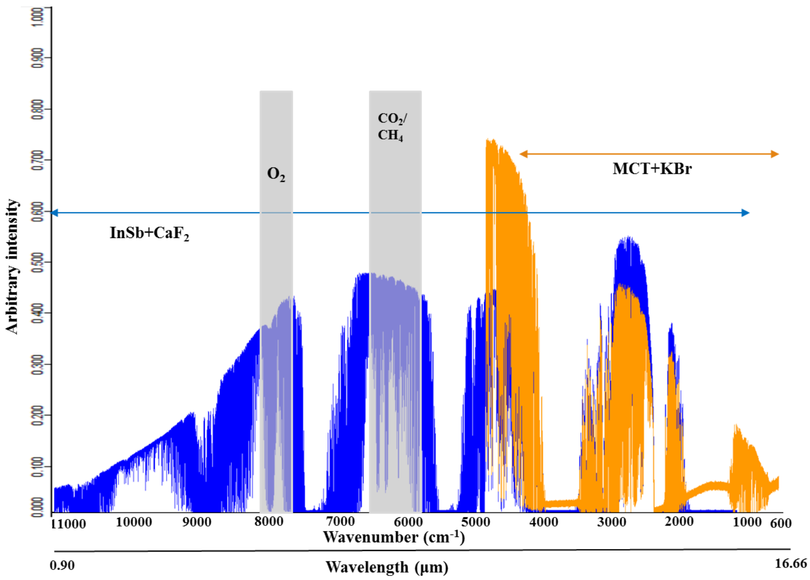

Figure 1 FTIR Measured Solar Spectra in the NIR and MIR spectral regions

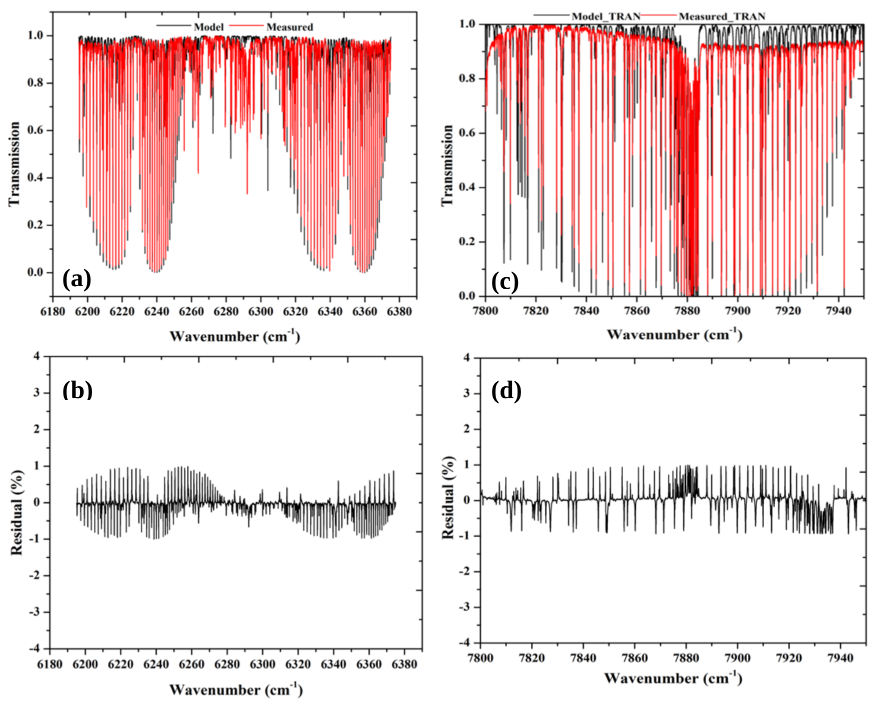

Figure 2 NIR spectra measured on 21st March 2016. a) Red lines indicate measured transmittance and black lines represent fitted transmittance for CO_2 b) residual error for CO_2 c) Transmittance fitted versus measured in O_2 spectral range d) residual error of O_2

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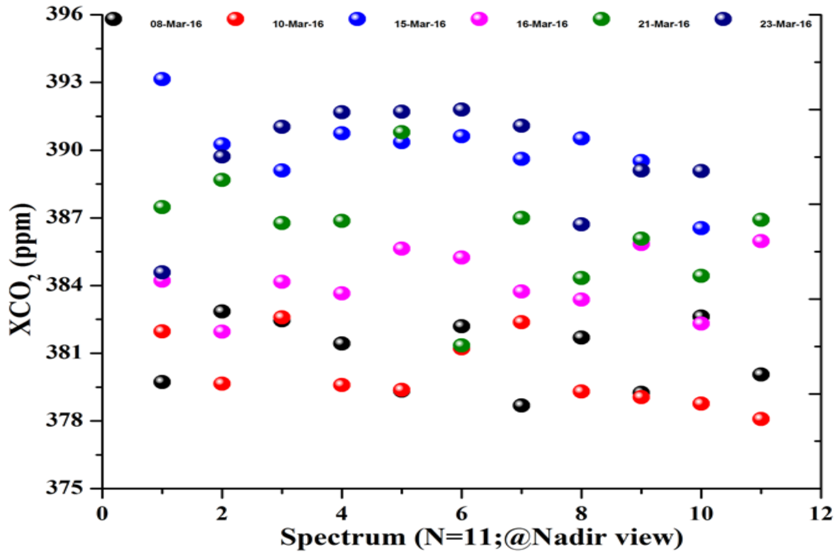

Figure 3 Time series column-averaged volume mixing ratio of CO_2 (XCO_2) over Shadnagar region

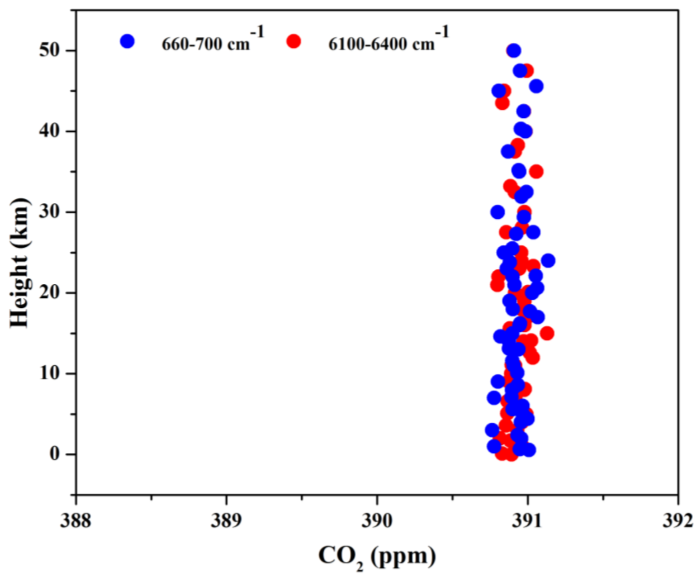

Figure 4 Volume mixing ratio of CO_2 retrieved on 21st April 2015 and 23rd March 2016