

# Atmospheric CO<sub>2</sub> retrieved from ground-based near IR solar spectra

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[1] The column-averaged volume mixing ratio (VMR) of CO<sub>2</sub> over Kitt Peak, Arizona, has been retrieved from high-resolution solar absorption spectra obtained with the Fourier transform spectrometer on the McMath telescope. Simultaneous column measurements of CO<sub>2</sub> at  $\sim 6300$  cm<sup>-1</sup> and O<sub>2</sub> at  $\sim 7900$  cm<sup>-1</sup> were ratioed to minimize systematic errors. These column ratios were then scaled by the mean O<sub>2</sub> VMR (0.2095) to yield column-averaged vmrs of CO<sub>2</sub>. These display similar behavior to the Mauna Loa in situ surface measurements. During the period 1977–1995, the column-averaged mixing ratio of CO<sub>2</sub> increased at an average rate of  $1.49 \pm 0.04$  ppmv/yr with seasonal variations of  $\sim 7$  ppmv peak-to-peak. Our retrievals demonstrate that this remote technique is capable of precisions better than 0.5%. **INDEX TERMS:** 0330 Atmospheric Composition and Structure: Geochemical cycles; 0394 Atmospheric Composition and Structure: Instruments and techniques; 1610 Global Change: Atmosphere (0315, 0325)

## 1. Introduction

[2] The atmospheric CO<sub>2</sub> VMR has increased from about 280 ppmv in pre-industrial times (before 1800) to about 360 ppmv by the 1990s [IPCC, 1995]. Previous studies based on observations from the in situ network of surface stations indicate that the biosphere and ocean sinks are absorbing about half of the anthropogenic CO<sub>2</sub> emission [Battle *et al.*, 2000]. The nature and geographic distribution of these sinks, however, remains too uncertain to predict their responses to future climate or land use changes [IPCC, 1995]. Although in situ measurements of CO<sub>2</sub> from the existing surface network are highly accurate (0.1 ppmv), their sparse spatial coverage (both vertical and horizontal) limits their usefulness in constraining models of CO<sub>2</sub> sources and sinks.

[3] Rayner and O'Brien [2001] have shown that global satellite measurements of the CO<sub>2</sub> column, even with poorer precision (2 ppmv, 0.5%), would provide a better constraint on geographic and temporal distribution of CO<sub>2</sub> sources and sinks than the existing surface network. This calculation assumes, however, that such space-borne observations are bias-free. To test and eliminate bias, an extensive correlative measurement effort will be required. These measurements, additionally, can be important for constraining aspects of the CO<sub>2</sub> behavior that will not be measurable from space in the foreseeable future (e.g. diurnal variations). In situ measurements of CO<sub>2</sub> from the existing surface network cannot alone be used to validate space-borne measurements of column CO<sub>2</sub> due to their much higher spatial resolution and their confinement to the planetary boundary layer.

[4] Ground-based spectral observations of the sun at high spectral resolution can, in principle, be used to determine the total

CO<sub>2</sub> column. The near IR is particularly attractive for this task because the sun is sufficiently bright that high signal-to-noise (S/N) at high spectral resolution can be obtained with minimal integration time and uncooled detectors.

## 2. Measurements

[5] Between 1979 and 1985, numerous high-resolution absorption spectra ( $\Delta\nu = 0.014$  cm<sup>-1</sup>) of the Sun were obtained with the 1-m Fourier transform spectrometer (FTS) at the McMath telescope complex on Kitt Peak (31.9 N, 111.6 W, 2.07 km above sea level). Observations covering the spectral range from 6000 cm<sup>-1</sup> to 8000 cm<sup>-1</sup> were used to determine the column-averaged dry air VMR of CO<sub>2</sub> and CH<sub>4</sub> [Wallace and Livingston, 1990]. In that work, equivalent width (EQW) analyses were performed on 19 well isolated lines of the CO<sub>2</sub> (21<sup>2</sup>) – (00<sup>0</sup>) band ( $\nu_o = 6348$  cm<sup>-1</sup>) and 14 lines of the O<sub>2</sub> 0–0 <sup>1</sup>Δ<sub>g</sub>–<sup>3</sup>Σ<sub>g</sub><sup>-</sup> band ( $\nu_o = 7882$  cm<sup>-1</sup>) to get the column amount of both gases. Assuming the O<sub>2</sub> VMR to be constant (0.20946), the column ratio (CO<sub>2</sub>/O<sub>2</sub>) was scaled to yield the column-averaged CO<sub>2</sub> VMR in the atmosphere over Kitt Peak.

[6] In this letter, we report a reanalysis of the Kitt Peak observations using a more sophisticated spectral retrieval algorithm with updated spectroscopic line lists for CO<sub>2</sub>, O<sub>2</sub> (including the collision induced absorption), H<sub>2</sub>O, and absorption in the solar atmosphere. This allows us to simultaneously fit the entire O<sub>2</sub> band (containing more than 200 significant lines) and two CO<sub>2</sub> bands centered at 6228 and 6348 cm<sup>-1</sup>. This allows us to include in our analysis spectra obtained at high airmasses, that Wallace and Livingston [1990] excluded due to limitations imposed by their EQW technique. In addition, we have analyzed spectra obtained more recently at the same facility.

## 3. Data Analysis

[7] Spectra are analyzed using a line-by-line algorithm developed at JPL for the analysis of solar absorption spectra. In the retrieval, least square analysis is performed over a prescribed spectral window to derive the slant column abundance of the target gases. The fitting residual is defined as:

$$\chi^2 = \sum_{i=1}^{NM} \frac{(Y_i^M - Y_i^C(x))^2}{\sigma_i^2} \quad (1)$$

$Y_i^M$  is one measurement in one spectrum,  $Y_i^C$  is the forward model calculation,  $x$  is the target gas scale factor,  $\sigma_i$  is the uncertainty of  $Y_i^M$ . In our forward model the atmosphere is represented by 70 vertical levels. Pressure- and temperature-dependent absorption coefficients are computed line-by-line for each level and used in the forward model to produce spectra  $Y_i^C(x)$  for comparison.

[8] Pressure and temperature profiles are obtained from NOAA's Climate Diagnostics Center (CDC), which are assimilated temperature data on 17 levels from 1000 to 10 mbar with  $1^\circ \times 1^\circ$  geographic resolution. Climatological temperature profiles are used for levels with pressure  $\leq 10$  mbar. A study of the temperature sensitivity of the retrieved CO<sub>2</sub>/O<sub>2</sub> ratio revealed a T-dependence of 0.07%/K. So if the CDC profiles were system-

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atically in error by 5 K at all levels, the CO<sub>2</sub>/O<sub>2</sub> error would be 0.35%, or about 1 ppmv.

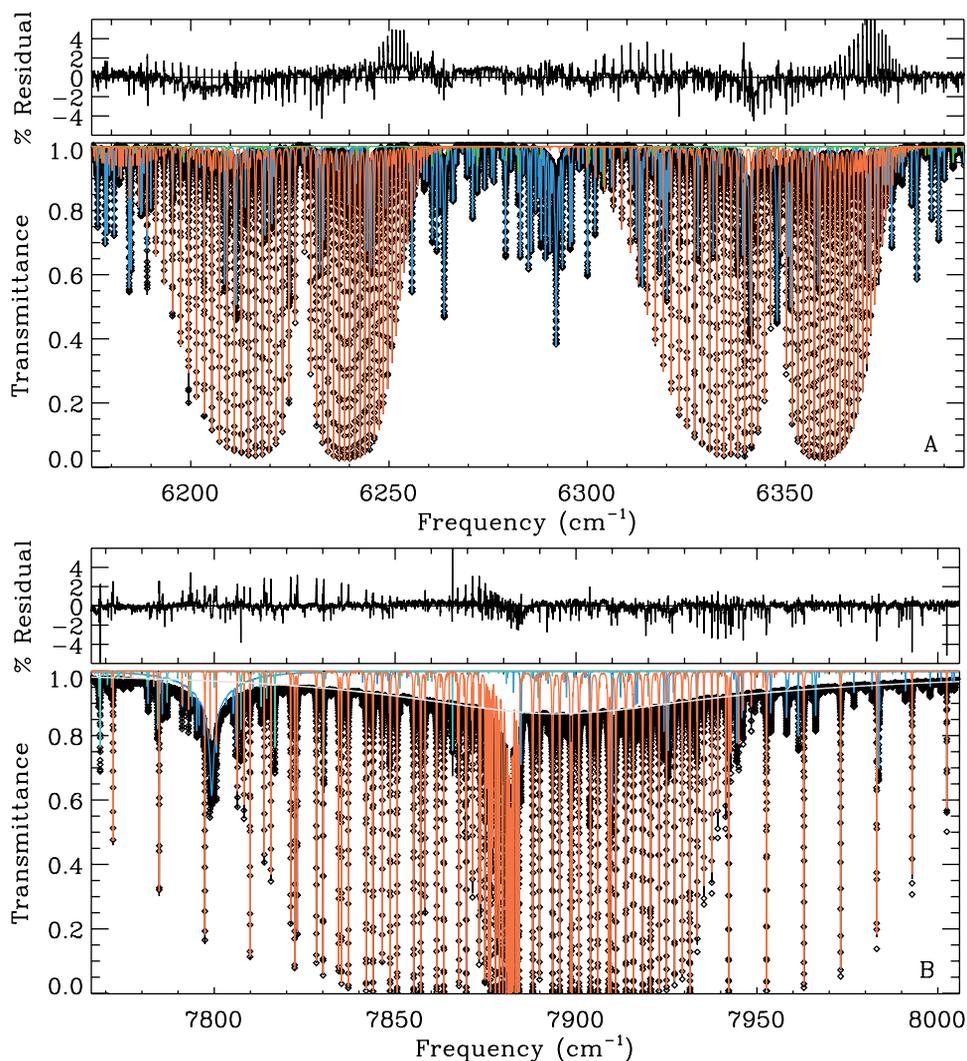
[9] The CO<sub>2</sub> spectral parameters are derived from the latest HITRAN compilation [Rothman *et al.*, 1998]. The background solar linelist is based on the work of Livingston and Wallace [1991]. For the O<sub>2</sub> lines, the HITRAN strengths were updated with a recent recalculation [Goldman, *private communication*] that was found to give improved agreement with laboratory data [Newman *et al.*, 2000]. In addition to the discrete O<sub>2</sub> lines of the <sup>1</sup>Δ band, there is also underlying O<sub>2</sub> continuum absorption [Smith and Newnham, 2000, 2001]. Although this O<sub>2</sub> collision induced absorption (CIA) was included in the line-by-line calculation to improve estimation of the continuum, only the discrete <sup>1</sup>Δ O<sub>2</sub> lines were used in the computation of the O<sub>2</sub> column amount.

#### 4. Results

[10] 414 spectra obtained at Kitt Peak over the period 1977–1995 have been analyzed. Due to other demands on the instru-

ment, solar observations in the 6000–8000 cm<sup>-1</sup> spectral region were generally made on only a few days each year. The spectra were measured at various times throughout the day from sunrise to sunset, weather permitting. The spectra analyzed are generally co-additions of 2–4 individual spectra, each taking 7 minutes to acquire. The effective solar zenith angle (SZA) was calculated as the average of the SZAs of the individual interferograms at their zero path difference (ZPD) times. At high airmasses (~10), this was often significantly different (5% in airmass) from the mean SZA, due to the fact that the ZPDs were typically not in the middle of the double-sided interferograms, and due to the non-linear nature of the variation of the airmass with time.

[11] Examples of the spectral analysis are shown in Figure 1. Two spectral bands of CO<sub>2</sub> and one of O<sub>2</sub> were fitted as shown. We have excluded from further analysis the 71 observations (17%) that produce rms spectral residuals greater than 6.0% for O<sub>2</sub> or 3.0% for CO<sub>2</sub>. The larger threshold for rejection of O<sub>2</sub> spectra is due to the difficulty in fitting the O<sub>2</sub> CIA at large SZAs. Most of these rejected spectra were not intended for use in the 6000–8000 cm<sup>-1</sup> region. In remaining spectra, those measured at low SZA generally have rms

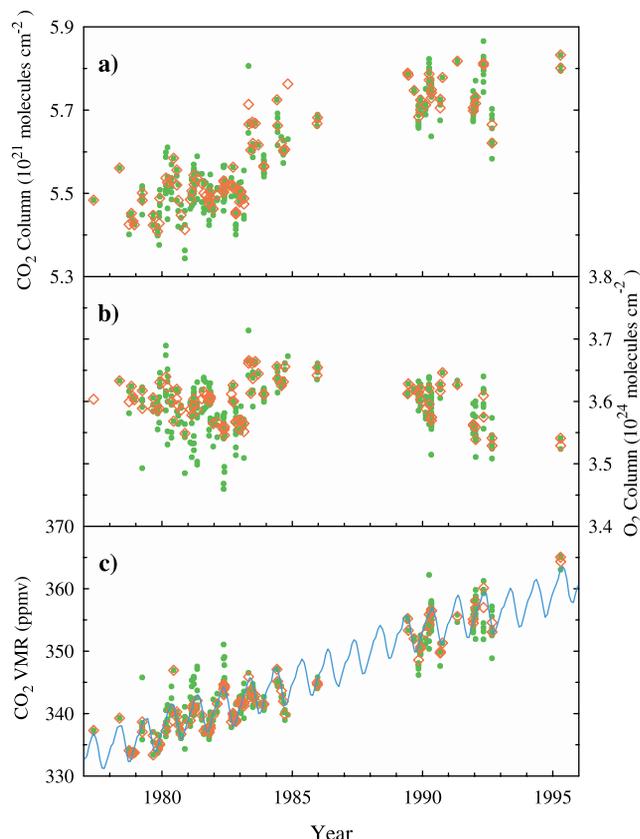


**Figure 1.** Examples of spectral fits to a Kitt Peak spectrum measured at 70.70° SZA on May 9, 1981. Diamonds are the measurements and black lines are the fitted transmittance. (a) The 6300 cm<sup>-1</sup> region, containing the (14<sup>1</sup>1)–(00<sup>0</sup>0) and (21<sup>2</sup>2)–(00<sup>0</sup>0) bands of CO<sub>2</sub>; (b) The 7900 cm<sup>-1</sup> region, containing the O<sub>2</sub> 0–0 <sup>1</sup>Δ<sub>g</sub>–<sup>3</sup>Σ<sub>g</sub><sup>-</sup> band. The contributions from CO<sub>2</sub>/O<sub>2</sub>, H<sub>2</sub>O and solar features are shown by the red, green and blue lines respectively. The O<sub>2</sub> CIA is represented by the grey line in (b). The residual traces (measured-calculated) are clearly dominated by systematic errors in both regions.

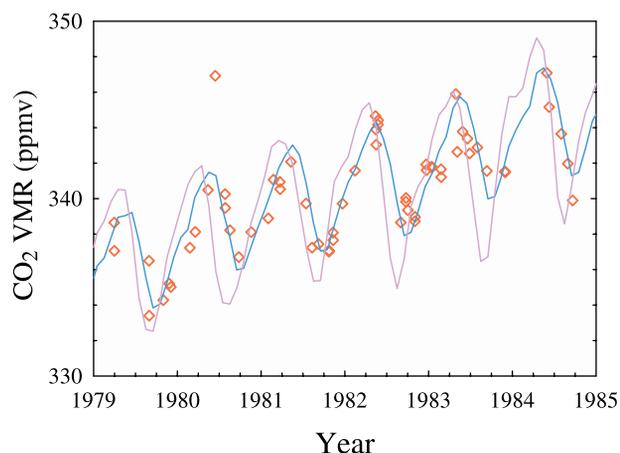
residuals of about 0.4–0.8% for O<sub>2</sub> and 0.7–0.8% for the CO<sub>2</sub>. These residuals are dominated by solar features and by the O<sub>2</sub>/CO<sub>2</sub> lines themselves. For spectra measured at high SZA (>75 deg) the residuals are larger (up to 3% in CO<sub>2</sub> and 5% in O<sub>2</sub>) due to the increasing strengths of the O<sub>2</sub>/CO<sub>2</sub> lines.

[12] The retrieved slant column amounts were divided by the calculated airmass to produce vertical column amounts. Account was taken of the 250 m optical path inside the telescope, which adds nearly 3% to the noontime O<sub>2</sub> slant column. The daily-average value of CO<sub>2</sub> and O<sub>2</sub> vertical column amounts and their ratio (CO<sub>2</sub>/O<sub>2</sub>) are shown in Figure 2. The long-term trend in the CO<sub>2</sub> column amounts (Panel A) is evident, but the seasonal variation is unclear. For the O<sub>2</sub> column amount (Panel B), no long-term trend is observed. The retrieved dry VMRs (converted from column amount after dividing by  $2.15 \times 10^{22}$  times the surface pressure in mbar) of O<sub>2</sub> fall within the range of 0.202 to 0.217, with a mean of about 0.209 — remarkably close to the actual O<sub>2</sub> VMR for dry air (0.2095).

[13] The ratio of the CO<sub>2</sub> and O<sub>2</sub> column amounts, scaled by the standard atmospheric O<sub>2</sub> fraction of 0.2095, gives the column-averaged dry volume-mixing ratio of CO<sub>2</sub> in the atmosphere (Figure 2, Panel C). Clearly, the precision of the CO<sub>2</sub>/O<sub>2</sub> ratio is improved over that of the CO<sub>2</sub> column. The high degree of correlation between error in CO<sub>2</sub> and O<sub>2</sub> suggests that much of the scatter in the unratiod observations is common to both spectral regions. We speculate that these



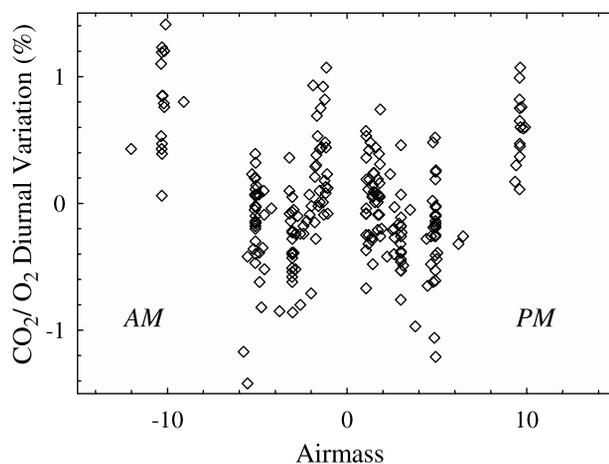
**Figure 2.** Time series of retrieved vertical columns of (a) CO<sub>2</sub> and (b) O<sub>2</sub>. (c) the column-averaged CO<sub>2</sub> VMR over Kitt Peak determined from the ratio of the individual CO<sub>2</sub> and O<sub>2</sub> spectra (green dots) and the daily-averaged value (red diamonds) are shown. The column measurements in panel (c) have been scaled by 1.058 to match the absolute value of the Mauna Loa record (blue). Error in the spectroscopic database for CO<sub>2</sub> is likely responsible for the discrepancy (see text).



**Figure 3.** Time series of daily averaged retrieved values of the Kitt Peak column CO<sub>2</sub> VMRs (red open diamonds) over period 1979–1985, compared with the Mauna Loa (blue) and the Niwot Ridge (pink) in situ measurements.

errors arise in the spectra (e.g. uncertainties in instrumental line shape) or in the calculated airmass (e.g. uncertainty in surface pressure or SZA). In Figure 2c, we have scaled the CO<sub>2</sub> column average dry mixing ratio by 1.058. This scaling was empirically determined to minimize bias between the Kitt Peak data and those from Mauna Loa, and probably reflects an error in the CO<sub>2</sub> line strengths and/or pressure broadening coefficients. Also shown in Figure 2 (Panel C) are the Mauna Loa CO<sub>2</sub> in situ measurements. Their trend and seasonal cycles are remarkably similar to the Kitt Peak data. The average CO<sub>2</sub> increase between 1977 and 1995 is  $1.49 \pm 0.04$  ppm/yr, the same as that measured from Mauna Loa ( $\sim 1.47$  ppm/yr) over the same period.

[14] Details of the seasonal cycles for CO<sub>2</sub>/O<sub>2</sub> in the period 1979–1985 are expanded in Figure 3. We compared the Kitt Peak data with two sets of in situ measurements: Mauna Loa (19.5N, 155.6W, 3397m above sea level) and Niwot Ridge (40.1N, 105.6W, 3475m above sea level). The phase of Kitt Peak data is nearly the same as Mauna Loa measurements but has a lag of about one month compared with the Niwot Ridge record, despite the latter site being much closer to Kitt Peak. The seasonal amplitude of Kitt Peak data ( $\sim 7$  ppm peak-to-peak) is also more similar to Mauna Loa record than to the Niwot Ridge



**Figure 4.** Diurnal variations of the CO<sub>2</sub>/O<sub>2</sub> ratio (see text for details).

record. We do not know the reason for the different behavior of the Niwot Ridge data, but we speculate that the Mauna Loa and Kitt Peak records might better represent the free tropospheric CO<sub>2</sub>, while the Niwot Ridge record is more heavily influenced by local sources and sinks of CO<sub>2</sub>.

[15] To understand the diurnal variation and to estimate the precision of the retrieval, 231 column results of 40 different days for which more than 4 column measurements exist were analyzed. For each day, the O<sub>2</sub> and CO<sub>2</sub> vertical column amounts were converted into VMRs and averaged to get the daily mean. The variation of one measurement from the daily mean is defined as

$$\text{Diurnal variation of } x = \frac{x}{\langle x \rangle} - 1 \quad (2)$$

where  $x$  is one measurement and  $\langle x \rangle$  is the mean of the day. The diurnal variations for O<sub>2</sub> and CO<sub>2</sub> obtained in this manner are partly correlated and therefore the CO<sub>2</sub>/O<sub>2</sub> ratios exhibit less error than CO<sub>2</sub> VMRs obtained by dividing the CO<sub>2</sub> column amount by pressure. The range for O<sub>2</sub> variation is  $\pm 2.0\%$ , whereas for CO<sub>2</sub> it is  $\pm 1.2\%$ .

[16] The diurnal variations in the CO<sub>2</sub>/O<sub>2</sub> ratios are shown in Figure 4. Most of the deviation is in the range of  $-0.5 \sim 0.5\%$ , except for a few measurements made at high airmasses ( $>10$ ). Assuming the CO<sub>2</sub> VMR over Kitt Peak is essentially constant during one day, the scatter in Figure 4 is a measure of the precision of the column measurements. The origin of the increase of CO<sub>2</sub>/O<sub>2</sub> at high airmass is likely non-geophysical. We speculate that the different behaviors of the continuum signal in the CO<sub>2</sub> and O<sub>2</sub> spectral regions as a function of airmass contributes to this anomalous diurnal behavior in CO<sub>2</sub>/O<sub>2</sub>. Since the integrating periods of the Kitt Peak measurements are quite long (about 30 minutes at 5 airmasses and 15 minutes at 10 airmasses), it is impossible to unambiguously assign an average airmass to these spectra.

## 5. Conclusions

[17] Reanalysis of near IR spectra obtained at Kitt Peak National Solar Observatory have demonstrated that the column-averaged CO<sub>2</sub> VMR can be retrieved with  $\sim 0.5\%$  precision. By simultaneously fitting all lines in one band and using new spectroscopic line lists, we decreased the temperature sensitivity of data retrieval and greatly improved the precision compared with Wallace and Livingston's analysis.

[18] We believe that remaining errors are dominated by deficiencies in the spectroscopic line lists, and by airmass ambiguities exacerbated by the long scan duration of the Kitt Peak spectrom-

eter. With improvements to the spectroscopic line lists and with modern, faster-scanning FTIR spectrometers dedicated to the measurement of CO<sub>2</sub>, substantially better results can be anticipated. We are confident that with these improvements, this technique will be more than adequate for ground-truthing future space-based CO<sub>2</sub> column observations.

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