

# O<sub>2</sub>-O<sub>2</sub> absorption band identification based on optical depth spectra of the visible and near-infrared

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**Abstract.** The first implementation of the rotating shadowband spectroradiometer allows the routine collection of direct normal solar spectral irradiance data at 512 wavelengths. These data are used on clear days to calculate spectra in optical depth. A persistent absorption band near 477 nm in the first optical depth spectra collected led to the eventual identification of six bands in the 400 to 1080 nm range resulting from absorption by O<sub>2</sub> collision pairs. All of these O<sub>2</sub>-O<sub>2</sub> bands were discovered earlier using atmospheric long pathlength or laboratory high pressure techniques, however, it is notable that this method's sensitivity permitted their detection at one air mass. These data suggest that there are no unexplained narrowband absorption features in the visible/near-infrared, that excess optical depth measured near 1000 nm may now have an explanation, and that the linearity of the O<sub>2</sub>-O<sub>2</sub> absorption may be exploited to investigate mean pathlengths in the atmosphere.

## Introduction

Water vapor, ozone, and oxygen have well known atmospheric absorption bands in the visible and near infrared spectrum. These molecular bands have been a part of the HITRAN data base since its inception, although weaker bands extending to shorter wavelengths have been added in later versions [Rothman, 1992]. Not included in the HITRAN data set are absorption bands that are not normally permitted by selection rules for dipole transitions, but which occur through simultaneous transitions of O<sub>2</sub> molecular pairs during collision. Janssen [1886] discovered several visible bands of O<sub>2</sub>-O<sub>2</sub> under laboratory conditions as early as 1885. Perner and Platt [1980] used long-path, differential optical absorption spectroscopy (DOAS) in the atmosphere to observe six O<sub>2</sub>-O<sub>2</sub> bands in the ultraviolet and visible using lamps viewed through a 10 km lightpath. In recent efforts Erle *et al.* [1995], Pfeilsticker *et al.* [1997], and Solomon *et al.* [1998] have used long-path DOAS to measure a subset of these bands in the solar spectrum to estimate their contribution to neglected absorption in models of the clear and cloudy atmospheres. Using very high resolution Fourier transform spectroscopy, Mlawer *et al.* [1998] identified three O<sub>2</sub>-O<sub>2</sub> bands in the spectra at 1.06, 1.27, and 1.58  $\mu\text{m}$  by differencing these observations with their line-by-line radiative transfer model (LBLRTM) results [Clough and Iacono, 1995].

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In this paper we briefly describe the rotating shadowband spectroradiometer and its operation at the Department of Energy's Atmospheric Radiation Measurement (ARM) program's Southern Great Plains (SGP) site. Results from Langley analyses performed on a clear day during the fall of 1997 are examined to identify six bands in the 400-1080 nm range. The significance that we place on these results is discussed in the final section.

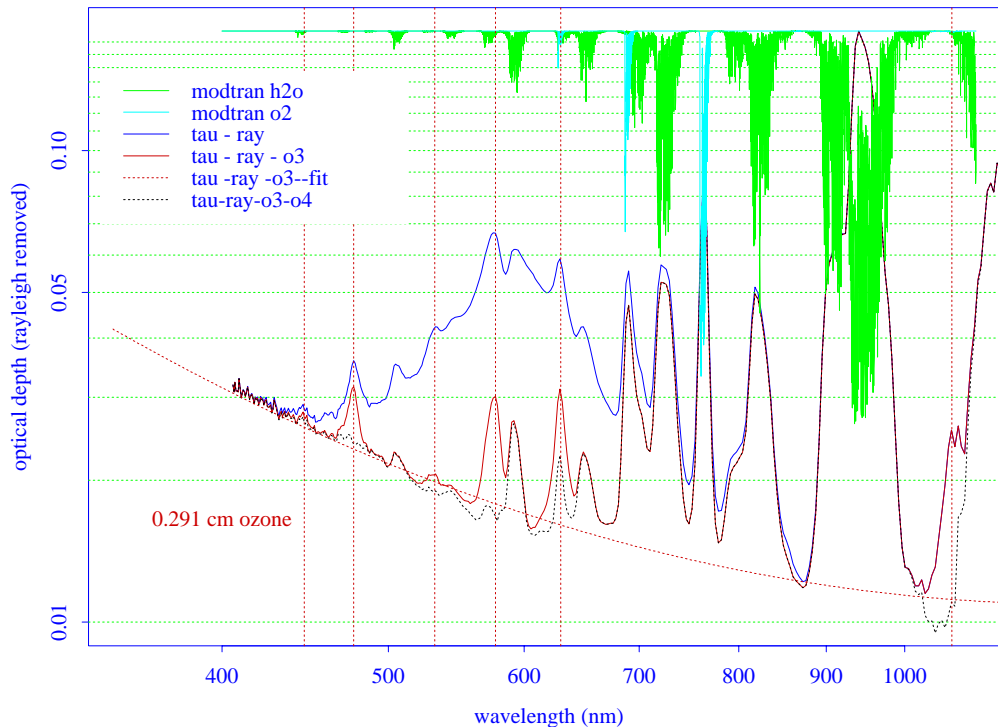
## Rotating Shadowband Spectroradiometer

The rotating shadowband spectroradiometer (RSS) is described in detail in Harrison *et al.* [1999]. The instrument is the latest in the rotating shadowband radiometer line [Michalsky *et al.*, 1986; Harrison *et al.*, 1994], and it differs from its predecessors fundamentally in that a prism-based, diode array spectrometer is used to spectrally separate and detect radiation rather than single filtered detectors. The first version of the RSS has 512 passbands with high spectral resolution in the ultraviolet (0.6 nm) and lower resolution (8 nm) in the near-infrared. The wavelength coverage is continuous from about 360 to 1080 nm. Before each measurement sequence, samples are taken to determine the correct exposure for the measurement. Samples are taken with the shadowing band out of the field of view, with it blocking the diffuser from the direct solar beam, and with the band to either side of the diffuser blocking forward scattered sunlight; the latter is used as a correction to the diffuse measurement, since that measurement includes both blocked direct beam and blocked forward-scattered sunlight. The difference between the corrected diffuse measurement and the total horizontal measurement is divided by the cosine of the solar-zenith angle and corrected for the angular response of the instrument (measured in the laboratory) to yield a direct normal irradiance. The product of the corrected direct normal irradiance and the cosine of the solar-zenith-angle is added to the corrected diffuse to yield an angle-corrected total horizontal spectral irradiance. However, only the direct normal irradiance is used in the following calculations.

## Langley Analyses

Langley plots are plots of the natural logarithm of the measured spectral irradiance versus the air mass relative to a zenith air mass of one. Using the spectra obtained over a range of air masses during stable conditions, we can obtain Langley plots at 512 passbands; from these we extract total optical depths from the slopes and calibrations of the extraterrestrial irradiance in instrument counts from the intercepts. In fact, we can only do this in the parts

## Optical Depth Spectrum for 97 Nov 03--PM



**Figure 1.** Optical depth spectrum based on Langley analyses of RSS spectra. Red solid line has Rayleigh scattering and ozone absorption removed. Red dashed line is quadratic fit to six chosen aerosol wavelengths. Vertical lines are O<sub>2</sub>-O<sub>2</sub> band centers. Black dashed line has the O<sub>2</sub>-O<sub>2</sub> bands subtracted from the Rayleigh and ozone corrected plot. This suggests that the features that remain are explained by the absorption assignments in MODTRAN3.7.

of the spectrum where the weak line approximation to the curve of growth holds, i.e., where adding absorbers increases the extinction approximately linearly. Moreover, it does not work for the water vapor and oxygen absorption bands in the wavelength range under discussion because some lines in these bands are saturated.

An optical depth spectrum based on a Langley plot from 3 November 1997 at the ARM SGP site is shown in Fig. 1. Narrow wavelength bands, low detector responsivity, and low irradiance conspire to produce noisy results below 406 nm, therefore, those data are not shown to allow us to concentrate on the rest of the spectral details. Plotted in this figure as the dark blue solid line are the optical depths after removal of the Rayleigh scattering optical depth. Ozone optical depth is estimated by fitting a quadratic in  $\ln(\text{optical depth})$  vs  $\ln(\text{wavelength})$  at six wavelengths affected only by aerosol and ozone, namely 415, 495, 615, 670, 873, and 1045 nm. The ozone optical depth that is subtracted from the dark blue solid line is incremented until the least-squares fit reaches a minimum (red dashed line in Fig. 1). This technique is explained in *King and Byrne* [1976] and *Michalsky et al.* [1995]. The estimate using this method yields 291 Dobson units versus the TOMS value of 291 DUs for that day and 293 DUs for the following day. The TOMS measurements are made near 11:45 am local time, and the midpoint of the Langley plot is centered some 3.5 hours later in the day than the TOMS instantaneous measurement. The exact agreement is fortuitous although differences of a few Dobson units would produce virtually the same red solid line in Fig. 1.

It should be noted that these observations are for an extremely clear day in Oklahoma with aerosol optical depths near 500 nm slightly larger than 0.02. The red solid line should approximate the aerosol optical depth wavelength dependence, but has several absorption features throughout this wavelength range. Many of these are associated with water vapor and oxygen and can be identified as such using the overplot of a MODTRAN3.7 [*Berk et al.*, 1989] transmission spectrum. The green solid lines are water vapor and the light blue solid lines are oxygen absorption bands. The water vapor abundance is nominal for a mid-latitude summer profile and should only be used for the purpose of locating bands and their relative strengths. Since the Langley plot does not strictly apply to the water and oxygen bands, there is no simple interpretation relating optical depths to column abundance. There exists a modified Langley technique introduced by *Reagan et al.* [1987] that can be used to retrieve water vapor from the water vapor bands, which will not be discussed here.

Even with these identified there remain unexplained absorption bands not included in MODTRAN or, therefore, HITRAN on which it is based. The vertical dashed lines are drawn through O<sub>2</sub>-O<sub>2</sub> absorption features at 446.7, 477.3, 532.2, 577.2, 630.0, and 1065.2 nm identified by *Greenblatt et al.* [1990] using their 89.5 cm absorption cell containing 55 atmospheres of O<sub>2</sub>. The absorption at 477.3 nm is the clearest signature of O<sub>2</sub>-O<sub>2</sub> because there is nothing else near this wavelength to identify with this feature. At 532.2 nm is a much smaller absorption feature that one might mistake for water; however, the O<sub>2</sub>-O<sub>2</sub> band is stronger than the

stronger of the water bands that bracket it, and, therefore could not be the weak water band that more nearly overlaps it. Moreover, the band center is appropriate for the O<sub>2</sub>-O<sub>2</sub> band. Similar arguments can be made for the 446.7 nm feature, but less convincingly because of the weakness of the absorption.

The next three O<sub>2</sub>-O<sub>2</sub> bands are blended with water vapor and oxygen bands. The O<sub>2</sub>-O<sub>2</sub> band at 577.2 nm is near water vapor bands of moderate strength, but nearer the weaker of the pair. Comparing the strengths of the two features in the solid red optical depth spectrum with the relative MODTRAN spectra, it is clear from the centering and the relative strengths that O<sub>2</sub>-O<sub>2</sub> is present at 577.2 nm. One further piece of evidence is the optical depth spectra calculated by *Pfeilsticker et al.* [1997] that suggests the 577.2 nm feature is about two-thirds stronger than the 477.3 nm feature, which is confirmed in Fig. 1. The 1065.2 nm O<sub>2</sub>-O<sub>2</sub> band is on the shoulder of a strong water vapor band. Again the band center and the strength as suggested by *Pfeilsticker et al.* [1997] is the evidence for this identification. The band at 630.0 nm is the least obvious assignment to O<sub>2</sub>-O<sub>2</sub> because it is blended with water and oxygen. Water cannot explain the strength of this feature if we compare to the next longer wavelength water band in the MODTRAN and optical depth spectra. However, free oxygen has a band exactly centered at 630.0 nm. Again, according to *Pfeilsticker et al.* [1997] optical depth calculations, we suspect that about half of the optical depth of this feature results from O<sub>2</sub>-O<sub>2</sub>.

## Discussion

Accepting the identifications of the O<sub>2</sub>-O<sub>2</sub> bands in the last section, we can use the laboratory measurements of absorbance of O<sub>2</sub>-O<sub>2</sub> by *Greenblatt et al.* [1990] to calculate and remove the optical depth contributions of these bands to the spectrum in Fig. 1. Absorbance data were obtained from Jim Burkholder (personal communication, 1998) covering the oxygen bands between 330 and 1140 nm [*Greenblatt et al.*, 1990]. Absorbance  $A$  is given by

$$A = L\alpha[O_2]^2,$$

where  $L$  is the length of the path used by *Greenblatt et al.* [1990],  $[O_2]$  is the concentration of oxygen, and  $\alpha$  is the absorption coefficient. If absorbance had a linear dependence on oxygen concentration,  $\alpha$  would be called a cross-section, but with units of cm<sup>5</sup>/molecule<sup>2</sup> we use the term absorption coefficient to avoid confusion. In their experiment  $L$  was 89.5 cm,  $[O_2]$  was 55 atmospheres, but at a temperature of 296 K; Loschmidt's number 2.687 × 10<sup>19</sup> molecules/cm<sup>3</sup> must, therefore, be scaled by 273.15/296. We determined that the correction for a non-ideal gas was much smaller than the errors in the measurement of absorbance, therefore, we assume ideal gas conditions. We solve for the absorption coefficients for these wavelengths using

$$\alpha = \frac{A}{89.5 \text{ cm} \times [55 \times 2.479 \times 10^{19} \text{ molecules} \cdot \text{cm}^{-3}]^2}.$$

The transmittance is related to the optical depth  $\tau$  and the absorbance through

$$\text{transmittance} = e^{-\tau} = 1 - \text{absorbance}$$

at all levels in the atmosphere. Therefore,

$$\tau = -\ln(1 - \text{absorbance}) = -\ln(1 - L\alpha[O_2]^2)$$

where  $L$  is the length of the atmospheric path in the layer,  $[O_2]$  is the concentration of oxygen in the layer, and  $\alpha$  is the absorption coefficient from the equation above. The pressure and temperature profiles of the MODTRAN mid-latitude summer model, scaled by 0.21—the oxygen fraction, are used to calculate  $[O_2]$  in each layer,

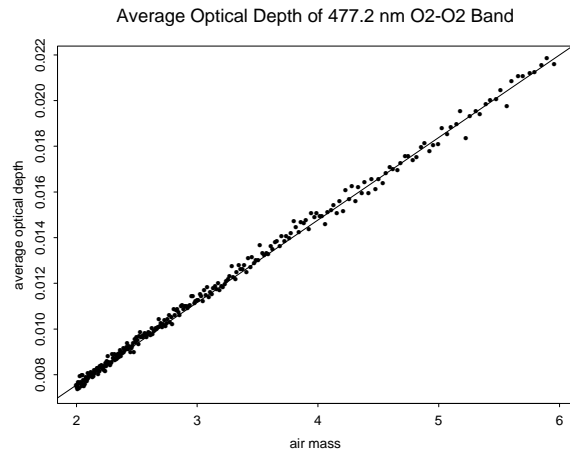
$$[O_2] = \frac{0.21 \times \text{pressure} \times 6.022 \times 10^{17} \text{ molecules} \cdot \text{cm}^{-3}}{R \times \text{temperature}}$$

where  $R$  is the universal gas constant; the only modification of the mid-latitude summer model is to start at the 320 m elevation of the ARM SGP site. The optical depth of O<sub>2</sub>-O<sub>2</sub> is then the sum of the optical depths of all the layers.

In Fig. 1 the black dashed line is the net result of removing optical extinction resulting from Rayleigh scattering, ozone absorption, and O<sub>2</sub>-O<sub>2</sub> absorption. What remains are absorption features associated with water vapor and oxygen absorption on a broad background of aerosol extinction. The O<sub>2</sub>-O<sub>2</sub> absorption bands at 446.7, 477.3, and 532.2 nm cannot be distinguished from the aerosol spectrum. The bands at 577.2, 630.0, and 1065.2 nm that are blended with other absorption bands are considerably altered. The water vapor band at wavelengths just shorter than the 577.2 nm O<sub>2</sub>-O<sub>2</sub> band was hidden by the stronger 577.2 nm O<sub>2</sub>-O<sub>2</sub> band. It can now be seen to be of comparable strength to the water vapor band at wavelengths just longward of 500 nm as suggested by the MODTRAN transmission model. The residual band at 630 nm appears comparable in extinction magnitude to the water vapor band at slightly longer wavelengths, but narrower, because this is a juxtaposition of a weaker water vapor band and a narrower oxygen absorption band. With the 1065.2 nm O<sub>2</sub>-O<sub>2</sub> band removed the structure of the extinction matches the structure seen in the overplotted MODTRAN results. This match suggests that any significant excess absorption relative to model calculations at these wavelengths (e.g., [*Halthore et al.*, 1998]) does not arise from an absorber with a spectral signature that exceeds an optical depth of about 0.002, but must come, if it exists, from a continuum source or enhancement of known absorption bands. While not conclusive, because we have not investigated all cases, we have results from days not shown that agree with the results in Fig. 1 that were obtained for conditions at the SGP ARM site similar to the days for which anomalous absorption is reported [*Halthore et al.*, 1998].

Optical depth measurements in the 1020-1060 nm range may have seemed higher than expected, but should be improved by removal of the O<sub>2</sub>-O<sub>2</sub> optical depth there. Fig. 1 clearly shows that the frequently used wavelength of 500 nm for sunphotometry is partly contaminated by a weak water vapor band, and that 495 might be a better choice for a filter near this wavelength.

*Pfeilsticker et al.* [1997] argued that the O<sub>2</sub>-O<sub>2</sub> bands were not saturated for clear skies. We investigated the linearity of the absorption in the 477.3 nm band by measuring the changes in this band's optical depth with increasing air mass. We chose this band because it is relatively strong and isolated from other absorption bands that would interfere with the analysis of optical depth.



**Figure 2.** Average optical depth of the 477.3 nm band vs air mass. The band appears to increase linearly with pathlength.

The procedure was to use the Langley calibrations for the wavelengths in the range of 450 to 500 nm to calculate instantaneous optical depths. For each optical depth spectrum the Rayleigh scattering and ozone absorption optical depth are removed from every wavelength. Next a quadratic in  $\ln(\text{optical depth})$  vs  $\ln(\text{wavelength})$  is fit to the points in the 450 to 500 nm range, but not in the O<sub>2</sub>-O<sub>2</sub> absorption feature. The average optical depth of the 477.3 nm band is then calculated by differencing the optical depth data and this fit over the 470 to 485 nm and normalizing by the sum over wavelength. Fig. 2 is a plot of the average optical depth thus calculated vs air mass over the range from two to six air masses. There is a clear tendency for the average optical depth to increase linearly with air mass. This result suggests that the 477.3 nm band could be used to assess photon pathlength in cloudy conditions as Erle *et al.* [1995] have done using DOAS techniques.

The linearity of the O<sub>2</sub>-O<sub>2</sub> absorption band provides a easier way to retrieve mean photon pathlengths from the RSS than using the O<sub>2</sub> A-band [Min and Harrison, 1998]. In contrast to the mean pathlength retrieved from the O<sub>2</sub> A-band, which is weighted by the atmosphere pressure, the mean pathlength inferred from O<sub>2</sub>-O<sub>2</sub> at 477.3 nm is, clearly, weighted by the pressure squared. Combining two mean pathlengths with different weighting functions might provide some information on the vertical profile of pathlength, which is crucial to understanding the geometry of clouds.

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