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Line positions and strengths of $^{16}O^{12}C^{18}O$, $^{18}O^{12}C^{18}O$ and $^{17}O^{12}C^{18}O$ between 2200 and 7000 cm^{-1}

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Abstract

Line positions and strengths of $^{16}O^{12}C^{18}O$ (628), $^{18}O^{12}C^{18}O$ (828) and $^{17}O^{12}C^{18}O$ (728) were measured between 2200 and 7000 cm^{-1} using 22 near infrared (NIR) absorption spectra recorded at 0.01–0.013 cm^{-1} resolution with the McMath–Pierce Fourier transform spectrometer located at the National Solar Observatory on Kitt Peak, Arizona. These data were obtained at room temperature using absorption cells with optical path lengths ranging from 2.4 to 385 m; the cells were filled with natural and ^{18}O-enriched samples of CO_2 at pressures ranging from 0.54 to 252 torr. The observed line positions were analyzed to obtain the upper state band centers and rotational constants for 17 bands of $^{16}O^{12}C^{18}O$, 19 bands of $^{18}O^{12}C^{18}O$ and 8 bands of $^{17}O^{12}C^{18}O$. The majority of the $^{18}O^{12}C^{18}O$ and $^{17}O^{12}C^{18}O$ bands were measured for the first time. In addition, the rotational constants for the lower states 00001, 01101*e* and 01101*f* were derived for all three species using the method of combination differences in which the averaged values obtained from the line positions of two or more bands were least-squares-fitted. Rovibrational parameters were also obtained for the 02201*e*, 02201*f*, 10002 and 10001 states of $^{18}O^{12}C^{18}O$. The line position analysis revealed that transitions of the levels $38 \leqslant J' \leqslant 46$ of the $11111f \leftarrow 01101f$ band of $^{18}O^{12}C^{18}O$ are perturbed. Perturbed transitions were also observed for the $12212 \leftarrow 02201$ band and in the high-*J* transitions ($J' \geqslant 49$) of the $20012 \leftarrow 00001$ band of $^{18}O^{12}C^{18}O$. Band strengths and Herman–Wallis-like *F*-factor coefficients were determined for 21 bands of $^{16}O^{12}C^{18}O$, 25 bands of $^{18}O^{12}C^{18}O$ and 8 bands of $^{17}O^{12}C^{18}O$ from least-squares fits to more than 3700 measured transition intensities; band strengths and line positions for 34 of these bands were obtained for the first time.

Keywords: Carbon dioxide; Isotopes; Line positions; Intensities; Near infrared

1. Introduction

This paper is a continuation of our systematic study of the near infrared spectroscopy of carbon dioxide, driven by the need for spectroscopic reference standards to support remote sensing of the planetary atmospheres of Mars, Venus and the Earth. We recently reported high accuracy line positions and strength parameters in the 4600–7000 cm^{-1} spectral region [1] for 54 bands of $^{16}O^{12}C^{16}O$ as well as self-broadened widths and frequency shifts for 15 of those bands [2]. Previously, we reported calibrated line positions for near-IR bands of $^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$ and $^{16}O^{13}C^{18}O$ [3,4]. In the present study, we extend our analysis to the line positions and line strengths for the ^{18}O isotopologues $^{16}O^{12}C^{18}O$, $^{18}O^{12}C^{18}O$ and $^{17}O^{12}C^{18}O$. Table 1 shows that the present study includes hot bands near 2300 cm^{-1}, ground state and hot bands in the 2400–2800 cm^{-1} window, and the Fermi dyad, triad and tetrad in the 3400–7000 cm^{-1} range.

The present study complements a dozen previous analyses of carbon dioxide isotopologues reported in the last decade [5–17]. For $^{16}O^{12}C^{17}O$, the line positions up to 3000 cm^{-1} were studied using Fourier transform spectrometers [5–9]. Concurrently with the present study, Perevalov et al. [16,17] analyzed the line positions using cavity ring-down spectroscopy and reported positions and rotational

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Table 1
Overview of present CO_2 measurements

Isotopologue	Range of obs. positions (cm^{-1})	# vib. (upper)	# vib. (lower)	Range of obs. strengths (cm^{-1})	# band strengths
$^{16}O^{12}C^{18}O$	2450–6960	17	2	2450–6960	21
$^{18}O^{12}C^{18}O$	2900–7490	19	6	3564–7490	25
$^{17}O^{12}C^{18}O$	2290–5560	8	2	3492–4879	8

constants for extremely weak bands of $^{16}O^{12}C^{18}O$, $^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$, $^{16}O^{13}C^{18}O$ and $^{16}O^{13}C^{17}O$ between 5957–6123 and 6745–6832 cm^{-1}. There have been very few laboratory studies of NIR line intensities for these rarer carbon dioxide isotopologues [11–15], and atmospheric remote sensing applications have been forced to rely upon unvalidated theoretical intensity predictions released in 1992 [18,19].

The present study vastly improves our knowledge of the band strengths for the $^{16}O^{12}C^{18}O$, $^{18}O^{12}C^{18}O$ and $^{16}O^{12}C^{17}O$ isotopologues. This is illustrated in Fig. 1 where the observed band strengths are plotted as a function of the band origin. These results are particularly important for remote sensing of terrestrial planets. For Venus [20] the atmospheric spectrum is so dominated by CO_2 absorption that astronomers must often detect other species in atmospheric windows contaminated by absorption from very weak isotopic carbon dioxide bands. The $^{16}O^{12}C^{18}O$ and $^{16}O^{12}C^{17}O$ bands in the 6100–6300 cm^{-1} region will be highly useful for determining $^{16}O/^{17}O$ and $^{16}O/^{18}O$ ratios in the Martian atmosphere [21]. Less abundant carbon dioxide isotopologues can interfere with remote sensing retrievals of absorptions from the parent $^{16}O^{12}C^{16}O$ species at levels above the 0.3% accuracy required for source/sink modeling in the Earth's atmosphere, such as the measurements to be obtained by the Orbiting Carbon Observatory [22]. Therefore, results from present study will be submitted for inclusion in future updates of the HITRAN [19] compilation.

2. Experiment

All CO_2 spectra were recorded with the McMath–Pierce Fourier transform spectrometer (FTS) located at the National Solar Observatory on Kitt Peak using quartz halogen lamps as the infrared source, a CaF_2 beamsplitter, and two liquid nitrogen cooled InSb detectors. The resolution was 0.01–0.013 cm^{-1}, and the time required to obtain an integration was generally 60–130 min. The experimental conditions (sample pressures, optical path lengths, etc.) for the 22 spectra analyzed in this study are listed in Table 2. Three sets of spectra (166-, 164- and 155-series) were recorded over a 2-year period. Spectra were obtained at room temperature using natural samples of CO_2 and two different ^{18}O-enriched samples (94% $^{18}O^{12}C^{18}O$ and 46% $^{16}O^{12}C^{18}O$) calibrated with mass spectrometry by the manufacturer.

Two absorption cells were used in our experiments. One cell was a stainless steel multi-traversal cell with a base path length of 6 m. Sample temperatures were monitored using three thermocouples in contact with the outside surface of the cell. The entire 6 m path was wrapped using aluminum insulation to reduce the temperature gradients along the entire cell length. The other cell was a single pass stainless steel cell, 2.46 m long, covered with insulation to reduce temperature gradients and to stabilize the cell temperatures during data acquisition. This cell had four high accuracy (0.05 K) platinum resistance thermometer probes (Hart Scientific) inserted through the cell walls at regular

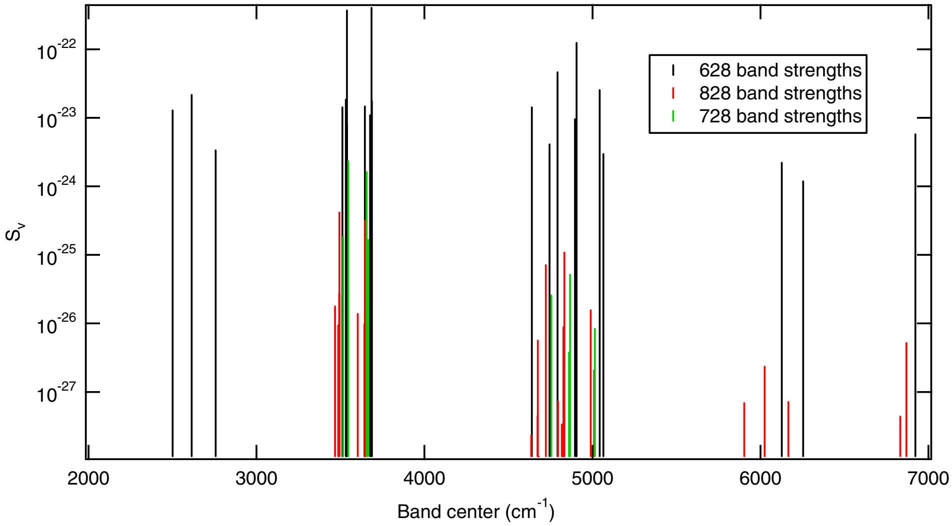

Fig. 1. Illustration of the observed band strengths S_v, in units of $cm^{-1}/(molecule\ cm^{-2})$ at 296 K and in natural abundance, as a function of the band centers for the three carbon dioxide isotopologues $^{16}O^{12}C^{18}O$, $^{18}O^{12}C^{18}O$ and $^{17}O^{12}C^{18}O$. Between 3400 and 5100 cm^{-1}, values are obtained for all three isotopologues. Below 2800 cm^{-1}, only values of $^{16}O^{12}C^{18}O$ are given while $^{16}O^{12}C^{18}O$ and $^{18}O^{12}C^{18}O$ bands are reported above 5900 cm^{-1}.