

Fourier transform spectroscopy of $^{12}\text{C}^{18}\text{O}_2$ and $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ in the 3800–8500 cm^{-1} region and the global modeling of the absorption spectrum of $^{12}\text{C}^{18}\text{O}_2$

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Abstract

The absorption spectrum of the ^{18}O enriched carbon dioxide has been recorded at Doppler limited resolution with a Fourier transform spectrometer in the spectral range 3800–8500 cm^{-1} . Seventeen cold bands ($14\Sigma-\Sigma$ and $3\Sigma-\Pi$) and nine hot bands ($9\Pi-\Pi$) of $^{12}\text{C}^{18}\text{O}_2$, nineteen cold bands ($18\Sigma-\Sigma$ and $1\Sigma-\Pi$) and eighteen hot bands ($6\Sigma-\Sigma$, $9\Pi-\Pi$ and $3\Delta-\Delta$) of $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ have been observed. Among them, 14 $^{12}\text{C}^{18}\text{O}_2$ bands and 12 $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ bands are observed for the first time. The spectroscopic parameters G_v , B_v , and centrifugal distortion constants, have been determined for all observed bands. Effective Hamiltonian parameters for the $^{12}\text{C}^{18}\text{O}_2$ isotopic species are retrieved from the global fitting of the observed line positions presented in this paper and collected from the literature. As the result, 65 obtained effective Hamiltonian parameters reproduce 5443 observed line positions of 73 $^{12}\text{C}^{18}\text{O}_2$ bands with $\text{RMS} = 0.00145 \text{ cm}^{-1}$.

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1. Introduction

The infrared absorption spectroscopy of carbon dioxide is of great interest for many important applications. This paper is one of the series of our publications devoted to the global modeling of high resolution spectra of carbon dioxide molecule [1–17]. In this paper we are concentrated on two ^{18}O consisted isotopologues: $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{18}\text{O}_2$ (natural abundance 0.0039471 and 0.0000039573, respectively). We have undertaken a systematic measurement of line positions of these isotopic species using Fourier Transform Spectrometer in Hefei. These isotopologues could have important contribution to the absorp-

tion by very dense Venus atmosphere which is dominated by CO_2 . When this work started there were no publications concerning the measurements of high resolution spectra of $^{12}\text{C}^{18}\text{O}_2$ in the region above 4000 cm^{-1} , except the band 20013–00001 centered at 4721.92 cm^{-1} which was detected in Venus spectra [18]. In parallel to our study, Toth et al. [19] reported the strong bands of $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{18}\text{O}_2$ in this region. The ro-vibrational transitions of $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ in the region 3600–8500 cm^{-1} have been reported in Refs. [13,18–21]. The present work provides a comparison with the available data of $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ and $^{12}\text{C}^{18}\text{O}_2$ and also fills some gaps in this region.

This paper is organized as following: Section 2 presents the experimental details, Section 3 gives the rotational analysis and vibrational assignments, Section 4 deals with the global fit of the effective Hamiltonian parameters of $^{12}\text{C}^{18}\text{O}_2$ and the conclusions are given in Section 5.

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2. Experimental details

The ^{18}O enriched carbon dioxide sample was purchased from Icon Services. The stated isotopic concentration for the oxygen atom is 84.3% of ^{18}O . The isotope abundance was studied by a photo-ionization mass spectroscopy (PIMS) experiment. PIMS was measured with an electron time-of-flight mass spectrometer in the photochemistry end-station of National Synchrotron Radiation Laboratory, Hefei. The abundances of $^{12}\text{C}^{18}\text{O}_2$ and $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ were determined as 63.8% and 28.4%, respectively. The accuracy of the PIMS measurement was estimated to be about 0.1%.

The absorption spectra were recorded in the spectral range from 4000 to 9500 cm^{-1} , with a Bruker IFS 120HR Fourier-transform spectrometer (FTS) equipped with a path length adjustable multi-pass gas cell. The maximum optical path length is 105 m. A tungsten source, CaF_2 beam splitter were used in all experiments. The cell was operated at room temperature, stabilized by an air-conditioning system. The pressure was measured using two capacitance manometers of 200 Pa and 133 hPa full-scale ranges with an overall accuracy of 0.5%. Different band-pass optical filters were applied to improve the signal to noise ratio. For accurate line position measurements, no apodization function was applied. The line positions were calibrated using the absorption lines of water (present as an impurity in the cell) given in HITRAN database [22]. The experimental conditions are presented in Table 1. The accuracy of the unblended lines recorded with a good signal to noise ratio was estimated to be better than 0.001 cm^{-1} . Altogether more than 4700 scans were co-added to improve the signal-noise-ratio. An overview and a small portion of the recorded spectrum are presented in Figs. 1 and 2, respectively.

3. Rotational analysis and vibrational assignment

The band by band rotational analysis was performed using the standard expression for the rotational energy levels in a given vibrational state:

$$E_v(J, \ell_2) = G_v + B_v[J(J+1) - \ell_2^2] - D_v[J(J+1) - \ell_2^2]^2 + H_v[J(J+1) - \ell_2^2]^3. \quad (1)$$

Table 1
Experimental conditions

Spectral region (cm^{-1})	Pressure (Pa)	Path length (m)	Resolution (cm^{-1})	Detector	Sample scans
3500–7500	3476	105	0.015	InSb	4752
3500–7500	3223	15	0.015	InSb	1386
3500–7500	531	15	0.01	InSb	938
5000–9000	3348	105	0.017	Ge	4928
5000–9000	3246	15	0.017	Ge	1792

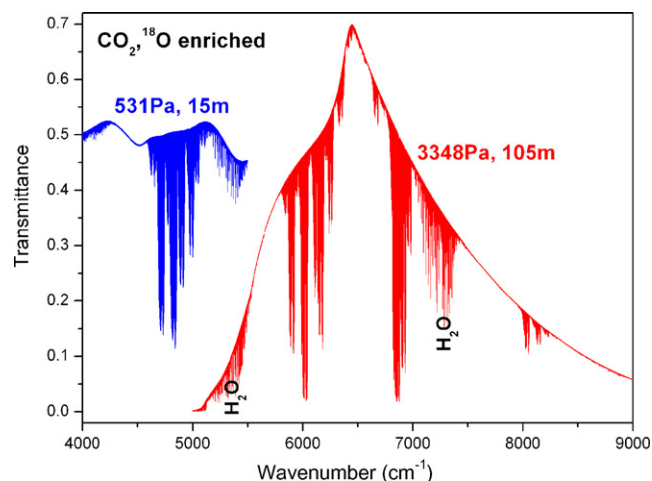


Fig. 1. An overview of the Fourier-transform absorption spectrum of O-18 enriched CO_2 in the region 4000–9000 cm^{-1} .

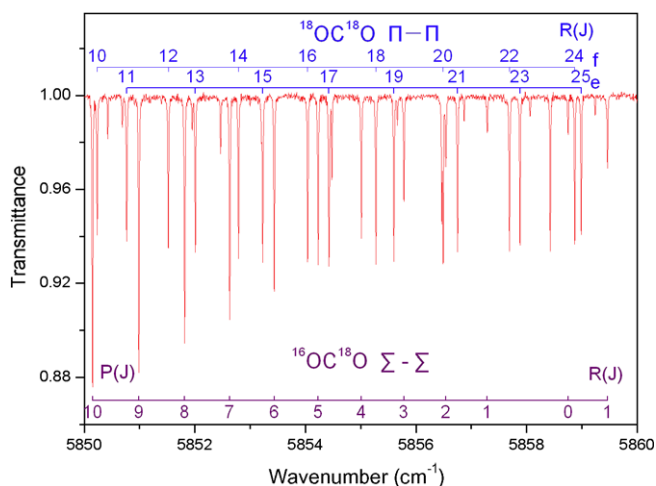


Fig. 2. A small portion of the Fourier-transform absorption spectrum in the region 5850–5860 cm^{-1} . The P-branch of the Σ - Σ cold band centered at 5858.02 cm^{-1} of $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ and the R-branch of the Π - Π hot band centered at 5842.86 cm^{-1} are shown. Experimental conditions: O-18 enriched CO_2 sample, total sample pressure: 3348 Pa, absorption path length: 105 m.

Here G_v is the vibrational term value, B_v is the rotational constant, D_v is centrifugal distortion constants, ℓ_2 is the quantum number associated to the vibrational angular momentum. These constants for an upper state have been fitted to the observed line positions of the respective observed band. The lower state constants (for the ground

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