

Note

Absorption spectra of $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$ near $1.05\ \mu\text{m}$

L. Wang^{a,b}, V.I. Perevalov^{a,c}, S.A. Tashkun^{a,c}, A.-W. Liu^{a,b}, S.-M. Hu^{a,b,*}

^a USTC-Shanghai Institute for Advanced Studies, University of Science and Technology of China, Shanghai 201315, China

^b Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

^c Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics SB RAS, 1, Akademicheskii av., 634055 Tomsk, Russia

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Abstract

The absolute line intensities of the Fermi triad 2003*i*-00001 ($i = 1, 2, 3$) of $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$ isotopic species of carbon dioxide were retrieved from Fourier-transform spectra recorded at Doppler limited resolution in the region $9200\text{--}9700\ \text{cm}^{-1}$. The accuracy of the line intensity determination is estimated to be better than 15% for most lines. The vibrational transition dipole moments squared and Herman–Wallis coefficients have been determined. The global fittings of the observed line intensities within the framework of the effective operators method have been performed. The fitting results reproduce the data within experimental uncertainty.

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The absorption spectrum of carbon dioxide in the short-wave region is of particular interest for the planetary atmospheres. As concerns the $9200\text{--}9700\ \text{cm}^{-1}$ region, which is important for many applications like remote sensing, HITRAN database [1] contains the line parameters only for the Fermi triad 2003*i*-00001 ($i = 1, 2, 3$) of the principal isotopic species $^{12}\text{C}^{16}\text{O}_2$ and there is no information in it about the line parameters of this triad for the second important isotopic species $^{13}\text{C}^{16}\text{O}_2$. The line intensities presented in HITRAN for the above-mentioned bands are based on the old measurements of Boese et al. [2]. The line positions of the $^{12}\text{C}^{16}\text{O}_2$ triad have been obtained by Mandin [3] from a Venus spectrum and recently by Ding et al. [4,5] from ICLAS measurements. In the last edition of HITRAN database, the line positions obtained by ICLAS in [4] are used. In this note, we present the

results of new measurements of the line intensities and line positions for both isotopic species $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$ performed by means of Fourier-transform spectroscopy in this region.

The absorption spectra were recorded with a Bruker IFS 120HR Fourier-transform spectrometer (FTS) equipped with a path length adjustable multi-pass gas cell. Two samples of carbon dioxide were used: the sample with the natural abundances of isotopic species and the ^{13}C enriched sample from Aldrich Chemical. A mass spectroscopy experiment has given the 98.5% abundance of $^{13}\text{C}^{16}\text{O}_2$ in the sample. (The $^{12}\text{C}^{16}\text{O}^{17}\text{O}$ isotopologue concentration in this sample should be no more than 0.1%, which was confirmed by the absorption spectrum in the MIR region.) The partial pressure was 200 and 53 hPa for $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$, respectively. In both cases, the path length was 105 m, and the spectral resolution was $0.021\ \text{cm}^{-1}$. A tungsten source and Ge-diode detector were used. The measurements were carried out at room temperature (293 K). Seven thousand scans were accumulated and the resulted signal-to-noise ratio

* Corresponding author. Fax: +86 551 360 2969.

E-mail address: smhu@ustc.edu.cn (S.-M. Hu).

is about 300. The line positions were calibrated with the lines of water vapor (presented as trace contamination in the sample cell) given by the HITRAN2000 [1] database. The accuracy of the line positions of unblended and not-very-weak lines was estimated to be better than 0.003 cm^{-1} . The overview spectra for both isotopic species in the region of $9200\text{--}9700 \text{ cm}^{-1}$ are presented in Fig. 1.

To retrieve line intensity, the calculated spectrum is fit to an experimental one, using a nonlinear least-squares procedure. A PC based program “Intwin” written in C++ was applied to obtain line parameters from the profile fitting to the observed spectrum. Voigt profile was adopted for each line. Line position, integrated line absorbance, Gaussian and Lorentzian widths of each line and a baseline (treated as a linear function) can be obtained from the fitting procedure. The Gaussian width was fixed at the corresponding Doppler width. The integrated absorbance of each line was converted to the line strength at the standard temperature $T = 296 \text{ K}$, then the transition moment squared was determined. All these values together with the line positions are presented in Supplementary materials. In our measurements, the pressure uncertainty is about 1% and the error from the temperature fluctuation and absorption path length is about 0.5%. The overall uncertainty of the line intensities mainly comes from the fitting error due to the weakness of the studied bands and the limited signal-to-noise ratio. It is estimated to be around 7% or better for the well-isolated lines of the 20032–00001 band of $^{12}\text{C}^{16}\text{O}_2$, 10% for two bands of $^{13}\text{C}^{16}\text{O}_2$ and the 20031–00001 band of $^{12}\text{C}^{16}\text{O}_2$, and about 15% for the weakest 20033–00001 band of $^{12}\text{C}^{16}\text{O}_2$. It can be worse for very-weak or blended lines.

The empirical data reduction of both line positions and line intensities have been performed. The usual

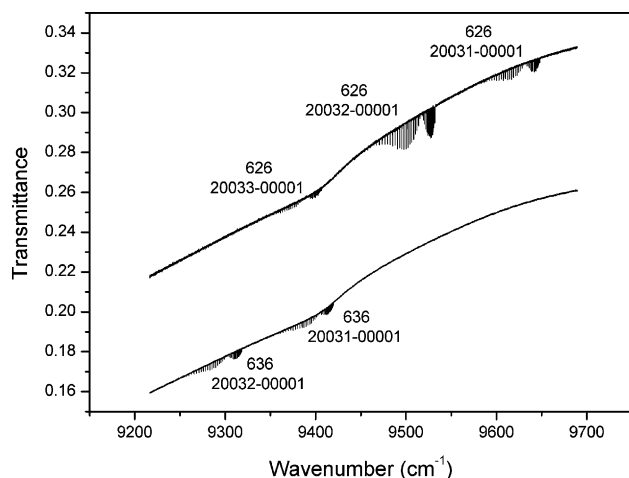


Fig. 1. Absorption spectra of $^{12}\text{C}^{16}\text{O}_2$ (upper) and $^{13}\text{C}^{16}\text{O}_2$ (lower) in the $9200\text{--}9700 \text{ cm}^{-1}$ region. The gas pressure was 200 and 53 hPa for $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$, respectively. Absorption path length was 105 m.

equation in terms of spectroscopic constants G_v , B_v , and D_v (see, e.g. [6]) has been used for the calculation of the vibration–rotation energies of a given vibrational state. These parameters have been fitted to the observed line positions for each observed band. The spectroscopic parameters G_0 , B_0 , and D_0 for the ground vibrational state have been taken from Rothman et al. [6]. The fitted parameters are presented in Table 1, where their comparison to the values obtained in [3,5] is also given.

The vibrational transition moment squared and Herman–Wallis coefficients have been determined for each band in the result of the least-squares fittings to the transition moments squared. The Herman–Wallis factor was used in the form presented in [7]. Unweighted fittings have been performed. The coefficients A_1 and A_2 determined in this article should be considered as the parameters reproducing the particular experimental data. All these parameters are presented in Table 1.

Using the effective operators approach presented, for example, in [8–10], we have performed the line intensity fittings for both isotopic species. The observed bands belong to $\Delta P = 13$ series of transitions according to our classification given in [9,10]. The values of the expansion coefficients of the eigenfunctions have been obtained from the global fitting of the effective Hamiltonian parameters to the observed line positions in [11] for $^{12}\text{C}^{16}\text{O}_2$ and in [12] for $^{13}\text{C}^{16}\text{O}_2$. The partition functions $Q(T)$ are taken from Gamache et al. [13]. The fitting procedure is aimed to minimize the value of the dimensionless weighted standard deviation χ , defined according to the usual formula

$$\chi = \sqrt{\frac{\sum_{i=1}^N \left(\frac{S_i^{\text{obs}} - S_i^{\text{calc}}}{\delta_i} \right)^2}{(N - n)}},$$

where S_i^{obs} and S_i^{calc} are, respectively, observed and calculated values of the intensity for the i th line; $\delta_i = \frac{S_i^{\text{obs}} \sigma_i}{100\%}$, σ_i is the measurement error of i th line in percentage, N is the number of fitted line intensities, and n is the number of adjusted parameters. For the weighting of the line intensities it was used $\sigma_i = 15\%$ for both isotopic species. The results of the least-squares fits are presented in Table 2. Together with weighted standard deviation the root mean square of residuals (*RMS*) is also given for both fits. Both fits achieved the experimental accuracy. The sets of the effective dipole moment parameters are given in Table 2.

It should be emphasized that our measured line intensities for the 20032–00001 band of $^{12}\text{C}^{16}\text{O}_2$ are in average 25% higher than those by Boese et al. [2]. The current HITRAN database line intensity data for the 2003*i*–00001 ($i = 1, 2, 3$) bands of $^{12}\text{C}^{16}\text{O}_2$ are based on [2]. But in this reference, due to relatively lower

Table 1

Spectroscopic constants G_v , B_v , and D_v (in cm^{-1}), vibrational transition moments squared $|R_v|^2$ (in D^2 ; D, Debye), Herman–Wallis parameters A_1 and A_2 for the Fermi triad 2003*i*-00001 ($i = 1, 2, 3$) of $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$

Band	Reference ^a	G_v	B_v	$D_v \times 10^7$	$J_{\text{MAX}} P/R$	N/N^b	RMS^c	$ R_v ^2 \times 10^{10}$	$A_1 \times 10^4$	$A_2 \times 10^4$
$^{12}\text{C}^{16}\text{O}_2$										
20033–00001	FTS	9388.9758(17) ^d	0.3823970(67)	1.930(56)	34/34	22/32	3.2	1.673(78)	1.22(41)	0.666(26)
	ICLAS	9388.98340(72)	0.3823801(17)	1.8088(37)	52/48	49/52	2.7			
	VENUS	9388.9937(4)	0.38238062(25)	1.851(35)	44/46		1.2			
20032–00001	FTS	9516.95601(69)	0.3804959(18)	1.3990(88)	44/48	42/45	2.5	7.768(26)	1.22(41)	0.666(26)
	ICLAS	9516.95800(58)	0.38049100(92)	1.3648(25)	62/64	61/65	2.4			
	VENUS	9516.9690(11)	0.3804955(24)	1.389(10)	54/56		4.1			
20031–00001	FTS	9631.33988(86)	0.3812380(23)	0.929(11)	40/48	35/44	2.7	2.883(24)		
	ICLAS ^c	9631.3412(6)	0.38123749(89)	0.9138(25)	58/62	59/60	2.3			
	VENUS	9631.3532(7)	0.3812447(36)	1.007(44)	48/36		2.1			
$^{13}\text{C}^{16}\text{O}_2$										
20032–00001	FTS	9302.13553(41)	0.3811499(16)	1.509(12)	36/38	37/39	1.3	4.211(94)	11.89(90)	2.087(34)
	ICLAS	9302.13825(74)	0.3811492(19)	1.4996(89)	50/40	45/46	2.7			
	VENUS	9302.1446(10)	0.3811439(70)	1.405(92)			2.1			
20031–00001	FTS	9404.12760(73)	0.3806616(27)	0.928(19)	38/38	35/39	2.1	4.058(62)		
	ICLAS	9404.12812(67)	0.3806759	0.9969(52)	56/38	47/48	2.6			
	VENUS	9404.1394(16)	0.380642	0.64(24)			2.6			

^a FTS, this work; ICLAS, [5]; VENUS, [3].

^b n , number of transitions included in the line position fit; N , number of assigned rotational transitions.

^c Root mean square deviation of the line position fit in 10^{-3}cm^{-1} .

^d The numbers in parentheses are one standard deviation in units of the last digit.

^e Ref. [4].

resolution (0.11cm^{-1}) achieved by a gating spectrometer, only the integrated intensities of heavily overlapped R -branches are given for 20031–00001 and 20033–00001 bands. Here, we measured the individual line intensities for all these bands of $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$. The uncertainty of our measured absolute line intensities is estimated to be about 15%. In Fig. 2, the comparison of HITRAN line intensities to our measured values is presented. Two approaches have been used for the modeling of the measured line intensities: approach based on

the band intensity and Herman–Wallis factor, and global approach based on the method of effective operators. Within the framework of the second approach, we performed fittings of the effective dipole moment parameters to the observed line intensities. In all cases, the experimental accuracy was achieved. The fitted sets of the dipole moment parameters will be used to update and enlarge atmospheric CDSD-296 and high-temperature CDSD-1000 versions of the Carbon Dioxide Spectroscopic Databank [14].

Table 2

Summary of the line intensities fits and effective dipole moment parameters for the Fermi triad 2003*i*-00001 ($i = 1, 2, 3$) of $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$

ΔP series	Number of lines	Number of bands	Number of branches	J_{max}	χ	RMS (%)	Number of adjusted parameters
$^{12}\text{C}^{16}\text{O}_2$							
13	80	3	6	40	0.68	9.4	2
$^{13}\text{C}^{16}\text{O}_2$							
13	57	2	4	38	0.71	10.4	2
ΔV_1	ΔV_2	ΔV_3	$\Delta \ell_2$	Value	Order		
Effective dipole moment parameters $M_{\Delta V_1 \Delta V_2 \Delta V_3}^{ \Delta \ell_2 }$ in Debye							
$^{12}\text{C}^{16}\text{O}_2$							
2	0	3	0	−0.10333(61) ^{a,b}	10^{-4}		
1	2	3	0	0.544(35)	10^{-6}		
$^{13}\text{C}^{16}\text{O}_2$							
2	0	3	0	−0.8906(69)	10^{-5}		
1	2	3	0	0.325(62)	10^{-6}		

^a Only relative signs of parameters are determined.

^b The numbers in parentheses are one standard deviation in units of the last digit.

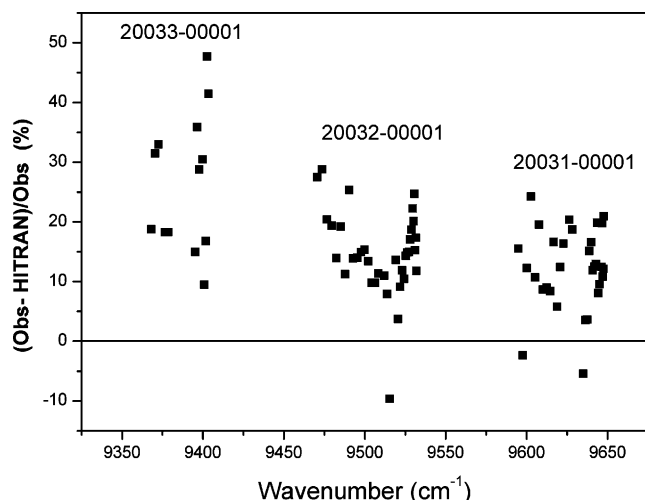


Fig. 2. The line strengths observed in this article compared with those presented in HITRAN database for the Fermi triad 2003*i*-00001 (*i* = 1, 2, 3) of $^{12}\text{C}^{16}\text{O}_2$.

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Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as

part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

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