Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Spectroscopy 246 (2007) 133–157
Journal of MOLECULAR SPECTROSCOPY
www.elsevier.com/locate/jms

Air-broadened halfwidth and pressure shift coefficients of $^{12}C^{16}O_2$ bands: 4750–7000 cm^{-1}

R.A. Toth [a,*], C.E. Miller [a], V. Malathy Devi [b], D.C. Benner [b], L.R. Brown [a]

[a] *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA*
[b] *The College of William and Mary, P.O. Box 8795, Williamsburg, VA 23187-8795, USA*

Received 25 July 2007; in revised form 4 September 2007
Available online 21 September 2007

Abstract

Previously we obtained self-broadened halfwidth and self-induced shift coefficients at room temperature for 15 near infrared CO_2 bands between 4750 and 7000 cm^{-1} [R.A. Toth, L.R. Brown, C.E. Miller, V.M. Devi, D.C. Benner, J. Mol. Spectrosc., 239 (2006) 243–271]. The present study expands our work on the near infrared line parameters of CO_2 to include air broadening coefficients. Here we report nearly 400 air-broadened half width and air-induced pressure shift coefficients spanning 11 different CO_2 vibrational bands in the 4750–7000 cm^{-1} region. Retrievals have been performed using Voigt line profiles over three distinct spectral intervals: (a) 4750–5200 cm^{-1}, covering the 20011 ← 00001, 20012 ← 00001, and 20013 ← 00001 Fermi Triad and three associated hot bands 21111 ← 01101, 21112 ← 01101, 21113 ← 01101; (b) 6100–7000 cm^{-1}, covering the 30011 ← 00001, 30012 ← 00001, 30013 ← 00001 and 30014 ← 00001 Fermi Tetrad; (c) near 6950 cm^{-1} for the 00031 ← 00001 overtone band. The air-broadened halfwidth and air-induced pressure shift coefficients have been modeled with empirical expressions and compared to other measurements available in the literature.

Keywords: Carbon dioxide; CO_2; Air-broadening; Near infrared; Lorentz widths; Pressure shift

1. Introduction

The current state of knowledge for CO_2 line-by-line parameters does not provide sufficient accuracies for OCO and other carbon cycle remote sensing applications [1]. Thus the HITRAN 2004 spectral line parameters [2] do not support the stringent 0.3% precision requirements for analysis of atmospheric measurements, despite efforts already underway to monitor atmospheric CO_2 from the ground [3,4] and from space [5,6] using near infrared detection. The need for more sensitive remote sensing measurements and the increasing sophistication in remote sensing instrumentation drives the demand for better line-by-line reference parameters.

Toward that end, we are performing a systematic reinvestigation of the near infrared CO_2 spectrum designed to provide spectroscopic reference parameters with the accuracy required to support current and planned CO_2 remote sensing measurements. Our analyses to date provide better accuracy for line positions and line intensities of over 150 bands involving eight isotopologues [7–10]. Self-broadened halfwidth and pressure shift coefficients are considered for 15 bands of $^{16}O^{12}C^{16}O$ [11], and the present study describes the corresponding analysis of air broadening. Accurate values of air-broadening parameters are important for analysis of atmospheric measurements and provide one part to meet the 0.3% requirement. Two other parts are accurate values of zero pressure line positions and line intensities of which our recent studies provide for $^{16}O^{12}C^{16}O$ [7,10]. Obviously the final part is to apply these parameters to the analysis of accurately obtained atmospheric measurements.

* Corresponding author. Fax: +1 818 354 5148.
E-mail address: ratoth@jpl.nasa.gov (R.A. Toth).

0022-2852/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2007.09.005

The experimental data cover the 4750–7000 cm^{-1} range and include 11 different vibrational bands: 20011 ← 00001, 20012 ← 00001, 20013 ← 00001, 21111 ← 01101, 21112 ← 01101, 21113 ← 01101, 30011 ← 00001, 30012 ← 00001, 30013 ← 00001, 30014 ← 00001, and 00031 ← 00001. We are reporting 389 halfwidth and 433 pressure-shift coefficients of $^{16}O^{12}C^{16}O$ (626) transitions determined using spectrum-by-spectrum retrieval and standard Voigt line shapes. Separate constrained multispectrum analyses of the 30012 ← 00001 [12] and 30013 ← 00001 bands [13] demonstrate the importance of speed-dependent line shapes and line mixing for further reducing measurement uncertainties.

Table 1 summarizes the previous studies of air, N_2 and O_2 broadening of CO_2 throughout the infrared, listing the band(s) studied, range of transitions with number of transitions measured, molecular species of CO_2, instrument used to obtain spectra, type of broadening gas and broadening parameters obtained. The previous studies involving air-broadening of CO_2 include four studies by Devi et al. [12–15]. Also considered are the measurements of N_2 and O_2 broadening from which air-broadened halfwidth coefficients, b^0(air), can be derived using the expression:

$$b^0(\text{air}) = 0.79b^0(N_2) + 0.21b^0(O_2). \quad (1)$$

Prior N_2 and O_2 broadening measurements of CO_2 include the following studies: Tanaka et al. [16], De Rosa et al. [17], Margottin-Maclou et al. [18]. Corsi et al. [19], Dana et al. [20], Hikida and Yamada [21], and Pouchet et al. [22]. As seen from Table 1, the present study substantially increases the air broadening information for near infrared bands of carbon dioxide.

2. Experimental details

All spectra were recorded over the 4750–7000 cm^{-1} range with the McMath-Pierce Fourier transform spectrometer (FTS) located at the Kitt Peak National Solar Observatory. A full description of the experimental details (pressure gauges, absorption cells, gas handling, and instrument) was given in our previous work of line positions and strengths of $^{16}O^{12}C^{16}O$ [10]. For the present work, the samples contained small amounts of CO_2 in natural abundance mixed with dry air. For each spectral run, the CO_2 gas was admitted into the evacuated absorption cell, the pressure was recorded; then dry air was added and the total pressure was recorded. The gas sample was allowed to stabilize thermally, after which a spectrum of 10 or more co-added interferograms was recorded over a period of ~90 min. The CO_2 partial pressure was checked by comparing retrieved line strengths with those of Ref. [10]. This procedure showed that the initial CO_2 pressures determined from the pressure gauge were accurate to better than 1% which is more than adequate for obtaining accurate air-broadening parameters. The total sample pressures were known to better than 0.5%.

Table 2 gives the experimental conditions for each run. The columns contain the run identification number, CO_2 partial pressure, air partial pressure, total pressure, CO_2

Table 1
Summary of previous air, N_2, and O_2 broadening studies of CO_2

Reference	Band	Range[a]	#Lines	Mol[b]	Instr.[c]	Air[d]	N_2[d]	O_2[d]	Widths	Shifts
Devi et al. [12]	30012–00001	P54–R52	54	626	FTS	x			x	x
Devi et al. [13]	30013–00001	P58–R56	58	626	FTS	x			x	x
Devi et al. [14]	00011-10001	P48-R48	49	626	FTS	x	x		x	x
	00011–10002	P52–R44	49	626	FTS	x	x		x	x
	00011–10001	P40–R40	41	636	FTS	x	x		x	x
	00011–10002	P40–R40	41	636	FTS	x	x		x	x
Devi et al. [15]	10002–00001	P46–R46	93	638	FTS	x	x		x	x
	10001–00001	P50–R45	93	638	FTS	x	x		x	x
Tanaka et al. [16]	11102-00001	P46-R44	30	626	FTS		x	x	x	x
	11101–00001	P60–R13	31	626	FTS		x	x	x	
De Rosa et al. [17]	30012–00001	P18–P10	5	626	TDL		x	x	x	x
Margottin-Maclou et al. [18]	00011–00001	R0–R82	12	626	Grat		x	x	x	
	10011–00001	R0–R48	9	626	Grat		x	x	x	
Corsi et al. [19]	20012–00001	R22–R46	13	626	TDL		x	x	x	x
Dana et al. [20]	11101–10002	P22–R26	13	626	FTS		x	x	x	
Hikida, Yamada [21]	30013–00001	P28–R28	10	626	TDL		x	x	x	
Pouchet et al. [22]	30013–00001	R2–R20	5	626	TDL		x	x	x	

[a] The range of quantum numbers reported.
[b] $^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$ and $^{16}O^{13}C^{18}O$ are written as 626, 636 and 638, respectively.
[c] The instrument types are Fourier transform spectrometer (FTS), Tunable diode laser (TDL) and grating (Grat).
[d] The perturbing gas in the studies.