# Temperature dependences for air-broadened Lorentz half-width and pressure shift coefficients in the 30013 $\leftarrow$ 00001 and 30012 $\leftarrow$ 00001 bands of CO<sub>2</sub> near 1600 nm $^1$

A. Predoi-Cross, A.R.W. McKellar, D. Chris Benner, V. Malathy Devi, R.R. Gamache, C.E. Miller, R.A. Toth, and L.R. Brown

Abstract: In this study, 39 high-resolution spectra of pure and air-broadened CO<sub>2</sub> recorded at temperatures between 215 and 294 K were analyzed using a multispectrum nonlinear least-squares technique to determine temperature dependences of airbroadened Lorentz half-width and air-induced pressure shift coefficients for over 100 individual  $^{12}C^{16}O_2$  transitions in the  $30012 \leftarrow 00001$  (at 6348 cm<sup>-1</sup>) and  $30013 \leftarrow 00001$  (at 6228 cm<sup>-1</sup>) bands. Data were recorded with two different Fourier transform spectrometers (Kitt Peak FTS at the National Solar Observatory in Arizona and the Bomem FTS at NRC, Ottawa), with absorption path lengths ranging between 25 and 121 m. The sample pressures varied between 11 torr (pure CO<sub>2</sub>) and 924 torr (CO<sub>2</sub>-air) with volume mixing ratios of CO<sub>2</sub> in air between ~1.5% and 11% (1 torr = 133.322 4 Pa). To minimize systematic errors and increase the accuracy of the retrieved parameters, a constrained multispectrum nonlinear least-squares fitting technique was used to include theoretical quantum mechanical expressions for the rovibrational energies and intensity parameters rather than retrieving the individual positions and intensities line by line. The results suggest no detectable vibrational dependence for the temperature dependences for the air-broadened Lorentz half-width coefficients and the air-induced pressure shift coefficients. The half-width coefficients and temperature dependence exponents were modeled using semiclassical calculations based upon the Robert–Bonamy formalism. A good agreement is seen between the measurements and theoretical calculations. Beyond |m| = 26, a simple scaling factor (0.96) has been applied to the calculated half-width coefficients to match the experimental measurements.

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**Résumé :** Trente-neuf spectres de  $CO_2$  élargis par l'air ont été enregistrés à haute résolution et entre 215 et 294 K. Leur analyse par une technique de moindres carrés multi-spectres non-linéaires a permis de déterminer la dépendance en température des coefficients d'élargissement Lorentzien et des coefficients de déplacement induits par l'air pour plus de 100 transitions individuelles de  ${}^{12}C{}^{16}O_2$  dans les bandes  $30012 \leftarrow 00001$  (à 6348 cm<sup>-1</sup>) et  $30013 \leftarrow 00001$  (à 6228 cm<sup>-1</sup>). Les spectres ont été enregistrés avec deux spectromètres à transformée de Fourier différents (le FTS du National Solar Observatory à Kitt Peak en Arizona, et le FTS Bomem du CNRC à Ottawa) et avec des chemins d'absorption variant de 25 à 121 m. La pression des échantillons s'étendait de 11 torr (CO<sub>2</sub> pur) à 924 torr (CO<sub>2</sub>-air) avec des rapports de mélange compris entre ~1.5% et 11% (1 torr = 133,3224 Pa). Pour diminuer les erreurs systématiques et accroître la précision des paramètres déterminés, une technique de moindres carrés multi-spectres, incluant une contrainte basée sur l'expression quantique de la dépendance rovibrationelle des énergies et intensités des raies, a été utilisée plutôt que des déterminations individuelles raie par raie. Les résultats suggèrent l'absence de dépendance vibrationnelle pour la dépendance en température des coefficients d'élargissement et de déplacement induits par l'air. Les coefficients d'élargissement et de dépendance en température ont été modélisés par une méthode semi-classique basée sur le formalisme de Robert–Bonamy. Un bon accord a été trouvé entre les résultats mesurés et calculés. Pour *lm* en dessus de 26, un simple facteur d'échelle (0,96) a été utilisé pour que le calcul des coefficients d'élargissement corresponde aux observations.

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A. Predoi-Cross.<sup>2</sup> Department of Physics and Astronomy, University of Lethbridge, Lethbridge, AB T1K 3M4, Canada.

**A.R.W. McKellar.** Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada. **D.C. Benner and V.M. Devi.** The College of William and Mary, Williamsburg, VA 23187-8795, USA.

C.E. Miller, R.A. Toth, and L.R. Brown. Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA.

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**R.R. Gamache.** Department of Environmental, Earth, and Atmospheric Sciences, University of Massachusetts Lowell, MA 01854, USA.

	Vibrational	Temp. range		No. of			
Ref.	band	(K)	Technique	lines	Transitions studied	Range of <i>n</i>	Broadener
7	Laser	290-600	Laser	1	R14	0.54	Self
8	$v_3$ (emission)	T>1000	Grating	6	R76 – R86	0.47- 0.53	Self
8	Laser	1200-3000	Grating	4	P20-P26	<i>n</i> <0.51	Self
9	$v_3$	160, 298	Diode laser	5	P6-P60	Averaged 0.86 (9)	$N_2$
10	$v_3$	295-815	Diode laser	3	R38 –R54	0.72 -0.73	$N_2$
11	V3	296-803	Diode laser	2	R66, R68	0.66, 0.67	$N_2$
12	$v_3$	198, 296	Grating	42, 1	R0-R82 (smoothed)	Ave = 0.72, R68 = 0.79	N <sub>2</sub> , O <sub>2</sub> , Self
12	$v_1 + v_2$	198, 296	Grating	42	R0-R82 (smoothed)	Ave = 0.72	N <sub>2</sub> , O <sub>2</sub>
13	$v_2$	202.2-297.5	Diode laser	7	Q4-Q16	0.646-0.831	$N_2$
14	$v_3 - v_1$	297, 387	Diode laser	1	P20	0.943, 0.827	$N_2$
	$v_3 - 2v_2$			1	R18		
15	$v_2$	200-325	Diode laser	9	R20-R50	0.608-1.296	Self, N <sub>2</sub>
	$2v_2 - v_2$			5	R19-R36		
16	$v_3$	217-299	Diode laser	8	R36-R66	0.748-0.799	$N_2$
	$v_3 + v_2 - v_2$			2	R46, R55		
17	$v_3$	218-343	Grating	9	R66- R82	0.8 and 0.82	N <sub>2</sub> , O <sub>2</sub>
18	mi-IR	197-620			select lines	0.48-1.5	Self, N <sub>2</sub> ,O <sub>2</sub>
19	$2v_1 + 2v_2 + v_3$	197, 233, 294	FTS	22	P2-P44, R2-R40	No values tabulated	Self, N <sub>2</sub> , Ar
20	$v_1 + 4v_2 + v_3$	197, 233, 294	FTS	22	P2-P54, R4-R50	No values tabulated	Self, N <sub>2</sub> , Ar

Table 1. Summary of previous studies of temperature dependence of self- and foreign-broadening in carbon dioxide.

# 1. Introduction

The Earth's atmosphere bears the fingerprint of human influences. Our knowledge and understanding of spatial and temporal patterns in the Earth's carbon cycle, and ultimately of global warming and climate change, are directly linked to our ability to monitor the atmospheric  $CO_2$ , a well-mixed greenhouse gas with a very long lifetime. A crucial objective in monitoring a greenhouse gas is to understand the spatial and temporal fluctuations in surface fluxes.

Satellite-based remote sensing of CO<sub>2</sub> can provide a global distribution of its concentrations with a precision better than 1%. Such a precision is difficult to achieve because the changes in the surface pressure can affect the retrievals of column concentrations of CO2 more than the natural variations due to its sources and sinks. Currently, there are several satellite remote sounding instruments designed to measure column concentrations of CO2 (e.g., the Atmospheric Infrared Sounder (AIRS) [1] and the Infrared Atmospheric Sounder Interferometer (IASI) [2]) using mid-infrared wavelengths; next year, two more (the Orbiting Carbon Observatory (OCO) [3] and the Greenhouse Gases Observing Satellite (GOSAT) [4]) are scheduled for launch, which will target near-IR transitions of CO<sub>2</sub>, particularly those near 1.6 µm. For tropospheric remote sensing, reliable pressure broadening spectroscopy is essential. For the new missions like OCO and GOSAT, accuracies better than 1% are needed for the CO<sub>2</sub> air-broadening coefficients. Unfortunately, the temperature dependence coefficients for air-broadening of all CO<sub>2</sub> bands used by the atmospheric community come from unpublished and unconfirmed predictions made 18 years ago [5].

To satisfy the new requirements, studies were undertaken to obtain air-broadened Lorentz widths of  $CO_2$  at room temperature. The most extensive study was that by Toth et al. [6], who reported air-broadened half-width and air-induced pressure shift coefficients for over 400 transitions belonging to 11  $^{12}CO_2$  bands between 4750 and 7000 cm<sup>-1</sup>. In contrast, no past infrared measurements were available for the temperature dependence of air-broadened CO<sub>2</sub> widths, as seen in Table 1. Instead, the older studies obtained self-, N<sub>2</sub>-, O<sub>2</sub>- and Ar-broadening at different temperatures, and most reported values for relatively few transitions. Many of these [6–18] involved mid-infrared bands; only two studies [19, 20] considered temperature dependence in 30012 $\leftarrow$ 00001 at 6348 cm<sup>-1</sup> and 30013 $\leftarrow$ 00001 at 6228 cm<sup>-1</sup>. Significantly, most of the temperature dependence analyses assumed Voigt line shapes.

Subsequently, independent studies at room temperature [21-24] found that Voigt profiles were insufficient to reproduce observed line shapes in high-quality laboratory spectra. Devi et al. [21, 22] measured the  $30012 \leftarrow 00001$  and 30013←00001 bands using comprehensive multispectrum nonlinear least-squares and concluded that the best results were obtained using a speed-dependent Voigt (SDV) profile, with line mixing effects determined via the relaxation matrix formalism [27]. Following this, Predoi-Cross et al. [23, 24] published an independent room temperature study of airand self-broadening and shifts and weak (Rosenkranz) line mixing coefficients for transitions of the same two bands, using spectra from a different spectrometer and a different multispectrum retrieval software. The absorption profiles were analyzed using both Voigt and speed-dependent Voigt profiles, with an associated asymmetric component due to line mixing. The air-broadened half-width and line mixing coefficients were then modeled using the energy power gap (EPG) and energy corrected sudden (ECS) scaling laws. One difference in the two sets of studies was that in Devi et al. [21, 22] the retrieval technique was modified to adjust the rovibrational constants and intensity parameters (including Herman-Wallis terms) of the entire band(s) in the fitted interval rather than to retrieve individual positions and intensities of the transitions, as was done by Predoi-Cross et al. [23, 24].

In one sense, the present study extends these multispectrum analyses to obtain the temperature dependence of air-

**Table 2.** Summary of experimental conditions of the CO<sub>2</sub> spectra analyzed in this work.

Temp (K)	Pressure (torr)	Path <sup>a</sup> (m)	CO <sub>2</sub> (VMR)
Pure CO <sub>2</sub>			
293.9	26.10 <sup>b</sup>	24.94	1.0
294.1	$11.04^{b}$	24.94	1.0
CO <sub>2</sub> in air			
292.9	923.52	121.2	0.0593
293.1	250.38	121.2	0.0595
292.8	100.86	121.2	0.0605
293.3	551.29	49.00	0.0152
293.1	549.55	49.00	0.0499
293.2	200.25	49.00	0.0155
293.0	100.00	49.00	0.0160
293.2	50.07	49.00	0.0749
292.9	49.79	49.00	0.0160
292.6	26.05	49.00	0.0679
292.8	25.09	49.00	0.0170
296.0	798.0	80.15	0.102
296.0	501.0	80.15	0.102
295.2	100.5	80.15	0.104
291.0	492.0	80.15	0.102
273.9	601.0	80.15	0.102
273.9	401.0	80.15	0.102
258.9	652.1	40.15	0.102
258.9	500.8	40.15	0.103
258.9	370.4	40.15	0.101
258.9	249.5	40.15	0.101
258.9	153.9	40.15	0.105
258.9	77.8	40.15	0.106
244.4	709.0	80.15	0.102
234.4	600.2	60.15	0.102
234.4	450.6	60.15	0.102
234.4	299.9	60.15	0.102
234.4	199.9	60.15	0.104
234.4	100.3	60.15	0.104
234.4	59.8	60.15	0.109
219.0	749.0	80.15	0.102
219.0	601.0	80.15	0.102
219.0	450.5	80.15	0.102
219.0	300.5	80.15	0.102
215.3	601.7	40.15	0.102
215.3	498.4	40.15	0.102
215.3	301.3	40.15	0.102

**Note:** 1 atm = 101.3 kPa = 760 torr, VMR = volume mixing ratio.

<sup>a</sup>Spectra with path lengths of 24.94, 121.2, and 49.00 m were recorded at ~0.011 cm<sup>-1</sup> resolution with the Kitt Peak FTS; the remaining spectra were recorded at NRC with a Bomem FTS at ~0.008 to 0.009 cm<sup>-1</sup> resolution.

<sup>b</sup>Pure natural CO<sub>2</sub> samples (volume mixing ratio = 1 with 0.9842  ${}^{16}O^{12}C^{16}O$ )

broadening coefficients (half-widths and pressure shifts) for  $30012 \leftarrow 00001$  and  $30013 \leftarrow 00001$  bands of carbon dioxide. The broadening coefficients (widths, shifts, and temperature dependences) were retrieved simultaneously using 39 spectra obtained with two different spectrometers. The positions, intensities, line mixing and speed-dependent Voigt coefficients were constrained to the values obtained by Devi et al. [21, 22]. The temperature dependence coefficients of the air-in-

duced pressure shifts were obtained for the first time. The measured air-broadened half-width coefficients and their temperature dependence exponents were found to be in satisfactory agreement with theoretical values.

### 2. Experimental details

The experiments described in this work were carried out using two different Fourier transform spectrometers (FTS). The spectra with path lengths of 24.94, 49.00, and 121.2 m were recorded at ~0.011 cm<sup>-1</sup> resolution with the Kitt Peak FTS and are part of the data set used in refs. 21 and 22. The long absorption paths were achieved using a 6 m base path White cell. The atmospheric path between the White cell and the entrance aperture of the FTS was purged with liquid nitrogen vapors through appropriate plexiglass tubing to minimize strong absorption features arising from CO<sub>2</sub> and H<sub>2</sub>O. Other experimental details are given in Toth et al. [6, 28].

All other spectra were recorded at the Steacie Institute for Molecular Sciences at the National Research Council in Ottawa using a Bomem DA3.002 Fourier Transform Spectrometer. The experimental details are very similar to those of the room temperature study in refs. 23 and 24. The spectra were recorded at nominal spectral resolutions of 0.008 and 0.009 cm<sup>-1</sup>. A large multiple-traversal gas cell described in refs. 25 and 26 and listed in ref. 23 with a base length of 5 m gave absorption paths of 40.15 to 80.15 m. A total of 26 spectra recorded between 215.3 and 296.0 K, with sample pressures varying from 59.8 to 798.0 torr (1 torr = 133.322 4 Pa), as summarized in Table 2, were combined with the 13 Kitt Peak spectra. Each spectrum represented the average of 24 to 32 interferograms, with a total data acquisition time of approximately 2 h.

The cell, which sits entirely inside a vacuum jacket, was cooled by means of methanol from a refrigerated cooling bath (Neslab Model ULT-80DD) that circulated through copper coils soldered to the outside of the cell. The gas temperature was monitored with readings from platinum resistance thermometers mounted on the cooling lines and inside the cell, as well as from the temperature of the cooling bath itself. We estimated the accuracy of the temperature determination to be  $\pm$  0.5 K, with a further uncertainty of  $\pm$  0.5 K due to possible variations along the 5 m length of the cell. The uncertainties and possible inhomogeneties were greatest at the lowest temperature of 215 K. The temperatures were checked spectroscopically using several line intensities retrieved in ref. 23, with an estimated accuracy of  $\pm$  0.2 K. The readings of the temperature monitor were corrected accordingly. As expected, the largest offset between the average temperature determined in this manner and that given by the temperature monitor was obtained at the lowest temperature.

The air and  $CO_2$  gas mixture were taken from a premixed commercial cylinder (BOC Gases Canada) and had a quoted volume mixing ratio of 0.096 CO<sub>2</sub> with an uncertainty of 2%. The volume mixing ratio (VMR) in each of the 26 spectra was determined by fitting these spectra first individually and finally simultaneously with the 13 Kitt Peak spectra such that the intensities of all transitions were identical to those reported in refs. 21 and 22 by constraining the rovi-

Table 3. Temperature dependences of air-broadened half-width and pressure shift coefficients in the 30013 - 00001 band of carbon dioxide.

Line	Position <sup>a</sup>	Intensity <sup>b</sup>	$b_{\rm L}^0({\rm air})^c$	Unc. (%)	$n^d$	%Unc. (%)	$\rho_{b-n}$	$\delta^0(air)^c$	Unc.	$\delta'(air)^e$	Unc.	$ ho_{\delta^0\delta'}$	$\mathrm{SD}^{d,f}$
P54e	6 175.528 178	$3.4509 \times 10^{-25}$	0.063 14	1.29	0.750	(F)		-0.006 98	(81)	0.000 000	(F)		0.100
P52e	6 177.856 086	$4.9553 \times 10^{-25}$	0.068 83	0.93	0.750	(F)		-0.003 78	(63)	0.000 000	(F)		0.100
P50e	6 180.152 596	$7.0003 \times 10^{-25}$	0.068 37	0.76	0.760	(F)		-0.004 66	(51)	0.000 000	(F)		0.100
P48e	6 182.417 925	$9.7279 \times 10^{-25}$	0.068 22	0.47	0.770	(F)		-0.005 55	(32)	0.000 000	(F)		0.100
P46e	6 184.652 290	$1.3296 \times 10^{-24}$	0.067 45	0.36	0.770	(F)		-0.004 73	(24)	0.000 000	(F)		0.060
P44e	6 186.855 909	$1.7871 \times 10^{-24}$	0.067 76	0.27	0.780	(F)		-0.006 45	(17)	0.000 000	(F)		0.099
P42e	6 189.028 995	$2.3616 \times 10^{-24}$	0.067 86	0.25	0.770	2.96	-0.496	-0.006 90	(16)	-0.000 056	(7)	+0.475	0.108
P40e	6 191.171 758	$3.0679 \times 10^{-24}$	0.068 43	0.19	0.876	1.92	-0.523	-0.006 11	(12)	-0.000 074	(5)	+0.497	0.088
P38e	6 193.284 405	$3.9168 \times 10^{-24}$	0.068 51	0.16	0.775	1.64	-0.544	-0.007 02	(10)	-0.000 059	(4)	+0.518	0.093
P36e	6 195.367 137	$4.9131 \times 10^{-24}$	0.068 86	0.13	0.798	1.25	-0.565	-0.006 70	(08)	-0.000 080	(3)	+0.533	0.105
P34e	6 197.420 146	$6.0531 \times 10^{-24}$	0.069 34	0.12	0.709	1.16	-0.586	-0.006 54	(07)	-0.000 054	(2)	+0.556	0.109
P32e	6 199.443 622	$7.3221 \times 10^{-24}$	0.069 30	0.10	0.755	0.91	-0.605	-0.006 96	(06)	-0.000 040	(2)	+0.570	0.105
P30e	6 201.437 743	$8.6923 \times 10^{-24}$	0.070 51	0.10	0.769	0.79	-0.623	-0.006 84	(06)	-0.000 051	(2)	+0.585	0.106
P28e	6 203.402 679	$1.0121 \times 10^{-23}$	0.070 59	0.08	0.763	0.71	-0.635	-0.007 16	(05)	-0.000 051	(1)	+0.595	0.110
P26e	6 205.338 591	$1.1552 \times 10^{-23}$	0.070 75	0.08	0.718	0.70	-0.645	-0.006 97	(05)	-0.000 058	(1)	+0.610	0.107
P24e	6 207.245 631	$1.2913 \times 10^{-23}$	0.072 35	0.08	0.725	0.65	-0.657	-0.006 66	(05)	-0.000048	(1)	+0.622	0.129
P22e	6 209.123 937	$1.4122 \times 10^{-23}$	0.072 78	0.08	0.719	0.63	-0.660	-0.006 88	(05)	-0.000 058	(1)	+0.625	0.130
P20e	6 210.973 638	$1.5090 \times 10^{-23}$	0.074 27	0.07	0.703	0.61	-0.664	-0.006 54	(04)	-0.000 060	(1)	+0.633	0.131
P18e	6 212.794 851	$1.5728 \times 10^{-23}$	0.075 59	0.08	0.714	0.60	-0.675	-0.006 64	(05)	-0.000 061	(1)	+0.639	0.141
P16e	6 214.587 680	$1.5951 \times 10^{-23}$	0.076 05	0.07	0.700	0.59	-0.672	-0.006 63	(04)	-0.000 057	(1)	+0.642	0.126
P14e	6 216.352 216	$1.5689 \times 10^{-23}$	0.078 02	0.08	0.706	0.58	-0.678	-0.006 11	(04)	-0.000 061	(1)	+0.649	0.147
P12e	6 218.088 537	$1.4892 \times 10^{-23}$	0.079 68	0.08	0.677	0.61	-0.681	-0.005 98	(05)	-0.000 070	(1)	+0.653	0.143
P10e	6 219.796 708	$1.3540 \times 10^{-23}$	0.081 62	0.07	0.713	0.59	-0.690	-0.006 01	(05)	-0.000 042	(1)	+0.660	0.140
P8e	6 221.476 778	$1.1644 \times 10^{-23}$	0.083 77	0.08	0.719	0.61	-0.697	-0.005 38	(06)	-0.000 053	(1)	+0.667	0.132
P6e	6 223.128 784	$9.2486 \times 10^{-24}$	0.085 87	0.09	0.817	0.59	-0.711	-0.005 18	(07)	-0.000 056	(2)	+0.673	0.131
P4e	6 224.752 748	$6.4331 \times 10^{-24}$	0.087 11	0.11	0.687	0.86	-0.723	-0.004 14	(09)	-0.000 073	(2)	+0.692	0.124
P2e	6 226.348 677	$3.3064 \times 10^{-24}$	0.090 61	0.19	0.699	1.35	-0.744	-0.004 79	(16)	-0.000 058	(3)	+0.707	0.117
R0e	6 228.689 986	$1.6745 \times 10^{-24}$	0.094 72	0.34	0.693	2.44	-0.757	-0.002 99	(31)	-0.000 086	(6)	+0.717	0.091
R2e	6 230.215 765	$4.9779 \times 10^{-24}$	0.089 65	0.13	0.723	0.95	-0.736	-0.004 09	(11)	-0.000 062	(2)	+0.699	0.125
R4e	6 231.713 419	$8.0947 \times 10^{-24}$	0.084 93	0.09	0.701	0.73	-0.719	-0.004 14	(07)	-0.000 057	(2)	+0.687	0.114
R6e	6 233.182 890	$1.0893 \times 10^{-23}$	0.083 73	0.08	0.688	0.65	-0.705	-0.004 37	(06)	-0.000 054	(1)	+0.676	0.139
R8e	6 234.624 105	$1.3264 \times 10^{-23}$	0.081 96	0.07	0.681	0.62	-0.696	-0.004 30	(05)	-0.000 055	(1)	+0.668	0.137
R10e	6 236.036 977	$1.5126 \times 10^{-23}$	0.079 77	0.08	0.706	0.58	-0.690	-0.004 61	(05)	-0.000 050	(1)	+0.660	0.134
R12e	6 237.421 403	$1.6431 \times 10^{-23}$	0.078 24	0.06	0.715	0.56	-0.685	-0.004 70	(04)	-0.000 063	(1)	+0.654	0.132
R14e	6 238.777 268	$1.7170 \times 10^{-23}$	0.076 42	0.07	0.699	0.57	-0.681	-0.005 02	(04)	-0.000 061	(1)	+0.651	0.135
R16e	6 240.104 444	$1.7362 \times 10^{-23}$	0.075 00	0.07	0.673	0.59	-0.678	-0.005 15	(04)	-0.000 072	(1)	+0.649	0.127
R18e	6 241.402 787	$1.7057 \times 10^{-23}$	0.073 71	0.07	0.676	0.61	-0.676	-0.005 47	(04)	-0.000 071	(1)	+0.646	0.120
R20e	6 242.672 143	$1.6326 \times 10^{-23}$	0.072 93	0.07	0.686	0.61	-0.675	-0.005 85	(04)	-0.000 064	(1)	+0.643	0.114
R22e	6 243.912 344	$1.5256 \times 10^{-23}$	0.072 03	0.07	0.700	0.62	-0.674	-0.006 05	(04)	-0.000 057	(1)	+0.639	0.126
R24e	6 245.123 209	$1.3939 \times 10^{-23}$	0.070 76	0.07	0.710	0.63	-0.671	-0.005 88	(04)	-0.000 061	(1)	+0.633	0.108
R26e	6 246.304 549	$1.2467 \times 10^{-23}$	0.070 23	0.09	0.750	0.63	-0.668	-0.006 04	(05)	-0.000 057	(1)	+0.624	0.104
R28e	6 247.456 161	$1.0925 \times 10^{-23}$	0.069 30	0.09	0.697	0.73	-0.660	-0.005 86	(05)	-0.000 076	(1)	+0.618	0.092
R30e	6 248.577 833	$9.3880 \times 10^{-24}$	0.069 88	0.09	0.835	0.68	-0.650	-0.006 20	(05)	-0.000 065	(2)	+0.598	0.097

	Position <sup>a</sup>	Intensity <sup>0</sup>	$b_{\rm L}{}^0({\rm air})^c$	Unc. (%)	$n^{d}$	%Unc. (%)	$\rho_{b-n}$	$\delta^0(air)^c$	Unc.	$\delta'(air)^e$	Unc.	$\rho_{\delta^0\delta'}$	$SD^{af}$
R32e	6 249.669 344	$7.9145 \times 10^{-24}$	0.069 15	0.10	0.812	0.79	-0.637	-0.006 32	(90)	-0.000054	(2)	+0.586	0.086
R34e	6 250.730 463	$6.5495  imes 10^{-24}$	$0.068 \ 46$	0.12	0.831	06.0	-0.619	-0.007 13	(01)	$-0.000\ 038$	(2)	+0.569	0.071
R36e	6 251.760 953	$5.3223 \times 10^{-24}$	0.068 57	0.13	0.754	1.21	-0.599	-0.007 12	(08)	$-0.000\ 030$	(3)	+0.557	0.096
R38e	6 252.760 567	$4.2488 \times 10^{-24}$	0.067 34	0.15	0.742	1.54	-0.577	-0.006 11	(60)	$-0.000\ 072$	(3)	+0.540	0.074
R40e	6 253.729 054	$3.3328 \times 10^{-24}$	0.068 02	0.18	0.826	1.79	-0.554	-0.007 14	(11)	-0.000074	(4)	+0.519	0.076
R42e	6 254.666 157	$2.5696 \times 10^{-24}$	0.066 68	0.22	0.711	2.77	-0.532	-0.006 65	(14)	-0.000064	(9)	+0.508	0.082
R44e	6 255.571 615	$1.9476 \times 10^{-24}$	0.06671	0.24	0.770	(F)		-0.006 94	(16)	$0.000 \ 0.000$	(F)		0.096
R46e	6 256.445 161	$1.4515 \times 10^{-24}$	0.06672	0.31	0.770	(F)		-0.008 92	(21)	$0.000 \ 0.000$	(F)		0.104
R48e	6 257.286 530	$1.0639 \times 10^{-24}$	0.068 01	0.43	0.760	(F)		-0.006 52	(29)	$0.000 \ 0.000$	(F)		0.100
R50e	6 258.095 453	$7.6701 \times 10^{-25}$	0.065 68	0.59	0.760	(F)		-0.00240	(38)	$0.000 \ 0.000$	(F)		0.100
R52e	6 258.871 660	$5.4396 \times 10^{-25}$	0.067 27	0.83	0.750	(F)		-0.012 16	(55)	$0.000 \ 0.000$	(F)		0.100

 Table 3 (concluded).

at 296 K for a natural CO<sub>2</sub> sample (<sup>16</sup>O<sup>12</sup>C<sup>16</sup>O fraction of 0.9842). These are calculated using the vibrational band intensity and Herman-Wallis factors [21]. Zero pressure line positions in  $cm^{-1}$ , calculated with rovibrational constants from ref. 21. <sup>5</sup>Line intensities are in cm/molecule<sup>-1</sup>

 $^{-}$ Measured air-broadened Lorentz half-width and pressure-shift coefficients are in cm<sup>-1</sup> atm<sup>-1</sup> at 296 K

Temperature dependence exponents of air-width coefficients as well as speed dependence (SD)parameters are unitless

as in ref. 21, and were fixed in the least-squares solution. air-shift coefficients are in cm<sup>-1</sup> atm<sup>-1</sup> K<sup>-1</sup> coefficients of parameters are the same "The temperature dependent ß

In (1) to (3),  $v_i$  denotes the wavenumber (cm<sup>-1</sup>) of the *i*th transition, and prime and double prime denote the upper and lower vibrational levels, respectively. In (2),  $L_i$  are the Hönl–London factors and  $C_2$  represents the second radiation constant; *m* is defined as -J'' in the P branch, J'' + 1 in the R branch, and zero in the Q branch. Other terms have their usual meanings. The terms  $a_1$  and  $a_2$  in (3) were sufficient to describe the bands to the noise level of the spectra, once the speed dependence and line mixing were utilized. The temperature dependences of pressure-broadened half-width and shift coefficients were determined using the expressions given below.

$$b_{\rm L}(p,T) = p \left[ b_{\rm L}^0(\operatorname{air})(p_0,T_0)(1-\chi) \left(\frac{T_0}{T}\right)^{n_a} + b_{\rm L}^0(\operatorname{self})(p_0,T_0)\chi \left(\frac{T_0}{T}\right)^{n_s} \right]$$
(4)

$$\nu = \nu_0 + p[\delta(\operatorname{air})(1 - \chi) + \delta(\operatorname{self})\chi]$$
(5)

$$\delta(T) = \delta^{0}(T_{0}) + \delta'(T - T_{0})$$
(6)

In (4) to (6),  $b_{\rm L}^0$  and  $\delta^0$  represent pressure-broadening and pressure shift coefficients (in cm<sup>-1</sup>atm<sup>-1</sup> at 296 K), respectively.  $b_{\rm L}$  (p, T) is the Lorentz half-width (in cm<sup>-1</sup>) of the spectral line at pressure p and temperature T, and  $b_{\rm L}^{0}({\rm Gas})(p_0, T_0)$  is the Lorentz half-width coefficient of the line at the reference pressure  $p_0$  (1 atm) and temperature  $T_0$ (296 K) of the broadening gas (either air or  $CO_2$ ), and  $\chi$  is the ratio of the partial pressure of CO2 to the total sample pressure in the cell. The temperature dependence exponents of air-broadened half-width coefficients are  $n_a$  and the temperature-dependent coefficients of air-induced shifts are  $\delta'$ . In the present study, the rovibrational constants (G' - G''), B', H', D', B'', D'', H''), intensity parameters (band strengths

# 3. Spectroscopic analysis

In each fitted interval (6120–6280 cm<sup>-1</sup> for  $30013 \leftarrow$ 00001 and 6280–6395 cm<sup>-1</sup> for  $30012 \leftarrow 00001$ ), the line parameters were retrieved using nonlinear multispectrum curve fitting technique [29], modified with constraints on positions and on intensities, as was done in refs. 21 and 22. Briefly, the software adjusted the constants in (1) for positions,

$$\nu_{i} = G' - G'' + \{B'J'(J'+1) - D'[J'(J'+1)]^{2} + H'[J'(J'+1)]^{3}\} - \{B''J''(J''+1) - D''[J''(J''+1)]^{2} + H''[J''(J''+1)]^{3}\}$$
(1)

and in (2) and (3) for intensities,

$$S_i = \frac{S_v v_i L_i F}{Q_r v_0} \exp\left(\frac{-C_2 E''}{T_0}\right) \left[1 - \exp\left(\frac{-C_2 v_i}{T_0}\right)\right]$$
(2)

where

$$F = [1 + a_1m + a_2m^2 + a_3m^3 + a_4J'(J'+1)]^2$$
(3)

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Table 4	. Tem	perature d	lependences	of ai	r-broadened	half-	width	and	pressure	shift	coefficients	in	the	30012-	←00001	band	of	carbon	dioxide	
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Line         Position"         Intensity <sup>b</sup> $b_1^{0}(air)^{c}$ Unc. (%) $p_{ba}$ $p_1^{0}(air)^{c}$ Unc. $\delta(air)^{c}$ Unc. $p_{ba}$ P34         6         293.53 + 10 <sup>-55</sup> 0.067         1.88         0.750         (F) $-0.0003$ 0         (124)         (F)           P30         6         299.831         1.88         0.007147         1.30         0.750         (F) $-0.0005$ 0.00         0.0000         (F)           P46         6         304.366 818         1.1813 \times 10 <sup>-24</sup> 0.066 70         0.44         0.770         (F) $-0.008$ 30         0.0000000         (F)           P44         6         306.552 45         1.6071 \times 10 <sup>-24</sup> 0.066 70         0.44         0.770         (F) $-0.006$ 1.20 $-0.0000$ 1.21         2.44           6         308.375 59         2.1484 \times 10 <sup>-24</sup> 0.066 80         0.25         5.49 $-0.574$ $-0.006$ 1.20 $-0.0000$ 1.21         2.44           F34         6         31.0244         3.6104 \times 10 <sup>-34</sup> 0.068 90         0.15         0.755         1.30		remperature der	pendences of an o	roudened han	widen und pr	essure sin		in the 500	12 00001 04		on dioxide.			
PS4         6         295.3         PC70         PL         PL         PL         PL         PL           PS6         6277.618 606         42.334 × 10 <sup>-23</sup> 0.067 70         0.90         0.700         (F)         -0.006 30         (Q)         0.000 000         (F)           PS0         6 299.891 138         6.0610 × 10 <sup>-33</sup> 0.067 16         0.90         0.700         (F)         -0.006 67         (31)         0.000 000         (F)           P44         6 30.612 42 51         8.5345 × 10 <sup>-53</sup> 0.068 12         0.47         0.770         (F)         -0.006 67         (31)         0.000 000         (F)           P44         6 30.637 559         1.448 × 10 <sup>-44</sup> 0.068 12         0.47         0.770         (F)         -0.006 67         (31)         0.000 070         (F)         +0.488           P40         6 310.833 404         2.821 × 10 <sup>-34</sup> 0.068 20         0.31         0.22         0.844         2.344         -0.066 67         (13)         -0.000 077         (5)         +0.533           P40         6 310.832 404         2.821 × 10 <sup>-34</sup> 0.068 80         0.15         0.753         1.30         -0.061         0.000         70         1.533         0.000 077 </th <th>e</th> <th>Position<sup>a</sup></th> <th>Intensity<sup>b</sup></th> <th><math>b_{\rm L}^0({\rm air})^c</math></th> <th>Unc. (%)</th> <th><math>n^d</math></th> <th>Unc. (%)</th> <th><math>\rho_{b-n}</math></th> <th><math>\delta^0(air)^c</math></th> <th>Unc.</th> <th><math>\delta'(air)^e</math></th> <th>Unc.</th> <th><math> ho_{\delta^0\delta'}</math></th> <th><math>\mathrm{SD}^{d,f}</math></th>	e	Position <sup>a</sup>	Intensity <sup>b</sup>	$b_{\rm L}^0({\rm air})^c$	Unc. (%)	$n^d$	Unc. (%)	$\rho_{b-n}$	$\delta^0(air)^c$	Unc.	$\delta'(air)^e$	Unc.	$ ho_{\delta^0\delta'}$	$\mathrm{SD}^{d,f}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	ŀ	6 295.319 760	$2.9053 \times 10^{-25}$	0.067 20	1.88	0.750	(F)		-0.003 70	(124)	(F)			0.100
$            Pso = 6 299.891 138 = 6.0610 \times 10^{-2} 0.067 76 0.90 0.760 (F) = -0.006 32 (60) 0.000 000 (F) =$	2	6 297.618 696	$4.2334 \times 10^{-25}$	0.071 47	1.30	0.750	(F)		-0.005 03	(92)	0.000 000	(F)		0.100
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	)	6 299.893 138	$6.0610 \times 10^{-25}$	0.067 76	0.90	0.760	(F)		-0.006 32	(60)	0.000 000	(F)		0.100
P46         6         304.366         818         1.181.3 × 10^{-24}         0.066         75         0.470         (F) $-0.006$ 77         (26) $-0.000$ 000         (2) $-0.488$ P42         6         308.8737         559         2.1484 × 10 <sup>-24</sup> 0.066         20         0.821         3.45 $-0.524$ $-0.006$ 10         (20) $-0.000$ 0.00         0.00         0.01         10 $-0.000$ 0.00         0.00         0.01         0.00         0.00         0.01         0.00         0.00         0.01         0.00         0.00         0.01         0.000         0.01         0.01         0.000         0.00         0.01         0.01         0.000         0.01         0.000         0.00 <td< td=""><td>3</td><td>6 302.142 651</td><td><math>8.5345 \times 10^{-25}</math></td><td>0.069 07</td><td>0.64</td><td>0.770</td><td>(F)</td><td></td><td>-0.008 30</td><td>(44)</td><td>0.000 000</td><td>(F)</td><td></td><td>0.100</td></td<>	3	6 302.142 651	$8.5345 \times 10^{-25}$	0.069 07	0.64	0.770	(F)		-0.008 30	(44)	0.000 000	(F)		0.100
P44       6       306.565       245       1.6071 × 10 <sup>-24</sup> 0.066       75       0.40       0.725       5.49       -0.004       0.006       10       0.00000000000000000000000000000000000	5	6 304.366 818	$1.1813 \times 10^{-24}$	0.068 12	0.47	0.770	(F)		-0.006 67	(31)	0.000 000	(F)		0.100
P42         6         308,737 559         2.1484 × 10 <sup>-24</sup> 0.068 22         0.31         0.821         3.45         -0.524         -0.006 10         (20)         -0.000 047         (9)         +0.498           P40         6         310.83 404         2.818 × 10 <sup>-24</sup> 0.068 60         0.25         0.884         2.34         -0.546         -0.006 69         (15)         -0.000 070         (5)         +0.533           P36         6         31.002 446         3.6404 × 10 <sup>-34</sup> 0.068 99         0.16         0.813         1.49         -0.371         -0.006 40         (11)         -0.000 077         (4)         +0.551           P34         6         317.158 873         5735 × 10 <sup>-24</sup> 0.069 36         0.13         0.719         1.14         -0.643         -0.006 84         (8)         -0.000 057         (2)         +0.652           P30         6         321.137 534         1.3101 × 10 <sup>-23</sup> 0.071 72         0.10         0.776         0.27         -0.062         -0.007 86         (6)         -0.000 065         (2)         +0.627           P26         6         325.137 354         1.3101 × 10 <sup>-23</sup> 0.071 74         0.10         0.722         0.75         -0.067         -0.00	ŀ	6 306.565 245	$1.6071 \times 10^{-24}$	0.066 75	0.40	0.725	5.49	-0.504	-0.007 31	(26)	-0.000 020	(12)	+0.488	0.100
P40         6         310.883 404 $2.8218 \times 10^{-24}$ 0.068 60         0.25         0.884         2.34         -0.571         -0.006 69         (16)         -0.000 050         (6)         +0.511           P36         6         315.004 369         4.6118 \times 10^{-24}         0.068 46         0.20         0.804         1.93         -0.571         -0.007 16         (11)         -0.000 077         (3)         +0.551           P34         6         315.094 369         4.6118 \times 10^{-24}         0.068 95         0.15         0.755         1.30         -0.015         -0.006 33         (9)         -0.000 057         (2)         +0.6062           P30         6         321.204 523         8.3778 \times 10^{-24}         0.070 08         0.11         0.743         0.96         -0.662         -0.006 18         (6)         -0.000 065         (2)         +0.617           P26         6         323.185 158         9.8306 \times 10^{-24}         0.071 74         0.10         0.722         0.75         -0.676         -0.007 11         (5)         -0.000 065         (2)         +0.617           P24         6         323.655 87         1.3993 \times 10^{-23}         0.071 14         0.10         0.722         0.75         -0.662	2	6 308.737 559	$2.1484 \times 10^{-24}$	0.068 22	0.31	0.821	3.45	-0.524	-0.006 10	(20)	-0.000 047	(9)	+0.498	0.100
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	)	6 310.883 404	$2.8218 \times 10^{-24}$	0.068 60	0.25	0.884	2.34	-0.546	-0.006 69	(16)	-0.000 050	(6)	+0.511	0.100
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3	6 313.002 446	$3.6404 \times 10^{-24}$	0.068 46	0.20	0.804	1.93	-0.571	-0.007 16	(13)	-0.000 070	(5)	+0.533	0.097
P346 317.158 8735.7353 \times 10^{-24}0.068 950.150.7551.30-0.0615-0.006 33(9)-0.000 077(3)+0.572P326 321.204 5238.3778 \times 10^{-24}0.070 080.110.7191.14-0.634-0.006 84(8)-0.000 057(2)+0.592P366 321.204 5238.3778 \times 10^{-24}0.070 0760.100.7700.82-0.662-0.007 16(7)-0.000 065(2)+0.617P266 325.137 3541.1301 \times 10^{-23}0.071 230.100.7860.73-0.671-0.007 05(6)-0.000 065(2)+0.647P266 325.068 871.2993 \times 10^{-23}0.072 630.080.7330.70-0.681-0.006 69(5)-0.000 067(1)+0.646P206 330.821 2421.5035 \times 10^{-23}0.074 130.080.7250.68-0.688-0.006 25(5)-0.000 057(1)+0.664P146 336.242 3841.5843 \times 10^{-23}0.077 600.090.7040.67-0.696-0.005 88(5)-0.000 057(1)+0.664P146 336.242 3841.3584 \times 10^{-23}0.077 600.090.6870.688-0.701-0.005 92(5)-0.000 050(1)+0.664P146 337.909 3591.5091 \times 10^{-23}0.081 580.090.6870.68-0.701-0.005 92(5)-0.000 050(1)+0.663P166 334.64 7871.6045 \times 10^{-23}0.081 68 <t< td=""><td>5</td><td>6 315.094 369</td><td><math>4.6118 \times 10^{-24}</math></td><td>0.068 99</td><td>0.16</td><td>0.813</td><td>1.49</td><td>-0.593</td><td>-0.006 40</td><td>(11)</td><td>-0.000 077</td><td>(4)</td><td>+0.551</td><td>0.095</td></t<>	5	6 315.094 369	$4.6118 \times 10^{-24}$	0.068 99	0.16	0.813	1.49	-0.593	-0.006 40	(11)	-0.000 077	(4)	+0.551	0.095
P226319.1956796.9991 $\times 10^{-24}$ 0.069360.130.7191.14 $-0.634$ $-0.006$ 84(8) $-0.000$ 059(2) $+0.592$ P306321.2045238.3778 $\times 10^{-24}$ 0.070080.110.7430.96 $-0.650$ $-0.007$ 16(7) $-0.000$ 057(2) $+0.606$ P266323.1851589.8306 $\times 10^{-24}$ 0.070760.100.7220.75 $-0.676$ $-0.007$ 05(6) $-0.000$ 062(2) $+0.627$ P266325.1373541.1301 $\times 10^{-23}$ 0.071230.100.7860.73 $-0.671$ $-0.007$ 75(6) $-0.000$ 049(1) $+0.640$ P206330.8212421.535 $\times 10^{-23}$ 0.072630.080.7410.68 $-0.684$ $-0.006$ 25(5) $-0.000$ 069(1) $+0.652$ P186332.6576331.5750 $\times 10^{-23}$ 0.07530.080.7410.667 $-0.696$ $-0.005$ 83(5) $-0.000$ 066(1) $+0.664$ P146336.2423841.5843 $\times 10^{-23}$ 0.0790.0090.6870.68 $-0.701$ $-0.005$ 83(5) $-0.000$ 071(1) $+0.669$ P126337.9903591.5091 $\times 10^{-23}$ 0.081880.09 $-0.709$ $-0.006$ 60 $-0.000$ 07	ŀ	6 317.158 873	$5.7353 \times 10^{-24}$	0.068 95	0.15	0.755	1.30	-0.615	-0.006 33	(9)	-0.000 077	(3)	+0.572	0.102
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	6 319.195 679	$6.9991 \times 10^{-24}$	0.069 36	0.13	0.719	1.14	-0.634	-0.006 84	(8)	-0.000 059	(2)	+0.592	0.114
P286 323.185158 $9.8306 \times 10^{-24}$ 0.070760.100.7700.82 $-0.662$ $-0.006$ 84(6) $-0.000$ 065(2) $+0.617$ P266 325.1373541.1301 \times 10^{-23}0.071230.100.7860.73 $-0.671$ $-0.007$ 05(6) $-0.000$ 062(2) $+0.647$ P246 328.9555871.3993 \times 10^{-23}0.072630.080.7330.70 $-0.681$ $-0.006$ (5) $-0.000$ 057(1) $+0.646$ P206 330.8212421.5035 \times 10^{-23}0.077130.080.7250.68 $-0.0684$ $-0.006$ 25(5) $-0.000$ 067(1) $+0.657$ P166 334.4647871.6045 \times 10^{-23}0.0770.080.080.7110.68 $-0.005$ 88(5) $-0.000$ 071(1) $+0.669$ P146 336.2423841.5843 \times 10^{-23}0.077900.090.6870.68 $-0.701$ $-0.005$ 92(5) $-0.000$ 071(1) $+0.669$ P126 337.903591.5091 \times 10^{-23}0.081580.090.6980.69 $-0.709$ $-0.006$ $-0.000$ 06 $-0.000$ 071(1) $+0.673$ P106 339.7086011.3760 \times 10^{-23}0.081580.090.6980.69 $-0.709$ $-0.006$ $-0.000$ 000(1) $+0.683$ P26 34	)	6 321.204 523	$8.3778 \times 10^{-24}$	0.070 08	0.11	0.743	0.96	-0.650	-0.007 16	(7)	-0.000 057	(2)	+0.606	0.094
P26       6       325.137       354       1.1301×10 <sup>-23</sup> 0.071       23       0.10       0.786       0.73 $-0.671$ $-0.007$ 05       (6) $-0.000$ 062       (2) $+0.642$ P24       6       327.060       897       1.2717×10 <sup>-23</sup> 0.071       74       0.10       0.722       0.75 $-0.676$ $-0.007$ 15 $-0.000$ 057       (1) $+0.646$ P20       6       330.821       24       1.5035×10 <sup>-23</sup> 0.074       13       0.08       0.725       0.68 $-0.6684$ $-0.006$ 55 $-0.000$ 0.667       (1) $+0.6652$ P18       6       332.657       693       1.5750×10 <sup>-23</sup> 0.076       38       0.08       0.711       0.65 $-0.688$ $-0.006$ (5) $-0.000$ 0.71       (1) $+0.6672$ P14       6       332.657       603       1.5750×10 <sup>-23</sup> 0.079       0.09       0.698       0.69 $-0.709$ $-0.000$ 0.71 $-0.000$ 0.71 $+0.673$ P10       6       337.908       601       1.3760×10 <sup>-23</sup> 0.0818 <t< td=""><td>3</td><td>6 323.185 158</td><td>9.8306×10<sup>-24</sup></td><td>0.070 76</td><td>0.10</td><td>0.770</td><td>0.82</td><td>-0.662</td><td>-0.006 84</td><td>(6)</td><td>-0.000 065</td><td>(2)</td><td>+0.617</td><td>0.108</td></t<>	3	6 323.185 158	9.8306×10 <sup>-24</sup>	0.070 76	0.10	0.770	0.82	-0.662	-0.006 84	(6)	-0.000 065	(2)	+0.617	0.108
P246327.0608971.2717 \times 10^{-23}0.071740.100.7220.75 $-0.676$ $-0.007$ 711(5) $-0.000$ 049(1) $+0.640$ P226328.9555871.3993 \times 10^{-23}0.072630.080.7330.70 $-0.681$ $-0.006$ 69(5) $-0.000$ 057(1) $+0.646$ P206332.6576931.5750 \times 10^{-23}0.075130.080.7210.68 $-0.684$ $-0.006$ 25(5) $-0.000$ 066(1) $+0.657$ P166334.4647871.6045 \times 10^{-23}0.075130.080.7410.66 $-0.693$ $-0.006$ 61(5) $-0.000$ 057(1) $+0.664$ P146336.2423841.5843 \times 10^{-23}0.077900.090.6870.68 $-0.701$ $-0.005$ 92(5) $-0.000$ 071(1) $+0.665$ P106337.086011.3760 \times 10^{-23}0.081580.090.6980.69 $-0.709$ $-0.005$ 92(5) $-0.000$ 050(1) $+0.663$ P166534.6243970141.1861 \times 10^{-23}0.083680.100.722 $-0.738$ $-0.004$ 78 $-0.000$ 050(1) $+0.663$ P266543.0555149.4379 \times 10^{-24}0.0860.100.722 $-0.738$ $-0.004$ 78 $-0.000$ 052	5	6 325.137 354	$1.1301 \times 10^{-23}$	0.071 23	0.10	0.786	0.73	-0.671	-0.007 05	(6)	-0.000 062	(2)	+0.627	0.112
P22       6       328.955       587       1.3993 × 10 <sup>-23</sup> 0.072       63       0.08       0.733       0.70 $-0.681$ $-0.006$ 69       (5) $-0.000$ 057       (1) $+0.646$ P20       6       330.821       242       1.5035 × 10 <sup>-23</sup> 0.074       13       0.08       0.725       0.688 $-0.006$ 25       (5) $-0.000$ 0661       (1) $+0.652$ P16       6       334.464       787       1.6045 × 10 <sup>-23</sup> 0.076       38       0.08       0.711       0.668 $-0.006$ 61       (5) $-0.000$ 057       (1) $+0.664$ P14       6       336.242       384       1.5843 × 10 <sup>-23</sup> 0.077       96       0.09       0.704       0.67 $-0.696$ $-0.005$ 88       (5) $-0.000$ 071       (1) $+0.669$ P10       6       337.90       359       1.5091 × 10 <sup>-23</sup> 0.081       88       0.09       0.698 $-0.701$ $-0.005$ 20       (7) $-0.000$ 058       (2) $+0.693$ P26       6       343.055       514       9.	ŀ	6 327.060 897	$1.2717 \times 10^{-23}$	0.071 74	0.10	0.722	0.75	-0.676	-0.007 11	(5)	-0.000 049	(1)	+0.640	0.109
$220$ 6 $330.821$ $242$ $1.5035 \times 10^{-23}$ $0.074$ $13$ $0.08$ $0.725$ $0.68$ $-0.684$ $-0.006$ $25$ $(5)$ $-0.000$ $069$ $(1)$ $+0.652$ $218$ $6$ $332.657$ $693$ $1.5750 \times 10^{-23}$ $0.075$ $13$ $0.08$ $0.741$ $0.65$ $-0.688$ $-0.006$ $33$ $(5)$ $-0.000$ $06661$ $(1)$ $+0.652$ $216$ $6$ $334.464$ $787$ $1.6045 \times 10^{-23}$ $0.077$ $96$ $0.09$ $0.744$ $0.67$ $-0.693$ $-0.006$ $61$ $(5)$ $-0.000$ $077$ $(1)$ $+0.664$ $214$ $6$ $332.425$ $84$ $1.5843 \times 10^{-23}$ $0.077$ $90$ $0.09$ $0.744$ $0.687$ $-0.696$ $-0.005$ $88$ $(5)$ $-0.000$ $070$ $(1)$ $+0.669$ $212$ $6$ $337.903$ $591 \times 10^{-23}$ $0.079$ $90$ $0.09$ $0.687$ $0.68$ $-0.709$ $-0.005$ $92$ $(5)$ $-0.000$ $070$ $(1)$ $+0.675$ $210$ $6$ $334.055$ $514$ $0.481$ $80.90$ $0.09$ $0.698$ $0.69$ $-0.709$ $-0.006$ $90$ $(6)$ $-0.000$ $050$ $(1)$ $+0.683$ $226$ $6$ $341.397$ $014$ $1.1861 \times 10^{-23}$ $0.081$ $88$ $0.10$ $0.782$ $0.72$ $-0.712$ $-0.006$ $90$ $(2)$ $+0.719$ $226$ $6$ $346.282$ $821$ $2.3809$	2	6 328.955 587	$1.3993 \times 10^{-23}$	0.072 63	0.08	0.733	0.70	-0.681	-0.006 69	(5)	-0.000 057	(1)	+0.646	0.122
2186332.6576931.5750 \times 10^{-23}0.075130.080.7410.65 $-0.688$ $-0.006$ 33(5) $-0.000$ 0.066(1) $+0.657$ 2166334.4647871.6045 \times 10^{-23}0.077960.090.7040.67 $-0.693$ $-0.005$ 88(5) $-0.000$ 0.77(1) $+0.664$ 2146336.2423841.5843 \times 10^{-23}0.077960.090.7040.67 $-0.696$ $-0.005$ 88(5) $-0.000$ 071(1) $+0.667$ 2126337.9903591.5071 \times 10^{-23}0.081580.090.6870.68 $-0.701$ $-0.005$ 92(5) $-0.000$ 070(1) $+0.667$ 286341.3970141.1861 \times 10^{-23}0.081580.090.6980.69 $-0.709$ $-0.005$ 42(7) $-0.000$ 058(2) $+0.693$ 266343.0555149.4379 \times 10^{-24}0.086080.100.7820.72 $-0.738$ $-0.004$ 37(8) $-0.000$ 072(2) $+0.711$ 276344.6840326.5732 \times 10^{-24}0.0870.220.6731.59 $-0.770$ $-0.004$ 81(19) $-0.000$ 072(2) $+0.736$ 286351.4100.4560.7251.09 $-0.762$ $-0.004$ 37(38) $-0.000$ 072(8) $+0.727$	)	6 330.821 242	$1.5035 \times 10^{-23}$	0.074 13	0.08	0.725	0.68	-0.684	-0.006 25	(5)	-0.000 069	(1)	+0.652	0.124
P166334.4647871.6045 \times 10^{-23}0.076380.080.7110.68 $-0.693$ $-0.006$ 61(5) $-0.000$ 0.77(1) $+0.664$ P146336.2423841.5843 \times 10^{-23}0.077960.090.7040.67 $-0.696$ $-0.005$ 88(5) $-0.000$ 0.701(1) $+0.669$ P126337.903591.5091 \times 10^{-23}0.079900.090.6870.68 $-0.701$ $-0.005$ 92(5) $-0.000$ 0.701(1) $+0.663$ P106337.905091 \times 10^{-23}0.081580.090.6980.69 $-0.709$ $-0.006$ 09(6) $-0.000$ 050(1) $+0.663$ P266341.3970141.1861 \times 10^{-23}0.085080.100.7520.71 $-0.721$ $-0.005$ 42(7) $-0.000$ 058(2) $+0.693$ P266343.0555149.4379 \times 10^{-24}0.086080.100.7820.72 $-0.738$ $-0.004$ 37(8) $-0.000$ 059(2) $+0.719$ P26344.6280326.5732 \times 10^{-24}0.087020.140.7090.94 $-0.771$ $-0.004$ 37(8) $-0.000$ 071(4) $+0.736$ P26346.6238211.7134 \times 10^{-24}0.089420.160.7251.09 $-0.762$ $-0.004$ 37(	3	6 332.657 693	$1.5750 \times 10^{-23}$	0.075 13	0.08	0.741	0.65	-0.688	-0.006 33	(5)	-0.000 066	(1)	+0.657	0.127
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5	6 334.464 787	$1.6045 \times 10^{-23}$	0.076 38	0.08	0.711	0.68	-0.693	-0.006 61	(5)	-0.000 057	(1)	+0.664	0.144
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	ŀ	6 336.242 384	$1.5843 \times 10^{-23}$	0.077 96	0.09	0.704	0.67	-0.696	-0.005 88	(5)	-0.000 071	(1)	+0.669	0.144
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	6 337.990 359	$1.5091 \times 10^{-23}$	0.079 90	0.09	0.687	0.68	-0.701	-0.005 92	(5)	-0.000 070	(1)	+0.675	0.143
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	)	6 339.708 601	$1.3760 \times 10^{-23}$	0.081 58	0.09	0.698	0.69	-0.709	-0.006 09	(6)	-0.000 050	(1)	+0.683	0.132
$266$ $6\ 343.055\ 514$ $9.4379 \times 10^{-24}$ $0.086\ 08$ $0.10$ $0.782$ $0.72$ $-0.738$ $-0.004\ 37$ $(8)$ $-0.000\ 072$ $(2)$ $+0.701$ $24$ $6\ 344.684\ 032$ $6.5732 \times 10^{-24}$ $0.087\ 02$ $0.14$ $0.709$ $0.94$ $-0.751$ $-0.005\ 26$ $(10)$ $-0.000\ 069$ $(2)$ $+0.719$ $22$ $6\ 346.282\ 512$ $3.3809 \times 10^{-24}$ $0.090\ 36$ $0.22$ $0.673$ $1.59$ $-0.770$ $-0.004\ 81$ $(19)$ $-0.000\ 072$ $(8)$ $+0.748$ $80$ $6\ 348.623\ 821$ $1.7134 \times 10^{-24}$ $0.095\ 75$ $0.41$ $0.646$ $3.00$ $-0.782$ $-0.004\ 37$ $(38)$ $-0.000\ 072$ $(8)$ $+0.748$ $82$ $6\ 350.147\ 049$ $5.0877 \times 10^{-24}$ $0.089\ 42$ $0.16$ $0.725$ $1.09$ $-0.762$ $-0.003\ 18$ $(13)$ $-0.000\ 055$ $(2)$ $+0.718$ $84$ $6\ 351.640\ 149$ $8.2642 \times 10^{-24}$ $0.085\ 97$ $0.12$ $0.701\ 0.83$ $-0.745\ -0.004\ 61$ $(9)$ $-0.000\ 055$ $(2)\ +0.715$ $86$ $6\ 353.103\ 126$ $1.1103 \times 10^{-23}$ $0.083\ 87$ $0.10$ $0.670\ 0.76$ $-0.730\ -0.004\ 73$ $(7)\ -0.0000\ 055$ $(2)\ +0.705$ $88$ $6\ 354.535\ 998$ $1.3490 \times 10^{-23}$ $0.082\ 02$ $0.09$ $0.701\ 0.68$ $-0.720\ -0.004\ 75$ $(6)\ -0.000\ 057\ (1)$ $+0.686$ $812$ $6\ 357.311\ 570\ 1.6613 \times 10^{-23}$ $0.079\ 93\ 0.09$ $0.696\ 0.66\ -0.707\ -0.004\ 30$ $(5)\ -0.000\ 057\ $		6 341.397 014	$1.1861 \times 10^{-23}$	0.083 68	0.10	0.705	0.71	-0.721	-0.005 42	(7)	-0.000 058	(2)	+0.693	0.139
P4 $6\ 344.684\ 032$ $6.5732 \times 10^{-24}$ $0.087\ 02$ $0.14$ $0.709$ $0.94$ $-0.751$ $-0.005\ 26$ $(10)$ $-0.000\ 069$ $(2)$ $+0.719$ P2 $6\ 346.282\ 512$ $3.3809 \times 10^{-24}$ $0.090\ 36$ $0.22$ $0.673$ $1.59$ $-0.770$ $-0.004\ 81$ $(19)$ $-0.000\ 071$ $(4)$ $+0.736$ R0 $6\ 348.623\ 821$ $1.7134 \times 10^{-24}$ $0.095\ 75$ $0.41$ $0.646$ $3.00$ $-0.782$ $-0.004\ 37$ $(38)$ $-0.000\ 072$ $(8)$ $+0.748$ R2 $6\ 350.147\ 049$ $5.0877 \times 10^{-24}$ $0.089\ 42$ $0.16$ $0.725$ $1.09$ $-0.762$ $-0.004\ 37$ $(38)$ $-0.000\ 058$ $(3)$ $+0.727$ R4 $6\ 351.640\ 149$ $8.2642 \times 10^{-24}$ $0.085\ 97$ $0.12$ $0.701$ $0.83$ $-0.745$ $-0.004\ 61$ $(9)$ $-0.000\ 055$ $(2)$ $+0.715$ R6 $6\ 353.103\ 126$ $1.1103 \times 10^{-23}$ $0.083\ 87$ $0.10$ $0.670$ $0.76$ $-0.730$ $-0.004\ 73$ $(7)$ $-0.000\ 055$ $(2)$ $+0.705$ R8 $6\ 354.535\ 998$ $1.3490 \times 10^{-23}$ $0.082\ 02$ $0.09$ $0.701$ $0.68$ $-0.720$ $-0.004\ 55$ $(6)$ $-0.000\ 057$ $(1)\ +0.693$ R10 $6\ 355.938\ 798$ $1.5342 \times 10^{-23}$ $0.079\ 93$ $0.09$ $0.696$ $0.66$ $-0.713\ -0.004\ 59$ $(6)$ $-0.000\ 057$ $(1)\ +0.678$ R14 $6\ 358.654\ 375\ 1.7295 \times 10^{-23}$ $0.076\ 53$ $0.08\ 0.672\ $		6 343.055 514	9.4379×10 <sup>-24</sup>	0.086 08	0.10	0.782	0.72	-0.738	-0.004 37	(8)	-0.000 072	(2)	+0.701	0.127
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		6 344.684 032	$6.5732 \times 10^{-24}$	0.087 02	0.14	0.709	0.94	-0.751	-0.005 26	(10)	-0.000 069	(2)	+0.719	0.115
R0 $6\ 348.623\ 821$ $1.7134 \times 10^{-24}$ $0.095\ 75$ $0.41$ $0.646$ $3.00$ $-0.782$ $-0.004\ 37$ $(38)$ $-0.000\ 072$ $(8)$ $+0.748$ R2 $6\ 350.147\ 049$ $5.0877 \times 10^{-24}$ $0.089\ 42$ $0.16$ $0.725$ $1.09$ $-0.762$ $-0.003\ 18$ $(13)$ $-0.000\ 055$ $(2)$ $+0.715$ R4 $6\ 351.640\ 149$ $8.2642 \times 10^{-24}$ $0.085\ 97$ $0.12$ $0.701$ $0.83$ $-0.745$ $-0.004\ 61$ $(9)$ $-0.000\ 055$ $(2)$ $+0.715$ R6 $6\ 353.103\ 126$ $1.1103 \times 10^{-23}$ $0.083\ 87$ $0.10$ $0.670$ $0.76$ $-0.730$ $-0.004\ 73$ $(7)$ $-0.000\ 055$ $(2)$ $+0.705$ R8 $6\ 354.535\ 998$ $1.3490 \times 10^{-23}$ $0.082\ 02$ $0.09$ $0.701$ $0.68$ $-0.720$ $-0.004\ 73$ $(7)$ $-0.000\ 051$ $(1)$ $+0.693$ R10 $6\ 355.938\ 798$ $1.5342 \times 10^{-23}$ $0.079\ 93$ $0.09$ $0.696$ $0.66$ $-0.713$ $-0.004\ 59$ $(6)$ $-0.000\ 057$ $(1)$ $+0.686$ R12 $6\ 357.311\ 570$ $1.6613 \times 10^{-23}$ $0.077\ 81$ $0.08$ $0.695$ $0.66$ $-0.707$ $-0.004\ 30$ $(5)$ $-0.000\ 053$ $(1)$ $+0.678$ R16 $6\ 359.967\ 286$ $1.7414 \times 10^{-23}$ $0.074\ 85$ $0.08$ $0.672$ $0.68$ $-0.701$ $-0.004\ 98$ $(5)$ $-0.000\ 063$ $(1)\ +0.676$ R18 $6\ 361.250\ 392$ $1.7026 \times 10^{-23}$ $0.073\$		6 346.282 512	$3.3809 \times 10^{-24}$	0.090 36	0.22	0.673	1.59	-0.770	-0.004 81	(19)	-0.000 071	(4)	+0.736	0.129
$R2$ 6 350.147 049 $5.0877 \times 10^{-24}$ $0.089 42$ $0.16$ $0.725$ $1.09$ $-0.762$ $-0.003 18$ $(13)$ $-0.000 068$ $(3)$ $+0.727$ $R4$ 6 351.640 149 $8.2642 \times 10^{-24}$ $0.085 97$ $0.12$ $0.701$ $0.83$ $-0.745$ $-0.004 61$ $(9)$ $-0.000 055$ $(2)$ $+0.715$ $R6$ 6 353.103 126 $1.1103 \times 10^{-23}$ $0.083 87$ $0.10$ $0.670$ $0.76$ $-0.730$ $-0.004 73$ $(7)$ $-0.000 055$ $(2)$ $+0.705$ $R6$ 6 354.535 998 $1.3490 \times 10^{-23}$ $0.082 02$ $0.09$ $0.701$ $0.68$ $-0.720$ $-0.004 55$ $(6)$ $-0.000 051$ $(1)$ $+0.693$ $R10$ 6 355.938 798 $1.5342 \times 10^{-23}$ $0.079 93$ $0.09$ $0.696$ $0.66$ $-0.713$ $-0.004 59$ $(6)$ $-0.000 057$ $(1)$ $+0.686$ $R12$ $6 357.311 570$ $1.6613 \times 10^{-23}$ $0.077 81$ $0.08$ $0.695$ $0.66$ $-0.707$ $-0.004 30$ $(5)$ $-0.000 063$ $(1)$ $+0.678$ $R14$ $6 358.654 375$ $1.7295 \times 10^{-23}$ $0.076 53$ $0.08$ $0.672$ $0.68$ $-0.701$ $-0.004 92$ $(5)$ $-0.000 063$ $(1)$ $+0.676$ $R16$ $6 359.967 286$ $1.7414 \times 10^{-23}$ $0.074 85$ $0.08$ $0.672$ $0.68$ $-0.701$ $-0.004 98$ $(5)$ $-0.000 068$ $(1)$ $+0.676$ $R18$ $6 361.250 392$ $1.7026 \times 10^{-23}$ $0.072 82$ $0.08$ <t< td=""><td></td><td>6 348.623 821</td><td><math>1.7134 \times 10^{-24}</math></td><td>0.095 75</td><td>0.41</td><td>0.646</td><td>3.00</td><td>-0.782</td><td>-0.004 37</td><td>(38)</td><td>-0.000 072</td><td>(8)</td><td>+0.748</td><td>0.097</td></t<>		6 348.623 821	$1.7134 \times 10^{-24}$	0.095 75	0.41	0.646	3.00	-0.782	-0.004 37	(38)	-0.000 072	(8)	+0.748	0.097
R46 351.640 149 $8.2642 \times 10^{-24}$ 0.085 970.120.7010.83-0.745-0.004 61(9)-0.000 055(2)+0.715R66 353.103 1261.1103 \times 10^{-23}0.083 870.100.6700.76-0.730-0.004 73(7)-0.000055(2)+0.705R86 354.535 9981.3490 \times 10^{-23}0.082 020.090.7010.68-0.720-0.004 55(6)-0.000 051(1)+0.693R106 355.938 7981.5342 \times 10^{-23}0.079 930.090.6960.66-0.713-0.004 59(6)-0.000 057(1)+0.686R126 357.311 5701.6613 \times 10^{-23}0.077 810.080.6950.66-0.707-0.004 30(5)-0.000 063(1)+0.680R146 358.654 3751.7295 \times 10^{-23}0.076 530.080.6720.68-0.701-0.004 92(5)-0.000 063(1)+0.678R166 359.967 2861.7414 $\times 10^{-23}$ 0.074 850.080.6530.72-0.699-0.005 60(5)-0.000 068(1)+0.674R206 362.503 7941.6211 $\times 10^{-23}$ 0.072 820.080.6930.6930.6930.6930.6930.6930.692(5)-0.005 60(5)-0.000 065(1)+0.670		6 350.147 049	$5.0877 \times 10^{-24}$	0.089 42	0.16	0.725	1.09	-0.762	-0.003 18	(13)	-0.000 068	(3)	+0.727	0.122
R6 $6\ 353.103\ 126$ $1.1103 \times 10^{-23}$ $0.083\ 87$ $0.10$ $0.670$ $0.76$ $-0.730$ $-0.004\ 73$ $(7)$ $-0.000055$ $(2)$ $+0.705$ R8 $6\ 354.535\ 998$ $1.3490 \times 10^{-23}$ $0.082\ 02$ $0.09$ $0.701$ $0.68$ $-0.720$ $-0.004\ 55$ $(6)$ $-0.000\ 051$ $(1)$ $+0.693$ R10 $6\ 355.938\ 798$ $1.5342 \times 10^{-23}$ $0.079\ 93$ $0.09$ $0.696$ $0.66$ $-0.713$ $-0.004\ 59$ $(6)$ $-0.000\ 057$ $(1)$ $+0.686$ R12 $6\ 357.311\ 570$ $1.6613 \times 10^{-23}$ $0.077\ 81$ $0.08$ $0.695$ $0.66$ $-0.707$ $-0.004\ 30$ $(5)$ $-0.000\ 070$ $(1)$ $+0.686$ R14 $6\ 358.654\ 375$ $1.7295 \times 10^{-23}$ $0.076\ 53$ $0.08$ $0.672$ $0.68$ $-0.701$ $-0.004\ 92$ $(5)$ $-0.000\ 063$ $(1)$ $+0.678$ R16 $6\ 359.967\ 286$ $1.7414 \times 10^{-23}$ $0.074\ 85$ $0.08$ $0.672$ $0.68$ $-0.701$ $-0.004\ 98$ $(5)$ $-0.000\ 083$ $(1)$ $+0.676$ R18 $6\ 361.250\ 392$ $1.7026 \times 10^{-23}$ $0.072\ 82$ $0.08$ $0.693$ $0.69$ $-0.700$ $-0.006\ 45$ $(5)$ $-0.000\ 068$ $(1)$ $+0.670$ R20 $6\ 362.503\ 794$ $1.6211 \times 10^{-23}$ $0.072\ 82$ $0.08$ $0.693$ $0.69$ $-0.700$ $-0.006\ 45$ $(5)$ $-0.000\ 065$ $(1)$ $+0.670$		6 351.640 149	$8.2642 \times 10^{-24}$	0.085 97	0.12	0.701	0.83	-0.745	-0.004 61	(9)	-0.000 055	(2)	+0.715	0.122
R8 $6\ 354.535\ 998$ $1.3490 \times 10^{-23}$ $0.082\ 02$ $0.09$ $0.701$ $0.68$ $-0.720$ $-0.004\ 55$ $(6)$ $-0.000\ 051$ $(1)$ $+0.693$ R10 $6\ 355.938\ 798$ $1.5342 \times 10^{-23}$ $0.079\ 93$ $0.09$ $0.696$ $0.66$ $-0.713$ $-0.004\ 59$ $(6)$ $-0.000\ 057$ $(1)$ $+0.686$ R12 $6\ 357.311\ 570$ $1.6613 \times 10^{-23}$ $0.077\ 81$ $0.08$ $0.695$ $0.66$ $-0.707$ $-0.004\ 30$ $(5)$ $-0.000\ 070$ $(1)$ $+0.686$ R14 $6\ 358.654\ 375$ $1.7295 \times 10^{-23}$ $0.076\ 53$ $0.08$ $0.695$ $0.66$ $-0.704$ $-0.004\ 92$ $(5)$ $-0.000\ 063$ $(1)$ $+0.678$ R16 $6\ 359.967\ 286$ $1.7414 \times 10^{-23}$ $0.074\ 85$ $0.08$ $0.672$ $0.68$ $-0.701$ $-0.004\ 98$ $(5)$ $-0.000\ 083$ $(1)$ $+0.676$ R18 $6\ 361.250\ 392$ $1.7026 \times 10^{-23}$ $0.072\ 82$ $0.08$ $0.693$ $0.69$ $-0.700$ $-0.006\ 45$ $(5)$ $-0.000\ 068$ $(1)$ $+0.670$ R20 $6\ 362.503\ 794$ $1.6211 \times 10^{-23}$ $0.072\ 82$ $0.08$ $0.693$ $0.69$ $-0.700$ $-0.006\ 45$ $(5)$ $-0.000\ 065$ $(1)$ $+0.670$		6 353.103 126	$1.1103 \times 10^{-23}$	0.083 87	0.10	0.670	0.76	-0.730	-0.004 73	(7)	-0.000055	(2)	+0.705	0.128
R10 $6\ 355.938\ 798$ $1.5342 \times 10^{-23}$ $0.079\ 93$ $0.09$ $0.696$ $0.666$ $-0.713$ $-0.004\ 59$ $(6)$ $-0.000\ 057$ $(1)$ $+0.686$ R12 $6\ 357.311\ 570$ $1.6613 \times 10^{-23}$ $0.077\ 81$ $0.08$ $0.695$ $0.66$ $-0.707$ $-0.004\ 30$ $(5)$ $-0.000\ 070$ $(1)$ $+0.686$ R14 $6\ 358.654\ 375$ $1.7295 \times 10^{-23}$ $0.076\ 53$ $0.08$ $0.695$ $0.66$ $-0.707$ $-0.004\ 92$ $(5)$ $-0.000\ 063$ $(1)$ $+0.678$ R16 $6\ 359.967\ 286$ $1.7414 \times 10^{-23}$ $0.074\ 85$ $0.08$ $0.672$ $0.68$ $-0.701$ $-0.004\ 98$ $(5)$ $-0.000\ 083$ $(1)$ $+0.676$ R18 $6\ 361.250\ 392$ $1.7026 \times 10^{-23}$ $0.073\ 55$ $0.08$ $0.653$ $0.72$ $-0.699$ $-0.005\ 60$ $(5)$ $-0.000\ 068$ $(1)$ $+0.674$ R20 $6\ 362.503\ 794$ $1.6211 \times 10^{-23}$ $0.072\ 82$ $0.08$ $0.693$ $0.69$ $-0.700$ $-0.006\ 45$ $(5)$ $-0.000\ 065$ $(1)$ $+0.670$		6 354.535 998	$1.3490 \times 10^{-23}$	0.082 02	0.09	0.701	0.68	-0.720	-0.004 55	(6)	-0.000 051	(1)	+0.693	0.131
R12 $6\ 357.311\ 570$ $1.6613 \times 10^{-23}$ $0.077\ 81$ $0.08$ $0.695$ $0.66$ $-0.707$ $-0.004\ 30$ $(5)$ $-0.000\ 070$ $(1)$ $+0.680$ R14 $6\ 358.654\ 375$ $1.7295 \times 10^{-23}$ $0.076\ 53$ $0.08$ $0.680$ $0.67$ $-0.704$ $-0.004\ 92$ $(5)$ $-0.000\ 063$ $(1)$ $+0.678$ R16 $6\ 359.967\ 286$ $1.7414 \times 10^{-23}$ $0.074\ 85$ $0.08$ $0.672$ $0.68$ $-0.701$ $-0.004\ 98$ $(5)$ $-0.000\ 083$ $(1)$ $+0.676$ R18 $6\ 361.250\ 392$ $1.7026 \times 10^{-23}$ $0.073\ 55$ $0.08$ $0.653$ $0.72$ $-0.699$ $-0.005\ 60$ $(5)$ $-0.000\ 068$ $(1)$ $+0.674$ R20 $6\ 362.503\ 794$ $1.6211 \times 10^{-23}$ $0.072\ 82$ $0.08$ $0.693$ $0.69$ $-0.700$ $-0.006\ 45$ $(5)$ $-0.000\ 065$ $(1)$ $+0.670$	)	6 355.938 798	$1.5342 \times 10^{-23}$	0.079 93	0.09	0.696	0.66	-0.713	-0.004 59	(6)	-0.000 057	(1)	+0.686	0.136
R14       6 358.654 375 $1.7295 \times 10^{-23}$ 0.076 53       0.08       0.680       0.67 $-0.704$ $-0.004 92$ (5) $-0.000 063$ (1) $+0.678$ R16       6 359.967 286 $1.7414 \times 10^{-23}$ 0.074 85       0.08       0.672       0.68 $-0.701$ $-0.004 92$ (5) $-0.000 063$ (1) $+0.678$ R18       6 361.250 392 $1.7026 \times 10^{-23}$ 0.073 55       0.08       0.653       0.72 $-0.699$ $-0.005 60$ (5) $-0.000 068$ (1) $+0.674$ R20       6 362.503 794 $1.6211 \times 10^{-23}$ 0.072 82       0.08       0.693       0.69 $-0.700$ $-0.006 45$ (5) $-0.000 065$ (1) $+0.670$	2	6 357.311 570	$1.6613 \times 10^{-23}$	0.077 81	0.08	0.695	0.66	-0.707	-0.004 30	(5)	-0.000 070	(1)	+0.680	0.132
R16       6 359.967 286 $1.7414 \times 10^{-23}$ $0.074 85$ $0.08$ $0.672$ $0.68$ $-0.701$ $-0.004 98$ $(5)$ $-0.000 083$ $(1)$ $+0.676$ R18       6 361.250 392 $1.7026 \times 10^{-23}$ $0.073 55$ $0.08$ $0.653$ $0.72$ $-0.699$ $-0.005 60$ $(5)$ $-0.000 083$ $(1)$ $+0.674$ R20       6 362.503 794 $1.6211 \times 10^{-23}$ $0.072 82$ $0.08$ $0.693$ $0.69$ $-0.700$ $-0.006 45$ $(5)$ $-0.000 065$ $(1)$ $+0.670$	4	6 358.654 375	$1.7295 \times 10^{-23}$	0.076 53	0.08	0.680	0.67	-0.704	-0.004 92	(5)	-0.000 063	(1)	+0.678	0.134
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5	6 359.967 286	$1.7414 \times 10^{-23}$	0.074 85	0.08	0.672	0.68	-0.701	-0.004 98	(5)	-0.000 083	(1)	+0.676	0.117
$320 + 6.362.503.794 + 1.6211 \times 10^{-23} + 0.072.82 + 0.08 + 0.693 + 0.693 + 0.693 + 0.700 + 0.006.45 + (5) + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.670 + 0.000.065 + (1) + 0.000.000.065 + (1) + 0.000.000.0000, 000.0000, 000.000.000, 000.000, 000.000, 000.000, 0$	8	6 361.250 392	$1.7026 \times 10^{-23}$	0.073 55	0.08	0.653	0.72	-0.699	-0.005 60	(5)	-0.000 068	(1)	+0.674	0.124
	)	6 362.503 794	$1.6211 \times 10^{-23}$	0.072 82	0.08	0.693	0.69	-0.700	-0.006 45	(5)	-0.000 065	(1)	+0.670	0.116
$R22  6  363.727  610  1.5060 \times 10^{-23}  0.071  91  0.08  0.705  0.71  -0.701  -0.006  11  (5)  -0.000  061  (1)  +0.668  0.705  0.71  -0.701  -0.006  11  (5)  -0.000  061  (1)  +0.668  0.705  0.71  -0.701  -0.006  11  (5)  -0.000  061  (1)  +0.668  0.705  0.71  -0.701  -0.006  0.70  0.705  0.71  -0.701  $	2	6 363.727 610	$1.5060 \times 10^{-23}$	0.071 91	0.08	0.705	0.71	-0.701	-0.006 11	(5)	-0.000 061	(1)	+0.668	0.123
$R24  6  364.921  972  1.3673 \times 10^{-22}  0.071  31  0.10  0.712  0.73  -0.699  -0.005  92  (5)  -0.000  062  (1)  +0.663  -0.699  -0.005  92  (5)  -0.000  062  (1)  +0.663  -0.699  -0.005  92  (5)  -0.000  062  (1)  +0.663  -0.699  -0.005  92  (5)  -0.000  062  (1)  +0.663  -0.699  -0.005  92  (5)  -0.000  062  (1)  +0.663  -0.699  -0.005  92  (5)  -0.000  062  (1)  +0.663  -0.699  -0.005  92  (5)  -0.000  062  (1)  +0.663  -0.699  -0.005  92  (5)  -0.000  062  (1)  +0.663  -0.699  -0.005  92  (5)  -0.000  062  (1)  +0.663  -0.699  -0.005  92  (5)  -0.000  062  (1)  +0.663  -0.699  -0.005  92  (5)  -0.000  062  (1)  +0.663  -0.699  -0.005  92  (5)  -0.000  062  (1)  +0.663  -0.699  -0.005  92  (5)  -0.000  062  (1)  +0.663  -0.699  -0.005  92  (5)  -0.000  062  (1)  +0.663  -0.699  -0.005  -0.$	4	6 364.921 972	$1.3673 \times 10^{-22}$	0.071 31	0.10	0.712	0.73	-0.699	-0.005 92	(5)	-0.000 062	(1)	+0.663	0.111
$R26  6  366.087  028  1.2146 \times 10^{-22}  0.070  01  0.10  0.703  0.78  -0.696  -0.006  36  (6)  -0.000  052  (1)  +0.657  -0.696  -0.006  36  (6)  -0.000  052  (1)  +0.657  -0.696  -0.006  36  (6)  -0.000  052  (1)  +0.657  -0.696  -0.006  36  (6)  -0.000  052  (1)  +0.657  -0.696  -0.006  36  (6)  -0.000  052  (1)  +0.657  -0.696  -0.006  36  (6)  -0.000  052  (1)  +0.657  -0.696  -0.006  36  (6)  -0.000  052  (1)  +0.657  -0.696  -0.006  36  (6)  -0.000  052  (1)  +0.657  -0.696  -0.006  -0.006  -0.000  052  (1)  +0.657  -0.696  -0.006  -0.$	5	6 366.087 028	$1.2146 \times 10^{-22}$	0.070 01	0.10	0.703	0.78	-0.696	-0.006 36	(6)	-0.000 052	(1)	+0.657	0.111
R28 $6\ 367.222\ 941$ $1.0566 \times 10^{-23}$ $0.070\ 73$ $0.10$ $0.790$ $0.76$ $-0.692$ $-0.005\ 74$ $(6)$ $-0.000\ 086$ $(1)$ $+0.645$	8	6 367.222 941	$1.0566 \times 10^{-23}$	0.070 73	0.10	0.790	0.76	-0.692	-0.005 74	(6)	-0.000 086	(1)	+0.645	0.112

Line	Position <sup>a</sup>	Intensity <sup>b</sup>	$b_{\mathrm{L}}{}^{0}(\mathrm{air})^{c}$	Unc. (%)	$n^d$	Unc. (%)	$\rho_{b-n}$	$\delta^0(air)^c$	Unc.	$\delta'(air)^e$	Unc.	$\rho_{\delta^0\delta'}$	$\mathrm{SD}^{df}$
R30	6 368.329 890	$9.0073 \times 10^{-24}$	0.070 42	0.11	0.808	0.82	-0.681	-0.006 60	(2)	-0.000 063	(1)	+0.630	0.101
R32	6 369.408 071	$7.5300 \times 10^{-24}$	0.069 45	0.13	0.834	06.0	-0.667	-0.006 68	(2)	-0.000052	(2)	+0.614	0.099
R34	6 370.457 696	$6.1759 \times 10^{-24}$	0.068 89	0.15	0.819	1.09	-0.650	-0.007 13	(6)	$-0.000\ 027$	(3)	+0.600	0.092
R36	6 371.478 994	$4.9716 \times 10^{-24}$	0.068 50	0.16	0.659	1.68	-0.634	-0.007 15	(10)	-0.000035	(3)	+0.596	$0.121^{g}$
R38	6 372.472 213	$3.9295 \times 10^{-24}$	0.067 98	0.19	0.733	1.88	-0.610	-0.006 46	(12)	$-0.000\ 080$	(4)	+0.571	0.088
R40	6 373.437 618	$3.0503 \times 10^{-24}$	0.068 98	0.23	0.821	2.21	-0.583	-0.007 21	(15)	$-0.000\ 051$	(5)	+0.545	$0.112^{g}$
R42	6 374.375 493	$2.3261 \times 10^{-24}$	0.067 36	0.30	0.771	3.17	-0.560	-0.006 12	(19)	$-0.000\ 031$	(2)	+0.529	0.100
R44	6 375.286 142	$1.7430  imes 10^{-24}$	0.068 43	0.38	0.782	4.40	-0.538	-0.006 67	(25)	-0.000085	(10)	+0.513	0.100
R46	6 376.169 887	$1.2835 \times 10^{-24}$	0.066 92	0.43	0.770	(F)		-0.006 69	(29)	$0.000 \ 000$	(F)		0.100
R48	6 377.027 072	$9.2908 \times 10^{-25}$	0.068 26	0.59	0.760	(F)		-0.00608	(40)	$0.000 \ 000$	(F)		0.100
R50	6 377.858 062	$6.6115 \times 10^{-25}$	0.067 33	0.83	0.760	(F)		-0.000 62	(55)	$0.000 \ 000$	(F)		0.100
<sup>a</sup> Zero	pressure line positio	ns in cm <sup>-1</sup> are calcul <sup>2</sup>	ated using the ro	ovibrational con	nstants repo	rted in ref. 22.	They are list	ed for convenie	nce to the r	eader.			

Table 4 (concluded)

The intensities in cm/molecule<sup>-1</sup> at 296 K for a natural CO<sub>2</sub> sample (<sup>16</sup>O<sup>12</sup>C<sup>16</sup>O fraction of 0.9842) are calculated using the vibrational band intensity and Herman–Wallis factors in ref. Measured air-broadened Lorentz width and pressure-shift coefficients are in cm<sup>-1</sup> atm<sup>-1</sup> at 296 K

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<sup>d</sup>Temperature dependence exponents of air-broadened half-width coefficients as well as speed dependence (SD) parameters are unitless

"The temperature dependent coefficients of air-shift coefficients are in  $cm^{-1}$  atm<sup>-1</sup> K<sup>-1</sup>. <sup>5</sup>SD parameters are the same as in ref. 22 and were fixed in the present least-squares solution.

Retained in the fit.

and Herman–Wallis coefficients), self- and air-line mixing coefficients were fixed to the appropriate values reported in refs. 21 and 22, respectively, for the two bands. However, the individual air-broadened half-width coefficients, air-induced pressure shift coefficients, and their temperature dependences were adjusted. The resulting line parameters are listed in Tables 3 and 4 along with their uncertainties (described later). The line positions and intensities are the same as in refs. 21 and 22 and are shown here for identification and convenience of the readers.

The final multispectrum fit for the region of the  $30013 \leftarrow 00001$  band is shown in Fig. 1, where the observed line shapes are modeled with speed-dependent Voigt profiles and asymmetric line mixing (off-diagonal relaxation matrix). The bottom panel (Fig. 1c) displays all 39 experimental spectra. The other two panels demonstrate that proper weighting schemes are employed by showing the weighted obs. – calcd. residuals for (Fig. 1*a*) all 39 (room and cold) spectra. In Fig. 2 is a short spectral interval from Fig. 1 replotted to show in detail the 3 transitions, R16 to R20.

# 4. Theoretical calculations

The half-width coefficients of self-,  $O_2$ - and  $N_2$ -perturbed carbon dioxide were modeled using semiclassical calculations based on the real components of the Robert–Bonamy theory [30] (RRB). In this theoretical approach we can express the half-width coefficient,  $\gamma$ , (which corresponds to  $b_L^0$ , used elsewhere in this article) of any given rovibrational transition  $f \leftarrow i$  as the real part of the corresponding diagonal element of the complex relaxation matrix. In this semiclassical framework, the half-width coefficients can be computed using the elements of the Liouville scattering matrix [31, 32],

$$\gamma_{i \leftarrow f} = \frac{n_2}{2\pi c} \left\langle v \left[ 1 - e^{-^R S_2\left(f, i, J_2, v, b\right)} \right] \right\rangle_{v, b, J}$$
(7)

where  $n_2$  is the number density of perturbers and  $\langle \rangle_{v,b,J}$  is an average over all possible molecular trajectories of impact parameter b, initial relative velocity v, and the initial rotational quantum number  $J_2$  of the collision partner. In (7),  $^{R}S_{2}$  is the real part of the second-order term in the expansion of the scattering matrix. The size of the  ${}^{R}S_{2}$  term depends on (i), the rovibrational states involved in the transition and associated collision induced jumps from these energy level, (ii), the intermolecular potential, and (iii), the collision dynamics. Not present in (7) are the vibrational dephasing term,  $S_1$ , which appears only for transitions where there is a change in the vibrational state, and the imaginary part of the  $S_2$  term. The potential leading to  $S_1$  is written in terms of the isotropic induction and London dispersion interactions that depend on the vibrational dependence of the dipole moment and the polarizability of the radiating molecule. Since these parameters are not available for  $CO_2$ , the  $S_1$  term has been omitted from the theoretical calculation. The effect of the imaginary part of  $S_2$  will be investigated in a future study.

The intermolecular potential used in our calculations has both an electrostatic component (quadrupole moments of  $CO_2$  with the quadrupole moment of N<sub>2</sub>, O<sub>2</sub>, or  $CO_2$ ) and an atom-atom component based on parameters published by Rosenmann et al. [33]. The expression of Sack [34] ex-

**Fig. 1.** Multispectrum fit of all 39 spectra in the 6120–6280 cm<sup>-1</sup> region of  ${}^{12}C^{16}O_2$  (30013 $\leftarrow$ 00001 and all other bands appearing in the fitted interval) using a Voigt profile modified with speed dependence and line mixing via relaxation matrix. (*a*) Weighted fit residuals (obs. – calcd. on an expanded scale) from all spectra. (*b*) Weighted fit residuals for the 13 room temperature spectra recorded at Kitt Peak and included in (*a*). (*c*) The 39 experimental spectra. The different colors correspond to various gas sample temperatures (black = room temperature Kitt Peak spectra, all other data are from NRC: red (296 K), light green (274 K), blue (259 K), dark green (244 K), cyan (234 K), pink (219 K), and dark cyan (215 K).



panded to the fourth order was used to express the atomatom distance  $r_{ij}$  in terms of the center of mass separation R. The Robert and Bonamy's second-order in time approximation is used to describe the dynamics of the collisional processes.

All the molecular parameters for the CO<sub>2</sub>-X (where X is N<sub>2</sub>, O<sub>2</sub>, or CO<sub>2</sub>) systems used in the calculations are taken from the work of Rosenmann et al. [33]. The molecular trajectories are assumed to be curved (parabolic) rather than straight lines [30]. In this approximation, the interaction potential is used to determine the distance, effective velocity, and force at closest approach. To simplify the trajectory calculations the isotropic part of the atom–atom expansion is approximated by a single isotropic Lennard–Jones 6–12 potential where the parameters are from ref. 33. The reduced

matrix elements of the radiating and perturbing molecules are evaluated using wave functions in the symmetric top basis, and the energies are given in terms of the molecular rotational constants.

The calculation of N<sub>2</sub>-, O<sub>2</sub>-, and self-broadened half-width coefficients were made for P-, Q-, and R-branch transitions of CO<sub>2</sub> for |m| values from 1 to 121, where m = -J'' for P-branch transitions, m = J'' + 1 for R-branch transitions, and m = 0 for the Q1 to Q121 transitions. The half-width coefficients were calculated at 200 K, 250 K, 296 K, 300 K, and 500 K by using the Gaussian method of moments to perform the averaging over the Maxwell–Boltzmann distribution of velocities. The air-broadened half-width coefficients at each temperature were determined assuming binary collisions and Dalton's law of partial pressures,

**Fig. 2.** An expanded portion from Fig. 1 illustrating the multispectrum fit for R16 to R20 transitions of the  $30013 \leftarrow 00001$  band. (*a*) Weighted fit residual for all 39 spectra. (*b*) Weighted fit residual for the 13 Kitt Peak room temperature spectra. (*c*) The 39 experimental spectra.



$$\gamma_{\rm air} = 0.79 \times \gamma_{N_2} + 0.21 \times \gamma_{O_2} \tag{8}$$

For atmospheric applications, both the temperature and pressure dependence of half-width coefficients are required on a line by line basis. The temperature scaling law [35] can be used to determine the temperature dependence exponents n of the half-width coefficient,

$$\gamma(T) = \gamma(T_0) \left\{ \frac{T_0}{T} \right\}^n \tag{9}$$

In recent years it has been shown that for some gas-perturber systems, such as foreign-broadened water, this scaling law does not apply [25–37]. However as seen later, this does not seem to be the case for the present data.

The theoretical values of the temperature dependence exponents *n* were determined for each transition by a least-squares fits of  $\ln[\gamma(T)/\gamma(T_0)]$  vs.  $\ln[T_0/T]$  over the tempera-

ture range 200 to 500 K. We were also able to determine the error in the temperature dependence exponents using the half-width values at any two of the five temperatures studied. This procedure provided ten 2-point temperature dependence exponents. The difference between each 2-point temperature dependence exponent and the 5-point fit value is calculated. The errors quoted in this work are the largest of these differences and believed to be more reliable than the statistical values taken from the fit. Table 5 gives the range of theoretical values for  $\gamma$  at 296 K and *n*.

### 5. Discussion of results

We performed a number of comparisons to assess the quality of our retrieved broadening coefficients (air-broadened widths, pressure shifts, and their temperature dependences). First, we noted that corresponding measurements for the two bands were in very close agreement for transitions

**Table 5.** Calculated minimum and maximum values for the Lorentz halfwidth coefficients and temperature dependence exponents for  $CO_2$  broadened by N<sub>2</sub>, O<sub>2</sub>, air, and  $CO_2$ .

System	$\gamma_{min}~(cm^{-1}~atm^{-1})$	$\gamma_{max}~(cm^{-1}~atm^{-1})$	$n_{\min}$	n <sub>max</sub>
CO <sub>2</sub> -N <sub>2</sub>	0.0496	0.0965	0.398	0.771
CO <sub>2</sub> -O <sub>2</sub>	0.0362	0.0728	0.185	0.787
CO <sub>2</sub> -air	0.0468	0.0915	0.364	0.769
CO <sub>2</sub> -CO <sub>2</sub>	0.0493	0.1239	0.488	0.748

**Fig. 3.** Experimental air-broadening coefficients for the  $30013 \leftarrow 00001$  and  $30012 \leftarrow 00001$  bands of  ${}^{12}C{}^{16}O_2$  retrieved using constrained multispectrum fits. The horizontal axis is *m*, equal to -J'' for P-branch lines and J''+1 for R-branch lines. (*a*) Half-width coefficients. (*b*) Percentage differences of averaged half-width coefficients to corresponding values in the  $30012 \leftarrow 00001$  band. (*c*) Pressure shift coefficients. (*d*) Percentage differences of averaged air-induced shift coefficients to corresponding values in the  $30012 \leftarrow 00001$  band. For simplicity, the percentage differences in (*b*) and (*d*) are computed using coefficients from  $30012 \leftarrow 00001$  band, because the values for the other band give only mirror images.



**Fig. 4.** Similar to Fig. 3, the temperature dependence exponents for air-broadening coefficients for the  $30013 \leftarrow 00001$  and  $30012 \leftarrow 00001$  bands of  ${}^{12}C^{16}O_2$  retrieved using constrained multispectrum fits. (*a*) *n* for half-widths. (*b*) Percentage differences from averaged *n* minus  $30012 \leftarrow 00001$  values. (*c*) Temperature dependent coefficients ( $\delta'$ ) of air-induced shift coefficients. (*d*) Percentage differences from averaged  $\delta'$  minus  $30012 \leftarrow 00001$  measurements.



with the same rotational quantum assignment ( $\Delta J, J''$ ). This is demonstrated in Figs. 3a and 3c and 4a and 4c, where the air-broadening measurements (widths, shifts, and their temperature dependences) for  $30012 \leftarrow 00001$  and  $30013 \leftarrow$ 00001 are plotted together as a function of m (where m =-J'' for P-branch lines and J''+1 for R-branch lines). Also, for each m value, we averaged the coefficients for transitions in the  $30012 \leftarrow 00001$  and  $30013 \leftarrow 00001$  vibrational bands. The percentage differences between the average and the individual measurements are displayed in panels (b) and (d) of Figs. 3 and 4. For the air-broadened widths and pressure shifts in Figs. 3a and 3c, the mean percentage differences are, respectively, +0.2(0.6) and +1(7), while for the temperature dependence coefficients of air-broadened widths and pressure shifts in Figs. 4a and 4c, the mean percentage differences are, respectively, +0.05(2.27) and +1(10). The larger scatter observed in panels (b) and (d) of Figs. 3 and 4 for high values of |m| was attributed to the weakness of the absorptions in the fitted data. As seen previously [e.g., 6, 21–24], the air-broadened half-width coefficients have minimal vibrational dependence, whereas the air-induced shift coefficients in the  $30012 \leftarrow 00001$  band are slightly larger than those for the  $30013 \leftarrow 00001$  band.

Encouraged by the excellent agreement seen in Figs. 3 and 4, we averaged the pairs of observed values with the same rotational quantum assignment in the two bands. The values for all four types of broadening coefficients (widths, shifts, and the temperature dependence of widths and shifts) are presented in Table 6, along with their respective percentage differences.

In Fig. 5, we compare the mean observed values from Table 6 and the theoretically predicted air-broadened halfwidth coefficients and their temperature dependences as a function of |m|. The error bars are plotted for the observed values, but these are usually smaller than the plot symbols. Note that P-branch values are of even |m|, while R-branch

Line	Width	RMS (%)	п	RMS (%)	Shift (unc.)	δ′	Error (%)
P(54)	0.0652	3.1			-5.34(74)		
P(52)	0.0702	1.9			-4.40(56)		
P(50)	0.0681	-0.4			-5.49(39)		
P(48)	0.0686	0.6			-6.93(27)		
P(46)	0.0678	0.5			-5.70(20)		
P(44)	0.0673	-0.8			-6.88(16)		
P(42)	0.0680	0.3	0.796	3.2	-6.50(13)	-5.13	-9.1
P(40)	0.0685	0.1	0.880	0.5	-6.40(10)	-6.20	-19.2
P(38)	0.0685	0.0	0.790	1.8	-7.09(08)	-6.39	8.2
P(36)	0.0689	0.1	0.806	0.9	-6.55(07)	-7.89	-1.9
P(34)	0.0691	-0.3	0.732	3.2	-6.44(06)	-6.53	17.5
P(32)	0.0693	0.0	0.737	-2.4	-6.90(04)	-4.99	19.0
P(30)	0.0703	-0.3	0.756	-1.7	-7.00(04)	-5.36	5.6
P(28)	0.0707	0.1	0.766	0.5	-7.00(04)	-5 79	11.9
P(26)	0.0710	0.3	0.752	4 5	-7.01(03)	-6.00	3.4
P(24)	0.0720	-0.4	0.723	-0.2	-6.89(04)	_4.85	1.2
P(22)	0.0727	_0.1	0.726	0.2	-6.78(03)	-5.75	_0.9
P(20)	0.0727	-0.1	0.720	1.5	-6.40(03)	-6.42	6.8
P(18)	0.0742	0.3	0.714	1.9	-0.40(03)	6 36	0.8
P(16)	0.0754	-0.3	0.727	0.8	6 62(03)	-0.50	4.4
P(14)	0.0702	0.2	0.700	0.0	-0.02(03) 5 00(03)	-5.00	7.9
D(12)	0.0708	0.0	0.705	-0.1	-5.99(03)	-0.58	0.4
P(10)	0.0798	0.1	0.082	0.8	-5.95(04)	-0.94	0.4 8.6
$\mathbf{D}(\mathbf{g})$	0.0810	0.0	0.700	-1.0	-0.03(04)	-4.03	8.0 4.4
$\mathbf{D}(6)$	0.0857	-0.1	0.712	-1.0	-3.40(04)	-5.59	4.4
P(0)	0.0800	0.1	0.600	-2.2	-4.78(03)	-0.58	12.0
$\Gamma(4)$ $\Gamma(2)$	0.0071	-0.1	0.098	1.0	-4.70(07)	-7.09	-3.2
$\Gamma(2)$ $\mathbf{P}(0)$	0.0905	-0.1	0.080	-1.9	-4.60(12)	-0.47	10.1
$\mathbf{K}(0)$	0.0932	0.5	0.009	-5.0	-3.08(24)	-/.0/	-0.0
$\mathbf{K}(2)$ $\mathbf{P}(4)$	0.0895	-0.1	0.724	0.1	-3.03(09)	-0.50	4.9
$\mathbf{R}(4)$	0.0033	0.0	0.701	0.0	-4.38(00)	-5.01	-1.3
$\mathbf{R}(0)$	0.0030	0.1	0.079	-1.3	-4.33(03)	-5.40	0.4
$\mathbf{R}(0)$ $\mathbf{R}(10)$	0.0820	0.0	0.092	1.4	-4.43(04)	-5.52	-3.8
R(10) R(12)	0.0799	0.1	0.701	-0.7	-4.00(04)	-5.55	5.0
R(12) R(14)	0.0765	-0.5	0.703	-1.4	-4.30(03)	-0.04	J.0 1.5
R(14) R(14)	0.0703	0.1	0.090	-1.4	-4.97(03)	-0.24	1.3
R(10)	0.0749	-0.1	0.072	-0.1	-3.00(03)	-/./4	7.5
$\mathbf{K}(10)$ $\mathbf{R}(20)$	0.0730	-0.1	0.005	-1.8	-3.33(03)	-0.97	-2.1
R(20)	0.0729	-0.1	0.089	0.3	-0.13(03)	-0.40	0.9
$\mathbf{K}(22)$	0.0720	-0.1	0.702	0.4	-0.08(03)	-3.90	5.0
$\mathbf{K}(24)$	0.0701	0.4	0.711	0.2	-5.90(03)	-0.12	1.0
R(20)	0.0700	-0.2	0.720	-3.2	-0.20(04)	-3.40	-4.1
$\mathbf{K}(2\delta)$	0.0700	1.0	0.743	0.3	-5.80(04)	-8.08	0.5
R(30)	0.0702	0.4	0.822	-1.6	-6.40(04)	-0.41	-1.2
R(32)	0.0693	0.2	0.823	1.3	-6.50(05)	-5.28	-2.0
K(34)	0.0687	0.3	0.825	-0.7	-7.13(05)	-5.21	-1/.0
K(36)	0.0685	-0.1	0.707	-6./	-/.14(06)	-5.23	8.7
R(38)	0.0677	0.5	0.738	-0.6	-6.28(08)	-7.62	5.7
K(40)	0.0685	0.7	0.823	-0.4	-/.18(10)	-6.25	-19.0
R(42)	0.0670	0.5	0.741	4.1	-6.38(11)	-4.77	-36.1
R(44)	0.0676	1.3			-6.81(15)		
R(46)	0.0668	0.2			-7.80(18)		
R(48)	0.0681	0.2			-6.30(25)		

**Table 6.** Air-broadening coefficients for  ${}^{12}C^{16}O_2$  averaged from measurements of  $30013 \leftarrow 00001$  and  $30012 \leftarrow 00001$  bands.

**Note:** Width coefficients (HWHM) are in units of  $\text{cm}^{-1}\text{atm}^{-1}$  at 296 K. The temperature dependence coefficients of widths (*n*) are unitless. The pressure shift coefficients are in  $10^{-3}$  cm<sup>-1</sup> atm<sup>-1</sup> at 296 K. The temperature dependence of shift coefficients ( $\delta'$ ) are in units of  $10^{-5}$  cm<sup>-1</sup> atm<sup>-1</sup> K<sup>-1</sup>.

**Fig. 5.** Observed air-broadened half-width coefficients of P and R branches of  $30013 \leftarrow 00001$  and  $30012 \leftarrow 00001$  of  ${}^{12}CO_2$  compared with theoretical predictions. The horizontal axis is |m|, equal to J'' for P-branch lines and J''+1 for R-branch lines. (*a*) Averaged measured half-widths from Table 6 (open and solid squares) with calculated values (solid line). The dash-dot-dash line shows the values recommended for atmospheric uses obtained by combining observed values (for |m| = 1-51) with calculated values (scaled by 0.96) for |m| = 52-101 (see text for details). (*b*) Averaged temperature dependence exponents (*n*) of air-broadened half-width coefficients for the P and R branches with the theoretical prediction (solid line). The horizontal dashed curve corresponds to the commonly used default value of n = 0.75.



transitions are odd |m|, and we use open and solid plotting symbols to reveal if the coefficients also vary as a function of  $\Delta J$ . The corresponding theoretical air-broadening widths and their temperature dependences are shown to |m| = 101by solid curves in Fig. 5*a* and for widths and temperature dependence of widths in Fig. 5*b*. As shown in Fig. 5*a*, the observed air-broadened half-width coefficients for the Pand R-branch transitions tend to lie on a smoothly changing curve that is below the calculated values for |m| > 6 and above them for |m| < 6.

In contrast in Fig. 5b, the temperature dependence of the widths for P and R branches do not fall on the same smoothly changing curve, and they are often different by more than the percent agreement in the average n. Normally, such differences would be attributed to experimental error, since the observed widths do follow the trends predicted by theory. However in the present study, two different bands are analyzed using the same spectral data, and as seen in Fig. 4, the observed differences in their temperature dependences are very similar at each m. In contrast, averaged temperature dependence in Fig. 5b is different from the calculation by larger amounts; the P-and R-branch lines also

have slightly different observed values. One possibility is that some systematic error in comparison with the calculations was introduced in the retrievals, because the temperature dependence of the line mixing could not be determined with the present dataset. Further investigation is needed to clarify this.

Nevertheless, both the measured widths and temperature dependence coefficients do fall reasonably close to the calculated values up to |m| < 40. The agreement between theory and empirical widths is best for  $6 \le m \le 26$ . Between  $|m| = \sim 26$  and 55, the measured widths are lower than the calculated values. There are two important exceptions, however. The "kink" predicted for the low |m| widths is not observed at all, while for the temperature dependence of widths, the local minimum at |m| = 14 is observed closer to |m| = 18.

Beyond the range of our empirical averages, the calculated widths and temperature dependences steadily decrease with increasing |m|, reaching widths of 0.055 cm<sup>-1</sup> atm<sup>-1</sup> at 296 K and *n* of 0.5 at |m| = 101. To match the calculated widths to the averaged measurements, a scaling factor of 0.96 was applied, and the resulting curve is shown by the dash-dot line in Fig. 5*a*. We feel that the best results for the

**Fig. 6.** Percentage differences between present air-broadened widths and other reported measurements (PW – others)/PW × 100 for transitions in the (*a*)  $30013 \leftarrow 00001$  band and (*b*)  $30012 \leftarrow 00001$  bands. All values are plotted as a function of the *m* value. The mean and standard deviation for each set of % differences are given in the legend.



scientific community are the averaged measured air-broadened half-width coefficients for |m| up to 50 (Table 6) and the scaled theoretical prediction above |m| = 50.

The recommendation for the temperature dependence of air-broadened widths is less clear. For the entire range of |m| where measurements are available, the power law model fits the calculated studies fairly well. Indeed, for most applications, the power law gives a reasonable description of the temperature dependence of the air-broadened half-width coefficients over the range T = 200-500 K. Depending on the requirements of atmospheric applications, the theoretical values might be sufficiently reliable. Measurements are needed to validate the theoretical model at higher J.

The temperature dependence coefficients  $\delta'$  for air-induced shifts displayed in Fig. 4*c* vs. |m| represent the first measure-

ments in any CO<sub>2</sub> band, but there is no obvious trend in the retrieved values of  $\delta'$  with |m| or vibrational band. We observe that within the scatter of the experimental data, most of the  $\delta'$  coefficients are about  $-6 \times 10^{-5}$  cm<sup>-1</sup> atm<sup>-1</sup> K<sup>-1</sup>, and this is our recommended value for this coefficient.

The panels in Fig. 6 present the percentage differences between the retrieved air-broadened half-width coefficients and similar data sets available in the literature, plotted for both the (Fig. 6a)  $30013 \leftarrow 00001$  and (Fig. 6b)  $30012 \leftarrow 00001$  bands as a function of *m*. The scatter in our percentage differences occurs at very low or very high *J* values or in spectral regions where the lines overlap with hot band transitions. The present results agree best with the results from the room temperature study of Devi et al. [21] (also a constrained multispectrum analysis) and those of Predoi-

Fig. 7. Ratios of present air-broadened pressure shifts to other reported measurements for transitions in (a) the  $30013 \leftarrow 00001$  band and (b) the  $30012 \leftarrow 00001$  band. The data are plotted as a function of m. The mean and standard deviation for each set of ratios are given in the legend.



Cross et al. [24]. where the same type of line shape model was used. The differences between the present set of airbroadened half-width coefficients and those of Toth et al. [6] or HITRAN 2004 [38] are largely due to the difference in values between the half-width coefficients retrieved with a speed-dependent Voigt model with line mixing and those retrieved with the standard Voigt model.

The panels in Fig. 7 present the ratios between the retrieved air-induced pressure shift parameters and data sets available in the literature, plotted as a function of *m* for both the (Fig. 7*a*)  $30013 \leftarrow 00001$  and (Fig. 7*b*)  $30012 \leftarrow 00001$ bands. For |m| > 40 and at very low *m* values, we can see that the air-pressure shift coefficients are different than those reported by Toth et al. [6] and Predoi-Cross et al. [24], but these are still in good agreement with those from the room temperature constrained analysis studies [21, 22].

### 6. Uncertainties

Ultimately, it is not the uncertainties in the half-width and pressure shift parameters that are important, but the uncertainty in the half-width and pressure shift at the temperature of the gas being simulated. When one uses a half-width at 296 K and its temperature dependence exponent from a database such as the HITRAN, it is assumed that the half-widths near 296 K are the best determined and the uncertainty in n increases the uncertainty in half-width as the temperature gets farther from 296 K. In fact, for each line the experimental values of the two half-width parameters and of the two

Fig. 8. (a) The uncertainty of air-broadened widths as a function of temperature for  $30013 \leftarrow 00001$  with (b) the corresponding minimum uncertainty where the plot symbol is equal to the lower state J. Traces for P10 through P32 overlap extensively and are not labeled individually.



pressure shift parameters are highly correlated and the uncertainty as a function of temperature looks quite different.

$$\varepsilon_{b_{\rm L}}^2 = \left(\frac{T_0}{T}\right)^{2n} \varepsilon_{b_{\rm L}}^2 + \left[b_{\rm L}(T) \ln\left(\frac{T_0}{T}\right)\right]^2 \varepsilon_n^2 + 2\rho_{b_{\rm L}^0 n} b_{\rm L}(T) \left(\frac{T_0}{T}\right)^n \ln\left(\frac{T_0}{T}\right) \varepsilon_{b_{\rm L}^0} \varepsilon_n \quad (10)$$

$$\varepsilon_{\delta}^2 = \varepsilon_{\delta^0}^2 + (T - T_0)^2 \varepsilon_{\delta'}^2 + 2\rho_{\delta^0\delta'}(T - T_0)\varepsilon_{\delta^0}\varepsilon_{\delta'}$$
(11)

In these expressions,  $\varepsilon$  is the uncertainty in the parameter in the subscript, and  $\rho$  is the correlation between the two parameters in the subscript. Tables 3 and 4 list these correlations  $(\rho_{b-n} \text{ and } \rho_{\delta^0 \delta'})$  for each spectral line.

Figure 8*a* displays the formal uncertainty in the air-broadened Lorentz half-width for each spectral line from P2 to P42 as a function of temperature for the  $30013 \leftarrow 00001$  band measured in this study. The uncertainties in half-width coefficients for the low J lines are relatively constant over the range of temperatures of the spectra in the fit, namely 215 to 294 K. For higher J lines, the strengths of the lines become small enough at lower temperatures that the fit does not constrain the half-widths at those temperatures, and the temperature region in which the half-widths are best determined narrows to only the higher temperatures. Figure 8b displays the minimum half-width uncertainty as a function of temperature for each of the spectral lines in Fig. 8a. The trend toward higher temperature at higher rotational quantum numbers is clear as is the trend toward lower uncertainties in the strongest lines at the intermediate J values. Figure 9 shows the corresponding effects in the pressure shift parameters. The minimum uncertainties are generally a bit smaller and occur at temperatures 2 to 5 K warmer than those of the half-widths. The small irregularity for P18 observed in Fig. 9b is due to a problem with a hot band line

**Fig. 9.** (*a*) The uncertainty of air-broadened pressure-induced shifts as a function of temperature for  $30013 \leftarrow 00001$  with (*b*) the corresponding minimum uncertainty where the plot symbol is equal to the lower state *J*. Traces for P10 through P26 overlap extensively and are not labeled individually.



blended with P18 that was not modeled as well as possible. Most of the irregularities in Fig. 8a, on the other hand, are due to a small round-off problem in the fitting software uncertainty analysis for Lorentz widths.

The uncertainties derived from the fits for both the Lorentz width and pressure shift parameters are smaller than the real uncertainties. Because of the large quantity of data within the solution, the uncertainty due to the noise levels of the spectra is very small. At this level there are various other problems with the fits that dominate the actual uncertainties. These include uncertainties in the measurement of the physical conditions of the gas, uncertainties in the spectral line shapes, and some modeling of the spectral line parameters used. In particular, there was no effort to model either line mixing or speed dependence as a function of temperature. Each has only a small effect upon the solution in the first place. While the speed dependence model represents all temperatures, the model is unlikely to hold rigorously for all collisional speeds. In the comparisons between the two bands, the half-widths and pressure shifts differ by a few times the formal uncertainties. For the half-widths the differences between the two bands seem to be random as a function of rotational quantum number, so it is likely that these differences are due not to vibrational effects in carbon dioxide but rather to some systematic problem in the fits. The general shape of the uncertainty with temperature is independent of these systematic effects, and the relative uncertainty from temperature to temperature is close to that shown in Figs. 8 and 9.

Combination of widths and shifts at 296 K with temperature dependence parameters determined from an unrelated study do not profit from the correlations displayed here. The smallest uncertainty becomes that at 296 K, and the uncertainty in n causes them to rise as the temperature moves farther from that temperature. To get high quality Lorentz halfwidths and pressure shifts requires that they be determined in the same study as their temperature dependences.

### 7. Conclusions

We confirmed earlier measurements of air-broadened Lorentz half-widths and air-induced pressure shifts [21–24] and determined extensive temperature dependence values up to J'' = 45 simultaneously for two near-IR bands of  ${}^{12}CO_2$  $(30012 \leftarrow 00001 \text{ at } 6348 \text{ cm}^{-1} \text{ and } 30013 \leftarrow 00001 \text{ at}$ 6228 cm<sup>-1</sup>). The broadening parameters were retrieved using constrained multispectrum nonlinear least-squares curve fitting, employing speed-dependent Voigt profiles and relaxation matrix line mixing. This procedure was applied to highresolution spectra (37 air-broadened CO<sub>2</sub> and two of pure CO<sub>2</sub>), recorded at temperatures between 215 and 294 K using two different Fourier transform spectrometers. We performed semiclassical theoretical calculations using the Robert-Bonamy formalism [30] and found small differences (<4%) between the measured and calculated air-broadened half-width coefficients and the corresponding temperature dependence coefficients. We observed no obvious vibrational dependence for the temperature dependence of air-broadened widths of CO<sub>2</sub>. The measured temperature dependences of the air-induced pressure shifts revealed no dependence on the rotational quantum numbers; therefore an average value of  $-6.0 \times 10^{-5}$  cm<sup>-1</sup> atm<sup>-1</sup> K<sup>-1</sup> was recommended for atmospheric calculations.

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