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Air-broadening in near-infrared carbon dioxide line shapes: Quantifying contributions from O_2 , N_2 , and Ar



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ABSTRACT

We measured air broadening in the (30012) \leftarrow (00001) carbon dioxide (CO₂) band up to J'' = 50 using frequency-agile rapid scanning cavity ring-down spectroscopy. By using synthetic air samples with varying levels of nitrogen, oxygen, and argon, multi-spectrum fitting allowed for the collisional broadening terms of each major air component to be simultaneously determined in addition to advanced line shape parameters at atmospherically relevant CO₂ mixing ratios. These values were compared to broadenerspecific line shape parameters from the literature. Fits to measured spectra were also constrained with results from requantized classical molecular dynamic simulations. We show that this approach enables differentiation between narrowing mechanisms in advanced line shape parameters retrieved from experimental spectra of limited signal-to-noise ratio.

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1. Introduction

The estimated global warming of 1°C above pre-industrial levels [1] has been primarily caused by anthropogenic emissions of carbon dioxide (CO₂) [2]. Climate models rely on accurate knowledge of the global carbon cycle to understand and forecast this trend. Satellite measurements can constrain the temporal and spatial variability in the CO₂ fluxes needed for climate models if the retrieved atmospheric-column-integrated CO₂ mole fraction has a relative uncertainty less than 0.3 % [3]. High-accuracy spectroscopic reference measurements across atmospherically relevant pressures and temperatures are necessary to meet these demanding sensing goals. Additionally, an understanding of the uncertainties and biases in the reference spectroscopy is critical for constructing error budgets in remote sensing applications [4].

HITRAN [5] and other spectroscopic databases store extensive lists of line-by-line parameters for use in high resolution molecular spectroscopy applications and remote sensing. HITRAN 2016 included 173,024 resonant lines spanning the visible to microwave spectral regions for the most abundant CO_2 isotopologue (${}^{12}C^{16}O_2$) [5]. The sheer number of CO_2 transitions included in this database makes it intractable to provide high accuracy spectroscopic measurements for each entry. Recent work by Hashemi et al. estimated air- and self- line shape parameters for the HITRAN 2020 CO_2 transitions based upon the available literature data [6]. That work highlighted the importance of modeling the rotational and vibrational quantum number dependence of spectroscopic line shape parameters in the construction of comprehensive line lists. However, experimental high-resolution spectroscopic reference data are also required to validate the theory and to ensure the accuracy of line lists [7].

Theoretical models for predicting the CO_2 line shapes in the atmosphere require line shape parameters of each major air component. Subtle effects such as the impact of the broadener on the spectroscopic parameters are important not only for the high precision needs of measurements taken in the Earth's atmosphere, but also for expanding the applicability of line-by-line databases to other atmospheres such as Venus and Mars [8]. A number of calculations and simulations of CO_2 broadening by atmospherically relevant species have previously been reported [7,9,10]. Laboratory reference data that is sensitive to the broadener effects on the CO_2 line shape parameters are needed to validate these theoretical studies.

The effects of foreign broadeners on CO_2 in the near-infrared have been well documented, however, most experimental spectra have been analyzed with single-spectrum fitting and the Voigt profile (VP) [11–14]. The VP has been found to be too simplistic to model high resolution spectra at intermediate pressures, leading to collisional broadening parameters that are 2 % to 6 % too small [15,16]. As more sophisticated line shapes are employed, it is critical to use multi-spectrum techniques to constrain the pressure and temperature relationships of fitted line parameters in or-

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der to prevent their numerical correlation. A series of papers by Devi et al. studied the effects of various atmospheric broadeners on CO_2 using Fourier-transform spectroscopy (FTS) with advanced line shapes and multi-spectrum fitting [16–18]. The multi-spectrum fitting software used in those studies could retrieve two pressurebroadened half-widths for each transition, one of which was the self-broadening width. As a result, a common set of pure CO_2 spectra were used in three separate multi-spectrum fits with samples containing roughly 1 % to 10 % CO_2 in bath gases of O_2 , Ar, or air [16–18].

Gamache et al. calculated the collisional broadening of CO₂ by O₂ and N₂ along with the temperature dependence and the pressure shifting terms using the semiclassical complex Robert-Bonamy theory [7,8]. In this methodology, the intermolecular potential was adjusted to optimize the agreement between experiment and theory. The Devi et al. measurements [17] were used as part of this refinement. The HITRAN 2016 air- and self- broadening values [5] are equal to those reported in the air and self-broadening CO₂ study up to J = 40 [16], whereas for J > 40 the HITRAN 2016 values are the half-widths calculated by Gamache et al. [8].

Nguyen et al. modeled CO₂ line shapes using requantized classical molecular dynamic simulations (rCMDS) evaluated at several temperatures for 50 % CO₂ in O₂ and N₂ [9,10], respectively. The Fourier-Laplace transform of the autocorrelation function of the dipole moment calculated by the rCMDS provides a simulated CO₂ absorption spectrum with the specified broadener. Multi-spectrum fitting of the speed-dependent Nelkin-Ghatak profile (SDNGP) with first-order line mixing to simulated spectra yielded advanced line shape parameters analogous to the analysis of experimental spectra. In this analysis, the simulations covered a range of Doppler widths and temperatures, and the shift terms were neglected because the theoretical spectra did not exhibit pressure shifts [9,10]. Hashemi et al. estimated speed-dependent Voigt profile (SDVP) airbroadened line shape parameters [6] from the SDNGP line lists provided by Nguyen et al. [9] to support atmospheric retrieval codes.

Here we report frequency-agile, rapid scanning cavity ringdown spectroscopy (FARS-CRDS) measurements of the (30012) \leftarrow (00001) $^{12}C^{16}O_2$ band up to J'' = 50. This band includes a proposed transition for the NASA Active Sensing of CO₂ Emissions over Nights, Days, and Seasons (ASCENDS) mission [19–21]. The present work leverages the fast data acquisition and high sensitivity of the FARS-CRDS technique [22–25] with a flexible multi-spectrum analysis fitting software program that we have recently developed [26]. This approach has allowed us to simultaneously determine the N₂-, O₂-, and Ar-broadened half-widths of CO₂ in addition to advanced line shape parameters at atmospherically relevant CO₂ mixing ratios. These values are compared to the semiclassical half-widths predicted using the model of Gamache and Hartmann [7,8] as well as the line shape parameters determined through rCMDS [6,9,10].

2. Methods

2.1. Instrument

Measurements were made with a FARS-CRDS spectrometer previously described in the literature [22,27,28]. Briefly, FARS-CRDS involves mode-to-mode scanning of a laser sideband between successive resonances of an optical cavity [29] using an electro-optic phase modulator. This technique enables rapid scanning as well as high sensitivity due to the use of a high finesse optical cavity. The spectrum frequency axis can then be referenced to an optical frequency comb which is referenced to an atomic frequency standard. For the present measurements a metrology-grade digitizer board, which had its response validated against synthetic exponential decay signals generated from an arbitrary waveform generator,

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Fig. 1. Broadband CO_2 -in-air FARS-CRDS spectrum of the (30012) \leftarrow (00001) band at 33.3 kPa. Sample composition is specified in Table 1.

was used to acquire the ring-down signals [25]. A typical full-band spectrum can be found in Fig. 1.

2.2. Sampling

All spectra were collected using static charges of the sample gases across a range of pressures below 40 kPa (i.e., in the spectrally isolated pressure domain [15]). Four sample cylinders containing different mole fractions of N2, O2, and Ar were used in this study, as described in Table 1. The N₂ sample contained CO₂ with N₂ as the buffer gas. The CO₂ mole fraction reported was measured by the specialty gas vendor. The uncertainty in the CO₂ mole fraction was determined from the standard deviation in the mole fraction measured across all lines in this study when constraining fit intensities to reference line intensities [28]. The air cylinder was unit A-29 of National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1721 Southern Hemisphere Air [30]. The 5 % Argon and 15 % Argon samples were previously described in Long et al. [31]. The CO₂, Ar, and O₂ mole fractions were analyzed as described in [31], where the N₂ contribution was determined as the sample balance with the uncertainty being equal to the quadrature sum of the O₂- and Ar-component uncertainties.

2.3. Multi-spectrum fitting

A multi-spectrum fitting software program, the Multi-spectrum Analysis Tool for Spectroscopy (MATS), has been developed by NIST to provide a Python-based spectral fitting toolkit [26]. MATS uses the advanced line shape definitions provided in the HITRAN application programming interface (HAPI) [32] and provides the capability to adapt fitting software to experimentally driven needs. The modeled spectra are calculated based on a combination of background parameters unique to each spectrum and spectroscopic parameters that have the option of being common across all spectra (i.e., multi-spectrum) or unique to each spectrum (i.e., singlespectrum). The flexible nature of the software also allows the manual incorporation of additional parameter constraints. MATS uses the Levenberg-Marquardt algorithm to minimize the residuals between the input spectra and the model and returns the standard uncertainty of each fitted parameter [33].

In this work, the ability to constrain the fits in terms of both pressure and diluent contributions enabled the simultaneous fitting of all 17 measured spectra. This approach allowed us to separate the N_2 , O_2 , and Ar collisional broadening contributions. The ability to extract meaningful broadener contributions was quantified by comparing the broadening coefficients for air determined by fitting only the air spectra and the coefficients determined from the sum of the air component contributions from the entire set of spectra.

For line-by-line analyses, each band-wide scan was segmented into ± 1 cm⁻¹-wide fitting windows centered on the target line.

Table 1

Sample compositions with corresponding combined standard uncertainties, nominal experimental pressures, and experimental temperature range.

Sample name	CO ₂ mole fraction (µmol/mol)	N ₂ diluent contribution (%)	O ₂ diluent contribution (%)	Ar diluent contribution (%)	Nominal pressure (kPa)	Temperature range (K)
Air	387.98(5)	78.13273(180)	20.93234(118)	0.93493(136)	10, 20, 33	296.67 - 296.77
N ₂	397.83(413)	100	0	0	5, 11, 16, 22, 27, 32	296.61 - 296.75
5 % Argon	409.8(10)	75.029(43)	19.8840(77)	5.087(42)	8, 16, 24, 32	296.63 - 296.75
15 % Argon	366.3(11)	67.0239(1200)	17.9961(69)	14.98(12)	8, 22, 27, 33	296.63 -296.73

The frequency axis for each spectrum was calculated by

$$\nu_q = \nu_0 + \nu_{FSR} \Delta q, \tag{1}$$

where v_q is the frequency at a given longitudinal mode order q, v_{FSR} is the average free spectral range determined over the range of modes corresponding to each laser grating tuning, and Δq is the relative longitudinal mode order. A heterodyne beat note with a self-referenced optical frequency comb (which was referenced to a Cs clock) was employed to give v_0 . The absorption coefficient for each measured spectrum was modeled by

$$\frac{1}{c\tau(v_{FSR}\Delta q)} = \tilde{\alpha}(v_{FSR}\Delta q) + \alpha_{et}(v_{FSR}\Delta q) + \alpha_{ab}(v_q),$$
(2)

where $\bar{\alpha}$ defines the linear baseline term, α_{et} represents the contribution of etalons to the base losses, and α_{ab} is the resonant molecular absorption. The approximate amplitude and frequency of the etalons are determined through Fourier analysis of an empty cavity spectrum. The amplitude and phase of the etalons as well as the linear baseline term are floated during fitting in order to minimize residuals.

The choice of theoretical line profile for modeling the observed line shapes of high resolution molecular spectra has been an active research topic for several decades [34,35]. An IUPAC task group has recommended a line profile that captures physical contributions beyond the VP, while still simplifying to other commonly used line profiles including the VP [35]. The recommended Hartmann-Tran profile (HTP) includes two additional narrowing mechanisms: the rate of collision-induced velocity changes (Dicke narrowing, ν_{VC}) and speed-dependence effects (quantified by the dimensionless speed-dependent broadening ratio, $a_w = \frac{\gamma_2}{\gamma_0}$, where γ_0 is the pressure broadening coefficient and γ_2 is the speed dependent

broadening coefficient), along with correlations between velocityand phase-changing collisions.

The line centers [36] and line intensities [28] were constrained to recent high accuracy measurements. The CO_2 mole fraction for each gas sample was floated because static charges were employed (which can lead to subtle changes in the CO_2 mole fraction based on CO_2 adsorption and desorption from the cavity walls) [28]. Initial parameters for the broadening and shift terms for each diluent were set equal to the HITRAN 2016 air values, while the CO_2 selfbroadening contribution was assumed to be negligible [5].

A variety of HTP-derived line shapes were employed in the present study including the Nelkin-Ghatak profile (NGP, where ν_{VC} is included), the SDVP (where a_w is included), and the SD-NGP (where both narrowing mechanisms are included). The full HTP profile (both narrowing mechanisms and correlation between velocity- and phase-changing collisions are included) was not included in the fits because of the limited SNR of the experimental data. The IUPAC task group that recommended the HTP also noted the need for sufficiently high experimental SNR in order to determine higher-order parameters of the HTP [35]. To maintain the extracted parameter fidelity in experimental data with limited SNR. additional constraints can be employed during the spectral fitting. In order to explore this approach, we performed additional fits to the measured spectra with the SDVP line shape where aw was constrained to the smoothed Hashemi et al. rCMDS air-broadened values [6]. Additionally, we performed SDNGP fits where v_{VC} was constrained by the v_{vc}/γ_2 smoothed ratio from the Nguyen et al. rCMDS O_2 and N_2 values, respectively [9,10]. By constraining the ratio of the two narrowing mechanisms, opposed to fixing one narrowing mechanism to the rCMDS values, both v_{vc} and a_w are adjusted to minimize residuals. This imposes a physically meaningful



Fig. 2. Typical experimental absorption spectra (top row, dots) and fitted profiles (top row, red lines) and corresponding fit residuals (lower rows) for each specified line profile and pressure. Each column depicts a sample used in the multi-spectrum analysis for the R20e line in the (30012) \leftarrow (00001) CO₂ band. All y-axes are in units of 10⁻⁶ cm⁻¹. Note the change of scale along y-axes for the VP case. The average and standard deviation for each QF value across the 17 spectra comprising the multi-spectrum fit are given under the y-axis label for each line profile.

Table 2

Uncertainty analysis for the line shape parameters reported in current study. All uncertainties are treated as 1 σ values.

		Type B rela	Type B relative uncertainties (%)				
Line shape paramet	er	Р	Т	χ	Combined Type B		
γo a _w v _{vc}		0.01 0.01 0.01	0.02 0.07 0.29	0.102 1.81 0.63	0.10 1.81 0.69		
Line shape	Broadener	Median Tyj	Median Type A relative uncertainties (%)				
parameter		SDVP	SDNGP				
γo a _w v _{vc}	N ₂ O ₂ Ar	0.05 0.28 0.52 1.1	0.06 0.28 0.52 2.27 26.47				
Line shape	Broadener	Median rel	Median relative combined uncertainties (%)				
parameter		SDVP	SDNGP				
γo a _w ν _{vc}	N ₂ O ₂ Ar	0.11 0.30 0.53 2.11	0.12 0.30 0.53 2.91 26.47				

ratio between the two narrowing mechanisms that can be difficult to differentiate between in experimental spectra with finite SNR. The two constrained fit cases will subsequently be referred to as SDVP – Hashemi and SDNGP – Nguyen, respectively.

Fig. 2 shows typical experimental spectra and the corresponding residuals for various HTP-derived line profiles. We observe significant increases in the quality-of-fit (QF) metric, (defined as the ratio of the peak-to-baseline height to the standard deviation in the model residuals) when higher-order line profiles are employed beyond the VP. This improvement is in agreement with previous work in this band by Long et al. [15] which concluded that both collisional narrowing and speed-dependence of collisional broadening are important mechanisms in this pressure region. However, at the signal-to-noise ratio (SNR) of the experimental measurements, differences in the shape or magnitude of the residuals and QF are subtle for the line shapes beyond the VP. The qualitative assessment is that the SDVP tends to result in larger QF then the NGP, indicating that in this pressure interval the observed line shape is more sensitive to speed-dependent effects than to Dicke narrowing effects. Differences between the QFs in the SDVP and SDNGP with and without the rCMDS constraints are very similar.

This indicates that the imposed theoretical constraints are not impeding the ability to model spectra at the experimental noise levels.

For the experimental SNR achieved in this study, it was not possible to extract statistically significant values of a_w or v_{VC} for each individual broadener. Therefore, these terms were constrained to be independent of broadener. The temperature dependences for the collisional and speed-dependent broadening terms were fixed to the HITRAN 2016 air broadening values [5]. In addition, the Dicke narrowing power-law temperature dependence was fixed to the theoretical value of unity based on mass diffusion. The SDVP - Hashemi and SDNGP - Nguyen fitting cases used the temperature dependences reported in the Hashemi et al. and Nguyen et al. studies for γ_0 , γ_2 , and ν_{VC} [6,9,10]. Additionally, the rCMDS line shape parameters and temperature dependences were smoothed based on their |m| dependence (*m* is -J'' for P-branch and J''+1 for R-branch) before being used as constraints in the current analysis (see the Supplemental Material for additional discussion) [6,9,10]. The HITRAN total internal partition sums algorithm (TIPS 2017) [5] was employed. For line intensities less than 10^{-24} cm molec.⁻¹, all advanced line profile parameters were constrained to zero.



Fig. 3. Relative deviation between literature N_2 (top panel), O_2 (middle panel), and Ar (bottom panel) broadened half-widths with respect to the SDVP half-widths measured in this work. Also shown is the relative deviation between the present SDNGP and SDVP results. The uncertainties shown for the NIST data are the relative combined standard uncertainties as summarized in Table 2. The uncertainties for the Devi et al. [16–18] and the Nguyen et al. [9,10] values are the reported standard fit uncertainties. No uncertainties are shown for the Gamache et al. values [8].

Table 3

 $^{12}C^{16}O_2$ (30012) \leftarrow (00001) SDVP line list. Measured SDVP line shape parameters and corresponding standard uncertainties as detailed in Table 2. Uncertainties are given in terms of last reported digit. Units: v₀ in cm⁻¹, γ_0 in MHz/Pa (cm⁻¹/atm = 0.29587215 MHz/Pa), and a_w is dimensionless.

Line	т	ν_0	γ0 - N2	γ_0 - O_2	γ_0 - Ar	a _w
P50e	-50	6299.893174	0.02034(8)	0.01796(47)	0.01593(80)	0
P48e	-48	6302.142664	0.02011(6)	0.01691(37)	0.01478(62)	0
P46e	-46	6304.366815	0.02028(6)	0.01663(27)	0.01420(47)	0.054(6)
P44e	-44	6306.565231	0.02004(4)	0.01675(13)	0.01446(25)	0.038(3)
P42e	-42	6308.737537	0.02035(4)	0.01723(14)	0.01494(24)	0.058(3)
P40e	-40	6310.883377	0.02116(3)	0.01737(10)	0.01579(16)	0.102(3)
P38e	-38	6313.002414	0.02127(3)	0.01808(8)	0.01529(12)	0.106(2)
P36e	-36	6315.094333	0.02092(2)	0.01741(6)	0.01573(10)	0.075(2)
P34e	-34	6317.158835	0.02124(2)	0.01759(5)	0.01572(9)	0.089(2)
P32e	-32	6319.195639	0.02133(2)	0.01788(4)	0.01602(6)	0.091(2)
P30e	-30	6321.204481	0.02149(2)	0.01796(5)	0.01618(6)	0.094(2)
P28e	-28	6323.185114	0.02143(2)	0.01804(3)	0.01617(5)	0.082(2)
P26e	-26	6325.13731	0.02177(2)	0.01842(4)	0.01673(6)	0.096(2)
P24e	-24	6327.060853	0.02191(2)	0.01854(4)	0.01699(6)	0.095(2)
P22e	-22	6328.955543	0.02204(2)	0.01894(3)	0.01707(4)	0.090(2)
P20e	-20	6330.821198	0.02249(2)	0.01934(3)	0.01774(5)	0.105(2)
P18e	-18	6332.65765	0.02262(2)	0.01962(3)	0.01787(4)	0.094(2)
P16e	-16	6334.464734	0.02320(2)	0.02005(3)	0.01848(5)	0.106(2)
P14e	-14	6336.242389	0.02345(3)	0.02031(4)	0.01870(5)	0.094(2)
P12e	-12	6337.990341	0.02409(3)	0.02091(3)	0.01942(5)	0.104(2)
P10e	-10	6339.708583	0.02450(3)	0.02131(5)	0.01968(6)	0.095(2)
P8e	-8	6341.396997	0.02511(3)	0.02191(4)	0.02021(6)	0.097(2)
P6e	-6	6343.055498	0.02587(3)	0.02249(9)	0.02108(14)	0.102(2)
P4e	-4	6344.684017	0.02617(3)	0.02287(6)	0.02136(8)	0.074(2)
P2e	-2	6346.282498	0.02822(4)	0.02467(13)	0.02319(24)	0.122(3)
R0e	1	6348.623807	0.02923(6)	0.02565(29)	0.02402(51)	0.093(5)
R2e	3	6350.147034	0.02709(3)	0.02387(9)	0.02200(14)	0.101(2)
R4e	5	6351.640133	0.02583(3)	0.02267(6)	0.02088(9)	0.083(2)
R6e	7	6353.103109	0.02523(3)	0.02160(9)	0.02040(14)	0.086(2)
R8e	9	6354.535981	0.02480(3)	0.02150(4)	0.01994(6)	0.103(2)
R10e	11	6355.938781	0.02428(3)	0.02105(4)	0.01939(6)	0.109(2)
R12e	13	6357.311577	0.02361(3)	0.02049(4)	0.01875(5)	0.101(2)
R14e	15	6358.654324	0.02306(2)	0.01997(4)	0.01834(6)	0.096(2)
R16e	17	6359.967244	0.02265(2)	0.01958(3)	0.01789(5)	0.096(2)
R18e	19	6361.25035	0.02236(2)	0.01922(3)	0.01756(5)	0.097(2)
R20e	21	6362.503752	0.02207(2)	0.01892(4)	0.01721(5)	0.096(2)
R22e	23	6363.727569	0.02190(2)	0.01866(3)	0.01692(5)	0.098(2)
R24e	25	6364.921932	0.02168(2)	0.01830(4)	0.01669(6)	0.095(2)
R26e	27	6366.086989	0.02151(2)	0.01813(4)	0.01635(6)	0.093(2)
R28e	29	6367.222904	0.02133(2)	0.01787(5)	0.01616(9)	0.088(2)
R30e	31	6368.329856	0.02110(3)	0.01777(11)	0.01562(18)	0.079(2)
R32e	33	6369.40804	0.02101(4)	0.01760(17)	0.01556(25)	0.078(4)
R34e	35	6370.457667	0.02103(5)	0.01773(21)	0.01547(35)	0.090(4)
R36e	37	6371.47897	0.02116(6)	0.01751(25)	0.01584(44)	0.095(5)
R38e	39	6372.472194	0.02094(3)	0.01745(10)	0.01558(27)	0.092(3)
R40e	41	6373.437606	0.02081(3)	0.01742(9)	0.01497(25)	0.089(3)
R42e	43	6374.375489	0.02061(3)	0.01704(12)	0.01502(34)	0.081(3)
R44e	45	6375.286149	0.02028(5)	0.01621(20)	0.01531(33)	0.065(5)
R46e	47	6376.16991	0.02005(5)	0.01668(24)	0.01452(40)	0.050(6)
R48e	49	6377.027117	0.02008(5)	0.01696(25)	0.01403(44)	0
R50e	51	6377.858138	0.02011(6)	0.01676(44)	0.01557(75)	0

2.4. Uncertainty analysis

Table 2 summarizes the median standard Type-A-evaluation (statistical), Type-B-evaluation (systematic), and combined uncertainties for each of the reported parameters. The Type A uncertainties were generated from the standard errors reported by the multi-spectrum fits, which do not account for numerical correlation between parameters. The only exceptions to this are a_w in the SDVP – Hashemi case and v_{VC} in the SDNGP – Nguyen case. In those cases the uncertainties were set equal to the standard deviation in the residuals after applying the smoothing function to the reported Hashemi et al. [6] and Nguyen et al. values [9,10]. We observed that for each line shape the N₂ collisional broadening term had the lowest Type A uncertainty. This result is expected because the CO₂-in-N₂ sample grounded this measurement and N₂ was a majority component in each of the other samples. In contrast, the Ar collisional broadening term tended to have the

highest Type A uncertainty given that it had the lowest mole fraction in each of the samples.

In addition to the statistical uncertainties in the measured values, systematic uncertainties in the pressure, temperature, and sample composition were evaluated as part of the combined uncertainty for each quantity. The sample pressure was measured with a NIST-calibrated pressure gauge which had a relative combined standard uncertainty of 0.01 %. This pressure uncertainty maps directly onto the uncertainty in each of the fitted line shape parameters.

The temperature dependences of γ_0 , γ_2 , and ν_{VC} are described by power law relationships, where a_w is the ratio of γ_2 and γ_0 at the reference temperature and has the uncertainty associated with its component values. The power law temperature correction for a generic parameter at the experimental temperature (b_T) as a function of the reference temperature parameter value (b_{296}), experiment temperature (T), and the temperature exponent (n) is given

Table 4

 $^{12}C^{16}O_2$ (30012) \leftarrow (00001) SDNGP line list. Measured SDNGP line shape parameters and corresponding standard uncertainties as detailed in Table 2. Uncertainties are given in terms of last reported digit. Units: v₀ in cm⁻¹, γ_0 and ν_{VC} are in MHz/Pa (cm⁻¹/atm = 0.29587215 MHz/Pa), and a_w is dimensionless.

Line	т	ν_0	γ0 - N2	γ ₀ - 0 ₂	γ_0 - Ar	a _w	v_{vc}
P50e	-50	6299.893174	0.02034(8)	0.01795(47)	0.01593(80)	0	0
P48e	-48	6302.142664	0.02010(6)	0.01695(37)	0.01477(62)	0	0
P46e	-46	6304.366815	0.02022(6)	0.01654(27)	0.01434(46)	0.000(56)	0.00329(270)
P44e	-44	6306.565231	0.02004(4)	0.01668(13)	0.01463(25)	0.001(24)	0.00260(111)
P42e	-42	6308.737537	0.02028(3)	0.01720(13)	0.01491(24)	0.000(25)	0.00346(119)
P40e	-40	6310.883377	0.02105(4)	0.01737(11)	0.01572(17)	0.089(5)	0.00082(29)
P38e	-38	6313.002414	0.02127(3)	0.01808(8)	0.01528(12)	0.106(3)	0.00000(19)
P36e	-36	6315.094333	0.02081(3)	0.01736(6)	0.01565(9)	0.030(6)	0.00282(31)
P34e	-34	6317.158835	0.02120(3)	0.01757(5)	0.01569(9)	0.078(3)	0.00079(16)
P32e	-32	6319.195639	0.02132(2)	0.01788(4)	0.01602(6)	0.088(2)	0.00020(11)
P30e	-30	6321.204481	0.02147(2)	0.01794(5)	0.01617(6)	0.090(2)	0.00034(12)
P28e	-28	6323.185114	0.02133(2)	0.01794(3)	0.01619(5)	0.049(2)	0.00229(12)
P26e	-26	6325.13731	0.02175(2)	0.01840(4)	0.01671(6)	0.092(2)	0.00039(10)
P24e	-24	6327.060853	0.02188(2)	0.01851(4)	0.01697(6)	0.086(2)	0.00069(10)
P22e	-22	6328.955543	0.02196(2)	0.01887(3)	0.01702(4)	0.069(2)	0.00168(6)
P20e	-20	6330.821198	0.02249(2)	0.01934(3)	0.01774(5)	0.104(2)	0.00004(6)
P18e	-18	6332.65765	0.02254(2)	0.01956(3)	0.01781(4)	0.074(2)	0.00156(6)
P16e	-16	6334.464734	0.02319(3)	0.02004(3)	0.01846(5)	0.105(2)	0.00009(6)
P14e	-14	6336.242389	0.02338(3)	0.02028(4)	0.01862(5)	0.076(2)	0.00160(11)
P12e	-12	6337.990341	0.02408(3)	0.02091(3)	0.01941(5)	0.102(2)	0.00020(6)
P10e	-10	6339.708583	0.02445(3)	0.02128(5)	0.01964(6)	0.084(2)	0.00117(13)
P8e	-8	6341.396997	0.02508(3)	0.02188(4)	0.02017(6)	0.089(2)	0.00083(10)
P6e	-6	6343.055498	0.02587(3)	0.02246(9)	0.02110(14)	0.101(3)	0.00002(22)
P4e	-4	6344.684017	0.02604(3)	0.02275(5)	0.02125(8)	0.022(6)	0.00466(44)
P2e	-2	6346.282498	0.02828(5)	0.02467(14)	0.02323(25)	0.126(4)	0.00000(39)
R0e	1	6348.623807	0.02923(8)	0.02563(31)	0.02404(51)	0.094(8)	0.00010(95)
R2e	3	6350.147034	0.02712(4)	0.02389(9)	0.02202(14)	0.104(3)	0.00000(24)
R4e	5	6351.640133	0.02573(3)	0.02259(6)	0.02078(9)	0.056(3)	0.00253(21)
R6e	7	6353.103109	0.02503(3)	0.02167(9)	0.02007(13)	0.025(10)	0.00475(61)
R8e	9	6354.535981	0.02479(3)	0.02149(4)	0.01992(6)	0.101(2)	0.00024(11)
R10e	11	6355.938781	0.02427(3)	0.02105(4)	0.01939(6)	0.108(2)	0.00000(10)
R12e	13	6357.311577	0.02357(3)	0.02047(3)	0.01871(5)	0.093(2)	0.00085(8)
R14e	15	6358.654324	0.02298(3)	0.01992(4)	0.01826(5)	0.077(2)	0.00165(9)
R16e	17	6359.967244	0.02258(2)	0.01953(3)	0.01781(5)	0.077(2)	0.00161(9)
R18e	19	6361.25035	0.02230(2)	0.01917(3)	0.01753(4)	0.083(2)	0.00119(8)
R20e	21	6362.503752	0.02202(2)	0.01888(4)	0.01718(5)	0.083(2)	0.00108(10)
R22e	23	6363.727569	0.02187(2)	0.01863(3)	0.01690(5)	0.092(2)	0.00054(6)
R24e	25	6364.921932	0.02164(2)	0.01828(4)	0.01666(6)	0.085(2)	0.00085(10)
R26e	27	6366.086989	0.02146(2)	0.01811(4)	0.01631(6)	0.080(2)	0.00102(12)
R28e	29	6367.222904	0.02123(3)	0.01780(5)	0.01611(9)	0.069(3)	0.00172(19)
R30e	31	6368.329856	0.02097(3)	0.01768(11)	0.01556(18)	0.031(11)	0.00300(55)
R32e	33	6369.40804	0.02088(5)	0.01748(16)	0.01561(25)	0.028(20)	0.00337(109)
R34e	35	6370.457667	0.02090(6)	0.01755(21)	0.01534(35)	0.058(14)	0.00191(83)
R36e	37	6371.47897	0.02096(3)	0.01737(8)	0.01559(13)	0.088(4)	0.00022(21)
R38e	39	6372.472194	0.02093(5)	0.01732(18)	0.01594(51)	0.089(8)	0.00014(50)
R40e	41	6373.437606	0.02077(3)	0.01738(9)	0.01505(24)	0.081(5)	0.00051(32)
R42e	43	6374.375489	0.02049(4)	0.01692(12)	0.01531(34)	0.040(12)	0.00248(62)
R44e	45	6375.286149	0.02016(5)	0.01619(20)	0.01515(33)	0.001(52)	0.00434(257)
R46e	47	6376.16991	0.02001(5)	0.01666(24)	0.01453(40)	0.000(45)	0.00313(210)
R48e	49	6377.027117	0.02007(5)	0.01693(25)	0.01410(42)	0	0
R50e	51	6377.858138	0.02012(6)	0.01681(45)	0.01546(76)	0	0

by

$$b_T = b_{296} \left(\frac{296}{T}\right)^n.$$
(3)

The quadrature sum of derivatives with respect to each term in Eq. (3) multiplied by the uncertainty in that term provides a measure of the systematic uncertainty caused by uncertainty in temperature:

$$\delta b_T = \sqrt{\left(\left(\frac{296}{T}\right)^n \delta b_{296}\right)^2 + \left(\frac{nb_T}{T} \delta T\right)^2 + \left(b_T \ln\left(\frac{296}{T}\right) \delta n\right)^2}.$$
(4)

The first term in this sum can be neglected because it is captured in the Type A uncertainties. The second and third terms describe the respective impacts of the temperature uncertainty and the temperature exponent uncertainty on the reported line shape parameter. For the present measurements a NIST-calibrated thermistor was employed with a standard uncertainty of 20 mK. Additionally, the maximum temperature excursion across a spectral fitting window in all spectra was 42 mK. The quadrature sum of these values, 47 mK, was used as the temperature uncertainty in the evaluation of Eq. (4).

The uncertainty in the temperature exponent for γ_0 was taken to be the difference between the employed HITRAN 2016 values [5] (which are based upon Gamache et al. [8]) and the average temperature exponents reported for each line in the lowtemperature FTS analysis of Wilzewski et al. [37] and the rCMDS experiments of Nguyen et al. [9,10]. The Nguyen et al. analysis provided measurements of the γ_0 temperature exponents for both N₂ and O₂ [9,10], however the impact of the broadener on the temperature dependence was not considered in the uncertainty quantification. Similarly, for γ_2 and ν_{VC} the difference between the temperature exponent used in the fits and the available literature data was used as a measure of the uncertainty. In the fitting we assumed that γ_2 had the same temperature dependence as γ_0 , resulting in a temperature-independent a_w . Further, we assumed v_{VC} had a temperature exponent equal to unity. Relative temperature uncertainties for γ_0 , γ_2 , and v_{VC} were evaluated for each line using Eq. (4) and subsequently averaged over all lines for each case. An additional uncertainty component given by the standard deviation of the ensemble of line-dependent uncertainties was added to yield the uncertainty for each of these three parameters reported in Table 2.

For a sample comprising multiple broadeners, the broadenerspecific line profile parameters, b_i are weighted by the sample mole fraction, χ_i , to represent the parameter for a given sample

$$b_{sample} = \chi_{N_2} b_{N2} + \chi_{O_2} b_{O2} + \chi_{Ar} b_{Ar} + \chi_{CO_2} b_{CO2}.$$
 (5)

The corresponding uncertainty caused by uncertainty in the sample composition is given by

$$\delta b^{\text{sample}} = \left[\left(\chi_{N_2} \delta_{b_{N_2}} \right)^2 + \left(b_{N_2} \delta_{\chi_{N_2}} \right)^2 + \left(\chi_{O_2} \delta_{b_{O_2}} \right)^2 + \left(b_{O_2} \delta_{\chi_{O_2}} \right)^2 + \left(\chi_{Ar} \delta_{b_{Ar}} \right)^2 + \left(b_{Ar} \delta_{\chi_{Ar}} \right)^2 + \left(\chi_{CO_2} \delta_{b_{CO_2}} \right)^2 + \left(b_{CO_2} \delta_{\chi_{CO_2}} \right)^2 \right]^{\frac{1}{2}}. (6)$$

The uncertainty in sample composition of a given parameter was then calculated using Eq. (6) for each sample weighted by the proportion of the total dataset in which that sample was used. The uncertainties in the mole fraction for each sample and broadener are given in Table 1.

Eq. (6) indicates that for each broadener, the Type B sample composition uncertainty of a parameter can be decomposed into the uncertainty in the parameter magnitude scaled by the relative amount of the broadener and the uncertainty in the relative amount of the broadener scaled by the parameter magnitude. For N₂, O₂, and Ar the uncertainty components of γ_0 that are proportional to δ_{γ_0} (first, third and fifth terms on the right-hand side of Eq. (6)) were neglected because they were estimated from the reported fit uncertainties. Because the CO2 self-broadening contribution was assumed to be negligible during fitting, the difference between the self-broadening reported in HITRAN 2016 [5] and the sample γ_0 (neglecting the self-broadening component calculated by Eq. (5)) was used to quantify the uncertainty in $\gamma_{0.CO2}$. The sample composition uncertainty and the assumption that selfbroadening can be ignored leads to a 0.10 % systematic uncertainty in the reported γ_0 .

We assumed that a_w and ν_{VC} were broadener independent given that SNR of the measured spectra was not high enough to distinguish such subtle differences in these quantities. This uncertainty can be estimated by the difference in the theoretical values of each broadener and the theoretical values of the sample, where the mass diffusion values [38,39] were used for ν_{VC} and theoretical values were employed for a_w [40]. The assumption that a_w is broadener independent leads to a 1.81 % systematic uncertainty on a_w , where the analogous assumption for ν_{VC} introduces a 0.69 % systematic uncertainty. The analysis of the sample composition systematic uncertainties for γ_0 , a_w , and ν_{VC} indicates that this is the largest source of systematic uncertainty in our analysis.

3. Results and discussion

SDVP and SDNGP line lists for the (30012) \leftarrow (00001) $^{12}C^{16}O_2$ band broadened by N₂, O₂, and Ar can be found in Tables 3 and 4. Analogous line lists for the VP, NGP, SDVP – Hashemi, and SDNGP – Nguyen cases are located in the Supplemental Material.



Fig. 4. Speed-dependent broadening, a_w, for the present SDVP fits (left panel) and SDNGP fits (right panel) in comparison with the values reported by Devi et al. [16–18] for the SDVP and Nguyen et al. [9,10] for the SDNGP. The plotted uncertainties for the Devi et al. and the Nguyen et al. values are the reported standard fit uncertainties.

3.1. Line shape comparison and analysis

On average the $\gamma_{0,N2}$ values are 18 % larger than those of O₂ and 32 % larger than those of Ar, such that the average ratio $\gamma_{0,O2}/\gamma_{0,Ar}$ is ~1.12. The general trends with |m| are similar, but not identical across all broadeners leading to an *m*-dependence in the ratio of broadening coefficients that deviates more at higher |m|. The relative differences between our measured N₂, O₂, and Ar foreign broadening values for CO₂ based on the SDVP and those reported by Devi et al. [16–18], Nguyen et al. [9,10], and Gamache et al. [8] can be found in Fig. 3. In addition, Fig. 3 shows the relative deviation between the present γ_0 measurements based on SDNGP and SDVP fits. The relative difference between the present SDVP and SDNGP fits is the smallest compared to the other data sets, however, the SDVP collisional broadening values are still roughly 0.4 % larger than the SDNGP values, highlighting the importance of the choice of line profile.

For each broadener there is good agreement between the Devi et al. [16-18] results for the collisional widths and the SDVP results reported here. The N₂-broadened γ_0 values reported by Devi et al. are 0.56 % larger than those reported here, the O₂ broadened values are 0.01 % larger, and the Ar broadened values are 0.14 % smaller. The differences between the Gamache et al. values [8] and the present measurements are on average similar to the differences between those with the Devi et al. values, but show significant deviations at low |m|. The Nguyen et al. rCMDS results [9,10] based upon SDNGP fits also show a large deviation from the measurements at low |m|, but with negative relative deviations. On average the Nguyen et al. N₂ broadened values were 0.23 % smaller and the O₂ broadened values were 0.51 % smaller than the SDNGP results reported in this study [9,10]. When comparing the Nguyen et al. simulations [9,10] and the Gamache et al. [8] calculations to the data reported here and the Devi et al. measurements [16-18], there are noticeable |m| deviations in the reported collisional broadening terms for both N₂ and O₂. These trends highlight the importance of multiple broadener experimental studies to provide insights for theoretical modeling and simulations.

We have also reported a_w values for the SDVP and a_w and ν_{VC} for the SDNGP. Fig. 4 compares the present SDVP and SDNGP a_w values to those in the literature. The a_w values reported for all broadeners in the Devi et al. studies [16–18] are significantly larger than the present values and have much larger values at low |m|. For the SDNGP fits, we observe much better agreement with the Nguyen et al. rCMDS values [9,10] and observe similar |m| dependence. Fig. 5 compares the present ν_{VC} SDNGP values to the Nguyen et al. rCMDS values [9,10].

The SDVP – Hashemi fits led to QFs that were nearly identical to those from the present SDVP fits. In addition, the a_w values from the SDVP fits and the SDVP – Hashemi fits show similar magnitude and |m| dependence (see Fig. 4). The a_w terms deter-



Fig. 5. Dicke narrowing, ν_{VC} , for SDNGP results from the present study and the values reported by Nguyen et al. [9,10]. The plotted uncertainties for the Nguyen et al. values are the reported standard fit uncertainties.

mined with the SDNGP – Nguyen fits show significantly smoother *m*-dependence than the unconstrained SDNGP fits and resulted in similar QFs. Additionally, Fig. 5 shows that the constrained SDNGP led to a much smoother v_{VC} *m*-dependence. These results illustrate that the ability to constrain advanced line profiles with theoretical values for high-order line parameters can greatly improve the precision of fitted parameters obtained from measured spectra with relatively low SNR.

4. Conclusions

In this work we report frequency-agile, rapid scanning cavity ring-down spectroscopy (FARS-CRDS) measurements of the (30012) \leftarrow (00001) CO₂ band up to J'' = 50. Spectra were analyzed using a flexible multi-spectrum fitting program [26] which offers the capability to impose pressure, temperature and broadening constraints. The high sensitivity of the FARS-CRDS technique enables the use of samples near atmospheric abundance of CO₂, where the flexibility of the MATS program enables simultaneous determination of major-air-component collisional broadening terms. These are key improvements over previous CO₂-in-air foreign broadening component studies. These values were compared to available broadenerspecific line shape parameters [8–10,16–18]. We find that the ability to constrain experimental data with theoretical results (e.g. rCMDS) can reduce scatter in the |m|-dependence of line shape parameters derived from multi-spectrum fits of advanced line profiles.

Declaration of Competing Interest

The authors declare no competing interests.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jqsrt.2021.107669.

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