

Predicting accurate line shape parameters for CO₂ transitions

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Abstract: The vibrational dependence of CO₂ half-widths and line shifts are given by a modification of the model proposed by Gamache and Hartmann [R. Gamache and J.-M. Hartmann, *J. Quant. Spectrosc. Radiat. Transfer* 83, 119 (2004)]. This model allows the half-widths and line shifts for a ro-vibrational transition to be expressed in terms of the number of vibrational quanta exchanged in the transition raised to a power and a reference ro-vibrational transition. Calculations were made for 24 bands for lower rotational quantum numbers from 0 to 160 for N₂-, O₂-, air-, and self-collisions with CO₂. These data were extrapolated to J''=200 to accommodate several databases. Comparison of the CRB calculations with measurement give very high confidence in the data. In the model a *Quantum Coordinate* is defined by $(c_1 \Delta v_1 + c_2 \Delta v_2 + c_3 \Delta v_3)^p$. The power p is adjusted and a linear least-squares fit to the data by the model expression is made. The procedure is iterated on the correlation coefficient, R, until $[|R|-1]$ is less than a threshold. The results demonstrate the appropriateness of the model. The model allows the determination of the slope and intercept as a function of rotational transition, broadening gas, and temperature. From these fit data, the half-width, line shift, and the temperature dependence of the half-width can be estimated for any ro-vibrational transition, allowing spectroscopic CO₂ databases to have complete information for the line shape parameters.

Keywords: Half-width, line shift, temperature dependence of the half-width, CO₂- CO₂, CO₂-N₂, CO₂-O₂, CO₂-air.

1. Introduction

While CO₂ is only present in the Earth's atmosphere at a concentration of 0.039445% [1] it is the second strongest absorber of infrared radiation [2]. Even at this seemingly low concentration CO₂ is the leading anthropogenic gas contributing to the greenhouse effect in the Earth's atmosphere [3]. This concentration of 390 ppm is also larger than it has been in at least 650 thousand years [4, 5]. Because of this fact CO₂ has become the standard by which other greenhouse gases are gauged in global climate change. Its concentration has been measured continuously since 1957 [6, 7] and proxy records extend the data back hundreds of thousands of years [4]. The abrupt rise in the concentration of CO₂ corresponds with the onset of the Industrial Revolution and this rise in concentration is thought to be of anthropogenic origin [8]. To address this question and the role of CO₂ in global climate change, the sources and sinks of CO₂ in the Earth's atmosphere must be well understood. This task is being accomplished by a number of satellite-based instruments, which are making remotely sensed measurements of carbon dioxide and other atmospheric trace gases in the Earth's atmosphere. Measuring in the mid-infrared region are the Infrared Atmospheric Sounder Interferometer (IASI) [9] onboard the METOP-A satellite [10] and the Atmospheric Infrared Sounder (AIRS) [11] onboard the AQUA satellite [12]. The Greenhouse Gases Observing Satellite (GOSAT)[13], launched by Japan in 2009, targets CO₂ transitions particularly in the 1.6 μm region. In 2009 the Jet Propulsion Laboratory launched the Orbiting Carbon Observatory (OCO) [14] which failed to reach orbit. However, due to the importance of the mission, NASA anticipates the launch of OCO-2 in 2013 [15]. The OCO-2 mission will need spectroscopic parameters with uncertainty of less than 0.3%, placing strong

demands on the spectroscopic community. The current databases, HITRAN2008 [2] or GEISA [16], will need to be improved to meet these needs.

Carbon dioxide is the principal gas in the atmospheres of Venus (at 96.5% [17, 18]) and Mars (at 95.2% [19]). Understanding the role of CO₂ in these atmospheres will help researchers better understand CO₂ in Earth's atmosphere. High temperature applications such as Venus [20] and monitoring CO₂ in the combustion process [21-23] to better understand the global carbon cycle complicate the problem. The characterization of CO₂ from spectra is further complicated by line mixing effects [24]. For the high-temperature applications the HITRAN and GEISA databases are not adequate. To address these applications several databases have been produced. HITEMP [25] contains spectroscopic parameters for H₂O, CO₂, CO, NO, and OH with an intensity cutoff derived at 1000 K. For CO₂ there are several databases (CDSD-296 [26] and CDSD-1000 [27]) with low intensity cutoffs making them applicable to high-temperature applications. CDSD-296 contains roughly four hundred thousand transitions with $J_{\max}=128$ and CDSD-1000 contains almost four million transitions with $J_{\max}=200$. More recently Tashkun and Perevalov [28] have released CDSD-4000 containing over 628 million transitions and Huang *et al.* [29] have compiled an *ab initio* database of CO₂-transitions (positions, intensity, and energy) for $J_{\max}=200$, for which the primitive database contains more than 734 million lines. For many of the transitions in these databases the line shape information is approximate or missing.

In this work accurate half-widths, line shifts, and the temperature dependence of the half-width are predicted using a model based on the number of vibrational quanta exchanged in the transition. The model was developed by Gamache and Hartmann [30]

in a study of a particular class of water vapor transitions using the Complex Robert-Bonamy (CRB) formalism [31]. Here the model is modified by allowing the exponents in the equations to be adjusted to better reproduce the data. In the following section the CRB formalism is presented and the vibrational dependence model derived. Section 3 describes the calculations for a number of perturbing molecules. Section 4 discusses the fitting of the model to the data followed by a description of the prediction algorithm in section 5. The paper ends with a discussion and conclusion of the work.

2. Theory

The complex Robert-Bonamy (CRB) formalism is a semi-classical approach to calculating the half-width and line shift for transitions of atmospheric gases. The internal states of the radiating and perturbing molecules are treated quantum mechanically and the dynamics are treated classically. For many molecules in planetary atmospheres semi-classical approaches are the only practical approaches since first principle quantum calculations are intractable. The quality of the semi-classical calculation is strongly dependent on the level of sophistication employed, e.g. the size of the intermolecular potential, whether the imaginary terms in the potential are included, trajectory model employed, velocity integral vs. mean relative thermal approximation, etc. These topics have been the subject of numerous studies [32-40]. Here the calculations were made using a potential expanded to 20 *order* and *rank* 4 [34] for the radiator and perturber, the calculations employed the real and imaginary terms, trajectories were determined using an isotropic 6-12 potential in Hamilton's equations, and the velocity integral was evaluated. For details of the calculations applied to CO₂ see Refs. [41-43].

The half-width, γ , and line shift, δ , of a ro-vibrational transition $v'f \leftarrow v''i$ in the CRB formalism are given by minus the imaginary part and the real part, respectively, of the diagonal elements of the complex relaxation matrix. Expressed in terms of the Liouville scattering matrix [44] one has

$$(\gamma - i\delta)_{f \leftarrow i} = \frac{n_2}{2 \pi c} \left\langle \mathbf{v} \times \left[1 - e^{-R S_2(f, i, J_2, v, b)} e^{-i[S_1(f, i, J_2, v, b) + {}^l S_2(f, i, J_2, v, b)]} \right] \right\rangle_{v, b, J_2} \quad (1)$$

where n_2 is the number density of perturbers and $\langle \dots \rangle_{v, b, J_2}$ represents an average over all trajectories (impact parameter b and initial relative velocity v) and initial rotational state J_2 of the collision partner. S_1 and $S_2 = {}^R S_2 + i {}^l S_2$ are the first and second order terms in the successive expansion of the Liouville scattering matrix. The expressions for S_1 and S_2 can be found in Refs. [41, 45, 46].

The vibrational dependence of the line shape parameters can be obtained by considering two transitions with identical rotational quantum numbers belonging to a reference band and to a vibrational transition starting from the ground state. Here, as in Refs. [30] and [47], the computed rotational band is taken as the reference band. The line shape parameters can then be written in a simplified form from Eq. (1)

$$\begin{aligned} (\gamma - i\delta)_{0f \leftarrow 0i} &= \left\langle 1 - \exp^{-R S_2(0f, 0i)} \left\{ \cos[{}^l S_2(0f, 0i)] - i \sin[{}^l S_2(0f, 0i)] \right\} \right\rangle, \\ (\gamma - i\delta)_{vf \leftarrow 0i} &= \left\langle 1 - \exp^{-R S_2(vf, 0i)} \left\{ \cos[{}^l S_2(vf, 0i) + S_1(v, 0)] - i \sin[{}^l S_2(vf, 0i) + S_1(v, 0)] \right\} \right\rangle, \end{aligned} \quad (2)$$

where it is noted that R and I denote the real and imaginary parts, $S_1(0,0) = 0$, and that the S_2 terms arise from anisotropic interactions only which are calculated here using a potential that does not depend on vibration. The differences in the collisional parameters for the two transitions are due to two main factors: The first is a spectroscopic effect associated with the fact that the energy structure and wave functions between the ground and the ν vibrational states are different. These differences affect the S_2 terms (real and imaginary components) since for a given ($i' \leftarrow i$) the reduced matrix elements are different for the 2 vibrational states and the arguments of the resonance functions change as the energy gap changes. The second factor arises because the S_1 (vibrational dephasing) term arises from purely vibrational effects.

Gamache and Hartmann [30] looked at conditions where one of the vibrationally dependent terms, spectroscopic effects or vibrational dephasing, dominated over the other. Conditions where the purely vibrational effects are negligible compared with the spectroscopic effects leads to Eq. (7) of their work and the opposite condition leads to their Eq. (10). The spectroscopic effects contain the differences $[{}^R S_2(\nu f, 0i) - {}^R S_2(0f, 0i)]$ and $[{}^I S_2(\nu f, 0i) - {}^I S_2(0f, 0i)]$. These terms are determined from the energy differences for the collisional transitions from state $i \rightarrow i'$ and $f \rightarrow f'$, and the reduced matrix elements $\langle J_f || D_{*,n}^\ell || J_{f'} \rangle$ in terms of the Wigner D matrices. For water vapor the spectroscopic effects tend to be small for a certain class of transitions (far off resonance) compared with the vibrational dephasing term [30] and allowed prediction of water vapor line shape parameters by Jacquemart *et al.* [48].

The energy of the vibrational states of CO_2 are given in terms of the G_ν , B_ν , D_ν , and H_ν molecular constants [49]. As the vibrational state increases only the G_ν constant

changes appreciably, the B_v , D_v , and H_v constants show only slight changes. Since collisional transitions occur within a vibrational state the energy differences do not depend greatly on vibration. The wavefunctions for CO_2 are given in terms of the Wigner D-matrix, $D'_{00}(\Omega)$, dependent only on J , hence the reduced matrix for the collisional transition $J \rightarrow J'$ are independent of vibrational state. The end result is that ${}^R S_2(vf, 0i)$ and ${}^R S_2(0f, 0i)$ nearly cancel each other and ${}^1 S_2(vf, 0i)$ and ${}^1 S_2(0f, 0i)$ do the same. Thus, for CO_2 as the radiating molecule in the collision process the off-resonance condition need not be satisfied for the S_1 term to be the dominant term for the vibrational dependence [47].

Gamache and Hartmann [30] have shown that for far off-resonance conditions the half-width and line shift are proportional to the vibrational dephasing term. Thibault *et al.* [50], following studies for diatomic molecules [39, 51-53], have shown that for CO_2 the vibrational dependence of the S_1 term is proportional to the change in vibrational quanta,

$$S_1[(v_1', v_2', v_3') \leftarrow (v_1'', v_2'', v_3'')] \propto c_1 \Delta v_1 + c_2 \Delta v_2 + c_3 \Delta v_3, \quad (3)$$

where $\Delta v_i = v_i' - v_i''$ ($i=1$ to 3) is the number of vibrational quanta exchanged in the i^{th} mode for the considered ro-vibrational transition. For CO_2 , the coefficients in Eq. (3) were reported in Ref. [41] in *au*; $c_1=0.14$, $c_2=0.07$, and $c_3=0.268$. The vibrational dependence of the half-width and line shift can thus be written

$$\begin{aligned}\gamma_{v_1 v_2 v_3, f \leftarrow 0i} &\propto [\Delta v_1 + \Delta v_2 / 10 + \Delta v_3]^2 \quad , \\ \delta_{v_1 v_2 v_3, f \leftarrow 0i} &\propto [\Delta v_1 + \Delta v_2 / 10 + \Delta v_3] \quad .\end{aligned}\tag{4}$$

As transitions involve larger and larger exchanges of vibrational quanta the linear development used in the derivation of Eq. (4) may come into question. To allow for this fact the powers in the expressions were generalized and solved for as described below and the expressions were rewritten for any ro-vibrational transition,

$$\gamma \left[(v_1', v_2', v_3') f \leftarrow (v_1'', v_2'', v_3'') i \right] = I_{f \leftarrow i}^\gamma + A_{f \leftarrow i} (c_1 \Delta v_1 + c_2 \Delta v_2 + c_3 \Delta v_3)^{p_\gamma} \tag{5a}$$

$$\delta \left[(v_1', v_2', v_3') f \leftarrow (v_1'', v_2'', v_3'') i \right] = I_{f \leftarrow i}^\delta + B_{f \leftarrow i} (c_1 \Delta v_1 + c_2 \Delta v_2 + c_3 \Delta v_3)^{p_\delta} \tag{5b}$$

where γ and δ are the half-width and line shift for the ro-vibrational transition

$(v_1', v_2', v_3') f \leftarrow (v_1'', v_2'', v_3'') i$, $I_{f \leftarrow i}^\gamma$ and $I_{f \leftarrow i}^\delta$ are the intercepts and $A_{f \leftarrow i}$ and $B_{f \leftarrow i}$ are

the slopes both with units of $\text{cm}^{-1} \text{atm}^{-1}$, and $(c_1 \Delta v_1 + c_2 \Delta v_2 + c_3 \Delta v_3)^{p_\gamma}$ and

$(c_1 \Delta v_1 + c_2 \Delta v_2 + c_3 \Delta v_3)^{p_\delta}$ are the *Quantum Coordinates* of the lines describing the

vibrational dependence of the half-widths and line shifts respectively. Note, this

modification has the effect of stretching or compressing the space of the model to allow

better prediction (described below). If data are available for a number of ro-vibrational

transitions with the same J' and J'' fits can be made to Eqs. (5) to determine the power,

slope, and intercept. The procedure is described below.

The notation of Toth *et al.* [54], given by 5 integers, is used for the vibrational states of CO_2 ; $v_1 v_2 \ell_2 v_3 n$. $v_1 v_2$ and v_3 give the number of active quanta for each

fundamental, ℓ_2 is the ℓ value for the ν_2 degenerate fundamental and its overtones, and n is the n^{th} component of the ν_1 and $2\nu_2$ Fermi interacting states (including their overtone and combination states). This notation can be put in generic normal-mode notation by removing one quantum of ν_1 and adding two quanta of ν_2 for each n^{th} component greater than 1. For example the vibrational state 20011 is $2\nu_1 + \nu_3$ in normal mode notation and 20012 is $\nu_1 + 2\nu_2 + \nu_3$.

Equations (3) and (5) and the coefficients of the vibrational dependence of the polarizability for CO_2 suggest that transitions where the only vibrational quantum number that changes is n should have identical half-widths and line shifts because for each increase in n , ν_1 decreases by 1, ν_2 increases by 2 but the coefficient for ν_1 is twice that for ν_2 .

3. Calculations

In order to make fits to Eqs. (5) half-width and line shift data must be available for a number of vibrational transitions for the same rotational transition. Because the *Quantum Coordinate* depends on the number of ν_1 , ν_2 , and ν_3 quanta exchanged in the transition the fits should contain data where the number exchanged is large. To get such data, CRB calculations were made following the methods of Refs. [41-43] for J'' from 0 to 160 for the 24 vibrational bands listed in Table 1, which considers vibrational transitions up to $\Delta\nu_1=3$, $\Delta\nu_2=5$, and $\Delta\nu_3=9$. To allow the prediction of all transitions (fundamental, hot, and overtone band) the calculations considered all rotational states, even and odd, even for the rotational states. The calculations were made for N_2^- , O_2^- , air-

, and self-broadening of CO₂. The molecular constants used in the CRB calculations are listed in Refs. [41-43] and the constants used for energies and wavefunctions of CO₂ in Ref. [47]. The data at 9 temperatures were used in the current study; 200, 250, 296, 350, 500, 700, 1000, 1500, 2000 K.

One important question arises. If fits are to be made to the CRB calculated half-widths and line shifts to determine parameters that will allow prediction of half-widths and line shifts for transitions that have not been measured or calculated, what is the accuracy of the CRB calculations? The CRB calculations have been compared with recent high accuracy measurement in Refs. [41-43, 47] and in general the half-widths agree with a standard deviation of 1-3 % and the line shifts show very small deviations. See the cited references for details.

The databases for high-temperature applications [28, 29] have data for transitions with J'' up to 200. The current limit of the CRB codes is $J''=160$. In order to obtain the needed data several extrapolations routines were developed to predict the half-width and line shift for these transitions for each temperature of the study. The half-widths were considered first. Plots of $\gamma(296\text{ K})$, $d\gamma/dJ''$ and $d^2\gamma/dJ''^2$ versus m were made in the range $J''=140-160$. From these data it was determined that a linear fit of the data from $J''=141$ to 160 could allow extrapolation from $J''=161$ to 200. Fits were made and the extrapolated half-width data produced at the temperatures considered in this work.

The study of the line shifts considered the three methods tested above. The first and second derivatives of the line shift show strong oscillations but over a small range. It is thought this is due to taking differences between a quantity (the line shift) with small magnitude. Fitting the line shifts from $J''=151-160$ to a straight line worked quite well

and allowed the extrapolation from $J''=161-200$. Extrapolated line shifts were produced for the 9 temperatures of the study.

As an example, Fig. 1 presents the half-widths, line shifts, and temperature dependence of the half-width in the range 200-350 K versus m for the $30012 \leftarrow 00001$ band of CO_2 with air as the buffer gas. Plotted are the data for the P-, Q-, and R-branch given by a black +, red \times , and solid blue circle symbols, respectively. Note, that while this band does not have Q-transitions the prediction routine allows Q-lines to be calculated and these data are included for comparison with data for the other branches. In general there is only a small variation in the P-, Q-, and R-branch data. The extrapolated data smoothly join the calculated data. These data were then used in fits of Eqs. (5) to determine the parameters that allow predictions to be made for transitions with J'' up to 200.

4. Fits to determine the coefficients in Eqs. 5

Equations (5) were fit to the CRB half-width and line shift data using a search algorithm that adjusts the power p_γ (or p_δ) then makes a least-squares fit to determine the slope ($A_{f \leftarrow i}$ or $B_{f \leftarrow i}$) and the intercept ($I_{f \leftarrow i}^\gamma$ or $I_{f \leftarrow i}^\delta$) of the line and the correlation coefficient, R , of the fit. The algorithm iterates by a simple stepping method, where the step size decreases when the direction changes, until the best fit determined by $1-|R|$ less than a threshold, ϵ , here set to 0.0001. Note, a correlation coefficient equal to $|1|$ implies the data perfectly fits the equation. The initial choices of the powers in the algorithm are 2.01 for p_γ and 1.01 for p_δ , with an initial step of -0.002, thus walking toward the theoretical values of 2 and 1 for γ and δ , respectively. When the value of $1-|R|$ increases

with the step, the step size is halved and the walk direction changed. Figures 2a and 2b show the fits for air-broadening of CO₂ at 296 K for the P16 and P116 transitions. Shown are the calculated data (blue + symbol), the fit of the data (red line) and in the top panel the measured data (black x symbol). Figs. 3a and b show the fits for the air-induced line shifts of CO₂ for the same transitions in the same format as Fig. 2. The CO₂-air measured half-width data are from the work of Tanaka *et al.* [55], Devi *et al.* [56, 57], Toth *et al.* [58], Predoi-Cross *et al.* [59, 60], and Gulidova *et al.* [61]. The air-induced line shift measurements are from the work of Devi *et al.* [57], Toth *et al.* [58], Predoi-Cross *et al.* [59, 60], and Gulidova *et al.* [61].

Fits were made for each rotational transition at each of the temperatures of the study. On average the algorithm took less than 10 iterations for low J'' lines and up to several hundred for high J'' lines. In general the correlation coefficients are 1 to three significant figures or better, even for the extrapolated data. The appropriateness of the model (Eqs. (5)) is evident from the plots or the correlation coefficients determined for the fits. Similar fit results were obtained for all the broadening molecules at all the temperatures of the study. Complete sets of plots for pressure -broadening and pressure shifting of CO₂ with the buffer gases N₂, O₂, air, and CO₂ for each temperature studied can be found on the corresponding author's web site (faculty.uml.edu/Robert_Gamache).

Tables 2 and 3 report the fit parameters for the air-broadened half-width and the air-induced pressure shift of CO₂ transitions for the temperature 296 K. Table 2 gives the results for P-branch transitions from J''=1 to 200 and Table 3 gives the results for R-branch transitions from J''=0 to 200. These data allow the recalculation of γ and δ data in Table 1 and the prediction of γ and δ data for other transitions for the CO₂-air collision

system. The complete set of fit data from the above work allows the prediction of γ and δ data for the other perturbing gases and temperatures.

5. Prediction algorithm

Using the intercept, slope, and power data from the fits line shape parameters, prediction routines were written for the CO₂-N₂, CO₂-O₂, CO₂-air, and CO₂-CO₂ collision systems at the 9 temperatures of this study. Because the line shape parameters can be determined at different temperatures, the prediction routines can be customized for particular application such as the atmospheres of Mars or Venus or high temperature applications. The authors are currently working with the CDS group [26-28] and with Huang *et al.* [29] to add line shape information to their databases. Researchers who would like CO₂ line shape information in a particular temperature range within 200-2000 K are encouraged to contact the corresponding author.

6. Discussion and Conclusion

An examination of the complex Robert-Bonamy equations for carbon dioxide as the radiating molecule revealed that for comparing vibrational transitions for the same rotational transition the S₂ components cancel each other to a large extent leaving the S₁ term as the dominant component in determining the vibrational dependence of the half-width and line shift. This result leads to a simple theoretical expression to model the vibrational dependence of a rotational transition, e.g. Eqs. 5. Using CRB calculations of

the half-width and line shift, which have shown excellent agreement with measurement, for 24 vibrational bands, fits of Eqs. (5) to the data were made at 9 temperatures ranging from 200-2000 K for rotational transitions with $J''=0$ to 160. The correlation coefficients of the fits clearly demonstrate the quality of Eqs. (5) to represent the vibrational dependence of γ and δ data. These data were extrapolated to $J''=200$ for application to the high temperature databases. The results of the fits for each rotational transition, the slope, intercept, and power in the *Quantum Coordinate*, can be used to predict γ and δ for the same rotational transition for any vibrational transition. Because the fitting data are available over a range of temperatures, the temperature dependence of the line shape parameters can also be determined for particular temperature ranges.

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Tables

- 1 Vibrational band for which CRB calculations were made.
- 2 p_γ , $I_{f \leftarrow i}^\gamma$, $A_{f \leftarrow i}$, and the correlation coefficient R from the fit of Eq. 5a for P-branch transitions from $J''=1$ to 200 for CO₂ broadened by air at 296K.
- 3 p_δ , $I_{f \leftarrow i}^\delta$, $B_{f \leftarrow i}$, and the correlation coefficient R from the fit of Eq. 5b for R-branch transitions from $J''=0$ to 200 for CO₂ broadened by air at 296K.

Table 1 Vibrational bands for which CRB calculations were made.

band	band
00001 ← 00001	30001 ← 00001
00011 ← 00001	01101e ← 00001
00021 ← 00001	02201e ← 00001
00031 ← 00001	03301e ← 00001
00041 ← 00001	04401e ← 00001
00051 ← 00001	05501e ← 00001
00061 ← 00001	20011 ← 00001
00071 ← 00001	20012 ← 00001
00081 ← 00001	20013 ← 00001
00091 ← 00001	30011 ← 00001
10001 ← 00001	30012 ← 00001
20001 ← 00001	30013 ← 00001

2 p_γ , $I_{f \leftarrow i}^\gamma$, $A_{f \leftarrow i}$, and the correlation coefficient R from the fit of Eq. 5a for P-branch transitions from $J''=1$ to 200 for CO₂ broadened by air at 296K.

J'	J''	p_γ	$I_{f \leftarrow i}^\gamma \dagger$	$A_{f \leftarrow i} * 100^\dagger$	R
0	1	2.008	0.09265	0.01681	0.9969
1	2	2.002	0.08920	0.02019	1.0050
2	3	2.004	0.08840	0.02170	1.0044
3	4	2.004	0.08779	0.02335	0.9985
4	5	2.002	0.08709	0.02581	0.9991
5	6	2.002	0.08625	0.02843	1.0007
6	7	1.948	0.08529	0.03302	0.9946
7	8	1.900	0.08424	0.03819	0.9989
8	9	1.832	0.08312	0.04498	0.9980
9	10	1.840	0.08197	0.05005	0.9994
10	11	1.786	0.08084	0.05780	0.9990
11	12	1.854	0.07978	0.05959	0.9987
12	13	1.768	0.07873	0.06971	0.9989
13	14	1.776	0.07770	0.07522	0.9991
14	15	1.752	0.07666	0.08253	0.9991
15	16	1.726	0.07565	0.08910	0.9995
16	17	1.742	0.07473	0.09128	0.9991
17	18	1.800	0.07391	0.08880	0.9991
18	19	1.832	0.07318	0.08717	0.9990
19	20	1.832	0.07252	0.08712	0.9991
20	21	1.816	0.07193	0.08785	0.9997
21	22	1.806	0.07140	0.08822	0.9995
22	23	1.872	0.07094	0.08349	0.9994
23	24	1.872	0.07051	0.08372	0.9995
24	25	1.872	0.07012	0.08392	0.9994
25	26	1.840	0.06977	0.08624	0.9996
26	27	1.824	0.06946	0.08726	0.9997
27	28	1.836	0.06921	0.08617	0.9997
28	29	1.872	0.06902	0.08337	0.9997
29	30	1.872	0.06885	0.08307	0.9996
30	31	1.872	0.06871	0.08284	1.0000
31	32	1.872	0.06859	0.08285	1.0001
32	33	1.872	0.06847	0.08318	0.9998
33	34	1.872	0.06836	0.08376	0.9998
34	35	1.872	0.06825	0.08441	0.9999
35	36	1.890	0.06815	0.08373	1.0000
36	37	1.922	0.06806	0.08181	0.9997
37	38	1.904	0.06796	0.08309	0.9998
38	39	1.908	0.06789	0.08275	0.9998

39	40	1.900	0.06782	0.08322	1.0000
40	41	1.948	0.06778	0.08006	0.9997
41	42	1.932	0.06770	0.08137	0.9998
42	43	1.892	0.06762	0.08451	1.0001
43	44	1.900	0.06753	0.08466	0.9998
44	45	1.948	0.06745	0.08243	0.9996
45	46	1.890	0.06732	0.08788	0.9999
46	47	1.884	0.06720	0.08970	0.9996
47	48	1.864	0.06707	0.09227	1.0000
48	49	1.878	0.06696	0.09186	0.9998
49	50	1.838	0.06684	0.09544	0.9996
50	51	1.872	0.06674	0.09343	0.9997
51	52	1.854	0.06662	0.09570	0.9998
52	53	1.832	0.06648	0.09846	0.9998
53	54	1.846	0.06634	0.09844	0.9996
54	55	1.806	0.06618	0.10322	0.9998
55	56	1.816	0.06602	0.10433	0.9997
56	57	1.796	0.06583	0.10839	0.9994
57	58	1.770	0.06564	0.11291	0.9996
58	59	1.766	0.06547	0.11479	0.9996
59	60	1.752	0.06530	0.11718	0.9998
60	61	1.770	0.06514	0.11651	0.9996
61	62	1.746	0.06496	0.12031	0.9996
62	63	1.742	0.06478	0.12244	0.9995
63	64	1.714	0.06457	0.12694	0.9996
64	65	1.688	0.06436	0.13104	0.9996
65	66	1.694	0.06417	0.13197	0.9996
66	67	1.648	0.06393	0.13958	0.9997
67	68	1.650	0.06371	0.14239	0.9996
68	69	1.640	0.06349	0.14639	0.9995
69	70	1.624	0.06327	0.15036	0.9996
70	71	1.630	0.06307	0.15107	0.9995
71	72	1.624	0.06286	0.15339	0.9996
72	73	1.606	0.06264	0.15771	0.9996
73	74	1.584	0.06241	0.16286	0.9995
74	75	1.594	0.06219	0.16350	0.9996
75	76	1.570	0.06196	0.16850	0.9995
76	77	1.586	0.06174	0.16806	0.9995
77	78	1.552	0.06149	0.17543	0.9994
78	79	1.558	0.06128	0.17746	0.9994
79	80	1.572	0.06107	0.17803	0.9995
80	81	1.554	0.06084	0.18275	0.9996
81	82	1.548	0.06063	0.18534	0.9996
82	83	1.564	0.06043	0.18474	0.9994
83	84	1.540	0.06019	0.19088	0.9994

84	85	1.532	0.05997	0.19473	0.9995
85	86	1.552	0.05977	0.19367	0.9995
86	87	1.558	0.05956	0.19443	0.9995
87	88	1.526	0.05932	0.20162	0.9995
88	89	1.516	0.05909	0.20579	0.9995
89	90	1.512	0.05888	0.20947	0.9995
90	91	1.520	0.05868	0.21109	0.9995
91	92	1.520	0.05848	0.21378	0.9995
92	93	1.512	0.05827	0.21776	0.9995
93	94	1.506	0.05806	0.22146	0.9994
94	95	1.494	0.05785	0.22651	0.9995
95	96	1.500	0.05766	0.22809	0.9995
96	97	1.502	0.05746	0.23015	0.9995
97	98	1.494	0.05727	0.23370	0.9995
98	99	1.512	0.05710	0.23200	0.9995
99	100	1.490	0.05689	0.23846	0.9995
100	101	1.512	0.05673	0.23638	0.9995
101	102	1.502	0.05654	0.24084	0.9995
102	103	1.506	0.05636	0.24230	0.9995
103	104	1.500	0.05618	0.24558	0.9996
104	105	1.512	0.05602	0.24496	0.9996
105	106	1.512	0.05585	0.24685	0.9996
106	107	1.516	0.05568	0.24788	0.9996
107	108	1.506	0.05551	0.25176	0.9996
108	109	1.502	0.05534	0.25423	0.9996
109	110	1.512	0.05518	0.25365	0.9996
110	111	1.484	0.05499	0.26153	0.9996
111	112	1.486	0.05483	0.26320	0.9996
112	113	1.478	0.05466	0.26738	0.9996
113	114	1.486	0.05452	0.26797	0.9996
114	115	1.474	0.05435	0.27298	0.9996
115	116	1.478	0.05421	0.27421	0.9996
116	117	1.472	0.05405	0.27773	0.9995
117	118	1.482	0.05392	0.27740	0.9996
118	119	1.478	0.05377	0.28021	0.9997
119	120	1.486	0.05365	0.27991	0.9996
120	121	1.484	0.05351	0.28173	0.9996
121	122	1.480	0.05337	0.28414	0.9997
122	123	1.484	0.05324	0.28496	0.9996
123	124	1.488	0.05311	0.28606	0.9997
124	125	1.486	0.05298	0.28874	0.9997
125	126	1.492	0.05286	0.28939	0.9997
126	127	1.486	0.05272	0.29291	0.9997
127	128	1.488	0.05260	0.29450	0.9997
128	129	1.494	0.05248	0.29529	0.9997

129	130	1.494	0.05235	0.29770	0.9997
130	131	1.496	0.05223	0.29965	0.9997
131	132	1.490	0.05210	0.30360	0.9997
132	133	1.490	0.05198	0.30599	0.9997
133	134	1.484	0.05185	0.31000	0.9997
134	135	1.478	0.05172	0.31416	0.9997
135	136	1.488	0.05162	0.31407	0.9997
136	137	1.490	0.05151	0.31589	0.9997
137	138	1.490	0.05140	0.31800	0.9997
138	139	1.494	0.05130	0.31881	0.9997
139	140	1.492	0.05119	0.32107	0.9998
140	141	1.492	0.05108	0.32277	0.9998
141	142	1.482	0.05096	0.32716	0.9997
142	143	1.486	0.05086	0.32767	0.9997
143	144	1.484	0.05075	0.32993	0.9997
144	145	1.486	0.05065	0.33125	0.9997
145	146	1.484	0.05055	0.33383	0.9997
146	147	1.474	0.05043	0.33894	0.9997
147	148	1.476	0.05033	0.34075	0.9997
148	149	1.478	0.05023	0.34265	0.9997
149	150	1.478	0.05012	0.34526	0.9997
150	151	1.474	0.05001	0.34920	0.9997
151	152	1.470	0.04990	0.35325	0.9997
152	153	1.474	0.04981	0.35497	0.9997
153	154	1.478	0.04971	0.35656	0.9997
154	155	1.478	0.04961	0.35923	0.9997
155	156	1.484	0.04952	0.35993	0.9997
156	157	1.474	0.04940	0.36542	0.9997
157	158	1.474	0.04930	0.36764	0.9997
158	159	1.474	0.04921	0.36961	0.9997
159	160	1.470	0.04911	0.37253	0.9997
160	161	1.478	0.04900	0.37306	0.9996
161	162	1.470	0.04888	0.37792	0.9996
162	163	1.470	0.04878	0.38024	0.9996
163	164	1.470	0.04868	0.38256	0.9996
164	165	1.470	0.04858	0.38488	0.9996
165	166	1.466	0.04847	0.38851	0.9996
166	167	1.470	0.04837	0.38952	0.9996
167	168	1.470	0.04827	0.39184	0.9995
168	169	1.474	0.04817	0.39282	0.9995
169	170	1.472	0.04807	0.39580	0.9995
170	171	1.462	0.04795	0.40151	0.9995
171	172	1.460	0.04784	0.40454	0.9995
172	173	1.464	0.04775	0.40550	0.9995
173	174	1.470	0.04766	0.40576	0.9994

174	175	1.460	0.04753	0.41156	0.9994
175	176	1.458	0.04743	0.41460	0.9994
176	177	1.456	0.04732	0.41765	0.9994
177	178	1.464	0.04724	0.41716	0.9994
178	179	1.454	0.04711	0.42307	0.9994
179	180	1.452	0.04701	0.42614	0.9994
180	181	1.456	0.04691	0.42705	0.9993
181	182	1.452	0.04680	0.43086	0.9993
182	183	1.452	0.04670	0.43321	0.9993
183	184	1.450	0.04659	0.43631	0.9993
184	185	1.450	0.04649	0.43867	0.9993
185	186	1.452	0.04639	0.44028	0.9992
186	187	1.446	0.04628	0.44490	0.9992
187	188	1.448	0.04618	0.44651	0.9992
188	189	1.448	0.04608	0.44887	0.9992
189	190	1.446	0.04597	0.45201	0.9992
190	191	1.448	0.04587	0.45360	0.9991
191	192	1.448	0.04577	0.45597	0.9991
192	193	1.444	0.04566	0.45990	0.9991
193	194	1.448	0.04557	0.46070	0.9991
194	195	1.448	0.04546	0.46306	0.9991
195	196	1.454	0.04537	0.46306	0.9990
196	197	1.442	0.04525	0.47019	0.9990
197	198	1.442	0.04514	0.47256	0.9990
198	199	1.442	0.04504	0.47494	0.9990
199	200	1.448	0.04495	0.47488	0.9990

† in units of $\text{cm}^{-1} \text{atm}^{-1}$

- 3 p_{δ} , $I_{f \leftarrow i}^{\delta}$, $B_{f \leftarrow i}$, and the correlation coefficient R from the fit of Eq. 5b for R-branch transitions from $J''=0$ to 200 for CO₂ broadened by air at 296K.

J'	J''	P_{δ}	$I_{f \leftarrow i}^{\delta} * 1000^{\dagger}$	$B_{f \leftarrow i} * 10^{\dagger}$	R
1	0	0.992	-0.02931	-0.06293	-1.0000
2	1	0.990	-0.04248	-0.06708	-1.0000
3	2	0.990	0.00560	-0.06812	-1.0000
4	3	0.990	0.09853	-0.06902	-1.0000
5	4	0.988	0.16167	-0.07017	-1.0000
6	5	0.988	0.17573	-0.07140	-1.0000
7	6	0.986	0.18050	-0.07304	-1.0000
8	7	0.982	0.17204	-0.07506	-1.0000
9	8	0.980	0.14911	-0.07721	-1.0000
10	9	0.974	0.13615	-0.07983	-1.0000
11	10	0.968	0.12333	-0.08246	-1.0000
12	11	0.964	0.12689	-0.08485	-1.0000
13	12	0.960	0.15839	-0.08718	-1.0000
14	13	0.956	0.18534	-0.8945	-1.0000
15	14	0.952	0.19910	-0.09173	-1.0000
16	15	0.948	0.20796	-0.09396	-1.0000
17	16	0.948	0.18957	-0.09570	-0.9999
18	17	0.946	0.19358	-0.09745	-0.9999
19	18	0.950	0.16874	-0.09848	-0.9999
20	19	0.952	0.15465	-0.09950	-1.0000
21	20	0.954	0.14517	-0.10041	-1.0000
22	21	0.954	0.15698	-0.10146	-1.0000
23	22	0.958	0.13609	-0.10201	-1.0000
24	23	0.958	0.13957	-0.10286	-1.0000
25	24	0.958	0.14027	-0.10361	-1.0000
26	25	0.958	0.13166	-0.10422	-1.0000
27	26	0.960	0.10762	-0.10456	-1.0000
28	27	0.958	0.11965	-0.10524	-1.0000
29	28	0.958	0.11697	-0.10565	-1.0000
30	29	0.960	0.09882	-0.10576	-1.0000
31	30	0.958	0.11239	-0.10624	-1.0000
32	31	0.958	0.11619	-0.10650	-1.0000
33	32	0.958	0.12495	-0.10680	-1.0000
34	33	0.958	0.13633	-0.10712	-1.0000
35	34	0.958	0.14388	-0.10739	-1.0000
36	35	0.958	0.14434	-0.10762	-1.0000
37	36	0.960	0.12497	-0.10757	-1.0000
38	37	0.960	0.11985	-0.10772	-1.0000
39	38	0.958	0.13410	-0.10807	-1.0000

40	39	0.958	0.13178	-0.10820	-1.0000
41	40	0.958	0.12389	-0.10827	-1.0000
42	41	0.958	0.12107	-0.10838	-1.0000
43	42	0.956	0.13838	-0.10879	-1.0000
44	43	0.958	0.12661	-0.10883	-1.0000
45	44	0.956	0.14371	-0.10930	-1.0000
46	45	0.958	0.12504	-0.10930	-1.0000
47	46	0.956	0.12769	-0.10968	-1.0000
48	47	0.956	0.11549	-0.10984	-1.0000
49	48	0.954	0.12258	-0.11024	-1.0000
50	49	0.954	0.11411	-0.11044	-1.0000
51	50	0.954	0.10344	-0.11062	-1.0000
52	51	0.952	0.10719	-0.11102	-1.0000
53	52	0.950	0.11428	-0.11149	-1.0000
54	53	0.948	0.12596	-0.11207	-1.0000
55	54	0.948	0.12280	-0.11246	-1.0000
56	55	0.946	0.12821	-0.11303	-1.0000
57	56	0.946	0.11308	-0.11333	-1.0000
58	57	0.944	0.11330	-0.11385	-1.0000
59	58	0.942	0.11817	-0.11440	-1.0000
60	59	0.940	0.12729	-0.11498	-1.0000
61	60	0.940	0.11548	-0.11530	-1.0000
62	61	0.938	0.11642	-0.11582	-1.0000
63	62	0.936	0.11715	-0.11640	-1.0000
64	63	0.934	0.12181	-0.11710	-1.0000
65	64	0.934	0.11546	-0.11767	-1.0000
66	65	0.932	0.12598	-0.11846	-1.0000
67	66	0.932	0.11227	-0.11894	-1.0000
68	67	0.928	0.12685	-0.11982	-1.0000
69	68	0.928	0.11080	-0.12022	-1.0000
70	69	0.924	0.13080	-0.12112	-1.0000
71	70	0.924	0.11632	-0.12158	-1.0000
72	71	0.922	0.11508	-0.12224	-1.0000
73	72	0.920	0.11126	-0.12289	-1.0000
74	73	0.918	0.10932	-0.12362	-1.0000
75	74	0.916	0.11612	-0.12449	-1.0000
76	75	0.914	0.12769	-0.12543	-1.0000
77	76	0.914	0.11964	-0.12608	-1.0000
78	77	0.912	0.12623	-0.12689	-1.0000
79	78	0.910	0.13152	-0.12764	-1.0000
80	79	0.910	0.12279	-0.12816	-1.0000
81	80	0.906	0.15216	-0.12923	-1.0000
82	81	0.906	0.14203	-0.12978	-1.0000
83	82	0.906	0.12769	-0.13030	-1.0000
84	83	0.904	0.13035	-0.13108	-1.0000

85	84	0.902	0.13441	-0.13191	-1.0000
86	85	0.902	0.12417	-0.13257	-1.0000
87	86	0.900	0.13627	-0.13353	-1.0000
88	87	0.900	0.12635	-0.13418	-1.0000
89	88	0.896	0.15310	-0.13529	-1.0000
90	89	0.896	0.14067	-0.13582	-1.0000
91	90	0.894	0.14707	-0.13659	-0.9999
92	91	0.892	0.15208	-0.13737	-0.9999
93	92	0.890	0.15791	-0.13816	-0.9999
94	93	0.888	0.16183	-0.13895	-0.9999
95	94	0.886	0.16722	-0.13974	-0.9999
96	95	0.884	0.17740	-0.14058	-0.9999
97	96	0.882	0.19078	-0.14146	-0.9999
98	97	0.882	0.18669	-0.14211	-0.9999
99	98	0.882	0.18376	-0.14276	-0.9999
100	99	0.880	0.20140	-0.14367	-0.9999
101	100	0.880	0.19637	-0.14425	-0.9999
102	101	0.880	0.18918	-0.14482	-0.9999
103	102	0.880	0.17963	-0.14538	-0.9999
104	103	0.878	0.19116	-0.14624	-0.9999
105	104	0.878	0.18216	-0.14683	-0.9999
106	105	0.876	0.19679	-0.14772	-0.9999
107	106	0.876	0.19069	-0.14831	-0.9999
108	107	0.874	0.20691	-0.14922	-0.9999
109	108	0.874	0.19980	-0.14982	-0.9999
110	109	0.874	0.19086	-0.15039	-0.9999
111	110	0.874	0.18060	-0.15094	-0.9999
112	111	0.872	0.19020	-0.15174	-0.9999
113	112	0.870	0.19812	-0.15252	-0.9999
114	113	0.868	0.20647	-0.15329	-0.9999
115	114	0.868	0.19299	-0.15377	-0.9999
116	115	0.866	0.20529	-0.15456	-0.9999
117	116	0.866	0.19742	-0.15506	-0.9999
118	117	0.864	0.21412	-0.15587	-0.9999
119	118	0.864	0.20864	-0.15639	-0.9999
120	119	0.862	0.22813	-0.15725	-0.9999
121	120	0.862	0.22527	-0.15783	-0.9999
122	121	0.862	0.22225	-0.15840	-0.9999
123	122	0.862	0.21736	-0.15893	-0.9999
124	123	0.862	0.20986	-0.15943	-0.9999
125	124	0.862	0.20089	-0.15991	-0.9999
126	125	0.862	0.19257	-0.16040	-0.9999
127	126	0.860	0.20943	-0.16122	-0.9999
128	127	0.860	0.20197	-0.16170	-0.9999
129	128	0.858	0.21743	-0.16247	-0.9999

130	129	0.858	0.20539	-0.16289	-0.9999
131	130	0.856	0.21548	-0.16362	-0.9999
132	131	0.854	0.22550	-0.16435	-0.9999
133	132	0.854	0.21089	-0.16474	-0.9999
134	133	0.854	0.19623	-0.16512	-0.9999
135	134	0.852	0.20808	-0.16582	-0.9999
136	135	0.850	0.22072	-0.16652	-0.9999
137	136	0.848	0.23556	-0.16724	-0.9998
138	137	0.848	0.22740	-0.16765	-0.9998
139	138	0.846	0.24645	-0.16841	-0.9998
140	139	0.846	0.23946	-0.16882	-0.9998
141	140	0.846	0.23177	-0.16924	-0.9998
142	141	0.846	0.22300	-0.16965	-0.9998
143	142	0.846	0.21302	-0.17005	-0.9998
144	143	0.844	0.22862	-0.17079	-0.9998
145	144	0.844	0.21768	-0.17117	-0.9998
146	145	0.842	0.23201	-0.17189	-0.9998
147	146	0.842	0.22022	-0.17225	-0.9998
148	147	0.842	0.20809	-0.17260	-0.9998
149	148	0.840	0.22127	-0.17328	-0.9998
150	149	0.840	0.20567	-0.17358	-0.9998
151	150	0.838	0.21451	-0.17420	-0.9998
152	151	0.836	0.21986	-0.17479	-0.9998
153	152	0.836	0.19739	-0.17501	-0.9998
154	153	0.834	0.20248	-0.17560	-0.9997
155	154	0.834	0.18137	-0.17584	-0.9997
156	155	0.832	0.18876	-0.17645	-0.9997
157	156	0.830	0.19921	-0.17708	-0.9997
158	157	0.830	0.18274	-0.17736	-0.9997
159	158	0.828	0.19693	-0.17803	-0.9997
160	159	0.826	0.21294	-0.17873	-0.9997
161	160	0.826	0.20186	-0.17908	-0.9997
162	161	0.824	0.20284	-0.17962	-0.9997
163	162	0.822	0.21392	-0.18026	-0.9997
164	163	0.822	0.19669	-0.18054	-0.9996
165	164	0.820	0.20801	-0.18119	-0.9996
166	165	0.820	0.19084	-0.18146	-0.9996
167	166	0.818	0.20244	-0.18212	-0.9996
168	167	0.816	0.21428	-0.18277	-0.9996
169	168	0.816	0.19719	-0.18305	-0.9996
170	169	0.814	0.20929	-0.18371	-0.9996
171	170	0.814	0.19227	-0.18399	-0.9995
172	171	0.812	0.20462	-0.18465	-0.9995
173	172	0.812	0.18765	-0.18492	-0.9995
174	173	0.810	0.20030	-0.18559	-0.9995

175	174	0.808	0.21317	-0.18626	-0.9995
176	175	0.806	0.22626	-0.18692	-0.9995
177	176	0.806	0.20944	-0.18721	-0.9995
178	177	0.806	0.19262	-0.18749	-0.9995
179	178	0.804	0.20605	-0.18816	-0.9994
180	179	0.804	0.18928	-0.18844	-0.9994
181	180	0.802	0.20298	-0.18912	-0.9994
182	181	0.800	0.21692	-0.18980	-0.9994
183	182	0.800	0.20027	-0.19008	-0.9994
184	183	0.798	0.21448	-0.19076	-0.9994
185	184	0.798	0.19788	-0.19104	-0.9994
186	185	0.796	0.21239	-0.19173	-0.9993
187	186	0.794	0.22712	-0.19242	-0.9993
188	187	0.794	0.21063	-0.19270	-0.9993
189	188	0.792	0.22566	-0.19339	-0.9993
190	189	0.792	0.20922	-0.19368	-0.9993
191	190	0.792	0.19278	-0.19397	-0.9993
192	191	0.790	0.20815	-0.19466	-0.9992
193	192	0.788	0.22376	-0.19536	-0.9992
194	193	0.788	0.20743	-0.19564	-0.9992
195	194	0.786	0.22334	-0.19635	-0.9992
196	195	0.784	0.23948	-0.19705	-0.9992
197	196	0.784	0.22327	-0.19734	-0.9991
198	197	0.784	0.20705	-0.19763	-0.9991
199	198	0.782	0.22356	-0.19833	-0.9991
200	199	0.780	0.24030	-0.19904	-0.9991
201	200	0.780	0.22420	-0.19933	-0.9991

† in units of $\text{cm}^{-1} \text{atm}^{-1}$

Figures

- 1 Predicted half-widths (top panel), line shifts (middle panel), and temperature dependence of the half-width in the range 200-350 K (bottom panel) versus m for the $30012 \leftarrow 00001$ band of CO_2 with air as the buffer gas. See text for description.
- 2 Fits of Eq. 5a to the calculated data for the half-widths of the P16 and P116 transition at 296 K for the CO_2 -air collision system. See text for description.
- 3 Fits of Eq. 5b to the calculated data for the line shifts of the P16 and P116 transition at 296 K for the CO_2 -air collision system. See text for description.