# Calculation of $CO_2$ broadening and shift coefficients for high-temperature databases

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A semiempiric approach has been developed for calculation of halfwidths and shifts of spectral lines. This approach incorporates corrections for the Anderson–Tsao–Curnutte approximation. Model parameters were determined by fitting the broadening and shift coefficients to experimental data. This allows sufficiently accurate prediction of the parameters of line profiles, which were not measured. The coefficients of $CO_2$ spectral lines broadening and shifting by air and nitrogen pressure are calculated, as well as the coefficients of thermal dependence of line profiles. The calculated parameters are intended for use in spectroscopic databases.

## Introduction

Various problems of atmospheric physics, astrophysics, and laser physics require a knowledge of spectral line parameters for carbon dioxide and its main isotopic species in a wide temperature range for different vibrational bands from the mid-infrared to visible spectral region. For example, for solution of problems of atmospheric physics, one should know the halfwidths of the $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, and $^{12}C^{18}O_2$ spectral lines (and some other isotopic species of carbon dioxide) in air accurate to no less than 10% at the temperature of 200–350 K. In this case, the fundamental, overtone, and combination bands must be calculated, as well as hot bands, i.e., the bands caused by transitions from the excited vibrational states. Besides, the broadening and shift coefficients and the parameters of temperature dependence must be determined. The amount of information needed for solution of the problems of atmospheric spectroscopy includes about 50 000 spectral lines. Even greater amount is needed for calculating the spectra of flame (as well as spectra of planets), because in this case one needs the information on spectra at the temperature of 2000–3000 K, which include a large number of hot bands.

Currently, there is not information on the coefficients of broadening by air pressure in the HITRAN-96 database; only mean values of the coefficients of temperature dependence of spectral line broadening can be found there. Thus, the available information is obviously insufficient, and the HITRAN database has to be expanded and supplemented with new data.

It should be noted that halfwidths of spectral lines only slightly depend on vibrational quantum numbers. The largest difference in the halfwidths of different bands is as small as several percent. Therefore, the broadening coefficients can be calculated for only one band and then extrapolated to other vibrational bands.

At the same time, the shift coefficients can vary significantly (several times) from one band to another. So, calculations should be performed for every band separately, or the shifts should be determined by some interpolation. Therefore, the amount of calculations for compilation of a more complete database increases tens times. On the other hand, the exponents of the temperature dependence of line halfwidths can vary widely depending on the rotational quantum number $J$ because of the strong temperature dependence of the population of a lower energy level. Therefore, these parameters are different for low and high values of $J$.

The use of the mean value of the temperature exponent in spectroscopic calculations is apparently a rather rough approximation. Consequently, this parameter should be determined separately for each line. This circumstance also complicates the problem, and the amount of necessary calculations increases several times. The isotopic effect in the shift coefficients can be significant, and therefore the parameters for isotopic species should be calculated separately as well.

Earlier, the broadening parameters of rotational-vibrational lines of molecular gases were calculated within the framework of the semiclassic Robert–Bonamy (RB) theory.[1] This theory is based on the exact simulation of the intermolecular potential and takes into account fine details of collisions and intramolecular dynamics. It requires rather complicated and long-time calculations (even for one line). Calculations for the entire IR spectrum prove to be very computationally expensive. So, there is a need to simplify the procedure of calculation without any loss in accuracy. That is, the impact theory should be modified so that to decrease computations, on the one hand, and to keep the quality, on the other hand. Such a modification may be based on the wider use of empiric data than in the semiclassic RB theory. For this purpose, general equations of the exact theory should

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be transformed to a simpler form similar to the equations of the Anderson–Tsao–Curnutte (ATC) theory.[2] Simultaneously, the additional parameters should be introduced to take into account the trajectory bending, effects of vibrational excitation, corrections to the scattering matrix obtained from the perturbation theory, etc. The parameters of the theory can be found by fitting line halfwidths and shifts to experimental data.

In this paper, we present the results calculated for the new database based on the ATC method. The calculated coefficients of line shifting by air pressure and exponents of the temperature dependence in the range from 200 to 350 K significantly supplemented the available databases. The calculated data can be used in spectroscopy of planetary atmospheres.

## Review of experimental and calculated data

The $CO_2$ broadening coefficients were measured by now in the IR region, and the shifts of various spectral lines by pressure of different buffer gases were found.[3–21] In Refs. 3–11, the measured results are given for the laser bands of 9 and 10 μm. The measurements for other bands: 1.4, 2.7, 4.3, 12.6, and 15 μm are presented in Refs. 12–21. The experimental values of line halfwidths were obtained for all types of bands and for all *P*-, *Q*-, and *R*-branches. The influence of line interference in *Q*-branches on halfwidths was studied. The measured shifts of lines in the $\nu_3$ and $3\nu_3$ bands are given in Refs. 21 and 22. For the $\nu_3$ band, the measurements at high temperature up to 815 K are available as well.[23]

Table 1 gives an idea on the measurement accuracy achieved by now. This table presents the smallest and largest halfwidths of $CO_2$–$CO_2$ lines obtained by different authors.

It can be seen that the typical measurement accuracy estimated as the difference between measurements by different authors is about 5%. At the same time, for some lines the difference exceeds 10%.

**Table 1. Maximum and minimum experimental halfwidths of $CO_2$–$CO_2$ lines, in $10^{-3}$ $cm^{-1} \cdot atm^{-1}$**

| $\lvert m \rvert$ | Largest experimental value | Smallest experimental value |
|---|---|---|
| 6 | 128 | 112 |
| 17 | 116 | 100 |
| 24 | 108 | 93 |
| 36 | 106 | 85 |
| 47 | 80 | 63 |
| 55 | 81 | 63 |

Note. $m = -J''$ for lines of *P*-branch and $m = J'' + 1$ for lines of *R*-branch.

The broadening coefficients were calculated by different methods. The ATC method was used for calculating the coefficients of self-broadening and broadening by nitrogen in Refs. 25–27, and the RB method was applied in Refs. 1 and 24. The calculations by the RB method are in closer agreement with the experimental data. The same is true for the exponents of the temperature dependence.

Line shifts were calculated in Ref. 24 by the RB method. As a result, a good agreement with the experimental data was obtained. It was found that the largest contribution to the shift is due to polarization interactions (inductive and dispersion forces); the linear pressure dependence of the shift coefficients was observed.

## Technique of calculation

For compilation of a new database on halfwidths and shifts of $CO_2$ spectral lines by air pressure, it is proposed here to use the following semiempiric technique that incorporates various corrections for deviation from the ATC approximation.

Within the framework of the semiclassic theory, the general equation for the halfwidth $\gamma_{if}$ and shift $\delta_{if}$ of the transition $i \to f$ can be written as

$$\gamma_{if} = \mathrm{Re} \sum_{\mathrm{int}} \int \mathrm{d}v v \int \mathrm{d}b b \left(\frac{v}{v_c'}\right)^2 \times$$
$$\times f[b, v, D^2 (ii' | l_1 l_2), D^2 (ffi | l_1 l_2)]; \quad (1)$$
$$\delta_{if} = \mathrm{Im} \sum_{\mathrm{int}} \int \mathrm{d}v v \int \mathrm{d}b b \left(\frac{v}{v_c'}\right)^2 \times$$
$$\times f[b, v, D^2 (ii' | l_1 l_2), D^2 (ffi | l_1 l_2)],$$

where $b$ and $v$ are the impact parameter and the initial impact speed; the integral $\sum_{\mathrm{int}} \int \mathrm{d}v ...$ is averaging over collisions; $f(b,...)$ is some function (see Ref. 1) including the line strengths $D(b, v, i, i' | l_1 l_2)$, which are connected with the scattering channel $i \to i'$ and depend only on molecular constants of an absorbing molecule [the function $f(b,...)$ also depends on the intermolecular potential, trajectory, constants of the buffer molecule, etc.].

The integrand can be expanded into a series. Thus, we obtain the equation similar to those resulting from the ATC theory:

$$\gamma_{if} = A + \sum D^2 (ii' | l_1 l_2) P_{l_1 l_2}(\omega_{ii'}) +$$
$$+ \sum D^2 (ff' | l_1 l_2) P_{l_1 l_2}(\omega_{ff'}) + ... ; \quad (2)$$
$$\delta_{if} = B + \sum D^2 (ii' | l_1 l_2) Q_{l_1 l_2}(\omega_{ii'}) +$$
$$+ \sum D^2 (ff' | l_1 l_2) Q_{l_1 l_2}(\omega_{ff'}) + ... .$$

Here $A = \frac{n}{c} \sum_{2} \rho(2) \int_{0}^{\infty} v\,\mathrm{d}v\; b_0^2(v, 2)$ is a usual term of the ATC theory due to integral cut-off ($b_0(v,2)$ is the cut-off parameter); $B = \frac{n}{c}\,(\alpha_i - \alpha_f) \sum_{2} \rho(2) \times \times \int_{0}^{\infty} v\,\mathrm{d}v\; b_0^{-3}(v, 2)$ is the contribution of the isotropic part of the potential. It includes the difference between the mean dipole polarizability in the ground ($\alpha_i$) and excited ($\alpha_f$) vibrational states. This term determines the vibrational dependence of the shift coefficients.

The functions of channel efficiency can be presented as

$$P_{l_1 l_2}(\omega) = P_{l_1 l_2}^{\mathrm{ATC}}(\omega)\,[1 + a_1\omega + a_2\omega^2 + \ldots]. \qquad (3)$$

In this equation, $\omega$ are the frequencies of quadrupole transitions, i.e., some functions of the rotational quantum number $J$. This allows the expression in the square brackets in the right-hand side of Eq. (3), i.e., the correction to the ATC theory, to be presented as $J$-dependent expressions, whose parameters are fitted to experimental halfwidths. Introducing a correction factor, we can take into account fine effects, which are usually ignored in the impact theory. At the same time, the use of the efficiency function $P_{l_1 l_2}^{\mathrm{ATC}}(\omega)$ obtained in the ATC theory as an initial approximation for $P_{l_1 l_2}(\omega)$ in Eq. (3) allows correct description of the behavior of halfwidths and line shifts at large values of quantum numbers, at high temperature, etc. The parameters $a_i$ determined in such a way well describe not only the $J$-dependence of line halfwidths, but also the shift coefficients. This confirms the correctness of the used approach.

## Discussion

Figure 1 shows the halfwidths of $CO_2$ lines (in the case of broadening by nitrogen) calculated by three different methods in comparison with the experimental data.[21] It is seen that calculation by the Anderson–Tsao–Curnutte method[2] does not agree with the measured values for high $J$. Calculations by the more accurate cut-off-free method[28] are closer to the experiment, but also disagree with the experimental data at $J > 25$. At the same time, the values obtained using the method proposed here coincide with the experimental ones within the measurement error for all the considered lines. As to the shift coefficients, the new technique gives good results (Fig. 2).

When calculating the shifts, we used one more fitting parameter – the mean dipole polarizability in the excited vibrational state. This parameter is responsible for the contribution of the isotropic part of the potential to the shift value. The isotropic part, in its turn, is responsible for the vibrational dependence of the shift coefficient. Figure 2 shows the calculated and measured[21,22] line shifts for $R$-branches of the $\nu_3$ and $3\nu_3$ bands. First of all, we would like to note the presence of the strong vibrational effect. At excitation of three quanta of the asymmetric stretching mode, the polarizability changes from 2.601 to 2.683 A$^3$. At the same time, the shift of lines corresponding to the same rotational transitions changes more than three times. The rotational dependence of the shift coefficients proves to be almost linear. It is well reproduced by our calculations (the rotational dependence is determined by the parameters $a_i$, which were found by fitting line halfwidths). The agreement between the calculated and experimental data is rather good. The calculated values, as a rule, coincide with the experimental ones within the measurement error (the typical measurement error is ±0.001 cm$^{-1}$·atm$^{-1}$).

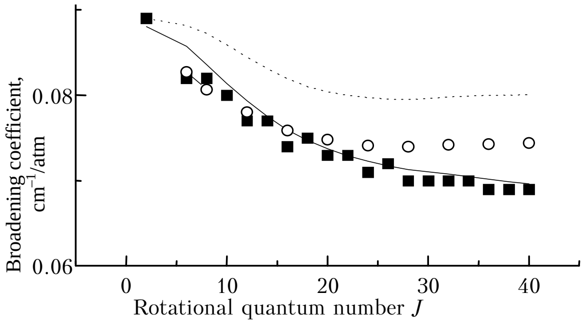

**Fig. 1.** Halfwidths of $CO_2$ lines (broadening by nitrogen) calculated by three different methods and the experimental data: Anderson–Tsao–Curnutte method[2] ( · · ), cut-off-free method[28] (   ), our method (—), and experiment[21] (   ).

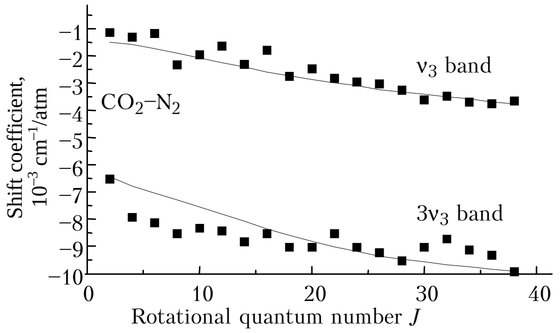

**Fig. 2.** Calculated and experimental line shifts for $R$-branches of $\nu_3$ and $3\nu_3$ bands (designations are the same as in Fig. 1).

The studies of the temperature dependence of $CO_2$ line halfwidths reported in Refs. 23 and 24 were performed for the temperature from 300 to 900 K. Our calculations for the same temperatures well agree with the experiment (Fig. 3). The exponents of the temperature dependence $N'$ and $N''$ are determined from the equations

$$\gamma(T) = \gamma(300)\left(\frac{T}{300}\right)^{-N'};$$

$$\delta(T) = \delta(300)\left(\frac{T}{300}\right)^{-N''}.$$

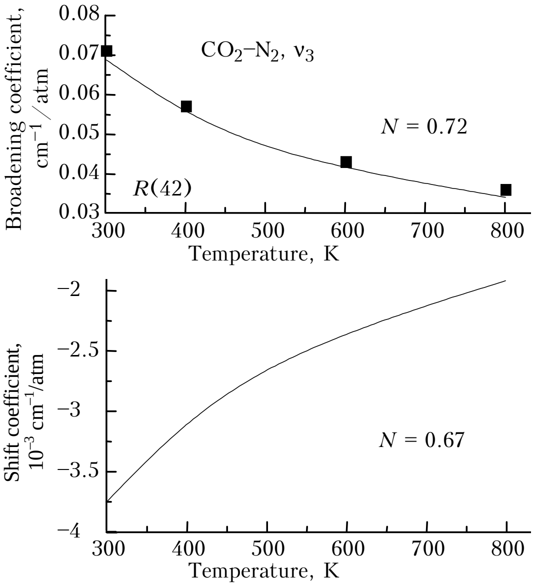

**Fig. 3.** Temperature dependence of line profile parameters of CO$_2$ (ν$_3$ band): broadening coefficients (upper panel) and shift coefficients (lower panel); calculation (—) and experiment$^{23}$ ( ).

Upon calculation of the coefficients of CO$_2$ spectral line broadening and shifting by nitrogen and oxygen by the above-described method for the temperature of 200–350 K, using the equations

$$\gamma_{\text{air}} = 0.79\gamma_{N_2} + 0.21\gamma_{O_2}$$
$$\delta_{\text{air}} = 0.79\delta_{N_2} + 0.21\delta_{O_2}, \tag{4}$$

we obtain the corresponding coefficients for shifting and broadening by the air pressure for transitions with $J'' \le 100$ and the exponents of their temperature dependence. Table 2 gives the parameters of CO$_2$ spectral lines broadening and shifting by air pressure, as well as the values of $N'$ and $N''$. The coefficients of temperature dependence are determined in the temperature range from 230 to 350 K. Nevertheless, they obviously can be used for some wider temperature interval.

In conclusion, we would like to note that the proposed method of calculation of broadening and shift coefficients of carbon dioxide can be applied to other molecules, whose line profile parameters should be included in the HITRAN and GEISA databases.

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**Table 2. Carbon dioxide coefficients of broadening and shifting by air pressure, exponents of temperature dependence *N* for broadening and shifting**

| $J''$ | $J'$ | Halfwidth, cm$^{-1}$/atm | Shift, cm$^{-1}$/atm | $N'$ | $N''$ |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| 1 | 0 | 0.0893 | −0.00133 | 0.7467 | 0.5059 |
| 3 | 2 | 0.0859 | −0.00151 | 0.7388 | 0.5137 |
| 5 | 4 | 0.0829 | −0.00164 | 0.7293 | 0.5257 |
| 7 | 6 | 0.0814 | −0.00173 | 0.7077 | 0.5593 |
| 9 | 8 | 0.0795 | −0.00189 | 0.6893 | 0.6387 |
| 11 | 10 | 0.0775 | −0.00206 | 0.6764 | 0.6788 |
| 13 | 12 | 0.0756 | −0.00225 | 0.6694 | 0.7238 |
| 15 | 14 | 0.0739 | −0.00243 | 0.6681 | 0.7416 |
| 17 | 16 | 0.0725 | −0.00259 | 0.6706 | 0.7371 |
| 19 | 18 | 0.0713 | −0.00279 | 0.6777 | 0.7623 |
| 21 | 20 | 0.0704 | −0.00293 | 0.6879 | 0.7436 |
| 23 | 22 | 0.0696 | −0.00308 | 0.6983 | 0.7323 |
| 25 | 24 | 0.0690 | −0.00321 | 0.7076 | 0.7184 |
| 27 | 26 | 0.0685 | −0.00332 | 0.7145 | 0.6918 |
| 29 | 28 | 0.0681 | −0.00348 | 0.7207 | 0.7062 |
| 31 | 30 | 0.0679 | −0.00357 | 0.7269 | 0.6814 |
| 33 | 32 | 0.0676 | −0.00366 | 0.7299 | 0.6663 |
| 35 | 34 | 0.0673 | −0.00376 | 0.7300 | 0.6658 |
| 37 | 36 | 0.0670 | −0.00384 | 0.7274 | 0.6547 |
| 39 | 38 | 0.0667 | −0.00397 | 0.7232 | 0.6735 |
| 41 | 40 | 0.0665 | −0.00406 | 0.7190 | 0.6695 |
| 43 | 42 | 0.0662 | −0.00414 | 0.7130 | 0.6731 |
| 45 | 44 | 0.0658 | −0.00424 | 0.7051 | 0.6880 |
| 47 | 46 | 0.0654 | −0.00433 | 0.6956 | 0.6943 |
| 49 | 48 | 0.0649 | −0.00446 | 0.6850 | 0.7193 |

*Table 2 (continued)*

| 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|
| 51 | 50 | 0.0645 | −0.00457 | 0.6754 | 0.7350 |
| 53 | 52 | 0.0640 | −0.00467 | 0.6656 | 0.7471 |
| 55 | 54 | 0.0635 | −0.00480 | 0.6551 | 0.7709 |
| 57 | 56 | 0.0629 | −0.00491 | 0.6442 | 0.7842 |
| 59 | 58 | 0.0623 | −0.00507 | 0.6331 | 0.8074 |
| 61 | 60 | 0.0617 | −0.00521 | 0.6234 | 0.8261 |
| 63 | 62 | 0.0611 | −0.00533 | 0.6145 | 0.8400 |
| 65 | 64 | 0.0605 | −0.00549 | 0.6057 | 0.8570 |
| 67 | 66 | 0.0599 | −0.00564 | 0.5979 | 0.8703 |
| 69 | 68 | 0.0592 | −0.00580 | 0.5905 | 0.8834 |
| 71 | 70 | 0.0586 | −0.00598 | 0.5840 | 0.8963 |
| 73 | 72 | 0.0579 | −0.00613 | 0.5790 | 0.9039 |
| 75 | 74 | 0.0573 | −0.00630 | 0.5747 | 0.9113 |
| 77 | 76 | 0.0567 | −0.00647 | 0.5713 | 0.9171 |
| 79 | 78 | 0.0561 | −0.00665 | 0.5688 | 0.9211 |
| 81 | 80 | 0.0555 | −0.00683 | 0.5672 | 0.9236 |
| 83 | 82 | 0.0549 | −0.00700 | 0.5665 | 0.9242 |
| 85 | 84 | 0.0543 | −0.00718 | 0.5669 | 0.9234 |
| 87 | 86 | 0.0538 | −0.00736 | 0.5683 | 0.9229 |
| 89 | 88 | 0.0533 | −0.00754 | 0.5707 | 0.9182 |
| 91 | 90 | 0.0527 | −0.00772 | 0.5736 | 0.9125 |
| 93 | 92 | 0.0523 | −0.00789 | 0.5772 | 0.9089 |
| 95 | 94 | 0.0518 | −0.00807 | 0.5815 | 0.9026 |
| 97 | 96 | 0.0514 | −0.00824 | 0.5866 | 0.8942 |
| 99 | 98 | 0.0510 | −0.00841 | 0.5921 | 0.8862 |
| 101 | 102 | 0.0506 | −0.00856 | 0.5979 | 0.8790 |

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