

# Collisional broadening of the spectral lines of molecules in intrinsic gas

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The collisional broadening of infrared spectral lines of molecules is analyzed. It is shown that the indistinguishability of the particles leads to additional collisional transitions which are due to the exchange processes. This produces an additional broadening of spectral lines which correspond to optical transitions from the electronic-vibrational ground state. © 1995 American Institute of Physics.

## INTRODUCTION

It is well known that as the density of intrinsic gas increases, the resonance lines of the gas atoms are broadened much more strongly than when a foreign gas is introduced<sup>1–3</sup> (self-broadening effect). This is connected with the fact that when two identical atoms, one of which is excited, collide, resonance transfer of excitation energy can occur. In the process the coherence of the radiation is disrupted, since the phases of the oscillations of the colliding oscillators are different (if only, because of the Doppler frequency shift, which is different for different atoms).

Collisional broadening of a line, which corresponds to a rotational-vibrational transition  $\mathbf{v}_i J_i \rightarrow \mathbf{v}_f J_f$  in an optically active molecule  $A(\mathbf{v}_i J_i - \mathbf{v}_f J_f)$  (the optically active particles are in superposition quantum states containing the vectors  $|\mathbf{v}_i J_i m_i\rangle$  and  $|\mathbf{v}_f J_f m_f\rangle$ :  $|\Psi\rangle = C_i |\mathbf{v}_i J_i m_i\rangle + C_f |\mathbf{v}_f J_f m_f\rangle$ ), as a result of the interaction with a molecule  $B(\mathbf{v}_b J_b)$  ( $\mathbf{v}$  is the collection of vibrational quantum numbers, and  $J$  is the rotational quantum number) is associated with the effective energy exchange between the translational and rotational degrees of freedom, i.e., RRT processes:<sup>4,5</sup>

$$A(\mathbf{v}_i J_i m_i - \mathbf{v}_f J_f m_f) + B(\mathbf{v}_b J_b m_b) \Rightarrow \begin{cases} A(\mathbf{v}_i J_i' m_i' - \mathbf{v}_f J_f m_f) + B(\mathbf{v}_b J_b' m_b') + \Delta E \\ A(\mathbf{v}_i J_i m_i - \mathbf{v}_f J_f' m_f') + B(\mathbf{v}_b J_b' m_b') + \Delta E \\ A(\mathbf{v}_i J_i m_i' - \mathbf{v}_f J_f m_f') + B(\mathbf{v}_b J_b' m_b') + \Delta E \end{cases} . \quad (1)$$

Here  $\Delta E$  is the energy released into the translational degrees of freedom. The RRT processes are virtually independent of the vibrational state of the colliding molecules. At first glance, in contrast to atoms, there are therefore no physical reasons here for additional broadening of spectral lines which correspond to the transitions from the vibrational ground state. In this respect, it is instructive to compare the widths of spectral lines for the same vibrational transition for molecules with different isotopic modifications. For example, for the well-known spectra of the molecules  $^{12}\text{C}^{16}\text{O}_2$  and  $^{13}\text{C}^{16}\text{O}_2$ , (Refs. 6 and 7) it can be assumed that molecules of both modifications collide only with  $^{12}\text{C}^{16}\text{O}_2$

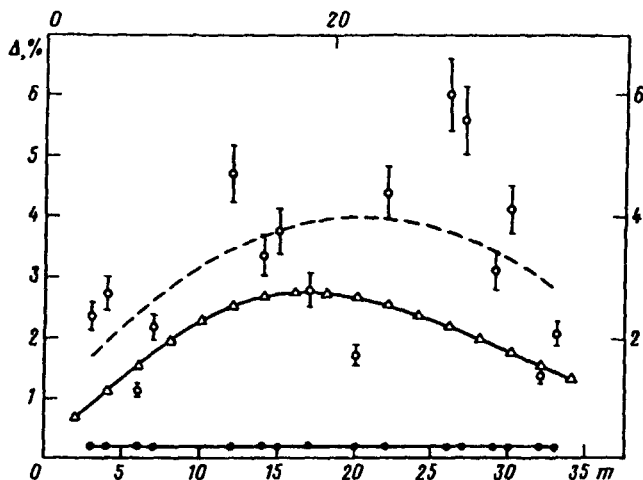


FIG. 1.  $\Delta(m)$  [Eq. (2)] for isotopic modifications of the  $\text{CO}_2$  molecule ( $m=J$  for lines on the  $P$  branch and  $m=J+1$  for lines on the  $R$  branch). The transition is  $00^0_0 \rightarrow 00^0_1$ ,  $T_g = T_1 = T_2 = T_3 = 300$  K;  $\circ$ —experiment;  $\bullet, \triangle$ —calculations with and without exchange processes, respectively. Dashed line—Average value for the experimental points.

molecules, because the  $^{13}\text{C}^{16}\text{O}_2$  concentration is low (1%). The rotational structure of the combining vibrational states in the transition  $00^0_0 \rightarrow 00^0_1$  for these molecules is virtually identical (the rotational constants  $B_v$  are identical to better than  $4 \times 10^{-2}\%$ ); i.e., the collisional widths  $\Delta\nu_{1/2}(^{12}\text{C}^{16}\text{O}_2)$  and  $\Delta\nu_{1/2}(^{13}\text{C}^{16}\text{O}_2)$  of the corresponding spectral lines must be the same. Figure 1 shows the experimental and computed curves

$$\Delta(m) = \frac{\Delta\nu_{1/2}(^{12}\text{C}^{16}\text{O}_2) - \Delta\nu_{1/2}(^{13}\text{C}^{16}\text{O}_2)}{\Delta\nu_{1/2}(^{12}\text{C}^{16}\text{O}_2)} \quad (2)$$

as a function of  $m$ . Here  $m=J$  for lines on the  $P$  branch and  $m=J+1$  for lines on the  $R$  branch, and the gas temperature is  $T=300$  K. The experimental curve lies above the computed curve—for small values of  $J$  the lines corresponding to the main component  $^{12}\text{C}^{16}\text{O}_2$  are broadened more strongly; i.e., a phenomenon is observed that in some sense is analogous to self-broadening for atoms but it is much weaker. All this means that for the transition  $00^0_0 \rightarrow 00^0_1$  of the main component  $^{12}\text{C}^{16}\text{O}_2$ , there is a mechanism which accounts for a small additional broadening for small values of  $J$ . Our objective is to determine this mechanism.

## 1. COLLISIONAL BROADENING OF MOLECULAR SPECTRAL LINES IN THE IR REGION OF THE SPECTRUM

The first paper in which the systematic features of collisional broadening of vibrational-rotational molecular lines were analyzed apparently was that published by Anderson,<sup>4</sup> which was later developed and extended by Tsao and Curnutte.<sup>5</sup> The starting assumptions of this analysis are as follows:

1) The relative motion of the colliding particles is quasi-classical, i.e., the particles move along trajectories and

2) the collisions are binary and the characteristic collision time is much shorter than the average time between collisions.

The collisions form a Lorentzian spectral-line contour.

The half-width  $\Delta\nu_{1/2}$  of a line at half-maximum is related to the average frequency  $z$  of optically active collisions as

$$\Delta\nu_{1/2} = \frac{z}{2\pi c} [\text{cm}^{-1}], \quad (3)$$

$$z = n_b \langle \mathbf{v}\sigma \rangle. \quad (4)$$

Here  $c$  is the speed of light,  $\mathbf{v}$  is the relative velocity of the colliding particles,  $\sigma$  is the effective broadening cross section, and  $n_b$  is the density of broadening particles.

The effective broadening cross section for the transition  $i \rightarrow f$  is defined as the sum of the partial cross sections  $\sigma(i \rightarrow f; \mathbf{v}, v_b, J_b)$ , where the summation extends over all possible states of the broadening particles ( $v_b, J_b$ )

$$\sigma(i \rightarrow f) = \sum_{v_b, J_b} \rho(v_b, J_b) \sigma(i \rightarrow f; \mathbf{v}; v_b, J_b), \quad (5)$$

and  $\rho(v_b, J_b)$  is the population of the state ( $v_b, J_b$ ) of the broadening particles

$$\sigma(i \rightarrow f; \mathbf{v}; v_b, J_b) = \int_0^\infty S(b; i \rightarrow f; \mathbf{v}; v_b, J_b) \cdot 2\pi b db. \quad (6)$$

Here  $b$  is the impact parameter, and the function  $S(b; i \rightarrow f; \mathbf{v}, v_b, J_b)$  determines the probability for phase interruption or cutoff of the radiation of the molecular oscillator in a collision with impact parameter  $b$ . The function  $S(b; i \rightarrow f; \mathbf{v}, v_b, J_b)$  is calculated in second-order perturbation theory.<sup>4,5</sup> The specific form of the function  $S_2(b)$  is calculated in the Anderson–Tsao–Cumutte (ATC) approximation with the simplifying assumptions that

1) the particles move with constant velocity along rectilinear trajectories and

2) the particle interaction potential is electrostatic. The electrostatic potentials  $v \rightarrow \infty$  as  $b \rightarrow 0$ . It is easy to see that in this case a convergence problem arises in the calculation of  $\sigma(i \rightarrow f)$ . To eliminate this problem, Anderson<sup>4</sup> proposed the following device:

$$\sigma(i \rightarrow f; \mathbf{v}; v_b, J_b) = \pi b_0^2 \sigma(i \rightarrow f; \mathbf{v}; v_b, J_b) + \int_{b_0(i \rightarrow f; \mathbf{v}; v_b, J_b)}^\infty S_2(b, i \rightarrow f; \mathbf{v}; v_b, J_b) 2\pi b db, \quad (7)$$

where  $b_0(i \rightarrow f; \mathbf{v}, v_b, J_b)$  is determined from the condition

$$S_2(b_0; i \rightarrow f; \mathbf{v}; v_b, J_b) = 1. \quad (8)$$

The concept of a critical impact parameter<sup>5</sup>  $b_m$ , which corresponds to the gas-kinetic diameter of a molecule, is often introduced in the calculations, and for  $b_0 < b_m$  it

is used instead of  $b_0$ . The procedure for eliminating the divergence,<sup>7,8</sup> and especially the use of a critical parameter, is not entirely correct (in the calculations  $b_m$  ordinarily serves as a free parameter and it is adjusted so as to obtain the best agreement with experiment). Studies which are based on more realistic assumptions than the ATS approximation have recently been published (see, for example, Refs. 9 and 10). Nonetheless, the physical meaning of the procedure<sup>7,8</sup> is quite clear and it appears to be fully justified for  $b_0 > b_m$ . Indeed, collisions with impact parameters  $b \leq b_0$  act so strongly on an optically active molecule that the probability of phase interruption or radiation cutoff is essentially equal to 1. We note that for small values of  $J$  (for  $\text{CO}_2$   $J < 30$ ) the electrostatic interaction plays the main role and all approximations<sup>4,5,8-10</sup> give the same results. In the calculations no distinctions are made between broadening by foreign-gas and self-broadening (see, for example, Refs. 8 and 10). From our viewpoint, this is not entirely correct.

## 2. SELF-BROADENING OF MOLECULAR LINES

In Refs. 4 and 5 the matrix elements of the interaction operator  $H_c(t)$  of the colliding molecules

$$\langle f|P|i\rangle = \frac{1}{\hbar} \int_0^\infty \exp(i\omega_f t) \langle f|H_c(t)|i\rangle dt$$

are used to calculate the function  $S_2(b; i \rightarrow f; v, v_b, J_b)$ . It is assumed that before and after the interaction the total wave function of the system of colliding molecules is a product of wave functions  $\Psi_A(r_a; v_a, J_a, m_a) \Psi_B(r_b; v_b, J_b, m_b)$ . In the case of self-broadening we are dealing with a system of identical particles. For such a system the wave function must have definite symmetry properties with respect to the permutation of the particles. The wave function is symmetric for bosons and antisymmetric for fermions. The molecule  $^{12}\text{C}^{16}\text{O}_2$  is a particle with an integral intrinsic angular momentum (the nuclear spin  $I=0$ ; the electronic state is  $^1\Sigma_g$ ; i.e., the electronic spin is zero and the projection of the orbital angular momentum onto the internuclear axis  $\Lambda=0$ ), i.e., it obeys the Bose-Einstein statistics, and correspondingly the wave function must be symmetric

$$|m\rangle = \frac{1}{\sqrt{2}} [\Psi(r_A; v_A, J_A, m_A) \Psi(r_B; v_B, J_B, m_B) + \Psi(r_A; v_B, J_B, m_B) \Psi(r_B; v_A, J_A, m_A)]. \quad (9)$$

In this case, in calculating  $S_2(b, i \rightarrow f; v, v_b, J_b)$  the wave function (9) must be used instead of the product  $\Psi(r_A; v_A, J_A, m_A) \Psi(r_B; v_B, J_B, m_B)$ . In accordance with Refs. 4 and 5, we have

$$S_2(b; i \rightarrow f; v, v_b, J_b) = S_2(b)_{\text{outer}} + S_2(b)_{\text{middle}}. \quad (10)$$

Substituting the wave function (9) into the expression for  $S_2(b)_{\text{outer}}$  (Ref. 5), we obtain

$$S_2(b)_{\text{outer}} = \frac{1}{2} \left\{ \frac{1}{(2J_i+1)(2J_b+1)} \sum_{m_i, m_b} \sum_{\substack{J'_i m'_i \\ J'_b m'_b}} \{ \langle v_i, J_i, m_i; v_b, J_b, m_b | P | \right. \\ \left. \times v'_i, J'_i, m'_i; v'_b, J'_b, m'_b \rangle \langle v'_i, J'_i, m'_i; v'_b, J'_b, m'_b | P | v_i, J_i, m_i; v_b, J_b, m_b \rangle \right.$$

$$\begin{aligned}
& + \langle v_i J_i m_i ; v_b J_b m_b | P | v_i J'_i m'_i ; v_b J'_b m'_b \rangle \\
& \times \langle v_i J'_i m'_i ; v_b J'_b m'_b | P | v_b J_b m_b ; v_i J_i m_i \rangle + \text{c.c.} \\
& + \langle v_i J_i m_i ; v_b J_b m_b | P | v_b J'_b m'_b ; v_i J'_i m'_i \rangle \\
& \times \langle v_b J'_b m'_b ; v_i J'_i m'_i | P | v_i J_i m_i ; v_b J_b m_b \rangle + \text{similar terms for the state } f \}. \quad (11)
\end{aligned}$$

Here the first and last terms correspond to the direct process

$$\begin{pmatrix} v_i J_i m_i \rightarrow v_i J'_i m'_i \rightarrow v_i J_i m_i \\ v_b J_b m_b \rightarrow v_b J'_b m'_b \rightarrow v_b J_b m_b \end{pmatrix}$$

and the exchange process

$$\begin{pmatrix} v_i J_i m_i \rightarrow v_b J'_b m'_b \rightarrow v_i J_i m_i \\ v_b J_b m_b \rightarrow v_i J'_i m'_i \rightarrow v_b J_b m_b \end{pmatrix},$$

and the second and third terms correspond to the cross process

$$\begin{pmatrix} v_i J_i m_i \rightarrow v_i J'_i m'_i \rightarrow v_b J_b m_b \\ v_b J_b m_b \rightarrow v_b J'_b m'_b \rightarrow v_i J_i m_i \end{pmatrix}.$$

It is ordinarily assumed that the permanent multipole moment of a molecule does not depend on the vibrational state. In this case, since the vibrational wave functions are mutually orthogonal, the expressions containing the exchange terms will be different from zero if  $v_b = v_i$  (or  $v_b = v_f$ ). For definiteness, let  $v_b = v_i$ . It is easy to show that  $\sum_{m_i, m_b}$  (exchange processes)  $\gg \sum_{m_i, m_b}$  (cross processes), so that in calculating  $S_2(b)_{\text{outer}}$  they can be dropped.

We now consider  $S_2(b)_{\text{middle}}$ . Again, for definiteness, let  $v_b = v_i$ . Then

$$\begin{aligned}
S_2(b)_{\text{middle}} = & - \sum_{\substack{m_i, m'_i, m_f, m'_f \\ m_b, m'_b, M}} \sum_{J'_b} \frac{(J_f \ l m_f M | J_i m_i)(J_f \ l m'_f M | J_i m'_i)}{(2J_i + 1)(2J_b + 1)} \\
& \times (\langle J_f m_f J_b m_b | P | J_f m'_f J'_b m'_b \rangle \langle J'_i m'_i J_b m'_b | P | J_i m_i J_b m_b \rangle \\
& + \langle J_f m_f J_b m_b | P | J_f m'_f J'_b m'_b \rangle \langle J'_b m'_b J_i m'_i | P | J_i m_i J_b m_b \rangle). \quad (12)
\end{aligned}$$

Analysis of expression (12) shows that the exchange part is due to the cross processes  $v_b J_b m_b \rightarrow v_i J'_i m'_i \rightarrow v_b J_b m_b$ . All terms corresponding to processes of this kind were already dropped in the calculation of  $S_2(b)_{\text{outer}}$ . Therefore, the exchange processes do not affect the form of  $S_2(b)_{\text{middle}}$ .

On the basis of what we have said above, and using the ATC approximation<sup>4,5</sup> for the quadrupole interaction, which is characteristic of  $\text{CO}_2\text{-CO}_2$  collisions (the  $\text{CO}_2$  molecule does not have a permanent dipole moment), we obtain the following expression for  $S_2(b)$ :

$$\begin{aligned}
S_2(b; v_i J_i - v_f J_f; v, v_b = v_i, J_b) \\
= \frac{1}{25} \left( \frac{q^2}{\hbar v} \right)^2 \frac{1}{b^8} \left\{ \sum_{J'_i J'_b} [\mathcal{Q}^2(J_i J'_i) \mathcal{Q}^2(J_b J'_b) \right. \\
+ \mathcal{Q}^2(J_i J'_b) \mathcal{Q}^2(J_b J'_i)] f_3(k) \\
+ \sum_{J'_f J'_b} [\mathcal{Q}^2(J_f J'_f) \mathcal{Q}^2(J_b J'_b) f_3(k)] \\
+ R(J_i J_f) \sum_{J'_b} [\mathcal{Q}^2(J_b J'_b) f_3(k)] \left. \right\}, \quad (13)
\end{aligned}$$

where  $q_A$  and  $q_B$  are the quadrupole moments of the colliding molecules,  $Q(JJ') = (J2K_0|J'K)$  is a Clebsch–Gordon coefficient, and  $R(J_i J_f)$  can be expressed in terms of the Racah coefficients  $W(J_i J_f J_i J_f; 12)$  as<sup>11</sup>

$$\begin{aligned}
R(J_i J_f) = 2(-1)^{J_i + J_f} \sqrt{(2J_i + 1)(2J_f + 1)} (J_i 2K_k 0 | J_i K_j) (J_f 2K_f 0 | J_f K_f) \\
\times W(J_i J_f J_i J_f; 12). \quad (14)
\end{aligned}$$

The resonance parameter  $k$  is defined as follows:

$$k = \frac{|\Delta E b|}{\hbar v}, \quad (15)$$

where  $\Delta E$  is the energy released in the collisions (1)

$$\Delta E = \begin{cases} E(J_i) + E(J_b) - E(J'_i) - E(J'_b) \\ E(J_f) + E(J_b) - E(J'_f) - E(J'_b) \end{cases} \quad (16)$$

The function  $f_3(k)$  is a resonance factor which can be expressed in terms of modified Bessel functions  $K_n$  as follows:<sup>5</sup>

$$f_3(k) = \frac{1}{2304} k^8 [K_4^2 + 8K_3^2 + 28K_2^2 + 56K_1^2 + 35K_0^2], \quad f_3(0) = 1. \quad (17)$$

For self-broadening the terms which are due to the exchange processes, which should give rise to additional broadening, appear in the expression used for calculating  $S_2(b)$ . The exchange terms contribute when either the initial ( $J_i; J_b$ ) or final ( $J'_i; J'_b$ ) states are the same. This means that a relatively small fraction of the molecules  $B(v_b = v_i; J_b)$  with  $J_b$  very close to  $J_i$  participate in the exchange processes; i.e., the contribution of exchange processes to the total broadening cross section  $\sigma(i \rightarrow f)$  [see Eq. (5)] is not large, and the maximum value is obtained when  $J_i$  corresponds to the maximum occupancy of the rotational levels of the molecules.

We calculated the widths of the spectral lines for the transition  $00^0 0 \rightarrow 00^0 1$  in the  $\text{CO}_2$  molecule under equilibrium conditions  $T_g = T_1 = T_2 = T_3$ , taking into account  $\Delta \nu_{1/2}(1)$  and ignoring  $\Delta \nu_{1/2}(2)$  exchange processes, at temperatures  $T = 15, 180, 300,$  and  $600$  K;  $b_m$  is assumed everywhere to be  $b_m = 4.88E$  (just as in Ref. 8). The computational results are presented in Fig. 2, where the quantity

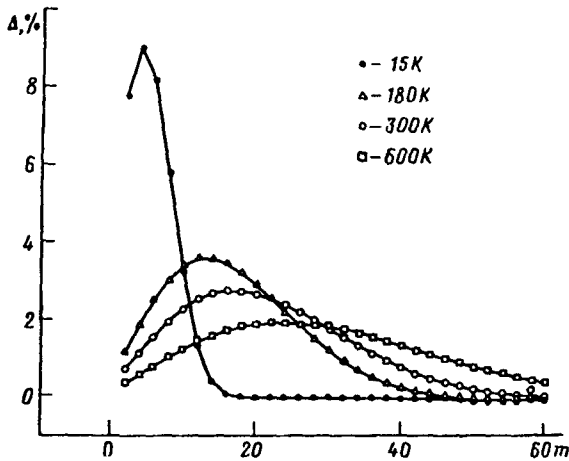


FIG. 2.  $\Delta(m)$  [see Eq. (18)] for  $T=15$  K (●), 180 K (Δ), 300 K (○), and 600 K (□).

$$\Delta = \frac{\Delta \nu_{1/2}(1) - \Delta \nu_{1/2}(2)}{\Delta \nu_{1/2}(1)} \quad (18)$$

is plotted as a function of  $m$ . We see from the figure that taking into account the exchange processes everywhere does indeed lead to additional broadening of spectral lines with small values of  $J$ ; specifically, it appreciably improves the agreement between the experimental results and the calculations for the isotopic modifications  $^{12}\text{C}^{16}\text{O}_2$  and  $^{13}\text{C}^{16}\text{O}_2$  (see Fig. 1).

The quantity  $\Delta$ , as expected, is maximum for  $J$  corresponding to the maximum occupancy of the rotational levels. As the temperature  $T$  increases, the additional exchange broadening decreases. For example,  $\Delta \approx 10\%$  at  $T=15$  K (this corresponds to the conditions of gas-dynamic cooling), whereas  $\Delta \approx 2\%$  at  $T=600$  K. It is easy to see that the additional broadening is manifested only for spectral lines corresponding to the optical transitions from the electronic-vibrational ground state, since the overwhelming majority of the molecules which are collision partners are, as a rule, in the vibrational ground state.

Taking into account the additional broadening due to exchange processes can also remove one other contradiction. Theoretical calculations in which the exchange processes are ignored<sup>8</sup> show that for rotational quantum numbers  $J < 30$  the lines corresponding to the vibrational transition  $00^00 \rightarrow 00^01$  should be slightly narrower than the lines from the transition<sup>8</sup>  $01^10 \rightarrow 02^20$ . This is explained by the fact that all rotational levels (with both even and odd  $J$ ) are present in the states  $01^10$  and  $02^20$ , whereas in the states  $00^00$  and  $00^01$  only levels with even  $J(00^00)$  or odd  $J(00^01)$  are present. In the case of collisions in the states  $01^10$  and  $02^20$  transitions with  $\Delta J = \pm 1$  can therefore occur, while for molecules in the states  $00^00$  and  $00^01$  such transitions are forbidden (a more detailed discussion is given in Ref. 8). The expected difference in the widths is small— not exceeding 5%, but the accuracy with which measurements of the widths can now be

made should make it possible to record this difference. Nonetheless, analysis of the measurements of the widths of spectral lines<sup>6,7</sup> does not reveal any differences in the widths of lines corresponding to transitions from the ground state and vibrationally excited states. Taking into account the additional broadening gives virtually complete agreement between the computational and experimental results.

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