

# ON THE PRESSURE DEPENDENCE OF THE CO<sub>2</sub> ABSORPTION COEFFICIENT IN THE WING OF THE 4.3 μm BAND

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*The CO<sub>2</sub> absorption coefficient in the wing of the 4.3 μm band at densities up to 80 amagat have been calculated using the spectral line wing theory. The calculated and measured data show a satisfactory agreement. The similarity and differences between our theoretical approach and that based on the calculation of the matrix elements of the relaxation operator are discussed.*

## 1. INTRODUCTION

The high-frequency wing of the 4.3 μm band of CO<sub>2</sub> is the classical object for which the deviation of the measured coefficients from the calculated as a sum of Lorentzian lines has been discovered and is still being studied.<sup>1,2</sup> A theoretical description of these deviations is generally related to a detailed study of molecular collisions in the presence of the radiation absorption. Such a treatment appeared to be rather complicated and failed to provide a prevailing opinion on the processes responsible for the line wings. This fact and the obvious importance of studying the nonresonance IR absorption for practical applications keep up unremitting interest in the experimental investigations of the behavior of the absorption coefficient under different thermodynamic condition. The objective of this paper is to discuss in terms of the line wing theory the interesting experimental results obtained by Hartmann et al. in Refs. 3 and 4.

The absorption measurements made for the CO<sub>2</sub>-N<sub>2</sub> gas mixture in the trough between the  $P_{66}$  and  $P_{68}$  lines of the 4.3 μm band of CO<sub>2</sub> at pressures of 1–7 atm and temperatures of 296 K and 370 K are given in Ref. 3. The absorption measurements for pure CO<sub>2</sub> in this band wing at normal temperature and high densities (1–80 amagat) have been presented in Ref. 4. As Hartmann et al.<sup>3,4</sup> note, the Lorentzian calculations greatly overestimate the absorption in the cases under consideration. The authors of Refs. 3 and 4 claim that their experimental results can be adequately described by taking into account the effect of spectral line mixing. The assumption about dominant role of the line mixing in the formation of the IR line wing absorption is being widely used.<sup>5–9</sup> The substantiation of this version generally proceeds from the relation for the absorption coefficient  $\kappa(\omega)$  in terms of the resolvent operator (see, for example, Ref. 4).

$$\kappa(\omega) \sim \Phi(\omega),$$

$$\Phi(\omega) = \sum_{\nu_i J_i \nu_j J_j} \rho_{\nu_i J_i} \langle \nu_i J_i | M | \nu_j J_j \rangle \sum_{\nu'_i J'_i \nu'_j J'_j} \langle \nu'_i J'_i | M | \nu'_j J'_j \rangle \otimes \text{Im} \{ \langle \nu_i J_i \nu_j J_j | \{ \omega - \omega_{\nu_i J_i \nu_j J_j} - iW \}^{-1} | \nu'_i J'_i \nu'_j J'_j \rangle \}. \quad (1)$$

Here the subscripts  $\nu_i$  and  $J_i$  number the states of the absorbing molecule,  $\langle \nu_i J_i | M | \nu_j J_j \rangle$  are the matrix elements of the dipole moment operator,  $\rho_{\nu_i J_i}$  is the density of states, and  $W$  in the resolvent operator  $\{ \}^{-1}$  is the relaxation operator. In the impact approximation  $W$  is independent of the frequency  $\omega$ .<sup>10,11</sup> The diagonal elements of  $W$  are related to the pressure broadening coefficients and shifts of the lines, i.e.,

$$\langle \nu_i J_i \nu_j J_j | W | \nu_i J_i \nu_j J_j \rangle = \gamma_{\nu_i J_i \nu_j J_j} - i\Delta_{\nu_i J_i \nu_j J_j}. \quad (2)$$

The off-diagonal elements  $W$  account for the line mixing. These are generally calculated using different fitting laws as well as sum rules which relate the diagonal and off-diagonal elements of  $W$ . Note that the calculations are valid for frequencies lying near the line centers.

The matrix elements of  $W$  were approximated in Ref. 3 using their exponential dependence on the energy difference of the corresponding levels. The matrix elements of  $W$  were determined in Ref. 4 based on their relation to the rotational cross section. The data on the absorption coefficient given in Ref. 3 were adequately described by these matrix elements of

$W$ , whereas the measurements reported in Ref. 4 disagreed with these calculations. The discrepancy increased with pressure and separation from the line centers. The authors of Refs. 3 and 4 arrived at the correct conclusion that the discrepancy was due to the inadequacy of the impact approximation for the description of the line wings. They saw possible way out of the situation in direct calculation of  $W$ , in particular in accounting for its frequency dependence. Their optimism was based on Refs. 12 and 7 in which the frequency dependence of the matrix elements of the relaxation operator  $W(\omega)$  for the CO<sub>2</sub>-Ar mixture was obtained using a certain theoretical approach. The latter will be discussed in Section 3.

It appears expedient at this point to make some remarks. Studying the transmission spectra the authors of Ref. 4 have compared their measurements with various calculations including the calculations which employ the so-called "modified" Lorentzian line shape:

$$k^{ML}(\omega) = \sum_{\nu_i J_i \nu_j J_j} k_{\nu_i J_i \nu_j J_j}^L(\omega) \chi(\omega - \omega_{\nu_i J_i \nu_j J_j}) \quad (3)$$

with the parameters for  $\chi$  taken from Ref. 13. The agreement between the calculations based on the line shape (3) and the

experiment was quite satisfactory.<sup>4</sup> Nevertheless, while recognizing the high accuracy of the modified Lorentzian model (3) and the inadequacy of the approximate account of the line mixing the authors of Ref. 4 still regarded this failure as being related to an insufficient accuracy of the calculations of the relaxation operator and made no question of the importance of the line mixing in the wings. Meanwhile the fact the line shape (3) has been successfully applied in practice can also be the evidence of the importance of using the proper line shape in the wing in the absence of line mixing. There remains a question whether the parameters in  $\chi$  account for the interference effects. However, in the case of line wings in the IR molecular spectra the line wing theory and its applications<sup>14–17</sup> make it possible to conclude that an adequate line shape is of critical importance. In Section 2 the measurements of Refs. 3 and 4 are interpreted from the standpoint of the above theory.

## 2. RESULTS OF CALCULATIONS

To begin with, we will make a general remark which appears to be essential for understanding the line wing problem. In the asymptotic case of small  $\Delta\omega$  near the line center the line contour is known to have a simple dispersive shape. When one passes over to larger values of  $\Delta\omega$  the impact approximation must be rejected. This fact is generally treated as the necessity to account for the collision dynamics, which naturally makes the mathematical problem of line shape calculations much more complicated. Stepping aside from the line center asymptotics, most theoretical studies of the line wing problem just cannot overcome the above difficulties. It may be justified, when intermediate frequencies are important in the problem. However, when the considerable separations from the line center are studied, the other asymptotics takes place – the large frequency detunings. This fact should lead to an expression for the line shape which is again simple enough and the collision details should appear unessential though for the other reasons than in the line center. It is this alternative asymptotics which is considered in the spectral line wing theory.<sup>14–17</sup>

The kinetic equation for the description of the line shape is obtained in Refs. 15 and 16 proceeding from the general assumptions. It contains the sum of two terms each of them being predominant in one of the asymptotic cases

$$i(\omega - \omega_{mn})Q_{mn} + (M\rho_1)_{mn} = (\omega - \omega_{mn})^2 I_{mn} + J_{mn},$$

$$\kappa(\omega) = (1/\pi) \text{ReSp}_1 M Q(\omega). \quad (4)$$

Here  $M$  is the dipole moment operator,  $\rho_1$  is the density of states of the absorbing molecule,  $I_{mn}$  and  $J_{mn}$  are rather complicated integrals including the operator  $Q$ . In the case of small  $\Delta\omega$  the first term on the right side of Eq. (4) is negligible, and the usual dispersive expression for  $\kappa$  is followed. In the case of large  $\Delta\omega$  the second term is negligible, and we arrive at the following relation for  $\kappa$  describing the far wing of the  $i$ th line

$$\kappa = D_a \sum S_i \Delta\omega^{-1-3/a} F(R_i(\Delta\omega), T) = D_a \sum S_i \Delta\omega^{-1-3/a} \times$$

$$\times \frac{1}{R_i} \int_0^{R_i} dR e^{-V(R)/kT} R (R_i^2 - R^2)^{-1/2}. \quad (5)$$

The advantages turned out to be realized in this relation which are conditioned by the asymptotics of "large frequency

detunings". Thus, in its derivation the integral over time in calculation of the spectrum of the correlation function is taken by the stationary phase method. The stationary points are determined by the energy conservation law

$$\Delta E_{mn} = \hbar \omega = C_a / R_i^a, \quad (6)$$

where  $\Delta E_{mn}$  is the energy difference of the states corresponding to the transition in the system of interacting molecules. In such a manner the quantum problem of solving the Schrodinger equation reduces to that of determining the roots of equation (6). The classical trajectory of the center-of-mass motion is also important only in the vicinity of the stationary point, and with a sufficient reason can be approximated by a straight line in this small zone. All the above discussed together with the use of the Gibbs factor containing the intermolecular interaction energy  $V(R)$  just give the required relation (5) describing the line wing. The parameters of the problem are the parameters of the relation approximating the quantum energy difference of interacting molecules (6). They are  $a$ ,  $C_a$  and  $D_a$ , which are determined from the comparison of the experimental and calculated absorption coefficients. The potential  $V(R)$  is derived from the potential  $E_{mn}$  by averaging over the quantum variables. We take it usually in the form of the Lennard-Jones potential for calculations in the framework of the spectral line wing theory.

According to this scheme which has become traditional for us we calculated of the absorption coefficient  $\kappa(\omega, P, T)$  for conditions specified in the measurements published in Refs. 3 and 4.

The line shape used in our calculations was obtained on the basis of the analysis of the  $\text{CO}_2$  absorption data at different temperatures published in Refs. 18 and 19. Its parameters are presented in Table I.

TABLE I. Line shape parameters.\*

$\text{CO}_2\text{-N}_2$		
$C_5, D_5$	$C_{14}, D_{14}$	$C_{10}, D_{10}$
6.6 0.005494	4.8412 0.0005230	5.891 0.00009352
$\text{CO}_2\text{-CO}_2$		
$C_5, D_5$	$C_8, D_8$	$C_{16}, D_{16}$
6.5 0.02418	6.73 0.001245	5.0601 0.0004945

\*) [ $C_a$ ] =  $\text{cm}^{-1-1/a}$ , [ $D_a$ ] =  $\text{cm}^{-3/a} \text{ amagat}^{-1}$

The simple fit of energy difference by monomial (6) cannot, certainly, be satisfactory for a wide range of separations. We have chosen the way of "piecewise" approximation of  $\Delta E$  by different monomials in the appropriate ranges of separations, that can be clearly traced in the line shape. Different sets of  $C_a$  and  $D_a$  refer to the different intervals  $\Delta\omega$ . Fig. 1 shows the portions of the "composite" contour. The line shape constructed in such a way is independent of  $\gamma$ , except for the central part. Therefore, for the comparison of the composite and empirical<sup>18,19</sup> line shapes the values  $\kappa^L \gamma / S$  are drawn in Fig. 1 in the case of  $\text{CO}_2\text{-Ne}$  mixture for  $\gamma$  varying from 0.055 to 0.115  $\text{cm}^{-1} \text{atm}^{-1}$  at  $T = 296$  K. This line shape allows us to reproduce the temperature variations of deviations of the experimental absorption data published in Ref. 5 from the results calculated with the dispersive line shape for  $\text{CO}_2\text{-CO}_2$  and  $\text{CO}_2\text{-N}_2$  mixtures (see Ref. 20).

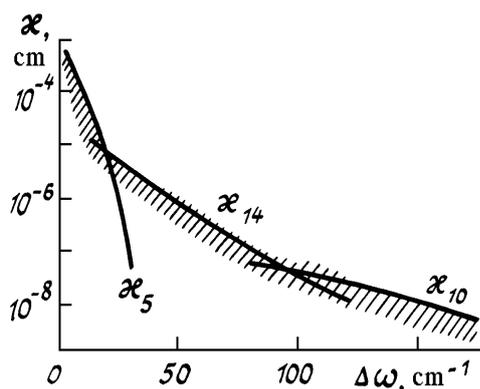


FIG. 1. Individual line shape of  $\text{CO}_2$  broadened by  $\text{N}_2$ ;  $\kappa_5$ ,  $\kappa_{14}$ , and  $\kappa_{10}$  are the portions of the composite shape at  $T = 296$  K. The range of variation of the line shape for different half-widths<sup>19</sup> is hatched.

The results of the absorption coefficient calculation using the above-discussed  $\text{CO}_2$ - $\text{N}_2$  line shape are shown in Figs. 2 and 3 and listed in Table II. The value  $N_\kappa$  is the absorption coefficient  $\kappa(\omega, P, T)$  divided by the  $\text{CO}_2$  mole fraction. The dependence of  $\kappa(\omega, P, T)$  on pressure and temperature is reproduced quite satisfactory.

TABLE II. Pressure dependence of the  $\text{CO}_2$ - $\text{N}_2$  absorption coefficient.

$T = 296$ K, $\omega = 2387.62$ $\text{cm}^{-1}$				$T = 370$ K, $\omega = 2387.64$ $\text{cm}^{-1}$			
$P$ , atm	$N_{\kappa}^{\text{exp}}$ , $\text{cm}^{-1}$	$N_{\kappa}^{\text{calc}}$ , $\text{cm}^{-1}$	$\frac{N_{\kappa}^{\text{calc}}}{N_{\kappa}^{\text{exp}}}$	$P$ , atm	$N_{\kappa}^{\text{exp}}$ , $\text{cm}^{-1}$	$N_{\kappa}^{\text{calc}}$ , $\text{cm}^{-1}$	$\frac{N_{\kappa}^{\text{calc}}}{N_{\kappa}^{\text{exp}}}$
1.00	—	0.490	—	1.0	0.115	0.107	0.93
1.46	0.104	0.102	0.99	2.11	0.490	0.451	0.92
2.42	0.274	0.264	0.96	2.76	0.800	0.738	0.92
3.41	0.489	0.485	0.99	3.34	1.120	1.032	0.92
4.44	0.744	0.751	1.01	3.75	1.350	1.248	0.92
5.35	0.980	1.009	1.03	4.19	1.610	1.500	0.93
6.35	1.230	1.312	1.07	4.90	2.040	1.908	0.94
8.0	—	1.858	—	8.0	—	3.763	—
10.0	—	2.609	—	10.0	—	4.981	—

The results drawn in Figs. 4 and 5 of Ref. 3 showed the division of the absorption coefficient into the constituent parts which depend on pressure in different ways. This division is fruitful in the study of the line wings. The analogous results of our calculation are shown in Fig. 4. The value  $N_{\kappa}^{\text{sel}}$  represents the part of the absorption coefficient which is calculated with the use of the dispersive line shape and contains mainly the contribution of the two nearest lines. The rest of absorption  $N_{\kappa}^{\text{cont}}$  is due to the contributions of the wings of distant lines. We denoted these parts as selective and continual absorption. Their relative contribution to the absorption coefficient depends significantly on the thermodynamic conditions. Thus, the selective absorption contribution increases with temperature at the given frequency and pressure. The rise in pressure, however, can result in increase of the continual absorption contribution, which becomes more and more pronounced, and for the "lower" frequency the lower is the temperature. At higher pressures the absorption is

completely determined by the line wings. The same pattern is also observed in the case of the pure  $\text{CO}_2$ . The corresponding curves are given in Fig. 5 for the frequency of  $2450$   $\text{cm}^{-1}$  beyond the band head, where the contribution of the hot bands could become significant with rise in temperature.

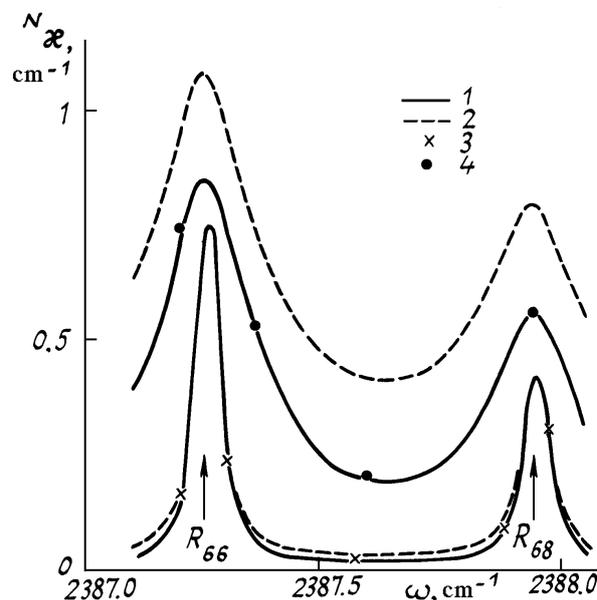


FIG. 2. The  $\text{CO}_2$ - $\text{N}_2$  absorption coefficient divided by the mole fraction of  $\text{CO}_2$  at  $T = 301$  K: 1)  $N_{\kappa}^{\text{calc}}$ , 2)  $N_{\kappa}^{\text{L}}$ , 3)  $N_{\kappa}^{\text{exp}}$  at  $P = 0.49$  atm, and 4)  $N_{\kappa}^{\text{exp}}$  at  $P = 1.94$  atm.

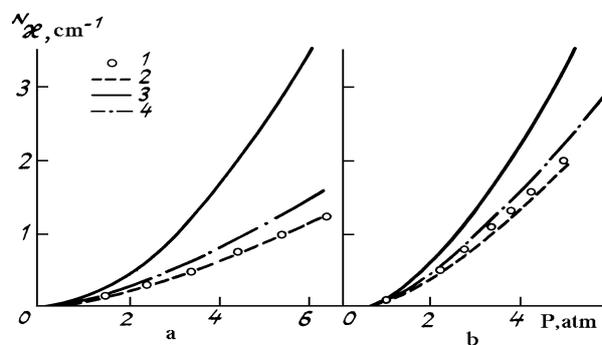


FIG. 3. Pressure dependence of the absorption coefficient  $N_{\kappa}(\text{CO}_2\text{-N}_2)$  at two temperatures: 1)  $N_{\kappa}^{\text{exp}}$ , 2)  $N_{\kappa}^{\text{calc}}$ , 3)  $N_{\kappa}^{\text{L}}$ , and 4)  $N_{\kappa}$  calculated on account of the line mixing effect.<sup>3</sup> a)  $T = 296$  K and  $\omega = 2387.62$   $\text{cm}^{-1}$ , b)  $T = 370$  K and  $\omega = 2387.64$   $\text{cm}^{-1}$ .

Beyond the head of the  $4.3$   $\mu\text{m}$  band the absorption at the normal temperature is practically completely determined by the line wings and, therefore, it is the most suitable object for the test of the line wing theory. As Fig. 6 shows, it stands this test successfully.

Thus, the experimental data of Refs. 3 and 4 are described adequately by the line wing theory, representing the absorption coefficient  $\kappa(\omega, P, T)$  as the sum of contributions of individual lines with the appropriate wings.

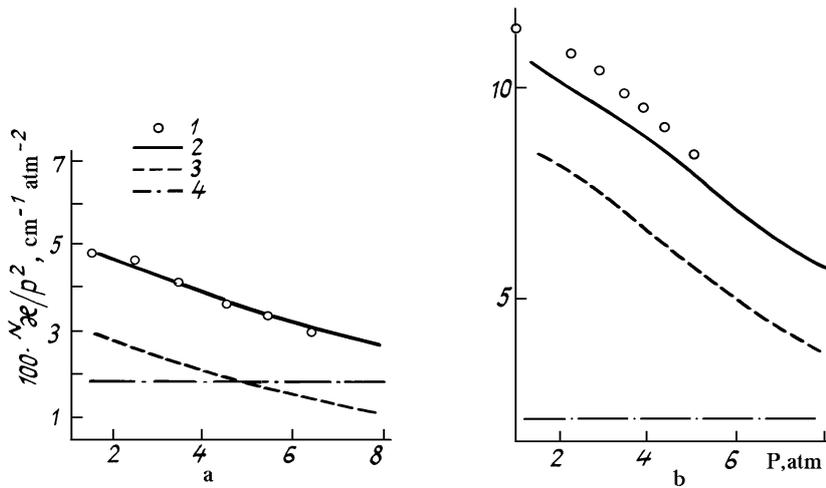


FIG. 4. Pressure dependence of different components of the absorption coefficient: 1)  $N_{\kappa}^{\text{exp}}/P^2$ , 2)  $N_{\kappa}^{\text{calc}}/P^2$ , 3)  $N_{\kappa}^{\text{sel}}/P^2$ , and 4)  $N_{\kappa}^{\text{cont}}/P^2$ . a)  $T = 296$  K and  $\omega = 2387.62$   $\text{cm}^{-1}$ , b)  $T = 370$  K and  $\omega = 2387.64$   $\text{cm}^{-1}$ .

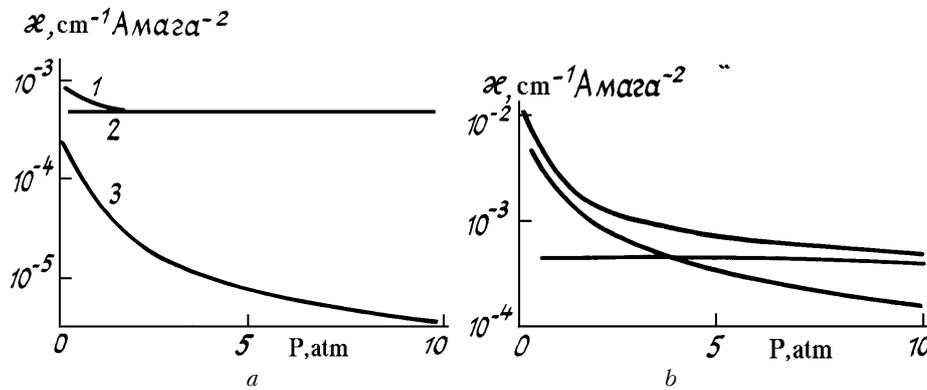


FIG. 5. Variations with pressure of the total  $\text{CO}_2$  absorption coefficient and its selective and continual parts at different temperatures and  $\omega = 2450$   $\text{cm}^{-1}$ : 1)  $\kappa^{\text{tot}}$ , 2)  $\kappa^{\text{cont}}$ , and 3)  $\kappa^{\text{sel}}$ . a)  $T = 300$  K and b)  $T = 627$  K.

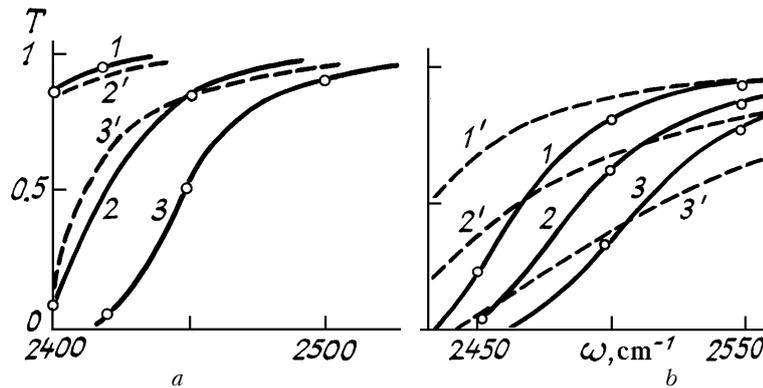


FIG. 6. The  $\text{CO}_2\text{-N}_2$  transmission spectrum at  $T = 291$  K for  $l = 4.4$  cm. Points denote the experimental data published in Ref. 4, dashed curves denote the calculation taking into account the line mixing effect, and solid curves denote our calculation. Case a: 1, 1')  $\rho = 1.62$  amagat; 2, 2')  $\rho = 7.27$  amagat; and 3, 3')  $\rho = 17$  amagat; Case b: 1, 1')  $\rho = 29.3$  amagat; 2, 2')  $\rho = 51.5$  amagat; 3, 3')  $\rho = 77.1$  amagat;

### 3. ON THE PECULIARITIES OF CALCULATIONS OF THE ABSORPTION IN THE LINE WING

In this concluding Section we note briefly the similarity and difference between two theoretical approaches

to the line wing problem with the use of calculation of the matrix elements of the relaxation operator<sup>1,2,7</sup> and with the use of the asymptotics "large frequency detunings",<sup>14-16</sup> contemplating the detailed publication of this comparative analysis later.

1. Relation (1) has been obtained by Fano in Ref. 21 using the factorization of the density matrix under condition  $V = 0$ . It is possible to make the factorization within the framework of the semiclassical representation<sup>22</sup> without excluding the intermolecular interaction potential. In this case the method of Fano's resolvent<sup>12,7</sup> and the kinetic equation method<sup>14-16</sup> are equivalent.

2. The use of the explicit form of the energy conservation law in the presence of the radiation absorption and of the intermolecular interaction in the process of the statistical averaging is the main point in the spectral line wing theory (see Ref. 14 for review of earlier references); this point is also available in Refs. 12 and 7.

3. The factors mentioned in item 2 are decisive for the spectral and temperature behavior of the absorption coefficient in the line wings (see Refs. 14-16 and references cited there). Their effect is so strong that, for example, the solution to the Schrodinger equation in Ref. 12, where the omitted and included terms were of the same order of magnitude, nevertheless, allowed us to obtain the CO<sub>2</sub>-Ar absorption coefficient<sup>12</sup> which was in a satisfactory agreement with the experiment and with the results of the calculations based on the line wing theory.<sup>23</sup>

4. If we bear in mind items 1-3 the opposite conclusions about the line mixing effect made on the basis of these two approaches seem to be unexpected. Thus, the authors of Refs. 12 and 7 have obtained for the diagonal and off-diagonal matrix elements the values of the same order of magnitude. According to the line wing theory evaluations,<sup>15</sup> the interference contribution to the absorption coefficient is not more than 15-20% and decreases with increase of the frequency detuning. As can be seen from items 1-3, the starting principles of both approaches are practically the same. The differences appear in the process of making approximations and in the computing realization.

Thus, both approaches are developing in one direction, though with some delay in time, and should lead to approximately analogous results. The differences pointed out in item 4 will be discussed in our further publication.

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