

SPECTRAL BEHAVIOR OF THE ABSORPTION COEFFICIENTS IN THE 4.3 μm CO_2 BAND WITHIN A WIDE RANGE OF TEMPERATURE AND PRESSURE

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Experimental data of some authors on the absorption coefficient of carbon dioxide in the cases of self-broadening and broadening by nitrogen of its spectral lines in the transmission microwindows and beyond the head of the 4.3 μm absorption band for temperature of 193 to 771 K and for pressure from the standard atmospheric to 60 Amagat are analyzed from the standpoint of the line wing theory. It is shown that the whole data set can be quite accurately described within the framework of this theory with the account for temperature behavior of the intermolecular interaction potential. Advantages and drawbacks of other theoretical approaches to description of spectral line wings are briefly discussed.

Recent experimental studies of the absorption coefficient within the 4.3 μm CO_2 band and beyond its head¹⁻⁶ provide a valuable information for theoretical analysis of mechanisms of forming the spectral line contour at different temperatures and pressures. We think that the absorption coefficient in the line wings is a sum of the absorption coefficients of individual lines with spectral and temperature behavior determined by the intermolecular interaction at a negligible effect of line mixing. Mathematical arguments in favour of this point of view have been discussed in a number of papers, see, for example, Refs. 7-10.

In this paper we will try to determine the place of our approach which we call the spectral line wing theory and the place of line mixing approaches in the general theory of line shape and the calculational results on the absorption coefficient within the 4.3 μm CO_2 band for gas mixtures $\text{CO}_2\text{-N}_2$ and $\text{CO}_2\text{-CO}_2$ at temperatures 193-771 K and pressures of 1-40 atm that corresponds to the conditions of measurements in Refs. 1-6.

In the problem on line shape two asymptotic cases, i.e., small frequency shifts (line center) and large frequency shifts (line wing), can naturally be separated out. The line center is described, in the absence of line mixing, by the Lorentz line shape. The line wing, in our opinion, is described by the line shape obtained in the line wing theory⁷⁻¹⁰ (see also Ref. 11). Theoretical studies of the line shape normally use two approaches, i.e., the kinetic equation method and Fano's resolvent method. The asymptotic cases mentioned above appear quite naturally in both these approaches, as it is shown below.

Let us introduce necessary designations. The below description of the spectral line shape uses the well-known expression

$$F(\omega) = \pi^{-1} \text{Re} \int_0^{\infty} \exp(i\omega t) \Phi(t) dt, \quad (1)$$

where the correlation function of the dipole moment (x is the dipole moment operator)

$$\Phi(t) = \text{Tr} x \exp[(t/i\hbar)H] \rho \exp[-(t/i\hbar)H], \quad (2)$$

H is the Hamiltonian of the system under study

$$H = H_1 + H_2 + H_3 + U = H^{(0)} + U, \quad (3)$$

$$\rho = Z^{-1} e^{-H/kT}, \quad (4)$$

$H_1(\xi_1)$ is the Hamiltonian of a light absorbing molecule (dynamic subsystem), $H_2(\xi_2)$ is the Hamiltonian of intramolecular motions of buffer gas molecules; $H_3(\xi_3)$ is the operator of the kinetic energy of the molecular centers of mass ($H_2 + H_3$ is a dissipative subsystem), and $U(\xi_1, \xi_2, \xi_3)$ is the intermolecular interaction potential (interaction between the dynamic and dissipative subsystems). Hereinafter $S(t) = e^{(t/i)H}$ is the evolution operator and the operation Tr_2Tr_3 from Tr in Eq. (2) can be treated as averaging over collisions.

Kinetic equation. The kinetic equation in the line shape theory is the equation whose solution is the operator $Q(t)$

$$Q(t) = \text{Tr}_2 \text{Tr}_3 S \rho x S^{-1}(t), \quad (5)$$

$$F(\omega) = \pi^{-1} \text{Re} \text{Tr}_1 x Q(\omega), \quad Q(\omega) = \int_0^{\infty} dt e^{i\omega t} Q(t). \quad (6)$$

Kinetic equation is written as follows

$$-\rho_1 x - i\omega Q(\omega) = (i\hbar)^{-1} \hat{L}_1 Q(\omega) + \hat{\Gamma}(\omega) Q(\omega), \quad (7)$$

where $\hat{\Gamma}(\omega)$ is the so-called relaxation operator.

It can be shown⁷⁻¹⁰ that the right-hand side of the kinetic equation for spectral components of the matrix elements Q_{nm} takes the form of the sum of two terms

$$i(\omega - \omega_{nm}) Q_{nm} + x_{nm} \rho_{nm} = Y_{nm} + (\omega - \omega_{nm})^2 Z_{nm}, \quad (8)$$

where

$$Y_{nm} = \int_0^{\infty} dt e^{i\omega t} \left(\text{Tr}_2 C \left[\frac{\partial U}{\partial t}, \rho_2 Q \right] C^{-1} \right)_{av}, \quad (9)$$

$$Z_{nm} = \int_0^{\infty} dt e^{i\omega t} (\text{Tr}_2 C \rho_2 Q C^{-1})_{av}. \quad (10)$$

Operator C after passing to a semiclassical representation obeys the equation

$$i\hbar \frac{\partial C}{\partial t} = (H_1(\xi_1) + H_2(\xi_2) + U(\xi_1, \xi_2, \mathbf{R}(t))) C, \quad (11)$$

where $\mathbf{R}(t)$ is the classical trajectory of a molecular center of mass motion.

Two terms of the right-hand side of Eq. (8) describe the line shape in alternative asymptotics.^{7,11} The equation, containing only the first term in the right-hand side, yields the Lorentz line shape. The equation containing only the second term $(\omega - \omega_{nm})^2 Z_{nm}$, in the right-hand side corresponding to the large frequency displacement asymptotics in the absence of the line mixing yields the expression for the absorption coefficient of an individual line conventional for the line wing theory

$$F(\omega) \sim \Delta\omega^{-1-3/a} \frac{1}{R'} \int_0^{R'} \frac{R e^{-V(R)/kT} dR}{\sqrt{R'^2 - R^2}}. \quad (12)$$

The value R' in Eq. (12) is the root of equation corresponding to the law of energy conservation for absorption

$$\Delta E(R) = \Delta\omega, \quad (13)$$

and $V(R)$ is the so-called "classical intermolecular interaction potential" connected to $U(\xi_1, \xi_2, \mathbf{R}(t))$ by the relation

$$V(\mathbf{R}) = \text{Tr}_1 \text{Tr}_2 C^{-1} \rho_1 \rho_2 C U. \quad (14)$$

Fano's resolvent. When $Q(t)$ in Eq. (6) is written in terms of the superoperator \hat{L}

$$\hat{L}y = [H, y] \quad (15)$$

($\hat{L} = \hat{L}_1 + \hat{L}_2 + \hat{L}_3 + \hat{L}' = \hat{L}^{(0)} + \hat{L}'$ what corresponds to partitioning (3) of H), the possibility appears of taking the integral over t in the explicit form

$$F(\omega) = -\pi^{-1} \text{Im Tr } x \frac{1}{\omega - \hat{L}} \rho x, \quad (16)$$

and the resolvent operator can be related to the operator $\hat{M}(\omega)$ which obeys the equation

$$\hat{M}(\omega) = \hat{L}'/\hbar + (\hat{L}'/\hbar) (\omega - \hat{L}^{(0)}/\hbar)^{-1} \hat{M}(\omega). \quad (17)$$

Solution of Eq. (17) can be written in terms of the amplitudes of a transition T between quantum states obeying Lippmann-Schwinger equation ($\hat{M} = \hat{N} \langle m \rangle$)

$$\begin{aligned} \hat{m}(\omega) &= [T(\omega + H^{(0)} - T^*(H^{(0)} - \omega))] + (2\pi i)^{-1} \times \\ &\times \int_{-\infty+i\eta}^{\infty+i\eta} dz \left(\frac{1}{z - H^{(0)}} - \frac{1}{z - \omega - H^{(0)*}} \right) T(z) T^*(z - \omega) \times \\ &\times \left(\frac{1}{z - H^{(0)}} - \frac{1}{z - \omega - H^{(0)}} \right). \end{aligned} \quad (18)$$

Representation of \hat{M} in terms of the scattering matrix (the first term of Eq. (18)) is typical of many equations written especially for studying resonant interactions, i.e., for the line center. As to the second term of Eq. (18), as far as we know, it has not been used in calculations. It can be shown that only small intermolecular distances are essential for its evaluation where intermolecular interactions are strong and therefore it should be important for the line periphery. Thus, in Fano's method the division into two asymptotic cases is in fact also assumed.

It should be noted that two approaches, i.e., the kinetic equations and Fano's resolvent turned out to be intrinsically interconnected (generally speaking, it is quite natural because both these approaches are aimed at the solution of one and the same physical problem),

namely, the operator \hat{M}_c in the resolvent method

$$\langle \hat{M}_c \rangle = \langle \hat{M} \rangle \left(1 - \left(\omega - \frac{1}{\hbar} \hat{L}_1 \right)^{-1} \langle \hat{M} \rangle \right)^{-1} \quad (19)$$

is in fact the relaxation operator from the kinetic equation

$$\langle \hat{M}_c \rangle = i\hat{\Gamma}(\omega). \quad (20)$$

Thus, there are two asymptotic cases in the line shape theory appearing as a result of definite mathematical approximations. They also imply different physical pictures of interaction of light with the molecular systems (see, for example, Refs. 7 and 12). We only note here that the presence in Eq. (8) of two, in a certain sense, alternative terms means, in fact, that the matrix elements of the relaxation operator or, what is the same because of Eq. (20), the resolvent operator are also the sum of two terms each prevailing in certain asymptotic cases. This situation is schematically illustrated in Fig. 1.

If the second term in the right-hand side of Eq. (8) or the integral term in Eq. (18) are neglected we shall deal only with the relaxation operator, i.e., with the asymptotic case of the line center. If, in this term, one makes a limiting transition to large $\Delta\omega$ neglecting the factor $\exp(-V/kT)$ one obtains the well-known statistical line shape, see Ref. 10. However, it may have nothing to do with the real line wing as it can be seen from the scheme in Fig. 1. It is also clear that if one deals with this term only even if the diagonal and off-diagonal matrix elements of the resolvent operator are of the same order of magnitude or if one takes into account the finite duration of collisions or makes the calculations of matrix elements more precise, etc. all that may tell nothing about the decisive role of the line mixing in the wing formation because it may have nothing to do with the real line wing at corresponding frequency shifts.

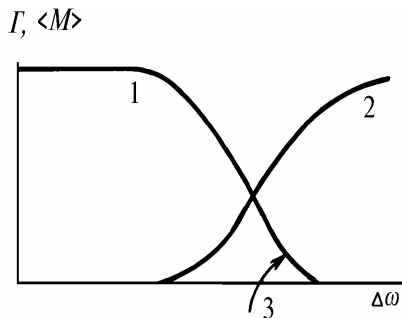


FIG. 1. Schematic picture of spectral behavior of matrix elements of the relaxation matrix. 1) Line center asymptotics, 2) line wing asymptotics, and 3) statistical line shape.

On the spectral line mixing. We think that the papers devoted to the study of line mixing by means of the resolvent method (see, for example, Refs. 4, 13–16) are not beyond the scope of the line center asymptotics and therefore have only a limited applicability, i.e., not very far from the center, where the line wing asymptotics is not yet dominating. Indeed, in order to use the analytical perturbation theory (see, for example, Ref. 19), as it was done in Refs. 4 and 16, the frequency at which the absorption occurs has to be beyond the half-width of a line at frequency ω_j contributing to the absorption at the frequency ω and there should be no absorption lines within the limits of the frequency shift $\Delta\omega = |\omega - \omega_j|$. These conditions are evidently violated at frequencies beyond the band head, but, generally speaking, may be satisfied at frequencies in microwindows under not very high pressures. However, even in the case of microwindows the frequency shifts are already so large ($\Delta\omega \geq 5\alpha$ for the 4.3 μm band) that they in fact are within the region of the wing asymptotics. This means that the matrix elements of the relaxation operator determined within the framework of the line center asymptotics ($\Gamma_{mm}(\Delta\omega) \sim \text{const}$), cannot be used here and their frequency dependence must be taken into account.

The other series of papers^{13–15} is the generalization of the approach proposed in Ref. 20, i.e., when the far line wing is studied based on the ideas resulting in the statistical line shape, see Ref. 10, in other words within the line center asymptotics, which is applicable only for not very large frequency shifts. Therefore the importance of the line mixing being underlined in these studies is valid just within this frequency region. Evaluation of the role of line mixing in the far-wing formation has to proceed from the line wing asymptotics. The role of line mixing in the formation of the far line wing is defined by other criteria and, as is shown in Ref. 7, it is inessential.

As follows from the literature the calculations made with the line mixing effects taken into account confirm all the above said. Thus, the results obtained using the line mixing approach are quite satisfactory for the microwindows at room temperature,^{4,16} whereas the results for frequency shifts beyond the 4.3 μm CO_2 absorption band head can hardly be considered successful (see, for example, Ref. 17), to say nothing about the temperature behavior of the absorption which is not described by line mixing theories. Moreover, even for the regions in which the agreement between calculations and experiment is reasonable, the evaluation of the line mixing effect may necessitate additional studies because in these cases both contributions may be comparable.

Results of calculations. Let us now consider the situations when the absorption coefficient is defined by the line-wing asymptotics and is described by the line wing theory. These are, first of all, the data concerning the region beyond the band head of the 4.3 μm CO_2 band.

Remind that the line-wing asymptotics is described by Eq. (12), where R' is the root of Eq. (13). The quantity $\Delta E(R)$ in Eq. (13) is the difference of quantum interaction energies of the molecular states between which the transition under study occurs. We approximate this difference with a set of monomials with the inverse power dependence on the distance between molecules

$$\Delta\omega = (C_a/R)^a, \quad (21)$$

so that each of them corresponds to some interval of frequency shifts. The corresponding piecewise approximations for $\text{CO}_2\text{--CO}_2$ and $\text{CO}_2\text{--N}_2$ mixtures are shown in Fig. 2.

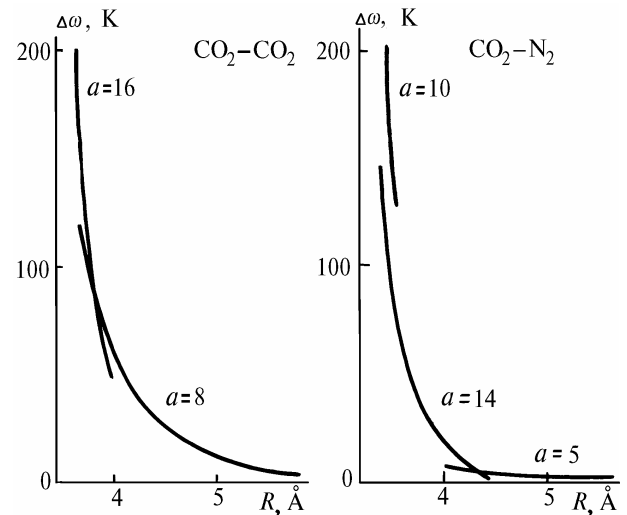


FIG. 2. Approximations of quantum interaction potential $\Delta E \sim \Delta\omega = (C/R)^a$ used in calculations.

The so-called "classical intermolecular interaction potential" (Eq. (14)) is approximated by Lennard—Jones potential with the parameters taken from thermodynamic measurements at room temperature. It is this potential that determines, to a considerable degree, the spectral behavior of the absorption coefficient resulting in the exponential fall off in the region of wing. It also leads to a nontrivial temperature dependence of the absorption coefficient, because $V(R)$ depends on temperature by its definition.²¹

Using the above approximations we have calculated the absorption coefficients. Deviations of the calculated values of the absorption coefficient from measured values are shown in Fig. 3. In addition to the conventional for us treatment of the case of large frequency shifts beyond the band head in terms of the line wing theory great attention was paid to joining the Lorentz line shape and the line wing contour and, accordingly, to the study of absorption within the band, particularly, in the gaps between the lines. Figure 4 depicts the deviations of calculated values of the absorption coefficients from the measured ones in the microwindows of the 4.3 μm CO_2 absorption band.

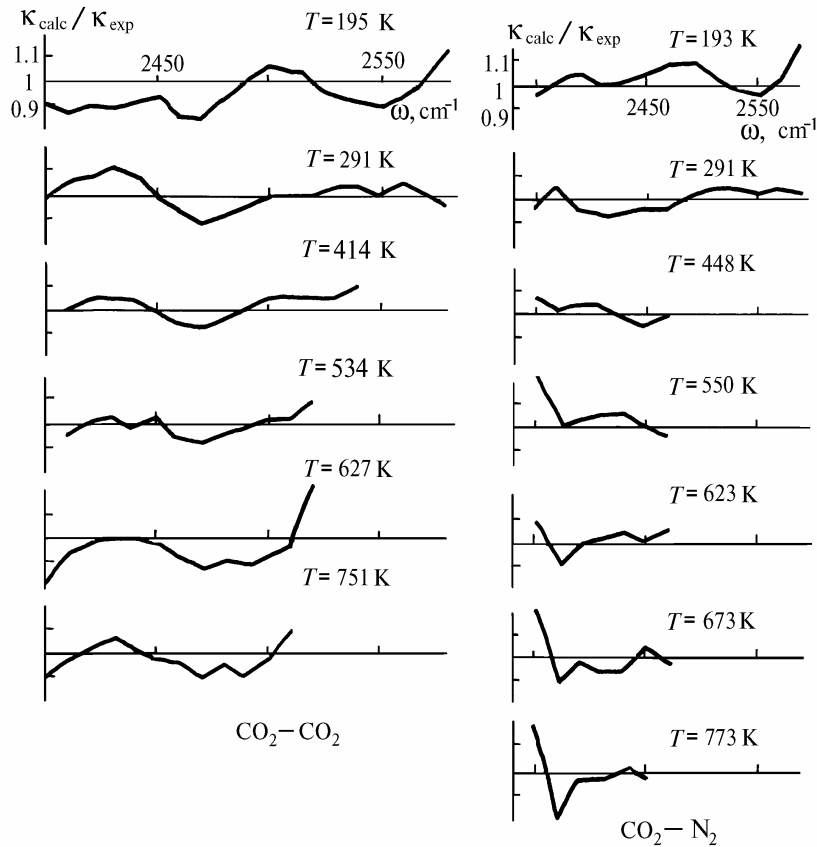


FIG. 3. Deviations of calculated values of the absorption coefficient from the measured for $\text{CO}_2\text{-CO}_2$ and $\text{CO}_2\text{-N}_2$ mixtures at different temperatures beyond the $4.3\ \mu\text{m}$ CO_2 band head.

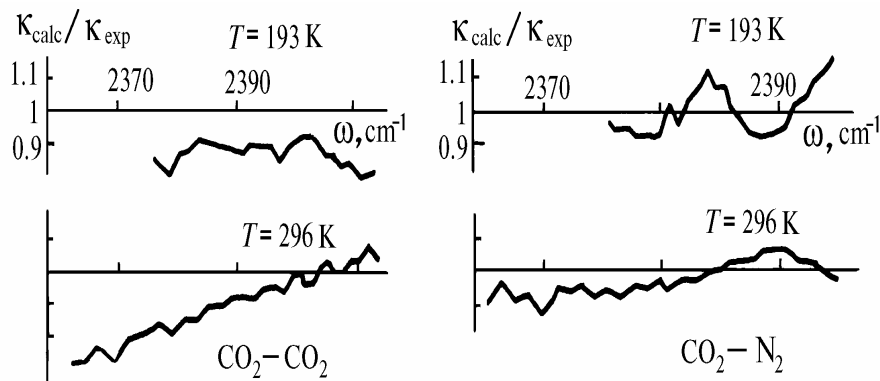


FIG. 4. Deviations of calculated values of the absorption coefficient from the measured ones for $\text{CO}_2\text{-CO}_2$ and $\text{CO}_2\text{-N}_2$ mixtures at different temperatures in the microwindows of the $4.3\ \mu\text{m}$ CO_2 absorption band.

The line shape parameters associated with the quantum intermolecular interaction potential remain unchanged at the temperatures and pressures under study. Both the quantum potential parameters and the temperature dependence of the "classical intermolecular interaction potential" were described earlier (see Ref. 7 for references therein). Temperature dependence of $V(R)$ is taken into account through the temperature dependence of the parameters of the corresponding Lennard-Jones potential.

The temperature dependences of ε and σ are depicted in Fig. 5. For the case of $\text{CO}_2\text{-N}_2$ the depth ε of the potential well does not vary with temperature. The behavior of σ shows some peculiarities. It appears that the data on $\kappa(\omega, T)$ in microwindows at low temperatures can be described only if the functional form of the potential is changing with temperature. That is, the necessary potential at low temperatures is, to some extent, narrower than the Lennard-Jones potential (Fig. 6).

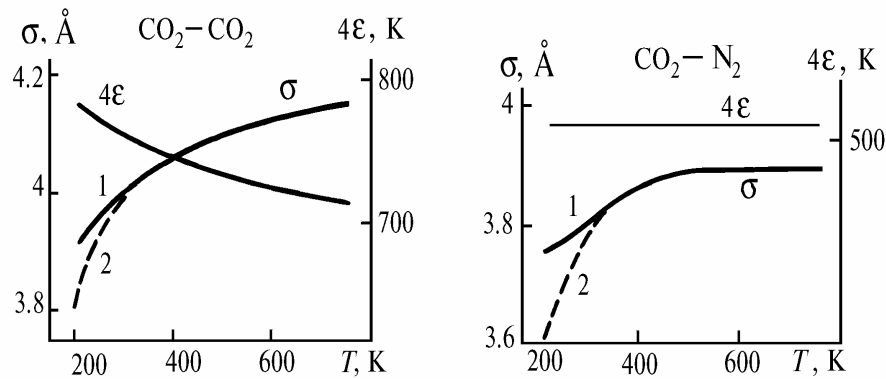


FIG. 5. Temperature dependence of the parameters of "classical potential" $V(R)$: 1) σ for $\Delta\omega < 20 \text{ cm}^{-1}$ and 2) σ for $\Delta\omega < 20 \text{ cm}^{-1}$.

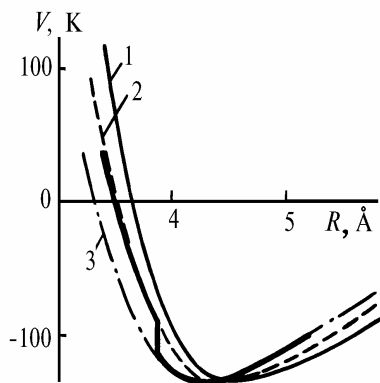


FIG. 6. Change of the shape of the classical potential for $\text{CO}_2\text{-N}_2$ mixture with temperature. The parameters of Lennard-Jones potential are: $4\epsilon = 528 \text{ K}$; 1) $\sigma = 3.8 \text{ \AA}$, 2) $\sigma = 3.76 \text{ \AA}$, and 3) $\sigma = 3.6 \text{ \AA}$. Bold curve shows the potential used in calculations.

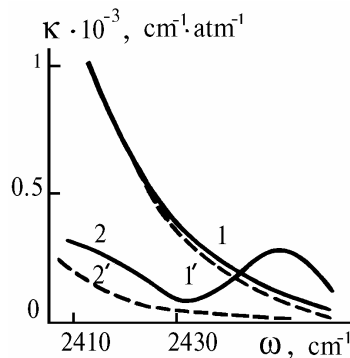


FIG. 7. Effect of hot bands on the absorption in the wing of the $4.3 \mu\text{m}$ CO_2 absorption band. $P = 0.2675 \text{ atm}$; 1 and 1' are for $T = 291 \text{ K}$ and 2 and 2' are for $T = 673 \text{ K}$. Dashed curves indicate calculations with κ from Ref. 6, solid lines denote the experimental data¹⁸ and the calculations by the line wing theory that coincide with each other in the figure scale.

Note that relative contributions of selective and continuous absorption (corresponding to small and large frequency shifts, respectively) to the total absorption

coefficient change essentially depending on the temperature and pressure, see, for example, Ref. 22. Thus, it appears that the absorption coefficients determined in Ref. 6 at high temperatures and at pressures up to $\sim 40 \text{ atm}$ in the band wing being applied to calculations at low pressure show poor agreement with the experimental data of Ref. 18 in which the absorption due to hot bands beyond the band head is distinctly observed (Fig. 7).

On the whole our results show that the line wing theory gives physically consistent and mathematically noncontradictory picture of the contour formation in the line wing and provides a quantitative description of the experimental data available.

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