The role of line mixing in the far wings of the CO_2 spectral lines

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Received September 8, 2003

Within the framework of the line wing theory, the line shape parameters related to the intermolecular interaction potential are obtained from a comparison between the calculated and measured absorption coefficients. At the same time, the relations for the characteristics considered as parameters in the line wing theory can be obtained from the general expression for the absorption coefficient in terms of the Möller operators taking into account the line mixing effect. These relations have a simple form in the case of no line mixing and can be easily estimated. Their comparison with the values obtained from approximation of the experimental data on the absorption coefficient, which implicitly include the line mixing, is indicative of its inessential role in the case of the 4.3 μm CO_2 band considered in this paper.

Introduction

The absorption coefficient in the transmission microwindows and wings of the CO_2 absorption band at 4.3 μm has been thoroughly studied experimentally at different temperatures in different buffer gases (see, e.g., Refs. 1–4). The temperature and frequency dependences of the absorption coefficient found experimentally are interpreted theoretically as being caused by the absorption in the far wings of spectral lines. However, in spite of the general agreement, different theoretical approaches give preference to one or another physical mechanisms of absorption in line wings. Two explanations can be separated out from those available in the literature. In some papers, (see, e.g., Refs. 2–6) the mixing of quantum states is given the main role in the formation of the absorption in line wings. Other approaches, in particular, the quasistatic[7–9] and asymptotic[10,11] theories of the line wings assume that the intermolecular interaction is decisive in the formation of the line shape at large frequency shifts with only insignificant role of line mixing.

The detailed analysis of arguments in favor of the concept on the major role of mixing of quantum states for the line periphery was carried out in Ref. 12, and it suggested their theoretical weakness. Sequential calculation of the absorption coefficients taking into account the line mixing effect, for example, for the CO_2 band at 4.3 μm could be the final evidence of the limited role of the line mixing in the far wings at normal pressure, but it is not accomplished yet because of its awkwardness. Taking the line mixing effect into account for a couple of water vapor absorption lines near 0.8 μm (see Ref. 13) showed that its contribution to atmospheric absorption between the mixed lines did not exceed 3%. The calculations of the absorption coefficient made in Refs. 7–11 neglecting the line mixing agree well with the experimental data, but include the parameters of intermolecular interaction potential as fitting parameters.

Recently, we have obtained a general equation for the absorption coefficient in the line wing through the Möller operators with regard for the line mixing. The closed equations including the Möller operators follow from the general equations for those characteristics, which are declared as parameters D_a and C_a in the asymptotic theory of line wings. The equations for D_a and C_a in the case of no line mixing have a rather simple form and can be readily estimated. Comparison of these parameters with the values obtained from approximation of the experimental values of the absorption coefficient, which should implicitly account for the effect of line mixing, if any, is indicative of only insignificant role of the line mixing in the experimental situations considered.

1. Equation for the absorption coefficient

The coefficient of absorption of radiation at the frequency ω by a molecule A in the binary approximation and at the classical motion of the centers of gravity is traditionally written in the following form (accurate to a constant factor):

$$\kappa(\omega) = \mathrm{Re}\,\mathrm{Tr}_x PQ = \sum_{n,n'} P_{n'n}\,\mathrm{Re}\,Q_{nn'}. \qquad (1)$$

The equation for Q involves the following characteristics:

$$H = H_1(x) + H_2(y) + H_3(q) + U(x,y;q)$$

is the complete quantum Hamiltonian of the problem; $H_1(x)$ is the Hamiltonian of an active molecule A; $H_2(y)$ is the Hamiltonian of a buffer molecule B; $H_3(q)$ is the Hamiltonian of motion of the centers of gravity; $U(x, y, q)$ is the potential of interaction of the active molecule A with B. In Eq. (1) P is the dipole moment of the active (interacting with the field) molecule A; Tr_x is the spur operation with respect to the intramolecular variables x of the molecule A; $|m\rangle$ are the eigenfunctions of the Hamiltonian $H_1(x)$ of the active molecule A; $(\ldots)_{mm'} = \langle m|\ldots|m'\rangle$ are matrix elements with the eigenfunctions of $H_1(x)$; $S(t)$ is the evolution operator, which is a solution of the Schrödinger equation for the molecule A interacting with the buffer molecule B (t is time).

For $Q_{nn'}$ the kinetic equation is presented in Section 3.

The equation equivalent to Eq. (1) for the absorption coefficient in the superoperator representation has the following form:

$$\kappa(\omega) = \frac{1}{\pi}\mathrm{Im}\,\mathrm{Tr}P\frac{1}{(\omega + i\varepsilon) - \hat{L}}\rho P, \quad \varepsilon \to 0, \tag{2}$$

where

$$\hat{L}W = \frac{1}{\hbar}[H,W], \tag{3}$$

$\hat{L}$ is the superoperator corresponding to the Hamiltonian H; $\dfrac{1}{(\omega + i\varepsilon) - \hat{L}}$ at $\varepsilon \to 0$ is the so-called resolvent operator; W in Eq. (3) is an arbitrary operator.

2. State mixing in the resolvent method

In the approximation of factorization of the density matrix

$$\rho \cong \rho^{(1)}R = \rho^{(1)}\rho^{(2)}\exp(-V(q)/kT), \tag{4}$$

where $\rho^{(1)}$, $\rho^{(2)}$ are the density matrices corresponding to H_1, H_2; and V is the potential describing the motion of the centers of gravity of the molecules, the equation for the absorption coefficient (2) can be written as (see, for example, Ref. 14)

$$\kappa(\omega) = -\frac{1}{\pi}\mathrm{Im}\,\mathrm{Tr}_1 P \; \frac{1}{\omega - \hat{L}_1}\left(1 + \langle\hat{M}\rangle \; \frac{1}{\omega - \hat{L}_1}\right)\rho^{(1)} P. \tag{5}$$

In Eq. (5) $\hat{M}$ is the superoperator including the interaction of the molecules in this representation:

$$\langle\hat{M}\rangle = \sum_{\alpha\alpha'} M_{b\alpha,a\alpha';b'\alpha',a'\alpha'} R_{\alpha'}. \tag{6}$$

The subscripts a and b enumerate eigenstates of the Hamiltonian H_1, while the subscripts α, α' enumerate the eigenstates of $H_2 + H_3$.

The absorption coefficient (5) can be also written as

$$\kappa(\omega) = -\frac{1}{\pi}\mathrm{Im}\mathrm{Tr}_1 P\frac{1}{\omega - \hat{L}_1 - \langle\hat{M}_c\rangle}\rho^{(1)}P. \tag{7}$$

The operator $\hat{M}_c$ is connected with $\hat{M}$ as follows:

$$\langle\hat{M}_c\rangle = \frac{1}{1 + \langle M\rangle(\omega - \hat{L}_1)^{-1}}\langle\hat{M}\rangle. \tag{8}$$

If the operator $\omega - \hat{L}_1 - \langle\hat{M}_c\rangle$ turns out diagonal in the chosen representation a, b, and $Z_{ba}(\omega)$ are its eigenvalues, then

$$\kappa(\omega) = \sum_{a,b}\rho_b^{(1)}\,|\,P_{ab}\,|^2\,\sigma_{ab}(\omega), \tag{9}$$

where

$$\sigma_{ab}(\omega) = \frac{1}{\pi}\frac{Z''_{ab}}{(Z'_{ab})^2 + (Z''_{ab})^2}, \tag{10}$$

$\sigma_{ba}(\omega)$ is the line profile; $S_{ab} = \rho_b^{(1)}\,|P_{ab}|^2$ is the line strength, and Eq. (9) is the absorption coefficient in the approximation of isolated lines.

Let now the operator $\omega - \hat{L}_1 - \langle\hat{M}_c\rangle$ be nondiagonal in the representation a, b, and N is the diagonalizing matrix. Then

$$\kappa(\omega) = -\frac{1}{\pi}\mathrm{Im}\mathrm{Tr}_1 P \;\; NN \; \frac{1}{\omega - \hat{L}_1 - \langle\hat{M}_c\rangle} \; NN \;\; \rho^{(1)}P. \tag{11}$$

After transition to matrix elements, the equation for the absorption coefficient acquires the form

$$\kappa(\omega) = \sum P_{ab}N_{ba,b'c'}\frac{1}{Z_{b'c'}}N^{-1}_{b'c',b''c''}\left(\rho^{(1)}P\right)_{b''c''}. \tag{12}$$

After regrouping of the terms, this equation can be reduced to the form (9), but the line strength proves to be a combination of elements with different a, b, just which is called line or state mixing.

3. State mixing in the method of kinetic equation

In the case of large shifted frequencies

$$\Delta\omega_{nn'} \equiv |\omega - \omega_{nn'}| \gg \gamma \tag{13}$$

(γ is the halfwidth) within the asymptotic theory of line wings, we obtain the kinetic equation for Q (see, for example, Ref. 15):

$$i(\omega - \omega_{nn'})Q_{nn'} + P_{nn'}\rho_{n'}^{(1)} = (\omega - \omega_{nn'})^2\left(\hat{Y}Q\right)_{nn'}, \tag{14}$$

where $\hat{Y}$ is the relaxation superoperator. Sequential solution of this equation for the binary problem on the interaction between the active and buffer molecules with the classical motion of the centers of gravity allows the absorption coefficient to be written as

$$\kappa(\omega) = \sum_{j\nu j'\nu'} \left|P_{j\nu j'\nu'}\right|^2 \rho_{j'}^{(1)} \sum_{\alpha} \rho_{\alpha}^{(2)} \frac{1}{2} \sum_{\sigma} 2\pi \left[\frac{1}{\left|\frac{\mathrm{d}\omega_{j\nu j'\nu'\alpha}}{\mathrm{d}t}\right|_{t^{(\sigma)}_{j\nu j'\nu'\alpha}}} + \right.$$

$$+\sum_{\nu_1} \frac{1}{\left|\frac{\mathrm{d}\omega_{j\nu_2 j'\nu'\alpha}}{\mathrm{d}t}\right|_{t^{(\sigma)}_{j\nu_1 j'\nu'\alpha}}} \left|\frac{P_{j\nu_1 j'\nu'}}{P_{j\nu j'\nu'}}\right|^2 \frac{\left\langle j\nu\alpha \middle| U(\mathbf{r}_{\min})\tilde{\Omega}_{+} \middle| j\nu_1\alpha \right\rangle}{V(\mathbf{r}_{\min})} +$$

$$+\sum_{\nu_2} \frac{1}{\left|\frac{\mathrm{d}\omega_{j\nu j'\nu_2\alpha}}{\mathrm{d}t}\right|_{t^{(\sigma)}_{j\nu j'\nu_2\alpha}}} \left|\frac{P_{j\nu j'\nu_2}}{P_{j\nu j'\nu'}}\right|^2 \frac{\left\langle j'\nu_2\alpha \middle| \tilde{\Omega}_{+}^{*} U(\mathbf{r}_{\min}) \middle| j'\nu'\alpha \right\rangle}{V(\mathbf{r}_{\min})} +$$

$$+\sum_{\nu_1\nu_2} \frac{1}{\left|\frac{\mathrm{d}\omega_{j\nu_1 j'\nu_2\alpha}}{\mathrm{d}t}\right|_{t^{(\sigma)}_{j\nu_1 j'\nu_2\alpha}}} \left|\frac{P_{j\nu_1 j'\nu_2}}{P_{j\nu j'\nu'}}\right|^2 \times$$

$$\left. \times \frac{\left\langle j\nu\alpha \middle| U(\mathbf{r}_{\min})\tilde{\Omega}_{+} \middle| j\nu_1\alpha \right\rangle \left\langle j'\nu_2\alpha \middle| \tilde{\Omega}_{+}^{*} U(\mathbf{r}_{\min}) \middle| j'\nu'\alpha \right\rangle}{V^2(\mathbf{r}_{\min})} \right]_{\mathrm{st}},$$

where $\tilde{\Omega}_{+}$, $\tilde{\Omega}^{*}_{+}$ are the Möller operators connecting the initial and final states in the process of the molecular interaction[16]; n, n' are the eigenstates of $H_1(x) + H_2(y) + U(x,y[\mathbf{r}(t)])$ that is the Hamiltonian of the binary problem at the classical motion of the centers of gravity ($n \to j\nu$); α, α' are eigenstates of $H_2(y)$ that is the Hamiltonian of the buffer molecule; $\mathbf{r}(t)$ is the vector connecting the centers of gravity.

After the approximations including approximation of the trajectory of the molecules by a straight line in the vicinity of a stationary point and approximation of the repulsive branch of the quantum potential of the intermolecular interaction in a limited range of distances by a function inversely proportional to the distance, we introduce the designation D for a certain combination of the matrix elements:

$$D = 32\frac{\pi^2}{a}\frac{\sqrt{m_1 m_2}}{m_1 + m_2} N \sum_{\nu\nu'} \sum_{\alpha} \rho_{\alpha}^{(2)} \frac{\left|P_{j\nu j'\nu'}\right|^2}{\sum\limits_{\nu\nu'}\left|P_{j\nu j'\nu'}\right|^2} \left(\left|C_{j\nu j'\nu'\alpha}\right|^{3/a} + \right.$$

$$+\sum_{\nu_1} \left|C_{j\nu_1 j'\nu'\alpha}\right|^{3/a} \left|\frac{P_{j\nu_1 j'\nu'}}{P_{j\nu j'\nu'}}\right|^2 \frac{\left\langle j\nu\alpha \middle| U\tilde{\Omega}_{+} \middle| j\nu_1\alpha \right\rangle}{V} +$$

$$+\sum_{\nu_2} \left|C_{j\nu j'\nu_2\alpha}\right|^{3/a} \left|\frac{P_{j\nu j'\nu_2}}{P_{j\nu j'\nu'}}\right|^2 \frac{\left\langle j'\nu_2\alpha \middle| \tilde{\Omega}_{+}^{*} U \middle| j'\nu'\alpha \right\rangle}{V} +$$

$$\left. +\sum_{\nu_1\nu_2} \left|C_{j\nu_1 j'\nu_2\alpha}\right|^{3/a} \left|\frac{P_{j\nu_1 j'\nu_2}}{P_{j\nu j'\nu'}}\right|^2 \frac{\left\langle j\nu\alpha \middle| U\tilde{\Omega}_{+} \middle| j\nu_1\alpha \right\rangle \left\langle j'\nu_2\alpha \middle| \tilde{\Omega}_{+}^{*} U \middle| j'\nu'\alpha \right\rangle}{V^2} \right). \tag{16}$$

In Eqs. (15) and (16), V is the classical potential describing the motion of the center of gravity of the interacting molecules;

$$\frac{m\mathbf{v}_0^2}{2} - \frac{m\mathbf{v}'^2}{2} = V(\mathbf{r}_{\min}),$$

$\mathbf{v}_0$, $\mathbf{v}'$ are the initial velocity of the center of gravity and the velocity at the point $\mathbf{r}_{\min}$ that is the point of maximum closeness of the molecules on the classical trajectory; N_m is the number of molecules in a unit volume. The rest part corresponding to the quantum problem of interaction of the two molecules includes the matrix elements of the Möller and dipole moment operators. They may be nondiagonal that corresponds to the presence of quantum states mixing.

In the absence of mixing

$$D_{\mathrm{calc}} = (32\pi^2/a)\sqrt{m_1 m_2}\,(m_1 + m_2)^{-1} N_m C^{3/a}. \tag{17}$$

In the theory of line wings, the quantum part of the equation for the absorption coefficient denoted by D_{emp} can be found from a comparison of the calculated and measured absorption coefficients. The comparison of the parameters D estimated theoretically and obtained experimentally allows one to assess the role of mixing for particular molecules in certain spectral ranges.

4. Equation for the absorption coefficient in the theory of line wings

Further in the calculations the parameter D is assumed to be a constant D_{emp}, and it is sought along with the constants determining the quantum potential of the intermolecular interaction from a comparison of the experimental and calculated values of the absorption coefficients:

$$\kappa_a(\omega) = \sum_{s} D_{\mathrm{emp}\,as} Z_s \frac{\omega}{\omega_s} \frac{1 - e^{-\hbar\omega/k\Theta}}{1 - e^{-\hbar\omega_s/k\Theta}} \times$$

$$\times \frac{1}{\left|\omega - \omega_s\right|^{1+3/a}} \frac{1}{r_s} \int_0^{r_s} \frac{e^{-V(r)/k\Theta}}{\sqrt{r_s^2 - r^2}}\, r\mathrm{d}r, \tag{18}$$

where

$$r_s = \frac{C_{\mathrm{emp}\,a}}{\left|\omega - \omega_s\right|^{1/a}}, \quad D_{\mathrm{emp}\,as} = D_{\mathrm{emp}\,a}\gamma_s, \tag{19}$$

γ_s is the line halfwidth. In the calculations, the profile of an isolated line is a piecewise-continuous function, each part of which corresponds to some value of a:

$$\kappa(\omega) = \begin{cases} \kappa_{\mathrm{Lor}}(\omega), & \Delta\omega < \Delta\omega_{\min 1}, \\ \left.\begin{matrix} \kappa_{\mathrm{Lor}}(\omega), & \kappa_{\mathrm{Lor}}(\omega) > \kappa_{a_1}(\omega) \\ \kappa_{a_1}(\omega), & \kappa_{\mathrm{Lor}}(\omega) < \kappa_{a_1}(\omega) \end{matrix}\right\} & \Delta\omega_{\min 1} < \Delta\omega < \Delta\omega_{\min 2}, \\ \left.\begin{matrix} \kappa_{a_1}(\omega), & \kappa_{a_1}(\omega) > \kappa_{a_2}(\omega) \\ \kappa_{a_2}(\omega), & \kappa_{a_1}(\omega) < \kappa_{a_2}(\omega) \end{matrix}\right\} & \Delta\omega_{\min 2} < \Delta\omega < \Delta\omega_{\min 3}, \\ \left.\begin{matrix} \kappa_{a_2}(\omega), & \kappa_{a_2}(\omega) > \kappa_{a_3}(\omega) \\ \kappa_{a_3}(\omega), & \kappa_{a_2}(\omega) < \kappa_{a_3}(\omega) \end{matrix}\right\} & \Delta\omega > \Delta\omega_{\min 3}. \end{cases} \tag{20}$$

The profile for the lines of the CO_2 band at 4.3 μm in the case of self-broadening is shown in Fig. 1. The estimate $D_{\mathrm{calc}\,a}$ and its comparison with $D_{\mathrm{emp}\,as}$ allow us to judge on the degree of mixing. In

Fig. 2 for the wing of the 4.3 μm band the values of the parameters D_a are depicted for the following mixtures CO_2–CO_2 ($C_{\text{emp}\,5} = 6.5906$, $D_{\text{emp}\,5} = 0.1847$, $C_{\text{emp}\,8} = 6.722$, $D_{\text{emp}\,8} = 0.011222$, $C_{\text{emp}\,16} = 5.0368$, $D_{\text{emp}\,16} = 0.00551$) and CO_2–N_2 ($C_{\text{emp}\,5} = 5.4848$, $D_{\text{emp}\,5} = 0.25$, $C_{\text{emp}\,14} = 4.8582$, $D_{\text{emp}\,14} = 0.0062$, $C_{\text{emp}\,10} = 5.8922$, $D_{\text{emp}\,10} = 0.0011$).

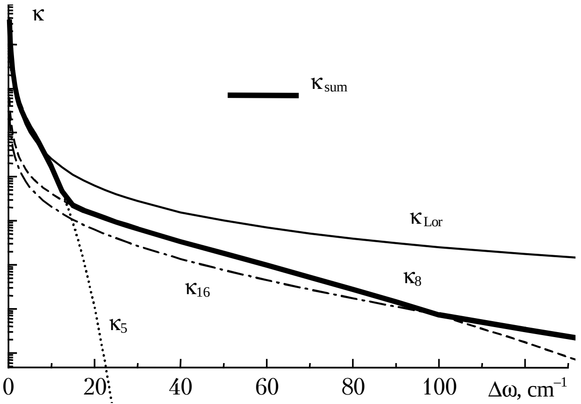

Fig. 1. The combined profile for the CO_2 band at 4.3 μm under self-broadening.

In estimating $D_{\text{calc}\,a}$, it should be kept in mind that r_s in Eq. (19) is measured in Å. Then $D_{\text{emp}\,a}$ is believed the same for all lines, and, because $D_{\text{emp}\,as}$ is connected with the halfwidth γ_s [see Eq. (19)], $D_{\text{emp}\,as}$ has the corresponding limits of variability. For CO_2–CO_2 we have $\gamma_s \sim 0.12$–0.06 and for CO_2–N_2 $\gamma_s \sim 0.1$–0.06 in the 4.3 μm band at normal temperature.

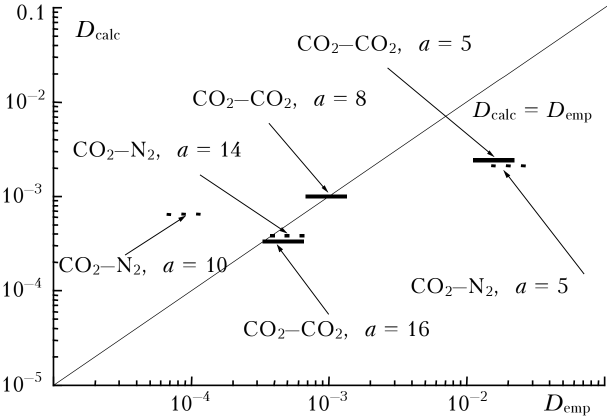

Fig. 2. Comparison of D_{calc}, Eq. (19), estimated in the absence of mixing and D_{emp} obtained experimentally for the wing of the CO_2 band at 4.3 μm.

The parameters D shown in Fig. 2 prove to be close to the diagonal $D_{\text{calc}} = D_{\text{emp}}$, which is indicative of an insignificant role of mixing in forming the line wings in the case under consideration. The constants corresponding to the near wing [$D_5(CO_2 - CO_2)$, $D_5(CO_2 - N_2)$] are somewhat farther from the diagonal $D_{\text{calc}} = D_{\text{emp}}$, which, in principle, may indicate that the role of mixing increases when closer to the line center. This also follows from the theoretical reasoning, since mixing is the effect that manifests itself at close-to-resonance frequencies.

Conclusions

The approximate consideration of the classical problem of motion of the centers of gravity allows separation of the function including the classical parameters as a factor in the general equation for the absorption coefficient. The rest part corresponding to the quantum problem of the interaction of two molecules includes the matrix elements of the Möller and dipole moment operators. They may be nondiagonal that corresponds to the presence of mixing of quantum states. In the absence of mixing, this part can be readily estimated.

In the theory of line wings, the quantum part of the equation for the absorption coefficient is assumed a parameter D_{emp}, which is determined from a comparison of the calculated and measured absorption coefficient values. The comparison of the estimated D_{calc} and the experimentally obtained D_{emp} parameters allows us to assess the role of mixing for particular molecules in certain spectral ranges. In the case of the CO_2 band at 4.3 μm, the estimated and measured parameters D turn out to be close, which is indicative of only insignificant role of the state mixing.

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