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SPECTROSCOPY OF AMBIENT MEDIUM

Collisional Self-Broadening Coefficients and Probabilities of Spontaneous Emission of the CO_2 10^00–00^01 Transition Lines

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Abstract—Using a tunable frequency-stabilized CO_2 laser, the pressure dependences of unsaturated absorption coefficients (AC) are measured in pure carbon dioxide in the pressure range from 5 to 30 Torr, where the spectral line shape is described by the Voigt profile. The absorption coefficients are measured in the centers of $R(8)$, $R(22)$, $R(34)$, $P(22)$, and $P(36)$ spectral lines of the 10^00–00^01 transition in the temperature range 300–700 K. By means of the least-squares method, the inverse problem is solved for the system of equations for AC at different pressures in the temperature range under study. The self-broadening coefficients $\gamma_{CO_2-CO_2}$ and the probabilities of spontaneous emission A_{ik} are derived. A new formula is proposed for $\gamma_{CO_2-CO_2}(T)$ dependence.

Keywords: carbon dioxide, absorption, self-broadening coefficient, spontaneous emission probability

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INTRODUCTION

Determination of carbon dioxide concentration in the atmosphere and in gaseous products of combustion of hydrocarbon fuels by optical methods, simulations of radiative transfer in the atmosphere, and diagnostics of active media of high-power CO_2 lasers, requires the knowledge of such CO_2 spectral line parameters as collisional self-broadening coefficients and probability of spontaneous emission [1–4]. The problem of the experimental determination of these parameters for the 10^00–00^01 transition lines is facilitated by the possibility of using methods that apply a tunable CO_2 laser as a probing radiation.

The purpose of this paper is to experimentally derive the self-broadening coefficients and probabilities of spontaneous emission for 10^00–00^01 transition CO_2 lines in the temperature range 300–700 K.

1. MEASUREMENT PROCEDURE

In the general case, the unsaturated absorption coefficient (AC) at the central frequency ν_0 of any 10^00–00^01 transition CO_2 line can be represented in the form [5]:

$$\alpha_{ki}(\nu_0) = N_C A_{ik} \frac{c^2}{8\pi\nu_0^2} \times g_i Q_V^{-1} Q_{Ri}^{-1} \left(e^{-\frac{E_k}{kT}} - e^{-\frac{E_i}{kT}} \right) F(0), \quad (1)$$

where the index k corresponds to the lower level 10^00 with the energy E_k; i corresponds to the upper level 00^01 with the energy E_i; N_C is the number density of CO_2 molecules; A_{ik} is the probability of spontaneous emission; Q_{Ri} and Q_V are the rotational and vibrational partition functions of the CO_2 molecule, respectively; g_i is the degeneracy of the level i; and $F(0)$ is the form factor at the center of an absorption line.

If the absorption lines of CO_2 molecules have a collisional-broadened profile with a width $\Delta\nu_L$, then the form factor at the center of such a line is given by the well-known expression

$$F_L(0) = \frac{2}{\pi\Delta\nu_L} = \frac{2}{\pi\gamma_{CO_2-CO_2}P_C}, \quad (2)$$

where $\gamma_{CO_2-CO_2}$ is the line width due to collision of CO_2 molecules with each other at the pressure $P_C = 1$ Torr or collisional self-broadening coefficient of a CO_2 spectral line.

Taking into account the relation $P_C = N_C kT$, it follows from Eq. (1) and (2) that in the case of collision-broadened profile of an absorption line, the value of AC α_L does not depend on the gas pressure P_C and at any fixed temperature is determined by the coefficient $\gamma_{CO_2-CO_2}$ and other spectroscopic parameters of the CO_2 molecule included in Eq. (1). Knowing these parameters and measuring the AC at a fixed temperature, we can determine $\gamma_{CO_2-CO_2}$. By measuring the AC at different temperatures, it is possible to derive the

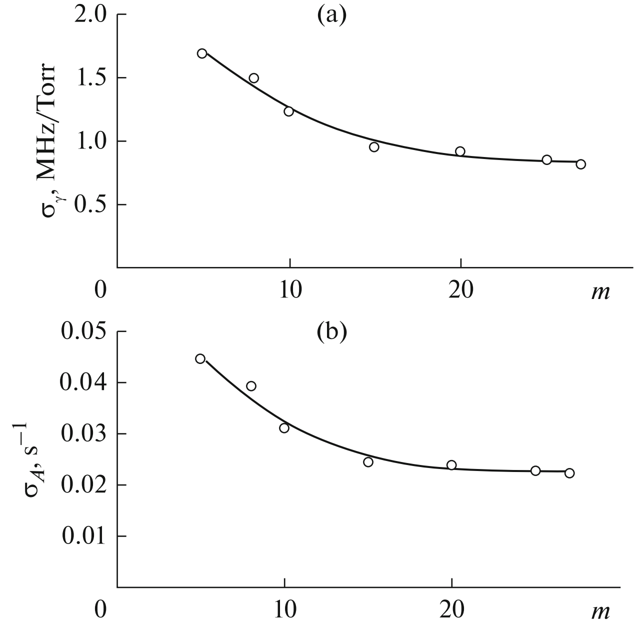

Fig. 1. Dependences of standard deviations of (a) collisional self-broadening coefficient σ_γ and (b) probability of spontaneous emission σ_A for $R(34)$ line of the $10^00{-}00^01$ transition in CO_2 molecule on the number m of equations for AC at a temperature of 300 K and the standard deviation of AC $\sigma_\alpha = 4 \times 10^{-5}$ cm^{-1}.

temperature dependence $\gamma_{CO_2-CO_2}(T)$, which is usually described in the form (see, for example, [1]):

$$\gamma_{CO_2-CO_2}(T) = \gamma_{CO_2-CO_2}(T_0)(T_0/T)^n, \qquad (3)$$

where $T_0 = 300$ K is the reference temperature and n is the exponent. The values of the spectroscopic parameters in Eq. (1), except for the probability of spontaneous emission A_{ik}, are known quite accurately. Therefore, to correctly determine the coefficient $\gamma_{CO_2-CO_2}$, it is necessary either to derive A_{ik} from independent measurements with sufficient accuracy or to apply a technique that does not use A_{ik}.

The Einstein coefficient A_{ik} can be determined if AC is measured in pure CO_2 at a fixed temperature and at a pressure which provides the Doppler shape of absorption ($P_C \leq 1$ Torr). However, at such pressures, the values of AC are small, and in order to perform measurements with the required accuracy, it is necessary to carry them out using a large optical path, which is quite difficult at temperatures other than room temperature.

In this paper, the collisional self-broadening coefficients $\gamma_{CO_2-CO_2}$ and the probabilities of spontaneous emission A_{ik} of the $10^00{-}00^01$ transition lines are determined from the ACs measured at the centers of absorption lines at pressures of carbon dioxide in the range 5–30 Torr. It is known that at such pressures, the line broadening is determined by the Doppler effect and molecular collisions, and the absorption line shapes are described by the Voigt profile. It is also known that molecular collisions lead not only to the broadening of the spectral lines, but also to their shift. According to [6], the shift coefficient of CO_2 spectral lines is much less than 2×10^{-4} cm^{-1} atm^{-1} or 8 kHz Torr^{-1}. Estimates show that under the experimental conditions of the present work, the shifts of the centers of absorption lines and probing radiation are on the same order of magnitude; their difference is much less than 0.1 MHz and, therefore, does not lead to noticeable errors in ACs measured at the centers of these lines.

The essence of the technique used is the following: a system of equations for AC of type (1) was written for each spectral line and a fixed temperature at different pressures from the range under study and the inverse problem of joint determination of $\gamma_{CO_2-CO_2}$ and A_{ik} was solved by the least-squares method. To solve this system of equations, the set of weighted squares of deviations (residuals) of the measured AC values $\hat{\alpha}$ from the calculated values $\alpha(A_{ik}; \gamma_{CO_2-CO_2})$ was minimized with respect to the sought parameters $\{A_{ik}, \gamma_{CO_2-CO_2}\}$. This technique is described in detail in [7].

2. RESULTS AND DISCUSSION

Figure 1 shows the standard deviations of unknown parameters σ_γ and σ_A calculated for the different number m of equations that describe the ACs measured at the different gas pressures and a fixed temperature.

It can be seen that the quasisolution of the fundamental system of equations under consideration depends on the number m of equations of type (1) that form the system, and the character of the change in uncertainty of parameters σ_γ and σ_A is the same: with m increasing, these parameters asymptotically approach their limiting minimum values. It was assumed in the calculations that the standard deviation of AC was $\sigma_\alpha = 4 \times 10^{-5}$ cm^{-1}; no less than 15 ACs were used.

Using the procedure described in section 1, the required $\gamma_{CO_2-CO_2}$ and A_{ik} coefficients were derived for $R(8)$, $R(22)$, $R(34)$, $P(22)$, and $P(36)$ spectral lines of the CO_2 $10^00{-}00^01$ transition.

Figure 2 shows an example of AC pressure dependences for the $R(34)$ line of the CO_2 $10^00{-}00^01$ transition, measured at different temperatures, which were used as inputs to find $\gamma_{CO_2-CO_2}$ and A_{ik} coefficients. For each experimental point, the standard deviation of AC σ_α did not exceed 10^{-4} cm^{-1}.

For the other lines, we obtained qualitatively similar dependences that differ quantitatively.

The $\gamma_{CO_2-CO_2}$ and A_{ik} values, derived from these data for $R(34)$ and $P(36)$ lines in the temperature

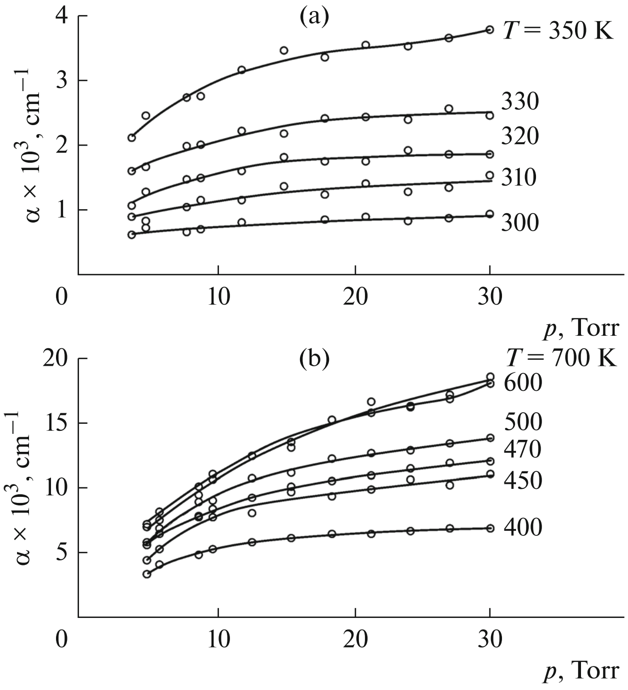

Fig. 2. Pressure dependences of AC in carbon dioxide for $R(34)$ line of the 10^00–00^01 transition at different temperatures.

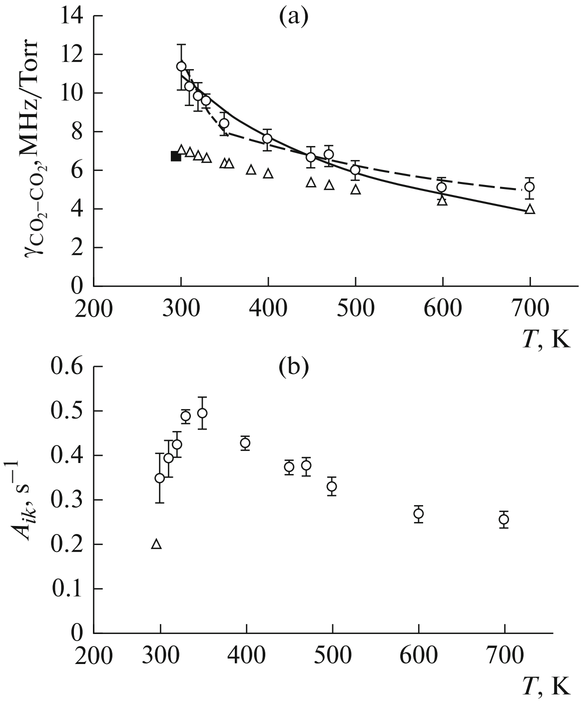

Fig. 3. (a) Collisional self-broadening coefficients $\gamma_{CO_2-CO_2}$ (○ – this work; ■ – [8]; Δ – [9]) and (b) probabilities of spontaneous emission A_{ik} (○ – this work; Δ – [8]) for $R(34)$ line of the 10^00–00^01 transition in CO_2 molecule at different temperatures.

range 300–700 K, are shown in Figs. 3 and 4, respectively.

It is clear from Figs. 3a and 4a that in the temperature range considered, the experimental data form $\gamma_{CO_2-CO_2}(T)$ dependences in which two regions (shown by dashed lines) with different slopes can be distinguished. From the analysis of experimental results using the least-squares method, it follows that $\gamma_{CO_2-CO_2}(T)$ temperature dependence is better approximated not by common Eq. (3) with one exponent n, in which the choice of the reference temperature T_0 = 300 K is not justified, but by a formula with two exponents n_1 and n_2 and the reference temperature T_C found experimentally and determined by the parameters of colliding molecules:

$$\gamma_{CO_2-CO_2}(T) = [\gamma_{CO_2-CO_2}(T_C)](T_C/T)^n, \qquad (4)$$

where

$$n = \begin{cases} n_1 & \text{at } T < T_C, \\ n_2 & \text{at } T > T_C. \end{cases}$$

Similar temperature dependences of the collisional self-broadening coefficient were obtained for the other spectral lines considered. Values of the parameters in analytical expressions of type (4) obtained for the lines studied in this work are given in the table 1.

Solid lines in Figs. 3 and 4 show approximations of the experimental self-broadening coefficients by functions of type (3). For the $P(36)$ line, we found $\gamma_{CO_2-CO_2}(T) = 9.6(300/T)^{1.1}$, and for the $R(34)$ line, $\gamma_{CO_2-CO_2}(T) = 11(300/T)^{1.2}$. As could be expected, the exponents obtained in Eq. (3) differ from those in Eq. (4) for the same lines.

Thus, it follows from the experimental results that the exponent in an equation of type (3) depends on the temperature range in question and the choice of the reference temperature in this range. This conclusion agrees qualitatively with the results of recent works [10, 11] where a strong dependence of the exponent on the chosen temperature range was also noted. To solve this

Table 1. Parameters of the temperature dependences of collisional self-broadening coefficients of the CO_2 10^00–00^01 transition lines

Line	n_1	n_2	$\gamma_{CO_2-CO_2}(T_C)$, MHz/Torr	T_C, K
$R(8)$	3.0	0.6	10.5	360
$R(22)$	1.6	1.1	8.7	355
$R(34)$	2.5	0.7	8.0	350
$P(22)$	1.5	0.9	8.0	360
$P(36)$	2.8	0.7	7.0	355

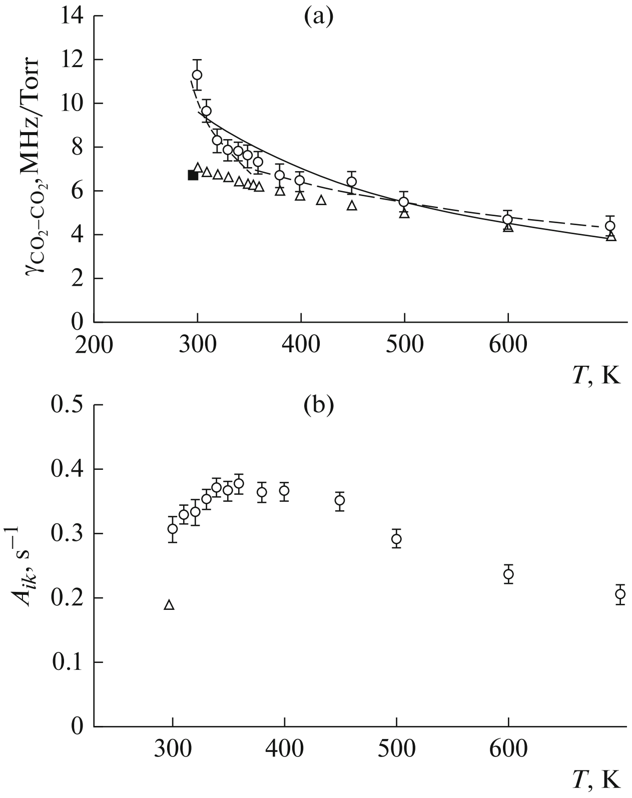

Fig. 4. (a) Collisional self-broadening coefficients $\gamma_{CO_2-CO_2}$ (○—this work; ■—[8]; Δ—[9]) and (b) probabilities of spontaneous emission A_{ik} (○—this work; Δ —[8]) for $P(36)$ line of the 10^00–00^01 transition in CO_2 molecule at different temperatures.

problem, it was proposed in the cited papers to consider several dependences of type (3) for temperature ranges corresponding, for example, to the atmospheres of different planets, and to choose its own reference temperature for each dependence. However, the authors of those works did not justify the choice of the reference temperature and do not explain the reasons for appearance of different exponents n in dependences of type (3).

The use of Eq. (4) in this work for describing $\gamma_{CO_2-CO_2}(T)$ dependence is based on the experimental results obtained for different lines of the 10^00–00^01 transition; it is consistent with common ideas about a change in the interaction of colliding CO_2 molecules with temperature in the range investigated (see, for example, [12]), and allows us to physically justify the choice of the reference temperature for Eq. (4). At high temperatures and high speeds of colliding molecules, short-range repulsive forces play the main role and $\gamma_{CO_2-CO_2}(T)$ temperature dependence has its own exponent. At low temperatures and lower molecular speeds, the nature of their interaction is different—the role of long-range multipole attraction forces increases. These forces can cause different orientation effects during collisions of CO_2 molecules, formation of clusters of these molecules, and appearance of induced dipole moments. This results in another exponent in the $\gamma_{CO_2-CO_2}(T)$ dependence at low temperatures. The reference temperature T_C in Eq. (4) separates two temperature intervals where different branches of the intermolecular interaction potential predominate.

The results of this work agree qualitatively with the results [13], where deviation of the temperature dependence of the relaxation rate constant of 00^01 CO_2 level from the Landau–Teller dependence, observed in the temperature range under consideration, is also explained by a change in the interaction mechanism of colliding molecules with temperature.

It should be noted that the temperature change in the interaction of colliding molecules was not taken into account in calculations of $\gamma_{CO_2-CO_2}(T)$ dependences for the CDSD-4000 base (see [9]). From Figs. 3a and 4a, where the experimental results of the present work are compared with the $\gamma_{CO_2-CO_2}$ values calculated in [9], it is clear that good agreement exists only in the temperature range 350–700 K, i.e., on one side from the obtained reference temperature $T_C = 350$ K. On the other side of this point, the difference between experimental and calculated $\gamma_{CO_2-CO_2}(T)$ dependences increases. This can be regarded as a confirmation of what was said above.

The reliability of the approximation of experimental data by model functions (3) and (4) was also estimated from the value of the determination coefficient R^2 [14]. It is considered that the model function is more suitable if its determination coefficient is closer to unity. The coefficients R^2 have the following values: 0.99986 for the line $P(36)$ and 0.99981 for the line $R(34)$ if we use Eq. (3), and 0.999985 for the line $P(36)$ and 0.99999 for the line $R(34)$ if we use Eq. (4). For all the lines studied, the determination coefficient R^2 was closer to unity when Eq. (4) was used. Even if we do not apply the R^2 estimate, it is clear from Figs. 3a and 4a that Eq. (4) better describes the experimental results than Eq. (3).

The data in Figs. 3b and 4b show that probability of spontaneous emission A_{ik}, which is considered to be a constant of optical transition, has different values at different temperatures. Similar results were obtained for all the lines considered. To explain this, additional research is required.

CONCLUSIONS

The paper presents the results of experimental studies of spontaneous emission probabilities A_{ik} and self-broadening coefficients $\gamma_{CO_2-CO_2}$ for $R(8)$, $R(22)$, $R(34)$, $P(22)$, and $P(36)$ vibrational-rotational lines of the 10^00–00^01 transition in CO_2 molecule in the temperature range 300–700 K. Using a frequency-stabilized CO_2-laser as a source of probing radiation, unsaturated absorption coefficients in carbon dioxide were measured at the central frequencies of the lines under study at pressures that correspond to the Voigt line profile. For each value of the gas temperature, the inverse problem is solved by the least-squares method from the system of equations for AC at different pressures; probabilities of spontaneous emission A_{ik} and self-broadening coefficients $\gamma_{CO_2-CO_2}$ are derived. Errors in the derived spectral parameters are estimated using the calculation formalism of covariance matrices; the diagonal elements of these matrices are variances of the required parameters. A new formula is proposed for describing $\gamma_{CO_2-CO_2}(T)$ dependence, which takes into account a change in the interaction of colliding CO_2 molecules with the gas temperature in the range under study. It was also found that probabilities of spontaneous emission of all lines considered have different values at different temperatures.

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