RESONANCE ABSORPTION OF 9.6-μm EMISSION BY CARBON DIOXIDE AT HIGH TEMPERATURES

R. I. Soloukhin and N. A. Fomin

The present interest in the resonance absorption coefficient of CO_2 at the frequency of the usually-employed laser transitions is due to 1) the direct effect of resonance self-absorption processes in the resonators on the output characteristics of CO_2 lasers, and 2) the possibility of using absorption processes for the diagnosis of gas flows. In addition, as a result of the physical correspondence between resonance amplification and absorption of laser emission, an analysis of the relations between the absorption index and various thermophysical parameters can be used to determine several quantities and to indicate the principles which must be understood for a description of the characteristics of laser devices based on CO_2 molecules. This applies, e.g., to determination of the Einstein coefficient of the transitions, as well as to cross sections for collisional line broadening and their dependence on temperature, partial pressure, and number of rotational sublevels.

In the 10.6-μm region ($10°0 \rightarrow 00°1$ transition) resonance absorption by carbon dioxide has been investigated fairly thoroughly [1-4], although not all the questions here can be regarded as conclusively settled. So far there have been no studies of absorption in the 9.6-μm region ($02°0 \rightarrow 00°1$ transition). At the same time, a knowledge of the absorption (or amplification) coefficients in two regions (9.6 and 10.6 μm) can be used in nonequilibrium conditions to determine two vibrational temperatures and the translational temperature if it is assumed that the bending and symmetric vibrations of the CO_2 molecule are in equilibrium and are characterized by a common temperature T_{12}, not equal to the temperature of the asymmetric vibration T_3 and the translational temperature T. If only the absorption (amplification) coefficients in the 10.6-μm region are available, the temperatures T_3 and T can be determined only by making the much greater assumption that T_{12} = T [5].

In this paper we present the necessary relations and make a numerical investigation of the dependences of the absorption coefficients in the 9.6-μm region on different thermophysical parameters. We devote particular attention to a description of absorption processes at high temperatures and pressures, where the effect of choice of the temperature dependence of the absorption-line collisional broadening cross section, and also the contribution of "hot" transitions to absorption, become particularly appreciable.

Basic Relations. To calculate the absorption we need the Einstein coefficients, the shape of the absorption line, and the position of the centers of the considered transition lines.

Until recently, the uncertainty in determination of the positions of the centers of the various CO_2 molecule transition lines was considerable; e.g., according to the data of [6, 7] it was about 10^{-1}-10^{-2} cm^{-1}. At the same time, for calculation of the contribution of particular transitions to the absorption coefficient an error in determination of the transition line center of even 10^{-3} cm^{-1} leads to an error of about 4%. (This estimate is obtained for a pressure of 1 atm and temperature 3000°K. With increase in pressure or reduction in temperature the error decreases.) Recently, however, the positions of the line centers for several transitions have been measured with sufficient accuracy. For instance, in [8] the positions of the lines are determined to an accuracy of 10^{-3} cm^{-1} and the rotational constants for seven CO_2 molecule transitions in the 9.6-μm region are determined more accurately. Generally speaking, a significant contribution to the value of the absorption coefficient in the 9.6-μm region at high temperatures can be made by the large number of high-lying transitions of the type $[n, m^l, p] \rightarrow [n, (m-2)^l, p+1]$. It is easy to show that the difference in populations for such transitions constitutes, e.g., 10% or more of the difference in populations for the main transition ($02°0 \rightarrow 00°1$) when we have the inequality

$$n\Theta_1 + (m-2)\Theta_2 + p\Theta_3 \leqslant 2.3T,$$

where Θ_1, Θ_2, and Θ_3 are the characteristic temperatures of the symmetric, bending, and asymmetric quanta of the molecules. An estimate shows that there is one such transition at T = 1000°K, nine at 2000°K, and 29 at 3000°K.

At moderate pressures (p $\leqslant$ 10 atm) the effect of "hot" transitions will be considerably less owing to the inexact coincidence of the transition line centers. In addition, there are no reliable data on the high-lying transitions and, hence, in this study we considered only seven of the transitions investigated in [8]. The constants obtained in [8] (see Table 1) enable us to determine the position of the line centers of the upper and lower levels of the selected transitions from the formula

$$G(n, m^l, p, J) = G_0(n, m^l,$$
$$p) + B(n, m^l, p)[J(J+1) - l^2] - D(n, m^l, p)[J(J+1) + l^2]^2 + H(n,$$
$$m^l, p)[J(J+1) - l^2]^3. \tag{1}$$

TABLE 1

Transition	Symmetry type	J'	E', cm⁻¹	B', cm⁻¹	$D'\cdot 10^7$, cm⁻¹	$H'\cdot 10^{14}$, cm⁻¹	E'', cm⁻¹	B'', cm⁻¹	$D''\cdot 10^7$, cm⁻¹	$H''\cdot 10^{14}$, cm⁻¹	$\left[\dfrac{R}{R_{10^00\to00^01}}\right]^2$
$02^00\to00^01$	$\Sigma_g^+\to\Sigma_u^+$	even	1285,412	0,390482	1,572	2,33	2349,147	0,387141	1,330	1,72	0,91
$02^01\to00^02$	$\Sigma_u^+\to\Sigma_g^+$	odd	3612,847	0,387502	1,563		4673,332	0,384066	1,326		1,81
$02^02\to00^03$	$\Sigma_g^+\to\Sigma_u^+$	even	5915,220	0,384526	1,542		6972,585	0,380995	1,329		2,68
$02^03\to00^04$	$\Sigma_u^+\to\Sigma_g^+$	odd	8192,557	0,381577	1,783		9246,943	0,377925	1,329		3,47
$04^00\to02^01$	$\Sigma_g^+\to\Sigma_u^+$	even	2548,373	0,391107	1,782		3612,847	0,387502	1,563		0,91
$03^10\to01^11$	$\Pi_g\to\Pi_{u,\,c-c}$	odd	1932,473	0,390752	1,498		667,381	0,390648	1,367		0,91
$03^10\to01^11$	$\Pi_g\to\Pi_{u,\,d-d}$	even	1932,473	0,391701	1,580		667,381	0,391267	1,387		0,91

The splitting of the levels of the $\Pi-\Pi$ transition due to Λ doubling

$$W = \frac{1}{2}\,[q_v + \mu_v J\,(J+1)]\,J\,(J+1)$$

is taken into account in the effective rotational constants

$$B = B_0 \pm (1/2)q_v,\quad D = D_0 \pm (1/2)\mu_v$$

given in Table 1.

Using relation (1) we obtain for the transition frequencies

$$E = G''(J-1) - G'(J)$$

for the P branch and

$$E = G''(J+1) - G'\,(J)$$

for the R branch. Here the superscripts " and ' refer to the upper and lower transition levels, respectively.

The shape of the absorption line was assumed to be Voigtian and was calculated numerically. The Doppler width of the profile was calculated from standard relations (see [9]). For the collision half-width we used the following relations:

$$\Delta v_c = \left(0.1254 - 0.98\cdot 10^{-3}J\right)\left(\frac{300}{T}\right)^n p\left(\xi_{CO_2} + 0.73\xi_{N_2} + 0.64\xi_{He} + 0.57\xi_{Ar}\right)$$

for the P branch and

$$\Delta v_c = \left(0.1301 - 1.13\cdot 10^{-3}J\right)\left(\frac{300}{T}\right)^n p\left(\xi_{CO_2} + 0.73\xi_{N_2} + 0.64\xi_{He} + 0.57\xi_{Ar}\right)$$

for the R branch (p, atm, Δv_c, cm⁻¹).

The dependence on the number of the rotational sublevel in these relations was obtained from an analysis of the data of [10, 11], in which the width of the absorption (emission) profile in different spectral intervals was investigated. The dependence on the partial pressures was selected in accordance with the recommendations in [10, 12]. The temperature dependence of the broadening cross section for the CO_2 molecule has been investigated in [2-4, 10, 13]. From the data of these papers the temperature dependence parameter n in the relations for the half-widths takes values from 0.5 to 1.5. The main series of calculations in this study was made with n = 1. Figure 1 illustrates the effect of n on the absorption coefficient.

The transition Einstein coefficients are expressed in terms of the square of the matrix element of the transition dipole moment

$$A_{21} = \frac{64\pi^4}{3h\lambda^3}\,\frac{S_{J'J''}}{g'},$$

where $S_{J'J''} = |R_{J'J''}|^2 S_J F_J$. Here $|R_{J'J''}|$ is independent of the rotational sublevel and characterizes the vibrational part of the transition dipole moment; S_J is the Hanley–London factor, which characterizes the rotational component of the dipole moment. For transitions of the $\Sigma\to\Sigma$ type for the P branch, and $S_J = J$ and $S_J = J+1$ for the R branch, F_J characterizes the interaction of vibrations and rotations in the molecule. If J is not too high, $F_J = 1$ to an accuracy of 5%. The squares of the transition matrix elements were calculated at our request by I. F. Golovnev by the method of [14] and are given in Table 1. Experiments (the apparatus and the method of measurement are described in [3]) showed that the value of the Einstein coefficient for the P20 line of the $02^00\to00^01$ transition was close to the calculated value given in Table 1.

The populations of the vibrational–rotational levels and the absorption coefficients for individual transitions were calculated from standard relations (see [9]).
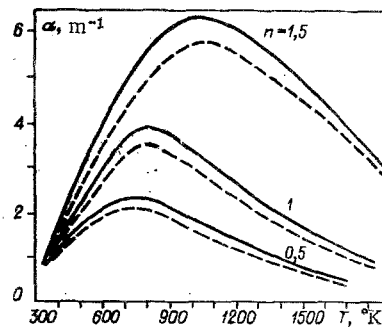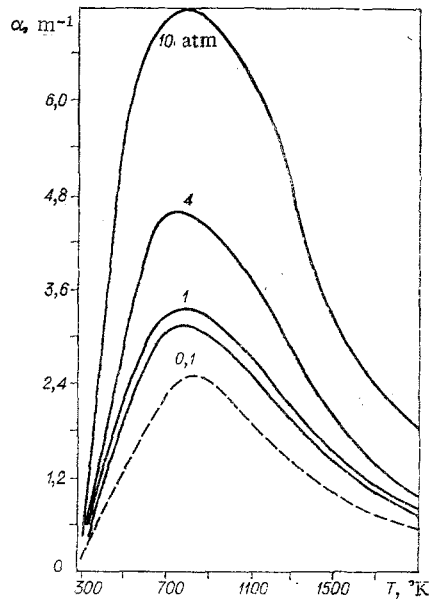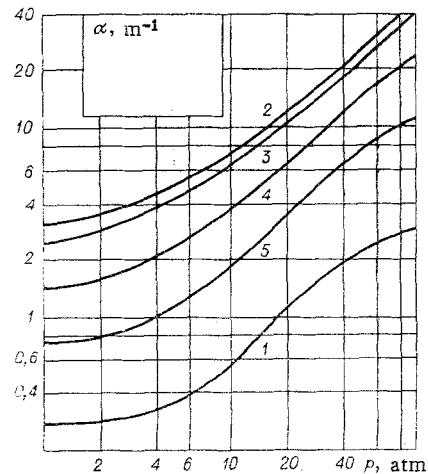
Fig. 1

Fig. 2

Fig. 3

Discussion of Results of Calculations. The calculated dependences of the absorption coefficient of the $02^\circ 0 \to 00^\circ 1$ transition (wavelength 9.6 μm) on the main parameters are shown in Figs. 1-5. Figure 1 illustrates the effect of the temperature dependence parameter n on the absorption coefficient and also gives data for the P18 line (dashed lines) and the P20 line (continuous lines) of the $02^\circ 0 \to 00^\circ 1$ transition. The pressure was 2 atm (here and henceforth the calculations are made for pure carbon dioxide). It is apparent that the errors associated with selection of the value of n become appreciable at $T \gtrsim 400^\circ$K and reach 100% at 600°K. Figure 2 compares the temperature dependences of the absorption coefficient of the P20 line of the $02^\circ 0 \to 00^\circ 1$ transition (wavelength 9.55 μm) for different pressures (figures on the curves). The value for n in these and subsequent calculations was 1. Figure 2 also shows the temperature dependence of the absorption coefficient of the P20 line of the $10^\circ 0 \to 00^\circ 1$ transition (wavelength 10.59 μm) for a pressure of 1 atm (dashed line). The higher values of the absorption coefficient on the $02^\circ 0 \to 00^\circ 1$ transition are due both to the lower position of the transition levels and to the large contribution of "hot" transitions to the value of the absorption coefficient owing to better coincidence of the lines. The difference in the absorption coefficients in the regions 10.6 and 9.6 μm will be particularly great in nonequilibrium conditions at low translational temperature of the gas [15].

The rate of growth of the absorption coefficient with pressure is different for different temperature regions: At low gas temperatures ($T \sim 300^\circ$K) it is due mainly to overlap of the rotational sublevels of the main transition and does not differ significantly for the $(10^\circ 0 \to 00^\circ 1)$ and $(02^\circ 0 \to 00^\circ 1)$ transitions. We note that the rate of growth of α for the R branch is always appreciably higher than for the P branch, owing to the smaller distance between the individual rotational sublevels.

At higher temperatures the half-width of the absorption line [$\Delta\nu_c \sim (1/T)^n$] is reduced and the effects of overlap of the rotational sublevels of the main transition become weaker. At the same time, with increase in T the populations of the "hot" transitions increase, which leads to an increase in the absorption coefficient due to overlap with individual lines of the "hot" transitions.

Hence, at $T \sim 1000^\circ$K and moderate pressures the rate of increase in α with pressure is maximal. The subsequent reduction of the growth rate of the absorption coefficient with pressure at higher temperatures is due to the further reduction of the collisional half-width with temperature increase.
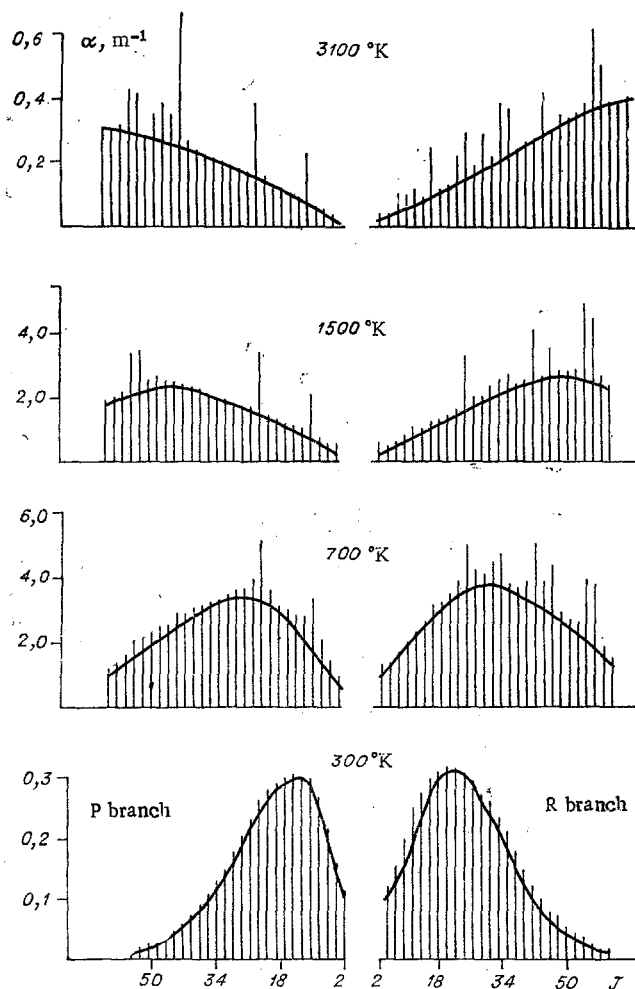
Fig. 4

The above effects are illustrated also by the data of Fig. 3, where the pressure dependence of the absorption coefficient of the P20 line of the $02^\circ 0 \to 00^\circ 1$ transition is shown in a wide range: from 1 to 100 atm. Curves 1-5 correspond to gas temperatures of 300, 700, 1100, 1500, and 1900°K. The spectral distributions of the absorption coefficient at different temperatures and pressures, shown in Figs. 4 and 5, are of interest.

The data of Fig. 4 correspond to a pressure of 2 atm, and those in Fig. 5 to a temperature of 700°K (the continuous curves correspond to a Boltzmann distribution over the rotational sublevels with the effects of overlap and the contribution of "hot" transitions ignored). An analysis of these results shows that at low pressures (p $\lesssim$ 0.1 atm) the distribution of the absorption coefficient over the rotational sublevels is of the Boltzmann type. This provides opportunities for the diagnosis of gas flows (determination of the rotational and, hence, translational temperatures) at low pressures (e.g., the nonequilibrium flows in gas dynamic lasers [5]). With increase in pressure to atmospheric and a little higher the situation becomes more complicated. We consider the data of Fig. 4, which represent the distribution of α over the rotational sublevels for different gas temperatures and a pressure of 2 atm. It is apparent that at T = 300°K the real distribution differs insignificantly from the Boltzmann type and, hence, in this case also CO_2-containing gas flows can be diagnosed by the technique proposed in [5]. At higher temperatures there is a great increase in absorption coefficient only on the lines which have resonance coincidences with the "hot"-transition lines. With further increase in temperature (see Fig. 4) all the higher-lying transitions are excited and in the absorption spectrum there appear new "spikes" corresponding to resonances with "hotter" transitions. Nevertheless, even in this situation, which is least favorable for diagnosis, the distribution in the P22-P36 lines is nearly Boltzmann, which allows determination of the parameters of a gas flow by a modification of the technique in [5].

Finally, with increase in the pressure above 10 atm (see Fig. 5) the spectral distributions begin again to follow the Boltzmann law, but to determine the absolute value of the absorption coefficient in this case we have to take into account overlap effects, which greatly increase the value of α. It may be noted that when p $\gtrsim$ 10 atm the distance between the rotational lines is much less than their width and, hence, probing with an ordinary radiation source will not distinguish the absorption lines. A tunable CO_2 low-pressure laser can be used in this case to detect absorption at resonance frequencies corresponding to the rotational sublevels of the main transition.
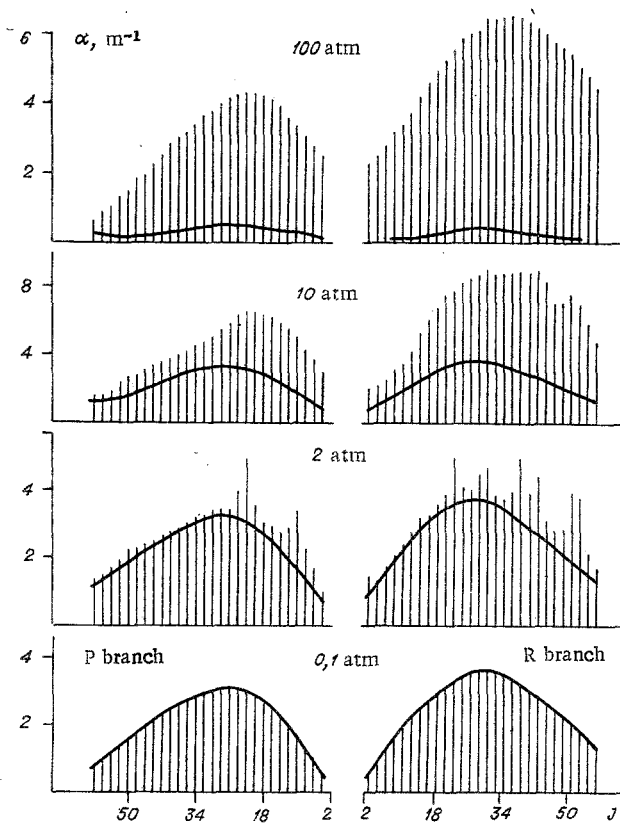
Fig. 5

We express our thanks to I. F. Golovnev for providing the results of calculations of the matrix elements of the "hot" transition dipole moments, and also to V. V. Churakov, Yu. A. Yakobi, and A. A. Vedeneev for useful discussions.

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