6. A. E. Sheindlin (ed.), Radiative Properties of Solid Materials (Handbook) [in Russian], Énergiya, Moscow (1974).
7. Yu. I. Prokhorov and V. I. Ivanov, "Emission spectra of infrared incandescent tubes," Elektrotermiya, No. 112-113, 24-26 (1971).

NUMERICAL STUDY OF SPECTRAL INTENSITY OF EMISSION AND ABSORPTION OF THE CO_2 AND CO MOLECULES UNDER VIBRATIONALLY NONEQUILIBRIUM CONDITIONS

N. N. Kudryavtsev and S. S. Novikov

UDC 631.375

Numerical calculations are performed of the spectral intensity of emission and absorption of the 4.3- and 2.7-μm bands of CO_2 and of the 4.7-μm band of CO under conditions of nonequilibrium excitation of the vibrational degrees of freedom.

The development of spectroscopic methods of studying vibrationally nonequilibrium molecular media requires a detailed study of transport processes of IR radiation in the absence of equilibrium between vibrational and translational—rotational degrees of freedom. In the present paper we provide a numerical study of the effect of the parameters of a vibrationally nonequilibrium gas on the spectral intensity of emission and absorption of CO_2 in the 4.3- and 2.7-μm bands of CO_2 and the 4.7-μm band of CO. Several results of studying the effect of parameters of a vibrationally nonequilibrium gas on the integral characteristics of emission and absorption of these bands are presented in [1].

The calculation of spectral characteristics of emission and absorption was performed in a wide region of variation of the dominating parameters: pressure, translational and vibrational temperatures, including the conditions in regions of CO_2-laser resonator, vibrationally nonequilibrium supersonic flows containing CO_2 and CO, etc. The populations of the lowest 5-10 levels of each mode, the transitions between which basically determine radiation transport of a vibrationally nonequilibrium gas under the conditions considered, can be described by a Boltzmann distribution with a corresponding vibrational temperature [2].

The distribution of CO_2 molecules over vibrational levels was described by two temperatures. The vibrational temperature T_3 characterizes the distribution of molecules within an asymmetric mode, where T_2 is the collective (symmetric and deformational) mode. The possibility of introducing a single temperature for the symmetric and deformational types of vibration is related to the strong interaction of these modes due to Fermi resonance. The vibrational distribution of CO molecules was characterized by the temperature T_5. The temperature of the rotational degrees of freedom of the CO and CO_2 was assumed equal to the translational one [2]. In the present paper we use the enumeration system of physical quantities for CO_2-lasers according to which the subscripts 2, 3 refer, respectively, to combined and asymmetric modes of CO_2, and 4 and 5 — to nitrogen and carbon monoxide [2].

The dependence of the emission intensity I_ω on the wave number at gas pressure $P = 10^{-3}$-10^{-1} atm, characteristic for a number of vibrationally nonequilibrium systems, changes strongly within narrow spectral regions, corresponding to a width of separate rotational lines and consisting of 10^{-2}-10^{-4} cm^{-1}. The use of methods of the theory of vibrational—rotational bands [3] makes it possible to determine values of spectral intensities of emission $\tilde{I}_\omega$ and absorption $\tilde{A}_\omega$ averaged over the rotational structure. The averaging range is chosen to be $\Delta\omega' = 2$-10 cm^{-1}, corresponding to a nonsignificant variation of the values $\tilde{I}_\omega$ and $\tilde{A}_\omega$, not exceeding 5-10% [3].

For the pressure values considered $P \leqslant 0.1$ atm the width of rotational lines γ in CO_2 and CO bands is smaller by 1-3 orders of magnitude than the separation between neighboring lines d [4]. Under these conditions the use of an isolated line model for calculating

---

Moscow Physicotechnical Institute. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 42, No. 5, pp. 805-813, May, 1982. Original article submitted March 26, 1981.

intensities of gas emission is justified. The determination of emission intensities by averaging over rotational structure according to this model is performed by summing the contributions to emission over the vibrational transitions forming the band [3]:

$$\tilde{I}_\omega = \sum_{v_r, v_p} \tilde{A}_\omega (v_r, v_p) B_\omega (v_r, v_p), \tag{1}$$

where $\tilde{A}_\omega(v_r, v_p)$ is the absorption of the isolated vibrational transition $(v_r, v_p \rightarrow v_r', v_p)$, $B_\omega(v_r, v_p) = 2hc^2\omega^3[g_{v'J'}N_{vJ}/g_{vJ}N_{v'J'} - 1]^{-1}$, v_r and v_p are sets of vibrational quantum numbers, respectively, of active (changing the number of quanta during transition) and passive (not changing the number of quanta) modes, and g is the level degeneracy. The vibrational and rotational quantum numbers belonging to the upper level of the transition are denoted by a prime.

Performing in (1) the average over the rotational structure, the absorption of an isolated vibrational transition $\tilde{A}_\omega(v_r, v_p)$ is, according to the isolated line model [3]:

$$\tilde{A}_\omega (v_r, v_p) = W_\omega (v_r, v_p)/d_\omega (v_r, v_p), \tag{2}$$

where $W_\omega = \int\limits_{-\infty}^{\infty} \{1 - \exp[-K_{vJ\rightarrow v'J'}(\omega) X]\} d\omega$ is the equivalent rotational line width for a line located in the wave number region $\left[\omega + \frac{d_\omega}{2}, \quad \omega - \frac{d_\omega}{2}\right]$, and $K_{vJ\rightarrow v'J'}(\omega)$ is the corresponding absorption coefficient.

The calculation of spectral band absorption was performed by the statistical model, according to which [3]

$$\tilde{A}_\omega = 1 - \exp\left[-\sum_{v_r, v_p} \frac{W_\omega (v_r, v_p)}{d_\omega (v_r, v_p)}\right], \tag{3}$$

and by the isolated line model

$$\tilde{A}_\omega = \sum_{v_r, v_p} \tilde{A}_\omega (v_r, v_p), \tag{4}$$

where $\tilde{A}_\omega(v_r, v_p)$ was determined by Eq. (2).

The results of calculating the spectral absorption of the 4.7- and 2.7-μm bands according to relations (3) and (4) practically coincide, since the gas absorption is small. For the central part of the 4.3-μm band the calculation according to isolated line model gives a value of $\tilde{A}_\omega$ 5-10% higher than that obtained with the statistical model. Consequently, approximately the same quantity provides an error in the determination of the emission intensity of the 4.3-μm band in using the isolated line model. Taking into account the relation obtained above between the width of rotational line and the separation between them $\gamma/d \lesssim 0.1$, one can conclude that due to reabsorption in the central portions of the rotational lines a significant part of the emission of the 4.3-μm band is due to their peripheral portions $|\omega - \rho_{vJ\rightarrow v'J'}| \gtrsim 5\text{-}10\gamma$.

Under the conditions considered the broadening of rotational lines is determined by the collision and Doppler mechanisms, and the line shape is described by the Voigt curve. The equivalent line width with a Voigt contour was calculated by an approximate method [5]. The starting parameters for this calculation are the integral absorption of a rotational line $S_{vJ\rightarrow v'J'} = \int\limits_{-\infty}^{\infty} K_{vJ\rightarrow v'J'}(\omega) d\omega$, and the Doppler γ_D and collision γ_L halfwidths.

The determination of collision broadening causes several difficulties, related to the lack of sufficient experimental data on the dependence of line widths on the rotational quantum number for various gas temperatures. Therefore, following [1], we used the mean values of halfwidths of rotational lines of the bands considered, recommended in [6]. Molecular nitrogen is assumed to be the main broadening component of the mixture. The calculations performed by using the minimum and maximum values of the halfwidths of the rotational lines of the band show that the error of the approximation made does not exceed 5-8% for characteristic conditions of the present work.

A method of calculating the integral absorption of rotational lines $S_{vJ\rightarrow v'J'}$ under vibrationally nonequilibrium conditions was described in [7-10]. The calculation is performed

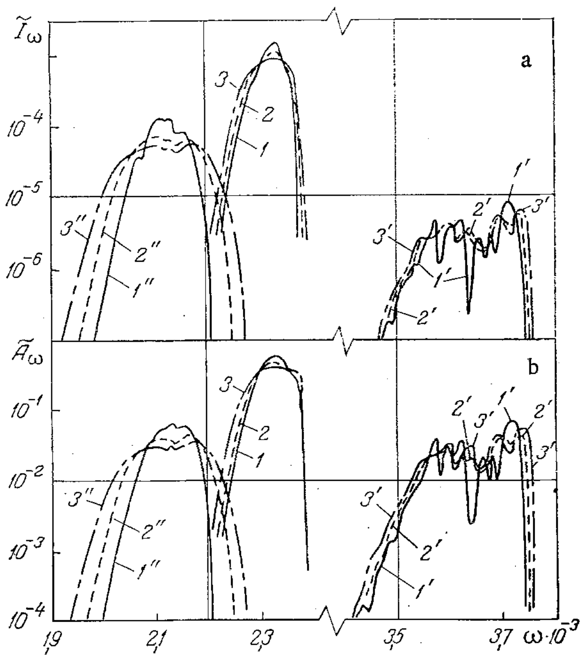

Fig. 1. Quantities $\tilde{I}_\omega$ (a) and $\tilde{A}_\omega$ (b) of the 4.3- and 2.7-μm CO_2 bands and the 4.7-μm CO band as a function of the gas translational temperature; $P = 5 \cdot 10^{-2}$ atm, T_3 or T_5 = 1500°K, T_2 = 500°K: 1, 1', 1'') T = 100°K; 2–2'') 300°K; 3–3'') 500°K. $\omega \cdot 10^{-3}$ cm^{-1}.

on the basis of integral absorptions of the corresponding vibrational—rotational bands, measured under the normal conditions P_0 = 1.0 atm, T_0 = 300°K, and the theoretical dependences of the squares of matrix elements of emission transitions on vibrational and rotational quantum numbers. The necessary parameter values for this calculation of integral absorption of rotational lines of the 4.3- and 2.7-μm bands of CO_2 and the 4.7-μm band of CO are given in [1].

In the present work we consider the "parallel" bands of CO_2 — 4.3 and 2.7 μm, forming vibrational transitions with changing quantum numbers $\Delta v_3 = 1$ (4.3 μm) and $\Delta v_1 = \Delta v_3 = 1$ or $\Delta v_2 = 2$, $\Delta v_3 = 1$ (2.7 μm). The projection of the rotational momentum of the CO_2 molecule, related to vibrational motion, on its axis does not change in this case. The asymmetric mode is active in the 4.3-μm band, and all types of vibration of carbon dioxide gas molecules are active in the 2.7-μm band.

The emission intensity $\tilde{I}_\omega$ and the absorption $\tilde{A}_\omega$ of a vibrationally nonequilibrium gas also depend, as under thermodynamic equilibrium conditions, on the optical path length $X = P_iD$, the pressure P, the temperature T, as well as on the vibrational temperatures of active and passive modes. By P_i we denote the partial pressure of the emitting gas, and by D the geometric width of the gas layer.

The calculations in the present work were performed for an optical path length X = 0.1 atm·cm (T = 300°K), being in the characteristic range for molecular lasers. The results of calculating the quantities $\tilde{A}_\omega$ and $\tilde{I}_\omega$ for varying translational temperature, pressure, vibrational temperature of CO or the asymmetric mode of CO_2 and the vibrational temperature of the collective mode of carbon dioxide gas are given in Figs. 1-4. In varying one parameter the values of the remaining ones were taken as characteristic values for molecular lasers. The digits without primes in Figs. 1-4 correspond to the 4.3-μm band, those with one prime — to the 2.7-μm band, and those with two primes — to the 4.7-μm band. The emission intensity values $\tilde{I}_\omega$ are given in W/sr·cm.

The gas temperature determines the Doppler broadening of spectral lines and, according to the assumption made of thermodynamic equilibrium of rotational and translational degrees of freedom, the population of rotational levels. The rotational distribution has a substantial effect on the quantities $\tilde{I}_\omega$ and $\tilde{A}_\omega$ due to the variation of populations of combined

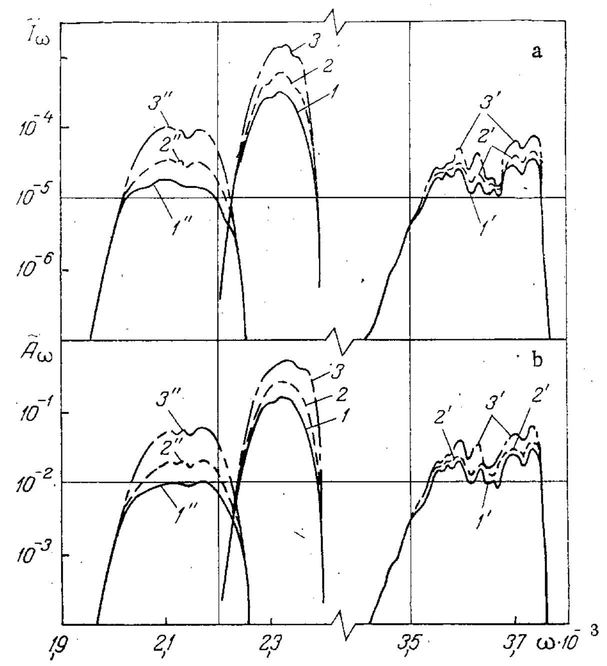

Fig. 2. The quantities $\tilde{I}_\omega$ (a) and $\tilde{A}_\omega$ (b) of the 4.3- and 2.7-μm CO_2 bands and the 4.7-μm CO band as a function of total gas pressure; T = 300°K, T_3 or T_5 = 1500°K, T_2 = 500°K: 1-1") P = 10^{-3} atm; 2-2") 10^{-2} atm; 3-3") 0.1 atm. The intensity values given of the 2.7-μm band are enhanced by 10 times.

vibrational—rotational states and, consequently, on the functions $B_\omega(v_r, v_p)$ and the equivalent widths $W_\omega(v_r, v_p)$ appearing in relations (1)-(4).

The results of calculating the spectral emission intensity $\tilde{I}_\omega$ and absorption $\tilde{A}_\omega$ of the bands considered are given in Fig. 1 for various gas temperatures. The curves presented were obtained for identical amounts of the emitting molecules, i.e., for a constant value of the mass optical path length $X_\rho = \rho_i D$, corresponding to the value $X_0 = 0.1$ atm·cm at T_0 = 300°K (ρ_i is the density of emitting molecules). For other temperatures, therefore, the calculation was performed for optical path length $X = X_0 \cdot T/T_0$.

It follows from the data of Fig. 1 that for identical gas parameters the magnitude of the spectral emission intensity $\tilde{I}_\omega$ in the 4.3-μm band is larger by orders of magnitude than for the 4.7-μm band, and exceeds by two orders of magnitude the emission intensity in the 2.7-μm band. The spectral absorption $\tilde{A}_\omega$ in the 4.3-μm band is higher by orders of magnitude than in the 4.7-μm band, and ≈20 times larger than in the 2.7-μm band. The absorption of the 4.7- and 2.7-μm bands is characterized by the low values $\tilde{A}_\omega \lesssim 0.05$.

The enhancement in the translational temperature leads to an approximately symmetric broadening of the 4.3- and 4.7-μm bands. At the same time, there is a lowering of emission intensities in their central portions. These features are determined by an increased population of high levels and a decreased population of low rotational levels at enhanced translational and, consequently, rotational temperatures.

For the 2.7-μm band one notes a smoothing of the frequency dependence of the quantities $\tilde{A}_\omega$ and $\tilde{I}_\omega$ with increasing temperature T. In the region of low gas temperatures T = 100°K the 2.7-μm band separates into two subbands, corresponding to different types of vibrational transitions: the long-wave part $\omega < 3640$ cm^{-1} — $\Delta v_2 = 2$, $\Delta v_3 = 1$, and the shortwave one $\omega >$ 3640 cm^{-1} — $\Delta v_1 = \Delta v_3 = 1$. On the whole, the dependences of the spectral emission and absorption intensities on the translational temperature are similar for the bands considered.

The spectral emission intensity $\tilde{I}_\omega$ and absorption $\tilde{A}_\omega$ of the bands considered for gas pressure varying within 10^{-3}-0.1 atm are given in Fig. 2. We note that the gas pressure determines the collision broadening of rotational lines. There exist three cases in which the quantities $\tilde{I}_\omega$ and $\tilde{A}_\omega$ are independent of the gas pressure [3]: a) weak reabsorption of radiation, when for all rotational lines of the band $K_{vJ \to v'J'}(\omega)\, X \ll 1$; b) emission of an optically

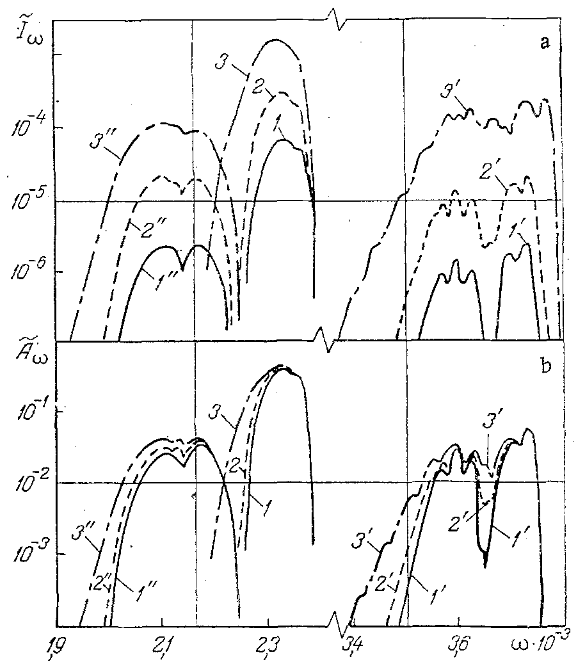

Fig. 3. The quantities $\tilde{I}_\omega$ (a) and $\tilde{A}_\omega$ (b) of the 4.3- and 2.7-μm CO_2 bands or the 4.7-μm CO band as a function of the vibrational temperature of the asymmetric mode T_3 or vibrational temperature T_5; $P = 5 \cdot 10^{-2}$ atm, T = 300°K, T_2 = 500°K: 1-1") T_3, T_5 = 600°K; 2-2") 1000°K; 3-3") 1800°K. The intensity of emission of the 2.7-μm band is enhanced by 10 times.

dense gas layer $\tilde{A}_\omega \to 1$; and c) significant predominance of the Doppler broadening mechanism of the gas over the collisional one.

The calculation performed shows that for $P \leqslant 10^{-3}$ atm the quantities $\tilde{I}_\omega$ and $\tilde{A}_\omega$ are practically independent of pressure. This case corresponds to a value of Doppler broadening mechanism predominating over the collision mechanism by significantly more than two orders of magnitude.

For $10^{-2} \leqslant P \leqslant 0.1$ atm the quantities γ_L and γ_D are approximately of the same order of magnitude. Since in this case $\tilde{A}_\omega \ll 1$, it can be concluded that the weak pressure dependence of the emission and absorption of the 2.7-μm band averaged over the rotational structure and of the peripheral parts of the 4.3- and 4.7-μm bands at $P = 10^{-2}$-0.1 atm corresponds to the limiting case of weak lines. For the central parts of the 4.3- and 4.7-μm bands, respectively, 2250-2350 cm^{-1} and 2050-2220 cm^{-1}, an increase in pressure by two orders of magnitude from 10^{-3} to 0.1 atm leads to an enhancement of the spectral emission intensity $\tilde{I}_\omega$ by approximately an order of magnitude. Thus, for characteristic pressures in molecular lasers $P = 10^{-3}$-10^{-1} atm the effect of pressure on the emission intensity of the central parts of the 4.3- and 4.7-μm bands is significant.

The spectral intensity of emission $\tilde{I}_\omega$ and absorption $\tilde{A}_\omega$ of the bands considered are shown in Fig. 3 for various vibrational temperatures of the active modes: the asymmetric T_2 for the 4.3- and 2.7-μm bands of CO_2 and T_5 for the 4.7-μm band of CO. The effect on the emission intensity $\tilde{I}_\omega$ of vibrational temperatures of active modes is determined by the dependence of the function $B_\omega(v_r, v_p)$ and of the equivalent widths $W_\omega(v_r, v_p)$ of rotational lines of separate vibrational transitions on the population of vibrational levels of molecules. The effect of vibrational temperatures of active modes on absorption is restricted by the dependence of equivalent widths $W_\omega(v_r, v_p)$ on the vibrational distribution in the modes.

The data of Fig. 3a show a strong dependence of the spectral emission intensity $\tilde{I}_\omega$ on the vibrational temperatures of active modes. The strongest dependence is observed in the region of decreasing values of T_3, T_5 = 600-1500°K. For T_3, T_5 values increasing from 600 to 1500°K the emission intensity of the 4.3-μm band increases by more than 50 times, and that of the

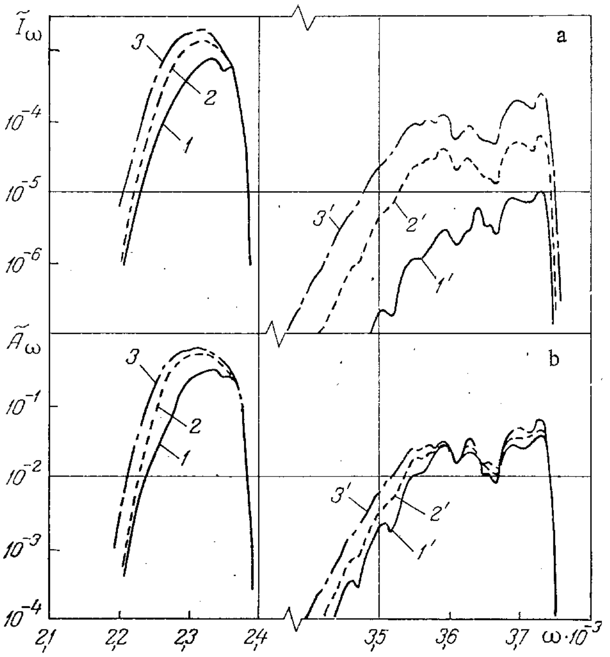

Fig. 4. The quantities $\tilde{I}_\omega$ (a) and $\tilde{A}_\omega$ (b) of the 4.3- and 2.7-μm CO_2 bands as a function of the vibrational temperature of the combined mode of CO_2 — T_2; $P = 5 \cdot 10^{-2}$ atm, $T = 300°K$, $T_3 = 1500°K$. Curves 1, 1' correspond to $T_2 = 300°K$, 2) 700, 2') 500, 3) 1100, 3') 700°K. The emission intensity of the 2.7-μm band is enhanced by 10 times.

4.7- and 2.7-μm bands by more than 100 times. The change in the spectral absorption A_ω in this case does not exceed 1.5-2.0 times in the central portions of the 4.3- and 2.7-μm bands.

In all bands considered there is a broadening of the spectral region of emission in the long-wave region, which corresponds to an increase in population of excited vibrational levels, the transitions between which are characterized by a lower frequency due to molecular anharmonicity. In the region of low values $T_3 = 600°K$ the 2.7-μm band separates into two parts, corresponding to the transitions $\Delta v_2 = 2$, $\Delta v_3 = 1$ and $\Delta v_1 = \Delta v_3 = 1$.

It follows from the results presented in Fig. 3 that the strong dependence of the emission intensity of a vibrationally nonequilibrium gas $\tilde{I}_\omega$ on vibrational temperatures is mostly due to the functions $B_\omega(v_r, v_p)$ of separate vibrational transitions.

Figure 4 shows the dependence of the spectral emission intensity $\tilde{I}_\omega$ and of the absorption $\tilde{A}_\omega$ of the 4.3- and 2.7-μm bands of CO_2 on the vibrational temperature of the combined mode of CO_2, T_2. The combined mode of CO_2 is active in the 2.7-μm band, and therefore the effect of the vibrational temperature of T_2 on the emission and absorption intensities averaged over the rotational structure is similar in its main features to the temperature effect of the asymmetric mode T_3. We note the stronger dependence of the quantities $\tilde{I}_\omega$ and $\tilde{A}_\omega$ in the 2.7-μm band on the vibrational temperature T_2, compared with its dependence on T_3. An increase of the vibrational temperature T_2 from 300 to 500°K leads to an increase in the emission intensity $\tilde{I}_\omega$ by more than an order of magnitude, and from 500 to 700°K, by 7-8 times.

The effect of vibrational temperatures of passive modes on the emission intensity and absorption averaged over the rotational structure reduces only to a change of the equivalent widths of rotational lines of the vibrational transitions $W_\omega(v_r, v_p)$ due to the redistribution of molecules over vibrational levels. It follows from the data of Fig. 4 that the quantity $\tilde{I}_\omega$ for the 4.3-μm band depends on the vibrational temperature of the combined mode of CO_2 (being passive in the given case) considerably more weakly. An enhancement of the vibrational temperature T_2 from 300 to 1100°K leads to an increase of the spectral emission intensity $\tilde{I}_\omega$ and of the absorption $\tilde{A}_\omega$ in the central part of the 4.3-μm band by not more than 2-3 times.

Comparison of the data shown in Figs. 3 and 4 makes it possible to draw conclusions on the approximately identical effect of vibrational temperatures of active and passive modes on the spectral absorption $\tilde{A}_\omega$ of CO_2 bands. The somewhat larger effect of the vibrational temperature T_2 on the value of $\tilde{A}_\omega$ for the CO_2 bands in comparison with the vibrational temperature of the asymmetric mode T_3 is related to the redistribution of molecules among the significant number of low-lying vibrational levels of the combined mode.

NOTATION

$\tilde{I}_\omega$, spectral emission intensity; $\tilde{A}_\omega$, spectral absorption; v, vibrational quantum numbers; ω, wave number; N, population; J, rotational quantum number; W_ω, equivalent line width; d_ω, separation between lines; γ, line half width; $K(\omega)$, absorption coefficient; S, integral absorption; P, pressure; X, optical path length; ρ, density; T_3 and T_2, respectively, vibrational temperatures of the asymmetric and combined modes of CO_2; and T_5, vibrational temperature of CO.

LITERATURE CITED

1. N. N. Kudryavtsev and S. S. Novikov, "A method of measuring vibrational temperatures in thermodynamic nonequilibrium flows," Inzh.-Fiz. Zh., 38, 411-419 (1980).
2. S. A. Losev, Gasdynamic Lasers [in Russian], Nauka, Moscow (1977).
3. R. M. Goody, Atmospheric Radiation, Clarendon Press, Oxford (1964).
4. N. N. Kudryavtsev, S. S. Novikov, and I. B. Svetlichnyi, "Methods and results of experimental determination of vibrational temperatures of CO_2 in nonequilibrium flows, using vibrational—rotational band models," Dokl. Akad. Nauk SSSR, 231, 1419-1421 (1976).
5. C. D. Rogers and W. Williams, "Integrated absorption for Voigt profiles," J. Quant. Spectr. Rad. Transfer, 11, 319-326 (1974).
6. R. M. Huffaker, "Current research of infrared radiation from rocket exhaust," J. Quant. Spectr. Rad. Transfer, 8, 87-98 (1968).
7. I. P. Hodgson, "The nonequilibrium emissivity of carbon dioxide near 4.3 μm," Aeronaut. Res. Current Paper, No. 1116, 3-26 (1970).
8. S. A. Losev, "Infrared radiation of carbon dioxide gas under nonequilibrium conditions," Mosk. Gos. Univ. Inst. Mekh. Nauch. Tr., No. 43, 79-85 (1976).
9. B. A. Khmelinin and Yu. A. Plastinin, "Emission and absorption of H_2O, CO_2, CO, and HCl molecules at temperatures 300-3000°K," Tr. TsAGI, No. 1656, 102-146 (1975).
10. L. I. Kopylova and M. V. Podkladenko, "Emission of heated carbon dioxide gas in the region of 2100-2500 cm^{-1} in the absence of thermodynamic equilibrium," Zh. Prikl. Spektrosk., 12, 811-816 (1970).