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Radiation of vibrationally nonequilibrium carbon dioxide in the 12 to 19 μm region

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Résumé. — On a fait des calculs numériques d'absorptivité et d'intensité de l'émission de CO_2 dans la bande vibro-rotationnelle de 15 μm en tenant compte des particularités de la structure de cette bande pour une large étendue de paramètres de flux du gaz incluant en particulier les conditions dans les résonateurs de lasers gazo-dynamiques à CO_2 qui fonctionnent dans le domaine spectral de $\lambda = 9\text{--}11\ \mu\text{m}$ et de $\lambda = 16\text{--}19\ \mu\text{m}$. Les calculs en P et R-branches ont été faits en utilisant un modèle statistique et un modèle de lignes isolées, et en Q-branches ; par une intégration directe « ligne par ligne » à travers le spectre.

On a trouvé les dépendances typiques des paramètres du gaz hors d'équilibre vibratoire. Les résultats ont été utilisés afin d'élaborer la méthode déterminant la température vibrationnelle du mode confondu selon l'intensité intégrale d'émission de bande, des populations de certains niveaux vibrationnels et de la température vibrationnelle du mode asymétrique selon l'absorptivité intégrale dans certaines Q-branches.

Abstract. — Numerical computations of CO_2 absorptivity and radiation intensity have been carried out with regard to specific features of the 15 μm vibrational-rotational band within a wide range of gas flow parameters, including, in particular, the conditions in the cavities of gasdynamic CO_2 lasers operating in the $\lambda = 9\text{--}11\ \mu\text{m}$ and $\lambda = 16\text{--}19\ \mu\text{m}$ spectral regions. The calculations in the P- and R-branches were carried out using the statistical model and the isolated line model, and in the Q-branches by direct « line-by-line » integration over the spectrum.

Typical dependences on the vibrationally excited gas parameters have been determined. The results have been used for developing a method of determination of the vibrational temperature of the bend-stretch manifold according to the integrated radiation intensity of the band, populations of certain vibrational levels, and the vibrational temperature of the asymmetric stretching mode according to integrated absorptivity in certain Q-branches.

List of symbols

$A(\omega)$	spectral absorptivity.	J	rotational quantum number.
A	integrated absorptivity in a spectral region (cm^{-1}).	$K(\omega)$	spectral absorption coefficient ($\text{atm}^{-1} \cdot \text{cm}^{-1}$).
$A_{\text{P,R}}, A_{\text{P,R,Q}}$	integrated absorptivities with allowance for the P, R- and P, R, Q-branches (cm^{-1}).	k	Boltzmann constant.
$B_{\text{c}}, B_{\text{d}}$	molecular rotational constant of the c- and d-type levels.	$L(\omega)$	analog of Planck's function under nonequilibrium conditions.
B_{v}	molecular rotational constant of a vibrational level (cm^{-1}).	l	quantum number of vibrational angular momentum for CO_2 bending mode.
c	light velocity ($\text{cm} \cdot \text{s}^{-1}$).	m	parameter allowing for the dependence on the rotational quantum number : $m = -J$ for P-branch, $m = J + 1$ for R-branch and $m = J$ for Q-branch.
D	geometric thickness of emitting volume (cm).	N	number of molecules per unit volume (parts/cm^3).
$g_{v,J}$	degeneracy of the vibrational-rotational level v, J .	P	gas pressure (atm).
$I(\omega), I$	spectral and integrated radiation intensities ($\text{W}/(\text{sterad} \cdot \text{cm}^2 \cdot \text{cm}^{-1})$ and ($\text{W}/\text{sterad} \cdot \text{cm}^2$)).	P_{n}	partial pressure of the radiating component.

Q_v, Q_r	vibrational and rotational partition functions.
$R_{J''l''}^{J'l'}$	a matrix element of rotational transition.
$S_{v'J'-v''J''}$	integrated intensity of rotational line ($\text{atm} \cdot \text{cm}^{-2}$).
T	translational temperature (K).
$T_{1,2}, T_3$	vibrational temperatures of the bend-stretch manifold and asymmetric stretching mode, respectively (K).
v_1, v_2, v_3	vibrational quantum numbers of the symmetric stretching, bending and asymmetric stretching modes.
$W_{v'J'-v''J''}$	equivalent black-line width (cm^{-1}).
X	optical path length ($\text{atm} \cdot \text{cm}$).
$\alpha_{v'-v''}$	integrated intensity of vibrational transition ($\text{atm} \cdot \text{cm}^{-2}$).
$\beta_{v'-v''}$	matrix element of vibrational transition.
$\gamma_{L,D}$	collisional and Doppler half-widths of rotational line (cm^{-1}).
δ	spectral line spacing (cm^{-1}).
η	a small parameter characterizing the vibrational-rotational intereffects.
θ	characteristic vibrational temperature (K).
λ	wavelength (μm)
$\psi(v_1, v_2, v_3, \pm l, J)$	unperturbed vibrational-rotational wave functions.
ψ_c, ψ_d	zero-approximation wave functions taking into account the vibrational-rotational interactions.
ω	wavenumber (cm^{-1}).
$\omega_{v'J' \leftarrow v''J''}$	wavenumber of rotational line centre.
$\Delta\omega_{v'_1, v'_2, l' \leftarrow v''_1 v''_2 l''}$	variation of the wave number of a vibrational transition due to excitation of one quantum of the asymmetric stretching mode.
$\Delta\omega_Q$	spectral width of Q-branch.
$\Delta\omega_{P,R}$	combined spectral width of the P and R-branches.
$\Delta\omega_1, \Delta\omega_2, \Delta\omega_3$	spectral regions in which effect of vibrational level population distributions on integrated radiation intensity have been studied.

1. Introduction.

Infrared radiation of a thermodynamically nonequilibrium gas bears wealth of information about molecular distributions among the internal degrees of freedom. The distribution may be determined from the relationships between gas emissivity in an appropriate spectral region and populations of the vibrational-rotational levels of the radiating molecules [1]. It can be done both by analytical [2] and numerical [1] methods. Radiation intensity and absorptivity of carbon dioxide have been calculated at 4.3 μm in

[3-13], at 2.7 μm in [6, 10-13] and at 15 μm in [10] with harmonic oscillator-rigid rotor approximation for determination of rotational lines intensities and spectral distribution for the conditions, where nonequilibrium Boltzmann population distribution in vibrational modes occurs.

In this work a systematic numerical calculation of the radiation at 15 μm has been carried out for arbitrary CO_2 vibrational distributions within a wide range of gas flow parameters, including, in particular, the conditions in the cavity of a gasdynamic CO_2 laser operating in the 9-11 μm [15] (Boltzman vibrational distribution) and 16-19 μm [16] (non-Boltzmann vibrational distribution) spectral regions.

The calculations of the 16-19 μm CO_2 Band radiation parameters have been based on precise determination of spectrum shape in the 15 μm band [17] and the recent results of determination of the individual vibrational-rotational transition parameters in this band [18], taking into account the influence of Fermi-resonance on vibrational transition intensities and rotational line spectral positions.

We have used the results of the calculations to develop and theoretically substantiate new methods of determining the vibrational distributions in CO_2 molecules and the populations of certain vibrational states of CO_2 according to radiation intensity and absorptivity measurements in the appropriate regions of the 15 μm band.

2. CO_2 radiation spectrum in 15 μm band.

The 15 μm band is generated by transitions between the levels of CO_2 bend-stretch manifold and, under vibrationally-nonequilibrium conditions, it extends through the spectral range of 12 to 19 microns [14]. This band possesses a number of features important for the calculation of the IR radiation transfer. These features include strong Q-branches and the dominating effect of the interaction between symmetric stretching and bending mode levels due to Fermi-resonance on the matrix elements and the spectral distribution of individual vibrational transitions which constitute the 15 μm band.

We will now consider in brief the CO_2 radiation spectrum in the 15 μm band. This band is made up of vibrational transitions with nonzero matrix elements of the dipole moment components perpendicular to the molecular axis. According to [19], the selection rules for a «perpendicular» vibrational transition in CO_2 can be written as :

$$\Delta l = \pm 1, g \leftrightarrow u, \Delta J = 0, \pm 1, + \leftrightarrow - \quad (2.1)$$

where l is vibrational moment of molecule, J is rotational quantum number, g and u stand for evenness and oddity of the vibrational wave functions with respect to inversion, respectively, $+$ and $-$ are signs of the rotational level [20]. In accordance with the selection rules (2.1), the variations of the vibrational

quantum number of the transitions responsible for the 15 μ band can be written in the following form :

$$\left\{ \begin{matrix} v_1 & v_2 & v_3 \\ v_1 - 1 & v_2 + 2^l & v_3 \end{matrix} \right\} \leftrightarrow \left\{ \begin{matrix} v_1 & v_2 + 1^{l\pm 1} & v_3 \\ v_1 - 1 & v_2 + 3^{l\pm 1} & v_3 \end{matrix} \right\} \quad (2.2)$$

where v_1, v_2, v_3 are vibrational quantum numbers of the symmetric, stretching, bending and asymmetric stretching modes. For each state the vibrational moment l can take values smaller or equal to the number of quanta v_2 in the bending mode. In this work the vibrational levels of CO₂ are represented by the quantum numbers of unperturbed states having the same relative energy distribution. The allowed transitions responsible for the 15 μ band are shown in figure 1 by solid lines.

The rotational levels corresponding to the vibrational states with $l > 0$ are doubly degenerate which corresponds to the two opposite directions of the vibrational moment l along the molecular axis. If the interaction between molecular rotation and vibrations is taken into account, each rotational level of the vibrational states with $l > 0$ will split into two levels with the wave functions [19] :

$$\begin{aligned} \psi_c &= [\psi(v_1, v_2, v_3, |l|, J) + \\ &\quad + \psi(v_1, v_2, v_3, -|l|, J)]/\sqrt{2} \\ \psi_d &= [\psi(v_1, v_2, v_3, |l|, J) - \\ &\quad - \psi(v_1, v_2, v_3, -|l|, J)]/\sqrt{2} \end{aligned} \quad (2.3)$$

Fig. 1. — Schematic representation of the lower vibrational levels of carbon dioxide. The vertical and slanted lines indicate transitions allowed by the selection rules and contributing to the radiation in the 15 μ band. The insert picture shows the rotational levels of the two combining states. The arrows indicate the allowed transitions for an even and odd rotational quantum number J .

where $\psi(v_1, v_2, v_3, \pm l, J)$ are the unperturbed vibrational-rotational wave functions. The degree of splitting may be represented as $\Delta E \sim [\eta^2 J(J+1)]^l$ [20], where η is a small parameter characterizing the interaction. Therefore, in the π -states all the rotational levels with wave functions having subscripts c and d have different rotational constants B_c and B_d . For the states with $l > 1$ the splitting is considerably smaller and is allowed for in the rotational energy equations by terms of the next order of smallness [20].

Carbon dioxide consists predominantly of molecules containing two ¹⁶O isotope atoms with a zero spin of nucleus disposed symmetrically about the ¹²C atom. Therefore, in the molecule ¹⁶O-¹²C-¹⁶O only those wave functions are allowed that are symmetrical relative to oxygen nucleus transposition and, consequently, half of the rotational states are absent. Depending on which level, c or d, is forbidden in the lowest state the transition which occurs, is either c-d or d-c in the Q-branch and c-c or d-d in the P and R-branches. Since the rotational wave function is symmetric, the type of transition alternates as the quantum number J varies [19]. Therefore, the vibrational-rotational band of an individual vibrational transition $v' \leftarrow v''$ may be considered as a superposition of two sub-bands in each of which the transitions take place from levels with either even or odd quantum numbers J .

Figure 1a illustrates the situation for the particular example of the 02²0-01¹0 transition.

Using the rotational energy formula and considering the difference of the rotational constants for combining levels we obtain that the interval between the adjacent rotational lines of the sub-bands is

$$\delta = 4 B'' + (B' - B'')(4m + 2) \quad \text{in P and R-branches} \quad (2.4a)$$

$$\delta = 2(B' - B'')(2m + 1) \quad \text{in Q-branches} \quad (2.4b)$$

where $m = -J$ for the P-branch, $m = J + 1$ for the R-branch and $m = J$ for the Q-branch, $|B' - B''| \ll B', B''$; for the adjacent lines it was assumed $J'' = J - 1$ and $J'' = J + 1$. It is seen that in the P and R-branches far from the band head in a system of the vibrational-rotational lines formed by two sub-bands, the mean line spacing is $2B$. The difference in the $B' - B''$ values for the c-d and d-c transitions is responsible for the marked difference of these sub-bands in the Q-branches. Thus a superposition of two sub-bands actually involves two Q-branches having different characteristics.

If one of the combining states has a zero vibrational moment l , the sub-band corresponding to the c-d, d-c or d-d transitions is missing, since in the Σ state the d-type levels are absent.

3. Determination of rotational structure-averaged radiation and absorption characteristics of P and R-branches of vibrational transitions in the 15 μm band.

The radiation intensity and absorptivity A were calculated by a procedure described elsewhere [12, 13]. The averaged $I(\omega)$ and $A(\omega)$ values were determined in the wave number range $\Delta\omega = 1\text{-}10\text{ cm}^{-1}$. The averaging range $\Delta\omega$ was chosen to meet the requirement of a small (less than 10 %) variation of rotational line intensity of an individual vibrational transition in the spectral range $[\omega, \omega + \Delta\omega]$.

To determine the averaged radiation intensity in the P and R-branches of the 15 μm band we used the isolated line model according to which [21, 22] :

$$I(\omega) d\omega = \sum_i A_i(\omega) L_i(\omega) d\omega \quad (3.1)$$

where $A_i(\omega) = \frac{1}{\Delta\omega} \int_{\Delta\omega} [1 - \exp(-K_i(\omega)X)] d\omega'$ is the averaged absorptivity of an individual vibrational transition numerated by subscript i , $K_i(\omega)$ is the corresponding absorption coefficient, $x = P_n D$ is optical path length in gas, P_n is the partial pressure of the radiating component, D is geometrical path length in the gas, $L_i(\omega) = 2 \frac{hc^2 \omega^3}{g_{v'J'} N_{v''J''}} (g_{v'J'} N_{v''J''} - 1)$; $g_{v'J'}$, $N_{v'J'}$, $g_{v''J''}$, $N_{v''J''}$ are the statistical weights and populations of the upper and lower vibrational-rotational levels, respectively. The absorptivity appearing in (3.1) is defined in the isolated line

model as [21] :

$$A_i(\omega) = W_{v'J' \leftarrow v''J''} / \delta_i \quad (3.2)$$

where $W_{v'J' \leftarrow v''J''}$ is the equivalent rotational line width, δ_i is the distance between the adjacent rotational lines of an individual vibrational transition.

Application of the isolated line model to the calculation of radiation intensity in the P and R-branches is justified in the pressure range $P < 0.1\text{ atm}$ and optical path lengths $X < 1.0\text{ atm}\cdot\text{cm}$, because under these conditions the rotational line width is one-two orders of magnitude smaller than the distance between the adjacent lines in the band [12, 13]. In determining the absorptivity in the P, R-branches of the 15 μm band we used a model [21] assuming a random line distribution in the spectrum and

$$A(\omega) = 1 - \exp\left[-\sum_i W_i(\omega)/\delta_i\right]. \quad (3.3)$$

The values of $A(\omega)$ in the P and R-branches calculated for the conditions considered in this work using the statistical and isolated line models agree to within 5 %. The equivalent width of the Voigt-contoured rotational lines were determined by the procedure described in [11-13]. The initial parameters for such calculations are the integrated line intensity $S_{v'J' \leftarrow v''J''} = \int_{-\infty}^{+\infty} K_{v'J' \leftarrow v''J''}(\omega) d\omega$ and the line half-width γ .

Ignoring the effect of the interaction between rotation and vibrations on the matrix elements of the vibrational and rotational transitions one obtains the following equation for the integrated intensity of the vibrational-rotational line [20] :

$$S_{v'J' \leftarrow v''J''} = \frac{8 \pi^3 \omega_{v'J' \leftarrow v''J''}}{3 hc} \frac{N_{v''J''}}{P_n g_{v''J''}} \beta^2 (R_{J''J'}^T)^2 \left(1 - \frac{N_{v'J'} g_{v''J''}}{N_{v''J''} g_{v'J'}}\right) \quad (3.4)$$

where $\omega_{v'J' \leftarrow v''J''}$ is the wave number at line centre, $\beta^2 = \beta_{v' \leftarrow v''}^2$ is squared matrix element of the dipole moment due to a variation of the molecular vibrational state, $R_{J''J'}^T$ is an amplitude factor due to molecular rotation.

To calculate the radiation in the vibrational-rotational bands it is convenient to use the integrated intensity of individual vibrational transitions $\alpha_{v' \leftarrow v''}$. The values of $\alpha_{v' \leftarrow v''}$ are determined as follows [21] :

$$\alpha_{v' \leftarrow v''} = \sum_{J', J''} S_{v'J' \leftarrow v''J''}. \quad (3.5)$$

The amplitude factors due to molecular rotation may, if the rotation-vibration interaction is ignored, be written as [21] :

$$(R_{J-1, l \pm 1}^J)^2 = \frac{(J \pm l)(J \pm l - 1)}{4J(2J + 1)}, \quad l \neq 0; \quad (R_{J-1, 0}^J)^2 = \frac{J - 1}{2(2J + 1)}$$

$$(R_{J, l \pm 1}^{J-1})^2 = \frac{(J \pm l)(J \pm l + 1)}{4J(2J - 1)}, \quad l \neq 0; \quad (R_{J, 0}^{J-1})^2 = \frac{J + 1}{2(2J - 1)}$$

for P and R-branches

$$(R_{J \pm 1}^{J \pm 1})^2 = \frac{(J \pm 1)(J \mp 1 + 1)}{4J(J+1)}, \quad l \neq 0; \quad (R_{J1}^{J0})^2 = \frac{1}{2} \quad (3.6)$$

for Q-branch.

Using the amplitude factor expression and assuming that $\omega = \omega_{v' \leftarrow v''}$, $g_{Jv} = (2 - \delta_{01})(2J+1)$ one may obtain from (3.5) [21]:

$$\alpha_{v' \leftarrow v''} = \frac{8\pi^3 \beta^2 \omega}{3hc} \frac{N_{v''}}{P_n g_{v''}} \left(1 - \frac{N_{v'} g_{v''}}{N_{v''} g_{v'}}\right) \quad (3.7)$$

where δ_{01} is the Kronecher symbol.

The above formulae establish the relationship between the integrated intensity of an individual vibrational-rotational line and that of the corresponding vibrational transition:

$$S_{v'J' \leftarrow v''J''} = \frac{\omega(\alpha_{v' \leftarrow v''})_0 P_0}{\omega_{v' \leftarrow v''} (N_{v''})_0 \left[1 - \frac{(N_{v'})_0 g_{v''}}{(N_{v''})_0 g_{v'}}\right]} \frac{N_{v''J''}}{P g_{J''}} (R_{J''J'}^{J''J'})^2 \left(1 - \frac{N_{v'J'} g_{v''J''}}{N_{v''J''} g_{v'J'}}\right) \quad (3.8)$$

where the subscript « 0 » refers to values under normal conditions: pressure $P_0 = 1.0$ atm, temperature $T_0 = 296$ K.

In calculating the radiation in the 15 μ m band it is essential to take into account the effect of Fermi-resonance between symmetric stretching and bending mode levels on the matrix elements of vibrational transitions and, consequently, on the integrated intensity $\alpha_{v' \leftarrow v''}$. Therefore, in this work we used the integrated intensity of individual vibrational transitions measured in [18] and these are listed in table I.

The broadening of the rotational lines in the pressure range of $10^{-4} < P < 0.1$ atm, typical of the vibrationally-excited gas in molecular lasers, is due to both Doppler and collisional mechanisms.

In this work the rotational line halfwidth of an individual transition occurring on collision between carbon dioxide molecules and various mixture components numerated by a superscript « n », $\gamma_L^{(n)}$, has been assumed to be equal to the $\gamma_L^{(n)}$ value of the strongest rotational lines in the vibrational band. The effect of the vibrational state of molecule on $\gamma^{(n)}$ was ignored because it was insignificant [23]. The $\gamma^{(n)}$ values under normal conditions $(\gamma_L^{(n)})_0$ were chosen as recommended in [2, 24-28] and were 0.087 cm^{-1} , 0.067 cm^{-1} , 0.04 cm^{-1} and 0.05 cm^{-1} for the collisions CO₂-CO₂, CO₂-N₂, CO₂-He and CO₂-Ar, respectively. The value of γ_L in a gas mixture under arbitrary temperature and pressure was determined using the formula reported in [26]:

$$\gamma_L = P \left(\frac{T_0}{T}\right)^{0.74} \sum_n \xi_n (\gamma_L^{(n)})_0 \quad (3.9)$$

where ξ_n are molar concentrations of the components. Calculation of absorptivity in the 15 μ m band for both the minimum and maximum halfwidths $(\gamma_L^{(n)})_0$ as regards the rotational quantum number gives the

maximum discrepancy of less than 5-10 % at the lowest investigated temperature $T = 100$ K. The maximum discrepancy for medium values of $(\gamma_L^{(n)})_0$ is within about one half of the above value and becomes even less than 1 % as the gas temperature is raised to 300 K.

The relationship between $S_{v'J' \leftarrow v''J''}$, $\delta(m)$, $R_{J''J'}^{J''J'}$ and the rotational quantum number J was transformed for the lines in the P and R-branches into a dependence on the wave number ω . This was done using the formulae following from the energy expressions for vibrational-rotational states of CO₂ [19, 21, 27] taking into account the interaction between molecular rotation and vibration.

4. Determination of rotational structure-averaged absorption in the Q-branches.

The use of band models for *a priori* calculation of absorption in the Q-branches is unjustified since the line arrangement (2.4b) is substantially different from that assumed in both the regular and statistical model and the choice of the averaging range which must contain a considerable number of lines is hampered because of the considerably differing intensities of the successive rotational lines in the Q-branch. Therefore, we used direct « line-by-line » integration over the spectrum to determine the absorption in the Q-branches of individual vibrational transitions:

$$A(\omega) = \frac{1}{2\Delta\omega} \int_{\omega-\Delta\omega}^{\omega+\Delta\omega} [1 - \exp(-K(\omega').X)] d\omega' \quad (4.1)$$

where $\Delta\omega$ is the averaging range, $K(\omega) = \sum_r K_r(\omega)$ is the absorption coefficient equal to the sum of the absorption coefficients of individual rotational lines.

Table I. — Spectroscopic parameters of transitions of the 15 μm CO_2 band ; $E_{v''}$ is the energy of the lowest vibrational state of transition ; $(\alpha_{v' \leftarrow v''})_0$ are integrated intensities of transitions $v' \leftarrow v''$; $\Delta\omega_{v_1'v_2'l' \leftarrow v_1'v_2'l''}$ is frequency shift of transition due to excitation of one quantum of the asymmetric mode ; $\Delta B_{v' \leftarrow v''}^{(c \leftarrow d)}$ and $\Delta B_{v' \leftarrow v''}^{(d \leftarrow c)}$ are differences in rotational constants of the combining levels for transition types $c \leftarrow d$ and $d \leftarrow c$. The figures in brackets appearing in the tables of this work indicate the order of magnitude of the value ; the braces span the levels in Fermi-resonance.

Transition $v' \leftarrow v''$	Transition type	$E_{v''}, \text{cm}^{-1}$	$\omega_{v' \leftarrow v''}$ cm^{-1}	$(\alpha_{v' \leftarrow v''})_0$ $\text{atm}^{-1} \cdot \text{cm}^{-1}$	$\Delta\omega_{v' \leftarrow v''}$ cm^{-1}	$\Delta B_{v' \leftarrow v''}^{(d \leftarrow c)}$ 10^{-5} cm^{-1}	$\Delta B_{v' \leftarrow v''}^{(c \leftarrow d)}$ 10^{-5} cm^{-1}
01 ¹ 0-00 ⁰ 0	$\Pi_u-\Sigma_g^+$	0.0	667.379	198.200	12.509	103.70	42.30
02 ² 0-01 ¹ 0	$\Delta_g-\Pi_u$	667.379	667.750	15.570	12.489	104.10	42.60
10 ⁰ 0	$\Sigma_g^+-\Pi_u$		720.808	4.448	10.043	— 45.30	— 106.70
02 ⁰ 0	$\Sigma_g^+-\Pi_u$		618.033	3.447	9.205	— 16.00	— 77.40
03 ³ 0-02 ² 0	$\Phi_u-\Delta_g$	1 335.129	668.109	0.918	12.473	73.80	73.80
11 ¹ 0	$\Pi_u-\Delta_g$		741.736	1.897(— 1)	10.385	— 33.80	— 126.60
03 ¹ 0	$\Pi_u-\Delta_g$		597.341	0.125	8.905	— 0.20	— 94.60
11 ¹ 0-10 ⁰ 0	$\Pi_u-\Sigma_g^+$	1 338.187	688.678	3.570(— 1)	12.831	115.50	22.70
03 ¹ 0	$\Pi_u-\Sigma_g^+$		544.283	6.536(— 3)	11.351	149.10	54.70
11 ¹ 0-02 ⁰ 0	$\Pi_u-\Sigma_g^+$	1 285.412	791.452	2.696(— 2)	13.668	86.20	— 6.63
03 ¹ 0-	$\Pi_u-\Sigma_g^+$		647.058	0.533	12.189	119.80	25.40
04 ⁴ 0-03 ³ 0	$\Gamma_g-\Phi_u$	2 003.238	668.452	4.794(— 2)	12.456	74.20	74.20
12 ² 0-	$\Delta_g-\Phi_u$		757.497	7.893(— 3)	10.634	— 88.50	— 88.50
04 ² 0	$\Delta_g-\Phi_u$		581.794	4.642(— 3)	8.737	— 48.20	— 48.20
12 ² 0-11 ¹ 0	$\Delta_g-\Pi_u$	2 076.865	683.870	2.170(— 2)	12.722	111.90	19.10
04 ² 0	$\Delta_g-\Pi_u$		508.167	1.239(— 4)	10.825	152.20	59.40
20 ⁰ 0	$\Sigma_g^+-\Pi_u$		720.289	1.148(— 2)	11.257	14.70	— 78.10
12 ⁰ 0	$\Sigma_g^+-\Pi_u$		594.248	2.180(— 3)	7.327	— 86.00	— 178.80
04 ⁰ 0-11 ¹ 0	$\Sigma_g^+-\Pi_u$	2 076.865	471.508	2.090(— 5)	8.516	69.10	— 23.70
12 ² 0-03 ¹ 0	$\Delta_g-\Pi_u$	1 932.470	828.265	4.825(— 4)	14.193	79.90	— 14.50
04 ² 0	$\Delta_g-\Pi_u$		652.536	3.965(— 2)	12.279	120.20	25.80
20 ⁰ 0	$\Sigma_g^+-\Pi_u$		864.684	1.037(— 4)	12.737	— 17.30	— 111.70
12 ⁰ 0	$\Sigma_g^+-\Pi_u$		738.643	7.251(— 3)	8.526	— 118.00	— 212.40
04 ⁰ 0	$\Sigma_g^+-\Pi_u$		615.903	1.654(— 2)	9.996	37.10	— 57.30
05 ⁵ 0-04 ⁴ 0	$H_u-\Gamma_g$	2 671.690	668.785	2.343(— 3)	12.440	74.60	74.60
13 ³ 0	$\Phi_u-\Gamma_g$		770.355	3.243(— 4)	10.646	15.00	15.00
05 ³ 0	$\Phi_u-\Gamma_g$		568.874	1.719(— 4)	8.504	— 46.60	— 46.60
13 ³ 0-12 ² 0	$\Phi_u-\Delta_g$	2 760.735	681.521	1.104(— 3)	12.679	77.70	77.70
05 ³ 0-	$\Phi_u-\Delta_g$		479.829	2.880(— 6)	10.325	116.10	116.10
21 ¹ 0	$\Pi_u-\Delta_g$		739.855	4.225(— 4)	11.052	16.50	— 107.40
13 ¹ 0	$\Pi_u-\Delta_g$		578.605	9.025(— 5)	7.621	— 39.00	— 150.00
05 ¹ 0	$\Pi_u-\Delta_g$		420.715	—	7.420	78.10	— 50.70
13 ³ 0-04 ² 0	$\Phi_u-\Delta_g$	2 585.032	857.224	2.640(— 5)	14.576	37.40	37.40
05 ³ 0	$\Phi_u-\Delta_g$		655.532	2.376(— 3)	12.223	75.80	75.80
21 ¹ 0	$\Pi_u-\Delta_g$		915.558	4.681(— 6)	12.949	— 23.80	— 147.70
13 ¹ 0	$\Pi_u-\Delta_g$		754.308	3.857(— 4)	9.518	— 79.30	— 190.30
05 ¹ 0	$\Pi_u-\Delta_g$		596.418	6.169(— 4)	9.317	37.80	— 91.00
21 ¹ 0-20 ⁰ 0	$\Pi_u-\Sigma_g^+$	2 797.154	703.436	5.905(— 4)	12.517	113.70	— 10.20
13 ¹ 0	$\Pi_u-\Sigma_g^+$		542.186	1.707(— 5)	9.086	58.20	— 58.80
05 ¹ 0	$\Pi_u-\Sigma_g^+$		384.296	—	8.885	175.30	46.50
21 ¹ 0-12 ⁰ 0	$\Pi_u-\Sigma_g^+$	2 671.113	829.477	2.760(— 5)	16.728	214.40	90.50
13 ¹ 0	$\Pi_u-\Sigma_g^+$		668.227	7.479(— 4)	13.297	158.90	47.90
05 ¹ 0	$\Pi_u-\Sigma_g^+$		510.337	9.601(— 6)	13.096	276.00	147.20
21 ¹ 0-04 ⁰ 0	$\Pi_u-\Sigma_g^+$	2 548.373	952.217	1.540(— 5)	15.258	59.30	64.60
13 ¹ 0	$\Pi_u-\Sigma_g^+$		790.967	1.315(— 4)	11.827	3.83	— 107.20
05 ¹ 0	$\Pi_u-\Sigma_g^+$		633.077	1.558(— 3)	11.626	120.90	— 7.87

The integration accuracy was 0.1 %. The choice of the averaging range $\Delta\omega$ in calculation of absorption in the Q-branches must be correlated with the spectral resolution of the optical systems used in the experiments. In this particular case we used two values of

$\Delta\omega$: 0.2 cm^{-1} for absorption averaging over the rotational structure of the Q-branch and 0.02 cm^{-1} at which the rotational structure is spectrally resolved. Table II presents the numeration used in this work for the strongest Q-branches of the 15 μm band, the

vibrational transitions responsible for these Q-branches and the spectral ranges in which the absorption of the branches was integrated.

The initial parameters for the calculation of absorption coefficient K in (4.1) are the integrated intensity and the rotational line shape. The S_r values were calculated in accordance with (3.8) using the rotational amplitude factors (2.6). The rotational line

shape was assumed to be the Voigt one. Calculations at the central portion of the line

$$|\omega - \omega_r|/\max(\gamma_L, \gamma_D) < 10$$

were based on an exact integral form of the Voigt function; at large distances from the centre the shape was approximated by [21]:

$$\varphi(\omega) = \frac{1}{\pi} \frac{\gamma_L}{\gamma_L^2 + (\omega - \omega_{v'J' \leftarrow v''J''})^2} \left\{ 1 + \frac{3}{2} \frac{1}{\left[\frac{(\omega - \omega_{v'J' \leftarrow v''J''})\sqrt{\ln 2}}{\gamma_D} \right]^2} \right\} \quad (4.2)$$

where γ_L and $\gamma_D = \frac{\omega_{v'J' \leftarrow v''J''}}{c} \sqrt{\frac{2RT \ln 2}{\mu}}$ are the collisional and Doppler halfwidths, μ is molecular weight. The γ_L values were found as described in section 3 of this paper.

5. Calculation procedure.

The following assumptions concerning the vibrational and rotational relaxation processes were made in population calculations of the vibrational-rotational levels of CO₂, N_{vJ} . Under the conditions normal in CO₂ lasers rapid rotational-translational relaxation takes place [29]. This makes it possible to describe the populations of the rotational levels of CO₂ vibrational states in terms of a Boltzmann distribution

$$N_{vJ} = N_v(2J + 1) Q_R^{-1} \exp\left[-\frac{hc}{k} \frac{BJ(J + 1)}{T_R}\right] \text{ with a rotational temperature } T_R \text{ equal to the translational}$$

temperature, $Q_R = kT_R/2hcb$ is rotational partition function.

In the cavities of gasdynamic CO₂ lasers operating in the spectral region $\lambda = 9-11 \mu\text{m}$ the distribution of CO₂ molecules between the vibrational levels was assumed to follow the Boltzmann's law at two vibrational temperatures T_3 and $T_{1,2}$ characteristic of the excitation of the asymmetric mode and bend-stretch manifold respectively [30, 31]:

$$N_v = Q_v^{-1} g_v \exp\left[-\left(\frac{E_{v_1v_2^l0}}{T_{1,2}} + \frac{E_{00^0v_3}}{T_3}\right) \frac{hc}{k}\right] \quad (5.1)$$

where $E_{v_1v_2^lv_3}$ is the energy of the corresponding vibrational level, Q_v is the vibrational partition function, the subscripts 1, 2 and 3 denote the symmetric, deformation and asymmetric modes of CO₂ vibrations respectively; $g_v = 1$ at $l = 0$ and $g_v = 2$ at $l > 0$.

At low gas temperatures the distribution in the bend-stretch manifold may become « non-Boltzmann » [32] so that the populations of the equidistant levels $0v_2^l0$ ($l = v_2$) are determined by the vibrational temperature $T_{1,2}$ characterizing the excitation of this type of vibrations and the relative level population in multiplets (states with $2v_1 + v_2 = \text{const.}$) is controlled by the translational temperature:

$$N_v \sim g_v \exp\left[-\left(\frac{E_{v_1v_2^l0} - E_{01^10}(v_2 + 2v_1)}{T} + \frac{E_{01^10}(v_2 + 2v_1)}{T_{1,2}} + \frac{E_{00^0v_3}}{T_3}\right) \frac{hc}{k}\right]. \quad (5.2)$$

In describing the vibrational level populations by (5.1) and (5.2) we ignored the intereffects between the asymmetric stretching mode and the bend-stretch manifold for the reason that the resultant vibrational level displacement is only about 10 cm^{-1} per vibrational quantum, that is, much below the vibrational quantum values for CO₂ ($700-2500 \text{ cm}^{-1}$). The shift of the vibrational levels of the bend-stretch manifold due to Fermi-resonance is within 50 to 100 cm^{-1} [19], which is comparable with the vibrational quantum value of the bending mode. Therefore, the vibrational level energies of the bending mode $E_{v_1v_20}$ have been determined from the experimental data reported in [18] and are listed in table I. The $L_i(\omega)$ functions for the two types of vibrational distributions in the CO₂ bend-stretch manifold (5.1) and (5.2) have the form:

$$L_i(\omega) = 2hc^2\omega^3 \left\{ \exp\left[\frac{hc}{k} \left(\frac{\omega_{v' \leftarrow v''}}{T_{1,2}} + \frac{\omega - \omega_{v' \leftarrow v''}}{T}\right)\right] - 1 \right\}^{-1} \quad (5.3)$$

$$L_i(\omega) = 2 hc^2 \omega^3 \left\{ \exp \left[\frac{hc}{k} \left(\frac{\omega_{01^1 0 \leftarrow 00^0 0}}{T_{1,2}} + \frac{\omega - \omega_{01^1 0 \leftarrow 00^0 0}}{T} \right) \right] - 1 \right\}^{-1}. \quad (5.4)$$

In describing the spectral distribution of radiation in the 15 μ band the positions of vibrational transition centres between the levels with unexcited states of the asymmetric mode $v_1' v_2'' 0 \leftarrow v_1'' v_2' 0$, the $\omega_{v_1' v_2'' 0 \leftarrow v_1'' v_2' 0}$ values were determined with allowance for the interactions between the different types of vibrations and their anharmonism on the basis of the data reported in [18] and listed herein in table I. Allowance for the displacement of the vibrational levels of the bend-stretch manifold due to the interaction with asymmetric vibrations at $v_3 \geq 1$ was determined in the linear approximation with respect to the quantum number v_3

$$\omega_{v_1' v_2'' v_3' \leftarrow v_1'' v_2' v_3''} = \omega_{v_1' v_2'' 0 \leftarrow v_1'' v_2' 0} - \Delta \omega_{v_1' v_2'' v_3' \leftarrow v_1'' v_2' v_3''} \cdot v_3. \quad (5.5)$$

Table II. — *The most intense Q-branches of the 15 μ band and wave number ranges in which the integrated absorptivity is calculated (i.e. the ranges covering 99.5 % of the total absorption of the Q-branch excluding the spectral region 10'). The numerals ascribed to the Q-branches in this table are used in the text of this work.*

Q-branch No.	Wave number range	Transition
1	595.3-597.5	03 ¹ 0-02 ² 0
2	606.8-609.0	02 ⁰ 1-01 ¹ 1
3	614.0-616.2	04 ⁰ 0-03 ¹ 0
4	616.0-618.2	02 ⁰ 0-01 ¹ 0
5	646.8-649.8	03 ¹ 0-02 ⁰ 0
6	654.7-657.7	01 ¹ 1-00 ⁰ 1 02 ² 1-01 ¹ 1 03 ³ 1-02 ² 1 04 ⁴ 1-03 ³ 1 05 ⁵ 1-04 ⁴ 1
7	667.2-670.2	01 ¹ 0-00 ⁰ 0 02 ² 0-01 ¹ 0 03 ³ 0-02 ² 0 04 ⁴ 0-03 ³ 0 05 ⁵ 0-04 ⁴ 0
8	688.4-690.6	11 ¹ 0-10 ⁰ 0
9	708.8-711.0	10 ⁰ 1-01 ¹ 1
10'	718.8-721.0	10 ⁰ 0-01 ¹ 0 20 ⁰ 0-11 ¹ 0
10	720.28-721.0	10 ⁰ 0-01 ¹ 0
11	729.3-731.5	11 ¹ 1-02 ² 1
12	739.7-741.9	11 ¹ 0-02 ² 0

The $\Delta \omega_{v_1' v_2'' v_3' \leftarrow v_1'' v_2' v_3''}$ values were calculated on the basis of the experimental data reported in [18] and given in table I. The table also presents the integrated intensities of the vibrational transitions between the bend-stretch manifold levels $(\alpha_{v_1' v_2'' 0 \leftarrow v_1'' v_2' 0})_0$ under normal conditions as well as rotational constant increment variations $\Delta B_{v' \leftarrow v''}^{(d \leftarrow c)} = B_{v'}^{(d)} - B_{v''}^{(c)}$, $\Delta B_{v' \leftarrow v''}^{(c \leftarrow d)} = B_{v'}^{(c)} - B_{v''}^{(d)}$ for the combining levels with $v_3 = 0$ borrowed from [18] that are also necessary for calculations. The interaction between the asymmetric mode and bend-stretch manifold was ignored in calculations of these values for states with the excited asymmetric mode which enabled us to put $\beta_{v' \leftarrow v''}^2 = \beta_{v_1' v_2'' 0 \leftarrow v_1'' v_2' 0}$.

and $\Delta B_{v' \leftarrow v''} = \Delta B_{v_1' v_2'' 0 \leftarrow v_1'' v_2' 0}$. From the data of [18] it follows that the excitation of the asymmetric mode little effects $\beta_{v' \leftarrow v''}$ and $\Delta B_{v' \leftarrow v''}$ for vibrational transitions in the 15 μ band. For instance, the difference between the respective values for the transitions 02⁰0-01¹0 and 02⁰1-01¹1, 10⁰0-01¹0 and 10⁰1-01¹1 does not exceed 5 %.

The spectral width of Q-branch is, according to [21], determined by the condition $N_J^*/N_{J_{\max}} = 10^{-3}$, where $J_{\max}$ is the rotational quantum number of the rotational state with maximum population, J^* is the rotational quantum number of the « boundary » level,

$$\text{and is } \Delta \omega_Q = 10.1 - \frac{B' - B''}{B''} \frac{kT}{hc}.$$

The combined width of the R- and P-branches is $\Delta \omega_{P,R} = 9 \sqrt{2 B \frac{kT}{hc}}$. Using the data of table I we find $B' - B'' \sim 5 \times 10^{-4} \text{ cm}^{-1}$, $B \sim 0.39 \text{ cm}^{-1}$, and at the characteristic temperature $T = 300 \text{ K}$ one obtains that the width of Q-branch does not exceed 4 % of the combined width of the P and R-branches. The rotational line density $1/\delta$ is determined by (3.4) and, therefore, the absorptivity in the Q-branches is 10-1 000 times as high as that in the P and R-branches. Thus the radiation intensity or absorptivity in the 15 μ band can be determined without allowance for the overlap between Q-branch and P and R-branches; correspondingly, $A(\omega) = A_Q(\omega) + A_{P,R}(\omega)$ and $I(\omega) = I_Q(\omega) + I_{P,R}(\omega)$. In case of strong absorption $A(\omega) \sim 1$ the contribution from Q-branches may be neglected.

To check the validity of the assumptions and determine the calculation error we calculated the integrated absorptivity in the 15 μ band of a thermodynamically equilibrium carbon dioxide under conditions corresponding to the experiment [33] and calculation [34] based on direct integration of the spectrum of the band. The comparative results are presented in figure 2.

For optical paths $x < 10 \text{ atm.cm}$ the integrated absorption in the 15 μ band was calculated by summation over the Q, P and R-branches and for $X > 10 \text{ atm.cm}$ the absorption in the Q-branches was ignored. From the data of figure 2 it follows that the discrepancy between the calculation results of

Fig. 2. — Integrated absorptivity of the CO₂ 15 μm band under thermodynamic equilibrium calculated in this work (the solid line), the experimental results of [33]-o, and the results calculated by direct integration over the spectrum [34] (the dash line), $P = 0.2$ atm, $T = 300$ K.

Fig. 3. — Integrated absorptivity of the 15 μm band of vibrationally-nonequilibrium CO₂ for different optical path lengths of the gas as function of the number of levels considered in the bend-stretch manifold: $T_3 = 1000$ K, $T_{1,2} = 500$ K, $T = 300$ K, $P = 10^{-2}$ atm. Curve 1 is for optical path length $X = 10^{-1}$, $2 \cdot 10^{-2}$, $3 \cdot 10^{-3}$ atm.cm (for distribution (5.1)).

this work and the experimental measurements of [33] and the results obtained by direct integration over the spectrum [34] does not exceed 5 %.

6. Results and discussion.

6.1 INTEGRATED BAND PARAMETERS. — The problem which is in the foreground is the choice of the number of vibrational levels which are to be considered in calculations. Figure 3 shows the relationship between the integrated absorptivity in the 15 μm band and the number of levels considered in the bend-stretch manifold $v_{2m} = \max \{ 2v_1 + v_2 \}$. Considered in calculations were transitions to the vibrational levels having larger populations than the « boundary » level, $N_{v_1 v_2 v_3} \geq N_{0v_2 m 0}$. The calculation has been carried out for three different optical paths X equal to 10^{-1} , 10^{-2} and 10^{-3} atm.cm (curves 1-3 respectively).

From the data of figure 3 it follows that the more levels are considered the higher is the absorptivity result which finally approaches the ultimate limit. The number of levels that have to be considered to attain a calculation accuracy of 10-15 % is, according to the data of figure 3 : three for the optical length $X = 10^{-3}$ atm.cm, four for $X = 10^{-2}$ atm.cm and about 6-7 for $X = 10^{-1}$. In further calculations we used $v_{2m} = 5$.

Under vibrationally nonequilibrium conditions it is important to select the form of the function of distribution between the levels of the bend-stretch manifold (5.1) or (5.2). In order to find out the effect of the form of the distribution function in the bend-stretch manifold on the absorptivity of different spectral regions of the 15 μm band we carried out calculations

Fig. 4. — Absorptivity of CO₂ in the 15 μm band averaged over the rotational structure. The vertical lines correspond to the absorption maximum in Q-branches for an averaging range of 0.2 cm⁻¹, $T_3 = 1500$ K, $T_{1,2} = 1000$ K, $T = 100$ K, $P = 5 \times 10^{-3}$ atm, $X = 3.3 \times 10^{-3}$ atm.cm. The results obtained for a Boltzmann distribution are marked with « a » and those for distribution (5.2) with subscript « b ».

the results of which are given in figure 4 and table III. The number of vibrational quanta in the bend-stretch manifold was constant. The conditions

Table III. — *Radiation intensities integrated over the spectral regions $\Delta\omega_1$, $\Delta\omega_2$ and $\Delta\omega_3$ and over the entire band $\Delta\omega_s$, I , in W/sterad cm^2 and absorptivity A in cm^{-1} calculated for population distributions between vibrational levels described by (5.1) and (5.2). $T_3 = 1\,500\text{ K}$, $T_{1,2} = 800\text{ K}$, $T = 200\text{ K}$, $P = 10^{-2}\text{ atm}$.*

Spectral region, cm^{-1}		$\Delta\omega_1 = 500\text{-}647$		$\Delta\omega_2 = 647\text{-}687$		$\Delta\omega_3 = 687\text{-}900$		$\Delta\omega_s = 500\text{-}900$	
optical path length atm.cm	distribution type	I	A	I	A	I	A	I	A
6.7(− 3)	(5.2)	5.80(− 5)	0.281	1.59(− 4)	1.01	4.10(− 5)	0.344	2.58(− 4)	1.64
	(5.1)	4.10(− 5)	0.277	1.61(− 4)	1.00	5.60(− 5)	0.338	2.58(− 4)	1.62
6.7(− 2)	(5.2)	4.04(− 4)	1.91	6.98(− 4)	4.38	2.58(− 4)	2.18	1.36(− 3)	8.47
	(5.1)	2.89(− 4)	1.90	7.06(− 4)	4.38	3.60(− 4)	2.12	1.36(− 3)	8.40

used in the calculations were typical of CO_2 gasdynamic lasers operating in the spectral regions $\lambda = 16\text{-}19\text{ }\mu$ and $\lambda = 9\text{-}11\text{ }\mu$. Under these conditions the absorption in the P and R-branches of the $15\text{ }\mu$ band is low not exceeding $A(\omega) \lesssim 0.02$ at maximum. The low absorptivity in the P and R-branches of the $15\text{ }\mu$ band under conditions typical of molecular lasers is due to an insignificant rotational line broadening as compared with the distance between the adjacent lines in the band. At the same time, one observes a considerable re-absorption at centres of the strong rotational lines. In certain Q-branches the absorption is considerable, 0.05 to 0.5, which is due to the high rotational line density exceeding by a factor of 20 to 500 the corresponding values for the P and R-branches. This enables one to determine the populations of individual levels of a CO_2 molecule according to emissivity measurements in the Q-branches of the $15\text{ }\mu$ band.

The spectral absorption of the P and R-branches located in the central portion ($A(\omega) > 0.01$) of the band depends little on the form of the distribution function in the combined mode, varying by not more than 10-20 %. The absorption in Nos. 6 and 7 Q-branches corresponding to transitions between the equidistant levels of the bend-stretch manifold $ov_2^l v_3$ ($l = v_2$) in case of equal numbers of vibrational quanta does not depend on the form of distribution function. For other Q-branches of the band, Nos. 2, 4, 5, 8, for example, the effect of the function form is tangible (Fig. 4). Since the absorptivity variations in transition from distribution (5.1) to (5.2) have different signs in different spectral regions of the $15\text{ }\mu$ band (Fig. 4), the integrated absorptivity in the $15\text{ }\mu$ band weakly depends on the distribution function form.

More detailed results of investigation of the effect of the function of distribution between the vibrational levels of CO_2 on the emissivity in the $15\text{ }\mu$ band are presented in table III. These results suggest that the

effect of the form of distribution function on the absorption in the central $\Delta\omega_2$ and peripheral $\Delta\omega_1$ and $\Delta\omega_3$ spectral regions of the $15\text{ }\mu$ band is small. Here, the variation of radiation intensity does not exceed 2-3 % in the central portion of the band $\Delta\omega_2$ but is as high as 30-40 % in the peripheral portions $\Delta\omega_1$ and $\Delta\omega_3$. The sign of I variation in the longwave $\Delta\omega_1$ and shortwave $\Delta\omega_3$ portions of the $15\text{ }\mu$ band is reversed in transition from the Boltzmann distribution in bend-stretch manifold (5.1) to non-Boltzmann distribution (5.2). Therefore, the effect of distribution function form in the combined mode on the integral radiation intensity in the entire $15\text{ }\mu$ band is also found to be relatively small and never exceeds 5-6 %. These results prompt a conclusion that measurements of the integrated radiation intensity or integrated absorption in the $15\text{ }\mu$ band allow to obtain information about the total number of vibrational quanta in bend-stretch manifold and, consequently, about its vibrational temperature $T_{1,2}$.

The Q-branches of the $15\text{ }\mu$ band extend through much narrower spectral ranges than P or R-branches. As a consequence, while having the integrated absorptivity comparable with that of the P and R-branches, Q-branches have a higher average absorptivity. The relative contribution of Q-branches into the integrated radiation of the $15\text{ }\mu$ band under different gas pressures is illustrated by figure 5. It shows the ratio of the integrated absorptivity of the $15\text{ }\mu$ band, $A_{P,R}$ (ignoring the Q-branches) to the total integrated absorptivity, $A_{P,R,Q}$ including P, R and Q-branches, as function of the optical path X . As X decreases, this ratio tends to 1/2 which is the theoretical limit for an optically thin layer ensuing from formula (3.6) and relationship $A \sim S.X$. When the optical path increases the relative contribution of the Q-branches into the radiation of the band decreases. The reason is that the higher absorptivity of Q-branch causes absorption saturation at much lower optical path length as compared with the P and R-branches.

Fig. 5. — Relationship between the integrated absorptivity of P and R-branches of the 15 μ m band and its total absorptivity under different gas pressures. Curve 1 is for $P = 10^{-4}$ atm, $2 \cdot 10^{-3}$, $3 \cdot 10^{-2}$, $4 \cdot 10^{-1}$ and $5 \cdot 1.0$. $T = 300$ K, $T_3 = 1500$ K, $T_{1,2} = 500$ K (distribution (5.1)).

The effects of the translational and vibrational temperatures of gas on the integrated radiation intensity of the 15 μ m band is illustrated in figure 6. The results are shown as relationships between radiation intensity and optical paths length $N_{\text{CO}_2} \cdot D \text{ cm}^{-2}$ (where N_{CO_2} is density of CO₂ molecules) which eliminates the effect of variation of the number of radiating molecules on gas absorptivity.

From the data of figure 6 it is seen that variation of temperature T from 100 to 800 K causes, throughout the investigated optical path range ($N_{\text{CO}_2} D = 5 \times 10^{17} - 10^{19} \text{ cm}^{-2}$), a variation of the integrated radiation intensity of not more than 20%. (The variations of I are shown by the hatched areas near curve 3.) In view of this fact it is possible to use less accurate translational temperature measurements in applications of the radiation characteristics in the 15 μ m band for prediction of vibrational distributions.

The effect of pressure on the integrated radiation intensity in the 15 μ m band is controlled by variations of the collisional broadening of the rotational lines. According to the results of figure 6, the pressure effect on the radiation intensity is particularly tangible for considerable optical lengths $N_{\text{CO}_2} D \sim 10^{19} \text{ cm}^{-2}$. At these $N_{\text{CO}_2} D$ values an increase of pressure by an order of magnitude results in doubling of the radiation intensity. At smaller optical lengths (10^{17} cm^{-2}) the dependence of I on pressure is much weaker, which corresponds to smaller radiation re-absorption. In the limiting case of « weak » lines $K_{v',j' \leftarrow v'',j''} X \ll 1$ the radiation intensity is independent of gas pressure. Note that since the pressure of the active medium of a gasdynamic laser varies in a wide range $P = 10^{-3}$

Fig. 6. — Relationship between the integrated radiation intensity of the 15 μ m band and vibrationally-nonequilibrium gas parameters. Boltzmann distribution (5.1) we assumed in calculations. Gas parameters were: 1 - $P = 10^{-3}$ atm, $1' - P = 10^{-2}$ atm, $1'' - P = 10^{-1}$ atm ($T_{1,2} = 200$ K, $T = 300$ K, $T_3 = 1500$ K); 2 - $T_3 = 1000$ K, $2' - T_3 = 1500$ K, $2'' - T_3 = 2000$ K ($T = 300$ K, $T_{1,2} = 500$ K, $P = 10^{-2}$ atm), 3 - $T = 100$ -800 K, $T_{1,2} = 800$ K, $T_3 = 1500$ K, $P = 10^{-2}$ atm.

to 0.1 atm, the $A(P)$ and $I(P)$ relationships are considerable. Temperature and pressure effect on the integrated absorptivity are similar in behaviour and comparable in magnitude. From the data of figure 6 it follows that the major factor affecting the radiation intensity in the 15 μ m band is the vibrational temperature of the combined mode $T_{1,2}$. A variation of the vibrational temperature $T_{1,2}$ from 200 to 800 K increases the radiation intensity 100-fold (Curves 1, 2 and 3, Fig. 6). The effect of the vibrational temperature of the asymmetric mode T_3 (curves 2, 2' and 2'') on I is much weaker than that of $T_{1,2}$. As a result of calculations carried out in this work it has been found that the effects of the vibrational temperatures T_3 and $T_{1,2}$ and gas pressure on the integrated absorptivity of the 15 μ m band under conditions typical of a CO₂ gasdynamic laser are comparable in magnitudes. Therefore, the vibrational temperature $T_{1,2}$ may be determined from measurements of the integrated radiation intensity of the 15 μ m band.

6.2 SPECTRAL Q-BRANCH PARAMETERS. — A detailed structure of the most intensive Q-branches of the 15 μ m band averaged with respect to the rotational lines is shown, under conditions of figure 4, in figure 7 in the bar chart form. It is seen that the particular form of the function of distribution between vibrational levels strongly affects the spectral distribution of absorption in a number of the Q-branches. The complex structure of the Q-branches numbered 6, 7

Fig. 7. — Absorptivity of the most intensive Q-branches of CO_2 in the $15 \mu\text{m}$ band. Solid lines are for the Boltzmann distribution (5.1) and dash lines for distribution (5.2). Triangles indicate the wave numbers of vibrational transition centres. Gas parameters were: $T_3 = 1\,500 \text{ K}$, $T_{1,2} = 1\,000 \text{ K}$, $T = 100 \text{ K}$, $P = 5 \times 10^{-3} \text{ atm}$, $X = 3.3 \times 10^{-3} \text{ atm.cm}$.

and 10 (in accordance with notations of Table II) is due to the fact that they are formed as a result of superposition of the rotational lines of several vibrational transitions shown in figure 7. Figure 8 shows, under the same conditions a histogram of the spectral absorption of No. 10 Q-branch with resolved rotational structure. The complex, irregular spectral structure is due to superposition in this spectral region of two Q-branches of the transitions $10^0 0-01^1 0$ and $20^0 0-11^1 0$.

Thus the data of figures 7 and 8 prompt a conclusion that the effect of distribution in the bend-stretch manifold on spectral and integrated absorption of the Q-branches in the $15 \mu\text{m}$ band is strong. The absorptivity in Q-branches (Nos. 1-12 in figure 4) is much higher than that in P and R-branches in the corresponding spectral regions. This allows to record absorption in individual intensive Q-branches of the $15 \mu\text{m}$ band. Since the absorptivities of individual Q-branches are determined by the populations of the combining vibrational levels, absorptivity measurements may be used for determining the populations of individual vibrational states of carbon dioxide.

In conclusion, we present comparison of the calculation of absorption in the Q-branches of the $15 \mu\text{m}$ band through the « line-by-line » integration over the spectrum with that based on the vibrational-rotational band theory. The results of comparison are illustrated in figure 9 for Q-branch No. 10. The solid curve represents the $A(\omega)$ calculation data obtained with the help of a statistical band model with the rotational structure averaging range $\Delta\omega = 0.01 \text{ cm}^{-1}$; the histogram gives the data obtained by the « line-by-line » integration over the spectrum; the dash line represents the $A(\omega)$ values averaged within the spectral ranges $\Delta\omega = 0.2 \text{ cm}^{-1}$ obtained *via* the statistical model. It is seen that the discrepancy between the $A(\omega)$ values obtained by the two methods in question

Fig. 8. — Absorptivity of Q-branch No. 10 with allowed rotational structure for the Boltzmann distribution in vibrational levels (5.1). The averaging spectral range was $\Delta\omega = 0.02 \text{ cm}^{-1}$. The gas parameters are the same as in figure 7.

does not exceed 10 %. The integrated absorptivity of Q-branch No. 10 is 3.84 cm^{-1} by the « line-by-line » integration and 3.92 cm^{-1} by the statistical model. Thus the application of the statistical model for Q-branch absorptivity calculations under conditions typical of gas dynamic CO_2 lasers results in an error of not more than 10 % for spectral and 5 % for integrated absorptivity.

6.3 INTEGRATED Q-BRANCH PARAMETERS. — Currently available spectral instruments have a resolution within the $15 \mu\text{m}$ band of the order of $0.2\text{-}2.0 \text{ cm}^{-1}$. Using them it is possible to determine the integrated characteristics of Q-branches having a spectral width

Fig. 9. — Comparison of Q-branch No. 10 absorptivity calculations *via* « line-by-line » integration over the spectrum (the bar chart represented by the solid line) and using the statistical model (solid curve); the dash line is the bar chart for calculation *via* the statistical model : $T_3 = 1\,500\text{ K}$, $T_{1,2} = 1\,000\text{ K}$, $T = 100\text{ K}$, $P = 5 \times 10^{-3}\text{ atm}$, $X = 3.3 \times 10^{-3}\text{ atm.cm}$. Boltzmann distribution.

of between 0.5 and 1.5 cm^{-1} . Therefore, further investigations in this work concerned the integrated absorption of Q-branches of which the most intensive were chosen where absorption is much higher than that in P and R-branches. The branches of the spectral regions Nos. 6 and 7 were not considered because the Q-branches of many transitions overlapped at these points. Besides, the strong re-absorption in spectral region No. 7 of atmospheric CO₂ adversely affects measurement accuracy.

The results of investigation of the relationships between the integrated absorption of Q-branches and optical path length are shown in figure 10. It is seen that the radiation in Q-branches is re-absorbed. As the optical path length increases the A *versus* X relationship becomes weaker. The data of figure 10 also illustrate the relative integrated absorptivity in the most intensive Q-branches of the $15\text{ }\mu\text{m}$ band.

Results of investigation of the effect of vibrationally-nonequilibrium gas parameters — pressure P , translational T and vibrational T_3 and $T_{1,2}$ temperatures — are shown in figures 10 to 13 under assumption of Boltzmann distribution.

The relationship between the integrated absorptivity of Q-branches of the $15\text{ }\mu\text{m}$ band, A , and gas pressure is shown in figure 11. For weak Q-branches (Nos. 1, 3, 9) a gas pressure variation by as much as three orders of magnitude from 10^{-4} to 0.1 atm results in no larger than a 30 % increase of absorption. For more intensive Q-branches the corresponding increase is a 2-4 fold one which is tangible. The increase of A dependence on pressure P in intensive Q-branches is

Fig. 10. — Integrated absorptivity of Q-branches as function of the optical path X : $T_3 = 1\,500\text{ K}$, $T_{1,2} = 1\,000\text{ K}$, $P = 5 \times 10^{-3}\text{ atm}$, $T = 100\text{ K}$. Distribution is Boltzmann.

Fig. 11. — Effect of gas pressure on integral absorption of Q-branches of the $15\text{ }\mu\text{m}$ band : $T_3 = 1\,500\text{ K}$, $T_{1,2} = 1\,000\text{ K}$, $T = 100\text{ K}$, $X = 3.3 \times 10^{-3}\text{ atm.cm}$.

due to the increased radiation re-absorption and line overlapping.

The effect of gas temperature on integrated absorptivity of Q-branches is illustrated in figure 12. For intensive branches (Nos. 4, 5, 8 and 10) the integrated absorptivity increases by 20-30 % as temperature T varies from 50 to 300 K. In the less intensive Q-branches the corresponding increases do not exceed 5 %. The increased absorption with increase of gas temperature is due to a smaller radiation re-absorption owing to molecular redistribution between a larger number of rotational levels.

Fig. 12. — Effect of translational gas temperature on integrated absorptivity of Q-branches (for a constant total number of molecules over the geometrical path) : $T_3 = 1\,500\text{ K}$, $T_{1,2} = 1\,000\text{ K}$, $P = 5 \times 10^{-3}\text{ atm}$, $X = X_0 \frac{T}{T_0} X_0 = 10^{-2}\text{ atm.cm}$ is the optical path under normal conditions.

The effect of vibrational temperature of the asymmetric mode on the absorption of these Q-branches is shown in figure 13. For all the investigated Q-branches, except No. 9, the dependence is weak and has a tendency to decrease. The reason is molecular redistribution over a larger number of vibrational levels resulting in smaller populations of the combining levels. For Q-branch No. 9 corresponding to the transition between the levels with excited asymmetric mode, $10^0 1-01^1 1$, the integrated absorptivity increases approximately 4 times as the temperature T_3 increases from 1 000 to 1 800 K. This is due to the dependence of the integrated intensity of the transition on the population of the lowest combining level

$$S \sim N_{i''} \sim \exp\left(-\frac{hc}{k} \frac{E_{000} v_3}{T_3}\right).$$

Therefore, it is possible to predict the vibrational temperature T_3 of the asymmetric mode according to the integrated absorptivity in Q-branches corresponding to the transitions between vibrational states with $v_3 \geq 1$ with a high degree of certainty.

The effect of vibrational temperature of the bend-stretch manifold on the integrated absorptivity of Q-branches is illustrated in figure 14 under assumption of Boltzmann distribution between the CO_2 vibrational levels. It is seen that for the intensive Q-branches (Nos. 4, 8, 9 and 10 [10]) the $A(T_{1,2})$ relationship is considerable and has a maximum within $T_{1,2} = 600\text{--}900\text{ K}$. The dotted line shows the variation (in relative units) of the integrated intensity

Fig. 13. — Relationship between integrated absorptivity of Q-branches in the $15\text{ }\mu\text{m}$ band and vibrational temperature of the asymmetric mode T_3 : $T_{1,2} = 1\,000\text{ K}$, $P = 5 \times 10^{-3}\text{ atm}$, $T = 100\text{ K}$, $X = 3.3 \times 10^{-3}\text{ atm.cm}$.

Fig. 14. — Relationship between integrated absorptivity (solid line) of Q-branches and vibrational temperature of the combined mode $T_{1,2}$: $T_3 = 1\,500\text{ K}$, $T = 100\text{ K}$, $P = 5 \times 10^{-3}\text{ atm}$, $X = 3.3 \times 10^{-3}\text{ atm.cm}$. Distribution of CO_2 molecules between vibrational levels was assumed to be Boltzmann. The dash line represents the integrated intensity calculation results for the vibrational transition $02^0 0-01^1 0$ generating Q-branch No. 4 (in relative units).

S_4 of the vibrational transition $02^0 0-01^1 0$. The S_4 versus $T_{1,2}$ relationship is given by the product [21] :

$$S_4(T_{1,2}) \sim e^{-\theta_2/T_{1,2}} (1 - e^{-\theta_2/T_{1,2}})^2 \times (1 - e^{-\theta_1/T_{1,2}}) (1 - e^{-\theta_2/T_{1,2}})$$

where the first factor is the ratio of the populations of the lowest level and the ground state, the second and the third factors are related with the vibrational partition function of carbon dioxide and the latter accounts for the effect of induced radiation. From figure 14 it is seen that the relationships $A(T_{1,2})$ and $S(T_{1,2})$ correlate neatly. Therefore, considering the above expression for $S(T_{1,2})$ one may assume that the decrease of the integrated absorptivity of Q-branches at elevated temperatures $T_{1,2}$ is due to molecular redistribution among a larger number of vibrational levels, equalization of combining level populations resulting in an increased contribution of stimulated radiation. On the basis of the data of figure 14 one may single out the Q-branches and the corresponding $T_{1,2}$ ranges in which the $A(T_{1,2})$ relationships are strong. Under conditions stipulating the Boltzmann distribution in CO₂ integrated absorptivity measurements in Q-branches Nos. 4 and 10 for $T_{1,2} < 600$ K and Nos. 5 and 8 for $T_{1,2} < 800$ K may be recommended for predicting the vibrational temperature of the combined mode $T_{1,2}$. For determination of the vibrational temperature T_3 one may recommend Q-branch No. 9 as the most intensive one for which, as it has been established in this work, the A versus T_3 relationship is considerable. The possibility of selection of Q-branches for which the dependence of integrated absorptivity on the vibrational temperatures of the asymmetric and combined modes prevail over the dependences on other parameters of vibrationally-excited gas — a condition necessary for the experimental determination of T_3 and $T_{1,2}$ — is illustrated by the data of table IV. Within the above mentioned range of gas parameters, the value $\frac{\partial \ln A}{\partial \ln T_{1,2}}$ characterizing the degree of A dependence on $T_{1,2}$ is as high as 1.7 for Q-branches Nos. 5 and 8 and 1.0 for Nos. 4 and 10, whereas the corresponding logarithmic derivatives with respect to pressure and temperature do not exceed 0.4-0.5 and 0.2, respectively. Note that in accordance with the abovesaid, the value of $\frac{\partial \ln A}{\partial \ln T_3}$ for Q-branch No. 9 is also high $\simeq 2.0$. Thus using the measurements of integrated absorptivity in the Q-branches it is possible to reproduce the vibrational temperatures of the asymmetric mode T_3 and bend-stretch manifold $T_{1,2}$.

If, eventually, the distribution in the combined mode is other than Boltzmann, the investigations carried out in this work have permitted to reproduce populations of individual vibrational levels according to the integrated absorptivity measurements in the Q-branches of the 15 μm band. The integrated intensity of an individual transition S_i and, consequently, the spectral and integrated absorptivities of Q-branches depend on the difference of populations of the combining levels $N_L - N_U$, where N_L and N_U are the populations of the lower and the upper levels, respectively. In the limiting cases of $N_L \ll N_U$ and

$N_L \gg N_U$, the radiation characteristics of Q-branches depend basically on the population of one of the combining levels. The values characterizing the dependence of the integrated absorption of Q-branches on the difference of combining level populations and populations of the upper and lower levels are listed in table V. Calculations were carried out for the distribution between the CO₂ vibrational levels defined by (5.2) under conditions typical of CO₂ gas dynamic lasers operating at wavelengths $\lambda = 16\text{-}19\text{ }\mu\text{m}$. The effects of pressure P , vibrational temperature of the asymmetric mode T_3 and rotational temperature on the integrated intensity of Q-branch are about the same as those in figures 11 to 14 where Boltzmann distribution between CO₂ vibrational levels was assumed. It is seen that the degree of dependence on $N_L - N_U$, N_L , N_U is 3 to 10 times as strong as that on T_3 , P and T (Table IV). Therefore, from measurements of the integrated radiation parameters of Q-branches one may obtain reliable estimates of the

Table IV. — *Logarithmic derivatives of integrated absorptivity of Q-branches with respect to vibrationally-nonequilibrium gas parameters : $T_3 = 1\,500\text{ K}$, $T_{1,2} = 1\,000\text{ K}$, $T = 100\text{ K}$, $P = 5 \times 10^{-3}\text{ atm}$, $X = 3.3 \times 10^{-3}\text{ atm.cm}$.*

Q-branch No.	$\frac{\partial \ln A}{\partial \ln T}$	$\frac{\partial \ln A}{\partial \ln T_3}$	$\frac{\partial \ln A}{\partial \ln P}$
1	0.05	− 0.15	0.3
3	0.05	− 0.24	0.2
4	0.15	− 0.14	0.3
5	0.25	− 0.15	0.4
8	0.25	− 0.15	0.4
9	0.01	2.0	0.01
10	0.20	− 0.15	0.46

Table V. — *Logarithmic derivatives of absorptivity of Q-branches with respect to the populations of the lower and upper combining levels, N_L , N_U and their difference $N_L - N_U$. Distribution over vibrational levels is (5.2).*

Q-branch No.	$\frac{\partial \ln A}{\partial \ln N_L - N_U }$	$\frac{\partial \ln A}{\partial \ln N_L}$	$\frac{\partial \ln A}{\partial \ln N_U}$
1	1.15	− 20.2	21.4
3	0.895	4.70	− 3.80
4	0.877	4.08	− 3.2
5	0.638	1.32	− 0.68
8	0.791	1.11	− 0.31
9	0.890	1.08	− 0.19
10	0.595	0.73	− 0.13
12	0.841	0.97	− 0.13

difference $N_L - N_U$ or populations of one of the combining levels N_L, N_U in the limiting cases $N_L \ll N_U$ and $N_L \gg N_U$. By measuring in the corresponding Q-branches it is possible to determine the populations of all the levels of the CO_2 bend-stretch manifold of interest. The populations of the equidistant levels $ov_2^l 0$ ($l = v_2$) should best be determined from integrated radiation measurements, as described above.

As an example consider evaluation of the population of the vibrational state $02^0 0$ which is the upper laser level for a CO_2 gasdynamic laser operating by the $02^0 0-01^1 0$ transition at $\lambda = 16.2 \mu\text{m}$. For populations of the combining levels $N_{02^0 0}$ and $N_{01^1 0}$ that typically have the same order of magnitude in this laser type, the value of $N_{01^1 0}-N_{02^0 0}$ is determined from integrated absorption measurements in Q-branch No. 4 of the transition $02^0 0-01^1 0$. If the equidistant level $01^1 0$ population is simultaneously determined according to the integrated radiation of the $15 \mu\text{m}$ band it is possible to evaluate the population of the level $02^0 0$.

When the population ratio $N_{02^0 0}/N_{01^1 0} \ll 1$, the accuracy of the above $N_{02^0 0}$ determination procedure is poorer. Basing on the vibrational relaxation kinetics data [31] one may safely state that under these

conditions $N_{03^1 0}/N_{02^0 0} \ll 1$. This permits the population of the $02^0 0$ level to be determined from the integrated absorptivity in Q-branch No. 5 (generated by the vibrational transition $03^1 0-02^0 0$) which depends basically on the population of the $02^0 0$ level: $A(N_{02^0 0}-N_{03^1 0}) \simeq A(N_{02^0 0})$. The population of $10^0 0$ may be determined in a similar manner from the absorption data for Q-branches Nos. 10 or 8 and that of $03^1 0$ from the data for Nos. 1 or 3, etc.

7. Conclusion.

A method for determination of vibrational level population distribution in CO_2 molecules has been developed on the basis of investigation of the relationship between the radiation characteristics of the $15 \mu\text{m}$ band of vibrationally excited CO_2 and gas parameters. According to this method the vibrational temperature $T_{1,2}$ is found from measurements of the integrated radiation intensity of the $15 \mu\text{m}$ band and the populations of individual vibrational levels and the asymmetric mode temperature T_3 from integrated absorptivity measurements in individual Q-branches.

References

- [1] KUDRYAVTSEV, N. N., NOVIKOV, S. S., SVETLICHNY, I. B., *Experimental investigation of vibrational energy exchange in laser-active chemically reacting gas mixtures*. In : Plasma Chemistry, Atomizdat, Moscow (1979), N° 6.
- [2] SMIRNOV, B. M., SHLYAPNIKOV, G. V., *Infrared radiation transfer in molecular gases*, *Usp. Fiz. Nauk*, **130** (1980) 377.
- [3] KOPYLOVA, L. I., PODKLADENKO, M. V., *The emissivity of heated carbon dioxide in the $2\,100-2\,500\text{ cm}^{-1}$ region in absence of thermodynamic equilibrium*. *Zh. Prikl. Spektro.* **12** (1970) 811.
- [4] HODGSON, J. K., *The non-equilibrium emissivity of carbon dioxide near $4.2 \mu\text{m}$* . Aeronaut. Res. Council. Current Paper, London (1970) N° 111b.
- [5] BIHL, S., FOUASSIER, J. P., JOECKLE, R., *Calcul de l'émission infrarouge de milieu laser CO_2* . *J. Quart. Spectrosc. Rad. Transfer* **14** (1974) 819.
- [6] KHMELININ, B. A., PLASTININ, Yu. A., *Radiation and absorption properties of H_2O , CO_2 , CO and HCl molecules at temperatures of $300-3\,000\text{ K}$* . In : Proc. Central Aero-Hydrodynamics Inst., Moscow (1975) N° 1656.
- [7] LOSEV, S. A., *On infrared radiation of carbon dioxide under nonequilibrium conditions*. In : Proc. Inst. Mech. Affiliated to the Moscow State University **43** (1976) 79.
- [8] KUDRYAVTSEV, N. N., NOVIKOV, S. S., SVETLICHNY, I. B., *Method and results of experimental determination of CO_2 vibrational temperature in nonequilibrium flows using vibrational rotational band models*. *Dokl. AN SSSR* **231** (1976) 1419.
- [9] VAGIN, S. P., VORONTSOV, S. S., YAKOBI, Yu. A., *Infrared luminescence of the active medium of CO_2 laser*. *Zh. Prikl. Spektro.* **29** (1978) 621.
- [10] BAKHIR, L. P., OVCHARENKO, B. V., *Determination of populations of CO_2 vibrational levels in gasdynamic lasers by the IR spectroscopy method*. *Zh. Prikl. Spektro.* **30** (1979) 44.
- [11] KUDRYAVTSEV, N. N., NOVIKOV, S. S., *A study of infrared radiation of vibrationally excited CO in the 4.7 micron band and CO_2 in the 2.7 and 4.3 micron bands*. *Revue Phys. Appl.* **16** (1981) 49.
- [12] KUDRYAVTSEV, N. N., NOVIKOV, S. S., *Numerical study of spectral emissivity and absorptivity of CO and CO_2 molecules under vibrationally-nonequilibrium conditions*. *Inzhenerno-Fiz. Zhurnal* **42** (1982) 805.
- [13] KUDRYAVTSEV, N. N., NOVIKOV, S. S., *Integral radiation and absorption characteristics of CO and CO_2 bands in vibrationally-nonequilibrium conditions*. *Zh. Prikl. Spektro.* **37** (1982) 125.
- [14] KRYUCHKOV, S. I., KUDRYAVTSEV, N. N., NOVIKOV, S. S., *On a method of CO_2 vibrational distribution determination in rarefield flows*. In : 13th Inter-

- national Symposium on Rarefied Gas Dynamics, Novosibirsk, July 5-9, vol. 1 (1982), p. 235.
- [15] BASOV, N. G., MIKHAILOV, V. G., ORAEVSKY, A. N., SHCHEGLOV, V. A., *Population inversion of molecules in a supersonic flow of binary gas in a Laval nozzle. Zhurn. Tekhn. Fiz.* **38** (1968) 2031.
- [16] MANUCCIA, T. I., STREGACK, J. A., HARRIS, N. W., WEXIER, B. L., *14 and 16-micron gasdynamic CO₂ lasers. Appl. Phys. Lett.* **29** (1976) 360.
- [17] ANDRADE E SILVA, M. H., AMAT, G., *Influence of Fermi-resonance on the rotational constants of linear triatomic molecules. J. Mol. Spectros.* **29** (1969) 384.
- [18] ROTHMAN, L. S., BENEDICT, W. S., *Infrared energy levels and intensities of carbon dioxide. J. Quant. Spectr. Rad. Transf.* **25** (1981) 505-524.
- [19] HERZBERG, G., *Infrared and Raman spectra of polyatomic molecules* (D. van Nostrand Company, Inc. New York) 1946.
- [20] LANDAU, L. D., LIFSHITS, E. M., *Nonrelativistic Quantum mechanics* (Nauka, Moscow) 1974 (in Russian).
- [21] PENNER, S. S., *Quantitative molecular spectroscopy and gas emissivities* (Addison-Wesley Publ. Co., Inc., reading, Mass.) 1959.
- [22] GOODY, R. M., *Atmospheric radiation* (Oxford Univ. Press, Oxford-London) 1963.
- [23] YAMAMOTO, T., TANAKA, M., AOKI, T., *Estimation of the rotational line width of carbon dioxide bands, J. Quant. Spectr. Rad. Transf.* **9** No 3 (1969) 371-382.
- [24] MADDEN, R. P., *A high-resolution study of CO₂ absorption between 15 and 18 microns. J. Chem. Phys.*, **35** No 6 (1961) 2083-2097.
- [25] DRAYSON, S. R., YOUNG, C., *Band strength and line half-width of the 10.4 micron CO₂ band. J. Quant. Spectr. Rad. Transf.* **7** No 6 (1967) 993-997.
- [26] PLANET, W. G., TEFFEMER, G. L., KNOLL, J. S., *Temperature dependence of intensities and widths of N₂-broadened lines in the 15 μm CO₂ band from tunable laser measurements. J. Quant. Spectr. Rad. Transf.* **20** (1978) 547-556.
- [27] LUDWIG, C. B., MALKMUS, W., REARDON, I. E., THOMSON, I. A. L., *Handbook of infrared radiation from combustion gases* (NASA Report, SP-3080, Washington) 1973.
- [28] ENG, R. S., MANTZ, A. W., *Tunable diode laser spectroscopy of CO₂ in the 10 to 15 micron spectral region. Lineshape and Q-branch head absorption profile. J. Mol. Spectros.* **74** (1979) 331.
- [29] COTTRELL, T. L., MCCOUBRAY, J. C., *Molecular energy transfer in gases* (Butterworths, London) 1961.
- [30] ANDERSON, L. D., *Gas dynamic lasers : an introduction* (Wiley-Acad. Press, New York-London) 1976.
- [31] LOSEV, S. A., *Gas dynamic lasers* (Nauka, Moscow) 1977 (in Russian).
- [32] LIHALTER, A. A., *On relaxation of CO₂ symmetric mode. Zh. Prikl. Mekh. Tekhn. Fiz.* **3** (1975) 8.
- [33] BURCH, D. E., CRYVNAK, D. A., WILLAMS, D., *Infrared Absorption of Carbon Dioxide. Appl. Optics* **17** (1962) 2605.
- [34] DRAYSON, S. R., *Atmospheric Transmission in the CO₂ Bands Between 12 μ and 18 μ. Appl. Optics* **5** (1966) 385.
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