In this case

$$\frac{R_j^1 S_{jJ}^1}{R_j^0} \approx \begin{cases} 3.3 \cdot 10^{-3} (S_j^1)^2 / R_j^0 & \text{for } \varkappa r = 1, \\ 3.54 \cdot 10^{-2} (S_j^1)^2 / R_j^0 & \varkappa r = 3, \end{cases}$$

$$\frac{R_j^2 S_{jJ}^2}{R_j^0} \approx \begin{cases} 5.7 \cdot 10^{-5} (S_{j,k\to k}^2)^2 / R_j^0 & \text{for } \varkappa r = 1, \\ 4 \cdot 10^{-3} (S_{j,k\to k}^2)^2 / R_j^0 & \varkappa r = 3. \end{cases} \quad (5.1)$$

Substituting in (5.1) the values given in Table 4 we can see that the cross sections of multiquantum transitions can be comparable with the cross sections of transitions with $\Delta j = 0$. Hence, the picture of rotational relaxation of the water molecules is very complex and a detailed analysis is required for determination of the main relaxation channels.

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RESONANCE ABSORPTION OF EMISSION (10.6 μm) IN CO_2–N_2 MIXTURES BEHIND A SHOCK FRONT

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An important parameter affecting the shape of the absorption (amplification) line is the collisional width of the spectral line. In application to flows of CO_2–N_2–H_2O (He) mixtures the accuracy of its assignment throughout the range of the translational temperature of the flow as the gas cools in a nozzle significantly affects the correctness of calculation of the amplification factor of the medium. The question of the temperature dependence of the CO_2 molecule spectral line width is of particular importance in the construction of mathematical models of vibrational energy transfer, if the criterion of their correctness in the comparison of theory and experiment is the amplification factor.

The value of the collisional width b_c of the spectral line for the CO_2 molecule is known sufficiently accurately at T = 300°K for CO_2–N_2–He mixtures [1]. Yet, despite the fairly large number of investigations of the temperature dependence $b_c(T)$ [2-5], this question still remains open. Different forms of $b_c = f(T)$ have been proposed to improve the agreement between the theoretical and experimental temperature dependences of the absorption coefficient in CO_2. For instance, in [2] the best agreement between theory and experiment at T = 360-400°K was obtained on the assumption that $b_c \sim T^{-3/2}$, whereas in [4] the relation $b_c \sim 1/T$ was used to explain the experimental results up to T = 1600°K and the contribution of the "hot" transitions $R23(01^11 \to 11^10)$ and $R4(02^01 \to 12^00)$ was taken into account. At the same time, in [3, 5] the charge in absorption coefficient k_ν with temperature could be explained on the assumption that $b_c \sim T^{-1/2}$, including a consideration of the contribution of additional transitions and the overlap of the rotational bands at $p > 1$ atm and $T > 1000$°K. It should also be noted that these investigations were mainly concerned with the relation $k_\nu(T)$ in pure CO_2, and there are hardly any data for CO_2–NO_2 mixtures.

To determine the temperature dependence of the collisional width of the collision line in CO_2–N_2 mixtures in the present investigations we considered the behavior of the absorption coefficient on the P20 ($00^01 \to 10^00$) transition of the CO_2 molecule behind a straight shock front for temperatures in the range 700-1250°K and N_2 content of the mixture 0-95%.

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In the general case the value of the absorption coefficient of the medium behind a straight shock front is not determined uniquely by the values of the translational temperature and pressure, but also depends on nonequilibrium parameters characterizing the distribution of energy over the internal degrees of freedom of the mixture molecules [6]. Hence, determination of the relation $k_\nu = f(T)$ requires the conduction of measurements at the end of the relaxation zone, when complete thermodynamic equilibrium has been established. For this purpose in this investigation we considered in each specific case the establishment of equilibrium in the relaxation zone behind a shock front, taking into account V–T and V–V processes of vibrational energy transfer in CO_2–N_2 mixtures. The nonequilibrium parameters in the flow were calculated by the method discussed in [6]. The amplification factor of the medium was determined in accordance with the calculated values of the nonequilibrium parameters at each point in the relaxation zone on the assumption of combined action of Doppler and collisional mechanisms of broadening [1, 7].

In the analysis of the temperature dependence of the absorption coefficient we considered two forms of $b_c(T)$: $b_c \sim 1/T$ and $b_c \sim T^{-1/2}$. The first corresponds to the hypothesis of variation of the collisional broadening cross sections $\sigma_i^{CO_2}$ with temperature as $T^{1/2}$, while the second corresponds to $\sigma_i^{CO_2} = \text{const}$.

The Einstein coefficient for the P20($00^\circ 1 \rightarrow 10^\circ 0$) transition is known sufficiently accurately at present and was taken, according to [1], as 0.187 sec^{-1}, while the values $b_{CO_2-CO_2} = 0.191$ $cm^{-1}\cdot atm^{-1}$ and $b_{CO_2-N_2} = 0.73\ b_{CO_2-CO_2}$ were taken from [1, 7].

The experiments were conducted in a large-diameter shock tube. We used the absorption measurement procedure described in [8] and modified so that the flow in two cross sections behind the shock front was probed simultaneously. The distance between the measurement sections was 19 mm. The error of experimental determination of the absorption coefficient was estimated for a sample of ten experiments, conducted in similar conditions by the method of [9], and did not exceed 10%. The simultaneous measurement of absorption for two independent channels enabled us to convert the systematic errors to random errors.

The width of the spectral line of the master CO_2 laser was much less than the corresponding value for the absorption line. Hence, all the calculations were made for the line center.

The establishment of thermodynamic equilibrium behind the shock front was determined from the leveling out of the absorption coefficient. The parameters behind the "viscous shock" front were calculated from known values of the shock wave velocity, pressure, and temperature of the motionless gas. The temperature was held constant at $T_1 = 293^\circ K$, while the pressure varied from 0.018 to 0.021 atm. The error in determination of the shock wave velocity did not exceed 2%, and its value lay in the range 0.89-1.48 mm/μsec. Since the boundary-layer thickness δ is small in comparison with the tube diameter ($\delta/D = 0.004$) its effect on the shock wave velocity and curvature of the front was ignored.

In the analysis of the experimental results obtained in measurement of the absorption coefficient we took into account the contribution of "hot" transitions to the value of k_ν, and its value was calculated from the relation

$$k_\nu = k_\nu[P_{20}(10^00 - 00^01)] + k_\nu[R_{23}(01^11 \rightarrow 11^10)] + k_\nu[R_4(02^01 \rightarrow 12^00)].$$

For the additional transitions of the R branch the values of the Einstein coefficients and collisional broadening cross sections were selected in accordance with the data of [5]. It should be noted that in the considered temperature range ($T = 700$-$1250^\circ K$) the contribution of these transitions to the value of the absorption coefficient did not exceed 0.1 k_ν [P20($10^\circ 0 \rightarrow 00^\circ 1$], as was mentioned in [5].

The pressure behind the shock front throughout the range of measurements did not exceed 0.55 atm. Hence, in accordance with [5], the effects of overlap of the rotational bands were ignored. Since there was some uncertainty in the frequency of the master laser in the experiment, we performed the calculations for two vibrational–rotational lines of the ($10^\circ 0 \rightarrow 00^\circ 1$) transition – P20 and P22 (Fig. 1, continuous and dot-dash lines, respectively). The results of comparison of the calculated [on the assumption of $b_c \sim T^{-1/2}$ (continuous lines) and $b_c \sim T^{-1}$ (dashed lines)] and measured values of the absorption coefficient (k_ν) for three different CO_2–N_2 mixtures with $\gamma_{CO_2} = 0.05$, 0.15, and 0.4 at temperatures from 700 to $1250^\circ K$ are shown in Fig. 1a-c, respectively. It is apparent that over the whole investigated temperature range the best agreement between theory and experiment is obtained when we assume that the collisional broadening cross sections are independent of the temperature ($b_c \sim 1/\sqrt{T}$) for CO_2– N_2 mixtures. At the same time, the assumption that $b_c \sim T^{-1}$ leads to a considerable overestimate of the theoretical values of k_ν in comparison with the experimental values, which for a CO_2–N_2 mixture (0.05-0.95) reaches 100%. The same trend is exhibited by CO_2–N_2 mixtures of other compositions. This is illustrated by Fig. 2, where the plots of $k_\nu = f(\gamma_{CO_2})$ for the two considered relations $b_c = f(T)$ are shown. The temperature behind the shock front for the whole range of CO_2 content ($\gamma_{CO_2} = 0.05$-0.1) in this case lay between 740 and $850^\circ K$, and the pressure between 0.216 and 0.266 atm.

Thus, our analysis of the variation of the absorption coefficient behind a straight shock front in relation to temperature and molecular nitrogen content of a CO_2–N_2 mixture shows that the best agreement between the calculated and

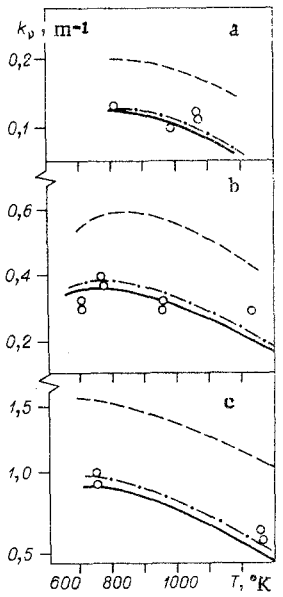

Fig. 1

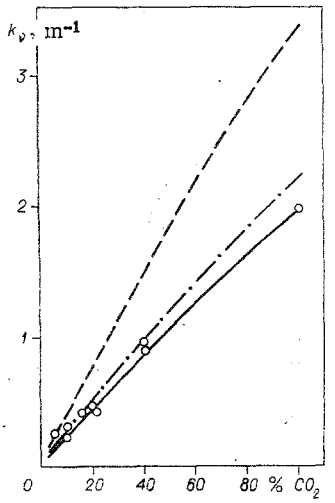

Fig. 2

measured values of the absorption coefficient is obtained by using the relation $b_c \sim T^{-1/2}$, i.e., on the assumption that the collisional broadening cross sections are independent of temperature.

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