INVERTED POPULATION OF CO_2 MOLECULES IN EXPANDING GAS STREAMS

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The system of equations of hydrodynamics, which describes the process of escape of the mixtures $CO_2 + N_2 + He$, H_2O from a nozzle, is solved numerically in conjunction with the equations of the kinetics of the excitation of the vibrational degrees of freedom of the molecules. It is found that an inverted population of the CO_2 molecules with respect to the transition [00°1] – [10°0], is produced under certain conditions at the exit from the nozzle. The magnitude of the inversion depends both on the nozzle configuration and on the initial values of the gas temperature and pressure. It is shown that for a specified nozzle configuration there exist optimal values of these parameters, at which the inverted population of the CO_2 molecules reaches approximately 10^{15} cm^{-3}.

The possibility of obtaining inverted population of the vibrational levels in rapidly expanding streams of molecular gas, particularly in a $CO_2 + N_2$ mixture, was indicated in [1, 2]. The theory of gas-dynamic quantum generators was developed in [3-6]. In these studies, the gas molecules were regarded as harmonic oscillators that exchange energy by collision. In the calculations they used a model proposed in [7] and based on the assumption that local thermodynamic equilibrium with a certain temperature T_i prevails over levels that belong to a definite normal oscillation mode i.

The vibrational relaxation of a $CO_2 + N_2$ system escaping from a Laval nozzle was investigated in [3]. The probability of exciting the vibrational levels of CO_2 by collisions with N_2 and CO_2 molecules and the probabilities of exchange of quanta between different modes of CO_2, and also between the molecules N_2 and CO_2, were determined in accordance with the Landau–Teller theory developed by Herzfeld and co-workers [8]. It should be noted, however, that the expression given in [8] for the transition probabilities does not take due account of either the attraction forces between the molecules, which play an important role at low temperatures, or the orientation of the molecules upon collision [9].

An important question in these problems is the determination of the energy-exchange probability near resonance. Thus, for example, experiment shows that the Landau–Teller theory does not give the correct temperature dependence for energy exchange between vibrational degrees of freedom of N_2 and asymmetric valence vibrations of CO_2. In this case, according to [10], the exchange probability is determined entirely by attraction forces and not by repulsion forces as assumed in the Landau–Teller theory.

The vibrational relaxation of $CO_2 + N_2 + He$ mixtures in free expansion was calculated in [4].

In [5], which reports the results of an investigation of the chemical and vibrational relaxation in supersonic streams of carbon dioxide, the expressions used for the probabilities take full account of the attraction forces within the framework of the Landau–Teller theory, but the orientation factor differs significantly from the data obtained in [9], which should perhaps be regarded as the most reliable.

On the other hand, for energy exchange close to resonance, the temperature dependence of the probabilities given in [5] does not agree with the experimental data.

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In [6], in a calculation of the behavior of the system $CO_2 + N_2 + H_2O$ in expanding streams, only the experimental values of the probabilities of transition between levels were used. It was assumed there that the exchange of quanta between the (10°0) and (02°0) state of CO_2, and also between $CO_2(00^\circ1)$ and N_2, occurs instantaneously.

The results of the calculation in [6] do not represent a systematic investigation of the vibrational relaxation following expansion of the gas in the nozzle; they pertain only to one variant, when $T_0 = 1500°K$ and $p_0 = 10$ atm. The case $T_0 = 5100°K$ without allowance for dissociation has no practical significance.

In the present paper we report a systematic study of the influence of nitrogen, helium, and water vapor on the degree of inverted population of the (00°1) level of the carbon dioxide molecule, and also its dependence on the temperature, gas pressure, and nozzle configuration. The probabilities of the processes of excitation and deactivation of the vibrational levels of the molecules CO_2, N_2, and H_2O were taken mainly from the experimental papers.

We consider adiabatic one-dimensional flow of a multicomponent mixture of relaxing gases in a nozzle of special configuration. The mass, momentum, and energy conservation equations and the equation of state for this flow are

$$A(x)\rho u = A_*\rho_* u_* \tag{1}$$

$$\rho u \frac{du}{dx} = -\frac{dp}{dx} \tag{2}$$

$${}^7/_2 kT + \alpha^{(1)} \sum_{i=1}^{3} E_i + \alpha_4^{(2)} E_4 + {}^1/_2 mu^2 = mH_0 \tag{3}$$

$$p = \rho \frac{k}{m} T \tag{4}$$

Here ρ, u, T, and p are respectively the density, velocity, temperature, and pressure; $\alpha^{(s)}$ are the molar fractions of the mixture component; $m = \sum_s \alpha^{(s)} m^{(s)}$; $m^{(s)}$ is the mass of the molecule of the s-th component; H_0 is the specific drag enthalpy; E_i is the vibrational energy of one gas particle. The indices s = 1, 2, 3, and 4 pertain to CO_2, N_2, He, and H_2O, respectively; and the indices i = 1, 2, 3 pertain to the symmetric-valent, deformation, and asymmetric-valent vibration modes of the CO_2 molecule; i = 4 denotes the vibrational motion of the N_2 molecule. The values in the critical cross section of the nozzle are marked with an asterisk.

We investigate in the present paper the vibrational relaxation of two mixtures $CO_2 + N_2 + He, H_2O$, for which the following scheme of reactions is assumed:

$$CO_2(01^10) + M \underset{K_{-1}}{\overset{K_1}{\rightleftarrows}} CO_2(00^00) + M + \Delta\varepsilon_1 \tag{5}$$

$$CO_2(00^01) + N_2(0) \underset{K_{-2}}{\overset{K_2}{\rightleftarrows}} CO_2(00^00) + N_2(1) + \Delta\varepsilon_2 \tag{6}$$

$$N_2(1) + H_2O(00^00) \underset{K_{-3}}{\overset{K_3}{\rightleftarrows}} N_2(0) + H_2O(01^10) + \Delta\varepsilon_3 \tag{7}$$

$$CO_2(00^01) + H_2O(00^00) \underset{K_{-4}}{\overset{K_4}{\rightleftarrows}} CO_2(00^00) + H_2O(01^10) + \Delta\varepsilon_4 \tag{8}$$

$$CO_2(00^00) + H_2O(01^10) \underset{K_{-5}}{\overset{K_5}{\rightleftarrows}} CO_2(01^10) + H_2O(00^00) + \Delta\varepsilon_5 \tag{9}$$

$$CO_2(00^01) + H_2O(00^00) \underset{K_{-6}}{\overset{K_6}{\rightleftarrows}} CO_2(01^10) + H_2O(01^10) + \Delta\varepsilon_6 \tag{10}$$

$$CO_2(00^00) + H_2O\,(01^10) \underset{K_{-7}}{\overset{K_7}{\rightleftarrows}} CO_2(10^00) + H_2O\,(00^00) + \Delta\varepsilon_7 \tag{11}$$

$$CO_2(10^00) + M \underset{K_{-8}}{\overset{K_8}{\rightleftarrows}} CO_2(02^00) + M + \Delta\varepsilon_8 \tag{12}$$

$$CO_2(00^01) + M \underset{K_{-9}}{\overset{K_9}{\rightleftarrows}} CO_2(03^10) + M + \Delta\varepsilon_9 \tag{13}$$

$$CO_2(00^01) + M \underset{K_{-10}}{\overset{K_{10}}{\rightleftarrows}} CO_2(11^10) + M + \Delta\varepsilon_{10} \tag{14}$$

$$CO_2(10^00) + H_2O \underset{K_{-11}}{\overset{K_{11}}{\rightleftarrows}} CO_2(00^00) + H_2O + \Delta\varepsilon_{11} \tag{15}$$

$$N_2(1) + M \underset{K_{-12}}{\overset{K_{12}}{\rightleftarrows}} N_2(0) + M + \Delta\varepsilon_{12} \tag{16}$$

Here M is any of the particles CO_2, N_2, He, H_2O; $\Delta\varepsilon_j$ is the heat of the j-th reaction; K_j and K_{-j} are the rate constants of the direct and inverse reactions, respectively ($j = 1, \ldots, 12$).

It is assumed that during the course of the development of reactions (5)-(16) there exists local thermodynamic equilibrium within the vibrational degrees of freedom of the molecules CO_2, N_2, and H_2O. This is correct, since we are considering sufficiently low temperatures and lower vibrational levels. Under these conditions, the exchange of vibrational quanta within each mode, which has probabilities close to unity, ensures the existence of a Boltzmann distribution over the levels [11] and consequently the existence of a vibrational temperature. The vibrational temperatures of different modes T_i, generally speaking, are not equal to each other and to the translational temperature T.

The energy E_i stored in each natural mode of vibration is expressed by

$$E_i = \frac{h\nu_i y_i}{1-y_i}, \qquad E_2 = \frac{2h\nu_2 y_2}{1-y_2}, \qquad y_i = \exp(-h\nu_i / kT_i)$$

In terms of the variables y_i, the system of relaxation equations takes the form

$$\begin{aligned}\frac{dy_1}{dx} = \frac{\rho}{mu}(1-y_1)^3(1-y_2)^2(1-y_3)\{&K_7\alpha^{(4)}[y_5 - y_1\exp(-\Delta\varepsilon_7/kT)]\\ &-\sum_{s=1}^{4} K_8^{(s)}\alpha^{(s)}[y_1 - y_2{}^2\exp(-\Delta\varepsilon_8/kT)] + \sum_{s=1}^{4} K_{10}^{(s)}\alpha^{(s)}[y_3\\ &- y_1y_2\exp(-\Delta\varepsilon_{10}/kT)] - K_{11}\alpha^{(4)}[y_1 - \exp(-\Delta\varepsilon_{11}/kT)]\}\end{aligned} \tag{17}$$

$$\begin{aligned}\frac{dy_2}{dx} = \frac{\rho}{2mu}(1-y_1)(1-y_2)^4(1-y_3)\Big\{&-\sum_{s=1}^{4} K_1^{(s)}\alpha^{(s)}[y_2 - \exp(-\Delta\varepsilon_1/kT)]\\ &+ 2K_5\alpha^{(4)}[y_5 - y_2\exp(-\Delta\varepsilon_5/kT)] + K_6\alpha^{(4)}[y_3 - y_2y_5\exp(-\Delta\varepsilon_6/kT)]\\ &+ 2\sum_{s=1}^{4} K_8^{(s)}\alpha^{(s)}[y_1 - y_2{}^2\exp(-\Delta\varepsilon_8/kT)] + 3\sum_{s=1}^{4} K_9^{(s)}\alpha^{(s)}[y_3 - y_2{}^3\\ &\times\exp(-\Delta\varepsilon_9/kT)] + \sum_{s=1}^{4} K_{10}^{(s)}\alpha^{(s)}[y_3 - y_1y_2\exp(-\Delta\varepsilon_{10}/kT)]\Big\}\end{aligned} \tag{18}$$

$$\begin{aligned}\frac{dy_3}{dx} = \frac{\rho}{mu}(1-y_1)(1-y_2)^2(1-y_3)^3\Big\{&-K_2\alpha^{(2)}(1-y_4)[y_3 - y_4\\ &\times\exp(-\Delta\varepsilon_2/kT)] - K_4\alpha^{(4)}[y_3 - y_5\exp(-\Delta\varepsilon_4/kT)] - K_6\alpha^{(4)}[y_3\\ &- y_2y_5\exp(-\Delta\varepsilon_6/kT)] - \sum_{s=1}^{4} K_9^{(s)}\alpha^{(s)}[y_3 - y_2{}^3\exp(-\Delta\varepsilon_9/kT)]\\ &-\sum_{s=1}^{4} K_{10}^{(s)}\alpha^{(s)}[y_3 - y_1y_2\exp(-\Delta\varepsilon_{10}/kT)]\Big\}\end{aligned} \tag{19}$$

$$\begin{aligned}\frac{dy_4}{dx} = \frac{\rho}{mu}(1-y_4)^3\Big\{&K_2\alpha^{(1)}(1-y_1)(1-y_2)^2(1-y_3)[y_3 - y_4\\ &\times\exp(-\Delta\varepsilon_2/kT)] - K_3\alpha^{(4)}[y_4 - y_5\exp(-\Delta\varepsilon_3/kT)]\\ &- [y_4 - \exp(-\Delta\varepsilon_{12}/kT)](K_{12}^{(3)}\alpha^{(3)} + K_{12}^{(4)}\alpha^{(4)})\Big\}\end{aligned} \tag{20}$$

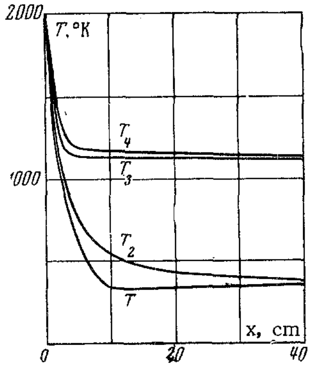

Fig. 1

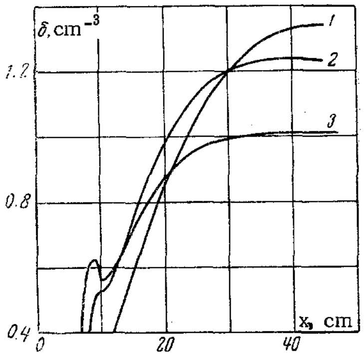

Fig. 2

In writing down the system (17)-(20) it was assumed that the density of the molecules in the vibrational state (m, n, p) is described by the relation

$$N(m, n, p) = N_{CO_2}[y_1^m(1-y_1)]\,[(n+1)\,y_2^n(1-y_2)^2]\,[y_3^p(1-y_3)] \qquad (21)$$

and the vibrational temperature T_5, corresponding to the deformational mode of the H_2O molecule, is equal to the translational temperature of the mixture, since it is known that the probability of excitation of the vibrational mode of water is extremely large, $P_{10} = 126\ T^{-3/2}$.

We analyze each of the 12 reactions (5)-(16) that take place in the relaxing systems $CO_2 + N_2 + He, H_2O$.

1. Among the most important reactions are the processes of relaxation of the deformation mode (5) in collisions with $M = CO_2, He, N_2, H_2O$. The kinetics of the excitation of the ν_2 vibrations of the CO_2 molecule in a medium consisting of carbon dioxide and helium has been sufficiently thoroughly investigated in a wide range of temperatures, using various procedures [12]. The results of these investigations for the probability of deactivation of the first vibrational level can be approximated by the following expressions:

$$P_{10} = 450T^{-1/2}\exp(-110T^{-1/3} + 100T^{-2/3}) \qquad (CO_2\text{—}CO_2)$$

$$P_{10} = 10T^{-1/2}\exp(-50T^{-1/3}) \qquad (CO_2\text{—}He)$$

where P_{10} is the probability of deactivation of the first vibrational level of one of the three modes. The processes of excitation and deactivation of the vibrations of CO_2 in collisions with N_2 have not been sufficiently fully investigated, and the results of different authors are different. In the present paper it is assumed, in accordance with the results of [13], that the nitrogen molecule is three times more effective than the CO_2 molecule

$$P_{10} = 1.3\cdot10^2T^{-1/2}\exp(-110T^{-1/3} + 100T^{-2/3})$$

Water vapor is particularly effective in the excitation of vibrations of all gases, including carbon dioxide. The reaction (5) in the case $M = H_2O$ has been sufficiently well investigated [12]. The results of the experiments show that the probability P_{10} in the case of CO_2-H_2O has a negative temperature dependence

$$P_{10} = 300/T^{3/2}$$

This expression for P_{10} is very similar in form to P_{10} for the system H_2O-H_2O.

2. As already noted earlier, exchange of vibrational quanta between the asymmetric valent mode of the CO_2 molecule and the N_2 molecule has a probability whose temperature dependence is not described by the Landau–Teller formula. Sharma and Brau [10] have shown that such a behavior is connected with the particular role of attraction in processes with a small energy defect. Under these conditions, the attraction forces can decisively influence the probability of the process. With increasing temperature, the role of the attraction forces decreases, and the contribution of the repulsion forces does not reach as yet a noticeable influence, so that the summary probability decreases. Finally, in a certain temperature region, the repulsion forces become decisive, and the probability of energy exchange increases in accordance with the Landau–Teller theory. This results in a parabolic temperature dependence of the probability of exchange of quanta between the asymmetric valent mode of the CO_2 molecules and the nitrogen molecule. The experimental values of this probability can be approximated by a parabola of the type

$$Q = 4\cdot10^{-9}(1100 - T)^2 + 6\cdot10^{-4}$$

where Q is the energy-exchange probability.

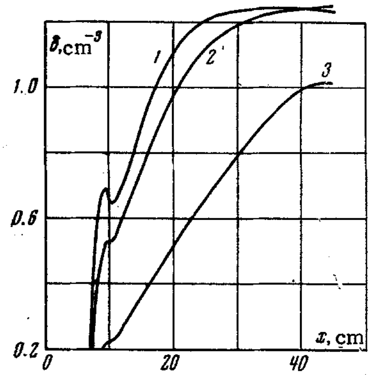

Fig. 3

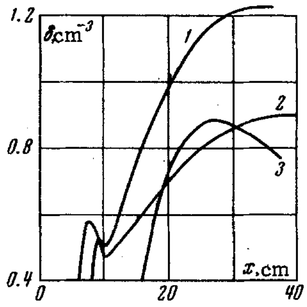

Fig. 4

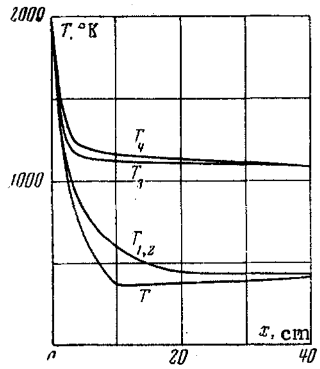

Fig. 5

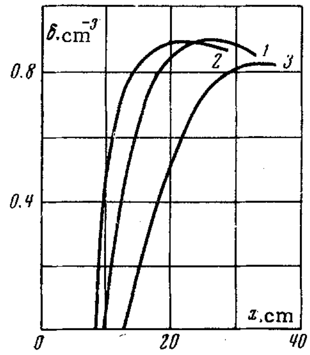

Fig. 6

3. The deactivation of the excited nitrogen in collisions with water molecules can be both as a result of exchange of quanta (7) and as a result of the transition of the vibrational energy N_2 into the energy of the translational motion of the molecules H_2O (16). Experiment [12] shows that exchange of vibrational quanta between nitrogen and water vapor occurs with a probability equal to

$$Q = 10\ \exp(-100T^{-1/3})$$

The rate of this reaction greatly exceeds the rate of the reaction (16), where

$$P_{10} = 5.5 \cdot 10^{-4}\ \exp(-57T^{-1/3})$$

At low water-vapor concentrations, the reaction (16) plays a negligibly small role. In the systems $CO_2 + N_2 + H_2O$ used to obtain inverted population in escape from nozzles, the concentration of the H_2O molecules usually does not exceed 2%.

4. The reactions (8)-(11) have not been investigated experimentally. Nonetheless, on the basis of the investigations carried out in [10] and [14] it can be assumed that the first of these processes has a probability $Q = 5 \cdot 10^{-2}T^{-1}$, the second and third have the probability $Q = 0.2/T$, and reaction (11) has the quite large probability $Q = 1/T$ (the quanta of the symmetrical valent mode of CO_2 and of the deformation mode of H_2O are close in magnitude).

5. Owing to the strong interaction between the ν_1 and ν_2 vibrations, the process (12) is exceedingly rapid. This is evidenced by the experiments of Rhodes and co-workers [15]. On the basis of the results of [7, 12, 13] it can be assumed that the probability of resonant exchange (one $h\nu_1$ quantum goes over into $2h\nu_2$) is described by the relation $Q = 30/T$.

6. The deactivation of the asymmetric-valent vibrations of the CO_2 molecule can proceed via several channels simultaneously. One such deactivation channel of the first vibrational level of the asymmetric-valent vibration is the reaction (13). The experimental results on this process are fully gathered in the review of Taylor and Bitterman [12]. It follows from the analysis of these results that in the case $M = N_2$, CO_2, H_2O the reaction (13) was experimentally investigated in a suffiently wide temperature range, whereas in a helium medium it was investigated only at room temperature. For M = He at temperatures T > 300°K, the probability of deactivation of the first vibrational level of the ν_3 mode can be extrapolated in accordance with the Landau–Teller formula, i.e., represented in the form

$$Q = 10^{-2}\exp(-52\ /\ T^{1/3})$$

In the case $M = N_2$, CO_2, H_2O, the reaction (13) has the respective probabilities

$$Q = \frac{8}{T^{1/2}} \exp(-78.5/T^{1/3}), \quad Q = \frac{1}{T^{1/2}} \exp(-57/T^{1/3}), \quad Q = 0.5/T$$

Just as for the deformation vibration, the deactivation of the asymmetric valent mode of CO_2 in collisions with molecules has a probability that is inversely proportional to the temperature. The difference lies only in the exponent of the temperature and in the absolute value of the probability.

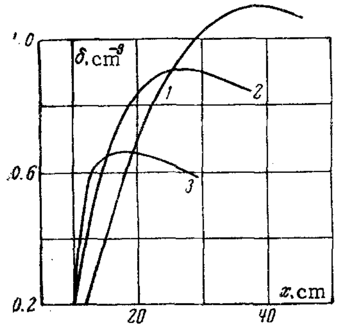

Fig. 7

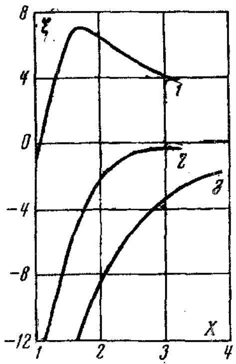

Fig. 8

7. Another channel for the deactivation of the asymmetric valent vibration of the CO_2 molecule is the process (14), where one quantum of the ν_3 mode goes over into two quanta with frequencies ν_1 and ν_2, and the remainder of the energy is converted into kinetic energy of the incoming particle. These processes were investigated experimentally by Rosser and Gerry [16] for M = He, O_2, H_2O in the temperature interval T = 400-1000°K. In a helium medium, the reaction (14) has a probability

$$Q = 0.4\exp(-80 / T^{1/3} + 60 / T^{2/3})$$

whose temperature dependence is in full agreement with the Landau–Teller theory. However, the system CO_2-H_2O, as before, is not described by this theory; the probability of the process in the entire temperature interval remains constant at $Q = 4 \cdot 10^{-3}$.

For the analogous reactions occurring in a medium of nitrogen and carbon dioxide there are no experimental data. However, only an insignificant error will result if it is assumed that the effectiveness of the nitrogen in these processes is close to the effectiveness of oxygen, i.e., if it is assumed that $Q = \exp(-80/T^{1/3} + 60/T^{2/3})$. With respect to the role of CO_2 we can state the following. First, the effectiveness of the CO_2 molecule is not higher than the effectiveness of the H_2O molecule, which in this case, as in all other reactions, is exceedingly large and apparently not lower than the effectiveness of the O_2 molecule, since it is known that the vibrational relaxation proceeds more rapidly in a medium of its own gas than in a medium of a diluent of the same mass (of course, no account is taken here of radicals or of molecules having a dipole moment). On the basis of the foregoing we can assume that in the CO_2-CO_2 system the probability of the process (14) is described by the expression

$$Q = 2.5\exp(-80 / T^{1/3} + 60 / T^{2/3})$$

The probability seems to be overestimated, and this leads to a decrease of the inversion at the upper laser level. In the systems that will be investigated subsequently, however, the concentration of the carbon dioxide is low, and therefore the role of this reaction will not be decisive.

8. A study of the vibrational relaxation of CO_2 molecules in shock waves [17] has shown that the deactivation rates of the states (10°0) and (02°0) are close in magnitude. These investigations were performed in a medium of its own gas. Apparently, it can be assumed that the probability of the processes (15) is described by a relation of the type $P_{10} = 300/T^{3/2}$.

Reactions of the type (1)-(4), (17)-(20) were solved numerically for two types of mixture, $CO_2 + N_2 + He$ and $CO_2 + N_2 + H_2O$, at different initial temperatures and pressures. The composition of the gas was also varied.

The calculations were performed for a nozzle whose convergent channel is rounded off to a radius equal to the diameter of the critical cross section, and the change of the area in the diffusor part of the nozzle is described by the function

$$A = A_* + \pi (x - x_*)^2 \operatorname{tg}^2 \theta$$

where x_* is the distance from the entrance to the nozzle to the critical cross section, and θ is half the angle at the apex of the cone, which is the asymptote of the diffusor part of the nozzle. The calculations were performed for a nozzle with a critical-section diameter 8 mm and $\theta = 15°$.

It follows from the calculations that the vibrational temperatures of the symmetrical valent and deformation modes of CO_2 remain practically constant over the entire length of the nozzle, independently of the conditions of the problem. This result is perfectly understandable since the ν_1 and ν_2 modes are quite strongly coupled with each other.

The temperatures T_1 and T_2 decrease considerably during the course of expansion of the gas, approaching the translational value T, and the difference between them depends strongly on the shape of the nozzle. In principle it is possible to choose a nozzle such that the approximate equality $T_1 \approx T_2 \approx T$ is obtained in a specified nozzle section.

Calculation shows that the vibrational temperature T_3 of the asymmetric-valent mode changes little during the expansion of the gas; an appreciable change takes place only during the initial period of the expansion. This can be attributed, first, to the insufficiently strong coupling of the ν_3 mode with the remaining modes of the CO_2 molecule and with the translational motion of the particles, and second, to the rather intense exchange of quanta with the nitrogen.

The almost resonant energy exchange between the CO_2 and N_2 molecules causes the temperatures T_3 and T_4 to remain close in magnitude along the nozzle. Since the probability of energy exchange between the ν_3 mode of CO_2 and the nitrogen molecule is inversely proportional to the temperature, it follows that when the translational temperature is decreased, i.e., when the degree of expansion of the gas is increased, the difference between T_4 and T_3 decreases and reached 20-30°K. In this case T_3 and $T_2 = T_1$ can differ by 600-700°K, which leads to inversion of the population of the ν_3 mode relative to the population of the vibrational levels of the deformation mode.

The inversion depends to a considerable degree on the nozzle configuration. The nozzle should be such that the rapid expansion of the gas causes quenching of the asymmetric valent vibration of CO_2, while the symmetric and deformation modes can continue to be deactivated for a certain time corresponding to the time of vibrational relaxations under these conditions. Therefore, the optimal nozzle for producing population inversion should consist of a diffusor part that goes over into a cylindrical channel at a certain distance from the throat. The location of the junction of these parts depends on many conditions, but at this junction the temperature T and the particle density should be such that the asymmetric-valent vibration is quenched, and that the deactivation of the ν_2 mode still continues to be sufficiently intense. The length of the cylindrical part of the nozzle depends on the duration of the deactivation of the lower laser level.

The calculations were performed for a nozzle with a diffusor part 10 cm long, continued by a cylindrical channel. The first series of the calculations were performed for three values of the initial temperature $T_0 = 1750, 2000, 2250$°K and three values of the initial pressure $p_0 = 10, 15, 20$ atm of a mixture 10% CO_2–40% N_2–50% He. Figure 1 shows the distributions of the temperatures $T_{1,2,3}$ of the different degrees of freedom of the CO_2 molecules, of the vibrational temperature T_4 of the nitrogen, and of the translational temperature T over the length of the nozzle, when $T_0 = 2000$°K and $p_0 = 15$ atm. The plots for other values of T_0 are similar to those in Fig. 1. It follows from an examination of these plots that at the indicated nozzle configuration the variation of all the temperatures stops at a length on the order of 40 cm, and $T_{1,2}$ becomes practically equalized with T. With increasing T_0, the difference between $T_{1,2}$ and $T_{3,4}$ increases. The difference between the populations of the asymmetric-valent and deformation modes $\Delta N = N(00^\circ 1) - N(10^\circ 0)$ also increases (Fig. 2). Curves 1, 2, and 3 of Fig. 2 pertain to the values $T_0 = 2250, 2000, 1750$°K, respectively. The ordinates represent the quantity $\delta = \Delta N \cdot 10^{-15}\ \mathrm{cm}^{-3}$. The population inversion sets in at a distance of about 8 cm from the throat of the nozzle. At $T_0 = 1750$°K, it appears earlier than at $T_0 = 2000$ or 2250°K. It should be noted that an optimal temperature, at which ΔN is the largest, exists for any specified nozzle configuration.

In the region x = 10 cm, a nonmonotonic variation of the δ curve is observed, due to the transition from the hyperbolic nozzle into a cylindrical tube. Indeed, calculation of the gas parameters in a hyperbolic nozzle without a cylindrical tube shows that ΔN reaches a maximum near x = 10 cm; with increasing gas expansion ΔN begins to decrease. Thus, the shape of the $\delta(x)$ curve depends on the location of the junction with the cylinder, whether it is before or after the maximum. In the case considered here, the cylinder junction is already located after the maximum. The difference in the populations of the ν_3 and ν_2 modes, expressed in relative units $\Delta N/N_{CO_2}$ increases strongly with increase of the initial temperature, although the absolute value of the inverted population tends to the optimum. The reason for it is that the growth of T_0 for a given nozzle configuration and for a constant pressure is accompanied by a growth of the final translational gas temperature T and by a decrease in the gas density.

Figure 3 shows the values of $\delta(x) = \Delta N \cdot 10^{-15}\ \mathrm{cm}^{-3}$ along the nozzle for $T_0 = 2000$°K. Curves 1, 2, and 3 pertain respectively to the values $p_0 = 20, 15$, and 10 atm. At $p_0 = 15$ atm the value of $\delta(x)$ reaches a maximum, from which it is clear that further increase of the pressure is meaningless. Indeed, an increase of p_0 (at constant T_0) leads, on the one hand, to an increase in the number of active particles, and on the other to an increase in the rate of deactivation of the vibrational levels of the CO_2 molecule. As a result, the temperature $T_{1,2}$ approaches the translational value during the course of gas expansion, while T_4 and T_3 decrease considerably in comparison with the case $p_0 = 15$ atm. The net effect reduces to a decrease of the difference between $T_{1,2}$ and $T_{3,4}$ at the same values of the translational temperature T, and consequently, to a decrease of ΔN.

The behavior of the ratio $\Delta N/N_{CO_2}$ is different from that of ΔN. The largest value of $\Delta N/N_{CO_2}$ is reached at the lowest pressure. The reason for such a behavior of $\Delta N/N_{CO_2}$ is that when the pressure is increased (at T_0 = const.) the particle density N_{CO_2} increases.

To determine the dependence of the inverted population ΔN of the asymmetric mode of the CO_2 molecule on the ratio of the nitrogen and carbon dioxide concentrations, we considered the vibrational relaxation of the mixtures 10% CO_2−40% N_2−50% He, 5% CO_2−45% N_2−50% He, and 20% CO_2−30% N_2−50% He at equal temperatures ($T_0 = 2000$°K) and pressures ($p_0 = 15$ atm). It turned out that ΔN has an optimal value for mixtures close in composition to 10% CO_2−40% N_2−50% He (curve 1 of Fig. 4). For the remaining two mixtures, the inversion is approximately the same, the only difference being that in the mixture with the larger CO_2 content (curve 3) the maximum value of ΔN is reached closer to the throat of the nozzle, and max ΔN has in this case a clearly pronounced character.

For the mixture 10% CO_2−89% N_2−1% H_2O, the calculations were performed at one and the same pressure, but at different temperatures $T_0 = 1750, 2000, 2250$°K. Figure 5 shows the profiles of all the temperatures for this mixture along the nozzle at $T_0 = 2000$°K and $p_0 = 15$ atm. They differ little from the corresponding values of the parameters obtained for the mixture 10% CO_2−40% N_2−50% He. A similar behavior is exhibited by $\delta = \Delta N \cdot 10^{-15}$ cm^{-3} as a function of x, the only difference being that max δ (x) is somewhat smaller in magnitude, and the inverted population begins somewhat later (Fig. 6). Curves 1, 2, and 3 in Fig. 6 pertain to $T_0 = 2000, 1750, 2250$°K, respectively. The relative magnitude of the inverted population $\Delta N/N_{CO_2}$ along the nozzle has qualitatively much in common with $\Delta N/N_{CO_2}$ for the mixture 10% CO_2−40% N_2−50% He.

From the analysis of the results above it follows that small additions of water vapor (about 1%) exert practically the same action as an appreciable amount of helium. The influence of water vapor depends strongly on its concentration in the mixture. Figure 7 shows the dependence of the inverted population of the molecules CO_2 on x for three different mixtures 10% CO_2−89.5% N_2−0.5% H_2O (curve 1), 10% CO_2−89% N_2−1% H_2O, and 10% CO_2−88% N_2−2% H_2O (curve 3) at $p_0 = 15$ atm and $T_0 = 2000$°K. It turned out that the largest inverted population is observed in the mixture with the smallest water-vapor content. This is apparently due to the fact that, starting with a certain concentration of the H_2O molecules, the rate of deactivation of the upper laser level of CO_2 becomes noticeable in comparison with the rate of deactivation of the deformation vibration.

Comparison of the data obtained by different authors with one another and with the present results is undoubtedly of interest. To this end we considered the variant proposed by N. G. Basov and co-workers [3], i.e., the system $CO_2 + N_2$. The calculation was carried out for the conditions of [3] using the probabilities assumed in the given paper. The results of the calculations are shown in Fig. 8, where the ordinates represent the quantity $\xi = \Delta N/N_0 \cdot 10^5$. Whereas in [3] (curve 1) they observed an appreciable population inversion, no such inversion exists according to the data of [6] (curve 2). The present results indicate to an even greater degree that there should be no inverted population under the conditions of [3] (curve 3). The point is that in [3] they apparently assumed too high a deactivation rate for the deformation mode of the molecule CO_2, an assumption that does not agree with the experimental data.

Thus the calculations have shown that expansion of the systems $CO_2 + N_2 + He, H_2O$ in a nozzle can yield an appreciable inverted population of the CO_2 molecules, equal approximately to 10^{15} cm^{-3}, and strongly dependent on the nozzle configuration and on the initial conditions. If the nozzle configuration and the mixture composition are specified, there exist optimal regimes with respect to the initial temperature and pressure.

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