

ROLE OF NONRESONANCE EXCHANGE PROCESSES IN GAS-DYNAMIC LASERS

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The role of nonresonance vibration exchange processes in gas-dynamic lasers is examined. The conditions under which these processes determine the kinetics of vibrational-level populations are elucidated. Detailed consideration is given to relaxation in $\text{CO}_2\text{-HCl}$ and CO-N_2 mixtures. It is shown that the initial pressures may be very considerable. The use of chemical reactions in expanding gas flows enables these pressures to be increased still further.

It was shown in [1-3] that nonresonance vibrational exchange played an important part in chemical and electrical-discharge lasers, and also in the process of nonequilibrium dissociation. This effect must also be allowed for in gas-dynamic lasers; during the dispersion of gas mixtures, processes of nonresonance exchange lead to a considerable redistribution of the populations of the vibrational levels, and also to a change in the effective relaxation times. Thus in the case of a mixture of gases in which the molecules constitute harmonic oscillators with different vibrational quanta E_A and E_B , on cooling the gas rapidly the effective relaxation time of the energy of the oscillator with the smaller quantum E_B may increase very substantially as a result of nonresonance exchange [2], the extent of this effect depending on the ratio between the cooling rate and the velocity of vibrational-translational (V-T) relaxation.

In the present investigation we shall consider the practical possibilities of gas-dynamic lasers after making careful allowance for nonresonance exchange effects. In order to analyze the kinetic characteristics of the processes we shall use a system of equations representing the balance of the vibrational energies for a mixture of gases in which the molecules are simulated by two varieties of harmonic oscillators. In each of the components we shall assume a Boltzmann distribution of the populations among the levels, each with its own vibrational temperature (the general case of these equations and their limits of applicability were considered in [4]).

The gas-dynamic laser is simulated by a long, narrow slit with a half-width R_0 , through which the gas mixture under consideration flows into empty space from a reservoir of large volume, so that the dispersion of the gas leaving the slit may be regarded as being limited to a plane, almost parallel channel (model of a plane nozzle with a critical cross section of width $2R_0$ and a small mouth angle). The flow in the channel is regarded as steady, this assumption being valid for times t satisfying the condition $t_1 \gg t \gg t_2$. Here t_2 is the time required for the leading edge of the travelling wave to pass from the slit to the point under consideration, t_1 is the time required for a substantial change to take place in the gas parameters (initial pressure P_0 and temperature T_0) in the reservoir. For the one-dimensional case under consideration, in which the test substance flows out into empty space, for large values of t the density falls in accordance with an $N \sim t^{-1}$ law [5]; in the cross section of the slit $N = N_0 = P_0/kT_0$.

The density distribution may be approximated by the following relationship:

$$N = N_0 R_0 / (R_0 + v_0 t) \quad (v_0 = c_0 \sqrt{2/(\gamma - 1)})$$

where v_0 is the maximum possible velocity of the gas for steady outflow into a vacuum, c_0 is the velocity of sound in the unperturbed gas (for P_0, T_0), γ is the adiabatic index. The foregoing expression quite ac-

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curately reflects the change in density at large distances ($x \gg 10R_0$) from the slit, while at shorter distances it differs from the exact values by a factor of 2-3 times [5], and so constitutes a satisfactory approximation when considering the kinetic characteristics of inversion in the vibrational levels of the molecules. Usually gas-dynamic lasers are characterized by values of $R_0 \sim 0.1$ cm, while inversion occurs in these at a distance of $x \gg 2$ cm from the slit; the vibrational degrees of freedom of the gas molecules are then still practically in equilibrium with the translational degrees of freedom up to $x \sim 1$ cm. For the two-dimensional case of the outflow of gas from a slit into vacuum (without assuming the existence of any limiting plane-parallel channel) there is a sharper change in the parameters of the mixture (density, velocity, temperature); however, the qualitative behavior of the results about to be presented remains intact.

On the assumption that molecules A may be formed as a result of chemical reactions, for the flow model under consideration the system of equations takes the form

$$\begin{aligned} \frac{d\varepsilon_A}{dt} &= -\frac{\varepsilon_A - \varepsilon_{0A}}{\tau_{VT}^A} - Q_{10}^{01} N_B \left[\varepsilon_A (\varepsilon_B + 1) \exp\left(\frac{E_A - E_B}{T}\right) - \right. \\ &\quad \left. - \varepsilon_B (\varepsilon_A + 1) \right] + (\chi - \varepsilon_A) \frac{1}{N_A} \left(\frac{dN_A}{dt} \right), \\ \frac{d\varepsilon_B}{dt} &= -\frac{\varepsilon_B - \varepsilon_{0B}}{\tau_{VT}^B} + Q_{10}^{01} N_A \left[\varepsilon_A (\varepsilon_B + 1) \exp\left(\frac{E_A - E_B}{T}\right) - \varepsilon_B (\varepsilon_A + 1) \right] \\ \frac{dT}{dt} &= -(\gamma - 1) \left(\frac{v_0 T}{R_0 + v_0 t} - \frac{W}{k} \right) \\ (\varepsilon_i - r_i x_i / (1 - x_i), \varepsilon_{0i} &= r_i x_{0i} / (1 - x_{0i}), x_i = \exp(-E_i / T), \\ x_{0i} &= \exp(-E_i / T), [\tau_{VT}^{(i)}]^{-1} = (P_{10}^{iB} N_B + P_{10}^{iA} N_A) (1 - x_{0i})) \end{aligned} \quad (1)$$

Here r_i is the multiplicity of degeneration of the oscillator, Q_{10}^{01} is the velocity constant of one-quantum exchange between the oscillators A and B, $[\tau_{VT}^{(i)}]$ is the vibrational-translational relaxation time of the oscillator, $(dN_A/dt)_*$ is the rate of change of the density of the A molecules as a result of chemical reactions, χ is the proportion of the chemical reaction energy passing into the vibrational degrees of freedom, expressed as the number of quanta E_A relating to one A molecule, and W determines the influence of the vibrational relaxation and the chemical reactions on the changes in gas temperature.

Generally speaking, the rate of dispersion (lateral motion) in the steady outflow condition is smaller than the velocity of the leading gas layers v_0 . However, this difference (which is very considerable in the transient case) does not play any major part in the kinetics of development of an inverted population under steady-state conditions.

The rate of exchange of the quanta between A and B (V-V exchange) usually exceeds the velocities of the processes determining the populations of the levels. A quasi-steady-state distribution is thus established in the system; this distribution "follows" the V-T processes and other processes slower than V-V, while the vibrational energies are related by the equation [2]

$$\varepsilon_A = \frac{\varepsilon_B}{(\varepsilon_B - 1) \exp(\Delta E / T) - \varepsilon_B} \quad (2)$$

If $T_B \ll E_B$ and $E_A > E_B$, then by using (1) and (2) we obtain an equation for the change in ε_B in the form [2]

$$\begin{aligned} \frac{d\varepsilon_B}{dt} &= -\frac{\varepsilon_B - \varepsilon_{0B}}{\alpha} \left(\frac{1}{\tau_{VT}^B} + \frac{\alpha - 1}{\tau_{VT}^A} \right) - \frac{\varepsilon_B}{\alpha} \left[\frac{(\alpha - 1) \Delta E}{T^2} \frac{dT}{dt} - \left(\frac{\chi}{\varepsilon_B} - \exp(-\Delta E / T) \right) \left(\frac{d\beta_A}{dt} \right)_* \right] \\ (\alpha &= 1 + \beta_A \exp(-\Delta E / T), \beta_A = N_A / N_B) \end{aligned} \quad (3)$$

Within the range of applicability of Eq. (3), the cooling of the gas for the case of $\Delta E > 0$, together with the effects of chemical reactions involving the formation of vibrationally-excited A molecules, increases the effective relaxation time τ . The following condition must then be satisfied: $\chi > \varepsilon_B \exp(-\Delta E / T) \sim 10^{-1}$ (for $E_B \sim 3000^\circ\text{K}$, $\Delta E \sim 500^\circ\text{K}$, $T \sim 1500^\circ\text{K}$). If, however, unexcited molecules ($\chi = 0$), or molecules which have been insufficiently excited, are formed, then the energy per particle falls, being redistributed among the newly formed particles, and the vibrational temperature T_B diminishes.

A change in τ also takes place on mixing two nonreacting gases. Thus if for simplicity we put $\Delta E = 0$, then for $\tau_{VT}^A > \tau_{VT}^B$ we shall have $\tau < \tau_{VT}^B$ and conversely.

Let us examine the conditions under which nonresonance exchange plays a substantial role in the operation of a gas-dynamic laser. It follows from system (1) that a quasi-steady-state distribution (2) occurs on satisfying the condition

$$\frac{1}{\varepsilon_i} \left| \frac{d\varepsilon_i}{dt} \right| + \frac{1}{\tau_{VT}^{(i)}} + \left| \frac{1}{\tau_1} \right| \ll \frac{1}{\tau_{VV}} \quad (4)$$

$$\left(i = B, A; \tau_1^{-1} = \frac{1}{N_A} \left(\frac{dN_A}{dt} \right); \tau_{VV}^{-1} = Q_{10}^{01} \min(N_A, N_B) \right)$$

Usually, in order to increase nonresonance pumping into molecule B, we use $\beta_A > 1$, so that $\tau_{VV}^{-1} = Q_{10}^{01} N_B$. For the majority of real mixtures the condition $(\tau_{VV}/\tau_{VT}) \ll 1$ is usually satisfied over a wide range of temperatures. Let us transform the first term on the left-hand side of (4):

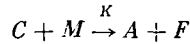
$$\frac{1}{\varepsilon_i} \left| \frac{d\varepsilon_i}{dt} \right| = \frac{1}{\varepsilon_i} \left| \frac{T}{\tau_2} \frac{d\varepsilon_i}{dT} \right| = \frac{r_i + \varepsilon_i}{r_i} \frac{E_i}{T_i} \frac{T}{T_i} \left| \frac{1}{\tau_2} \frac{dT_i}{dT} \right| \sim \left| \frac{1}{\tau_2} \right|$$

$$\left(\tau_2 = \left(\frac{1}{T} \frac{dT}{dt} \right)^{-1} \right)$$

Here τ_2 is the characteristic gas cooling time. Condition (4) takes the form

$$\frac{1}{T} \left| \frac{dT}{dt} \right| + \frac{1}{N_A} \left(\frac{dN_A}{dt} \right) \ll Q_{10}^{01} N_B \quad (5)$$

For the model based on the adiabatic expansion of gas into space, if we neglect the term W/k in (1), and assume a chemical reaction taking place in accordance with the equation



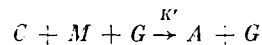
we obtain

$$\frac{v_0(\gamma-1)}{R_0} + \frac{K}{\beta_A} \frac{N_C^0 N_M^0}{N_B^0} \ll Q_{10}^{01} N_B^0$$

where K is the velocity constant of the chemical reaction, N_C^0 and N_M^0 are the initial densities of the original substances. Thus Eq. (3) is applicable over the ranges of temperatures and densities for which the following condition is satisfied:

$$N_B^0 \gg \max \left\{ \frac{v_0(\gamma-1)}{R_0 Q_{10}^{01}}, \sqrt{\frac{K N_C^0 N_M^0}{\beta_A Q_{10}^{01}}} \right\} \quad (6)$$

An analogous relationship is obtained when the reaction involves triple collisions (greater initial densities):



Here the reaction rate is $K' N_C N_M N_G$ (in the case of a binary reaction it was $K N_C N_M$), and for initial densities greater than 10^{20} - 10^{21} cm^{-3} the condition of type (6) may not be satisfied, so that Eq. (3) will no longer be valid.

At the same time, in order to ensure an effective use of the mechanism of nonresonance exchange, it is essential that the corresponding influx of energy into the B molecule should be no less than the loss of energy by virtue of V-T relaxation. Then we obtain from (3)

$$\frac{1}{\tau_{VT}^B} + \frac{\alpha-1}{\tau_{VT}^A} \ll \frac{\beta_A \Delta E}{T^2} \left| \frac{dT}{dt} \right| + \left(\frac{d\beta_A}{dt} \right) \quad (7)$$

or

$$\max\{N_A P_{10}^A, N_B P_{10}^B\} \leq \frac{1}{T} \left| \frac{dT}{dt} \right| \frac{\Delta E}{T} + \frac{1}{\beta_A} \left(\frac{d\beta_A}{dt} \right)$$

Let us assume that $\max\{N_A P_{10}^A, N_B P_{10}^B\} = N_B P_{10}^B$; then for the present model of the changes taking place in the gas-dynamic parameters we find that for

$$N_B^{\circ} \leq \min \left\{ \frac{v_0(\gamma-1)}{R_0 P_{10}^B} \frac{\Delta E}{T}, \sqrt{\frac{K N_C^{\circ} N_M^{\circ}}{\beta_A P_{10}^B}} \right\} \quad (8)$$

condition (7) always holds.

Let us consider a case in which there are no chemical reactions. Here

$$\frac{1}{Q_{10}^{\text{oi}}} \ll \frac{N_B^{\circ} R_0}{v_0(\gamma-1)} \ll \frac{\Delta E}{T} \frac{1}{P_{10}^B} \quad (9)$$

If $\Delta E \approx 0$, we have the usual V-T relaxation of the A + B system with a characteristic time

$$\tau = \alpha \left(\frac{1}{\tau_{VT}^B} + \frac{\alpha-1}{\tau_{VT}^A} \right)^{-1}$$

If we assume that conditions (9) are satisfied and take $\Delta E \sim E_1/2$, relaxation is so retarded that a rise in T_B may occur, the magnitude of this rise being determined by the velocity of the V-T transitions.

On allowing for nonresonance exchange, the relaxation processes and the efficiency of a gas-dynamic laser depend very substantially on the particular mixtures and conditions employed. We shall now consider the particular features characterizing the two mixtures CO-N₂ and CO₂-HCl.

Let us first consider the CO-N₂ mixture and use Eq. (3) to describe the behavior of the vibrational temperature for CO. It follows from Eq. (6) that the rate of V-V exchange between CO and N₂ is not very high; however, it is higher than the velocity of the V-T processes. Hence up to a certain stage of cooling Eq. (3) remains applicable.

For the solution of (3) we require an analytical expression for the probabilities P_{10} entering into τ_{VT} . It was shown in [7] that for diatomic molecules an expression of the following form yielded good agreement with experiment:

$$P_{10} = AT \exp(-BT^{-1}) \quad (10)$$

where A and B are constants depending for any particular pair of colliding molecules on the energy defect and the reduced mass of the collision μ . Since in the case under consideration μ is the same for all three pairs (N₂-N₂, N₂-CO, and CO-CO), we have $P_{10}^{N_2-N_2} = P_{10}^{N_2-CO}$ and $P_{10}^{CO-N_2} = P_{10}^{CO-CO}$. The relaxation times τ_{VT} thus have the form

$$\begin{aligned} (\tau_{VT}^{CO})^{-1} &= T_0 N_{CO} \left(\frac{T}{T_0} \right)^{\gamma(\gamma-1)} (1 + \beta_{N_2}) A_1 \exp(-B_1 T^{-1}) \\ (\tau_{VT}^{N_2})^{-1} &= T_0 N_{CO} \left(\frac{T}{T_0} \right)^{\gamma(\gamma-1)} (1 + \beta_{N_2}) A_2 \exp(-B_2 T^{-1}) \end{aligned} \quad (11)$$

Using the cooling model under consideration and Eq. (11), we may integrate Eq. (3) on the assumption that $(\alpha-1)/\alpha$ depends very little on temperature. The result of the integration is illustrated in Fig. 1, which represents the vibrational temperature T_{CO} and the mean store of vibrational quanta $\bar{\epsilon}_{CO}$ per CO molecule as functions of the gas temperature for a CO:N₂ = 1:10 mixture expanding into vacuum (these data relate to a temperature of $T_0 = 2000^\circ\text{K}$, $R_0 N_{CO}^{\circ} = 5 \cdot 10^{19} \text{ cm}^{-2}$, $A_1 = 4 \cdot 10^{-12}$, $A_2 = 7.8 \cdot 10^{-12}$, $B_1 = 195.2$, $B_2 = 217.8$). We see that the store of vibrational energy (and hence T_{CO}) increases with falling gas temperature, while no such effect occurs in pure CO. This rise is due to the existence of a nonresonance exchange process, which for the weak V-T relaxation of the CO-N₂ system leads to the development of a considerable difference between the vibrational and gas temperatures. In any real case there will, of course, be no unlimited growth of T_{CO} , since, starting from a certain gas temperature (in the present case $\sim 800^\circ\text{K}$), condition (6) will no longer be satisfied, and Eq. (3) cannot be used for smaller T. At such temperatures the role of collisions is so weak that the vibrational energies in the two molecules will no longer vary and will pass out to the "frozen" values (broken curves in Fig. 1).

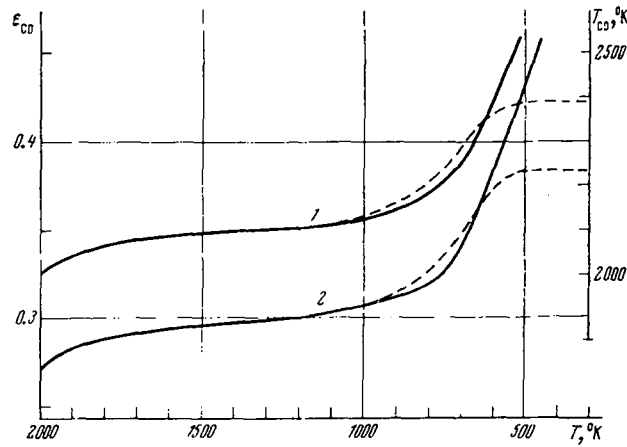


Fig. 1

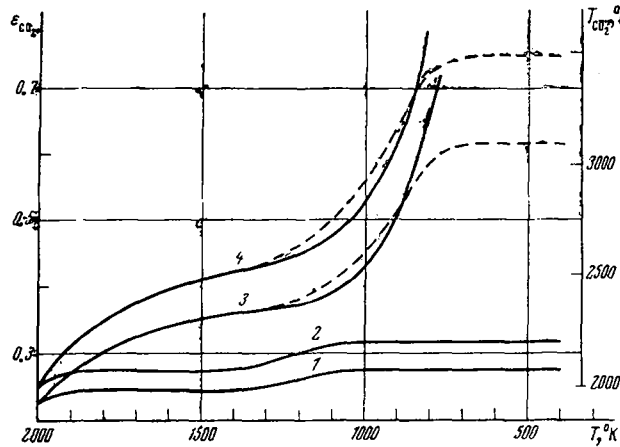


Fig. 2

On increasing N_{CO^0} to values of the order of 10^{22} cm^{-3} , the range of applicability of Eq. (3) expands considerably in the low-temperature direction, and greater values of the "frozen" T_{CO^*} (Fig. 1) may be obtained. Such large values of the initial densities are quite possible for a $CO-N_2$ mixture in view of the very low rate of $V-T$ relaxation, as indicated by Eq. (9). It should be noted that for densities of $>10^{21}-10^{22} \text{ cm}^{-3}$, triple collisions may play an appreciable part in vibrational relaxation. However, this question has not yet been studied, and there is no information as to the cross sections of the processes. The results agree with experimental data [8, 9]. Thus a relationship of the (2) type was obtained for a $CO-N_2$ mixture in [8], and experimental relationships were given for the vibrational temperatures in the N_2 and CO as functions of the initial gas-dynamic parameters; from this result it is clear that for mixtures with large β_{N_2} , T_{CO^*} may greatly exceed T_0 . Generation was obtained for the CO of a $CO-N_2$ mixture in [9]. The parameters employed were $T_0 \sim 2000^\circ K$ and $P_0 \sim 100-250 \text{ atm}$, in agreement with Eq. (9).

Let us apply the same type of consideration to a CO_2-HCl mixture. We shall assume that the temperatures of the deformation (shear) and symmetrical vibrations of CO_2 are close to the gas temperature, which is certainly true for high T , when the relaxation rates are high. Thus, in the same way as before we shall consider two oscillators: the asymmetric vibrations of CO_2 and the HCl molecule. It is well known [10] that HCl relaxes quite strongly; however, even in this case $V-V$ exchange takes place faster [11]. We may therefore make use of Eq. (3); the time $\tau_{VT}^{CO_2}$ corresponds to the time required for the energy of the asymmetric mode to pass to all the remaining vibrations of CO_2 . We obtain analytical expressions for $P_{10}^{HCl-HCl}$ and $P_{10}^{CO_2-CO_2}$ on the basis of the experimental data of [12] in the form of Eq. (10), and assume that $P_{10}^{CO_2-CO_2} \approx P_{10}^{CO_2-HCl}$, $P_{10}^{HCl-CO_2} \approx 4P_{10}^{HCl-HCl}$ [11]. In the temperature range $700-2000^\circ K$, by using the results of [10] we have

$$P_{10}^{HCl-HCl} = 7.2 \cdot 10^{-14} T \exp(-58.3 T^{-1.3}) \text{ cm}^3/\text{sec}$$

while for CO_2 from [12]

$$P_{10}^{\text{CO}_2-\text{CO}_2} = 1.2 \cdot 10^{-14} T \exp(-38.3 T^{-1}) \text{ cm}^3/\text{sec}$$

Substituting these expressions into Eq. (3) and integrating, we obtain $\varepsilon_{\text{CO}_2}$ as a function of the gas temperature (Fig. 2, curve 1; the result is given for a mixture of CO_2 : $\text{HCl} = 1:10$, $T_0 = 2000^\circ\text{K}$, $R_0 = 0.1 \text{ cm}$, $N_{\text{CO}_2}^\circ = 10^{17} \text{ cm}^{-3}$). We see a slight rise in T_{CO_2} (curve 2), which does not occur in the pure gas. However, in view of the relatively high rate of V-T relaxation the rise in the vibrational temperature is fairly small, while on increasing the parameter $R_0 N_{\text{CO}_2}^\circ$ above $\sim 5 \cdot 10^{17} \text{ cm}^{-2}$, no rise occurs at all and T_{CO_2} falls to $T_{\text{CO}_2}^*$, the value of which is determined by the specific value of $R_0 N_{\text{CO}_2}^\circ$.

Nonresonance exchange "operates" more effectively if vibrationally excited HCl molecules are formed as a result of a chemical reaction; the most important links in this reaction include the processes



Let us assume that conditions conducive to the effective formation of atomic chlorine are provided (for example, by means of ultraviolet radiation, decomposing the Cl_2). Then reaction (12) will take place vigorously, with the formation of the H required for (13), so that the H and Cl_2 concentrations may be regarded as only weakly dependent upon temperature. In this case the equilibrium of reaction (13) is moved to the right, and the equation determining the change in the density of HCl^* takes the simple form

$$\left(\frac{dN_{\text{HCl}}}{dt} \right)_* = N_{\text{H}}^\circ N_{\text{Cl}_2}^\circ K \left(\frac{R_0}{R_0 + v_0 t} \right)^2 \quad (14)$$

In the temperature range 700-2000°K the velocity constant of reaction (13) is excellently approximated by $K = 2.8 \cdot 10^{-10} \text{ cm}^3/\text{sec}$. On these assumptions we obtain

$$N_{\text{HCl}}(t) = \left[N_{\text{HCl}}^\circ + \frac{N_{\text{H}}^\circ N_{\text{Cl}_2}^\circ K R_0}{v_0} \left(1 - \frac{R_0}{R_0 + v_0 t} \right) \right] \frac{R_0}{R_0 + v_0 t} \quad (15)$$

$$\beta_{\text{HCl}} = \beta_{\text{HCl}}^\circ + \frac{D R_0}{v_0} \left(1 - \frac{R_0}{R_0 + v_0 t} \right)$$

$$\left(\frac{d\beta_{\text{HCl}}}{dt} \right)_* = D \left(\frac{R_0}{R_0 + v_0 t} \right)^2 \quad (D = N_{\text{H}}^\circ N_{\text{Cl}_2}^\circ K / N_{\text{CO}_2}^\circ) \quad (16)$$

Substituting (15) and (16) into (3) and integrating with respect to temperature, we obtain the result given in Fig. 2 (curves 3 and 4; the calculations are performed for a mixture with $\beta_{\text{HCl}}^\circ = 10$ with $T_0 = 2000^\circ\text{K}$, $R_0 = 0.1 \text{ cm}$, $N_{\text{CO}_2}^\circ = 10^{17} \text{ cm}^{-3}$, $\chi = 0.2$, $D = 2 \cdot 10^7$). As in the case of the $\text{CO}-\text{N}_2$ mixture, the rise in the vibrational temperature as a result of nonresonance exchange is limited by the increasing value of τ_{VV} (broken curves in Fig. 2). Any increase in the initial density $N_{\text{CO}_2}^\circ$ leads to a fall in $T_{\text{CO}_2}^*$. However, in the present case this density may be 5-10 times higher than in the absence of a chemical reaction. Thus for $R_0 N_{\text{CO}_2}^\circ \sim 5 \cdot 10^{18} \text{ cm}^{-2}$ there is no rise in the vibrational temperature, but the value of $T_{\text{CO}_2}^* \sim T_0$ is high enough to obtain an inverted population between the different vibrational modes. For $R_0 N_{\text{CO}_2}^\circ \geq 10^{19} \text{ cm}^{-2}$ there is no inversion, and in order to obtain the latter it is necessary to increase the intensity of the chemical reaction (for example, by increasing the parameter D).

It should be noted that in the present case, in which the reaction involves the participation of atomic and molecular hydrogen which may also accelerate vibrational relaxation, the value of $T_{\text{CO}_2}^*$ will be somewhat lower than that given in Fig. 2. However, the quasi-equilibrium density of these components is quite low, since they take part in a chain of reactions, and the corresponding corrections are small.

Thus we have established the limits of applicability of Eq. (3) and indicated the range of variation of the parameters within which the mechanism of nonresonance exchange "operates" effectively, so that in a number of cases it allows extremely high initial pressures. The use of chemical reactions in expanding gas flows enables us to increase the density still further. On the basis of the relationships here obtained we may choose a mixture of molecules for which the principal mechanism determining the vibrational temperature is nonresonance exchange (here, however, we must know the probabilities P and Q).

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