VIBRATIONAL RELAXATION AND POPULATION INVERSION IN THE CO^2 MOLECULE IN NONSTATIONARY CONDITIONS

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The vibrational relaxation is calculated and an analysis is made of the possibilities of obtaining population inversion of CO_2 molecule vibrational levels under nonstationary conditions, by free expansion of a gas mixture or by pulsed electron excitation. In the former case some suggestions are made regarding the choice of optimal gas composition, initial gas density and temperature, and of the characteristic dimensions. It is shown that a combination of chemical processes and expansion should yield some new possibilities. Calculations performed for pulsed electron excitation yield the experimental conditions for obtaining information on the probabilities of the various processes; the effective probability for electron excitation of symmetric and deformed modes in CO_2 molecules is also estimated. A detailed analysis of various operation conditions ensuring an appreciable increase in the power of pulsed CO_2 lasers is presented.

1. INTRODUCTION

A THEORETICAL analysis of the main physical processes in a laser based on the vibrational levels of polyatomic molecules, particularly the CO_2 molecule, was carried out for the stationary regime in [1-3]. At present, however, more and more attention is being paid to problems connected with nonstationary methods of producing inverted level populations. This uncovers new interesting possibilities for the practical utilization of molecular lasers. Since they reveal a number of distinguishing features, these methods call for a special theoretical analysis.

In the development of nonstationary methods for creating population inversion of vibrational levels of the CO_2 molecule, one can distinguish two main trends: thermal methods and pulsed electron excitation. From among the thermal methods, the most effective is the abrupt cooling accompanying the expansion of the gas.[4][1] Estimates reported in [6] have shown that the rates of adiabatic cooling of molecular gases in a chemical shock tube and following expansion through a slit (nozzle) can be sufficient to produce population inversion. In a note by Konyukhov and Prokhorov[7] they consider the possibility of obtaining inversion in a CO_2–N_2 mixture by rapid escape of heated gases from a nozzle. Recently, Basov et al.[8] investigated relaxation and obtained inverted population of vibration levels of the CO_2 molecule by supersonic flow of gas from a Laval nozzle. Population inversion by thermal pumping was obtained experimentally in [9,10]. For further experimentation, we need at present a detailed analysis of the possibility of the thermal method, and calculations of the optimal parameters of the system and of the operating conditions of the laser. Particular attention attaches in this case to free gas dynamic outflow, since it can be quite readily realized experimentally (for example, by flow of gas through a narrow slit) and yields the strongest deviations from thermodynamic equilibrium (owing to the rapid cooling and decrease of the gas density).

The second trend is pulsed excitation, by means of electrons, of the vibrational levels of polyatomic molecules. The inverted population and generation in the pulsed regime were investigated experimentally for CO_2 in [11-17]. In [11,12,16] generation occurs at the instant of the current pulse, while in [13,14] afterglow was also observed. The choice of the instant of Q switching and a changeover from a continuous to a pulsed discharge[15] have made it possible to increase the output power by a factor of several times, and a generated pulse power ~ 200 kW was obtained at large pressures (~ 60 Torr) and high-discharge-tube voltages (~ 200–1000 kV).[16] The relaxation times of CO_2 laser levels in molecular collisions were obtained in [17] by using short current pulses of duration $\sim 5\ \mu$sec.

We present in this paper a theoretical analysis of the vibrational relaxation of the CO_2 molecule under nonstationary conditions following adiabatic expansion of the gas and following pulsed electron excitation. This analysis makes it possible to clarify the conditions for the existence of inverted population of the levels $00^\circ1$–$10^\circ0$ of the CO_2 molecule, to determine the optimal parameters at which this inversion is maximal, and to indicate ways of increasing the output power of a pulsed laser with electron pumping. Comparison of the results of the theoretical calculation with the experimental data makes it also possible to estimate the cross sections of the various transitions, particularly the probabilities of electron excitation of vibrational levels of CO_2. The latter circumstance is important also for ordinary stationary CO_2 laser, where the role of the electron excitation of the CO_2 molecule vibrations in the kinetics of the processes has not yet been clarified.

In the analysis of the relaxation processes in the CO_2 molecule, we shall start with the model developed in [1,2] and based on the assumption of a local thermodynamic equilibrium with a certain temperature T_i over

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[1] The use of plasma expansion to produce atomic-level population inversion was considered in [5].

the levels belonging to a definite normal mode i. Since the vibrational temperatures can be quite high in the phenomena under consideration, it is necessary to take into account the contributions of the combination levels to the total vibrational energy E_i of a given mode. By summing the energy over all the vibrational levels, including the combination levels, we obtain for the value of E_i pertaining to an individual molecule the expression

$$E_i = \frac{h\nu_i x_i}{1 - x_i}, \quad i = 1, 3, 4; \quad E_2 = \frac{2h\nu_2 x_2}{1 - x_2}. \tag{1}$$

Here $x_i = \exp(-h\nu_i/kT_i)$ and ν_i are the fundamental frequencies of the different modes. The indices i = 1, 2, 3 pertain respectively to symmetrical, deformational, and asymmetrical oscillation modes of CO, and the index 4 pertains to the molecule N_2.

Calculations[1,2] have shown that practically in all cases, by virtue of the resonant interaction, the temperatures of the symmetrical and of the deformation types of oscillations are close in value. We shall therefore assume for simplcity $T_1 = T_2$, and also $h\nu_1 = 2h\nu_2$. From this we get $x_1 = x_2^2$, i.e., the relaxation of the sum of the vibrational energies $E_1 + E_2$ is determined by the time dependence of x_2.

When considering vibrational relaxation in the gases CO_2, CO_2–N_2, CO_2–He, and CO_2–N_2–He, we shall assume the same collision-relaxation channels as in [1,2], namely, resonant exchange via the lower vibrational level of the N_2 molecule and the 00°1 level of the CO_2 molecule (with probability W_{43}), the transition of the energy of the asymmetrical oscillation mode of CO_2 via the level 00°1 into the deformational and symmetrical mode (with probability $W_{3\Sigma}$), and the simultaneous relaxation of the energies $E_1 + E_2$ on the translational degrees of freedom via the levels $0v^l0$ (with probability W_{20}). The direct collisional relaxation of the energies E_1, E_3, and E_4 on the translational degrees of freedom and radiative transitions are disregarded, owing to their low probabilities. We note that the resonant exchange of vibrational quanta of N_2 and CO_2, and the relaxation of the energy of the asymmetrical oscillation mode via the upper levels, are insignificant (owing to the decreased populations). However, the use of the experimental probabilities makes it also possible to take these transitions effectively into account.

2. PRODUCTION OF INVERTED POPULATION OF VIBRATIONAL LEVELS BY ADIABATIC EXPANSION

To describe vibrational relaxation in a molecular gas (or a gas mixture) previously heated to a temperature T_0 and cooled by free expansion in vacuum, it is necessary to solve simultaneously the relaxation and gasdynamics equations. The differential equations describing the time variation of the vibrational energies E_i for each individual molecule can be written, under the assumptions made above, in the form

$$\begin{aligned}
\frac{dx_4}{dt} &= (1 - x_4)^3 (1 - x_3)(1 - x_2)^2 (1 - x_2^2)(x_3 - x_4) W_{43}(N_{CO_2}),\\
\frac{dx_3}{dt} &= (1 - x_4)(1 - x_3)^3 (1 - x_2)^2 (1 - x_2^2)(x_4 - x_3) W_{43}(N_{N_2})\\
&\quad - (1 - x_3)^3 (1 - x_2)^2 (1 - x_2^2)(x_3 - x_2^3 e^{-500/T})[W_{3\Sigma}(N_{CO_2})\\
&\quad + W_{3\Sigma}(N_{N_2}) + W_{3\Sigma}(N_{He})],\\
\frac{dx_2}{dt} &= \frac{3}{2}\,\frac{(1 - x_3)(1 - x_2)^5 (1 + x_2)^3}{1 + 4x_2 + x_2^2}(x_3 - x_2^3 e^{-500/T})[W_{3\Sigma}(N_{CO_2})\\
&\quad + W_{3\Sigma}(N_{N_2}) + W_{3\Sigma}(N_{He})] - \frac{(1 + x_2)^2 (1 - x_2)}{1 + 4x_2 + x_2^2}[x_2(1 - e^{-960/T})\\
&\quad - e^{-960/T}(1 - x_2)][W_{20}(N_{CO_2}) + W_{20}(N_{N_2}) + W_{20}(N_{He})].
\end{aligned} \tag{2}$$

In writing down (2) we have assumed that $h\nu_3 = h\nu_4$, we have used the formulas (1), the relation

$$\frac{dE_i}{dt} = \frac{dE_i}{dx_i}\,\frac{dx_i}{dt}$$

and the known connection between the probabilities of the direct and inverse transitions. To simplify the calculations, we shall henceforth assume the gas temperature T and the partial gas densities N_{CO_2}, N_{N_2}, and N_{He}, which enter in (2), to be independent of the spatial coordinates, i.e., we shall operate with gas parameters averaged over the entire volume.

Let us consider cooling of the gas by expansion. Assume that free escape of the gas into vacuum begins at the instant of time t = 0 (temperature T_0, density N_0, characteristic dimension R_0). As is well known,[18] the forward layers of the gas expand with a constant escape velocity $v_0 = 2c_0/(\gamma - 1)$, where γ is the adiabatic exponent and c_0 the velocity of sound in the unperturbed gas. The motion of the gas boundary is described by $r = R_0 + v_0 t$, and the average gas density N_{av} varies with time in accordance with

$$N_{cp} \sim N_0 (R_0 + v_0 t)^{-\beta}, \tag{3}$$

where β is the dimensionality of the problem.

We assume that the energy for each rotational degree of freedom of the CO_2 and N_2 molecules is kT/2, and that equilibrium obtained between the rotational and translation degrees of freedom. Then, denoting by Q the vibrational energy transformed per unit time into translational and rotational degrees of freedom (per single particle of the gas), and using the energy conservation law, the state law for an ideal gas, and relation (3), we obtain for the average temperature of the translational degrees of freedom of the gas

$$\frac{dT}{dt} + \left(\frac{3}{2} + \frac{1 + K_{N_2}}{1 + K_{N_2} + K_{He}}\right)^{-1} \frac{\beta v_0 T}{R_0 + v_0 t} = Q \Bigg/ \left(\frac{3}{2} + \frac{1 + K_{N_2}}{1 + K_{N_2} + K_{He}}\right) k, \tag{4}$$

where $K_{N_2} = N_{N_2}/N_{CO_2}$ and $K_{He} = N_{He}/N_{CO_2}$ are the relative concentrations of N_2 and He; k is Boltzmann's constant. For the quantity Q, starting from Eqs. (2), we get

$$\begin{aligned}
Q &= -\left(\frac{dE_4}{dt} + \frac{dE_3}{dt} + \frac{dE_2}{dt} + \frac{dE_1}{dt}\right) = \Big\{(h\nu_3 - 3h\nu_2)(1 - x_3)\\
&\quad \times (1 - x_2)^2 (1 - x_2^2)(x_3 - x_2^3 e^{-500/T})[W_{3\Sigma}(N_{CO_2}) + W_{3\Sigma}(N_{N_2})\\
&\quad + W_{3\Sigma}(N_{He})] + h\nu_2\left[\frac{x_2}{1 - x_2}(1 - e^{-960/T}) - e^{-960/T}\right]\Big\}[W_{20}(N_{CO_2})\\
&\quad + W_{20}(N_{N_2}) + W_{20}(N_{He})].
\end{aligned} \tag{5}$$

In determining the expansion velocity $v_0 = 2c_0/(\gamma - 1)$, we calculated the average speed of sound c_0 in the unperturbed gas mixture, and in determining the effective adiabatic exponent γ we assumed that the vibrational degrees of freedom of CO_2 and N_2 are "frozen."[2)]

[2)] We note that the change of the effective adiabatic coefficient γ in the course of cooling of the gas is taken into account by the term in the right side of Eq. (4).

The probabilities of transitions between vibrational levels, which enter in (2), depend strongly on the translational temperature and are proportional to the partial densities of the gases. To find their values and their temperature dependences, we used the data given in [1, 19] and calculated in addition the transition probabilities for high temperatures in the interval 1000–2500°K (for details see [20]).

The solution of the system (2) together with (4) with account taken of relations (3) and (5) was carried out with an electronic computer for different mixtures of the gases CO_2, N_2, He, for different initial temperatures T_0, for different pressures and different characteristic dimensions R_0, and also for $\beta = 1, 2, 3$ ($\beta = 1$ corresponds to expansion of a planar layer of gas, which can be simulated by expansion of gas from a narrow long slit of dimension $2R_0$; $\beta = 2$ corresponds to expansion of the cylindrical gas volume or to expansion from a round aperture of radius R_0, while $\beta = 3$ corresponds to expansion of a gas sphere with initial radius R_0). The results of the calculation are shown in Figs. 1–5.

Figure 1 shows a typical time dependence of the vibrational temperatures T_i for N_2 and CO_2, of the temperature of the translational degrees of freedom T, and of the inverted population ($\Delta N = N_{00^\circ 1} - N_{10^\circ 0}$, in an adiabatically expanding gas. We see that during the initial stage of the expansion, when the gas temperature T and its density are still high, the vibrational temperatures differ little from the gas temperature, by virtue of the high relaxation rate. However, as the gas expands, owing to the rapid decrease of its temperature and density, the relaxation rates of the vibrational energies decrease and a gap is produced between the different vibrational temperatures and the gas temperature. Starting with a certain instant of time, when the density and temperature of the gas have dropped considerably, the process of vibrational relaxation practically ceases, and the remaining reserve of the vibrational energy of the molecule remains unchanged. This is the effect of "freezing" of the vibrational energy.[3] Since in the mixture $W_{3\Sigma} < W_{20}$ "frozen" temperature T_3^* can be much higher than T_2, and the difference between T_3 and T_2 is sufficient to produce inverted population of the levels 00°1–100°0 of the CO_2 molecule. The resultant inversion increases rapidly (owing to the growth of the difference $x_3 - x_2^2$), reaches a maximum value, and then begins to decrease, and since by that instant $T_3 = T_3^* = \text{const}$, the decrease of the inversion is due to the decrease of the density of the molecules CO_2 as a result of the expansion of the gas. The rate of cooling of the gas, the values of the "frozen" vibrational temperatures T_i, the instant of time at which the inversion reaches a maximum, and the magnitude of this inversion are all determined by the different parameters of the gas mixture before the start of the expansion process.

An analysis has shown that addition of nitrogen to CO_2 in the ratio $CO_2 : N_2 = 1:3-1:5$ greatly increases the inversion.[20] If $W_{43} \gg W_{3\Sigma}$, the results become independent of W_{43}. Thus, calculation with a probability W_{43} smaller by one order of magnitude (while still satisfying the inequality $W_{43} > W_{3\Sigma}$) yielded only a 25% decrease of $\Delta N_{\max}$.

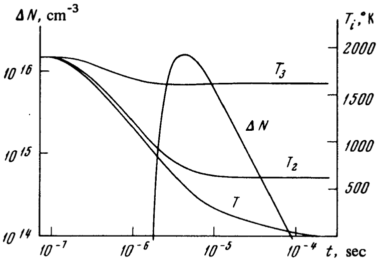

FIG. 1

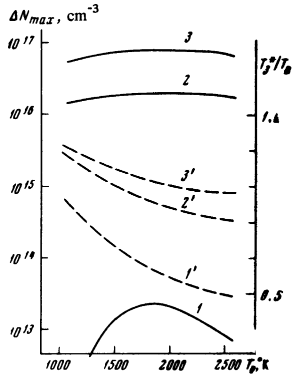

FIG. 2

FIG. 1. Typical time variation of the gas temperature T, of the vibrational temperatures T_i, and of the inversion ΔN for an adiabatically expanding gas mixture (CO_2: N_2 = 1.5, $P_0(CO_2) = 7.6 \times 10^2$ torr (at 300°K), T_0 = 1900°K, R_0 = 0.3 cm, $\beta = 2$).

FIG. 2. Dependence of the maximum inversion (1, 2, 3) and of the degree of "freezing" T^*_3/T_0(1', 2', 3') on the initial gas temperature for the following mixtures: pure CO_2(1, 1'); CO_2: N_2 = 1:5 (2, 2'); CO_2: N_2: He = 1:5:10 (3, 3'). Throughout, $P_{0(CO_2)} = 7.6 \times 10^2$ torr (at 300°K), R_0 = 0.1 cm, $\beta = 1$.

The dependence of $\Delta N_{\max}$ and of the quantity T_3^*/T_0 (degree of "freezing") on the initial gas temperature T_0 for different mixtures is illustrated in Fig. 2. We see that for the mixtures CO_2–N_2 and CO_2–N_2–He the inversion is little sensitive to the initial temperature of the gases in the range 1100–2000°. The optimal values T_0 = 1800–2000° are explained, on the one hand, by the increase in the number of vibrationally-excited molecules and the initial rate of cooling of the gas with increasing T_0 and, on the other, by the increase in the relaxation rate of the energy of the asymmetrical type of vibration of the CO_2 molecule. For the same reason, the degree of "freezing" T_3^*/T_0 also decreases with increasing T_0.

The influence of the characteristic dimension R_0 and of the initial partial pressure of CO_2 on the inversion magnitude of the "frozen" temperature T_3^* is shown in Figs. 3 and 4. The presence of optimal R_0 and $P_{0(CO_2)}$ for the inverted population are due to the competition between different factors: the increase of the initial cooling rate, the faster decrease of the gas density with time (with decreasing R_0), the growth of the density of the active molecules, and the increase of the rate of relaxation of the 00°1 level (with increasing $P_{0(CO_2)}$).

The problem of obtaining inversion by gas expansion is essentially nonstationary, since it is necessary to consider the time dependence of the processes. However, by simulating free expansion by means of continuous escape of gas from a slit or an aperture, it is possible to obtain a stationary picture. In this case, a time scan of the expansion is produced along the escape axis. Figure 5 shows the variation of the inversion along the expansion axis for several R_0, $P_{0(CO_2)}$, and β (in determining the distance *l*, it was assumed that the velocity of the gas along the expansion axis is constant and equals v_0).

We note that in the described method of adiabatic

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[3] This effect lasts until radiative decay of the vibrational levels begins. For the CO_2 molecule this time is $\gtrsim 10^{-2}$ sec.

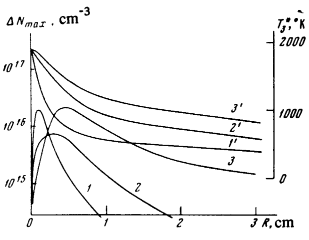

FIG. 3

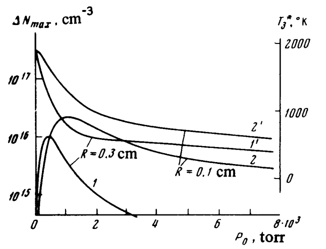

FIG. 4

FIG. 3. Dependence of the maximum inversion (1, 2, 3) and of the "frozen" temperature T^*_3(1', 2', 3') on the initial characteristic dimension of the gas R_0, for the mixture CO_2: N_2 = 1:5; T_0 = 1900°K; β = 1 (1, 1', 2, 2'), 2 (3, 3'); $P_0(CO_2) = 7.6 \times 10^2$ torr (1, 1', 3, 3'), $P_0(CO_2) = 2.3 \times 10^2$ torr (2, 2') (the pressure is referred to 300°K).

FIG. 4. Dependence of the maximum inversion ΔN_{max}(1, 2) and of the "frozen" temperature T^*_3(1', 2') on the initial partial pressure of CO_2 (referred to 300°K) for different R_0 (CO_2: N_2 = 1:5, T_0 = 1900°K; β = 1).

cooling of the gas, the possible laser efficiency is low. Estimates yielded an efficiency $\lesssim 0.3\%$, which is much lower than that of a CO_2 laser with electronic excitation of the vibrational levels. However, the use of the thermal pumping method is of interest because of its specific features and the possibility of obtaining large gains. The maximum inversion $\Delta N_{max} \sim 2 \times 10^{16}$ cm^{-3} (cf. Figs. 1–5) greatly exceeds the corresponding value for a stationary CO_2 laser.4) The experimental realization of thermal pumping methods encounters both technical difficulties and difficulties connected with the fact that the conditions for the creation of inverted population are quite critical to the choice of a number of parameters (for free expansion, these are the initial pressure and the characteristic dimensions). From among the experiments performed in this region,[9, 10] we shall stop to interpret the results of Dronov et al.[10]

Dronov et al.[10] observed experimentally an inverted population of the 00°1–10°0 levels of the CO_2 molecule following adiabatic cooling of the gas in a shock tube. The initial temperature was ~3400°K, the degree of dissociation $\varphi = N_{CO}/(N_{CO} + N_{CO_2}) \approx 0.5$, and the initial pressure was 2×10^4 Torr (at 3400°). According to the author's data, when the gas was expanded it was cooled at a constant rate $dT/dt \approx -5 \times 10^6$ deg/sec, and the inversion occurred at $T \approx 2000°$. However, estimates and calculations performed for a system of equations of the type (2) with a specified law and rate of cooling of the gas have shown that the inversion can occur only if $|dT/dt| > 5 \times 10^6$ deg/sec, or else in the case of much deeper cooling. Therefore the results of [10] can be explained only by assuming either that the rate of cooling of the gas in the experiment is larger than indicated in [10], or that there exists an additional mechanism that slows down effectively the rate of relaxation of the energy of the asymmetrical oscillation mode of the CO_2 molecule. Such a mechanism may be the chemical recombination reaction $CO + O + M \rightarrow CO_2 + M$.

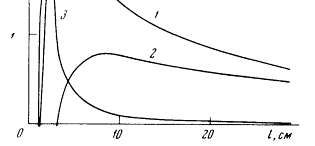

FIG. 5. Variation of the inversion along the expansion axis at R_0 = 0.1 cm, $P_0(CO_2) = 7.6 \times 10^2$ torr, β = 1 (curve 1); R_0 = 0.3 cm, $P_0(CO_2) = 2.3 \times 10^2$ torr, β = 1 (curve 2); R_0 = 0.3 cm, $P_0(CO_2) = 7.6 \times 10^2$ torr, β = 2 (curve 3). Mixture CO_2: N_2 = 1:5. T_0 = 1900°, pressure indicated at 300°K.

Kuznetsov[21] has shown that when atoms recombine to form a diatomic molecule, the rates of relaxation of the vibrational temperature can be greatly reduced. Estimates performed for the polyatomic molecule CO_2 under the assumption that the recombination reaction $CO + O + M \rightarrow CO_2 + M$ causes the production of excited CO_2 molecules at levels of a predominantly asymmetrical mode, have shown that rate of relaxation of the corresponding vibrational energy can be decelerated by approximately two orders of magnitude (at $\varphi \approx 0.5$). In this case, the requirements with respect to the rates of cooling of the gas during the expansion are greatly reduced, and inversion can be obtained under conditions that take place in the experiment of [10]. This shows that chemical processes of the type $CO + O \rightarrow CO_2$, in combination with gasdynamic expansion, can be quite effective for the development of lasers. Owing to such processes, the inverted population of the levels and the generation power increase (effective increase of the vibrational temperature T_3). Moreover, chemical pumping may turn out to be quite appreciable even in the already existing sealed CO_2 laser. It is not excluded that it can yield, if suitable conditions are created, a larger power in a sealed laser than in a flow-through laser.

3. POPULATION INVERSION BY PULSED ELECTRONIC EXCITATION OF THE VIBRATIONAL LEVELS

The second nonstationary method of obtaining inversion on the CO_2 molecule is a pulsed discharge in a mixture of molecular gases. In this case the vibrational relaxation should be considered together with the change of the state of the free electrons. Let us write down the equations for these electrons. Let the gas CO_2 (or the gas mixture CO_2–N_2, CO_2–He, or CO_2–N_2–He) be placed in a cylindrical tube of radius R. We assume that when an electric pulse of duration τ acts on the gas the electron density N_e and their temperature T_e remain constant during the time of the entire pulse. After the pulse terminates, N_e and T_e begin to decrease, and their time variation is determined by volume recombination, ambipolar diffusion (for N_e), and the cooling law (for T_e). Thus, the time variations of N_e and T_e are given by the formulas

$$\frac{dN_e}{dt} = \begin{cases} 0; & 0 < t \leqslant \tau \\ -\dfrac{D_{\text{amb}}}{\Lambda^2} N_e - \alpha N_e^2 \dfrac{I_2}{I_1}; & t > \tau \end{cases}, \tag{6}$$

$$\frac{dT_e}{dt} = \begin{cases} 0; & 0 < t \leqslant \tau \\ -\delta_{\text{eff}}\, \nu_{\text{eff}}\, (T_e - T); & t > \tau \end{cases}. \tag{7}$$

Here D_{amb} is the coefficient of ambipolar diffusion, Λ is the diffusion length, α is the coefficient of volume recombination, and δ_{eff} and ν_{eff} are the effective values of the specific energy losses and the frequencies of

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4) Allowance for the temperature and density inhomogeneities of the gas makes the inversion averaged over the volume slightly smaller than the calculated value.

collisions between the electrons and the heavy particles of the gas, respectively;[5)] the electron density N_e is rereferred to the value on the tube axis, and

$$I_1 = \int_0^R rJ_0\left(\frac{r}{\Lambda}\right) dr, \quad I_2 = \int_0^R rJ_0^2\left(\frac{r}{\Lambda}\right) dr.$$

The recombination heating of the electrons plays no role at the densities N_e under consideration. For simplicity, we assume also that the electrons have a radial distribution described by a Bessel function of zero order $J_0(r/\Lambda)$.

The equations describing the vibrational relaxation under electronic excitation are similar to Eqs. (2) for an expanding gas. It is necessary, however, to take additional account of the energy pumping in different oscillation modes under the influence of the electron impact, and also the diffusion decay of the vibrationally excited molecules. In this case there are added to the right sides of (2) the corresponding terms

$$\begin{gathered}(1-x_4)^3\left\{\left[W_{e4}-W_{4e}\frac{I_2}{I_1}x_4\right]\alpha_4 N_e-\frac{D_{N_2}}{\Lambda^2}x_4\right\},\\ (1-x_3)^3(1-x_2)^2(1-x_2{}^2)\left\{\left[W_{e3}-W_{3e}\frac{I_2}{I_1}x_3\right]\alpha_3 N_e-\frac{D_{CO_2}}{\Lambda^2}x_3\right\}, \quad (8)\\ \frac{(1-x_3)(1-x_2)^5(1+x_2)^3}{1+4x_2+x_2{}^2}\left\{\left[W_{e(1,2)}-W_{(1,2)e}\frac{I_2}{I_1}x_2{}^2\right]\alpha_2 N_e-\right.\\ \left.-\frac{D_{CO_2}}{\Lambda^2}x_2(2+x_2)\right\},\end{gathered}$$

where W_i is the probability (per electron) of exciting the vibration i by electron impact, W_{ie} is the probability of the inverse process, α_i is the average number of vibrational quanta excited by the electrons, and D_{N_2} and D_{CO_2} are the diffusion coefficients of the excited molecules N_2 and CO_2 in the gas mixture. For such molecules we assume a Bessel radial distribution, and the quantities x_i in (2) and (8) are referred to the tube axis.

As is well known,[1-3] the thermal regime and the temperature of the gas play an important role in molecular lasers. Therefore, besides (2), (6), (7), and (8) it is necessary to consider the nonstationary equation of thermal conductivity. Using the results[1,22] for the average gas temperature T, we can obtain

$$\frac{dT}{dt} = -\frac{18{,}9}{\pi}\frac{\lambda_{mix}(T)}{c_p\rho R^2}(T-T_w)+\frac{Q_{av}}{c_p}, \tag{9}$$

where $\lambda_{mix}(T)$ is the coefficient of thermal conductivity of the gas mixture, T_w is the temperature of the wall of the gas-discharge tube,

$$c_p = \left(\frac{5}{2}+\frac{1+K_{N_2}}{1+K_{N_2}+K_{He}}\right)k$$

is the effective specific heat of the mixture at constant pressure, $\rho = (1 + K_{N_2} + K_{He})N_{CO_2}$ is the specific density of the gas mixture, and Q_{av} is the average energy released per unit time (per gas particle). Since heating of the gas is due to relaxation of the vibrational energy,[1] we have $Q_{av} \approx 2QI_1/R^2$, and the expression for Q is given by formula (5).

To find D_{N_2}, D_{CO_2} and λ_{mix} we use the expressions given in [1]; the temperature dependence for the diffusion coefficients was assumed to be $\sim T^{2/3}$, and for the thermal-conductivity coefficients of pure gases it was obtained by approximating the data given in [23].

Simultaneous solution of Eqs. (2), (6), (7), and (9) with allowance for (5) and (8), with a choice of the concrete probabilities W_{ei} and W_{ie}, gives the time dependence of the vibrational temperatures T_i, of the populations of the vibrational levels, of the electron and gas temperatures, and of the electron density. To find α_i and W_{ei}, we used the results of Schulz,[24] who measured the cross sections for excitation of the vibrational levels of the molecules N_2 and CO_2 by electron impact (for details see [20]). We note that in the calculation of $W_{e(1,2)}$ we used the cross section obtained by Schulz only for the level 10°0. However, a comparison of the results of the calculation of the relaxation with experiment[17] has made it possible to determine the effective probability $\alpha_2 W_{e(1,2)}$ and to take into account the contributions of the remaining levels v0°0 and $0v^l0$ to the total excitation cross section.

To determine the rates of relaxation of the levels 00^01 and 10^00 in molecular collisions, the gas mixture CO_2–He was excited in [17] by an electric pulse with a current ~40 A ($N_e \sim 2 \times 10^{12}$ cm^{-3}) of duration $\tau = 5 \times 10^{-6}$ sec. The inversion on the transition 00^01–10^00, produced in the pulse, increased after the termination of the pulse as a result of relaxation of the lower level 10^00, reaching a maximum value, and then beginning to decrease as a result of the decrease of the population of the 00^01 level (Fig. 6, dashed curve). It is clear that the relative increase of the inversion by a factor ~7, observed in the experiment, is possible only if the level 10^00 is appreciably populated during the time of the current pulse. However, calculation with $N_e = 2 \times 10^{12}$ cm^{-3}, $T_e^0 = 3.3 \times 10^4$ °K, and the data of Schulz[24] for the conditions of the experiment of [17] did not yield the required growth of inversion in the afterglow, this being attributed to the growth of the population of the 10^00 level in the pulse, i.e., to the small value of the quantity $\alpha_2 W_{e(1,2)}$ chosen for the calculation. Agreement with experiment takes place if one takes for $\alpha_2 W_{e(1,2)}$ a quantity exceeding by 2.4×10^2 times the value obtained in [24]. Therefore we used in all subsequent calculations precisely this value for $\alpha_2 W_{e(1,2)}$. If it is assumed that $\alpha_2 = 3.5$, we then obtain for the cross section of excitation of the entire set of levels of symmetrical and deformation types of oscillation, in the electron energy region $T_e \sim 3$ eV, the value $\sim 1.5 \times 10^{-15}$ cm^2, which agrees well with the total cross section for the collision between CO_2 molecules and electrons.[25]

The result of a simultaneous solution of Eqs. (2), (6), (7), (9), with relations (5) and (8) taken into account and with initial data $T_e^0 = 3.3 \times 10^4$ °K, $T_0 = T_w = 300°$, $x_i^0 = \exp(-h\nu_i/kT_0)$, for a tube of radius R = 1.7 cm, are shown in Figs. 6–11.

Figure 6 shows the typical time dependence of the

[5)] We note that the choice of α and $\delta_{eff}\nu_{eff}$ for the calculation has little influence on the results.

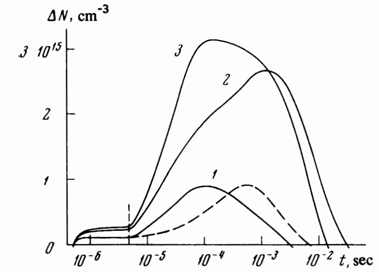

FIG. 6

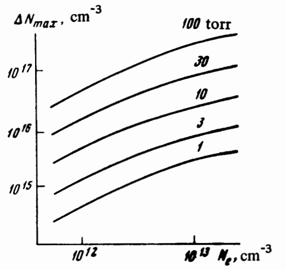

FIG. 7

FIG. 6. Time variation of the inverted population under pulsed electronic excitation of the vibration levels for the mixtures CO_2: He = 1:7 (1), CO_2: N_2 = 1:3 (2), CO_2: N_2: He = 1:3:7 (3) ($N_e = 2 \times 10^{12}$ cm^{-3}, $\tau = 5 \times 10^{-6}$ sec, R = 1.7 cm, T_0 = 300°K). The dashed curve is constructed from experimental data [17].

FIG. 7. Dependence of the maximum inversion in a single pulse on the electron density N_e at a constant current pulse duration $\tau = 5 \times 10^{-6}$ sec and at different partial pressures P_{CO_2}, as marked on the curves (mixture CO_2: He = 1:3, R = 1.7 cm, C_0 = 300°K).

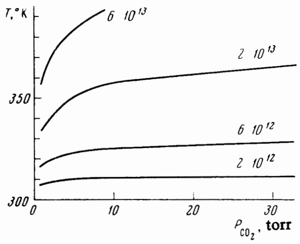

FIG. 8

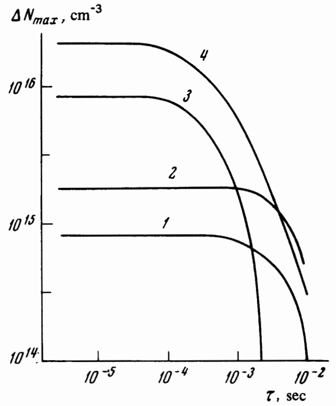

FIG. 9

FIG. 8. Maximum heating of the gas as a function of the partial pressure P_{CO_2} following single electric pulses with different N_e, as indicated on the curves in cm^{-3} ($\tau = 5 \times 10^{-6}$ sec, T_0 = 300°K, R = 1.7 cm, mixture CO_2: He = 1.3).

FIG. 9. Dependence of the maximum inversion on the current pulse duration τ at $N_e\tau$ = const and different partial pressures. $N_e\tau$ is equal to 10^7 sec/cm^3 (1, 3) or 3×10^7 sec/cm^3 (2, 4); P_{CO_2} is equal to 1 torr (1, 2) or 10 torr (3, 4) (mixture CO_2: He = 1:3, R = 1.7 cm, T_0 = 300°K).

inverted population of the level 00^01-10^00 of the CO_2 molecule following application of a short current pulse to the gas mixture.[6] The parameters were the same as in the experiment of [17]. Since the pulse duration τ is shorter than the relaxation time of the 10^00 level, the i inversion produced during the time of the pulse increases after the pulse is terminated, and starts to decrease, as a result of relaxation of the asymmetrical oscillation mode, only after a certain time. Good quantitative agreement between calculation and experiment[17] was obtained for the relative growth of the inversion in a mixture 1 Torr CO_2 + 7 Torr He. The disparity in the times of the inversion maxima is not fundamental and is attributed to the choice of the probability $W_{20}(CO_2-He)$.

Figures 7 and 8 show plots of the maximum inversion and the maximum gas temperature following a single pulse, as functions of the electron density N_e (current density) and partial CO_2 pressure for the mixture CO_2 : He = 1 : 3 at $\tau = 5 \times 10^{-6}$ sec. In the range $N_e = 6 \times 10^{11}-2 \times 10^{13}$ cm^{-3} and P_{CO_2} = 1–100 Torr, the inversion increases approximately linearly with increasing N_e and P_{CO_2}. Further increase of the inversion with increasing N_e is limited by the dissociation of CO_2. Estimates have shown that as a result of a single pulse of duration $\tau = 5 \times 10^{-6}$ sec, 10% of the CO_2 molecules can dissociate at $N_e \sim (4-20) \times 10^{12}$ cm^{-3}.

Notice should be taken of an important feature when working with current pulses whose duration is smaller than the relaxation time of the upper laser level 00^01. In this case the maximum population of the level 00^01, and consequently also the maximum inversion, do not depend on its relaxation rate and are determined by the total reserve of vibrational energy E_3 obtained from the electrons. This is precisely the reason why at $\tau = 5 \times 10^{-6}$ sec the inversion increases linearly with pressure, up to $P_{CO_2} \approx 100$ Torr. In addition, temperature effects play here a much lesser role and a certain decrease of inversion with increasing temperature can occur only as a result of the increase of the equilibrium population of the lower laser level 10^00.

In the case of electronic pulsed excitation, a characteristic parameter determining the reserve of vibrational molecule energy, the maximum inversion, the gas temperature, and the degree of dissociation is the product $N_e\tau$. Figure 9 shows the dependence of ΔN_{max} on the pulse duration τ at constant $N_e\tau$, equal to 10^7 and 3×10^7 sec/cm^3 and at different partial pressures P_{CO_2}, equal to 1 Torr and 10 Torr. We see that at sufficiently small τ the inversion is independent of τ and is determined by the value of N_e. However, if $\tau > \tau_1$, where τ_1 is the time of relaxation of the 00^01 level, the maximum obtained inversion begins to decrease with increasing pulse duration. This is due to the fact that when $\tau > \tau_1$ the relaxation of the upper laser level, which limits the inversion, begins already during the time of action of the current. On the other hand, an increase of the relaxation rate of this level with increasing pressure leads to the presence of an optimal CO_2 pressure (unlike in the case of small $\tau \sim 10^{-5}$ sec, when the inversion increases linearly with pressure, see Fig. 7).

The dependence of the inversion on the pressure at high pulse durations $\tau < \tau_1$ is illustrated in Fig. 10. The shift $P_{CO_2}^{opt}$ towards the larger side with decreasing τ (at constant $N_e\tau$) and with increasing $N_e\tau$ is due to the smaller influence of the relaxation of the level 00^01 on its population in these cases.

Figure 11 shows the change of ΔN_{max}, due to heating of the gas, in a sequence of pulses. The establishment of the thermal regime and of a constant value of ΔN_{max} at a repetition frequency 50 Hz occurs after

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[6] In order for equations of the type (2) to be valid it is necessary that the duration of the current pulse τ and the characteristic times of electron pumping $1/\alpha_i W_{ei} N_e$ be larger than the time of establishment of the Boltzmann equilibrium in each oscillation mode and of equilibrium between the symmetrical and deformation oscillation modes. When $\tau \gtrsim 5 \times 10^{-6}$ sec, $N_e < 2 \times 10^{13}$ cm^{-3}, and P > 1 torr, these conditions are satisfied.

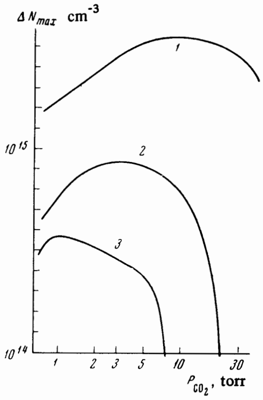

FIG. 10

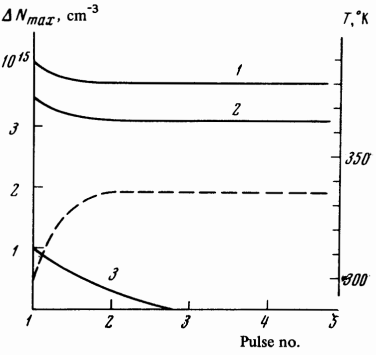

FIG. 11

FIG. 10. Dependence of the maximum inversion in a single pulse on the partial pressure for different $N_e\tau$ and different current pulse durations τ: curve 1 – $N_e = 2 \times 10^{10}$ cm^{-3}, $\tau = 1.5 \times 10^{-3}$ sec; 2 – $N_e = 5 \times 10^9$ cm^{-3}, $\tau = 2 \times 10^{-3}$ sec; 3 – $N_e = 2 \times 10^9$ cm^{-3}, $\tau = 5 \times 10^{-3}$ sec (mixture CO_2: He = 1:3, R = 1.7 cm, $T_0 = 300$°K).

FIG. 11. Variation of the maximal inverted population and of the gas temperature (at the instant of switching on of the pulses) in a sequence of pulses for different N_e (1 – $N_e = 5 \times 10^{11}$ cm^{-3}, 2 – $N_e = 6 \times 10^{10}$ cm^{-3}, 3 – $N_e = 6 \times 10^9$ cm^{-3}) and P_{CO_2}. Curves 1, 2 – ΔN_{max} at $P_{CO_2} = 1$ torr, 3 – ΔN_{max} at $P_{CO_2} = 5$ torr, dashed curve – dependence of T at $N_e = 6 \times 10^9$ cm^{-3} and $P_{CO_2} = 1$ torr (mixture CO_2: H = 1:3, $\tau = 10^{-2}$ sec, R = 2.5 cm, $C_0 = 300$°K, pulse repetition frequency 50 Hz).

2–3 pulses. The decrease of the inversion due to the heating is particularly large for current pulses with duration $\tau > \tau_1$. In this case, owing to the increase of the relaxation rate of the 00^01 level, the optimal pressures of CO_2 will be smaller than for a single pulse (Fig. 10). In addition, gas heating leads to a limitation of inversion with increasing current and to the occurrence of optimal values of N_e.

As seen from the foregoing analysis, in the case of short exciting pulses ($\tau < \tau_1$) with large current density ($N_e \sim 10^{12}$–10^{13} cm^{-3}), at large partial pressures $\sim 10^2$ Torr, one can obtain for the 00^01–10^00 transition an inversion $\gtrsim 10^{17}$ cm^{-3}, i.e., larger by two orders of magnitude than its value for a stationary discharge or for a pulse discharge with low pressures. A similar gain can be expected also for the power when a pulsed laser is operated both in the ordinary regime and in the Q-switched regime. In the latter case, the output power is proportional to the inversion at the instant of Q switching, so that to obtain maximum power the instant of switching should correspond to attainment of ΔN_{max} in the pulse.

The main data of the experimental papers[11–17] are in qualitative agreement with the results obtained above. Some of the calculated dependences of the maximum inversion on the pressure, shown in Fig. 10, are given for typical experimental conditions.[15] Just as in [15], the calculation yields optimal values of the pressure. The conclusions of the present paper are in good agreement with the results of Hill,[16] who obtained a large output power without limitation on its growth up to pressures ~ 60 Torr at current pulse durations $\tau = 5$–50 μsec.

4. ORGANIZATION OF EXPERIMENTS

A study of the kinetics of physical processes in nonstationary CO_2 lasers allows us to make concrete recommendations, both in the case of gasdynamic expansion and in the case of pulsed electronic excitation, concerning the organization of experiments and obtaining the optimal conditions for the operation of existing lasers. Let us point out some of the consequences of our calculations.

The experiments with gas dynamic expansion can be organized in two ways: a) using expansion of a CO_2–N_2 mixture of fixed chemical composition, b) using recombination reactions.

When population inversion is produced in an expanding CO_2–N_2 gas mixture, the optimal mixture composition is $CO_2 : N_2 = 1:3$–$1:5$, with initial gas temperature ~ 1200–2000°K. This temperature is not a critical parameter and its choice within the indicated limits has little influence on the magnitude of the inversion. The inversion is very sensitive, however, to the initial pressure and to the initial characteristic gas dimension. In the case of the escape of gas through a long slit ("plane" problem), the optimal partial pressure of CO_2 is $P_0^{opt} \sim 7.6 \times 10^2$–$1.5 \times 10^3$ Torr (300° K) and the optimal slit dimension is $2R_0 \sim 2$ mm, while in the case of escape through a round aperture $P_0^{opt} \sim 7.6 \times 10^2$ Torr and $R_0 \sim 5$ mm.

The distance from the expansion plane at which the maximum inversion is obtained depends on the initial gas pressure and on the dimension of the aperture. For the indicated cases it equals ~ 4 cm and 2 cm, respectively.

A very effective combination is that of chemical processes of the type $CO + O \rightarrow CO_2$ and gasdynamic expansion. In this case, however, more detailed studies of the recombination kinetics are necessary to determine the optimal conditions.

For pulsed electronic excitation, as shown theoretically in the present paper, the output power in the pulse, for CO_2 lasers, can in principle be increased by two orders of magnitude. To this end it is necessary to work with pulses whose duration is shorter than the relaxation time of the upper laser level, to use high pressures $P_{CO_2} \gtrsim 10^2$ Torr, and to maintain $N_e \sim 10^{12}$–10^{13} cm^{-3} at increasing pressure it is necessary to increase the voltage on the discharge tube. Since pulsed electronic excitation with short current pulses eliminates a number of difficulties encountered in the stationary regime (large relaxation rates of the upper laser level), other polyatomic molecules, besides CO_2, are promising. For example, one can expect appreciable generation powers with the 00^01–02^00 transition of the N_2O molecule at large pressures of the N_2O–N_2 mixture.

Great interest attaches to the organization of experiments to determine the probabilities of the elementary processes with the aid of pulsed electronic excitation, particularly the probability of excitation of symmetrical and deformation oscillation modes of CO_2 by means of electrons. As was shown above, on the basis of the experiment of [17], the latter quantity amounts to $\sim 5.0 \times 10^{-8}$, which is 240 times larger than the value obtained by Schulz[24] for the 10^00 level. More accurate values of this and other probabilities of excitation of vibration levels can be obtained by organizing suitable experiments. It is necessary here that the current-pulse duration in the experiment be shorter than the time of the collisional molecular relaxation of the vibrational level or of the group of levels whose electronic-excitation probability is being determined. The electron density in the pulse should be measured and should be sufficient to to produce a noticeable change in the level populations. The probability of the electronic excitation can be determined from the change in the populations of the levels or of the inversion.

On the whole, the nonstationary methods of excitation are of great theoretical and applied interest, and include many still unused possibilities.

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