POWERFUL GAS LASERS

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INTRODUCTION

NEW trends have developed in recent years in gas-laser technology, involving the use of monotonic gases as active media and a more extensive utilization of physico-chemical processes. This has become manifest primarily in the development of molecular lasers, delivering continuous power on the order of several hundred watts at 10—15% efficiency, and the development of lasers with molecule photodissociation, proposed by I. I. Sobel'man and S. G. Rautian[1].

We review in this survey the work on CO_2 molecular lasers, to which much attention has been paid during the last year in the periodical literature.

There is still no unified point of view concerning the inversion mechanism in CO_2 and the role of the different elementary processes. The published articles on this subject contain in many cases contradictory opinions concerning these questions. This is connected to a considerable degree with the complexity of the phenomena occurring in the molecular systems and with the lack of a theory of multilevel lasers with due allowance for relaxation processes. The critical analysis of publications on CO_2 lasers may also be of interest because the inversion mechanism in CO_2 lasers has unique features that are peculiar to a broad class of molecular and chemical lasers.

It is known that until most recently the efficiency of lasers did not exceed several tenths of one per cent and was in many cases even much lower than that. The main reason of such low efficiencies was that a negligible fraction of the total number of excitation events in the gas discharge led to the emission of stimulated photons.

An analysis of the kinetics of the processes in the active medium has led G. Gould[2] and others, at the end of 1963, to the conclusion that the use of relaxation processes in conjunction with inelastic electron and atom collisions is an important factor in the construction of powerful gas lasers. Such lasers are called collision lasers.

In the fall of 1964, G. Gould delivered to the conference on chemical lasers a paper called "Collision Lasers[2]," in which he expounded the fundamental principles of high-efficiency gas lasers and predicted the possibility of obtaining power densities on the order of 1 W/cm^3 at efficiencies exceeding 10%. The proposed working media were atom pairs of several elements (manganese and lanthanum) having a relatively large number of fine-structure levels.

Gould's paper apparently did not attract the deserved attention, and was not cited in subsequent papers on molecular lasers, although, as will be shown below, the premises formulated by him have become most successfully embodied just in molecular lasers, and not in lasers with atomic pairs of elements with developed fine structure. The gist of Gould's premises[2] consists in the following. To produce a high-efficiency laser, the upper working levels should have relatively long lifetime ($\tau_1 \simeq 10^{-4}$ sec) and should not disintegrate noticeably under the influence of inelastic collisions with other atoms or by diffusion to the walls.

For effective utilization of the excitation energy of the upper level, the probability of stimulated transitions should be at least one order of magnitude larger than the reciprocal lifetime of the upper level, i.e.,

$$\frac{\overline{P}}{N_1 h\nu} \gg 10^5 \text{ sec}^{-1},$$

where $\overline{P}$ is the generation power density and N_1 is the population of the upper level.

The maintenance of population inversion will be ensured if the lifetime of the lower working level τ_1 will be smaller by one order of magnitude than the quantity $N_1 h\nu/\overline{P}$, i.e., $\tau_2 \lesssim 10^{-6}$ sec.

Such second-level lifetimes cannot be ensured by radiative decay if this level is located sufficiently low above the ground state, all the more when account is taken of reabsorption of the radiation. The high position of the second level leads unavoidably to a lowering of the laser efficiency $\eta_{max} = h\nu/E_1 = 1 - E_2/E_1$. A way out of this contradiction is, according to Gould, to use inelastic atom collisions for the disintegration of the lower level. At a colliding-particle potential energy $\Delta E \lesssim kT_{gas}$. The cross sections of the inelastic collisions can reach 10^{-15} cm^2 and are in a position to ensure short level lifetimes. However, in order for the population of the second level to be much lower than that of the ground state in the presence of a Boltzmann distribution, the energy of the second level should be much higher than the translational-motion energy, i.e.,

$$E_2 > kT_{gas}.$$

These conditions can be satisfied if the nonradiative decay of the lower level occurs in several stages in a system of closely-spaced levels that couple the lower working state with the ground state.

It would be natural to assume that such a situation can occur in molecular systems, but Gould has expressed the misgiving that in the presence of a developed level system in the molecules it will not be possible to concentrate the excitation in the working transition.

According to[2]; a laser with high efficiency and large power density should satisfy the following requirements:

a) The probability of the laser transition should be low (partial forbiddenness).

b) The upper level should not decay noticeably under inelastic collisions ($E_1 - E_2 \gg kT_{gas}$).

c) The working levels should lie low, so as to ensure large absolute populations and electron-excitation rates.

d) The cross section for inelastic collision between the working and adjacent levels should be large ($\Delta E \lesssim kT_{gas}$).

e) All levels with noticeable population should contribute to the passage of the atoms through the working transition.

f) The total energy interval $\Sigma\Delta E_i$ in a sequence of closely lying levels should ensure the existence of inversion ($N_1 > N_2$), in which connection the Boltzmann factors in the distributions of the electrons and the atoms should satisfy the inequality

$$e^{-\Sigma\Delta E_i/kT}{}_{gas} < e^{-(E_1-E_2)/kT_e};$$

g) The gas density should be low, so as to satisfy in the discharge the inequality $T_e \gg T_{gas}$, but at the same time it should be sufficient for the inelastic collisions to be effective (tentative atom density $\sim 3 \times 10^{17}$ cm^{-3}).

The excitation of the upper level should occur not directly, but with the aid of a gas impurity that concentrates the maximum population density at the isolated level.

It is easy to verify that the foregoing requirements can be satisfied also in molecular lasers. The aggregate of the rotational levels ensures the necessary rates of decay of the lower working level even at gas pressures on the order of several mm Hg, owing to the short rotational relaxation times.

Of great importance for the operation of molecular lasers, as will be shown later, are also the competition of the vibrational-rotational transitions, the saturation of the working transition, inelastic molecule collisions, the presence of Fermi resonance, etc. Therefore the list of requirements that must be satisfied by powerful high-efficiency lasers can presently be substantially increased.

The first to report laser generation with CO_2 molecules was Patel, at the session of the American Physical Society in April 1964.[3] Patel's first publications[4,5] reported generation at 13 lines of the 00^01-10^00 band and 7 lines of the 00^01-02^00 band, and the total power was approximately 1 milliwatt.

The operation of the laser was explained on the basis of a four-level scheme with radiative decay of the lower level, while the role of the relaxation process was not noted.

In subsequent investigations Patel[6,7], Legay-Sommaire[8], and Moeller and Ridgen[9] obtained an appreciable increase in the power and efficiency by introducing nitrogen and helium into the discharge. Investigations in the pulsed mode[10-12] and in a Q-switched mode[13-16] has made it possible to estimate the lifetimes of the vibrational levels and to calculate a number of relaxation processes in the mechanism of the decay of the lower working level. Investigations in the Q-switched mode have also made it possible to understand better the competition between the vibrational-rotational transitions. These phenomena greatly reduce the number of lines in the laser emission spectrum.

Research on molecular lasers has attracted much attention, and within a short time, in 1966, continuous power up to 700 W and efficiencies up to 15% were attained, mostly by increasing the laser length.* It has been proposed[18] that the efficiency can reach 30—40% and that the power will amount to many kilowatts. For a detailed survey of the experimental work on CO_2 lasers we can recommend the review of N. N. Sobolev and V. V. Sokovikov[19]. Experimental investigation of the elementary processes in molecular lasers have explained a number of important details in the population-inversion mechanism.

In light of the foregoing requirements imposed on high-efficiency lasers, let us consider the main elementary processes occurring in discharges in a mixture $CO_2 + N_2 + He$ and the scheme of the lower levels of the electronic ground state of the molecule CO_2.

1. ELEMENTARY PROCESSES IN CO_2 LASERS

a) Scheme of Lower Levels of CO_2 Molecule

CO_2 is a linear symmetrical molecule with zero dipole moment and belongs to the point-symmetry group $D_{\infty h}$ and has three normal oscillation frequencies (see Fig. 1)[20]:

$\nu_1 = 1388.3$ cm^{-1} — symmetrical valence oscillation,

$\nu_2 = 667.3$ cm^{-1} — deformation valence oscillation,

$\nu_3 = 2349.3$ cm^{-1} — antisymmetrical valence oscillation.

The foregoing values hold for the molecule $C^{12}O_2^{16}$[21]. The deformation oscillations are doubly degenerate, since oscillations with the same frequency can occur in two orthogonal planes passing through the molecule axes.

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*According to the latest data (Electronic News 11, No. 573, 44 (1966) the maximum attained power is 1100 W.
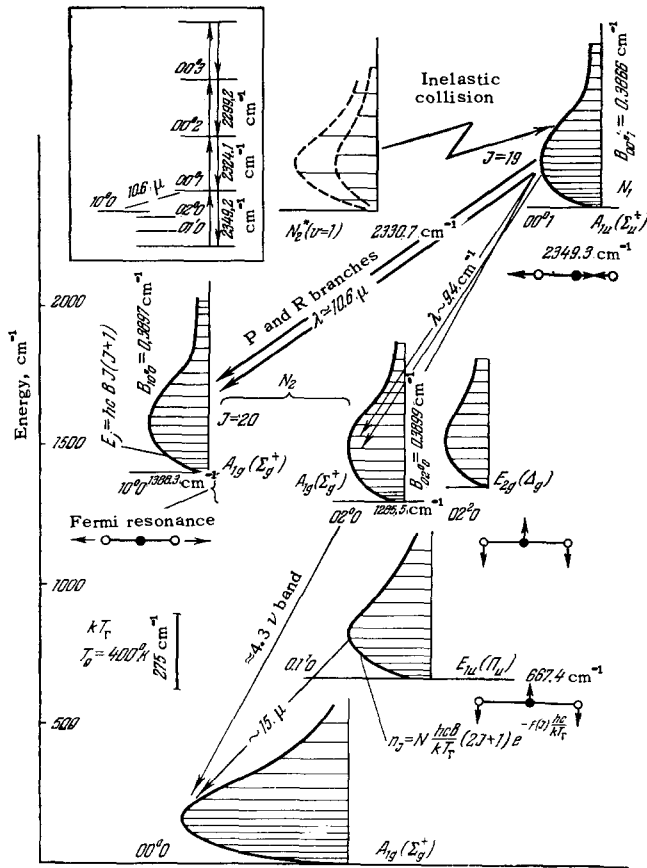
FIG. 1. Scheme of lower vibrational levels of the electronic ground state of the CO_2 molecule. To each vibrational state there corresponds a system of rotational levels with population distribution n_J. Each vibrational level is tagged with the energy (in cm^{-1}), the value of the rotational constant B, the type of symmetry of the state, and with a schematic designation of the vibrational motion of the atoms. The first vibrational level of the nitrogen molecule $N_2^*(v = 1)$ has a large cross section for inelastic collision with the 00^01 level. On the upper left is shown the arrangement of the 00^0v levels. On the lower left (to show the scale) is given the energy of the thermal motion kT_{gas}.

The structure of the vibrational levels of the molecule CO_2 are determined by the set of normal frequencies (ν_1, ν_2, and ν_3), their overtones, and composite combination frequencies.

The corresponding levels are designated by a combination of quantum numbers (v_1, v_2^l, v_3). Figure 1 shows the scheme of the lower vibrational levels of the electronic ground state of the CO_2 molecules and the aggregate of the rotational levels belonging to them.

On the upper left of Fig. 1 we show the position of the higher vibrational levels 00^0v.

For clarity, the lengths of the rotational-level lines are chosen proportional to the populations of the corresponding levels. The indices on the left denote the aggregate of the quantum numbers characterizing the level energy, and the indices on the right the types of symmetry of the state and the point group.

The additional quantum number l over the second index is due to the double degeneracy of the deformation oscillation. It takes on the values:

l = v, v − 2, ..., 0 − for even v_2,

l = v, v − 2, ..., 1 − for odd v_2,

and determines the value of the angular momentum $M_p^{vib} = \hbar l$, connected with the vibrations and directed along the molecule axis.

Levels with $l = 0$ are not degenerate, and those with $l > 0$ are doubly degenerate. When $v_2 > 1$, the degeneracy is lifted, owing to the anharmonicity of the CO_2 molecule.

The levels 02^20 and 02^00 belong to different point-symmetry groups[20].

The same figure shows, to illustrate the scale, the energy kT_{gas} of the thermal motion of the molecules, and the position of the first vibrational level of the nitrogen molecule N_2^* (v = 1) and its rotational structure.

Owing to the accidental coincidence of the frequency ν_1 and the second harmonic $2\nu_2$ of the deformational vibration (02^00), a shift of the corresponding levels takes place in the CO_2 molecule (Fermi resonance), and the states of the molecule at the levels 10^00 and 02^00 are mixed. A detailed treatment of this question is found in books on molecular spectroscopy[20,22], and the calculated values of the perturbed and unperturbed frequencies are contained in[21]. In[21], in particular, it is indicated that the Fermi resonance can explain the short vibrational-relaxation time of the lower working level 10^00, since the deformation oscillations (01^00 and 02^00) have the smallest relaxation time of all three types of oscillations.

This remark agrees with the strong influence of the generation power on the conductivity of the plasma in CO_2 discharge, described in[23]. Indeed, a lowering of the generation power, say by introducing losses in the resonator, leads to a decrease in the population of the lower working level (10^00), since its population depends significantly on the rate of the induced processes. The connection between the levels (10^00) and (02^00), which have the same parity, should lead, as a result of the Fermi resonance, to a change in the population of the 02^00 level, which has apparently a large cross section for interacting with the electron component[13] and a short vibrational-relaxation time[21,24].

According to the selection rules for the molecular systems in the dipole approximation, transitions between vibrational levels belonging to states of different parity g − u, with change of one of the vibrational quantum numbers by unity, are allowed. Accordingly, only two strong bands are observed in the emission spectrum of CO_2, with $\nu_2 = 667.4$ cm^{-1} and $\nu_3 = 2349.3$ cm^{-1}. The bands that follow them in intensity correspond to transitions to the ground state from the level 02^01 and 10^01. The remaining bands in the emission spectrum are weak or very weak. This

confirms the well known premise that in molecular systems electron collision excited only the lowest vibrational levels, connected with dipole transition with the ground state.

The bands corresponding to transitions between levels of like parity, g-g and u-u, are observed only in the Raman scattering spectrum. Owing to the Fermi resonance, the Raman-scattering spectrum of CO_2 contains a strong double band with $\nu_1 = 1285.5$ and 1388.3 cm^{-1}, with relative intensity $1:0.59$[22], in lieu of one unperturbed band with $\nu_1 = 1345$ cm^{-1}[21].

Transitions with a simultaneous change of two and three quantum numbers, and also of one quantum number by more than one unity, are forbidden in the dipole approximation. These include, in particular, also the working transitions (00^01-10^00) and (00^01-02^00), observed in the form of weak bands in the emission spectrum of CO_2. Recent investigations of the CO_2 spectrum have also shown the presence of (10^00-01^10) and (02^00-01^10) bands[12].

A more complete scheme of the vibrational levels of CO_2 is given in the book by Herzberg[22]. The same book gives information on the observed CO_2 bands in the Raman spectrum and in the spontaneous-emission spectrum. From an examination of these data it is seen that even weak lines terminating at the (00^01) level were not observed in the CO_2 spectra.

Information on the probability of transitions between levels of the CO_2 molecule is practically nonexistent. Recently, the probability of the vibrational-rotational transition of the 00^01-10^00 band to the lines of the P-branch $(J = 18 - 22)$ was measured and found to be (0.21 ± 0.03) sec^{-1}[25]. (For the 10^00-02^00 band, according to the measurements of I. K. Babaev and S. N. Tsys', the probability of the transition $P = 18$ is 0.25 ± 0.02 sec^{-1}.)

The measurement procedure consisted of the following. The beam from a laser oscillating at three lines of the P branch was directed to an absorption cell. From the known population of the vibrational and rotational levels, which were calculated by using the equilibrium temperature of the gas in the cell, and the radiative lifetime of the transition, averaged over the indicated lines, was determined from the measured absorption coefficient.

According to the calculations of[26], the probability of the other transitions, which are forbidden in the dipole approximation, is of the order of several tenths of an sec^{-1}. The probability of dipole transitions from the ground state from the levels 00^01 and 01^10 is of the order of 10^2 sec^{-1}.

Population inversion at the vibrational-rotational transitions and the number of generating lines depend on the distribution of the population over the rotational levels.

In vibrational-rotational spectra of spontaneous emission of symmetrical molecules having equivalent nuclei with spin $I \neq 0$, there is observed alternation

of the line intensity as the rotational quantum number J is varied. Since the oxygen isotope O^{16}, which has an abundance of 99.76%, has a nuclear spin $I = 0$, only symmetrical rotational states with even values of J for the lower level exist in the CO_2 molecule[20].

The molecule rotational energy is determined by the formula

$$E = hcBJ(J+1) = hcF(J),$$

where B is the rotational constant and the energy of the rotational-vibrational-transition quantum is given by

$$E' - E'' = h\nu_{00} + hc[F(J') - F(J'')],$$

where ν_{00} is the frequency of the zeroth line (for a pure vibrational transition).

The dipole transitions of CO_2 satisfy the selection rule $\Delta J = J' - J'' = +1, 0, -1$, corresponding to the observed R, Q, and P branches of the emission spectrum. For parallel bands with a transition dipole moment directed along the molecule axis, we obtain the additional hindrance $\Delta J = 0$ and there is no Q branch. Since the upper working level 00^01 corresponds to an asymmetrical valence oscillation with dipole moment directed along the molecule axis, only parallel bands of the R and P branches are observed in the generation spectrum. For transitions from the (01^10) level, corresponding to deformational vibration, perpendicular bands are observed. The selection rule for the quantum number l in parallel bands is $\Delta l = 0$, therefore the spectrum does not contain the transitions $00^01 - 02^20$.

For an equilibrium distribution of the molecules at a temperature $T_{rot} \simeq T_{gas}$, the population of the J-th rotational level, with allowance for its statistical weight $g_J = 2J + 1$, is determined by the formula

$$n_{Jv} = \frac{N_v}{Q} g_J \exp\left[-F(J)\frac{hc}{kT_{gas}}\right] \approx N_v \left(\frac{hcB}{kT_{gas}}\right)(2J+1)e^{-F(J)\frac{hc}{kT_{gas}}},$$

where

$$Q = \sum_J (2J+1) e^{-F(J)\frac{hc}{kT_{gas}}} \approx \frac{hcB}{kT_{gas}}\cdots, \qquad (1)$$

N_V is the total number of molecules at the vibrational level. This distribution over the vibrational levels, and also the values of the rotational constants B for different vibrational levels, are indicated in Fig. 1.

The values of J_{opt} corresponding to the maximum of the distribution, are determined by the expression

$$J_{opt} = \sqrt{\frac{kT_{gas}}{2hcB}} - \frac{1}{2} \approx 0.95\sqrt{T_{gas}} - \frac{1}{2}. \qquad (2)$$

For the usually observed intense line $P(20)(J' = 19)$ this corresponds to $T_{gas} \sim 400°K$. When the gas is cooled[27], a tendency is noted towards generation at transitions with lower values of J.

According to (1), the distribution n_{Jv} for a system of rotational levels is determined by the total number

of molecules N_V of the vibrational state and by an exponential factor. For the levels 10^00 and 02^00, which are connected by the Fermi resonance, the values N_{10^00} and N_{02^00} are not independent.

It can be shown that if the rotational relaxation leads to establishment of an equilibrium distribution in the rotational structure of the levels 10^00 and 02^00, then the ratio of their populations will be determined by the Boltzmann factor

$$\frac{N_{10^00}}{N_{02^00}} = \exp\left[-\frac{\Delta E}{kT_{gas}} \right],$$

where ΔE is the difference in the energies of the ground states of the levels, equal to 103 cm^{-1}, $N_{10^00}/N_{02^00} \simeq 0.6$ for $T = 300°K$ and ~ 0.7 for $T = 400°K$. Under the indicated assumption, the distribution (1) for the 10^00 level can be expressed in terms of the total number of molecules N_2 at the bound levels 10^00 and 02^00:

$$n_{J_2} = \frac{N_2 e^{-\Delta E/kT}_{gas}}{1 + e^{-\Delta E/kT}_{gas}} \frac{hcB}{kT_{gas}} (2J+1) e^{-F(J)\frac{hc}{kT}_{gas}}. \quad (3)$$

Therefore the lifetimes of the levels 10^00 and 02^00 should not be regarded separately as independent quantities, but it is necessary to determine the lifetime of a system of two levels.

b) Lifetimes of Vibrational Levels

In lasers using the CO_2 + N_2 + He mixture, the time of rotational relaxation of the CO_2 molecule is sufficiently small, and it can be stated that, at least in the continuous mode, the distribution of the rotational-level populations differs little from equilibrium. Under these conditions, the inverse population can be expressed simply in terms of the total populations of the upper and lower vibrational levels $N_{1,2}$. The stationary distribution N_i can be obtained by solving the system of kinetic equations

$$\frac{dN_i}{dt} = \sum_j M_{ij} - N_i \left[\tau_i^{-1} + \sum_j (A_{ij} + K_{ij}N_j) \right], \quad (4)$$

where $\sum_j M_{ij}$—rate of excitation of the i-th level due to collisions with particles of species j (molecules, electrons);

τ_i—total relaxation time of the i-th vibrational level in a mixture of given composition;

$\sum_j A_{ij}$—sum of probabilities of the radiative transitions to other levels; and

$K_{ij}N_j$—probability of decay of the i-th level by inelastic collisions with particles of species j.

The quantity τ_A^{-1}, which is a reciprocal of the time of natural vibrational relaxation of the pure gas, is defined as the ratio of the average number of collisions per second at a given pressure p_A to the number of effective collisions Z_{AA} leading to a conversion of the internal energy of the molecule to the energy of translational motion.

If we define the number of collisions Z for a certain expression, for example, 1 torr, then

$$\tau_A^{-1} = \frac{Z}{Z_{AA}} p_A = t_{AA}p_A.$$

The usual method of measuring the relaxation time is by determining the dispersion of ultrasound at normal temperatures and yields values only for the lower vibrational levels [28].

For polyatomic molecules having several normal oscillation frequencies, the relaxation can proceed in several ways. For the CO_2 molecule, just as for SO_2, the most probable mechanism of vibrational relaxation of the 10^00 and 00^01 levels is apparently the sequence [28]

$$CO_2(00^01) \rightarrow CO_2\begin{pmatrix} 10^00 \\ 02^00 \end{pmatrix} \rightarrow CO_2(01^10) \rightarrow CO_2(00^00),$$
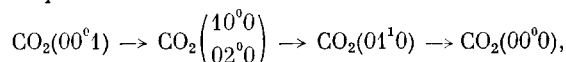
with

$$\tau_{00^01} > \tau_{\substack{10^00 \\ 02^00}} > \tau_{01^10}.$$

The relaxation of the 02^00 level occurs principally as a result of exchange processes $CO_2(02^00)$ + $CO_2(00^00) \rightleftharpoons 2CO_2(01^10)$.

In the case of a mixture of two gases, relaxing (A) such as CO_2 and nonrelaxing (B) such as helium, the exchange of the translational and vibrational energies can be the result of two processes: [28]:

a) $A^* + A \rightarrow A + A$ – intrinsic relaxation,

b) $A^* + B \rightarrow A + B$ – relaxation on the impurity B.

The resultant relaxation time is determined by the ratio $\tau^{-1} = t_{AA}p_A + t_{AB}p_B$, where p_A and p_B are the partial pressures of the gases, in torr, t_{AB} = Z/Z_{AB}, where Z_{AB} is the average number of collisions necessary for the molecule A^* to lose one quantum of vibrational energy, and Z is the total number of $A \rightarrow B$ collisions per second at a pressure of 1 torr.

Table 1 lists the values of the effective numbers of the collisions Z_{AB} and of t_{AB} at p_A and $p_B = 1$ torr for mixtures of CO_2 with other gases. The high probability of energy transfer in $CO_2 - H_2O$ collisions can apparently be attributed to the formation of an intermediate intermolecular complex.

The values of Z_{AB} in Table I are valid for the lower vibrational state of the CO_2 molecule, most likely 01^10, since the measurements were made at normal temperature (293°K). The value of Z_{AB} for the $CO_2 -$ He mixture decreased with increasing gas temperature [28].

There is no assurance that these values can be

Table I

| Mixture	Z_{AB}	t_{AB}	Mixture	Z_{AB}	t_{AB}
CO_2-CO_2	108 000	520	CO_2-H_2O	130	—
CO_2-He	1 500	$(4\cdot10^4)$	CO_2-CO	230	—
CO_2-N_2	1 200	$(4.5\cdot10^4)$			

used to estimate the lifetimes of higher vibrational levels. Indeed, the values τ_{00^01} reported in the literature[13,16] lie in the intervals 0.8 – 3 msec and greatly exceed those calculated in accord with the data of Table I.

Moreover, there are indications[13] that the intensity of the spontaneous emission from the 00^01 level is increased by addition of helium. This fact is difficult to explain if it is assumed that the helium reduces greatly the lifetime of the 00^01 level. At the same time, there are reliable data confirming that the helium decreases the lifetime of the 10^00 by two orders of magnitude[32]. It follows therefore that the time of vibrational relaxation on the impurities greatly depends on the energy level.

In a mixture of two relaxing gases such as CO_2 and N_2, the processes become much more complicated. At small resonance defects of the colliding molecules, equilibrium in the mixture should become rapidly established as the result of excitation-exchange processes:

$$A^* + B \rightleftarrows A + B^*.$$
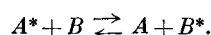
The relaxation of the entire system will be described by two exponential functions $\exp[-\tau_A^{-1}t]$ and $\exp[-\tau_B^{-1}t]$, where

$$\tau_A^{-1} = t_{AA}p_A + t_{AB}p_B, \quad \tau_B^{-1} = t_{BB}p_B + t_{BA}p_A.$$

The values of the coefficients t_{ij} for the working levels 00^01 and 10^00 of the CO_2 molecule are unknown, but nevertheless it is possible to draw a number of qualitative conclusions from the publications on CO_2 lasers.

The relaxation time τ_1 of the upper level changes little in relatively wide nitrogen and helium pressures and exceeds the relaxation time τ_2 of the lower level.

As is well known, only under these conditions is cw generation possible.

Consequently, $t_1^{CO_2-CO_2} < t_2^{CO_2-CO_2}$ and $t_1^{CO_2-N_2} < t_2^{CO_2-N_2}$. When a small amount of water vapor is added to the discharge[29], an increase is observed in the generation power, and this gives grounds for assuming that $t_1^{CO_2-H_2O} < t_2^{CO_2-H_2O}$.

The level relaxation times, and consequently the coefficients $t_{1,2}^{ij}$ depend on the gas temperature. Thus, for example, when the temperature increases from 300 to 500°K, τ_{01^10} decreases by approximately one-half. The lack of data on the temperature coefficients of the working levels makes an estimate of τ at the working temperatures of the gas difficult.

Information on the effect exerted by admixtures of other molecular gases on the generation power of a CO_2 laser are contained in[31]. The relative change in generation power following addition of 25% of impurity is listed in Table II. The power obtained with pure CO_2 is taken as unity. The influence of the in-

Table II

Gas	N_2	Air	CO	H_2	O_2	N_2O	C_2H_2	C_2H_4
P/P_{CO_2}	3	2.6	1.5	1	0.5	0.5	0	0

dicated impurities on the generation power can be connected with different factors – change in the electron temperature and electron density, change in the level lifetime, absorption in the gas, etc.

Comparing the positions of the lower vibrational levels of the indicated molecules with the working levels of CO_2, we can reach the conclusion that in some cases the influence of the impurity is connected with resonant transfer of excitation in inelastic collisions.

Figure 2 shows the position of the lower levels of CO_2, N_2, CO, O_2, H_2O, and N_2O. The role of N_2, as indicated earlier, consists essentially in increasing the rate of exchange of the upper level and decreasing the lifetime of the lower one. The CO molecule has a first-excited level with small resonance-energy defect relative to E_{00^01}:

$$\Delta E = E_{00^01} - E_{CO}(v=1) \approx -150\,\text{cm}^{-1} < kT_{\text{gas}}.$$

The lifetime of the intrinsic relaxation and $p_{CO} = 1$ torr is approximately 76 msec[28], and therefore the inelastic collisions $CO^* + CO_2 \rightarrow CO + CO_2^*$ (00^01) can increase to a certain degree the rate of excitation of the upper working level.

The drop in power when molecular oxygen is introduced into the discharge can be partially explained as being due to the small resonance defect of the O_2 level ($^3\Sigma_g^-$) relative to the CO_2 levels (10^00, 02^00). Then, in the presence of excited O_2 ($^3\Sigma_g^-$) molecules in the discharge, an increase takes place in the rate of excitation of the lower working level and the population inversion decreases. The time of the intrinsic vibrational relaxation of $O_2(v=1)$ at $p_{O_2} = 1$ torr is approximately 2.4 sec, and that of $N_2(v=1)$ at $p_{N_2} = 1$ torr is 14.5 – 16 msec[28,33].

The quenching action of N_2O can also be due to an increase in the population of the lower working level of CO_2 (10^00, 02^00), since the resonance defect for this level is much smaller than for the upper one. Cessation of generation upon introduction of ethylene (C_2H_4) into the discharge is more likely to be connected with intense absorption by the latter at the 10.6 μ wavelength. In addition, it is well known that hydrocarbon molecules have small vibrational-relaxation times and have a strong de-activating effect.

It is impossible to present any quantitative estimates of the time of the vibrational relaxation of the working levels of CO_2 mixed with other molecular gases, for the time being. The intrinsic relaxation time of the 00^01 level for $T_{\text{gas}} = 300°K$ was meas-
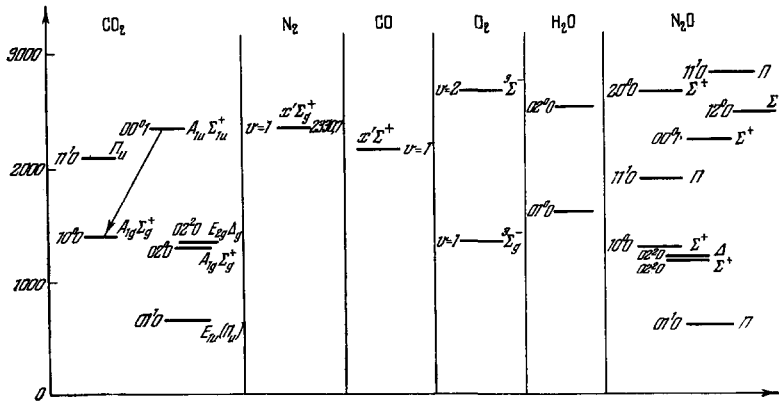
FIG. 2. Comparative position of the lower vibrational levels of the molecules CO_2, N_2, CO, H_2O, and N_2O.

ured in [30]. The measurement method consisted in observing the rate of decay of the 00^01 level after excitation by a short pulse from an external source.

It was shown there that the reciprocal time τ_1^{-1} increases linearly with the pressure:

$$\tau_1^{-1} = t_1^{CO_2-CO_2} p_{CO_2},$$

where $t_1^{CO_2-CO_2} = 385$ sec^{-1} torr^{-1}.

At working temperatures 400—500°K, $t^{CO_2-CO_2}$ apparently increases.

Measurements of τ_2 for the lower level were not made, but it can be assumed that $t_2^{CO_2-CO_2} \gtrsim 500$—700 sec^{-1} Torr^{-1}.

Since helium greatly reduces the relaxation time τ_2, we can conclude that $t_2^{CO_2-He}$ is large and can exceed ~700—800 sec^{-1} torr^{-1}.

Witteman's results [24,29] point to large values of $t_2^{CO_2-H_2O}$ but a quantitative estimate of this value is not given. We know likewise of no published data with which to determine $t_{1,2}^{CO_2-N_2}$.

Direct measurements of the rate of decrease of the spontaneous radiation after an excitation pulse do not give the true values of the level lifetime in the presence of resonance with the mixture components, for in this case a complicated process is observed, described by several exponentials. Thus, for example, upon relaxation in the system

$$CO_2(00^01) + N_2(0) \rightleftarrows CO_2(00^00) + N_2(v = 1)$$
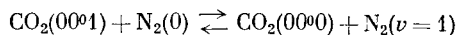
the observed relaxation times of the mixture λ_1^{-1} and λ_2^{-1} will be (see Appendix I)

$$\lambda_{1,2} = -\frac{\tau_1^{-1} + \tau_y^{-1} + k\,(y_0 + x_0)}{2}$$

$$\pm \left\{ \left[\frac{\tau_1^{-1} - \tau_y^{-1} + k\,(y_0 - x_0)}{2} \right]^2 + k^2 x_0 y_0 \right\}^{1/2},$$

where the subscripts 1 and y pertain to $CO_2(00^01)$ and N_2, $k = \langle \sigma v \rangle$ is the rate constant of the process indicated above, and x_0 and y_0 are the partial gas pressures of CO_2 (000) and N_2 (0).

Consequently, only at small values of k and at concentrations x_0 and y_0 will the values of $\lambda_{1,2}^{-1}$ coincide with the intrinsic relaxation times of the components in the mixture τ_1 and τ_y.

When $\tau_1^{-1} - \tau_y^{-1} + k\,(y_0 - x_0) \gg k\,(x_0 y_0)^{1/2}$, the observed relaxation times in the gas mixture will include a correction for the exchange of excitation with the other component of the impurity:

$$-\lambda_1^{-1} \simeq \tau_1^{-1} + ky_0, \qquad -\lambda_2^{-1} \simeq \tau_y^{-1} + kx_0.$$

Therefore the level lifetimes obtained in the Q-switching mode [13] are smaller than the intrinsic times of the vibrational relaxation. The same holds for the results of [16], where the measurements were made in the reactive Q-switching mode and the lifetime of the lower level was determined as the minimum relaxation time of the system in the presence of a discharge in the gas.

From an analysis of the population inversion in the molecular system (see Appendix II) we see that the intrinsic relaxation time of the molecular component τ is only one of the terms of the effective lifetime of the level $\tilde{\tau}$, which depends on the excitation transfer to other components of the mixture, on the probability of the inelastic collisions of the second kind, etc.

This can explain at first glance the paradoxical phenomenon noted in [15], namely the weak dependence of the measured lifetime of the lower level on the partial pressure of the gases. The misunderstanding vanishes if it is assumed that when the Q-switching mode was used, the measurements pertained to one of the effective relaxation times of the system, which depended both on the gas pressures, the temperature, as well as on the characteristics of the electronic component (n_e, T_e). The authors of [15] have proposed that inelastic electron collisions exert a noticeable influence on the relaxation processes.

The use of the concept of level effective lifetime, which takes into account exchange with other components of the system, may be fruitful, since it is easy to express in its terms such quantities as the inverse population, the saturation parameter, etc.

(see Appendix II). However, before we use the experimental data on the lifetimes in the calculations, we must check that the measurements are indeed equivalent to determining the value of $\tilde{\tau}$ used in the calculations.

We present quantitative estimates of the effective lifetimes of the CO_2 levels, $\tilde{\tau}_1$ and $\tilde{\tau}_2$, in the $CO_2 + N_2 + He$ mixture.

By definition (see formula (k) of Appendix II), we have

$$\tilde{\tau}_1^{-1} = \tau_1^{-1} + \mu_{01} + y_0 k_{01} - \frac{k_{10} k_{01} x_0 y_0}{\mu_{0y} + k_{10} x_0 + \tau_y^{-1}},$$

$$\tilde{\tau}_2^{-1} = \tau_2^{-1} + \mu_{02} + z_0 l_{01} - \frac{l_{10} l_{01} x_0 z_0}{\mu_{0z} + l_{10} x_0 + \tau_z^{-1}},$$

where $\tau_{1,2}^{-1}$ are the intrinsic reciprocal relaxation times of CO_2:

$$\tau_1^{-1} = \sum_j t_1^j p_j, \quad \tau_1^{-1} = \sum_j t_2^j p_j, \quad j - CO_2, N_2, He;$$

$\mu_{01} = n_e \langle \sigma_0 v \rangle$ is the probability of decay to the ground state of the CO_2 molecule from the first level as a result of an inelastic impact of the second kind:

$$\mu_{01} = \mu_{10} e^{E_1/kT_e} \simeq 1.35 \mu_{10} \quad \text{for } E_1 = 2349 \text{ cm}^{-1}, \ T_e \simeq 1 \text{eV};$$

$\mu_{02} = n_e \langle \sigma_{02} v \rangle = \mu_{20} \exp(E_2/kT_e) \simeq 1.2 \mu_{20}$ is the same for the second level;

$$\mu_{0y} = \mu_{y0} e^{E_1/kT_e} = 1.35 \mu_{y0},$$

$\mu_{y0} = n_e \langle \sigma_y v \rangle$ is the probability of excitation of N_2; $k_{01} \simeq 0.75 \times 10^{-14} \text{ cm}^3 \text{sec}^{-1}$ is the rate constant for inelastic collision of CO_2 and N_2, while x_0 and y_0 are the concentrations of CO_2 and N_2 in the ground state.

Inasmuch as there is no resonant excitation transfer to the lower level in the $CO_2 + N_2 + He$ mixture, we shall assume that the component z_0 vanishes and that $l_{10} = l_{01} = 0$. The influence of the helium will be taken into account in the intrinsic relaxation times of the molecules of the mixture, τ_1 and τ_2.

We assume for concreteness (see Sec. 1c)

$$\sigma_{10} = 4 \cdot 10^{-16} \text{cm}^2, \ \sigma_{20} = 2 \cdot 10^{-16} \text{cm}^2, \ \sigma_y = 1.15 \cdot 10^{-15} \text{cm}^2,$$

$$x_0 = 5 \cdot 10^{15} \text{cm}^{-3}, \ y_0 = 5 \cdot 10^{16} \text{cm}^{-3}, \ n_e = 10^{10} \text{ cm}^{-3}$$

$$v = 6 \cdot 10^7 \text{ cm} \cdot \text{sec}^{-1}, \ p_{CO_2} = 0.3 \text{torr}, \ p_{N_2} = 2 \text{torr},$$

$$p_{He} = 4 \text{torr}.$$

Then $\mu_{01} \simeq 320 \text{ sec}^{-1}$, $\mu_{02} = 160 \text{ sec}^{-1}$, $\mu_{0y} = 950 \text{ sec}^{-1}$, $\tilde{\tau}_1 \simeq 300 \text{ sec}^{-1}$ (120 sec^{-1} is the contribution of the intrinsic relaxation at $t_1^{CO_2-CO_2} = 400 \text{ sec}^{-1} \text{torr}^{-1}$, and the remainder is due to the impurity), $\tau_2^{-1} \simeq 3000 \text{ sec}^{-1}$ (200 sec^{-1} - intrinsic relaxation at $t_2^{CO_2-CO_2} \simeq 700 \text{ sec}^{-1} \text{torr}^{-1}$ and 2800 sec^{-1} - contribution of the helium at $t_2^{CO_2-He} \simeq 700 \text{ sec}^{-1} \text{torr}^{-1}$),

$$\tau_y^{-1} \geqslant 125 \text{ sec}^{-1} \ (t_1^{N_2-N_2} \simeq 62 \text{ sec}^{-1} \text{torr}^{-1}).$$

The contribution of the last term to $\tilde{\tau}_1^{-1}$ is negligible under the indicated conditions ($\sim 15 \text{ sec}^{-1}$), and

$$\tilde{\tau}_1^{-1} = \tau_1^{-1} + \mu_{01} + y_0 k_{01} \simeq 1000 \text{ sec}^{-1},$$

$$\tilde{\tau}_2^{-1} \simeq \tau_2^{-1} + \mu_{02} \simeq 3200 \text{ sec}^{-1}.$$

The lifetimes of the lower $10^0 0$ level, given in [12] for pulsed excitation of $CO_2 + He$ mixture, and found to be 0.25—0.3 msec, is apparently close to the effective lifetime $\tilde{\tau}_2$, since resonant excitation transfer is impossible in this mixture.

For the lifetime of the upper level, the literature cites values from 0.8 to 3 msec. At the indicated partial pressures of the gases in the mixture, the most likely value of $\tilde{\tau}_1$ will be 1—1.5 msec. An estimate of the rate of excitation of the levels and of the populations will be carried out in Sec. 4 for $\tilde{\tau}_1 = 1$ msec and $\tilde{\tau}_2 = 0.3$ msec.

The time $\tilde{\tau}_1$ characterizes not the level $00^0 1$ alone, but the entire system of levels $00^0 v$ ($v = 1 - 4$), between which a strong coupling exists as the result of the large collision cross section in processes of the type

$$CO_2(00^0 v) + CO_2(00^0 0) \rightleftarrows CO_2(00^0 v - 1) + CO_2(00^0 1).$$
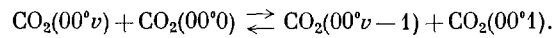
Indeed, the measurements [30] of the rate of radiative decay of the upper ($00^0 v$) vibration levels in the presence of intense radiation at the $00^0 1 - 10^0 0$ transitions have shown that the $00^0 v$ levels make a noticeable contribution to the excitation of the $00^0 1$ level. In the cited investigation, a short measuring cell with windows inclined at the Brewster angle and with a window in a side stub was placed in common resonator with a CO_2 laser operating in the Q-switched mode. The temporal characteristics of the spontaneous emission at the $00^0 1 - 10^0 0$ and $00^0 v - 00^0 (v - 1)$ bands were registered through the side stub with the aid of a monochromator and oscilloscope.

The emission spectrum of the indicated bands was observed in the measuring cell under the ordinary discharge conditions at a normal filling with a $CO_2 + N_2 + He$ mixture. Comparison of the intensities of the corresponding lines has shown that the population distribution at the level $00^0 v$, up to $v = 4$, can be described by a positive vibrational temperature $T_{vib} \simeq 3000°K$. When the radiation passed through the measuring cell, the population of the $00^0 v$ levels began to decrease rapidly (delay time 10 μsec), whereas in the continuous generation mode the intensity of the bands from the $00^0 v$ levels was reduced only by a factor of 2 and the distribution was conserved. Such a strong coupling between the $00^0 1$ upper working level and the $00^0 v$ level cannot be connected with radiative processes, which have transition probabilities of the order of 10^2 sec^{-1}. This leaves only one explanation, namely exchange of vibrational excitation between the $00^0 v - 00^0 (v - 1)$ states ($v = 1 - 4$).

In connection with the high efficiency of CO_2 lasers, the presence of upper excited $00^0 v$ levels

gives grounds for assuming that their energy is transferred in final analysis to the upper operational 00^01 level, and that their role consists of increasing the effective excitation cross section of the 00^01 level.

Naturally, in the Q-switched mode, at pulse durations $\tau = 20$ nsec, the energy of the 00^0v levels will not be transferred to the 00^01 level.

For simplicity, we shall henceforth take the level 1 to mean the entire aggregate of the 00^0v levels ($v = 1, 2, 3, 4$).

c) Certain Elementary Processes in the Electric Discharge in the $CO_2 + N_2 + He$ Mixture

In experimental lasers using the $CO_2 + N_2 + He$ mixture, the inversion of the population of the vibrational CO_2 levels is the result of excitation of an independent glow discharge at direct or alternating (~ 50 Hz) current. Exceptions were the first experiments of Patel[6] and Legay-Sommaire[8], where the externally excited nitrogen molecules were injected into the resonator cavity and mixed there with the CO_2 molecules,

For a quantitative analysis of the kinetics of the elementary processes it is necessary to know at least the following discharge characteristics:

1) electron density n_e,

2) electron distribution functions with respect to the energy (or T_e),

3) exact chemical composition of the gas in the working mode,

4) concentrations of the ions of different components,

5) excitation and level-ionization cross sections.

It is known from the literature on gas-discharge physics that at low current densities and moderate pressures (approximately several torr) the positive column is a non-isothermal plasma. The main losses of the supplied energy are connected with the processes of volume recombination and the relative magnitude of the losses connected with resonant and non-resonant radiation is small.

The published papers on molecular lasers contain no data on the gas-discharge characteristics, other than the values of the limiting field gradients and the partial pressures of the gases. Naturally, the partial pressure and the composition of the reagents do not determine uniquely the pressure and the chemical composition of the final products. Moreover, it is known[4] that the discharge contains intense CO bands (4830 Å), and also atomic and molecular oxygen, the CN radical, and other products. The instability of the chemical composition is apparently the main cause of the need for working with gas pumping[18]. Nonetheless, Witteman[42] succeeded in producing a laser without gas pumping using the $CO_2 + N_2 + H_2O$ mixture.

When the gas is pumped through at linear velocity on the order of several meters per second, the com-

position of the gas in the mixture can be regarded as close to the initial composition.

The ionization potentials[36] and the dissociation energies for four fundamental components of the gas are as follows:

$$CO_2(13.79\,eV\;;\;2.8\,eV),\quad N_2(15.58eV;\;9.76\;eV),$$
$$O_2(12.2\,eV\;;\;5.084\,eV),\quad He(24.58\;eV);$$

One can expect the discharge to contain principally the ions O_2, O_2^-, O^-, and CO_2^+. The relatively low dissociation energies of CO_2 and O_2 favor the formation of the ions O^- and O_2^-.

In the case of discharge in molecular gases, inelastic collisions between electrons and molecules, at which the lower vibrational levels are excited, play an important role.

The values of the total scattering cross sections, both maximal and at electron energies ~ 1 eV, are listed below[36]:

$$CO_2 \begin{cases} \sigma_{max}\,(4\;eV) = 1.4 \cdot 10^{-15}\;cm^2, \\ \sigma \quad (1\;eV) = 0.56 \cdot 10^{-15}\;cm^2, \\ \sigma \quad (0.5eV) = 2 \cdot 10^{-15}\;cm^2; \end{cases}$$

$$N_2 \begin{cases} \sigma_{max}\,(2.25eV) = 2.54 \cdot 10^{-15}\;cm^2, \\ \sigma \quad (1eV) = 1.15 \cdot 10^{-15}\;cm^2; \end{cases}$$

$$O_2 \begin{cases} \sigma_{max}\,(3.5eV) = 10^{-15}\;cm^2, \\ \sigma \quad (1eV) = 0.6 \cdot 10^{-15}\;cm^2; \end{cases}$$

$$He\;\sigma\,(1-2\;eV) = 0.6 \cdot 10^{-15}\;cm^2\,(elastic\;scattering).$$

A noticeable fraction of the indicated cross sections may be due to inelastic collisions.

The large cross sections for electron excitation of the vibrational levels of molecular gases are attributed to the formation of short-lived negative complexes[36].

In connection with the large cross sections, we can expect the maximum of the electron-energy distribution function, at appreciable concentration of N_2 molecules in the discharge, to occur at $T_e < 1.5-2$ eV (see also[19]).

There are no published data at all on the concentration of the electrons in the $CO_2 + N_2 + He$ discharge. Approximate estimates of this quantity can be made on the basis of tentative values of the field gradient in the positive discharge column and the drift velocity of the electrons v_{dr} as given by plots of $v_{dr}(E/p)$ in the book of S. Brown[37]. Certain difficulties in using these plots are connected with the fact that they are valid only for pure gases and not for mixtures.

According to Patel[7], for an initial mixture composition $p_{CO_2} = 0.33$ torr, $p_{N_2} = 1.2$ torr, and $p_{He} = 7$ torr we see that the field gradient in column was approximately 35 V/cm at a current of 200 mA and an internal tube diameter 77 mm.

It is well known that addition of a noticeable amount of helium to nitrogen greatly increases the field gradient, which was approximately half as large at

the indicated values of p_{CO_2} and p_{N_2} but without helium. Under such conditions, for $\bar{E}/P$ = 15 V/cm-torr, the plots of $v_{dr}(E/p)$ yield v_{dr} = 6×10^6 cm/sec for electrons in nitrogen. The increase in the gradient following addition of helium should not lead to a noticeable change of v_{dr}, since the growth of the gradient is offset by the increased cross section for scattering by the He atoms.

Naturally, this argument claims no rigor and does not eliminate the need for a thorough experimental investigation of the discharge characteristics.

For an average current density j $\simeq$ 5 mA/cm^2 at the indicated value of v_{dr}, the electron density can be approximately 5×10^9 cm^{-3}. The maximum density in the central region of the column is approximately twice as large ($\sim 10^{10}$ cm^{-3}).

The indicated values of n_e and T_e would depend on the gas pressure, current density, and other discharge parameters, and should be regarded as tentative. But even using these approximate values of n_e and T_e we can compare the rates of different processes, including inelastic collisions of the second kind, excitation of the working levels, etc. (see Sec. 4).

2. ROTATIONAL RELAXATION AND COMPETITION OF TRANSITIONS

The energy of the quanta of rotational motion of the molecules is usually much smaller than the thermal energy kT_{gas} of the molecule translational motion. During the collisions, the molecules exchange translational and rotational energy quite vigorously, and the time of establishment of thermodynamic equilibrium for the corresponding degrees of freedom is usually small. In particular, for CO_2 the time of rotational relaxation at pressure 1 torr is τ_{rot} = 1.75×10^{-6} sec [33]. The role of the rotational relaxation for the inversion mechanism in molecular lasers can be seen from the following reasoning.

As is known from experiment, generation from CO_2 occurs at a limited number of vibrational-rotational transitions. Excitation of the upper vibrational level (by electron impact or as a result of collisions with N_2^* (v = 1) is distributed over all of its rotational states.

The stationary distribution of the populations of the rotational levels is described by formula (1) and is established within a time on the order of τ_{rot}. When oscillations set in at frequencies corresponding to vibrational-rotational transitions $J' - J''$, the volume energy density $\rho_{J'J''}$ in the resonator increases markedly and the levels J'' begin to decay intensely.

The stationary inverse population in the generation mode $\Delta n = n_{J'} - n_{J''}(g'/g'')$ is determined from the condition that the gain of the active medium be equal to the loss in the resonator per pass. So long as the
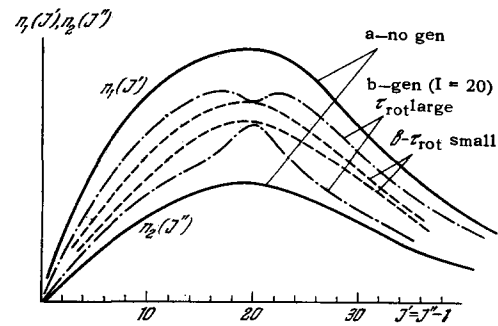

FIG. 3. Distribution of CO_2 molecules over rotational levels of the upper and lower states. a—no generation, b—generation at transition P = 20, τ_{rot} large; c—generation at transition P = 20, τ_{rot} small.

probability of the stimulated transitions $J' - J''$ is smaller than τ_{rot}^{-1}, the mechanism of rotational relaxation is capable of maintaining the equilibrium distribution $n_{J'}$ and switches the molecules to the decaying levels.

The "dissolution" of the excess population from the lower levels J'' of the working vibrational-rotational transitions proceeds in similar fashion.

Figure 3 shows schematically the distribution of $n_{J'}/g_{J'}$ and $n_{J''}/g_{J''}$ over the rotational levels of the upper and lower states: in the absence of generation (a), in the presence of generation at one transition and a large rotational relaxation time τ_{rot}(b), and in the presence of generation at one transition and small τ_{rot} (c).

For the sake of clarity, the abscissas represent the quantity $J' = J'' - 1$. With this variable, transitions of the P branch correspond to vertical lines.

In case (b), the stationary population inversion is larger for neighboring transitions than at the generating transition. If the resonator does not contain selective elements, then it is obvious that the generation conditions can be simultaneously satisfied for a number of vibrational-rotational transitions and the competition between them at large values of τ_{rot} will be negligible. Each of the generating transitions will produce a "hole" in the $n_{J'}$ distribution, and the envelope will differ little from that in case (c).

The form of the function n_J, the stationary value of the radiation density, and the number of generation transitions will be determined by the entire aggregate of parameters of the resonator and of the active medium, including the times τ_1, τ_2, and τ_{rot}.

It follows from these qualitative considerations that there apparently exists a certain analogy between the effect of formation of holes in the inhomogeneously broadened line [34] and the n_J distribution of a system of rotational levels.

In nonstationary processes, for example in the case of pulsed generation or Q-switched generation, τ_{rot} determines the time interval during which equilibrium is established in the system. For pulses

with duration $\tau_{pulse} < \tau_{rot}$, this condition can be strongly violated.

There is no information on rotational relaxation in a mixture of gases, particularly in the $CO_2 + N_2 +$ He mixture, but from a comparison of the number of generating lines of the P branch in pure CO_2 (P(12) – P(38)) [4], in $CO_2 + N_2$ (P(18) – P(28)) [8], in CO_2 + He (P(20) – P(26)) [9], and in the ternary mixture $CO_2 + N_2 +$ He (P(20) and P(24)) [35] it can be assumed that the relaxation time is greatly reduced by addition of N_2, and especially by addition of He. Thus, when the helium pressure is increased to 20 torr the number of lines in the Q-switching mode began to decrease, and at $p_{He} = 50$ torr it was the same as in the continuous mode. It was established in an indirect manner [13] that $\tau_{rot} = 2 \times 10^{-8}$ sec $= \tau_{pulse}$ when $p_{He} = 20$ torr. For the reciprocal rotational relaxation time τ_{rot}^{-1} in a mixture of gases we likewise have a linear dependence on the partial pressure of the admixture, τ_{rot}^{-1} $= \Sigma_{rot} t_{ij} p_j$. On the basis of the results of [13] we get $t_{rot}^{CO_2-He} \simeq 2.5 \times 10^6$ sec^{-1}torr^{-1}, and from [33] we get $t_{rot}^{CO_2-CO_2} \simeq 0.57 \times 10^6$ sec^{-1}torr^{-1}.

It follows from experiments of [13] that in the presence of rotational relaxation, competition is possible between the vibrational–rotational transitions with close J′, and this competition reduces the number of generating lines. In the Q-switching mode, the system of rotational levels ensures accumulation of excitation during the pause between pulses.

The foregoing review of the basic properties of the CO_2 molecule enables us to compare a laser operating with the $CO_2 + N_2 +$ He mixture with Gould's ideal laser and ascertain to what degree Gould's requirements are satisfied.

It is obvious that the conditions a), b), c), d), and h) are ensured by the positions of the working levels, by the difference between the vibrational–relaxation times τ_1 and τ_2, by rotational relaxation, and by transfer of excitation via inelastic collisions with N_2^* (v = 1) and relaxation from the levels 00^0v. The aggregate of rotational levels plays the role of the first stage in the process of decay of the lower level. The next stage consists of vibrational relaxation of the $10^0 0 – 02^0 0$ levels to the $01^1 0$ and 000 levels. As will be shown later, the vibrational relaxation processes ensure in the continuous mode the required rates of removal of molecules from the lower level. At a total molecule and atom concentration 3×10^{17} cm^{-3} (p $\simeq 10$ torr) we can still expect T_e to be noticeably higher than T_{gas}.

At a large electron density, the effective electron temperature may turn out to be so low that the rate of excitation of the upper working level is insufficient to produce population inversion. In addition, with increasing current, the gas temperature increases and the level lifetime decreases. This may explain ade-
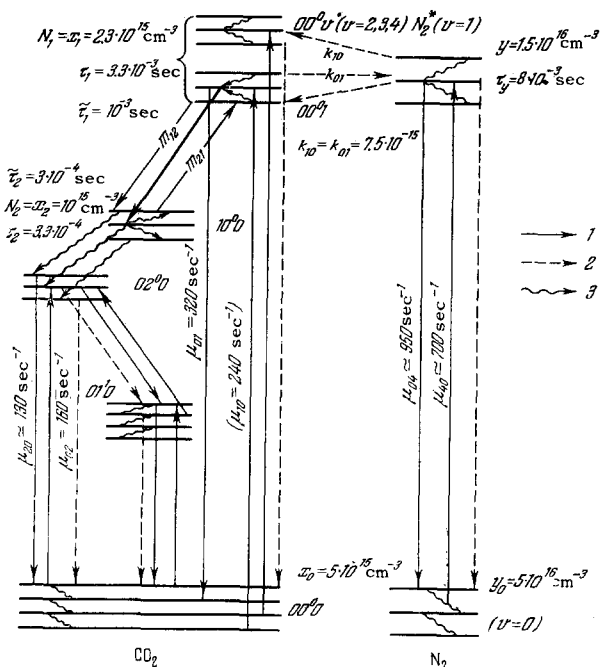

FIG. 4. Diagram of fundamental elementary processes in the $CO_2 + N_2 +$ He mixture. The thin lines show electronic-excitation processes, the dashed lines show vibrational relaxation, and the wavy lines rotational relaxation. x_1, x_2, x_0 are the populations, y_1 and y_0 the N_2 level populations, $\tilde{\tau}$ and τ respectively the effective and the intrinsic lifetime of the level with account of relaxation in the mixture, and μ_{ij} the probability of direct and inverse excitation processes.

quately the observed dependence of the generation power on the discharge current [9].

To illustrate the main elementary processes occurring in $CO_2 + N_2 +$ He, lasers let us use the diagram shown in Fig. 4. The diagram shows schematically the excitation and de-activation of the levels. We use the following notation:

$k_{10} \simeq k_{01}$ – rate constant for inelastic collisions between CO_2 and N_2^* (v = 1), μ_{10} – probability of exciting the $00^0 1$ level by direct electron impact from the ground state, μ_{01} – the same to the ground state, m_{21} and m_{12} – probabilities of transitions via inelastic collisions with electrons and gas molecules respectively, $x_{1,2,0}$ and $y_{1,0}$ – level populations, $\tilde{\tau}$ and τ – effective and intrinsic lifetimes of the level. The rotational relaxation processes are designated by wavy lines. The figure shows tentative estimates of the populations, the excitation probabilities, and the level lifetimes for the static mode (see Sec. 4).

3. GAIN IN MOLECULAR SYSTEMS

The gain in an active medium at a low signal level at the center of the Doppler contour is given by the formula

$$G_0 = \exp [K^0 l],$$

where

$$K^0 = \left(\frac{\ln 2}{\pi}\right)^{1/2} \frac{A_{12}\lambda^2 g_1}{4\pi\Delta\nu_D}\left[\frac{n_1}{g_1} - \frac{n_2}{g_2}\right]; \qquad (5)$$

A_{12} is the spontaneous-emission probability, $\Delta\nu_D$ - width of the line contour with allowance for impact broadening, $n_{1,2}$ - population density, and $g_{1,2}$ - statistical weight of the level. The same formula holds also for vibrational-rotational transitions of a molecular system, if n is taken to mean the populations of the corresponding rotational levels, A_{12} is the transition probability, and

$$J' = J'' \pm 1.$$

Taking expression (1) into account, we can express K^0 in the form

$$K^0 = \left(\frac{\ln 2}{\pi}\right)^{1/2} \frac{A_{12}\lambda^2 (2J+1)}{4\pi\Delta\nu_D} \frac{hcB_1}{kT_{gas}} e^{-F(J)\frac{hc}{kT_{gas}}} \qquad (6)$$

$$\times \left\{N_1 - N_2 \frac{B_2}{B_1} e^{\frac{hc}{kT_{gas}}[F(J\pm1)-F(J)]}\right\}.$$

For the P and R branches (in accordance with the selection rules $J' = J'' - 1$ and $J' = J'' + 1$) we have

$$K^0_P(J) = \left(\frac{\ln 2}{\pi}\right)^{1/2} \frac{A_{12}\lambda_P^2 (2J+1)}{4\pi\Delta\nu_D} \frac{hcB}{kT_{gas}} e^{-F(J-1)\frac{hc}{kT_{gas}}} \Delta N_P.$$

$$K^0_R(J) = \left(\frac{\ln 2}{\pi}\right)^{1/2} \frac{A_{12}\lambda_R^2 (2J+3)}{4\pi\Delta\nu_D} \frac{hcB_1}{kT_{gas}} e^{-F(J+1)\frac{hc}{kT_{gas}}} \Delta N_R. \qquad (7)$$

Unlike in the preceding formula, in (7) J denotes the rotational quantum number of the lower level

$$\Delta N_P = N_1 - N_2 p, \quad p = \frac{B_2}{B_1} e^{\frac{hc}{kT_{gas}}[F(J-1)-F(J)]},$$

$$\Delta N_R = N_1 - N_2 r, \quad r = \frac{B_2}{B_1} e^{\frac{hc}{kT_{gas}}[F(J+1)-F(J)]}. \qquad (8)$$

The superscript 0 of K^0 denotes amplification for a weak signal.

Patel [4] gives plots of the gains $K^0_{P,R}$ for the P and R branches in relative units.

The parameter for the plots is the relative level population $N_1/N_2 = N_{00^01}/N_{00^00}$. It is seen from these plots that for the same values of J the gain for the P branch is much higher than for the R branch (Fig. 5).

Using the well known value of A_{12} (P = 20) 'and also $B_{00^01} = 0.3866$ cm^{-1}, $B_{10^00} = 0.3879$ cm^{-1}, and $\Delta\nu_D = 5.2 \times 10^7$ Hz (at T = 400°K), we can determine the numerical value of the scale for the plots of Fig. 5 of Patel's paper [4]:

$$\frac{8\pi^3 c^4 k_{12} N_2}{3kT_{gas}\left(\frac{2\pi kT_{gas}}{M}\right)^{1/2}} \simeq 0.45 \cdot 10^{-18} N_2.$$

In Patel's derivation [4] of expression (6) for the gain, no account was taken of the coupling between the 10^00 and 02^00 levels. When this coupling is taken into account, it is necessary to use for the lower level the value n_{J_2} given by formula (3). The formu-

las (7) for the gain will take the same form as before, but in formulas (8) for p and r there will appear the coefficient

$$\frac{e^{-\Delta E/kT_{gas}}}{1 + e^{-\Delta E/kT_{gas}}},$$

where $\Delta E = E_{10^00} - E_{02^00}$, and N_2 will now denote the summary population of the levels 10^00 and 02^00.

For $T_{gas} = 400°K$ and $\Delta E = 103$ cm^{-1}, the numerical value will be $e^{-0.375}/(1 + e^{-0.375}) \simeq 0.405$. When calculating the gain for this case by means of the plots on Fig. 5, it is necessary to make use of the parameter value indicated in the parentheses.

To facilitate subsequent estimates, it is advantageous to separate the temperature-dependence factors of formula (7). To this end we rewrite (7) for J = 20 in the form

$$K^0_p = \varepsilon\Delta N_p \overline{K}(t),$$

where

$$\varepsilon = \left(\frac{\ln 2}{\pi}\right)^{1/2} \frac{A_{12}\lambda_P^2 (2J-1)}{4\pi\Delta\nu_D|_{T=400}} \frac{hcB}{k\cdot400} e^{-F(J-1)\frac{hc}{k\cdot400}}$$

$$\simeq 5.45\cdot10^{-18}\cdot\text{cm}^2,$$

$$\overline{K}(t) = t^{-3/2}e^{0.527(1-t^{-1})} \qquad (9)$$

is the temperature-dependence factor, normalized to unity at t = T/400 = 1. It should be noted that ΔN_P and ΔN_R also depend on the temperature.

A plot of the temperature dependence of $\overline{K}(t)$ is shown in Fig. 6. It is seen from the figure that when T is reduced from 400°K to 130° the gain doubles (provided ΔN_P remains unchanged).

At higher temperatures, $\overline{K}(t)$ is sufficiently well approximated by $t^{-3/2}$.
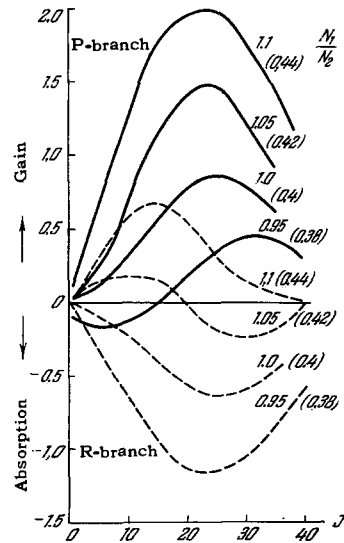

FIG. 5. Theoretical gain curves for rotational-vibrational transitions of P and R branches for different values of N_1/N_2, taken from [4]. The values of N_1/N_2 with allowance for the Fermi resonance are indicated in the parentheses.
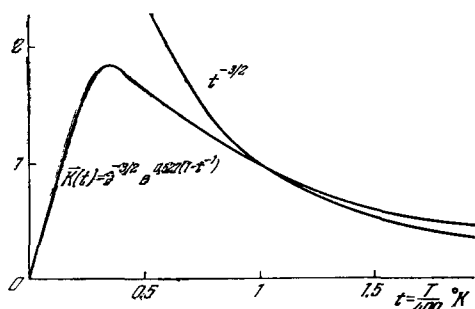
FIG. 6. Normalized temperature-dependence function of the gain K(t).

The measurements of the dependence of the power on the tube-wall temperature, reported in [27], show that the power changes from 4.5 to 2.2 W in the interval $T = -60°C - +40°C$. The corresponding theoretical variation of the gain should be approximately 50%, which agrees approximately with the $t^{-3/2}$ law. It is still difficult to speak of a more rigorous experimental verification, since the radical temperature drop of the gas was not accurately known.

Since it is possible the generation conditions can be simultaneously satisfied for the $00^0 1 - 10^0 0$ and $00^0 1 - 02^0 0$ transitions of the P and R branches in a nonselective resonator at sufficiently high population of the vibrational $00^0 1$ level, mode competition sets in. This competition, as is well known from experience with helium-neon and neon lasers, usually appears when the active transitions have common upper or lower levels.

Stimulated transitions between a pair of levels having more favorable conditions for the occurrence of generation (a lower threshold) will reduce the population inversion for the adjacent transition. In molecular systems, a similar phenomenon should occur, the only difference being that the common vibrational level unifies a relatively large number of adjacent vibrational-rotational transitions and the coupling between them will depend on the efficiency of the rotational relaxation mechanism. At a small relaxation time, adjacent transitions will be strongly coupled, and vice versa.

In CO_2 molecular lasers, the gain at the transitions of the $00^0 1 - 02^0 0$ band ($\lambda \approx 9.4 \mu$) is smaller than at the transitions of the $00^0 1 - 10^0 0$ band ($\lambda \approx 10.6 \mu$), and generation in the $00^0 1 - 02^0 0$ band has been observed only in pure CO_2 and at low power levels [4,23]. At a pressure $p_{CO_2} = 0.2$ torr (without addition of nitrogen or helium), Patel [4] observed in a laser 5 m long simultaneous generation at the P branch ($P = 12 - 38$) of the $00^0 1 - 10^0 0$ band and at the P branch ($P = 22 - 34$) of the $00^0 1 - 02^0 0$ band. According to his estimates, the band gain ratio is 1.5 : 1, and the level populations satisfy the relation

$$N_{00^0 1} = N_{02^0 0} = 1.05 N_{10^0 0}.$$

These estimates do not agree with the assumption

that the $10^0 0$ and $02^0 0$ levels are coupled by Fermi resonance.

It is interesting to note that no generation was observed at the transitions of the $00^0 1 - 02^0 0$ band in subsequent work with powerful CO_2 lasers using a tenary mixture and high gas pressure. The generation is apparently hindered not only by the presence of a common upper level but also by the coupling between the lower levels via the Fermi resonance.

The competition between the transitions of the P and R branches was also explained by Patel [4] on the basis of gain calculations (see Fig. 5).

When generation occurs at the $J' -- J''$ transition of the P branch, the populations of the corresponding levels become equalized, and this leads to a lowering of the inverse population and of the gain of the R branch of the transition $J' \rightarrow J'' - 1$. This notion of competition between the P and R branches, based on calculated gains for an equilibrium distribution over the rotational levels, is apparently not always valid, since an estimate of the temperatures on the basis of the rotational quantum numbers of the intense lines of the P and R branches yields divergent values for the CO_2 + air mixture (~450 and 500°K respectively) [31].

The competition of the vibrational-rotational transitions belonging to one branch was considered above in connection with rotational relaxation.

The importance of the phenomena of competition and limitation of the spectra of the generated frequencies was confirmed by research by Moeller and Ridgen [38] on a CO_2 and N_2O laser with selective resonator. The laser tube was 6 m long and had an inside diameter of 22 mm. One one end of the tube was located an internal mirror with 2% transmission, and on the other an NaCl window at the Brewster angle, and at a distance of 5 m there was a diffraction grating of 70 lines/mm.

The resonator was tuned in a wide frequency interval by rotating the diffraction grating.

It was possible in this manner to effect generation at individual rotational-vibrational transitions of the P and R branches of the bands $00^0 1 - 10^0 0$ and $00^0 1 - 02^0 0$ with total number of 103 lines for CO_2 and 67 for N_2O. The maximum values of J for P and R branches in both bands reach 48—52. The $00^0 1 - 02^0 0$ band of N_2O was not excited. The power of the most intense N_2O lines was smaller by more than one order of magnitude than the power of the strong CO_2 lines.

Figure 7 shows the generation spectrum of the P and R branches of the $00^0 1 - 10^0 0$ band.

The tuning range at the discrete lines was approximately 6%, and apparently can be made even wider [23].

Using the same system, but a mirror in lieu of the grating, generation was observed at a small number of P-branch lines of the $00^0 1 - 10^0 0$ band of CO_2.
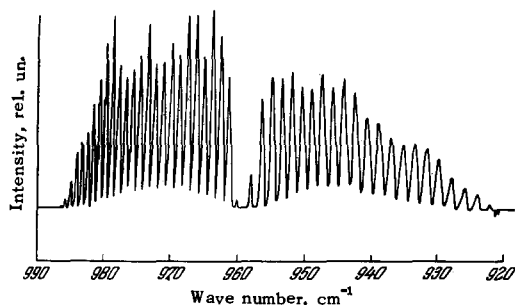
FIG. 7. Emission spectrum obtained from a laser with selective resonator. Left—R-branch lines, right—P-branches of the $00^{\circ}1-10^{\circ}0$ band of CO_2.

4. INVERSION MECHANISM IN CO_2 LASERS

The characteristics of the transitions in CO_2 molecules and of the discharge in molecular gases, considered in the preceding sections, make it possible now to proceed to a discussion of the inversion mechanism and certain quantitative estimates. The physical gist of the phenomenon consists in the following. The discharge in the $CO_2 + N_2 + He$ mixture gives rise to ionization of the molecules CO_2 and N_2. Inelastic electron collisions cause excitation of the lower vibrational levels of the nitrogen and of the CO_2 molecule, and an appreciable fraction of the excitation occurs at $00^{\circ}1$ level, which has large cross sections for inelastic collision with N_2^* ($v = 1$) and also for direct excitation by electrons.

The lower levels $10^{\circ}0$ and $02^{\circ}0$ are excited relatively little and have a relatively low population, owing to the short lifetime. Population inversion arises between the $00^{\circ}1$ level on the one side and the $10^{\circ}0$ and $02^{\circ}0$ levels on the other; this population inversion leads, in the presence of a resonator, to self excitation of the system.

The self-excitation conditions are satisfied for a relatively large number of vibrational-rotational transitions of the P and R branches of both bands, but owing to the nonlinear interaction between the oscillations (competition) of different transitions, a rather limited number of lines is observed in the stationary mode. Rotational relaxation contributes to transfer of excitation to the upper rotational level from the neighboring levels of the upper vibrational states, and to a uniform distribution of the overpopulation over the lower vibrational state.

The other components of the mixture (helium, oxygen, water vapor, etc.) are chosen such as to increase the inverse population as a result of interaction with the main gas (CO_2) and the electronic component.

With increasing current density, the electron temperature decreases, the gas temperature rises, and the role of inelastic collisions increases.

Quantitative estimates of the populations and of the rates of excitation can be carried out on the basis

of the quantities for which data are known in the literature, such as pressure, volume density, radiation power, cross sections, etc., using a number of formulas given in Appendix II and in Sec. 6. When the gain of the active medium greatly exceeds the resonator loss, the volume power density $\bar{P}$ is connected with the inverse population in the absence of generation $\Delta N(0)$ and the effective level lifetimes $\tilde{\tau}_1$ and $\tilde{\tau}_2$ by the relation $\bar{P} \simeq h\nu\Delta N(0)[\tilde{\tau}_1 + p\tilde{\tau}_2]^{-1}$, and the value of $\Delta N(0)$ is connected with the total rates of excitation of the levels M_1 and M_2 by the relation $\Delta N(0) \simeq \tilde{M}_1\tilde{\tau}_1 - \tilde{M}_2 p\tilde{\tau}_2$, where

$$p \simeq \frac{e^{-\Delta E/kT_{gas}}}{1+e^{-\Delta E/kT_{gas}}} \simeq 0.4.$$

The influence of the terms containing m_{12} and m_{21} is disregarded here.

In most cases $\tilde{M}_2 p\tilde{\tau}_2$ is noticeably smaller than $\tilde{M}_1\tilde{\tau}_1$, and then $\tilde{M}_1\tilde{\tau}_1 \simeq \Delta N(0)$ and $\bar{P} \lesssim h\nu\tilde{M}$. Naturally, in the case of generation $\Delta N(\rho) < \Delta N(0)$. Since, according to the published data, the range of variation of the laser parameters is sufficiently large, we assume, for concreteness, the characteristics of certain hypothetical laser operating in the cw mode:

a) mixture composition $p_{CO_2} = 0.3$, $p_{He} = 4$, $p_{N_2} = 2$ torr;

b) radiation power density $\bar{p} = 40$ mW/cm^3;

c) current density $j \simeq 7.5 \times 10^{-3}$ A/cm^2;

d) longitudinal potential gradient $E = 30$ V/cm;

e) gas temperature $T_{gas} = 500^{\circ}$K;

f) transparency of exit mirror $1 - r = 10\%$;

g) length of active part $l = 130$ cm;

h) rotational relaxation time $\tau_{rot} \sim 10^{-7}$ sec;

i) effective lifetimes of vibrational levels $\tau_1 = 1$ msec and $\tau_2 = 0.3$ msec.

We assume also that generation occurs at one rotational-vibrational transition $P(20)$.

The foregoing parameters are either certain averages of the values cited in the papers, or have been established indirectly from these papers.

Under the foregoing assumptions we obtain from the lower limit of the excitation rate of the upper level:

$$\tilde{M}_1 \gg \frac{\bar{p}}{h\nu} \simeq 2.1 \cdot 10^{18} \text{ cm}^{-3} \text{ sec}^{-1}$$

in the absence of stimulated transitions.

Bearing in mind the approximate character of the estimates, we shall henceforth put

$$\tilde{M}_1 \simeq 2.3 \cdot 10^{18} \text{ cm}^{-3} \text{sec}^{-1}.$$

By definition (see (l) in Appendix II)

$$\tilde{M}_1 = \mu_{10}x_0 + \mu_{y0}y_0 \frac{k_{10}x_0}{\mu_{0y} + k_{10}x_0 + \tau_y^{-1}} = \tilde{M}_{1e} + \tilde{M}_{1N_2}.$$

For $T_e \simeq 1$ eV ($v_e \simeq 6 \cdot 10^7$ cm/sec), $n_e \simeq 10^{10}$ cm^{-3}

we have

$$\mu_{10} \simeq n_e \langle \sigma_{1CO_2} v \rangle \simeq 240 \, \text{sec}^{-1} \quad (\text{for } \sigma_{1CO_2} \sim 4 \cdot 10^{-16} \, \text{cm}^2),$$

$$\mu_{y0} \simeq n_e \langle \sigma_{N_2} v \rangle \simeq 700 \, \text{sec}^{-1} (\text{for } \sigma_{N_2} \sim 1 \cdot 15 \cdot 10^{-15} \, \text{cm}^2).$$

For the rate constant of the process $CO_2 + N_2^* (v = 1) \rightleftarrows CO_2 (00^0 1) + N_2$ we have in accord with [7]

$$k_{01} = k_{10} = 0.75 \cdot 10^{-14} \, \text{cm}^3 \text{sec}^{-1}$$

and for the indicated partial pressures we have $x_0 \simeq 5 \times 10^{15} \, \text{cm}^{-3}$ (approximately 50% of the CO_2 are assumed to be in the ground state), $y_0 = 5 \times 10^{16} \, \text{cm}^{-3}$ ($\sim$70% of the N_2 molecules in the ground state), and $\tau_y^{-1} = 125 \, \text{sec}^{-1}$.

In addition,

$$\mu_{0y} \simeq \mu_{y0} e^{E_y/kT_e} \simeq 1.35 \mu_{y0} \simeq 950 \, \text{sec}^{-1}.$$

Substituting the foregoing values, we can determine the contribution of the direct electronic excitation to $\widetilde{M}_1$

$$\widetilde{M}_{1e} = \mu_{10} x_0 \simeq 1.2 \cdot 10^{18} \, \text{cm}^{-3} \text{sec}^{-1},$$

and the excitation from N_2^*

$$\widetilde{M}_{1N_2} = \mu_{y0} y_0 \frac{k_{10} x_0}{\mu_{0y} + k_{10} x_0 + \tau_y^{-1}} \simeq 1.1 \cdot 10^{18} \, \text{cm}^{-3} \text{sec}.$$

From a comparison of $\widetilde{M}_{1e}$ and $\widetilde{M}_{1N_2}$ we see that at the indicated values of the cross sections they make approximately equal contributions to $\widetilde{M}_1$.

It is of interest to note in this connection that in the first experiments of Patel [6] and Legay-Sommaire [8], in which externally excited N_2^* molecules were injected into the cavity, good agreement was obtained between the flow rate of the gas (N_2) and the generation power. According to [8], at $p_{N_2} = 1.8$ torr and a linear gas velocity $v = 14$ m/sec, the generation power was $P \simeq 1$ W.

The excitation power transferred to the N_2^* molecules at $N_{N*_2} \simeq 0.3 \, N_{N_2}$ will be

$$P_{N_2} = N_{N_2^*} s v E_y \simeq 0.3 N_{N_2} s v E_y = 3.6 \, \text{W},$$

where s is the cross section of the tube ($\sim$3 cm^2) and E_y the energy of the excited N_2^* molecule.

Consequently, in systems with injection [6,8], the coefficient of excitation-energy utilization $P/P_{N_2} = 28\%$ was close to the limit ($\eta_{max} = 41\%$). This indicates that the deactivation of the N_2^* molecules was due primarily to inelastic collisions with CO_2.

Comparison of $\widetilde{M}_{1e}$ and $\widetilde{M}_{1N_2}$ explains one of the reasons for the increase in the generation power when N_2 is added to CO_2. The second reason is, apparently, that the vibrational and rotational relaxation times are greatly reduced in the presence of N_2. Therefore, in the pulsed mode, when operating with pulse durations $\tau = 0.5$ msec, the power increases in the presence of N_2 and O_2 [10], in spite of the fact that the contribution of M_{1N_2} to $\widetilde{M}_{10}$ at short pulses is apparently quite small. Indeed, the time constant for the deactivation of N_2^* at $P_{CO_2} = 0.3$ torr is approx-

imately 12 msec [7], and within the time 0.5 msec the N_2^* molecules transfer a negligible fraction of their energy, whereas the electronic component $\widetilde{M}_{1e}$ has practically no inertia and increases in proportion to n_e, i.e., to the density of the current pulse.

There are at present no data with which to estimate the excitation rate $\widetilde{M}_2$ of the bound levels $10^0 0$ and $02^0 0$. It is possible that their excitation cross section has a value $\sim 10^{-16} \, \text{cm}^2$. It is probable that further research on the elementary processes in CO_2 lasers, including direct measurements of the excitation rates, will yield a more accurate value of this quantity.

Estimates show that the rates of the processes connected with the terms m_{21} and m_{12} can make a noticeable contribution to $\widetilde{M}_1$ and $\widetilde{M}_2$.

It is known that the electron temperature drops and the role of the inelastic collisions increases when the current density increases. The CO_2 molecule is characterized by an increase in the total scattering cross section in the low-energy region. This, however, can hardly be the only cause, since in the pulsed mode larger powers were obtained at current densities exceeding by tens of times the densities in the continuous modes.

It is possible that this is connected with the difference between the working temperatures of the gas in these modes and the temperature dependence of the rate of the relaxation process $CO_2 (00^0 1) + CO_2 (000) \rightleftarrows 2CO_2 (0^0 20)$. An estimate of the temperature effects for the continuous and pulsed modes is given in Sec. 5.

Let us assume further that the hypothetical laser in question operates in the Q-switching mode. If the time interval between the successive switchings of the cavity is sufficiently large to restore stationary values of N_1 and N_2, then the energy density in each generation pulse will be

$$\widetilde{W}_{max} \sim h\nu \frac{\Delta N(0)}{2} \simeq 0.8 \cdot 10^{-5} \, \text{J/cm}^3$$

and the density of the peak power at $\tau_{pulse} \simeq \Delta \nu_D^{-1}$

$$\overline{P}_{pulse} = \frac{\widetilde{W}}{\tau_{pulse}} \simeq \widetilde{W} \Delta \nu_D \simeq 400 \, \text{W/cm}^3$$

At the excitation rates indicated above, the interval between the cavity switchings should be of the order of the effective lifetime of the upper level $\tilde{\tau}_1$.

In [15], in the Q-switching mode, the energy density in the pulse was $\overline{W} = 1.4 \times 10^{-6} \, \text{J/cm}^3$, and in the continuous mode the power density was $\overline{P} \simeq 4 \, \text{mW/cm}^3$. The lower experimental values of $\overline{P}$ and $\overline{W}$ are apparently due to large losses in the Brewster windows [15].

It follows from the foregoing estimates that electronic collisions play an appreciable role in the excitation of the upper vibrational levels. This agrees also with the results of Frapard [11] who investigated generation in the pulsed mode, and with his conclusions that resonant transfer of excitation from N_2^*

or as a result of some other chemical process is incapable of explaining the slight delay of the generation pulse relative to the current pulse. The apparent contradiction to the 300-μsec delay observed in earlier experiments [4] in the generation pulse relative to the current pulse must be attributed to the fact that in pure CO_2 the relaxation of the lower vibrational level is relatively long and population inversion was produced in the afterglow of the discharge. In the described experiments, the large peak value of the current (approximately 15 A) has apparently led to a noticeable population of the lower level. An analysis of the time variation of the visible radiation in the Angstrom bands ($\lambda \sim 4830$ Å) of the CO molecule indicates that the process of dissociation of CO_2 by electron impact, $CO_2 + e + \Delta E \rightarrow CO^*(B'\Sigma) + O + e$ occurs with practically no inertia.

To explain the increase of the generation power in the presence of helium, it is proposed in [35] that the excitation energy of the metastable helium atom is consumed in dissociation of nitrogen, in accord with the scheme

$$He\,(2^3S_1) + 2N_2 \rightarrow He + 4N - 0.1 \text{ eV.}$$
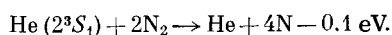
The atomic nitrogen then recombines into the N_2^* molecule, which is excited at high vibrational levels. This hypothesis contradicts the observed high efficiencies, since an appreciable fraction of the excitation energy of the helium atoms cannot be fully utilized. In addition, in the literature available to us we found no report of observation of helium lines in discharges in the $CO_2 + N_2 + He$ mixture.

A number of papers give data on the optimal composition of the working mixture [9,35] and advance ideas concerning the roles of individual components in the inversion mechanism. The optimal composition apparently depends on the diameter of the discharge tube and on the potential gradient established in the positive column at small current densities.

A composition that is optimal with respect to power is given in [9], for a tube diameter 21 mm.

The partial pressures for CO_2, He, and N_2 are respectively 2.7, 7.8, and 3.5 torr, and for a diameter ~ 77 mm we have in [35]:

$$p_{CO_2} = 0.33 \text{ torr,} \quad p_{He} = 7.0 \text{ torr,} \quad p_{N_2} = 1.2 \text{ torr.}$$

The existence of an optimal composition is connected with the complicated processes occurring in the gas discharge, and with external and internal characteristics, and cannot be clearly explained at the present time. The total pressure of the molecular gases CO_2, N_2, and O_2 should apparently not exceed several torr, for otherwise the electron temperature at small E/p ratios will be insufficient to maintain an independent discharge and for effective excitation of N_2^* ($v = 1$) and CO_2^* (00^01). In addition, at high pressures of N_2 ($p_{N_2} > 3$ torr), the intrinsic relaxa-

tion time ($\tau_{N_2} < 5$ msec) becomes commensurate with the time of deactivation by collision with CO_2. The partial pressure P_{N_2} should exceed by several times p_{N_2} in order that the equilibrium in the reaction $CO_2 + N_2^* \rightleftarrows CO_2^* + N_2$ be shifted toward larger CO_2^* concentrations.

On the other hand, when p_{CO_2} is small, the number of active molecules decreases and degeneration power is reduced. In the pulsed mode, especially for short pulses when large potential gradients can be obtained and the current density can be increased without the danger of increasing the gas temperature, the optimal partial pressure of the molecular gases can be noticeably higher. The pressure of helium is less critical, since it does not influence strongly the electron temperature.

The increase in the generation power of CO_2 lasers in the presence of helium can be attributed to several factors:

a) the decrease in the time of rotational relaxation of the lower level [12],

b) the decrease in the radial temperature gradient, which makes it possible to operate with larger discharge-tube diameter [23] and larger current densities [9],

c) its role as a buffer gas,

d) the decrease in the time of vibrational relaxation [32,28].

The increase in the excitation rate of the upper level in the presence of helium, observed in an investigation [12] under pulsed conditions, makes the following explanation probable. When the helium pressure is increased, the ratio of the longitudinal voltage gradient to the pressure (E/p) is decreased, and the electron drift velocity v_{dr} decreases somewhat. To maintain a specified current density in the discharge it is accordingly necessary to increase the electron concentration, which in turn leads to an increase in the rate of excitation in the upper level [12]. This statement is true if $kT_e \gg E_1$.

The influence of generation on the plasma conductivity can be connected with the electron temperature. Indeed, in the presence of generation, owing to the Fermi resonance, an increase takes place in the concentration of the CO_2 molecules at the 02^00 and 01^10 levels, and a change takes place in the electron temperature, owing to elastic collisions of the second kind.

In concluding this section, let us consider briefly the peculiarities of operation of lasers with $CO_2 + N_2 + He$ mixture in the pulsed mode.

It is reported in [10] that the following pulse powers were obtained with a laser having a useful gas volume 460 cm³ ($l \sim 180$ cm, dia ~ 1.8 cm):

in pure CO_2 — 220 W at $\tau = 0.5$ msec,

in $CO_2 + N_2 + O_2$ — 450 W at $\tau = 0.5$ msec,

in $CO_2 + N_2 + He$ — 825 W at $\tau = 0.15$ msec.

No delay was observed between the current pulse and the generation pulse.

Simple calculations based on the data given in[10] show that the power density in the pulsed mode reaches $\overline{P} \simeq 1.8 - 2.0$ W/cm^3 and that the energy density is $\overline{W} = 2.7 \times 10^{-4}$ J/cm^3, with a high efficiency ~12% maintained. It is natural to assume that when working with such relatively short pulses the main contribution to the excitation of the upper vibrational level is made by electron impact, since the transfer of the excitation from the N_2^* occurs with a delay amounting to several tenths of a millisecond. Consequently, an increase in P can be connected principally with an increase in the electron density n_e. This agrees with the current density $j \sim 400$ mA/cm^2 indicated in[10], which exceeds by 30—40 times the optimal values for continuous operation. The ratio of the potential gradient ($E \simeq 50$ V/cm) to the pressure of the molecular gases has approximately the same magnitude as for the continuous operation, and therefore we can expect T_e to have likewise a value of approximately one electron volt.

It is interesting to note that in a pulsed mode, a high degree of inversion is obtained: to obtain $\overline{W} \simeq 2.7 \times 10^{-4}$ J/cm^3 it is necessary to have $\Delta N(0)$ ~ 2.8×10^{16} cm^{-3}, which is more than 50% of the total number of molecules per cm^3 at $p_{CO_2} = 1.5$ torr.

At the indicated values of the rate of the stimulated transitions in the pulsed mode, a Boltzmann distribution over the rotational levels is apparently still maintained.

Indeed, in accord with the definition of the rotational relaxation time, we have

$$\frac{dn_J}{dt} = -\frac{n_J - n_J^0}{\tau_{rot}}. \tag{10}$$

This ratio can be used to estimate the population difference $n_J - n_J^0$ at a stationary rate of arrival of the molecules at lower rotational level $\tilde{M}_1 = dn_J/dt$, or a loss from the upper level under the influence of the stimulated emission. For the conditions of the experiment of[10] $\tilde{M}_{1e} = 10^{20}$ cm^{-3} sec^{-1}, and $n_J - n_J^0 \approx \tilde{M}_{1e}$ we have $\tilde{\tau}_{rot} 10^{13}$ cm^{-3}, which amounts to less than 1% of the value $n_J^0 10^{15}$ cm^{-3}.

In the Q-switching mode, as follows from[13], the deviations from equilibrium distribution over the rotational levels can be appreciable at small helium pressures.

5. TEMPERATURE EFFECTS IN CO$_2$ LASERS

The high efficiency of the inversion mechanism is one of the main conditions which determine the possibility of producing a high-power laser. Indeed, at low efficiencies and at large power-supply densities it is difficult to avoid an appreciable increase in gas temperature. An inescapable consequence of the high temperature is a drop in the gain and a reduction in the density of the generated power.

In this section we shall estimate the temperature effects in gas lasers. The stationary distribution in a homogeneous gas column can be obtained by solving the equation of heat conduction

$$C\frac{\partial T}{\partial t} = \text{div}(K \text{ grad } T) + F = 0,$$

or, in a cylindrical coordinate system, assuming that the temperature is independent of z:

$$\frac{d^2T}{dr^2} + \frac{1}{r}\frac{dT}{dr} + \frac{1}{K}F(r) = 0, \tag{11}$$

where C is the heat capacity of the gas, K the coefficient of thermal conductivity (assumed independent of the temperature), and F(r) is the source distribution density. The electron concentration distribution over the radius of the discharge tube is described by the function[39]

$$n_e(r) = n_e(0) J_0(2.4 \ r/r_0),$$

and approximately the same distribution will hold for the volume density of the sources F(r)
$$= (1 - \eta_\Sigma) j(r) E = (1 - \eta_\Sigma) en_e v_{dr} E.$$

We solve Eq. (11) with the boundary conditions

$$\frac{dT}{dr}\Big|_{r=0} = 0 \text{ and } T(r_0) = \text{const:}$$

$$T(r) = T(r_0) + \left(\frac{r_0}{2.4}\right)^2 \frac{(1-\eta) \, n_e(0) \, ev_{dr}E}{K} J_0\left(\frac{2.4r}{r_0}\right)$$

$$= T(r_0) + 0.127\frac{\overline{W}_l}{K} J_0\left(\frac{2.4r}{r_0}\right)\ldots, \tag{12}$$

where $\overline{W}_l = (1 - \eta) \, Eev_{dr} 2\pi \int_0^{r_0} n_e(r) \, e dr$ in the linear density of the energy dissipated in the tube.

Formula (12) agrees with a circumstance already noted in print – an increase in the diameter beyond 70—80 mm does not lead to an increase in power. Another reason is the instability of the uniform distribution of the current density in the positive column when the temperature is increased (the so-called pinching of the discharge).

We present quantitative estimates for the temperature drop in different mixtures at the following values of the thermal conductivity of the gases:

$$K_{He} = 0.344 \cdot 10^{-3} \text{ cal-sec}^{-1} \text{ deg}^{-1},$$

$$K_{N_2} = 0.057 \cdot 10^{-3} \text{ cal-sec}^{-1} \text{ deg}^{-1},$$

$$K_{CO_2} = 0.034 \cdot 10^{-3} \text{ cal-sec}^{-1} \text{ deg}^{-1},$$

A temperature drop $T(0) - T(r_0) = 200°C$ is obtained for $W_l = 1.04$ W in 1 cm of discharge-tube length for the CO$_2$ + N$_2$ + He mixture when the helium pressure noticeably predominant, and 0.375 W/cm for the CO$_2$ + N$_2$ mixture with nitrogen predominating.

Naturally, these estimates cannot claim to be accurate, owing to the assumptions made, but they illustrate the influence of the thermal conductivity of helium and explain the increase in the current density for tubes filled with helium.[9]. If we assume that the efficiency of the active medium is 15—17%, then the estimated power, 45—50 W/m, agrees with the published results[35,40].

In the pulsed mode, when operating with a high off-duty cycle and short pulses (τ = 20—50 msec), the stationary temperature distribution apparently does not have time to become established and the heating of the gas will be determined by its specific heat. In this case the temperature increases linearly with time:

$$T(r, t) - T(r, t_0) = \frac{F(r)}{C}(t - t_0) = \frac{\overline{W}_\Sigma}{C}, \tag{13}$$

where $F(\underline{r})$ is the volume power density of the sources, $\overline{W}_\Sigma$ the volume density of the delivered pulsed energy, $C \approx i k N_\Sigma / 2$ the specific heat of the gas, i the average number of degrees of freedom for the working gas, and N_Σ the total number of molecules per unit volume. Assuming that the gas has time to be cooled in the process between pulses, we find that the average power in the continuous and pulsed modes will be approximately the same. For a maximum delivered energy density $\overline{W}_\Sigma$ in the pulsed mode, at p_{He} = 10 torr and ΔT = 200°C, we obtain $\overline{W}_\Sigma = (\frac{3}{2}) k N_\Sigma \Delta T = 1.2 \times 10^{-3}$ J/cm^3, which is in satisfactory agreement with the results given in [10], where the maximum density of the delivered energy was 2.2×10^{-3} J/cm^3.

The indicated role of thermal effects explains the tendency of attaining an increased power in the continuous mode as a result of using longer discharge tubes, and the appearance of new active gas mixtures will hardly cause a radical change in the situation.

Consequently, although the relaxation mechanism of destruction of the lower working level has eliminated the limitations imposed by radiation reabsorption on the diameter of the discharge tubes, the limited thermal conductivity of the gas and the dependence of the gain on the temperature have set a new limit. Naturally, the power density in gas lasers will always be smaller by several orders of magnitude than in solid-state lasers.

Simple calculations show that pumping of the gas at reasonable flow rates does not reduce the temperature appreciably.

6. ENERGY RELATIONS IN MOLECULAR LASERS

In this section we shall derive relations for the generation power and the efficiency of molecular lasers. From an analysis of these relations we can determine the main characteristics of the active medium and carry out quantitative estimates of the power and efficiency.

From the formula for the inverse population (see Appendix II)

$$\Delta N = \frac{\Delta N(0)}{1 + \beta \rho} \tag{14}$$

and the expression for the gain

$$K(\rho) = \varepsilon \overline{K}(t) \Delta N \tag{15}$$

we can obtain the stationary value of the volume radiation density ρ, since in the generation mode we have

$$e^{2K(\rho)l} = (r_1 r_2)^{-1}. \tag{16}$$

Here l is the length of the active medium and $r_{1,2}$ are the reflection coefficients of the mirrors of the optical resonator.

When the gain exceeds greatly the losses, the volume radiation density ρ can be regarded as constant and the power flux through the output mirror, with transparency $1 - r_1$, will be

$$P = \frac{cs(1 - r_1)}{2} \rho, \tag{17}$$

where c is the speed of light and s the effective area of the cross section of the active medium, taking into account the distribution of ρ in the transverse cross section.

The coefficient 2 in the denominator of (17) is brought about by the fact that only half of the total volume density of the radiation is connected with the power flux in the direction of the semitransparent mirror.

Substituting the values of ρ from (14)—(16), we get

$$P = \frac{cs(1 - r_1)}{2\beta_0}\left(\frac{K^0}{\chi} - \overline{K}^{-1}\right), \tag{18}$$

where

$$K^0 = \varepsilon \Delta N(0), \quad \chi = -\frac{1}{2l}\ln(r_1 r_2). \tag{19}$$

Formula (18) is similar to the well known formulas for the laser power, and differs only in the concrete dependence of the saturation parameter β_0 on the characteristics of the active medium and in the presence of the temperature factor $\overline{K}(t)$. As indicated in Appendix II,

$$\beta_0 = \frac{\lambda^3 A_{12} cB \left(\frac{\ln 2}{\pi}\right)^{1/2}(2J-1)e^{-F(J-1)\frac{hc}{kT_0}}}{4\pi \Delta v_D |_{T_0} kT_0} \cdot \frac{\tilde{\tau}_1 + p\tilde{\tau}_2}{1 + m_{12}\tilde{\tau}_1 + m_{21}\tilde{\tau}_2}. \tag{20}$$

Substituting the numerical values of the quantities entering in (20), we get

$$\beta_0 = 8.8 \cdot 10^{12} \frac{\tilde{\tau}_1 + p\tilde{\tau}_2}{1 + m_{12}\tilde{\tau}_1 + m_{21}\tilde{\tau}_2}. \tag{21}$$

For the hypothetical-laser parameters assumed in Sec. 4, assuming further that the resonator loss is determined essentially by the transparency of the output mirror (r_1 = 0.9, r_2 = 1, χ = 3.85 × 10^{-4} cm^{-1}), we find that at $\tilde{\tau}_1$ = 10^{-3} sec the radiation power density will be P/s = 5 W/cm^2. When the gain of the active medium exceeds noticeably the loss in the resonator, putting $(1 - r_1)/\ln r_1^{-1} \approx 1$, we can transform (18) into

$$P \simeq c(sl)\frac{K^0}{\beta_0} \simeq hv(sl)\frac{\Delta N(0)}{\tilde{\tau}_1 + p\tilde{\tau}_2}(1 + m_{12}\tilde{\tau}_1 + m_{21}\tilde{\tau}_2)$$

$$\simeq hv(sl)\frac{\tilde{M}_1\tilde{\tau}_1[1 + \tilde{\tau}_2(m_{21} - pm_{12})] - \tilde{M}_2\tilde{\tau}_2[p - \tau_1(m_{21} - pm_{12})]}{\tilde{\tau}_1 + p\tilde{\tau}_2}. \tag{22}$$

For $p\tilde{\tau}_2 \ll \tilde{\tau}_1$, $\tilde{M}_2\tilde{\tau}_2 p \ll M_1\tau_1$, and $\tilde{\tau}_1 m_{21} < p$, the volume density of the power is expressed simply in

terms of the rate of excitation of the upper level

$$\overline{P} = \frac{P}{(sl)} = h\nu\tilde{M}_1.$$

Consequently, $\overline{P}$ is proportional to the ratio $\Delta N(0)/(\tau_1 + p\tau_2) \cong M_1$ - the useful part of the excitation rate of the upper level.

The quantity $\tilde{\tau}_1 + p\tilde{\tau}_2$ can be obtained from β_0 from the results of measurements of the generation power P, the weak-signal gain K^0, and the resonator losses (x, r_1, r_2). The laser efficiency η_Σ can be represented by the product

$$\eta_\Sigma = \eta_r \eta_{|tr},$$

where η_r is the efficiency of the resonator with allowance for the coefficient of excess over threshold, and $\eta_{tr} = [h\nu\Delta N(0)/(\tilde{\tau}_1 + p\tilde{\tau}_2)]/(\tilde{M}_1 E_1 + \tilde{M}_2 E_2 + \Sigma)$ is the efficiency of the transition. Here Σ is the loss of delivered power per unit volume to excitation of the nonworking levels (01^10, 11^10, 02^20, etc.), and the loss due to vibrational relaxation. In the ideal case, when $\tilde{M}_2 = \Sigma = 0$,

$$\eta_{tr} = \eta_{max} = \frac{h\nu}{E_1} = 0.41.$$

The real values of η_{tr} reach 0.15—0.2 according to [17,40]. From this we can conclude that $\tilde{M}_2 E_2 + \Sigma \simeq (1-1.7) \tilde{M}_1 E_1$. If we assume $\tilde{M}_2 E_2 = \tilde{M}_1 E_1$ and $\Sigma \simeq 0.5 \tilde{M}_1 E_1$, then we find at the values of $\tilde{M}_1$ indicated in Sec. 4, that $\tilde{M}_2 = 6 \times 10^{18}$ cm^{-3} sec^{-1}. Inclusion of the value of $\tilde{M}_2$ in the expression for $\Delta N(0)$ at $\tau_1 \approx 10^{-3}$ sec and $\tau_2 = 0.3 \times 10^{-4}$ sec leads to a reduction of approximately 30% in $\Delta N(0)$; this is within the limits of accuracy of the estimates given in Sec. 4.

CONCLUSION

Lasers using the $CO_2 + N_2 + He$ mixture have incorporated successfully the main premises formulated by Gould for an ideal gas laser: low position of the working levels relative to the ground state of the molecules, high degree of concentration of the excitation at the upper working level of the vibrational-rotational transition (owing to the large cross section for the excitation of the level 00^01 by electrons and nitrogen molecules), relatively short lifetime of the lower vibrational level (Fermi resonance, vibrational and rotational relaxations), relatively large gas density. A consequence of all this is a large inverse population ($\sim 10^{15}$ cm^{-3}). The appearance of competition between the $00^01 - 10^00$ and $00^01 - 02^00$ bands, the P and R branches of these bands, and individual vibrational-rotational transitions of the P branch ensures generation at a rather limited number of transitions, although the population inversion takes place at more than 100 transitions.

The system of rotational levels of the upper vibrational states forms a high capacity "reservoir" which effectively accumulates the excitation of the molecules and transfers this excitation to a small number of decaying rotational levels. The long lifetime of the upper vibrational state has made it possible to realize a Q-switching mode in a CO_2 laser. A nonradiative mechanism of decay of the lower level has made it possible to use large discharge-tube diameters.

The foregoing properties of the inversion mechanism have made it possible to obtain with the aid of CO_2 lasers, within a short time, power levels and efficiencies which heretofore appeared to be fantastic. This is evidence of the large promise afforded by molecular systems.

On the other hand, comparison of the characteristics of the CO_2 laser with results of experimental investigations of other systems (N_2O, OCS, H_2O) offer evidence that the CO_2 molecule has certain unique properties which favor the production of large inversion.

It is still not clear whether this is connected with the symmetry properties of the CO_2 and its level system, or with physical properties such as relaxation times, electron-collision cross sections, etc.

It is known, for example, that the nitrous oxide molecule N_2O (structure N-N-O) is linear and has no symmetry center, while the CS_2 molecule is linear and symmetrical (like CO_2), whereas H_2O and H_2S are symmetrical but not linear. These molecules differ greatly in their physical and chemical properties (dissociation energy, relaxation time, discharge characteristics) and it is not known which factors are decisive, since it was impossible to obtain large powers or efficiencies with these compounds.

Investigations of chemical reactions in the gas phase point to the existence of processes which have a high energy yield of vibrationally-excited products. This uncovers prospects for creating chemical or physical-chemical lasers which make complete or partial use of the energy of chemical reactions. The first work in the field of chemical lasers was published in the collection [2]. The most noticeable practical success in this direction has been attained with lasers using photodissociation of the molecules CH_3I, CF_3I, $CS_2 + O_2$, HCl, etc.

A common limitation of molecular systems is the small (compared with solid-state lasers) volume density of the energy of radiation and the need for using large gas volumes to obtain large powers (energies).

In addition, discharge in molecular systems is always accompanied by dissociation and a change in the initial composition of the gas, and this is the main cause for maintaining continuous gas flow. Prospects for producing powerful static systems are in this connection not perfectly clear. For devices of small and medium power (5—20 W), the static mode is more realistic.

There is still little information on commercially developed molecular lasers. It is known that the Raytheon Company has produced the model LG-14 (power 20 W, divergence 2 mrad), operating with gas flow [41], and the model LG-16 (power exceeding 700 W in the mode)[17].

The questions of applications of high-power gas lasers, modulation of radiation, interaction with matter, etc. are beyond the scope of the present review.

APPENDIX I

We consider a system of kinetic equations for the gas mixture - the working component X with level populations (x_1, x_2, and x_0) and impurities $y(y_1, y_0)$ and $z(z_1, z_0)$. We assume that the admixture y has a larger cross section for inelastic collision with the first level of the main gas, and impurity z - with the second level. Such a model will describe, for example, the behavior of the CO_2 + N_2 + H_2O mixture, where x, y, z, are the level populations of CO_2, N_2, and H_2O. For simplicity we shall assume that the ground-state populations (x_0, y_0, z_0) greatly exceed the populations of the corresponding excited states ($x_{1,2}$, y_1, z_1). For the upper working level of the CO_2 molecule the equation takes the form

$$\frac{dx_1}{dt} = \mu_{10}x_0 - (\mu_{01}y_0k_{01} + \tau_1^{-1} + p_{12}) x_1 + p_{21}x_2 + k_{10}x_0y_1\ldots, \quad \text{(a)}$$

where $\mu_{10} = n_e \langle \sigma v \rangle_{10}$ is the probability of excitation by electron impact from the ground state; μ_{01} is the probability of decay to the ground state as a result of inelastic electron collisions of the second kind, and y_0k_{01} is the same for collisions with the molecule N_2 in the ground state, τ_1^{-1} - as a result of vibrational relaxation of $CO_2(00^01)$; $p_{12} = m_{12} + f_1g_1 \int B_{12}(\nu)\rho(\nu)d\nu$ is the probability of the transition to the second level as a result of inelastic collisions, and also of stimulated emission

$$f_1 = \frac{hcB}{kT_{gas}} e^{-F(J-1)\frac{hc}{kT_{gas}}} = \frac{n_{1J}}{(2J-1)N_1},$$

p_{21} is the probability of the processes that are the inverse of p_{12}, and $k_{10}x_0$ is the probability of excitation of the upper level via inelastic collisions with N_2^* (v = 1).

The system of equations for x_1, x_2, y_1, z_1 can be written in the form

$$\frac{dx}{dt} = B + Ax,$$

where

$$x = \{x_i\} = \begin{Bmatrix} x_1 \\ x_2 \\ y_1 \\ z_1 \end{Bmatrix}, \quad B = \{b_i\} = -\begin{Bmatrix} \mu_{10}x_0 \\ \mu_{20}x_0 \\ \mu_{y0}y_0 \\ \mu_{z0}z_0 \end{Bmatrix}, \quad \text{(b)}$$

$$A = \{a_{ik}\} = \begin{Bmatrix} a_{11} & a_{12} & a_{13} & 0 \\ a_{21} & a_{22} & 0 & a_{24} \\ a_{31} & 0 & a_{33} & 0 \\ 0 & a_{42} & 0 & a_{44} \end{Bmatrix}, \quad \text{(c)}$$

$$a_{11} = -(\mu_{01} + y_0k_{01} + \tau_1^{-1} + p_{12}), \quad a_{12} = p_{21}, \quad a_{13} = k_{10}x_0,$$
$$a_{21} = p_{12}, \quad a_{22} = -(\mu_{02} + z_0l_{01} + \tau_2^{-1} + p_{21}), \quad a_{24} = l_{10}x_0,$$
$$a_{31} = J_0k_{01}, \quad a_{33} = -(\mu_{0y} + k_{10}x_0 + \tau_y^{-1}),$$
$$a_{42} = l_{01}z_0, \quad a_{44} = -(\mu_{0z}l_{10}x_0 + \tau_z^{-1}). \quad \text{(d)}$$

We consider first the behavior of the mixture of relaxing gases in the nonstationary mode.

Assume that at the instant of time t = 0 excitation due to the electronic component has stopped in the mixture (the electron-recombination coefficient is assumed large).

The solution of the system of equations (b) takes the form

$$x_i = \sum_j C_{ij}e^{\lambda_j t},$$

where λ_j are the eigenvalues of the matrix (c) and C_{ij} are coefficients determined from the initial conditions.

Let us establish a connection between the system relaxation times λ_j^{-1} and the intrinsic level relaxation times τ_i in the simplest case, when the stimulated emission is absent and the populations x_1 and x_2 are independent quantities. This corresponds to the conditions for the observation of the intensity of the spontaneous-emission lines from the working level in a decaying plasma[12]. Then the eigenvalues for the relaxation of the system x_1y_1 (for example CO_2 (00^01) and N_2^* (v = 1)) are determined by the condition

$$\begin{Bmatrix} a_{11} - \lambda & a_{13} \\ a_{31} & a_{33} - \lambda \end{Bmatrix} = 0. \quad \text{(e)}$$

The solution of (e) yields

$$\lambda_{1,2} = \frac{a_{11} + a_{33}}{2} \pm \left[\left(\frac{a_{11} - a_{33}}{2} \right)^2 + a_{13}a_{31} \right]^{1/2}. \quad \text{(f)}$$

From (f) we see that only at small degrees of inelastic collision, when $4a_{13}a_{31}(a_{11} - a_{33})^{-2} \ll 1$, do the relaxation times of the mixture coincide with the intrinsic relaxation times of the components:

$$\lambda_1 \approx a_{11} = -(\tau_1^{-1} + y_0k_{01}) \approx -\tau_1^{-1},$$
$$\lambda_2 \approx a_{33} = -(\tau_y^{-1} + k_{10}x_0) \approx -\tau_y^{-1}.$$

APPENDIX II

To calculate the gain and the saturation parameter of the active medium in the continuous mode, it is necessary to know the stationary populations of the working levels x_1 and x_2. From the system (b) with dx/dt = 0 we can obtain

$$x_1 = \frac{1}{\Delta} \{(a_{13}b_3 - a_{33}b_1)(a_{42}a_{24} - a_{22}a_{44}) + a_{12}a_{33}(a_{24}b_4 - a_{44}b_2)\} = \frac{\bar{x}_1}{\Delta},$$

$$x_2 = \frac{1}{\Delta} \{(a_{24}b_4 - a_{44}b_2)(a_{13}a_{31} - a_{11}a_{33}) + a_{21}a_{44}(a_{13}b_3 - a_{33}b_1)\} = \frac{\bar{x}_2}{\Delta},$$

where

$$\Delta = \det A = (a_{13}a_{31} - a_{11}a_{33})(a_{42}a_{24} - a_{22}a_{44}) - a_{12}a_{21}a_{33}a_{44}. \quad \text{(g)}$$

The gain of the molecular system can be expressed in terms of the level population difference $\Delta N = x_1 - px_2$ (see formula (5)).

According to (g)

$$\Delta N = \frac{1}{\Delta}(\bar{x}_1 - p\bar{x}_2) = \frac{\Delta N\,(0)}{1+\beta\rho}.\qquad\text{(h)}$$

where $\Delta N(0) = (1/\Delta)(\bar{x}_1 - p\bar{x}_2)\,|_{\rho=0}$ is the inverse population in the absence of stimulated transitions $(\rho = \int\rho(\nu)\,d\nu = 0)$, and β is the saturation parameter of the transition $1 \rightarrow 2$. Separating in Δ the terms containing ρ, we can obtain from (g) an analytic expression for β

$$\beta = B_{12}(\nu_0)\,f_1 g_1 \frac{\left\{\left(\bar{a}_{11}+\frac{a_{13}a_{31}}{a_{33}}\right)^{-1}+p\left(\bar{a}_{22}+\frac{a_{24}a_{42}}{a_{44}}\right)^{-1}\right\}}{1+m_{12}\left(\bar{a}_{11}+\frac{a_{13}a_{31}}{a_{33}}\right)^{-1}+m_{21}\left(\bar{a}_{22}+\frac{a_{24}a_{42}}{a_{44}}\right)^{-1}},\qquad\text{(j)}$$

where

$$\bar{a}_{11} = \mu_{01}+y_0 k_{01}+\tau_1^{-1} = -a_{11}-p_{12}.\quad \bar{a}_{22} = -a_{22}-p_{21}.$$

In the derivation of (j) we took into account the well known relation $g_1 B_{12}(\nu) = g_2 B_{21}$, and we put $\int B_{12}(\nu)\,s(\nu)\,d\nu = B_{12}(\nu)\rho$ and $f_2 = pf_1$. Expression (j) can be represented in a form more convenient for calculations, using the connection between the Einstein coefficients and separating the temperature-dependent factor

$$\beta = \beta_0 \bar{K}\,(t);$$

$$\beta_0 = \frac{\lambda^3 A_{12}cB\left(\dfrac{\ln 2}{\pi}\right)^{1/2}(2J-1)^{-F\,(J-1)\frac{hc}{kT_0}}}{4\pi\Delta\nu_D\,|_{T_0}kT_0}\cdot\frac{\tilde{\tau}_1+p\tilde{\tau}_2}{1+m_{12}\tilde{\tau}_1+m_{21}\tilde{\tau}_2},\qquad\text{(k)}$$

where

$$\tilde{\tau}_1^{-1} = \tau_1^{-1}+\mu_{01}+y_0 K_{01}-\frac{k_{10}k_{01}x_0 y_0}{\mu_{0y}+k_{10}x_0+\tau_y^{-1}}.$$

$$\tilde{\tau}_2^{-1} = \tau_2^{-1}+\mu_{02}+z_0 l_{01}-\frac{l_{10}l_{01}x_0 z_0}{\mu_{0z}+l_{10}x_0+\tau_z^{-1}}$$

are the effective reciprocal lifetimes of the levels in the presence of excitation in the system.

For the population inversion we obtain, following the transformations (h),

$$\Delta N\,(0) = \frac{\tilde{M}_1\tilde{\tau}_1\,[1+\tilde{\tau}_2\,(m_{21}-pm_{12})]-\tilde{M}_2\tilde{\tau}_2\,[p-\tilde{\tau}_1\,(m_{21}-pm_{12})]}{1+m_{12}\tilde{\tau}_1+m_{21}\tilde{\tau}_2}.$$

where

$$\tilde{M}_1 = \mu_{10}x_0+\mu_{y0}y_0\frac{k_{10}x_0}{\mu_{0y}+k_{10}x_0+\tau_y^{-1}}.$$

$$\tilde{M}_2 = \mu_{20}x_0+\mu_{z0}z_0\frac{l_{10}z_0}{\mu_{0z}+l_{10}z_0+\tau_z^{-1}}\qquad\text{(l)}$$

are the total excitation rates of the levels, with allowance for the influence of the impurity. From the detailed balancing principle it follows that

$$m_{21}/m_{12} = \exp\,[-(E_1-E_2)/kT_\Gamma].$$

[1] I. I. Sobel'man and S. G. Rautian, JETP 43, 2018 (1962) [sic!].

[2] G. Gould, Appl. Optics, Suppl. II, 59 (1965).

[3] C. K. N. Patel, W. L. Faust, R. A. McFarlane, Bull. Amer. Phys. Soc. 9, 500 (1964).

[4] C. K. N. Patel, Phys. Rev. Letts 12 (N 21), 588 (1964).

[5] C. K. N. Patel, Phys. Rev. 136 (5A), 1187 (1964).

[6] C. K. N. Patel, Phys. Rev. Letts 13 (N 21), 617 (1964).

[7] C. K. N. Patel, Appl. Phys. Letts 7 (N 1), 15 (1965)

[8] N. Legay-Sommaire, L. Henry, F. Legay, Compt. Rend. 260, 3339 (1965).

[9] G. Moeller, J. D. Rigden, Appl. Phys. Letts 7 (N 10), 274 (1965).

[10] C. Frapard, M. Roulot, K. Ziegler, Phys. Letts 20 (N 4), 384 (1966).

[11] C. Frapard, IEEE J. Quant. Electron. QE-2 (N 4), p. XXV, paper 4B-3 (1966).

[12] T. F. Deutsch, M. J. Weber, IEEE J. Quant. Electron. QE-2 (N 4), p. XXIV, paper 4B-2 (1966).

[13] G. W. Flynn, M. A. Kovacs, C. K. Rhodes, A. Javan, Appl. Phys. Letts 8 (N 3), 63 (1966).

[14] G. Flynn, L. Hocker, M. Kovacs, C. K. Rhodes, IEEE J. Quant. Electron. QE-2 (N 4), p. XXV, paper 4B-5 (1966).

[15] M. A. Kovacs, G. W. Flynn, A. Javan, Appl. Phys. Letts 8 (N 3), 62 (1966).

[16] T. J. Bridges, Appl. Phys. Letts 9 (N 4), 174 (1966).

[17] I. B. Brinton, Microwave News 5 (N 8), 16 (1966).

[18] Electronics News 11 (N 527) (1966).

[19] N. N. Sobolev and V. V. Sokovikov, UFN 91, 425 (1967), this issue p. 153.

[20] M. A. El'yashevich, Atomnaya i molekulyarnaya spektroskopiya (Atomic and Molecular Spectroscopy), Fizmatgiz, 1962.

[21] I. Wieder, G. B. McCurdy, Phys. Rev. Letts 16 (N 13), 565 (1966).

[22] G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand, 1945.

[23] G. Moeller, I. D. Rigden, IEEE J. Quant. Electron. QE-2 (N 4), p. XXIV, paper 4B-1 (1966).

[24] W. J. Witteman, J. Chem. Phys. 35, 1 (1961); J. Chem. Phys. 37, 655 (1962).

[25] E. T. Gerry, D. A. Leonard, Appl. Phys. Letts 8 (N 9), 227 (1966).

[26] H. Statz, C. L. Tang, G. F. Coster, IEEE J. Quant. Electron. QE-2 (N 4), p. XXVI, paper 4B-6 (1966).

[27] T. J. Bridges, C. K. N. Patel, Appl. Phys. Letts 7 (No. 9), 244 (1965).

[28] Atomic and Molecular processes, D. Bates, editor (Russian Transl.), Mir, 1964.

[29] W. J. Witteman, IEEE J. Quant. Electron. QE-2 (N 4), p. XXV, paper 4B-4 (1966).

[30] L. O. Hocker, M. A. Kovacs, C. K. Rhodes, G. W. Flynn, A. Javan, Phys. Rev. Letts 17 (N 5), 233 (1966).

[31] J. A. Howe, Appl. Phys. Letts 7 (N 7), 21 (1965).

[32] N. O. Cobrey, Mc. Gratt, Quart. Rev. (London), 11, 87 (1957).

[33] Ya. B. Zel'dovich and Yu. P. Raĭzer, Fizika udarnykh voln i vysokotemperaturnykh gidrodinamicheskikh yavleniĭ (Physics of Shock Waves and High-temperature Hydrodynamic Phenomena), Fizmatgiz, 1963.

[34] W. R. Bennet, in: Lazery (Lasers) (Russian Transl.), IL, 1963, p. 207.

[35] C. K. N. Patel, P. K. Tien, I. H. McFee, Appl. Phys. Letts 7 (N 11), 290 (1965).

[36] J. Husted, Physics of Atomic Collisions (Russ. Transl.), Mir, 1965.

[37] S. C. Brown, Elementary Processes in Gas-Discharge Plasma (Russ. Transl.), Gosatomizdat, 1961.

[38] G. Moeller, J. D. Rigden, Appl. Phys. Letts 8 (N 3), 69 (1966).

[39] N. A. Kaptsov, Elektricheskie yavleniya v gazakh i vakuume (Electric Phenomena in Gases and Vacuum), Gostekhizdat, 1950.

[40] Electronic News 11 (N 539) (1966).

[41] Electronic Component 5 (N 9), 850 (1965).

[42] W. J. Witteman, J. Appl. Phys. 37, 2919 (1966).

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