The carbon monoxide laser. Population inversion mechanism[1)]

N. N. Sobolev and V. V. Sokovikov
P. N. Lebedev Physics Institute, Academy of Sciences of the USSR
Usp. Fiz. Nauk 110, 191-212 (June 1973)

A review is given of the investigations of the mechanism of population inversion of vibrational levels in gas-discharge CO lasers operating at room and liquid nitrogen temperatures. Special attention is paid to the published theoretical and experimental information on the probabilities of vibrational transitions in molecules. Calculations of the populations of vibrational levels in the CO laser are discussed in detail. An analysis of these investigations demonstrates the correctness of the hypothesis postulating that the vibrational degrees of freedom of the CO molecule are pumped by electron impact and the higher levels are populated by the relaxation of carbon monoxide, which can be regarded as the relaxation of a system of anharmonic oscillators as first suggested by Treanor.

CONTENTS

1. GENERAL COMMENTS. BASIC RATE EQUATIONS

The mechanism of population inversion in CO_2 lasers suggested in[2-4] has been confirmed in a large number of investigations carried out at the Lebedev Physics Institute in Moscow and by investigations performed in other laboratories in the USSR and abroad. This mechanism is now generally accepted.[5,6]

The operation of the CO laser is, in many respects, similar to that of the CO_2 laser. There is little doubt that the CO laser is pumped by direct electron excitation of the vibrational levels of CO and N_2, in the same way as in the CO_2 laser. The distribution of molecules over the vibrational levels in the CO laser is governed (as in the case of the CO_2 laser) primarily by the vibrational relaxation, i.e., by collisions between heavy particles and particularly between CO molecules.

The quantitative analysis of the population of the CO_2 laser levels has been simplified considerably by the use of the well-developed theory of the relaxation of harmonic oscillators.[7] It is known that, irrespective of the method of excitation of a system of harmonic oscillators, the resonance exchange between vibrational quanta (VV relaxation) produces a Boltzmann distribution with a vibrational temperature governed by the total number of vibrational quanta. The vibration-translational (VT) relaxation alters only the vibrational temperature of the Boltzmann distribution over the vibrational levels. A system of harmonic oscillators behaves in this way because the VV relaxation is much faster than the VT relaxation. This model can be used in an analysis of the operation of the CO_2 laser because only a small number of the lower levels of three vibrational modes of the CO_2 molecule participates in the stimulated emission and these modes can be regarded as three harmonic oscillators. Each of these oscillators has its own vibrational temperature. This approach makes it possible to dispense with the solution of the system of rate equations describing the populations of individual levels and to consider the relaxation equations for the energy of each vibration mode of the CO_2 molecule.

An attempt was made in 1959 (at the Lebedev Institute) to represent the active medium in the CO laser by a system of harmonic oscillators with a Boltzmann distribution governed by a vibrational temperature. The absolute vibrational inversion is not necessary for the stimulated emission in the P-branch lines of the CO molecule. At low rotational temperatures a partial inversion may appear even in the case of a Boltzmann distribution of the vibrational levels. However, since the stimulated emission is observed for high vibrational levels ($v > 5$) but not for low levels, it follows that the vibrational temperature of CO should be of the order of 20 000–30 000°K. The gains calculated for these temperatures were found to be one or two orders of magnitude higher than the experimental values. This considerable discrepancy and the possibility of stimulated emission for a large number of high levels have suggested that in order to explain the operation of the CO laser one should invoke the model of a relaxing system of anharmonic oscillators[8] and solve the system of rate equations for the populations of the individual levels. The changes in the populations of the vibrational levels of the CO molecule in a glow discharge can be described by the following system of rate equations:

$$\begin{aligned}\frac{dN_v}{dt} &= K_{v+1,\,v}N_{v+1}N-(K_{v,\,v-1}+K_{v,\,v+1})\,N_vN+K_{v-1,\,v}N_{v-1}N\\ &+\Big\{\Big(\sum_{v'}K_{v+1,\,v}^{v'-1,\,v'}N_{v'-1}\Big)N_{v+1}-\Big[\Big(\sum_{v'}K_{v,\,v-1}^{v',\,v'+1}N_{v'}\Big)+\Big(\sum_{v'}K_{v,\,v+1}^{v',\,v'-1}N_{v'}\Big)\Big]N_v\\ &+\Big(\sum_{v}K_{v-1,\,v}^{v'+1,\,v'}N_{v'+1}\Big)N_{v-1}\Big\}+\Big(\sum_{v'}N_{v'}N_ek_{v'v}^{(e)}-N_vN_e\sum_{v'}k_{vv'}^{(e)}\\ &+(N_{v+1}A_{v+1,\,v}-N_vA_{v,\,v-1});\end{aligned} \tag{1}$$

here, N_v is the population of the v-th level; N is the total number of molecules per unit volume; $K_{v,v-1}$ and $K_{v,v-1}^{v',v'+1}$ are the rate constants of the vibration-translational and vibration-vibrational transitions, respectively; N_e is the electron density; $k_{vv'}^{(e)}=\langle\sigma_{vv'}^{(e)},u_e\rangle$ are the rate constants of the excitation of the vibrational levels by electron impact averaged over the electron velocities; $\sigma_{vv'}^{(e)}$, is the cross section of the excitation process; u_e is the electron velocity; $A_{v,v-1}$ is the probability of spontaneous emission (Einstein coefficient).

In the presence of helium or other gases the system (1) has additional terms describing vibrational transitions as a result of collisions between the CO molecules and the molecules of the additive. However, the effect of additives such as O_2, Xe, and H cannot be described simply by their collisions and it is not yet fully understood.

Under steady-state conditions the change in the level populations dN_v/dt is 0 and the system of nonlinear differential equations (1) reduces to a system of nonlinear algebraic equations of the first order. The number of equations in this system is governed by the dissociation energy and the anharmonicity constants; in the case of CO, it is ~60. The CO laser is a typical multilevel system and cannot be reduced to a model with two, three, or four levels.

We must stress that the system (1) does not describe completely the behavior of a real medium in a gas-discharge laser because it ignores various processes such as the deactivation of vibrationally excited molecules at the walls of a discharge tube, the dissociation of CO molecules in collisions with electrons, etc. Allowance for these processes would complicate the system even further and would make its solution practically useless because no data are available on the probabilities of these processes. In particular, nothing is known about the rate of dissociation of the CO molecules in specific vibrational states and, moreover, it is not known whether a vibrationally excited molecule is completely deactivated at the wall or whether it undergoes simply a one-quantum transition.

We shall see later that the agreement between the experimental and calculated results obtained without allowance for these processes justifies, to some degree, our neglect of these processes in the calculations.

The next chapter deals with the relationships between the rate constants of the processes resulting in the population of the vibrational levels of CO, included in Eq. (1).

2. PROBABILITIES OF VIBRATIONAL TRANSITIONS IN CO MOLECULES

In view of the fact that, until recently, there have been no experimental data on the probabilities of vibrational transitions between separate levels, it has been usual to perform rate calculations on the basis of the formulas derived by Herzfeld et al. by quantum-mechanical methods.[9] In the present chapter we shall give the theoretical formulas and compare the transition probabilities calculated on their basis with the recently published experimental results.[10–13] We shall also give data on the probabilities of radiative transitions and the electron-impact excitation cross sections of the vibrational levels of CO.

A. Collisional Vibrational Transitions

In the case of collisions between two molecules A and B, the probability that the molecule A undergoes a transition from a level v + 1 to a level v and the molecule B from a level v′ − 1 to a level v can be written as follows ($v \neq v' - 1$):[9]

$$\begin{aligned}P_{v+1,v}^{v'-1,v'}(a,b) &= P_0(a)\,P_0(b)\,P_c\,(v+1)\,v'\,(\Delta E_{v+1,v}\Delta E_{v',v'-1})^{-1}\\ &\times(\lambda^2/M_a)^2\,8\,(\pi/3)^{1/2}\,(\pi\mu\Delta E_{v+1,v}^{v'-1,v'})^2\,(\chi_{v+1,v}^{v'-1,v'})^{1/2}\\ &\times\exp[-3\chi_{v+1,v}^{v'-1,v'}+(\Delta E_{v+1,v}^{v'-1,v'}/2kT_g)+\varepsilon/kT_g],\end{aligned} \qquad (2)$$

which reduces to the following form under exact resonance conditions ($v = v' - 1$):

$$\begin{aligned}P_{v+1,v}^{v'-1,v'}(a,b) &=\\ &= P_0(a)\,P_0(b)\,P_c\,(v+1)^2\,[(\alpha^*)^2\,\lambda^4h^2\mu kT_g/\pi^2M_a^2\,(\Delta E_{v,v-1})^2]\,e^{\varepsilon/kT_g}.\end{aligned} \qquad (3)$$

The dimensionless transition probabilities P and the rate constants K in Eq. (1) are related by ZP = NK, where Z is the number of gas-kinetic collisions of the CO molecules per second. The coefficients in Eqs. (2)–(3) are:

$$P_0(a)\,P_0(b)=Z_0^{-1}\approx 1/3, \qquad P_c=1{,}364\,[1+(1{,}1\varepsilon/kT_g)],$$

where ϵ is the depth of a potential well described by the Lennard-Jones curve:

$$\chi_{v+1,v}^{v'-1,v'}=[2\pi^4\mu\,(\Delta E_{v+1,v}^{v'-1,v'})^2/\alpha^2\,h^2kT_g]^{1/3},$$

$\mu = m_Am_B/(m_A + m_B)$ is the reduced mass of the colliding molecules; M_a is the reduced mass of an oscillator A; $\lambda \approx 1/2$; α is a measure of the dimensions of the interaction region; $\Delta E_{v+1,v}$ is the energy of the (v + 1)-th vibrational quantum; $\Delta E_{v+1,v}^{v'-1,v'}$ is the difference between the energies of the (v + 1)-th and v′-th vibrational quanta; T_g is the gas temperature.

In the case of collisions between harmonic oscillators, the quantities $\Delta E_{v+1,v}$ are independent of the number of the vibrational level and $\Delta E_{v+1,v}^{v'-1,v'} = 0$. However, in collisions of anharmonic oscillators we have

$$\begin{aligned}\Delta E_{v,v-1}=E_v-E_{v-1}=hc\omega_e\,(1-2\chi_e v),\ \Delta E_{v,v-1}^{v',v'-1}\\ =\Delta E_{v,v-1}-\Delta E_{v',v'-1}=2hc\omega_c\chi_e\,(v'-v),\end{aligned}$$

where ω_e and χ_e are the anharmonicity constants.

Equations (2)–(3) represent the generalization of the Herzfeld formulas to collisions between anharmonic oscillators. The possibility of such generalization has been discussed in [14].

The probabilities of the direct and reverse transitions are related by expressions which follow from the principle of detailed equilibrium:

$$\begin{aligned}P_{v+1,v}&=P_{v,v+1}\exp[(E_{v+1}-E_v)/kT_g],\\ P_{v+1,v}^{v'-1,v'}&=P_{v,v+1}^{v',v'-1}\exp[(E_{v+1}-E_v-E_{v'}+E_{v'-1})/kT_g].\end{aligned} \qquad (4)$$

For a collision between two CO molecules the formulas (2)–(3) become[15]

$$\begin{aligned}P_{v+1,v}^{v'-1,v'}(a,a)&=\frac{2{,}17\cdot10^{-3}}{1+(98/T_g)}\,\frac{(v+1)\,v'\,(|v'-v-1|)^{7/3}}{(1-0{,}012v')\,[1-0{,}012\,(v+1)]}\,\frac{1}{T_g^{1/6}}\\ &\times\exp\left[-13{,}7\left(\frac{v'-v-1}{T_g}\right)^{1/3}+\frac{18{,}8\,(v'-v-1)}{T_g}+\frac{88}{T_g}\right] \quad (v\neq v'-1),\end{aligned} \qquad (5)$$

$$\begin{aligned}P_{v+1,v}^{v'-1,v'}(a,a)&=\{(v')^2\,T_g/[1+(98/T_g)]\,(1-0{,}012v')\}\times\\ &\times 2{,}54\cdot10^{-6}\exp(88/T_g)\quad(v=v'-1),\end{aligned} \qquad (6)$$

whereas in the case of a collision between a CO molecule and an atom of He

$$\begin{aligned}P_{v+1,v}(a,b)&=(v+1)\,\frac{335}{(1+33/T_g)}\left\{\frac{[1-0{,}012\,(v+1)]^2}{T_g}\right\}^{1/6}\\ &\times\exp\left\{-144\left[\frac{[1-0{,}012\,(v+1)]^2}{T_g}\right]^{1/3}+\frac{1560\,[1-0{,}012\,(v+1)+30]}{T_g}\right\}.\end{aligned} \qquad (7)$$

The probabilities of vibrational transitions in the CO molecule were calculated in [16] using the Herzfeld formulas modified for convenience by the approximation of the adiabatic factor

$$F(y)=8\,(\pi/3)^{1/2}\,y^{7/3}\exp(-3y^{2/3})$$

with the expression[17,18]

$$F(y)=(1/2)\,[3-\exp(-2y/3)]\exp(-2y/3),$$

where

$$y = \begin{cases} y_{v,\,v-1} = \delta(1-2\chi_e v), \\ y_{v,\,v-1}^{v',\,v'+1} = 2\chi_e\delta(|v-v'-1|), \end{cases}$$

$$\delta = (1/2)^3(\theta'/T_g)^{1/2}, \qquad \theta' = 16\pi^4\mu\nu^2/\alpha^2 k.$$

In this way, we obtain the following formulas for the rate constants of the vibrational transitions:

$$K_{v,\,v-1}^{v'-1,\,v'}(a, a) = \\ = Z'(a, a)\,P^{VV}(a, a)\,T_g\,[vv'/(1-\chi_e v)(1-\chi_e v')]\,F(y_{v,\,v-1}^{v'-1,\,v'}(a, a)), \tag{8}$$

$$K_{v,\,v-1}(a, a) = Z'(a, a)\,P^{VT}(a, a)\,T_g\,[v/(1-\chi_e v)]\,F(y_{v,\,v-1}(a, a)), \tag{9}$$

$$K_{v,\,v-1}(a, b) = Z'(a, b)\,P^{VT}(a, b)\,T_g\,[v/(1-\chi_e v)]\,F(y_{v,\,v-1}(a, b)); \tag{10}$$

Here, $Z'(a, a) = 4\sigma_{aa}^2(\pi k T_g/2\mu_{aa})^{1/2}$ cm^3/sec is the number of collisions between the CO molecules themselves (per second) reduced to one molecule (σ_{aa} is the collision diameter in the hard-sphere model and μ_{aa} is the reduced mass of two CO molecules); $Z'(a, b)$ is the corresponding quantity for collisions of the CO molecules with the He atoms; $P^{VV}(a, a)$, $P^{VT}(a, a)$, and $P^{VT}(a, b)$ are the dimensionless constants representing the relevant processes. These constants were found in [16] by comparing Eqs. (8)–(10) with the measured relaxation times of CO given in [19,20]. Some values of the transition probabilities calculated in [16] for 175°K from the formulas (8)–(10) are listed in Table I. It is clear from this table that the probabilities of transitions in the CO–CO collisions are practically always many orders of magnitude smaller than the probabilities of the VV transitions or the probabilities of the VT transitions in collisions with the He atoms.

The normalization constants were selected in [16] using all the experimental data and the value of τ for $T_g = 175$°K was found by extrapolating the high-temperature data [19] in accordance with the Landau-Teller temperature dependence of the relaxation time.[21] According to more recent measurements,[10] the VT relaxation time of the CO–He mixture at $T_g = 100$°K is two orders of magnitude smaller than the value found by extrapolation. This discrepancy is due to the fact that the long-range forces have been neglected in the calculations reported in [22]. Recent [12] experimental values of the probabilities of the VT transitions ($P_{1,0} = 3.1\times10^{-8}$) for $T_g = 298$°K in the CO–He collisions (v = 1–13) are approximately two orders of magnitude smaller than the values calculated by the Herzfeld method (7.0×10^{-6}).

In view of the considerable differences between the experimental values and those calculated by the Herzfeld method, the VT transition probabilities were also calculated in [23] allowing for the long-range forces at temperatures of 325 and 550°K. The results of these calculations are presented in Fig. 1. It is evident from this figure that at 325°K we have $P_{1,0} \approx 10^{-9}$.

TABLE I. Rates of vibrational transitions (sec^{-1}) at $T_g = 175$°K, $p_{CO} = 0.2$ Torr, and $p_{He} = 6.0$ Torr

v	$N_b K_{v,\,v-1}(a, b)$	$N_a K_{v,\,v-1}(a, a)$	$N_a K_{v,\,v-1}^{v-1,\,v}(a, a)$
1	$5.572\cdot10^{-2}$	$8.728\cdot10^{-12}$	$1.644\cdot10^{3}$
8	1.415	$1.695\cdot10^{-9}$	$1.146\cdot10^{5}$
9	1,878	$3.010\cdot10^{-9}$	$1.470\cdot10^{5}$
10	2.462	$5.274\cdot10^{-9}$	$1.837\cdot10^{5}$
11	3.195	$9.152\cdot10^{-9}$	$2.251\cdot10^{5}$
12	4.112	$1.575\cdot10^{-8}$	$2.714\cdot10^{5}$
15	8,442	$7.735\cdot10^{-8}$	$4.409\cdot10^{5}$
20	$2{,}576\cdot10^{1}$	$1.009\cdot10^{-6}$	$8.383\cdot10^{5}$
30	$2{,}032\cdot10^{2}$	$1.455\cdot10^{-4}$	$2.171\cdot10^{6}$
40	$1{,}432\cdot10^{3}$	$1.875\cdot10^{-2}$	$4.490\cdot10^{6}$
50	$9.501\cdot10^{3}$	2.279	$1.216\cdot10^{7}$
60	$6{,}070\cdot10^{4}$	$2.679\cdot10^{2}$	$1.422\cdot10^{7}$

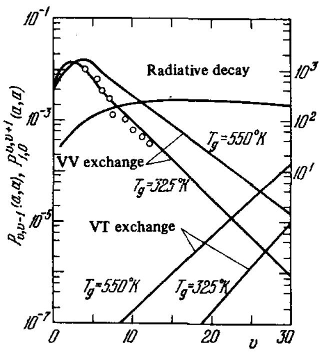

FIG. 1

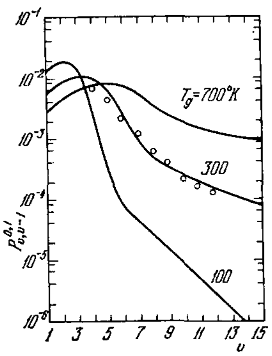

FIG. 2

FIG. 1. Dependences of the probabilities of the vibrational transitions on the level number at gas temperatures of 325 and 550°K. Circles denote the experimental values of $P_{1,0}^{v,v+1}$, obtained in [12] at 298°K.

FIG. 2. Dependences of the probabilities of the VV transitions on the level number at temperatures of 100, 300, and 700°K. The circles represent the experimental data reported in [12] and obtained at 298°K.

The probabilities of the VV transitions at room temperature were also found experimentally in [12]. They differed from the theoretical values and the discrepancy between the experimental probabilities and those calculated using the Herzfeld formulas increased with increasing level number, reaching one order of magnitude for the eighth level: $P_{87}^{01} = 5.9\times10^{-4}$ (exper.) and 5.6×10^{-5} (theor.). The origin of this discrepancy was analyzed in [25] and it was found that, as in the VT transitions, allowance should have been made not only for the short-range but also for the long-range forces.[26] The relative contributions of the short- and long-range forces are primarily a function of the gas temperature and of the energy defect of a given transition. Figure 2 shows the dependences of the probabilities of the VV transitions on the level number for three values of the gas temperature, obtained in [25]. The VV transition probabilities calculated allowing for the long-range forces in [23] are also included in Fig. 1. The agreement between the calculated and measured room-temperature transition probabilities shows that the calculations which include the long-range forces are more reliable.

By way of illustration we shall now quote several values of the transition probabilities. At room temperature and 1 atm the relaxation time τ of pure CO is approximately 1 sec,[13] whereas the relaxation time of a mixture of carbon monoxide and He is three orders of magnitude smaller;[10] the transition probabilities $P_{1,0}(a, a)$ and $P_{1,0}(a, b)$ are, respectively, 10^{-11} and 10^{-8}. These probabilities of the VT transitions are many orders of magnitude smaller than the value of $P_{1,0}^{01}$, which is approximately 5×10^{-3}. It is evident from Fig. 1 and Table I that the probabilities $P_{v,v-1}(a, a)$ and $P_{1,0}^{v,v+1}(a, a)$ are equal ($\approx2\times10^{-6}$) for $v \approx 27$ and the probabilities $P_{v,v-1}(a, b)$ and $P_{1,0}^{v,v+1}(a, a)$ are equal ($\approx4\times10^{-5}$) for $v \approx 18$. Thus, the VV transitions predominate in the range of the vibrational levels active in the stimulated emission. At a gas temperature $T_g = 175$°K all the values of P decrease by about an order of magnitude but the VV transitions remain dominant.

B. Radiative Vibrational Transitions

For an anharmonic molecule the dependence of the Einstein coefficient on the vibrational quantum number can be written in the form:[16,27]

$$A_{v,\,v-1}=[(E_v-E_{v-1})/E_1]^3\,|R_{v,\,v-1}/R_{1,\,0}|^2 A_{10}, \tag{11}$$

where

$$R_{v,\,v-1}/R_{1,\,0}=-(\chi^{1-}_{e}-2)[(\chi_e^{-1}-1)/(\chi_e^{-1}-3)\,(\chi_e^{-1}-5)]^{1/2}$$
$$\times[(-1)^{2v-1}/(\chi_e^{-1}-2v)]\,[v\,(\chi_e^{-1}-2v-1)\,(\chi_e^{-1}-2v-3)\,(\chi_e^{-1}-v)^{-1}]^{1/2}, \tag{12}$$

A_{10} is the Einstein coefficient for the 1–0 transition. For the CO molecule we have $A_{10}=30.303\ \mathrm{sec}^{-1}$;[16] the values of the other coefficients calculated using Eqs. (11)–(12) are given in Fig. 1 and in Table II.

We can see that the anharmonicity of the carbon monoxide molecule gives rise to a nonlinear dependence of $A_{v,v-1}$ on the level number and the transition probabilities remain constant for $v > 10$. Table II gives also the probabilities of two-photon radiative transitions. At a CO pressure of 1 Torr their contribution is significant for transitions between sufficiently high levels ($v > 10$).

A comparison of the probabilities of collisional and radiative vibrational transitions shows that in a CO–He laser with partial pressures $P_{CO}=0.2$ Torr and $P_{He}=6$ Torr the room-temperature deactivation of the vibrational levels with $v < 15$ occurs mainly because of radiative transitions.

C. Excitation of CO and N_2 Vibrational Levels by Electron Impact

An analysis of the operation of the CO_2 laser[2] has shown that the upper laser level of the CO_2 molecule is pumped mainly by the direct electron excitation of the vibrational levels of the CO and N_2 molecules present in the discharge, followed by the transfer of energy to the vibrational levels of CO_2. This conclusion has been drawn from the experimental data on the cross sections of collisions between electrons and molecules, reported by Schulz.[28] The same excitation mechanism obviously also applies to the CO laser.[11,14]

According to Schulz's results (Fig. 3), the electron-impact excitation cross sections of the vibrational levels of CO are large: the total excitation cross section of eight levels is 8×10^{-16} cm^2 for electrons of 1.8 eV energy. Figure 4 shows the dependences of the partial excitation cross sections of individual levels on the electron energy. It is clear from this figure that the excitation cross sections of the first two levels are several times larger than the excitation cross sections of the other levels. We can show that about four vibrational quanta are excited in one collision.

The rate constants of the excitation of molecules in a laser discharge can be found by averaging the quantities σu over the electron velocity distribution. The dependences of the excitation cross sections on the electron energy are described approximately in [16] by the Gaussian functions:

$$\sigma_{v'v}(\varepsilon)=\bar{\sigma}_{v'v}\exp[-(\varepsilon-\varepsilon_{v'v})^2/\alpha_{v'v}],$$

where $\bar{\sigma}_{v'v}$, $\epsilon_{v'v}$, and $\alpha_{v'v}$ are the constants selected in such a way that the Gaussian curves are as close as possible to the experimental dependences reported by Schulz (here, the averaging is carried out over a Maxwellian distribution). This procedure yields the rate constant of the excitation of the first level, which is reported in [16], 2.87×10^{-9} cm^3/sec (for $T_e = 20\,000$°K).

TABLE II. Probabilities of radiative transitions at T_g = 300°K [12]

v	$A_{v,\,v-1}$, sec^{-1}	$A_{v,\,v-2}$, sec^{-1}	v	$A_{v,\,v-1}$, sec^{-1}	$A_{v,\,v-2}$, sec^{-1}
1	33.4	—	8	200.1	25.1
2	64.5	0,9	9	214.1	32.0
3	92.9	2.8	10	227.1	39.3
4	118.0	5.6	11	238.8	47.7
5	142.0	9.3	12	248.5	56.2
6	164.3	13,9	13	256.3	65.6
7	182.0	19.0	14	262.5	75.0

Recently the distribution function of electrons in the CO laser plasma was determined by probe measurements[29] (see also [1]). An investigation was made of Co–He–O_2 mixtures (pressures in the ratios 1:10:0.1 and 1:30:0.1) at pressures of 3–7 Torr and for discharge currents of 20–60 mA in continuous-flow and static systems. It was found that in mixtures with large amounts of He the electron distributions were close to the Maxwellian form and the average energies were 2.5–4 eV. These energies corresponded to the excitation rate constants of $(1.2-2.0)\times10^{-8}$ cm^3/sec. Typical energy distribution functions of electrons in CO–He mixtures are plotted in Fig. 5 for p = 5 Torr and i = 40 mA. For a CO pressure of 0.3 Torr in a discharge at 100°K and an electron density $N_e = 2.5\times10^9$ cm^{-3}, the excitation rate was approximately 10^{18} cm$^{-3}\cdot$sec^{-1}. Since an average of four vibrational quanta was excited in one collision, the pumping power should be 0.1 W/cm^3. The experimental value [30] was of the same order of magnitude but somewhat larger (~0.4 W/cm^3). In view of this, we may conclude that the electron-impact pumping is sufficient to ensure the experimentally found values of the power density. The slight discrepancy between the values quoted above suggests that multistage excitation processes play some role in the electron-impact population.

3. VIBRATIONAL RELAXATION OF A SYSTEM OF ANHARMONIC OSCILLATORS

If the rate equation system (1) is simplified by dropping the last two terms in parentheses, which represent the pumping by electron impact and radiative transitions,

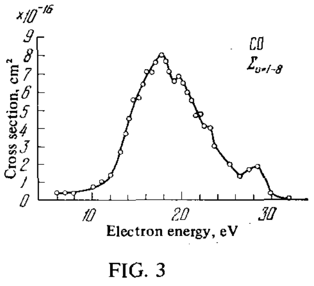

FIG. 3

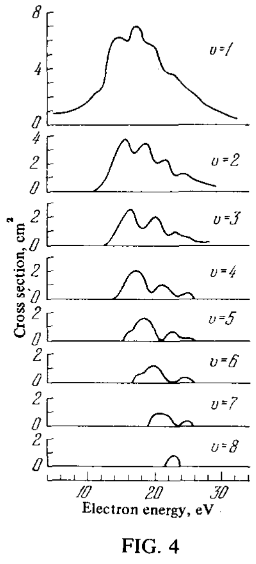

FIG. 4

FIG. 3. Dependence of the total electron-impact excitation cross section of eight vibrational levels of CO on the electron energy. [28]

FIG. 4. Dependence of the partial electron-impact excitation cross sections of the vibrational levels of CO on the electron energy. [28]

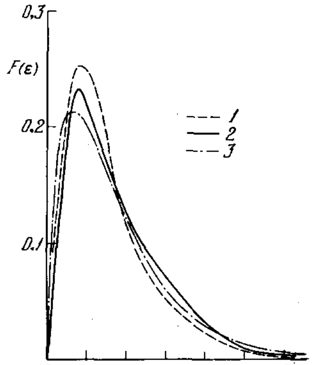

FIG. 5. Distribution of electron energies in CO–He mixtures: [29] 1) $p_{CO}:p_{He} = 1:10$, average electron energy $\bar{\epsilon} = 2.98$ eV; 2) $p_{CO}:p_{He} = 1:30$, $\bar{\epsilon} = 3.38$ eV; 3) Maxwellian curve for $\bar{\epsilon} = 3.38$ eV.

the system describes a purely vibrational relaxation of a diatomic gas (in this case, CO). An analysis of this system shows[7] that because of the difference between P(VV) and P(VT) [P(VV) ≫ P(VT)], the relaxation process in the harmonic oscillator model has two time scales $\tau_{VV} = O[(NP^{01}_{1,0})^{-1}]$, $\tau_{VT} = O[(NP_{1,0})^{-1}]$ ($\tau_{VV} \ll \tau_{VT}$) and it takes place in two stages. In the first (fast) stage a Boltzmann distribution of the vibrational levels is established and this distribution is a function of the total number of vibrational quanta. In the second (slow) stage the Boltzmann distribution is retained but the vibrational temperature decreases. The vibrational relaxation of a diatomic gas which can be represented by a system of anharmonic oscillators has been considered in [8,18,21] and a new result (compared with the relaxation of a system of harmonic oscillators) was first obtained in [8]: in this case, the relaxation process may give rise to a non-Boltzmann and even an inverse level population. In view of the basic importance of this result, we shall now present the main steps by which it was reached in [8].

It follows from Chap. 2 that in the anharmonic case we may find, in contrast to the case of harmonic oscillators, that the inequality P(VV) ≫ P(VT) is not satisfied in all cases but only up to a certain vibrational level v_0. For all values of v in excess of v_0 the relationship between the transition probabilities is the reverse of that just stated. The value of the level number v_0 at which the probabilities P(VV) and P(VT) become equal is a function of the gas temperature T_g and decreases with increasing T_g. Thus, there are two intervals of the vibrational level numbers, in which the relaxation mechanisms are different. At sufficiently low temperatures, when v_0 is high, the VV relaxation predominates. These are the conditions discussed in [8].

In the case of predominance of the VV transitions ($\epsilon = P_{1,0}/P^{01}_{1,0} \ll 1$) we may introduce, as in the harmonic oscillator case, two different time scales τ_{VV} and τ_{VT} ($\tau_{VV} \ll \tau_{VT}$) and use the Chapman-Enskog expansion in terms of a small parameter ϵ, retaining only the terms describing the vibrational energy exchange in the rate equations.

Direct substitution shows readily that the solution of the new system is

$$N_v = N_0 e^{-\gamma v} \exp(-E_v/kT_g), \tag{13}$$

where γ is a certain parameter. It is convenient to rewrite Eq. (13) in the form

$$N_v = N_0 \exp(-E_v/kT^*_v),$$

where T^*_V is the "vibrational temperature," which is—generally speaking—different for different levels. The parameter γ can be represented in the form

$$\gamma = (E_1/kT^*_1) - (E_1/kT_g). \tag{14}$$

the quantities γ and T^*_V depend on time (the time scale is governed by the probabilities of the VT transitions). On reaching an equilibrium with the translational degrees of freedom all the values of T^*_V become equal to T_g.

Substituting the value of γ into Eq. (13), we find that the population of the v-th level is

$$N_v = N_0 \exp\{(-E_1 v/kT^*_1) + [(E_1 v - E_v)/kT_g]\}. \tag{15}$$

Clearly, in the case of a system of harmonic oscillators ($E_V = E_{V1}$), this expression is a Boltzmann distribution. We can derive the following relationship between T^*_V and T^*_1:

$$T^*_v/T^*_1 = \{(vE_1/E_v) - (T^*_1/T_g)[(vE_1 - E_v)/E_v]\}^{-1}. \tag{16}$$

Hence, we can see that if $T^*_1 = T_g$ we have a Boltzmann distribution with a vibrational temperature $T^*_V = T^*_1 = T_g$. If $T_1 \neq T_g$, the distribution deviates from the Boltzmann form: for $T^*_1 > T_g$ it follows from Eq. (16) that $T^*_V > T^*_1$ (the "vibrational temperature" of a level increases with the level number); if $T^*_1 < T_g$, we find that $T^*_V < T^*_1$ (the "vibrational temperature" decreases with increasing level number). The main feature of Eq. (16) is that it demonstrates the possibility of a population inversion of the vibrational levels for $T^*_1 > T_g$. The population distributions described by Eq. (15) or (16) are plotted in Fig. 6. We can see that whereas the lower levels have the Boltzmann populations, an inversion of the populations of the higher levels is extremely strong. One must remember, however, that this formula is derived considering only the VV transitions, whereas in the case of high levels the VT transitions are important or even predominant (Fig. 1).

The second type of relaxation of anharmonic oscillators, characterized by the predominance of the VT transitions, is considered in [32]. However, the treatment given there is hardly justified [33] because the VT relaxation occurs only for high levels and cannot be treated in isolation, i.e., it cannot be discussed without allowance for the VV transitions between lower levels.

The overpopulation of the higher vibrational levels in an anharmonic oscillator compared with that corresponding to a Boltzmann distribution characterized by a

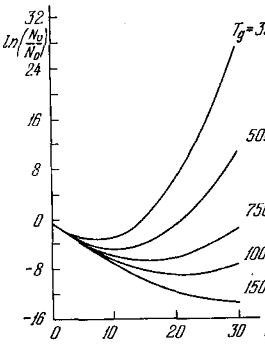

FIG. 6

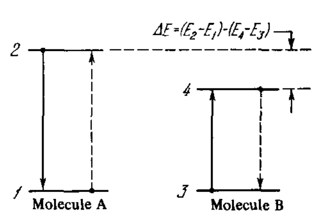

FIG. 7

FIG. 6. Treanor distributions of the populations of the vibrational levels at gas temperatures T_g = 334-1500°K and for T^*_1 = 4000°K. [8]

FIG. 7. Energy levels of molecules A and B.

vibrational temperature T_V can be understood qualitatively by considering two molecules A and B, each of which can be only in the states 1, 2 and 3, 4, respectively (Fig. 7). Let us assume that their quanta differ by $\Delta E=(E_2-E_1)-(E_4-E_3)$. The molecule B simulates a higher state of an anharmonic oscillator and the molecule A a lower state. We shall assume that the molecule A is in the state 2 and the molecule B in the state 3. Collision between the molecules A and B may transfer the former from the state 2 to the state 1 ($2\rightarrow 1$), which then gives up its energy to the molecule B. This excites the molecule B which is transferred from the state 3 to the state 4 ($3\rightarrow 4$). These processes are represented by the continuous arrows in Fig. 7. The reverse processes are represented by the dashed arrows. It follows from Eq. (4) that the rates of the direct and reverse processes are related by

$$P_{1;\,2}^{4;\,3}=\exp\left(-\Delta E/kT_g\right)P_{2;\,1}^{3;\,4}.$$

It is clear from this formula that at low gas temperatures $P_{2;1}^{3;4} \gg P_{1;2}^{4;3}$ the system B is pumped at the expense of the system A and this may give rise to a population inversion between the levels 3 and 4.

Although the conclusion about the possibility of population inversion of the vibrational levels has been obtained for conditions which are too idealized, there is little doubt that allowance for the anharmonicity is essential to the mechanism of population inversion in a laser medium.

Chapters 4 and 5 will deal with the calculations of the populations of the vibrational levels of CO in a laser discharge carried out bearing in mind that, apart from collisional transitions, the CO molecules may be excited by electron impact and radiative transitions.

4. POPULATIONS OF VIBRATIONAL CO LEVELS IN ACTIVE MEDIA OF CO LASERS

In the present chapter we shall discuss the calculations of the populations of the vibrational levels of the CO molecules in the active media employed in CO lasers.[15 16 23] In contrast to Treanor et al.,[8] these calculations were carried out making allowance for the radiative processes, VT transitions, electron excitation, etc. [see system (1)]. The radiative and VT transitions were considered, alongside the VV transitions, in [34] and an analytic solution of the system (1) was obtained for the first time in the linear approximation. This solution is the generalization of that obtained by Treanor et al. and it reduces to the latter if we consider only the VV transitions. In the other investigations[15,16,23] the system (1) was solved by numerical calculations.

A. CO Laser at Liquid Nitrogen Temperature

1. Results of calculations of populations. The populations of the vibrational levels of CO molecules in the plasma of a gas discharge in a CO–He laser operating at low temperatures was considered in [15,16]. Because of the absence of accurate data on the properties of plasma in laser discharges, the calculations in [16] were carried out for a wide range of the discharge parameters ($N_e=2.5\times10^8-2.5\times10^{11}$ cm^{-3}, $T_g=150-500$°K, $T_e=5000-30\,000$°K); it was assumed that the distribution of the electron velocities was Maxwellian.

Out of a large number of curves given in [16] we selected for illustration only those which matched closely

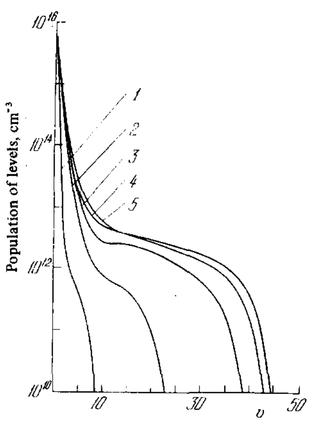

FIG. 8

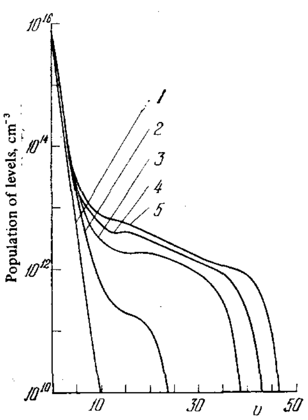

FIG. 9

FIG. 8. Distributions of the populations of the vibrational levels in a CO–He mixture with the following parameters: p_{CO} = 0.2 Torr; p_{He} = 6 Torr; N_e = 2.5 × 10^9 cm^{-3}, T_g = 175°K, T_e (10^3 °K): 1) 5, 2) 10, 3) 15, 4) 20, 5) 30.

FIG. 9. Distributions of the populations of the vibrational levels in a CO–He mixture with the following parameters: p_{CO} = 0.2 Torr; p_{He} = 6 Torr; N_e = 2.5 × 10^9 cm^{-3}, T_e = 20 000°K; T_g: 1) 500, 2) 300, 3) 200, 4) 175, 5) 150.

the parameters of a laser discharge plasma (see [11]). The results of calculations for $p_{CO}=0.2$ Torr, $p_{He}=6$ Torr, $N_e=2.5\times10^9$ cm^{-3}, $T_e=5000-30\,000$°K, and $T_g=150-500$°K are plotted in Figs. 8 and 9. We can see that a complete inversion does not appear in any of the cases considered. At high values of T_e and low values of T_g the distribution curves have a plateau between the levels 10 and 15, i.e., the populations of these levels are almost equal. The formation of this plateau is due to the contribution of the VV processes. This conclusion was checked by solving the equations free of the terms representing the VV transitions. It was found that only the levels excited by electron impact ($v\leq 8$) were significantly populated and their populations decreased much faster than in the Boltzmann distribution corresponding to the electron temperature (this was primarily due to radiative transitions). The fall following the plateau in the curves was due to an increase in the importance of the VT transitions and of the radiative losses.

One of the characteristic features of the population distribution curves of Fig. 8 is the low sensitivity to the electron temperature between 20 000 and 30 000°K. Evidently, these temperatures are optimal for the pumping of the CO vibrational levels. It is likely that at temperatures in excess of 30 000°K the level populations decrease with increasing T_e. Another feature which follows from Fig. 8 is the weak dependence of the vibrational temperature T_1^* on T_e in the range $T_e=10\,000-30\,000$°K. At lower electron densities N_e (2.5×10^8 cm^{-3}) the sensitivity of T_1^* to T_e is stronger than at higher values of N_e ($2.5\times10^{10}-2.5\times10^{11}$ cm^{-3}), as demonstrated in Figs. 3–6 in [16].

An important attribute of the anharmonic oscillator model is the considerable influence of the translational temperature of the gas T_g on the populations of the vibrational levels. It is evident from Fig. 9 that the plateau disappears completely when T_g rises from 150 to 500°K. This is due to the fact that the importance of the excitation of high levels associated with the VV transitions decreases with increasing temperature. Moreover, the role of the VT transitions becomes greater because the probabilities of these transitions have a strong temperature

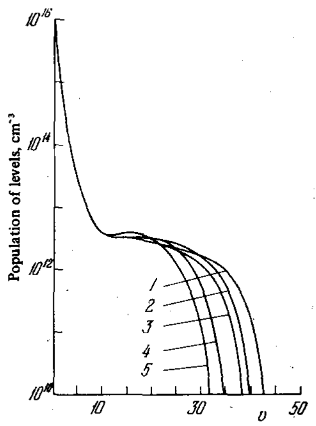

FIG. 10. Distributions of the populations of the vibrational levels in a CO–He mixture with the following parameters: $p_{CO} = 0.2$ Torr; $N_e = 2.5 \times 10^9$ cm^{-3}; $T_g = 175$°K, $T_e = 20\,000$°K, p_{He} (Torr): 1) 6, 2) 10, 3) 15, 4) 30, 5) 50.

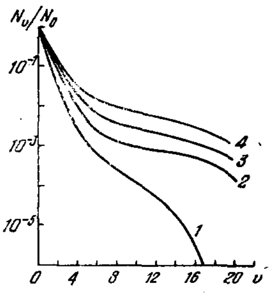

FIG. 11

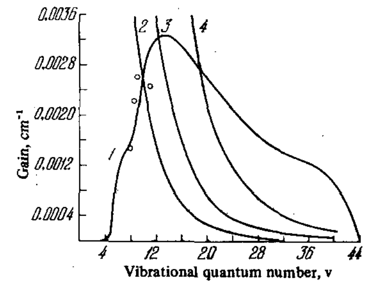

FIG. 12

FIG. 11. Distributions of molecules over the vibrational levels for various values of T_1^* (°K): 1) 1700, 2) 2000, 3) 2300, 4) 2900; $p_{CO}:p_{He} = 1:10$, p = 4 Torr, $T_g = 150$°K.

FIG. 12. Dependences of the gain on the vibrational level number. [16] Curve 1 is calculated allowing for the anharmonicity. Curves 2 ($T_V = 7500$°K), 3 ($T_V = 8500$°K), and 4 ($T_V = 10\,000$°K) are obtained for a Boltzmann population of the levels. The circles represent the results of measurements reported in [24].

dependence. These two factors are responsible for the rise of the CO laser output power as a result of cooling of the walls of its gas-discharge tube with liquid nitrogen. The role of helium is also to reduce the translational and rotational temperatures of the gas by increasing the rate of heat transport to the cold walls. In contrast to the CO_2 laser, an increase in the rate of the VT transitions under the influence of helium is undesirable (Fig. 10). However, an increase in the He pressure from 6 to 50 Torr does not alter T_1^* or even the populations of the first ten levels; the populations of the levels from 10 to 20 change slightly. In the case of high helium concentrations (~50 Torr) we must allow for the effect of CO–CO–He triple collisions which help in the exchange of the vibrational energy between the CO molecules.[35]

The calculations reported in [15] included not only a numerical solution of the system (1) but also the solutions of the system of equations from which the electron-pumping terms were excluded. Instead, it was assumed that the "temperature" T_1^* of the first vibrational level of the CO molecule was constant. It should be remembered that in the limiting case of pure VV transitions the parameter T_1^* was found to govern the distribution over all the levels.[8] The use of the parameter T_1^* avoided the difficulties due to the lack of data on the effective electron-impact excitation cross sections of the vibrational levels of CO, because the "vibrational temperature" of the first CO level could be found experimentally.[1]

Figure 11 shows the distributions over the vibrational levels obtained in [15] for different values of the parameter $T_1^* = 1700–2900$°K, representing the pumping rate. The calculations were carried out for a CO:He mixture with a 1:10 ratio of the partial pressures of CO and He; it was assumed that the total pressure was 4 Torr and that $T_g = 150$°K. All the curves in Fig. 11 (like those in Figs. 8–10) exhibited a plateau, characterized by the highest vibrational temperature, in the range of vibrational levels from 7 to 12.

2. Comparison of theory with experiment. Rich[16] was the first to compare the theory given above with the experimental results. His comparison is illustrated in Fig. 12, which shows the dependence of the maximum gain on the vibrational quantum number. Curve 1 was calculated on the basis of the theory developed above. It was assumed that the electron temperature and concentration were, respectively, $20\,000$°K and 2.5×10^{10} cm^{-3}; the gas temperature was taken to be 175°K and the partial pressures were assumed to be $p_{CO} = 0.2$ Torr and $p_{He} = 6$ Torr. Curves 2–4 were calculated on the assumption of a Boltzmann distribution over the vibrational levels with temperatures of 7500, 8500, and $10\,000$°K. The circles represent the experimental values of Havey,[24] obtained by illuminating a CO amplifier with the radiation produced by a CO laser, as reported in [36]. In the calculation of curve 1 the electron concentration and temperature were selected so as to ensure the best agreement between the theory and experiment. Therefore, the more important factor was not the absolute agreement between the gains but the nature of the dependence on the vibrational quantum number. It is evident from Fig. 12 that the experimental values of the gain increased on transition from the band 7–6 to the band 10–9 and then fell again. According to the theory, represented by curve 1, the gain should become significant for v = 4, should rise with v, reach a maximum at v = 14, and then fall to zero at v = 44. The dependence of the gain on v for a Maxwellian distribution (curves 2–4) differs considerably from the experimental dependence obtained by Havey and from the theoretical dependence represented by curve 1. In the case of a Boltzmann distribution with a temperature in the range 7500–$10\,000$°K the gain maxima should be observed at low values of v and the absolute values of these maxima α_{max} should be large ($\alpha_{max} = 9.4 \times 10^{-3}$ cm^{-1} for v = 3 and $T_V = 7500$°K, $\alpha_{max} = 1.6 \times 10^{-2}$ cm^{-1} for v = 3 and $T_V = 8500$°K, $\alpha_{max} = 2.7 \times 10^{-2}$ for v = 4 and $T_V = 10\,000$°K). Moreover, large values of α should also be observed near the maxima, i.e., for transitions from v = 1–0 to v = 8–7. A better agreement of the relative values of the gain and the positions of the maxima in the dependence of the gain on v may be obtained at higher vibrational temperatures,[1] but this not only fails to remove the problem of the difference between the theoretical and experimental absolute values of α but makes this problem more acute.

Thus, the assumption of a Boltzmann distribution of the vibrational levels in the CO laser is in conflict with the experimental results and even a qualitative agreement requires the application of the theory developed above. It should be stressed that the reported comparison suffers from an important defect: Rich did not know the electron temperature or concentration and he should have selected both these quantities in such a way as to obtain the best agreement between theory and experiment.

A more correct comparison of the theory given above with the experimental results was made in [37] (in this case the authors knew the electron concentrations). The

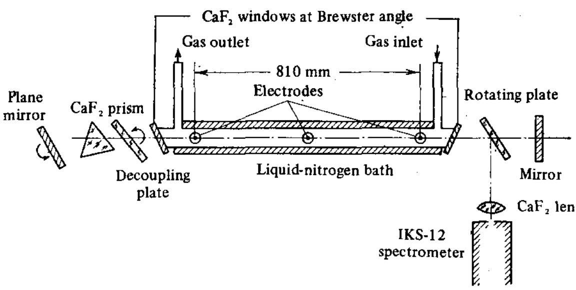

FIG. 13. Apparatus used in measurements of the gain. [37]

experimental results were obtained by the method of calibrated losses using the apparatus shown schematically in Fig. 13. A CaF_2 prism, a rotating plate for the loss regulation, and a plate for extraction of radiation were placed inside the resonator of a CO laser with a gas-discharge tube 810 mm long and 20 mm in diameter. The radiation was directed from the resonator to a spectrometer. When the rotating plate was aligned at the Brewster angle no more than three lines participated in the stimulated emission and when the losses were increased only one line remained. The losses corresponding to the suppression of the stimulated emission of this line (found allowing for constant losses) yielded the small-signal gain of the line. The measurements were carried out on 27 vibration-rotational lines. The populations of the vibrational levels and the gas temperature were deduced from a system of equations based on the measured gains of vibration-rotational lines with different values of v and J. Each of these equations was of the form

$$\alpha(J) = (8\pi^3/k)(Mc^3/2\pi k)^{1/2} T_g^{-3/2} K_{12} J \times (N_1 B_1 e^{-F_1(J-1)hc/kT_g} - N_2 B_2 e^{-F_2(J)hc/kT_g}),$$

where $\alpha(J)$ is the gain of a line whose lower level has a rotational quantum number J; B_1 and B_2 are the rotational constants; N_1 and N_2 are the populations of the vibrational levels; $F_1(J) = B_1J(J+1)$ and $F_2 = B_2J(J+1)$; F_1, N_1, and B_1 refer to the upper level and F_2, N_2, and B_2 to the lower level; $K_{12} = [(2J-1)/J](2h\lambda^3/64\pi^4)A_{12}$, where A_{12} is the Einstein coefficient.

The measurements were carried out for a current $i = 15$ mA which corresponded—according to [38]—to an electron concentration 2.9×10^9 cm^{-3}. The experimental results are compared with the calculations of Rich[16] in Fig. 14. It is evident from this figure that the agreement is satisfactory for $T_e = 15\,000$°K. Figure 15 shows a comparison of these experimental results[37] with the calculations reported in [15]. We can see that the experimental points lie between the curves corresponding to $T_1^* = 1700$ and 2000°K. The experimentally determined values of T_1^* are located, under similar conditions, between the same limits (see [1]).

B. CO Laser at Room Temperature

1. Results of calculations of populations. The populations of the vibrational levels of CO in the active medium of a CO–N_2 laser were calculated in [23,39] for room temperature. The first theoretical conclusion of a non-Boltzmann distribution over the levels, which was practically identical with the distribution obtained experimentally by Legay et al.,[40] was reported briefly in [29], where a mixture with CO and N_2 at pressures of 0.3 and 6.0 Torr, respectively, was considered for a temperature of 330°K.

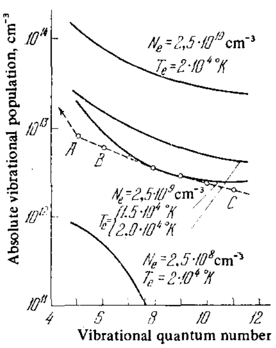

FIG. 14

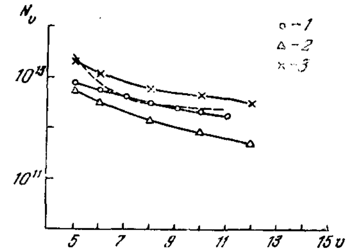

FIG. 15

FIG. 14. Comparison of the vibrational level populations calculated in [16] and deduced from measurements of the gain in [37].

FIG. 15. Comparison of the calculated population distributions [15,16] with the experimental data: [37] 1—experimental values (T_g = 180°K, p_{CO} = 0.2 Torr, p_{He} = 6.0 Torr, p_{O_2} = 0.1 Torr); 2, 3—results of calculations [15] for T_1^* = 1700 and 2000°K, respectively. The dashed curve represents Rich's calculations [16] for $N_e = 2.5 \times 10^9$ cm^{-3} and T_e 20 000°K. All the calculations were carried out for p_{CO} = 0.2 Torr, p_{He} = 6 Torr, T_g = 175°K.

The vibrational temperature of N_2 was assumed to be 1700°K and the exchange of the vibrational energy between N_2 and CO was assumed to take place between the first excited levels of these molecules.

The calculations reported in [23] were carried out for several values of the gas temperatures of pure CO and of CO–N_2 mixtures. As in the previous calculations by the same authors[39] and in [15], the pumping was assumed to be governed by the population of the first vibrational level of CO whose "vibrational temperature," was usually assumed to be 2700°K. Figure 16 shows the relative populations of the vibrational levels in pure CO, calculated without allowance for the radiative process. The results are plotted for the VT transition probabilities given in Fig. 1 or the probabilities increased ($r = 10^2$) or decreased ($r = 10^{-2}$) by two orders of magnitude. The upper curve in Fig. 16 describes the Treanor distribution. It is evident from Fig. 16 that a "high" vibrational temperature is retained up to very high values of v.

Figure 17 shows the deformation of the distribution over the vibrational levels for some artificially selected dependences of the transition probabilities on the level number. We can see that if $P_{1,0}^{v,v+1}$ is independent of the level number, we can have an absolute inversion (curve 1).

Since the energies of the first vibrational levels of CO and N_2 differ quite considerably (by 188 cm^{-1}), their vibrational temperatures are also different. For example, if $T_g = 325$°K, a CO vibrational temperature of 2700°K may be maintained at a vibrational temperature of N_2 amounting to 1700°K. Thus, the vibrational quanta are concentrated mainly in the first three levels of the N_2 molecule because of the relatively low vibrational temperature of nitrogen. Therefore, the nature of the distribution over the higher vibrational levels of N_2 cannot affect significantly the distribution of the levels of CO. The populations of the N_2 levels in CO–N_2 mixtures were not calculated in [23]. It was assumed that these populations could be represented by the Treanor curve right down to its minimum value and the populations of higher levels were assumed to be the contact.

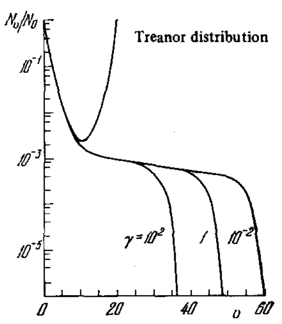

FIG. 16

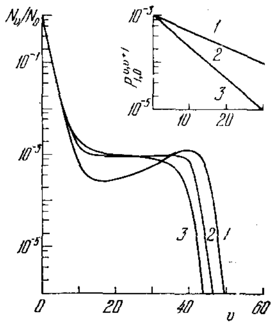

FIG. 17

FIG. 16. Distributions of the populations of the vibrational levels in pure CO calculated for the VT transition probabilities given in Fig. 1 (r = 1) and for probabilities increased (r = 10^2) or reduced (r = 10^{-2}) by two orders of magnitude. [23]

FIG. 17. Distributions of the populations of the vibrational levels in pure CO obtained for three (curves 1-3) artificially selected dependences of the transition probabilities $P^{v,v+1}_{1,0}$ on the level number, shown in the top right-hand corner.

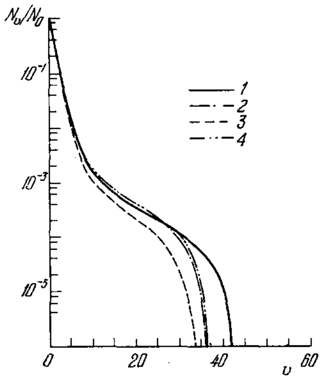

FIG. 18

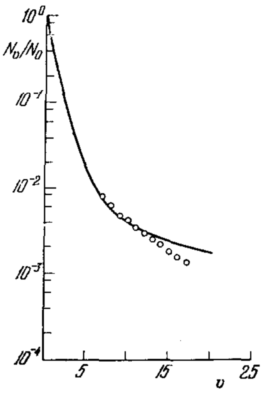

FIG. 19

FIG. 18. Distributions of the populations of the vibrational levels in pure CO (p_{CO} = 0.1 Torr): 1—P_{VT} corresponding to curves in Fig. 1; 2—P_{VT} increased by a factor of 20. Curves 3 and 4 give the corresponding distributions for a CO—N_2 mixture with the following parameters: p_{CO} = 0.1 Torr; p_{N_2} = 2.0 Torr; T_g = 325°K; T_1^*(CO) = 2700°K; $T_1^*(N_2)$: 3) 1700°K, 4) 1732°K.

FIG. 19. Comparison of the populations of the vibrational levels calculated in [23] (continuous curve) and measured in [40] (circles) for T_g = 325°K, T_1^* = 3000°K, and p_{CO} = 0.3 Torr.

Figure 18 shows the distributions of the populations of the vibrational levels of CO, calculated for a pure CO pressure of 0.1 Torr and a CO–N_2 mixture with partial pressures of 0.1 and 0.2 Torr, respectively. We can see that the curves differ only at high level numbers. This is due to the fact that the rates of the VT transitions rise at high values of v, compared with the case of pure CO, because the amount of N_2 is sufficiently large.

2. Comparison of theory with experiment. Only one experimental investigation was made in which the populations of the vibrational levels of CO were measured under conditions which could be expected realistically for CO lasers operating at room temperature. This investigation was carried out by Legay et al.[40] As in all previous investigations of this group of workers, the study was carried out using apparatus in which N_2 was first excited in a high-frequency discharge and then mixed with CO (see also Fig. 8 in [11]). The N_2 and CO pressures were 6.0 and 0.3 Torr, respectively. Oxygen (O_2) was added to the mixture in an amount corresponding to 0.005 Torr. The flow velocity of the mixture was 13 m/sec. The part of the tube filled with the active medium was 180 cm long and the resonator length was 290 cm. The measurements were carried out by the calibrated loss method, employing rotation of a plane-parallel CaF_2 plate located inside the resonator. Measurements of the gain for 20 vibration-rotational lines (v = 8–17, J = 15–22) were used to determine the gas temperature, which was 325°K, and the populations of the vibrational levels. It was established that the distribution of the populations of the laser levels of CO could be described by the Boltzmann formula with a temperature of 15000°K, whereas under similar conditions the temperature of the lower vibrational levels of CO was found to be 2000–3500°K.

Caledonia and Center[23] calculated the populations of the levels of CO under the conditions corresponding to the experiments of Legay et al. In these calculations it was assumed that the temperature of the lower levels was 3000°K, in the same way as was done in[40] in a comparison of the results with the Treanor distribution. The results of these calculations and experimental results are plotted in Fig. 19. It is evident from this figure that there is a generally satisfactory agreement between theory and experiment. However, we can see that the experimentally determined populations of the high vibrational levels are lower than the theoretical values. It is not possible to provide a definite explanation of this discrepancy. All that we can do is to suggest several reasons. It is possible that the discrepancy is due to the experimental errors associated with the nonsimultaneous measurements of the populations of different levels. Some role may be played also by the indeterminacy in the vibrational temperature of the lower levels and the inhomogeneity of the active medium along the laser. It is also very likely that the presence of small amounts of oxygen in the mixture results in a more effective deactivation of the upper levels of CO since the first vibrational quantum of O_2 is energetically close to the high quanta of CO.

Apart from the investigations of Legay et al., the populations of the CO levels in CO–N_2 mixtures were investigated by two other groups.[41,42] A characteristic feature of these investigations was the use of much lower CO and N_2 pressures than those usually employed in the working mixtures in CO–N_2 lasers. For example, the carbon monoxide pressure in [42] was p_{CO} = 0.08 Torr, whereas in [41] it was p_{CO} = 0.038 and 0.056 Torr for nitrogen pressures p_{N_2} = 1.1 and 1.0 Torr, respectively. In these investigations, as in [40], the nitrogen (N_2) admixture was excited first in a high-frequency discharge and then mixed with CO. At some distance from the mixing region, at right-angles to the direction of motion of the gas mixture, these workers measured the intensity of the infrared radiation as a function of the wavelength in the 2.3–2.7 μ region corresponding to the first harmonic of the CO bands (from 2–0 to 13–11). The radiation was recorded with a PbS detector and an infrared spectrometer with a moderate dispersion. The rotational structure was not resolved and the bands overlapped. A part of the 2–0 band did not overlap any other bands and the rotational temperature was deduced from this part by the matching method. The populations of the vibrational levels were found by the matching method from all the bands.

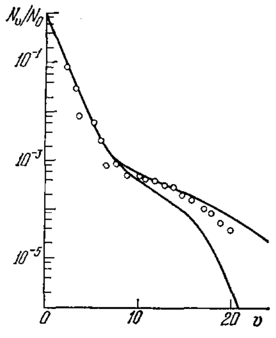

FIG. 20

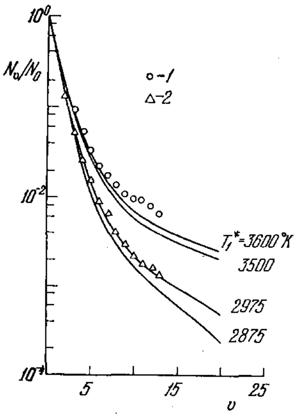

FIG. 21

FIG. 20. Comparison of the populations of the vibrational levels calculated in [23] (continuous curves, the upper curve corresponding to the doubled VV transition probabilities) and measured in [42] (circles) for $T_1^* = 2500°K$, $T_g = 350°K$, and $p_{CO} = 0.08$ Torr.

FIG. 21. Comparison of the populations of the vibrational levels calculated in [23] (continuous curves corresponding to different values of T_1^* and a fixed value of $T_g = 350°K$) and measured in [41] for CO pressures of 0.038 Torr (1) and 0.056 Torr (2).

A comparison of the results of calculations given in [23] with the experimental data reported in [41,42] is made in Figs. 20 and 21. Figure 20 shows two calculated curves illustrating the influence of an increase in the probability of the VV transitions by a factor of 2. We can see that this increase results in a significant rise of the populations of the upper levels and a better agreement between the theoretical and experimental results, whereas the distribution of the populations of the lower levels is not affected.

The results of a comparison of the calculations with the experimental data reported in [41] are given in Fig. 21: they correspond to higher vibrational temperatures T_1^* and lower pressures than those employed in [42]. The calculations were made for two vibrational temperatures at each pressure and they illustrate the sensitivity of the distribution of the populations to the vibrational temperature T_1^*. We can see that the change of T_1^* by 100°K alters significantly the calculated distribution.

We can summarize the results of comparisons of the experimental and calculated results by saying that the agreement is much better at room temperature than at liquid nitrogen temperature. This is not surprising because the experimental data on the probabilities of collisional transitions are known for room temperature and can be used in the calculations.

5. CONCLUSIONS

Considerable progress has been made in the development and construction of CO lasers. As reported in the first part of this review,[1] output powers of 10 W have been obtained for sealed lasers and the corresponding powers for a continuous flow and Q-switching conditions are 100 W and 10 kW. We shall not consider here the various possible applications of the CO laser because this would require a separate article. We shall simply point out the extremely fruitful uses of this laser in the nonlinear conversion of the frequency of light as a result of the scattering of a laser beam in InSb crystals subjected to a magnetic field.[43]

The comparison of the calculated and experimental results given above shows clearly that the assumption of the direct electron pumping of the vibrational levels is correct and that the anharmonicity plays a decisive role in the population inversion in CO lasers. However, the theory of the CO laser described here is not yet complete because it ignores certain processes which make a definite contribution to the population of the vibrational levels. These processes include: 1) the vibrational excitation of molecules by electron impact not only from the ground state but also from excited vibrational levels; 2) the deactivation of vibrationally excited molecules at the walls of a gas-discharge tube; 3) the exchange of vibrational quanta between CO molecules as a result of triple collisions of two CO molecules and one He atom. However, there are as yet no theoretical or experimental data on the rates of these processes.

It should also be pointed out that although it would be very desirable to measure directly the probabilities of collisional vibration-vibrational transitions at liquid nitrogen temperature, there is as yet no criterion for the reliability of the theoretical values of these probabilities used in calculations. This is also true of the measurements of the concentrations and of the electron-velocity distribution functions at low temperatures.

We shall conclude by mentioning a communication by Center and Caledonia[44] reporting calculations of the populations of the vibrational levels of CO under stimulated emission conditions. In this case, the absolute values of the populations are lower but the non-Boltzmann nature of the distribution is retained.

[1)] This is the second part of a review of CO lasers; the first part was concerned with the results of experimental investigations and was published in Kvantovaya Elektron. (Moscow) No. 4(10), 3,(1962) [Sov. J. Quantum Electron. 2, 305 (1973)]. [1]

[1] N. N. Sobolev and V. V. Sokovikov, Kvantovaya Elektron. (Moscow) No. 4(10), 3 (1972) [Sov. J. Quantum Electron. **2**, 305 (1973)].

[2] N. N. Sobolev and V. V. Sokovikov, ZhETF Pis. Red. **4**, 303 (1966); **5**, 122 (1967) [JETP Lett. **4**, 204 (1966); **5**, 99 (1967)].

[3] N. N. Sobolev and V. V. Sokovikov, Usp. Fiz. Nauk **91**, 425 (1967) [Sov. Phys.-Usp. **10**, 153 (1967)].

[4] N. N. Sobolev and V. V. Sokovikov, in: The Physics of Electronic and Atomic Collisions, Boulder, Colorado, 1968.

[5] D. C. Tyte, Advan. Quantum Electron. **1**, 129 (1970).

[6] P. K. Cheo, Advan. Lasers **3**, 111 (1971).

[7] E. V. Stupochenko, S. A. Losev, and A. I. Osipov, Relaksatsionnye protsessy v udarnykh volnakh (Relaxation Processes in Shock Waves), Nauka, M., 1965.

[8] C. E. Treanor, J. W. Rich, and R. G. Rehm, J. Chem. Phys. **48**, 1798 (1968).

[9] K. F. Herzfeld and T. A. Litovitz, Absorption and Dispersion of Ultrasonic Waves, Academic Press, New York, 1959.

[10] D. J. Miller and R. C. Millikan, J. Chem. Phys. **53**, 3384 (1970).

[11] J. T. Yardley, J. Chem. Phys. **52**, 3983 (1970).

[12] G. Hancock and I. W. M. Smith, Chem. Phys. Lett. **8**, 41 (1971); Appl. Opt. **10**, 1827 (1971).

[13] M. Margottin-Maclou, L. Doyennette, and L. Henry, Appl. Opt. **10**, 1768 (1971).

[14] N. N. Sobolev and V. V. Sokovikov, Elektron. Tekh., Ser. 3 No. 4, 3 (1970).

[15] N. N. Sobolev, V. V. Sokovikov, and V. N. Strelets,

Kratk. Soobshch. Fiz. FIAN No. 9, 13 (1971); N. N. Sobolev and V. V. Sokovikov, Preprint No. 108, P. N. Lebedev Physics Institute, M., 1971; N. N. Sobolev, V. V. Sokovikov, and V. G. Taranenko, Preprint No. 34, P. N. Lebedev Physics Institute, M., 1973.

[16] J. W. Rich, J. Appl. Phys. **42**, 2719 (1971).

[17] J. Keck and G. Carrier, J. Chem. Phys. **43**, 2284 (1965).

[18] K. N. C. Bray, J. Phys. B (Solid State Phys.) **1**, 705 (1968).

[19] R. C. Millikan and D. R. White, J. Chem. Phys. **39**, 3209 (1963).

[20] D. Rapp, J. Chem. Phys. **43**, 316 (1965).

[21] L. D. Landau and E. Teller, Phys. Z. Sowjetunion **10**, 34 (1936).

[22] H. K. Shin, J. Chem. Phys. **55**, 5233 (1971).

[23] G. E. Caledonia and R. E. Center, J. Chem. Phys. **55**, 552 (1971).

[24] M. E. Havey, Thesis (Air Force Institute of Technology, Ohio, 1970).

[25] W. Q. Jeffers and J. D. Kelley, J. Chem. Phys. **55**, 4433 (1971).

[26] R. D. Sharma and C. A. Brau, Phys. Rev. Lett. **19**, 1273 (1967); J. Chem. Phys. **50**, 924 (1969); R. D. Sharma, J. Chem. Phys. **54**, 810 (1971); R. D. Sharma, Phys. Rev. **177**, 102 (1969).

[27] S. S. Penner, Quantitative Molecular Spectroscopy and Gas Emissivities, Addison-Wesley, Reading, Mass., 1959 (Russ. Transl., IL, M., 1963).

[28] G. J. Schulz, Phys. Rev. **135**, A988 (1964).

[29] M. Z. Novgorodov, A. G. Sviridov, N. N. Sobolev, and P. Shvarts, Preprint No. 57, P. N. Lebedev Physics Institute, M., 1972.

[30] R. M. Osgood Jr, W. C. Eppers Jr, and E. R. Nicols, IEEE J. Quantum Electron. **QE-6**, 145, 567 (1970).

[31] E. R. Fisher and R. H. Kummler, J. Chem. Phys. **49**, 1075 (1968).

[32] C. T. Hsu and L. D. McMillen, J. Chem. Phys. **53**, 4107 (1970).

[33] K. N. C. Bray and N. H. Pratt, J. Chem. Phys. **53**, 2987 (1970).

[34] B. F. Gordiets, A. I. Osipov, and L. A. Shelepin, Zh. Eksp. Teor. Fiz. **59**, 615 (1970); **60**, 102 (1971); **61**, 562 (1971) [Sov. Phys.-JETP **32**, 334 (1971); **33**, 58 (1971); **34**, 299 (1972)].

[35] N. N. Sobolev and V. V. Sokovikov, Kratk. Soobshch. Fiz. FIAN No. 9, 11 (1972).

[36] M. E. Havey and J. D. Barry, IEEE J. Quantum Electron. **QE-7**, 370 (1971).

[37] É. N. Lotkova, G. N. Mercer, and N. N. Sobolev, Appl. Phys. Lett. **20**, 309 (1972); É. N. Lotkova, G. N. Mercer, V. F. Savchenko, and N. N. Sobolev, Preprint No. 151, P. N. Lebedev Physics Institute, M., 1972.

[38] M. Z. Novgorodov, A. G. Sviridov, and N. N. Sobolev, Preprint No. 115, P. N. Lebedev Physics Institute, M., 1971.

[39] C. A. Brau, G. E. Caledonia, and R. E. Center, J. Chem. Phys. **52**, 4306 (1970); R. E. Center, R. L. Taylor, C. A. Brau, and G. E. Caledonia, Abstracts of Papers presented at Sixth Intern. Conf. on Quantum Electronics, Kyoto, 1970.

[40] F. Legay, N. Legay-Sommaire, and G. Taieb, Can. J. Phys. **48**, 1949 (1970).

[41] K. P. Horn and P. E. Oettinger, J. Chem. Phys. **54**, 3040 (1971).

[42] R. Joeckle and M. Peyron, J. Chim. Phys., **67**, 1175 (1970).

[43] C. K. N. Patel, Appl. Phys. Lett. **19**, 400 (1971).

[44] R. E. Center and G. E. Caledonia, Appl. Phys. Lett. **19**, 211 (1971).

Translated by A. Tybulewicz