Kinetic model of formation of inverse populations in a carbon monoxide gas-discharge laser

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Numerical calculations of the populations of CO vibrational levels in the plasma of a CO–He laser are carried out. The set of kinetic equations for excitation and deactivation of CO vibrational levels in the discharge is solved for various values of the gas temperature and pressure and of the parameter T_1* characterizing the magnitude of pumping. The vibrational transition probabilities, which enter as coefficients in the kinetic equations, are calculated by the Herzfeld formulas modified to take into account the anharmonicity of the molecules. The population distributions thus calculated differ considerably from the Boltzmann distributions. The initial sections of the distribution curves can approximately be described by the Treanor formula and depend weakly on the transition probabilities. The further behavior of the curves is defined by the relations between the rate constants of the processes encountered in the equation set. The plateaus on the curves, that is, the regions of high temperature are a consequence of the allowance for the anharmonicity of the molecules. The results of the calculations are compared with available experimental data. The good agreement between them indicates that the model underlying the calculations is essentially correct.

1. INTRODUCTION

Theoretical investigations of the mechanism of production of population inversion of vibrational levels in the electric-discharge plasma of a CO laser, which reduced to a numerical solution of the system of kinetic equations for the populations, were carried out in[1-3]. The kinetic equations included terms describing the pumping of the CO by electron impact[4], in analogy with the case of the CO₂ laser[5], and also vibrational and vibrational-translational transitions in the CO molecules, with account taken of the dependence of the vibrational-transition probabilities on the anharmonicity of the molecule[6,7].

The CO molecule level distributions obtained as a result of the investigation of such a model turned out to differ strongly from the Boltzmann distributions that should obtain in the stationary case of electron excitation and relaxation of a gas consisting of molecules (harmonic oscillators). This fact has confirmed the important role played by anharmonicity in the formation of the vibrationally-excited CO molecules in the laser discharge.

It can be noted that in view of the absence of reliable experimental data, the vibrational-transition probabilities used in[1-3] differed greatly. Recent measurements[8-10] have made it possible to ascertain which of them are the most reliable and to analyze the extent to which the results of the kinetic calculations depend on the values of the probabilities. In the present paper, in addition to such an analysis, we calculate also the populations for the concrete case of the laser mixture experimentally investigated in[11,12].

2. SOLUTION OF THE SYSTEM OF KINETIC EQUATIONS

We consider a laser discharge in a CO-He mixture[1]. The system of kinetic equations describing the processes of excitation and deactivation of the vibrational levels of the CO molecule in the electric discharge can be represented in the following form[2,3]:

$$
\begin{aligned}
dN_v/dt = {} & K_{v+1,v}N_{v+1}N - (K_{v,v-1} + K_{v,v+1})N_vN + K_{v-1,v}N_{v-1}N \\
& + \tilde{K}_{v+1,v}N_{v+1}\tilde{N} - (\tilde{K}_{v,v-1} + \tilde{K}_{v,v+1})N_v\tilde{N} + \tilde{K}_{v-1,v}N_{v-1}\tilde{N} + \\
& + \Big(\sum_{v'} K_{v+1,v}^{v'-1,v'} N_{v'-1}\Big) N_{v+1} - \sum_{v'} (K_{v,v-1}^{v',v'+1} + K_{v,v+1}^{v',v'-1}) N_{v'}N_v \\
& + \Big(\sum_{v'} K_{v-1,v}^{v'+1,v'} N_{v'+1}\Big) N_{v-1} + N_e \sum_{v'} N_{v'}k_{v'v}^{(e)} - N_eN_v \sum_{v'} k_{vv'}^{(e)} \\
& + N_{v+1}A_{v+1,v} - N_vA_{v,v-1}.
\end{aligned}
\tag{1}
$$

Here N_v is the population of the v-th vibrational level; N is the concentration of the CO molecules; $\tilde{N}$ is the concentration of the helium atoms; $K_{v,v-1}$ and $K_{v,v-1}^{v',v'+1}$ are the rate constants of the vibrational-translational and proper vibrational-vibrational transitions in collisions between the CO molecules; $\tilde{K}_{v,v-1}$ is the rate constant of the vibrational-translational transition in the collision of the CO molecule with the He atom; N_e is the electron concentration; $k_{vv'}^{(e)} = \langle \sigma_{vv'}^{(e)} v_e \rangle$ are the rate constants, averaged over the electron energies, for the excitation of the vibrational CO levels by electron impact, $\sigma_{vv'}^{(e)}$ is the effective cross section of the indicated process, v_e is the electron velocity; $A_{v,v-1}$ is the probability of the spontaneous photon emission (the Einstein coefficient).

Under stationary conditions, the level-population change dN_v/dt is equal to zero, and the system of nonlinear differential equations is transformed into a system of nonlinear algebraic equations. The number of equations in this system is determined, generally speaking, by the dissociation energy of the molecule and by its anharmonicity constants.

The probabilities of the vibrational transitions are calculated in accordance with the Herzfeld formulas[13], in which account is taken of only the dependence, due to anharmonicity of the molecule[14,15], of the vibrational-quantum energy on the number of the level. It should be noted that at sufficiently small numbers of the vibrational levels ($v \lesssim 8$), vibrational-vibrational transitions predominate. In this region of values of v, one can introduce the small parameter $\epsilon = K_{10}/K_{10}^{01}$ and use the Chapman-Enskog expansion. The zeroth-order expansion, corresponding to allowance for only the vibrational-vibrational transitions, was considered by Treanor et et al.[6], who obtained an analytic solution for the populations:

$$N_v = \exp\left[-vE_1 / kT_1^* + (vE_1 - E_v) / kT_g\right], \qquad (2)$$

where T_1^* is the "vibrational temperature" of the first level. Thus, the level-population distribution in the region of values of v in which the vibrational-vibrational transitions predominate can be described with the aid of formula (2). As the role of the vibrational-translational and radiative transitions increases with increasing number of the level, the terms that are linear in N_v begin to make the principal contribution to the solution of the problem, so that in the limiting case of large v we can rewrite the system (1) in the form

$$k_{v+1,v}N_{v+1} + A_{v+1,v}N_{v+1} - k_{v+1,v}\exp\left\{-\frac{E_{v+1}-E_v}{kT_g}\right\}N_v + $$
$$+ k_{v,v-1}\exp\left\{-\frac{E_v-E_{v-1}}{kT_g}\right\}N_{v-1} - N_v(k_{v,v-1}+A_{v,v-1}) = 0, \qquad (3)$$

where($k_{v+1,v} = NK_{v+1,v}$), the solution of which, unlike (2), has a Boltzmann character

$$N_v = \frac{k_{v,v-1}}{k_{v,v-1}+A_{v,v-1}} N_{v-1} \exp\left(-\frac{E_v-E_{v-1}}{kT_g}\right). \qquad (4)$$

The presence of solutions (2) and (4), corresponding to the two limiting cases indicated above, points to the existence of an inflection point on the plot of the distribution of the vibrational-level populations, in the vicinity of which population with large vibrational temperatures, and even inversion, were realized. The limiting case of gas relaxation in the presence of only vibrational-translational transitions is considered in[16]. An approximate analytic solution of the system (1) in the presence of all three energy-transfer processes indicated above, but without pumping by electrons, was obtained in[7,17].

In the present article we give a numerical solution of the system (1) in which, however, the pumping is described by imposing an additional condition, namely that the population of the first vibrational level be constant; more accurately, we specify its experimentally measured[12] "vibrational temperature" T_1^* as a parameter. Such an approach is more reliable when it comes to quantitative results, since the cross sections for vibrational excitation of the CO molecules by electron impact are known for a limited number of levels[4]. Since amplification is usually observed experimentally on 5–12 levels, we thought it sufficient to consider a system of 20 kinetic equations. The system of equations was solved for different gas temperatures, the partial pressures of the carbon monoxide and helium, and also the parameters T_1^*. The solutions are shown in the figures in the form of plots of N_v/N_0 against the number of the vibrational levels.

3. DISCUSSION OF RESULTS

Figure 1 illustrates the influence of a 30-fold increase of the probabilities of vibrational-translational transitions on the form of the distribution over the vibrational levels in the absence of radiative transitions. By virtue of the homogeneity of the initial equations, this corresponds in fact to a change of the ratio $\tilde{k}_{v+1,v}/\tilde{k}^{v'-1,v'}_{v+1,v}$ by the same factor. It is seen from the figure that in both cases one obtains qualitatively identical results, namely a non-Boltzmann distribution over the levels. Moreover, the curves describing the level populations practically coincide at $v \lesssim 8$, and differ significantly only at $v > 11$. Thus, the results of the calculation of the distribution over the levels on which generation is usually observed ($v = 6$–11) change insignificantly when the employed probabilities are increased by a factor of 30.

Figure 2 shows the distributions of the CO molecules over the vibrational levels at different partial pressures of CO and He and a total mixture pressure 4 Torr. It is seen that the vibrational temperatures of the higher levels are lowered when the He content in the mixture is increased. The reason is that both curves were obtained at equal pump values determined by the value of the constant T_1^*, namely 2000° K. On the other hand, the influence of the helium in the gas discharge reduces not only to an increase in the rates of the vibrational-translational transitions, which leads to a faster drop of the curve, but also to an increase in the pumping rate, which is not taken into account here.

A change in the total pressure does not change the ratio of the probabilities of the vibrational-vibrational and vibrational-translational transitions, and reduces only to a clarification of the role of $A_{v,v-1}$ in the case of the considered system of equations, which contain no

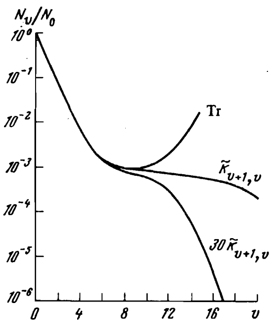

FIG. 1

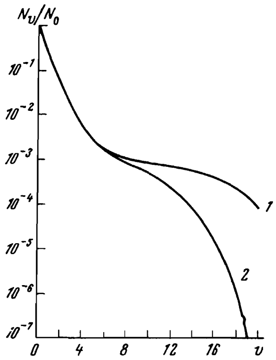

FIG. 2

FIG. 1. Molecular vibrational-level distributions obtained using the transition probabilities $\tilde{K}_{v+1,v}$ and $30\tilde{K}_{v+1,v}$. The radiative transitions were not taken into account. The curve labeled Tr describes the Treanor distribution.

FIG. 2. Molecular vibrational-level distributions at a ratio of the partial pressures of CO and He 1:10 (curve 1) or 1:30 (curve 2), and p = 4 Torr, T_g = 150°K, and T_1^* = 2000°K.

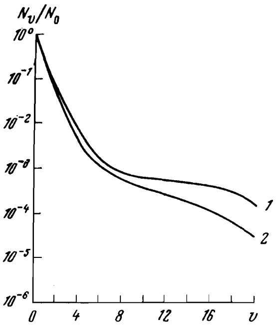

FIG. 3

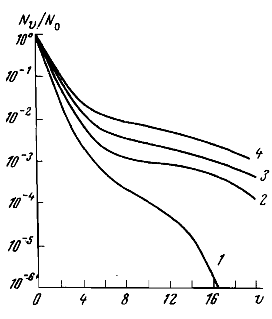

FIG. 4

FIG. 3. Influence of the radiative terms on the form of the vibrational-level distribution. Curve 1 was calculated without allowance for the radiative transitions, and curve 2 was calculated with kinetic equations that include terms containing $A_{v,v-1}$. $p_{CO}:p_{He}$ = 1:10, p = 4 Torr, T_g = 200°K, and T_1^* = 200°K.

FIG. 4. Distribution of CO molecules over the vibrational levels at different values of the parameter T_1^*: 1–1700, 2–2000, 3–2300, 4–2900°K; $p_{CO}:p_{He}$ = 1: 10, p = 4 Torr, T_g = 150°K.

terms describing the electron pumping. In other words, a change in the total pressure is equivalent to a change in the values of $A_{v,v-1}$. It should possibly be emphasized that such a solution of the pressure problem is valid only if fixed values of T_1^* are chosen and no account is taken of the diffusion of the excited molecules to the walls, the dissociation of the molecules by electron impact, and triple collisions[18].

The influence of the radiative terms on the form of the distribution over the levels is shown in Fig. 3. It can be assumed that the radiative transitions make a significant contribution to the character of the population, starting with the 7-th or 8-th level.

Figure 4 shows the distributions over the vibrational levels at different values of the parameter T_1^* (1700–2900° K) characterizing the value of the pumping. A numerical solution was also obtained of the complete system of equations (1) with allowance for the electron pumping. The cross sections for the excitation of the CO molecules by electron impact were assumed to be equal to the experimental values of Schulz[4]. The missing cross sections were estimated by starting from a comparison of the Schulz data with the Chen's calculations for N_2 molecules[19], assuming the behavior of the relative values of the cross sections in the case of CO and N_2 to be analogous. The concentration (N_e) and the temperature T_e) of the electrons were assumed respectively to be 5×10^9 cm^{-3} and 20,000° K[20]. The curve calculated under such conditions lies somewhat higher than curve 4 of Fig. 4, i.e., the corresponding temperature of the first level exceeds 2900° K. Such a value of T_1^* is much larger than the values measured experimentally under similar conditions[12], and is due, of course, to the inaccuracy of the employed rate constants of the electron pumping. Since the indicated calculation is only an estimate, the corresponding curve is not shown in the figure.

An important factor in the kinetic calculations is the choice of the gas temperature T_g. We have considered T_g = 150, 200, and 300° K. These temperatures are most realistic for lasers operating under conditions when the gas-discharge tube walls are cooled with liquid nitrogen, as well as without cooling[11,21-23].

The influence of T_g on the distribution of the populations of the vibrational levels is illustrated in Fig. 5. It can be seen that on going from T_g = 150° K to 300° K the section with large vibrational temperatures on the distribution curves vanishes and we obtain an almost Boltzmann distribution with a single vibrational temperature, T_1^* = 2000° K. Such a behavior of the curves as functions of T_g agrees well with the conclusions of Treanor et al.[6], that it is necessary to reduce the gas temperature to obtain repopulation of the levels in comparison with the Boltzmann population.

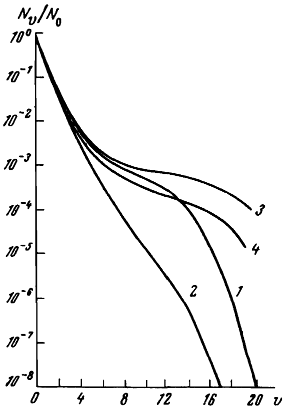

FIG. 5. Influence of the gas temperature on the distribution of the populations of the vibrational levels of the CO molecules at p = 4 Torr, T_1^* = 2000°K, $p_{CO}:p_{He}$ = 1:30 (curves 1, 2), 1:10 (3, 4), T_g = 150 (1, 3), 200 (4), 300°K (2).

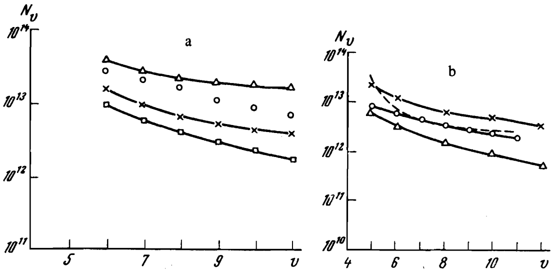

FIG. 6. Comparison of the calculated and experimental distributions over the levels: a) O—experimental values [11], T_g = 140°K; calculation results: □—T_g = 150°K, T_1^* = 1700°K; Δ—T_g = 150°K, T_1^* = 2000°K; X—T_g = 200°K, T_1^* = 2000°K. The measurements and calculations were performed at $p_{CO}:p_{He}$ = 1:10, p = 4 Torr. b) O—experimental values [11], T_g = 180°K, p_{CO} = 0.2 Torr, p_{He} = 6.0 Torr, p_{O_2} = 0.1 Torr; the results of the calculations in the present paper: Δ—T_1^* = 1700°K, X—T_1^* = 2000°K. The dashed lines show the results of the calculations by Rich [3], performed at N_e = 2.5 X 10^9 cm^{-3} and T_e = 20 000°K. All the calculations were performed for P_{CO} = 0.2 Torr, p_{He} = 6 Torr, and T_g = 175°K.

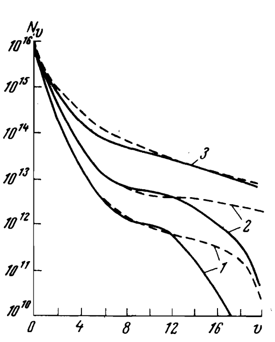

FIG. 7

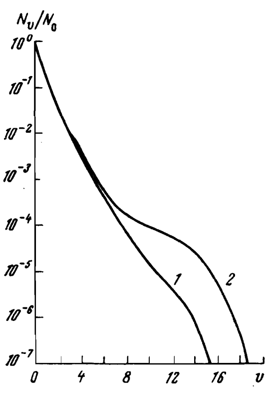

FIG. 8

FIG. 7. Comparison of the results of the calculations obtained in the present paper using the parameter T_1^* (solid lines) with the results of Rich [3] obtained by taking into account the terms that describe electron pumping (dashed curves). p_{CO} = 0.2 Torr; p_{He} = 6.0 Torr; T_g = 175°K. 1—Pair of curves: T_1^* = 1700°K; N_e = 2.5 · 10^9 cm^{-3}; T_e = 10 000°K; 2—pair of curves: T_1^* = 2000°K, N_e = 2.5 · 10^{10} cm^{-3}, T_e = 5000°K; 3—pair of curves: T_1^* = 2900°K, N_e = 2.5 · 10^{11} cm^{-3}, T_e = 20 000°K.

FIG. 8. Dependence of the populations of the vibrational levels on the level number in the case when the Herzfeld probabilities are used for the vibrational-vibrational transitions (curve 1) and the probabilities calculated in [24] with allowance for the long-range forces (curve 2).

Figure 6 shows a comparison of the calculated and experimental distributions over the levels. It is seen that the experimental points[11] lie in both considered cases between the curves obtained at values of T_1^* equal to 1700 and 2000° K. It is precisely in this range, as shown experimentally in[12], that the "vibrational temperatures" of the first level of the molecule CO are located under the conditions of the measurements in[11].

The same figure shows for comparison one of the curves calculated by Rich[3]. This curve was chosen to agree best with the experimental points. It turns out that it corresponds to $N_e = 2.5 \times 10^9$ cm^{-3} and $T_e = 20{,}000°$ K.

To illustrate the extent to which the calculations using the parameter T_1^* agree with the calculations of Rich[3] with allowance for the electron pumping, Fig. 7 shows a comparison of the results of both calculations. We chose from Rich's paper three curves and calculated the populations for the three corresponding values of the parameter T_1^* (1700, 2000, 2900° K).

We see that in all cases the two curves are quite close to each other at $v \lesssim 12$, i.e., precisely for those values of v at which generation usually takes place. Thus, if the temperature T_1^* is specified on the basis of the experimental data[12], then the populations can be calculated without considering the electron pumping. This, of course, is clear also from the fact that the rates of the vibrational transitions, which determine the distribution over the levels, greatly exceed the electron-pumping rate.

Recent measurements[10], as already mentioned, point to a difference between the experimental values of the transition probabilities in the CO molecule and the values calculated by the Herzfeld method[13]. It was shown in[24] that good agreement with the experimental results is obtained from probability calculations in which, unlike[13], account is taken of the contribution of the long-range force energy to the transition.

Figure 8 shows a comparison of the populations calculated using the Herzfeld values $K_{v,v+1}^{v',v'-1}$, and the probabilities calculated in[24] with allowance for the long-range forces. It is easily seen that the curve obtaining with allowance for the long-range forces has a section with a higher vibrational temperature, this being due to the larger contribution of the vibrational-vibrational transitions. It can also be noted that the initial sections of both curves ($v \lesssim 6$) practically coincide, i.e., they depend little on the transition probabilities.

4. CONCLUSION

From an analysis of the foregoing curves, obtained as a result of the calculations, we can draw a number of conclusions concerning the character and relative contribution of the processes that lead to the population of the vibrational levels of the CO molecules in the laser discharge. It can be noted that in practically all the considered cases the initial sections of the distributions over the levels ($v \lesssim 6$) depend little on the vibrational-transition probabilities used in the calculations. Such a behavior is due to the fact that in this region of values of the vibrational numbers v the predominant role is played by the vibrational-vibrational transitions, and consequently the corresponding sections of the curves should be described approximately by the Treanor formula (2). The subsequent behavior of the curves is already determined by the ratios of the rate constants of the different processes, which enter in the system of kinetic equations (1).

We emphasize that in the present paper the calculations of the probabilities were performed for a laser system that has been thoroughly investigated experimentally[11,12], i.e., for which the distribution of the populations of the laser levels, and also the "vibrational temperature" of the first level, were measured. The comparison of the results of the calculations with the indicated experimental data and their good agreement undoubtedly enables us to state that whereas the excitation of the lower vibrational levels of CO in the discharge is produced by direct electron impact, pumping to high vibrational levels is the result of the relaxation of anharmonic oscillators, the CO molecules. We note, however, this process does not lead, generally speaking, to formation of vibrational inversion, and makes it only possible to produce for a number of levels "vibrational temperatures" that are higher than T_1^* and favor the onset of partial vibrational-rotational inversion on these levels.

[1)] It is customary to use in CO lasers a mixture consisting of CO, He, and small amounts of O_2. We assume that the role of the O_2 reduces only to the elimination of the CN molecules that exist as an undesirable impurity in the discharge, i.e., it is not connected with the here-discussed mechanism of formation of the vibrationally-excited levels.

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