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KINETICS OF NONRESONANT VIBRATIONAL EXCHANGE AND MOLECULAR LASERS

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We investigated the kinetics of nonresonant vibrational exchange in molecular systems, under conditions when the equilibrium with respect to the vibrational degrees of freedom is established more rapidly than the transfer of energy to the translational degrees of freedom. We determine the distributions of the vibrational energies (with allowance for two-quantum transitions) in a binary mixture of harmonic oscillators and in a single-component system of anharmonic oscillators. These distributions depend strongly on the relations between the vibrational quanta. A number of applications of nonresonant exchange for molecular lasers are considered. The possibilities are investigated of "amplifying" the inverted population by changing the gas and vibrational temperatures via expansion and chemical pumping. The possibility of obtaining a second generation zone at the upper vibrational levels of diatomic molecules is indicated. The results make it possible to select gas mixtures that are effective for generation.

1. INTRODUCTION

QUESTIONS of kinetics of nonresonant exchange in molecular systems are now becoming very timely for a number of applied problems, including molecular lasers.

Of particular significance for applications are the kinetic relations which do not depend on numerous concrete probabilities of elementary processes. Thus, in [1] the relaxation of diatomic molecules was analyzed by using the existence of a disparity between the vibrational-exchange time τ^{VV} and the characteristic time τ^{VT} of the transfer of energy to the translational degrees of freedom:

$$\tau^{VV} \ll \tau^{VT}. \tag{1}$$

When (1) is satisfied, a Boltzmann distribution of the vibrational energy is established over the levels in a system of harmonic oscillators under nonequilibrium conditions.

In [2, 3], the approach of [1] was generalized to include polyatomic molecules. A Boltzmann distribution with vibrational temperature T_i was assumed for each type of oscillations i. The time of exchange within each type of oscillation, τ^{VV}, was assumed to be much smaller than the time of exchange between different oscillations and the time τ^{VT}:

$$\tau^{VV} \ll \tau^{VV'}, \tau^{VT}. \tag{2}$$

There exists, however, a very wide circle of phenomena for which the time of vibrational exchange (between arbitrary vibrations) is much smaller than the characteristic times of transfer of energy to the translational degrees of freedom:

$$\tau^{VV}, \quad \tau^{VV'} \ll \tau^{VT}. \tag{3}$$

Among the systems of this type are mixtures of different molecules, different types of vibrations in polyatomic molecules, and anharmonic oscillations.

Several recent papers have been devoted to the kinetics of single-quantum vibrational exchange in a system of anharmonic oscillators and in a mixture of harmonic oscillators with vibrational-quantum energies E_A and E_B.[4-7] It is shown in these papers that the vibrational exchange leads to a quasistationary state with vibrational temperatures T_A and T_B, which are connected with the gas temperature T by the formula

$$\theta_B = \theta_A - \theta_A^0 + \theta_B^0,$$
$$\theta_B = \frac{E_B}{kT_B}, \quad \theta_B^0 = \frac{E_B}{kT}, \quad \theta_A = \frac{E_A}{kT_A}, \quad \theta_A^0 = \frac{E_A}{kT}. \tag{4}$$

For anharmonic oscillators, such an expression relates the effective vibrational temperature at the upper levels with the temperature of the two lower ones.

However, in the distributions considered so far, only single-quantum transitions were taken into account, thereby limiting the region of their applicability and making it impossible to describe many features of the vibrational relaxation. In addition, the kinetics of nonresonant vibrational exchange has hardly ever been used for the analysis of processes in molecular lasers.

The present paper is devoted both to the study of the general aspect of the kinetics of nonresonant exchange (including two-quantum transitions) and to its applications. In the next two sections we investigate the distributions of the vibrational energy in a system of harmonic oscillators with different vibrational quanta and in a system of anharmonic oscillators. The possibilities of using nonresonant exchange for molecular lasers, particularly gasdynamic and chemical ones, are considered in Sec. 4.

2. QUASIEQUILIBRIUM DISTRIBUTION OF VIBRATIONAL ENERGY IN A SYSTEM OF HARMONIC OSCILLATORS OF DIFFERENT FREQUENCIES

There exists a large class of molecular vibrational systems that can be regarded in first approximation as sets of harmonic oscillators. Let us consider the characteristic features of the vibrational exchange, using as an example a system consisting of two groups of oscillators A and B, having vibrational quanta E_A and E_B. In reality, such a system is a binary gas mixture of diatomic molecules or a single-component system of polyatomic molecules with two separated different types of oscillations. According to the main assumption (3), we shall neglect here the transition to the translational degrees of freedom and consider only the vibrational exchange. As a result of this exchange, a certain quasiequilibrium distribution of the vibrational energy is established among the groups of different oscillators, and in each system of oscillators there will exist a Boltzmann distribution of the populations over the levels with vibrational temperatures T_A and T_B, respectively. (To this end, when account is taken of the two-quantum exchange, it is necessary to satisfy the additional condition $\tau^{VV} \ll \tau^{VV'}$.) When the vibrational temperatures differ from the gas temperature, the vibrational temperatures in each system of oscillators will be different. For the case of only single-quantum exchange, the connection between T_A and T_B was obtained in [4-6] and is given by formula (4) above. In the general case, however, when the frequencies differ greatly from one another, an important role may also be assumed by multiquantum transitions that limit the applicability of (4).

The qualitative features of such a relaxation are seen already from an examination of a three-level system. Let the value of the vibrational quantum E_A lie between the limits

$$E_B < E_A < 2E_B. \tag{5}$$

Since the vibrational quantum E_B is smaller than E_A, then pumping of energy into the system B takes place in single-quantum transitions. However, since $E_A < 2E_B$, energy is pumped from B into A in two-quantum transitions. The distribution of the vibrational temperatures in a system of two oscillators depends strongly in the case (5) on the probability ratio of the single-quantum and two-quantum transition. For three-quantum transitions, the quantitative features remain the same. Therefore we shall henceforth confine ourselves for simplicity to a consideration of single- and two-quantum exchange processes, i.e., we shall consider transitions of the type $i, n \to i \pm 1,\ n \mp 1$; $i, n \to i \pm 2,\ n \mp 1$ (n, i—numbers of the levels in oscillators A and B, respectively; $E_A > E_B$). In the quasiequilibrium case, when $\tau^{VV'} \ll \tau^{VT}$, we have for the population N_n^A of the n-th level of oscillator A the equation

$$\begin{aligned}
&\sum_i [Q_{n+1,\,n}^{i,\,i+1} N_i^B N_{n+1}^A - Q_{n,\,n+1}^{i+1,\,i} N_{i+1}^B N_n^A] \\
&+\sum_i [Q_{n-1,\,n}^{i+1,\,i} N_{i+1}^B N_{n-1}^A - Q_{n,\,n-1}^{i,\,i+1} N_i^B N_n^A] \\
&+\sum_i [Q_{n+1,\,n}^{i,\,i+2} N_i^B N_{n+1}^A - Q_{n,n+1}^{i+2,\,i} N_{i+2}^B N_n^A] \\
&+\sum_i [Q_{n-1,\,n}^{i+2,\,i} N_{i+2}^B N_{n-1}^A - Q_{n,\,n-1}^{i,\,i+2} N_i^B N_n^A] = 0.
\end{aligned} \tag{6}$$

The first two sums in (6) describe the single-quantum exchange between oscillators A and B with probabilities $Q_{n-1,\,n}^{i+1,\,i}$ (per molecule), and the second two sums describe the two-quantum exchange with corresponding probabilities $Q_{n-1,\,n}^{i+2,\,i}$.

To transform (6), we use the following relations:

$$\begin{aligned}
&Q_{n,\,n+1}^{i+1,\,i} = (n+1)(i+1)Q_{01}{}^{10}, \quad Q_{01}{}^{10} = Q_{10}{}^{01}\exp\{\theta_B{}^0 - \theta_A{}^0\}, \\
&Q_{n,\,n+1}^{i+2,\,i} = (n+1)Q_{01}^{i+2,\,i} \quad Q_{01}^{i+2,\,i} = Q_{10}^{i,\,i+2}\exp\{2\theta_B{}^0 - \theta_A{}^0\}, \\
&N_n{}^A = N_0{}^A\exp\{-n\theta_A\}, \quad N_i{}^B = N_0{}^B\exp\{-i\theta_B\}.
\end{aligned} \tag{7}$$

Then, after substituting (7) in (6) and performing a number of transformations, we obtain

$$\exp\{\theta_B - \theta_A\} = \exp\{\theta_B{}^0 - \theta_A{}^0\}\frac{1+\chi\exp\{-\theta_B\}}{1+\chi\exp\{-\theta_B{}^0\}}, \tag{8}$$

where

$$\chi = \Big[Q_{01}^{10}\sum_i (i+1)\exp\{-i\theta_B\}\Big]^{-1}\sum_i Q_{01}^{i+2,\,i}\exp\{-i\theta_B\}. \tag{9}$$

If we represent the probability of two-quantum exchange in the form $Q_{01}^{i+2,i} = \frac{1}{2}(i+2)(i+1)Q_{01}^{20}$, then we get for χ

$$\chi = \varkappa[1-\exp\{-\theta_B\}]^{-1}, \quad \varkappa = Q_{01}{}^{20}/Q_{01}{}^{10}. \tag{10}$$

Thus, in place of relation (4), which takes into account only single-quantum transitions, we obtain from (8)

$$\theta_A = \theta_B - \theta_B{}^0 + \theta_A{}^0 - \ln\left[\frac{1+\chi\exp\{-\theta_B\}}{1+\chi\exp\{-\theta_B{}^0\}}\right]. \tag{11}$$

The parameter κ characterizes the influence of two-quantum transitions on the energy distribution among the oscillators. Neglecting two-quantum processes, we get $\kappa = 0$, and relation (11) goes over into (4). In the other limiting case, when $Q_{01}^{20} \gg Q_{01}^{10}$, $\kappa \gg 1$, we have

$$\theta_A = 2\theta_B - 2\theta_B{}^0 + \theta_A{}^0. \tag{12}$$

The value of κ for different pairs of molecules varies in a wide range. Using for the probability calculation the method of Herzfeld[8] and of Nikitin et al.,[9] and assuming for simplicity the characteristic length of the interaction potential l to be the same for all pairs of molecules ($l = 0.183$ Å), we get for κ

$$\begin{aligned}
\varkappa = \frac{Q_{01}{}^{20}}{Q_{01}{}^{10}} = \frac{7{,}4\cdot 10^2}{M_B E_B{}^2}\left(\frac{2E_B - E_A}{E_A - E_B}\right)^{7/3} \\
\times\exp\left\{-\frac{0{,}445\mu^{1/3}[(2E_B - E_A)^{2/3} - (E_A - E_B)^{2/3}]}{T^{1/3}} + \frac{3E_B - 2E_A}{2T}\right\}.
\end{aligned} \tag{13}$$

Here M_B is the reduced mass of the oscillator B (in atomic units), μ is the effective mass of the collision (in atomic units), and E_A and E_B are expressed in degrees K.

Figure 1 shows the values of κ calculated for several pairs of molecules at T = 300°. The abscissas represent the quantity $\gamma = 10^{-2}\mu^{1/3}(E_B - \frac{2}{3}E_A)$. The values of κ for all pairs of molecules (with the exception of H_2–HF) fit relatively well the straight line

$$\lg\varkappa = 0{,}75 - 0{,}44\,\gamma. \tag{14}$$

Figure 1 makes it possible to estimate the parameter κ also for other pairs of molecules. We note that for the pair H_2–HF, the departure from the general rule may be connected with the influence of the large rotational quantum of H_2 and the large difference between $E_A - E_B$ and $3E_B - 2E_A$.

Figure 2 characterizes the relation between the vibrational temperatures and the difference of the quanta for different pairs of molecules under non-equilibrium

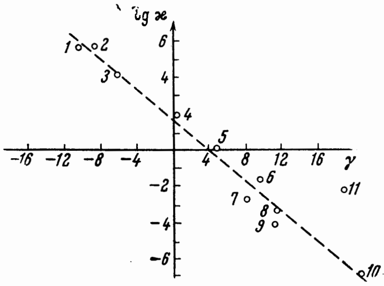

FIG. 1

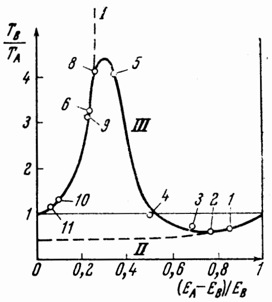

FIG. 2

FIG. 1. The parameter κ for a number of molecule pairs A–B: 1–HF–CO; 2–HF–N_2O; 3–HF–CO_2; 4–N_2–O_2; 5–HCl–CO; 6–HCl–CO_2; 7–DF–N_2O; 8–N_2–N_2O; 9–DF–CO_2; 10–N_2–CO; 11–HF. T = 300°K. For polyatomic molecules, only the asymmetrical type of oscillation is considered. (The ordinates represent the quantity $1 + \log \kappa$.)

FIG. 2. The ratio T_B/T_A for unlike-molecule pairs A–B at $T_A E_B/E_A = 1000°K$; the pair numbers (1–11) correspond to Fig. 1; T = 300°K. The values of T_B/T_A as functions of $(E_A-E_B)/E_B$ fall on the smooth curve III; the dashed curves correspond to allowance for only single-quantum (I) or two-quantum (II) transitions.

conditions. At a constant value of $T_A E_B/E_A$, the values T_B/T_A as functions of $(E_A - E_B)/E_B$ for different pairs of molecules lie on a single smooth curve. The dashed curves in Fig. 2 correspond to allowance for only single-quantum transitions (curve I) and only two-quantum transitions (curve II). In the region $(E_A - E_B)/E_B = 0.25$–0.75, the real relation between the vibrational temperatures differs noticeably from distributions of the type (4) and (13). The maximum disparity in the temperatures is reached at $(E_A - E_B)/E_B \sim 0.3$. The plots in Figs. 1 and 2, constructed at different values of the gas temperature T and of $T_A E_B/E_A$, can be used to select the proper pair of molecules needed to obtain the maximum vibrational temperature in one of the oscillators; this is an important factor for molecular lasers operating on vibrational-rotational transitions.

We note that in the intermediate region $0.3 \lesssim (E_A - E_B)/E_B \lesssim 0.8$, where, owing to the large energy defect, the probabilities of both the single-quantum and the two-quantum exchange are small, it is necessary, for certain pairs of molecules, to take additional account of transitions to translational degrees of freedom. For a set of three or more oscillators, and also for three-quantum transitions, the qualitative features of the nonresonant vibrational exchange remain the same.

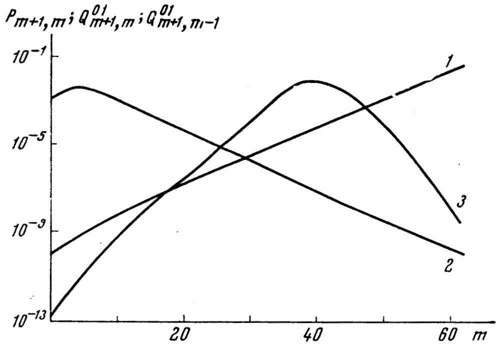

FIG. 3. Dependence of the probabilities of vibrational-translational relaxation $P_{m+1,m}$ (curve 1), of single-quantum exchange $Q_{m+1,m}$ (curve 2), and of two-quantum exchange $Q^{01}_{m+1,m-1}$ (curve 3) for the CO molecule on the number of the level m; the probabilities are given per collision. T = 300°K.

3. QUASIEQUILIBRIUM DISTRIBUTION OF VIBRATIONAL ENERGY IN A SYSTEM OF ANHARMONIC OSCILLATORS

Besides the set of harmonic oscillators, the anharmonic oscillator is an interesting system. The energy distribution in a system of such oscillators in [5] was obtained under the assumption that the principal role in the formation of this distribution is played by single-quantum exchange processes. The results of [5], however, have a limited region of applicability, as was already noted in [7], owing to the fact that at the upper levels the probabilities of the single-quantum exchange and the probabilities of the transfer of energy to translational degrees of freedom are of the same order of magnitude. For highly-excited levels, however, the distribution of [5] is subject to an additional limitation, connected with the purely vibrational exchange and due to the increased role of two-quantum exchange. Figure 3 shows, for the CO molecule, the dependence of the probabilities (per collision) of the vibrational-translational relaxation $P_{m+1,m}$, of single-quantum exchange $Q^{01}_{m+1,m}$, and of two-quantum exchange $Q^{01}_{m+1,m-1}$ with the lower quantum, as functions of the number of the level m. The calculation was made by the Herzfeld method. It is seen from Fig. 3 that for highly-excited levels the probabilities of two-quantum exchange may greatly exceed the probabilities of all the other processes and may determine the character of the distribution over the levels.

Let us now find the distribution over the levels in a system of anharmonic oscillators, with all three relaxation processes taken into account. We consider a stationary case, assuming that the non-equilibrium reserve of vibrational energy is maintained in the system by some sort of pumping mechanism that acts only on the lower levels. The balance equation, which determines the population N_n of the upper level of the oscillator, is

$$\sum_i [Q^{i,i+1}_{n+1,n} N_i N_{n+1} - Q^{i+1,i}_{n,n+1} N_{i+1} N_n] + \sum_i [Q^{i+1,i}_{n-1,n} N_{i+1} N_{n-1} - Q^{i,i+1}_{n,n-1} N_i N_n]$$

$$+ \sum_i [Q^{i,i+1}_{n+2,n} N_i N_{n+2} - Q^{i+1,i}_{n,n+2} N_{i+1} N_n] + \sum_i [Q^{i+1,i}_{n-2,n} N_{i+1} N_{n-2} - Q^{i,i+1}_{n,n-2} N_i N_n]$$

$$+ P_{n+1,n} N N_{n+1} - (P_{n,n+1} + P_{n,n-1}) N N_n + P_{n-1,n} N N_{n-1}. \quad (15)$$

Here, just as in (6), the first two sums describe single-quantum exchange, the second two-quantum exchange, and the remaining terms the vibrational-translational relaxation; $N = \sum_i N_i$.

Using relations similar to (7) between the probabilities of the direct and inverse transitions, and summing (15) from zero to m, we obtain

$$\Big[\sum_i Q^{i,i+1}_{m+2,m} N_i\Big] N_{m+2} + \Big[\sum_i (Q^{i,i+1}_{m+1,m-1} + Q^{i,i+1}_{m+1,m}) N_i + P_{m+1,m} N\Big] \cdot N_{m+1}$$

$$= \Big[\sum_i Q^{i,i+1}_{m+2,m} N_i \exp\{\theta^0_{i+2} - \theta^0_{2m+4} - \theta^0_i\} + \sum_i Q^{i,i+1}_{m+1,m} N_i \exp\{\theta^0_{i+1} - \theta^0_{m+1}\}$$

$$+P_{m+1,\,m}N\exp\{-\theta^0_{m+1}\}\Big]N_m$$
$$+\Big[\sum_i Q^{i,\,i+1}_{m+1,\,m-1}N_i\exp\{\theta^0_{i+2}-\theta^0_{2m+2}-\theta_1{}^0\}\Big]N_{m-1}. \qquad (16)$$

Here $\theta^0_{m+1} = (E_1 - 2m\Delta E)/kT$, E_1 is the energy of the lower quantum of the oscillator and ΔE is its anharmonicity.

To solve nonlinear equations of the type (16) we shall employ the device used in [7]. Since the sums in (16) depend weakly on the form of the distribution and are determined mainly by the reserve of vibrational energy of the oscillator, we shall use for the zeroth approximation in their calculation the Treanor distribution[5] for a cut-off harmonic oscillator with the same energy reserve. The number of the limiting level i* for such an oscillator is approximately determined from the condition

$$Q^{01}_{i^*,\,i^*-1} \approx \min[P_{i^*,\,i^*-1};\ Q^{01}_{i^*,\,i^*-2}]. \qquad (17)$$

For the levels $i > i^*$, where $Q^{01}_{i,\,i-1} < Q^{01}_{i^*,\,i^*-1}$, the Treanor distribution[5] does not exist, and the terms with $i > i^*$ make a small contribution to the sought sums. Following such a procedure, we obtain a linear relation of the type

$$A_mN_{m+2}+B_mN_{m+1}=C_mN_m+D_mN_{m-1}, \qquad (18)$$

which connects the populations of the four levels in the harmonic oscillator, with the coefficients A_m, B_m, C_m, and D_m depending on the energy of the system and on the number of the level.

To find the effective temperature of two levels m + 1 and m, we assume that the levels m + 2, m + 1, m, and m − 1 are characterized by a single temperature T_{m+1} and are equidistant, so that

$$E_{m+2}-E_{m+1}\approx E_m-E_{m-1}\approx E_{m+1}-E_m=E_1-2m\Delta E.$$

In (16) it is then necessary to make the appropriate corrections in the arguments of the exponentials. It is easy to see that under such an assumption, the relative error in (16) does not exceed $1 - \exp\{2m\Delta E/kT\}$. For the effective temperature T_{m+1} characterizing the distribution at the upper levels, we get

$$kT_{m+1}=\frac{E_1-2m\Delta E}{\ln y_{m+1}}, \qquad (19)$$

where y_{m+1} is the solution of the equation

$$A_my^3_{m+1}+B_my^2_{m+1}=C_my_{m+1}+D_m.$$

If the reserve of the vibrational energy is relatively small, so that we can confine ourselves in the sums of (16) to the first terms, then we obtain from (16) after a number of algebraic transformations

$$\theta_1=\theta_{m+1}-\theta^0_{m+1}+\theta_1{}^0+\ln\varphi_{m+1}, \qquad (20)$$

where

$$\varphi_{m+1}=[Q^{01}_{m+1,\,m}+P_{m+1,\,m}+W_m]^{-1}[Q^{01}_{m+1,\,m}+P_{m+1,\,m}\exp\{\theta_1-\theta_1{}^0\}$$
$$+W_m\exp\{\theta_{m+1}-\theta_{m+1}\}],$$
$$W_m=Q^{01}_{m+1,\,m-1}+Q^{01}_{m+2,\,m}\exp\{-\theta_{m+1}\};\qquad \theta_{m+1}=\frac{E_1-2m\Delta E}{kT_{m+1}}. \qquad (21)$$

If the condition

$$Q^{01}_{m+1,\,m-1}\gg Q^{01}_{m+2,\,m}\exp\{-\theta_{m+1}\} \qquad (22)$$

is satisfied, we can obtain from (20) a relatively simple analytic expression for the vibrational temperature T_{m+1}.

We note that the structure of expressions (20) and (21) with $P_{m+1,\,m} = 0$ is close to that of formula (11) for a system of harmonic oscillators.

Let us consider some limiting cases. Let the two-quantum transitions play no role. Then

$$\varphi_{m+1}\approx[Q^{01}_{m+1,\,m}+P_{m+1,\,m}]^{-1}[Q^{01}_{m+1,\,m}+P_{m+1,\,m}\exp\{\theta_1-\theta_1{}^0\}],$$
$$\theta_{m+1}=\theta_1-\theta_1{}^0+\theta^0_{m+1}-\ln\varphi_{m+1}. \qquad (23)$$

These expressions coincide with those obtained in [7]. In another limiting case, when only two-quantum transitions matter, we have

$$\varphi_{m+1}\approx\exp\{\theta_{m+1}-\theta_{m+1}\},\qquad 2\theta_{m+1}=\theta_1-\theta_1{}^0+\theta^0_{m+1}. \qquad (24)$$

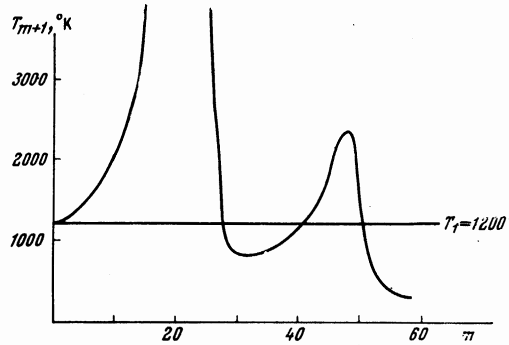

FIG. 4. Dependence of the effective vibrational temperature T_{m+1} on the number of the level m for the CO molecule. T_1 = 1200°K, T = 300°K.

Figure 4 shows the vibrational temperature as a function of the level number m for the CO molecule, as calculated from formulas (20) and (21) at T_1 = 1200° and T = 300°, using the probabilities shown in Fig. 3. First, when m increases, T_{m+1} increases, owing to the decrease of the vibrational quantum, so that absolute population inversion occurs for the levels 21–23. The change of T_{m+1} is described here by a formula of the type (4), which was derived earlier in [5] with only single-quantum exchange taken into account. However, for the levels $m \gtrsim 23$, the Treanor distribution[5] does not hold, owing to the large role of the two-quantum processes. For $23 \lesssim m \lesssim 32$, the character of the distribution is determined by the competition between the processes of single-quantum and two-quantum exchange, and for $32 \lesssim m \lesssim 47$ the change of T_{m+1} is due only to two-quantum exchange. At high levels $m \gtrsim 48$, an important role is assumed by transitions to the translational degrees of freedom, which lower the temperature T_{m+1} appreciably, down to the value of the gas temperature.

We note that since the radiative probabilities were not taken into consideration, the distribution shown in Fig. 4 takes place for the molecule CO at gas pressures $\gtrsim$ 20 Torr. This distribution is typical for arbitrary molecules. The specific character of the relation between the probabilities $P_{m+1,\,m}$, $Q^{01}_{m+1,\,m}$, $Q^{01}_{m+1,\,m-1}$ for different molecules may become manifest in the value of the minimum of T_{m+1}. This distribution is characterized by the presence of a second maximum of T_{m+1}. If the pumping is sufficiently strong and the gas temperature low, we obtain here a high vibrational temperature. Therefore a second band of levels suitable for lasing can exist in the region of this maximum.

We note also that the results obtained here, which dedetermine the populations of the upper vibrational levels of the molecule, are quite important for the analysis of the kinetics of nonequilibrium dissociation.

4. "ENHANCEMENT" OF INVERTED POPULATION IN MIXTURES OF MOLECULAR GASES UPON CHANGE OF THE GAS TEMPERATURE AND CHEMICAL PUMPING

Under nonequilibrium conditions, when the vibrational temperatures deviate from the gas temperature, there arise several specific effects that are important for molecular lasers operating on vibrational-rotational transitions, and also for a number of other applications.

Let us consider the main qualitative features of the effects arising here, using as an example a mixture of two types of diatomic molecules, A and B, simulated by harmonic oscillators. Let the gas temperature T vary in time, and in addition, let a chemical reaction result in the production, at a rate $(dN_A/dt)_{\text{chem}}$, of molecules A having a reserve of vibrational quanta ϵ_{chem}. Then the equations for the relaxation of the numbers of vibrational quanta ϵ_A and ϵ_B per molecule A and B, respectively, take the form

$$\frac{d\varepsilon_A}{dt} = -\frac{\varepsilon_A - \varepsilon_A{}^0}{\tau_A{}^{VT}} - Q_{10}{}^{01} N_B [\varepsilon_A(\varepsilon_B + 1)\exp\{\theta_A{}^0 - \theta_B{}^0\} - \varepsilon_B(\varepsilon_A + 1)]$$
$$+ (\varepsilon_{\text{хим}} - \varepsilon_A)\frac{1}{N_A}\left(\frac{dN_A}{dt}\right)_{\text{Chem}}, \quad (25)$$
$$\frac{d\varepsilon_B}{dt} = -\frac{\varepsilon_B - \varepsilon_B{}^0}{\tau_B{}^{VT}} + Q_{10}{}^{01} N_A [\varepsilon_A(\varepsilon_B + 1)\exp\{\theta_A{}^0 - \theta_B{}^0\} - \varepsilon_B(\varepsilon_A + 1)],$$

where ϵ_A^0 and ϵ_B^0 are the equilibrium values of the vibrational quanta of molecules A and B; τ_A^{VT} and τ_B^{VT} are the times of vibrational-translational relaxation of these molecules, and N_A and N_B are the densities of molecules A and B. For simplicity we consider here only single-quantum transitions.

In (25), all the terms in the right-hand sides can be of the same order. However, since it is assumed that the times of relaxation exchange between the molecules $\tau^{VV'} = 1/N_A Q_{10}^{01}$, $1/N_B Q_{10}^{01}$ satisfy the condition

$$\tau^{VV'} \ll \tau_A{}^{VT}, \qquad \tau_B{}^{VT}, \qquad \frac{N_A}{(dN_A/dt)_{\text{Chem}}}, \qquad \frac{T}{dT/dt}, \quad (26)$$

we can assume for the instants of time $\tau^{VV'} < t < \tau^{VT}$, that the expression in the square brackets in (25) is equal to zero (i.e., in first approximation, equilibrium is established between the oscillators A and B [10]). Differentiating it with respect to the time, we can determine the connection between $d\epsilon_A/dt$, $d\epsilon_B/dt$, and dT/dt:

$$\frac{d\varepsilon_A}{dt} = \frac{\exp\{\theta_A{}^0 - \theta_B{}^0\}}{[(\varepsilon_B + 1)\exp\{\theta_A{}^0 - \theta_B{}^0\} - \varepsilon_B]^2} \quad (27)$$
$$\times \left[\frac{d\varepsilon_B}{dt} + \varepsilon_B(\varepsilon_B + 1)(\theta_A{}^0 - \theta_B{}^0)\frac{1}{kT}\frac{d(kT)}{dt}\right].$$

Then, using (27), we can obtain from the system (25) an equation for ϵ_B, which in the case when the vibrational temperature of the molecule B is much lower than the characteristic temperature (i.e., $\epsilon_B \ll 1$), simplifies and takes the form

$$\frac{d\varepsilon_B}{dt} = -(\varepsilon_B - \varepsilon_B{}^0)\left[\frac{1}{\tau_B{}^{VT}\alpha} + \frac{K_A}{\tau_A{}^{VT}\alpha}\exp\{\theta_B{}^0 - \theta_A{}^0\}\right]$$
$$- \varepsilon_B\frac{\alpha - 1}{\alpha}(\theta_A{}^0 - \theta_B{}^0)\frac{1}{kT}\frac{d(kT)}{dt} \quad (28)$$
$$+ \varepsilon_B\left[\frac{1}{\alpha}\frac{\varepsilon_{\text{Chem}}}{\varepsilon_B} - \frac{1}{\alpha}\exp\{\theta_B{}^0 - \theta_A{}^0\}\right]\left(\frac{dK_A}{dt}\right)_{\text{Chem}}$$

where

$$K_A = N_A / N_B, \qquad \alpha \approx 1 + K_A \exp\{\theta_B{}^0 - \theta_A{}^0\}.$$

We see from this that the effective relaxation time of the reserve of vibrational quanta (and consequently, also of vibrational energy) of the molecule B changes in a gas mixture where the gas temperature changes and the chemical reaction results in vibrationally-excited molecules of the impurity gas A. The first term in the right-hand side of (28) characterizes the change of the proper time of the vibrational relaxation of the molecule B, due to the appearance of an additional reservoir of vibrational energy in the form of excited molecules A and due to the occurrence of an additional channel of relaxation of the energy of molecules B via the molecule A. However, besides these usual terms, characterizing the rate of vibrational relaxation in gas mixtures, the effective relaxation time can change also under conditions where there is a chemical reaction or the gas temperature changes. The last term in the right side of (28) is due precisely to the chemical reaction of formation of vibrational-excited molecules A. The second term, on the other hand, differs from zero if the gas temperature changes and the vibrational quanta of the molecules are different. The presence of this term is due to the existence of a distribution of type (4) and characterizes the transfer of energy from one type of oscillation to another when the gas temperature T changes, and when it becomes different from the vibrational temperatures T_A and T_B.

One of the effective methods of producing a difference between the vibrational and gas temperatures is cooling of the gas as it expands. The effect of energy transfer is insignificant for a preheated mixture of diatomic molecules A and B ($T_A = T_B = T$) at the initial period of the expansion, when the temperature difference is small. Subsequently, as the gas temperature drops and the rate of vibrational-translational relaxation decreases, the role of the second term in (28) increases and the transfer of energy to the molecules B ($E_A > E_B$) increases. The relaxation of the vibrational energy in the system of molecules B slows down, and a high vibrational temperature is maintained and in principle can even increase (see [4]).

The use of the kinetics of nonresonant exchange uncovers a number of possibilities for gasdynamic lasers (slowing down of the relaxation, increase of the inversion). Their analysis can be carried out by simultaneously solving the equations of gas dynamics and equations of the type (25).

Besides mixtures of molecules, the expansion can also be used to produce inverted population in a system of anharmonic oscillators. When the gas temperature is decreased, pumping takes place (see (20)) to the upper levels, at which generation can occur (for example, in CO or HCl).

Besides lasers, interest also attaches to analysis of the possibilities of dissociation upon expansion.

It should also be noted that when the sign of dT/dt is reversed in formula (27) (heating of the gas), energy is drawn from the molecules B in the binary mixture. The effect of energy outflow in the case of fast heating of the gas can greatly influence the kinetics of the dissociative and chemical processes in shock waves. To produce a difference between the vibrational and gas temperatures one can use successfully, besides gasdynamic processes, also chemical pumping. According to the foregoing results, it may turn out to be more convenient here to effect generation not on the excited molecules A, which are produced as a result of the chemical reactions, but on other molecules—B, introduced in the form of an impurity. If the molecules are suitably chosen (for relatively small admixtures B), the redistribution of the energy in the vibrational system gives rise to a high vibrational temperature for the molecules B, and consequently to a gain.

If the conditions (3) are satisfied, then the actual levels at which the pumping takes place are immaterial. All that matters is the energy yield of the reaction. One example of a scheme of this type is a laser with a DF-CO_2 mixture. The vibrational energy is transferred from the DF molecules, which are produced as a result of the chemical reaction, to the asymmetrical type of oscillations of CO_2. Generation on the 10.6-μ transition in CO_2 was obtained for this mixture in [11, 12], and generation on DF was observed in the absence of CO_2. Our estimates of the probabilities have shown that for the asymmetrical type of the oscillations of CO_2 and DF, the ratio of the probabilities of the single-quantum and two-quantum transitions is such that energy is transferred from the DF ($E_A = 4170\,^\circ K$) to the asymmetrical type of the oscillations of CO_2 ($E_B = 3340\,^\circ K$), where a higher vibrational temperature is produced (see Fig. 2).

We note that in the case of a nonresonant exchange it is possible to pump a higher energy into the CO_2 from the DF than from N_2, other conditions being equal. The HF–CO_2 mixture is much less effective compared with DF–CO_2. Pumping due to the large temperature difference of the vibrational quanta ($E_A = 5700\,^\circ K$ for HF) is slower than the disintegration of the upper laser level in CO_2. In addition, two-quantum transitions also play a role here (see Fig. 2).

One should also bear in mind the possible adverse role played by the indicated effects. Different impurities can contribute strongly to the inverted population by pumping energy from the molecules produced in the chemical reactions. Thus, the generation power in DF gradually decreased in an experiment[12] where CO_2 gas was progressively added to DF. Therefore in concrete analysis of the operation of chemical lasers it is necessary to consider in detail the distributions of the vibrational energy in the gas system, including all the impurities.

On the whole, the use of the kinetics of nonresonant exchange is quite promising for both gasdynamic and chemical lasers.

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