DISTRIBUTION OF VIBRATIONAL ENERGY IN A BINARY REACTIVE MIXTURE OF MOLECULAR GASES IN A FIELD OF RESONANCE LASER RADIATION

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There has recently been a considerable increase in interest in the theory of vibrational relaxation of molecular gases in systems having intensive external action. Such action occurs, for example, in the creation of a population inversion in molecular gas lasers through the absorption of resonance radiation, as well as in the laser initiation of chemical reactions and isotope separation. Until now, however, the principal attention has been paid to the change in the relaxation rate (or the chemical reaction rate) under the effect of the perturbing factors, and the question of the final state arising under a steady external action has not been considered. The question of the final state was first discussed on the example of a system containing sources of fast particles in [1]. The distribution of vibrational energy in a one-component gas in which a "dissociation—three-particle recombination" reaction, initiated by laser radiation, takes place was subsequently studied in [2, 3].

The purpose of the present report is to analyze the distribution of molecules by vibrational levels and the dependence of the number of vibrational quanta in a binary mixture of reactive molecular gases on the intensity and character of the laser pumping.

1. Let us consider a two-component system of molecules of types A and B. Let the radiation be efficiently absorbed only by molecules of type A, which is easily realized in the case of $\Delta\omega_{\text{mol}} \equiv |\omega_A - \omega_B| \gg \Delta\omega_{\text{las}}$ (ω_A and ω_B are the vibrational frequencies of the molecules and $\Delta\omega_{\text{las}}$ is the half-width of the laser radiation line), with $\Delta\omega_{\text{mol}}$ being such that the efficient exchange of vibrational energy in the collision of oscillators of different types is still possible. To describe the action of the laser radiation on such a two-component molecular system we adopt the following model: a) The molecules are modeled by truncated harmonic oscillators with frequencies ω_A (number of levels μ) and ω_B (number of levels ν); b) the vibrational relaxation in the system is due to one-quantum vibrational—vibrational and vibrational—translational exchange; c) rotational relaxation is assumed to have ended and is not considered; d) with steady excitation by laser radiation with a frequency ω_{las} either vibrational transitions $n \rightleftarrows n+1$ with probabilities $W_{n,n+1}$ and $W_{n+1,n}$, $n = 0, 1, 2, \ldots, k$ (cascade excitation of vibrations up to level k), or transitions $n = 0 \rightleftarrows n = k$ with probabilities W_{0k} and W_{k0} (multiquantum excitation) occur only in the oscillators of type A; the value $n = k$ is determined by the excitation conditions and by the relationships between ω_{las} and ω_A and ω_B; e) collisional dissociation of molecules of each component takes place from the limiting vibrational level; recombination of the product atoms during triple collisions leads to the formation of molecules at the limiting vibrational level of the discrete spectrum (if the reaction products recombine into molecules of a new type C then their concentration is assumed to be low in comparison with the concentrations of molecules of types A and B); f) the flow of energy into translational degrees of freedom due to the optical pumping is compensated by the removal of heat outside the system, so that the temperature of the translational degrees of freedom can be taken as constant.

Within the framework of this model the system of basic gas-kinetic equations for the populations of the vibrational levels can be represented in the following form:

$$\begin{aligned}\frac{dx_n}{dt} = {} & P_{10}(A)\{(n+1)x_{n+1} - [(n+1)e^{-\theta_A} + n]x_n + ne^{-\theta_A}x_{n-1}\} + \\ & + N_A Q_{10}^{01}(AA)\{(n+1)(1+\alpha_A)x_{n+1} - [(n+1)\alpha_A + n(1+\alpha_A)]x_n + \\ & + n\alpha_A x_{n-1}\} + N_B Q_{10}^{01}(AB)\{(n+1)(1+\alpha_B)x_{n+1} - \\ & - [(n+1)\alpha_B e^{\Delta} + n(1+\alpha_B)]x_n + n\alpha_B e^{\Delta} x_{n-1}\} + W - \\ & - \sum_{\beta}[P_{\mu d}(A\beta)N_\beta x_\mu - P_{d\mu}(a\beta)N_\beta N_a^2]\delta_{n\mu}, \quad n = 0, 1, \ldots, \mu; \end{aligned} \tag{1.1}$$

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$$\frac{1}{2}\frac{dN_a}{dt}=\sum_{\beta}\left[P_{\mu d}(A\beta)\,N_\beta x_\mu-P_{d\mu}(a\beta)\,N_\beta N_a^2\right]. \tag{1.2}$$

For the molecules of type B the equations for the populations y_n of the levels have an analogous form (where $W_{k0} = 0$, however). Here $\Delta = \theta_B - \theta_A$; $\theta_A = \hbar\omega_A/kT$; $\theta_B = \hbar\omega_B/kT$; T is the temperature of the gas; N_a and N_b are the total numbers of product atoms per unit volume formed through the dissociation of molecules A and B; $P_{\mu d}$ and $P_{d\mu}$ are the numbers of collisions per unit time transferring molecules from the limiting level μ to the continuous spectrum and the reverse, respectively (with a unit concentration of molecules and atoms); $P_{10}(AA)$, $Q_{10}^{01}(AA)$, and $Q_{10}^{01}(AB)$ are the probabilities of one-quantum processes of vibrational–translational energy exchange (V–T process) and of vibrational–vibrational energy exchange within (V–V process) and between (V–V' process) components, respectively, normalized to a unit time and a unit concentration of the partners in the collision.

The probabilities $P_{10}(A)$ and $P_{10}(B)$ of the V–T processes in each component are determined from the equations $P_{10}(A)=\sum_\beta N_\beta P_{10}(A\beta)$; $P_{10}(B)=\sum_\beta N_\beta P_{10}(B\beta)$, where N_β is the number of particles of type β per unit volume (here and below the indices β = a and b pertain to the concentrations of the product atoms while the indices β = A and B pertain to the concentrations of molecules of types A and B).

The term W in the right side of (1.1) describes the variation in the population x_n due to pumping. In the cases of cascade and multiquantum pumping W has the respective forms [4]

$$W=\begin{cases}(1-\delta_{nk})\,W_{n+1,n}x_{n+1}-[(1-\delta_{nk})\,W_{n,n+1}+W_{n,n-1}]\,x_n+W_{n-1,n}x_{n-1};\\ (W_{kn}x_k-W_{nk}x_n)\,\delta_{n0}+(W_{0n}x_0-W_{n0}x_n)\,\delta_{nk},\end{cases}$$

where $W_{n+1,n}$ and W_{nk} are the transition probabilities in $\sec^{-1}$.

The variation in the average supply $\alpha_A=\sum_{n=0}^{\mu} nx_n/N_A$ of vibrational quanta per molecule is described by an equation obtained from the system (1.1) by multiplying each equation of (1.1) by n/N_A and then summing [5]:

$$\begin{aligned}\frac{d\alpha_A}{dt}=-\frac{\alpha_A-\alpha_A^{(0)}}{\tau_{VT}^{(A)}}-\frac{(1-\alpha_A)\,\alpha_B e^{\Delta}-(1+\alpha_B)\,\alpha_A}{\tau_{VV'}^{(AB)}}-\\ +W'-\sum_\beta\left[P_{\mu d}(A\beta)\,N_\beta x_\mu-P_{d\mu}(a\beta)\,N_\beta N_a^2\right]\frac{\mu}{N_A},\end{aligned} \tag{1.3}$$

where

$$W'=\begin{cases}W_{10}\left(\sum_{n=0}^{k-1}x_n-kx_k\right)\frac{1}{N_A} & \text{— for cascade excitation,}\\ kW_{k0}(x_0-x_k)\frac{1}{N_A} & \text{— for multiquantum excitation;}\end{cases}$$

$\alpha_B=\sum_{n=0}^{\nu} ny_n/N_B$; $\alpha_A^{(0)} = e^{-\theta_A}/(1 - e^{-\theta_A})$ and $\alpha_B^{(0)} = e^{-\theta_B}/(1 - e^{-\theta_B})$ are the equilibrium values of α; $\tau_{VT}^{(A)} = 1/P_{10}(A)(1 - e^{-\theta_A})$; $\tau_{VT}^{(B)} = 1/P_{10}(B)(1 - e^{-\theta_B})$; $\tau_{VV'}^{(AB)} = 1/N_B Q_{10}^{01}(AB)$; $\tau_{VV'}^{(BA)} = 1/N_A Q_{10}^{01}(AB)$. In the derivation of Eq. (1.3) it was assumed that $W_{n,n-1} = nW_{10}$ and $W_{n0} = W_{0n}$. The equation for α_B has a form analogous to (1.3) with W' = 0.

The relationships between the particle concentrations

$$N_A+\frac{1}{2}N_a=N_A^0;\quad N_B+\frac{1}{2}N_b=N_B^0, \tag{1.4}$$

where N_A^0 and N_B^0 are the number densities of particles in the system, also follow from the gas-kinetic equations for x_n and y_n.

Equations (1.1)-(1.4) form a rather complicated system of nonlinear differential equations. In the future, therefore, we will examine a number of particular cases when the problem admits an analytical solution.

2. The form of the vibrational distribution function and the dependence of α on the probability of optical pumping in the final (steady) stage of the "dissociation—triple recombination" reaction, for which the recombination of product atoms is important, are of interest for clarifying the possibility of obtaining high steady concentrations of product atoms and high coefficients of enrichment in a binary isotope mixture. In this stage of the reaction one is able to obtain analytical expressions for the vibrational distribution functions from the kinetic equations (1.1) by the method of double summation [5, 6]. In the case of multiquantum optical pumping they have the form

$$\begin{gathered} x_n = x_0 \frac{\xi_A^n + \dfrac{W_{k0}}{D_1}\left[\sum\limits_{r=1}^{k} \dfrac{1}{r}\,\xi_A^{n+k-r} + \left(1-\xi_A^k\right)\sum\limits_{r=1}^{n} \dfrac{1}{r}\,\xi_A^{n-r}\right]}{1 + \dfrac{W_{k0}}{D_1}\sum\limits_{r=1}^{k} \dfrac{1}{r}\,\xi_A^{k-r}}, \\ 1 \leqslant n \leqslant k; \\ x_n = x_k \xi_A^{n-k}, \qquad 1 + k \leqslant n \leqslant \mu, \end{gathered} \tag{2.1}$$

where x_0 is determined from the normalization condition $\sum\limits_{n=0}^{\mu} x_n = N_A$;

$$\begin{gathered} \xi_A = C_1/D_1, \\ C_1 = P_{10}(A)\,e^{-\theta_A} + N_A Q_{10}^{01}(AA)\,\alpha_A + N_B Q_{10}^{01}(AB)\,e^{\Delta}\alpha_B, \\ D_1 = P_{10}(A) + N_A Q_{10}^{01}(AA)\,(1+\alpha_A) + N_B Q_{10}^{01}(AB)\,(1+\alpha_B); \end{gathered} \tag{2.2}$$

and similarly for component B

$$\begin{gathered} y_n = y_0 \xi_B^n, \qquad 1 \leqslant n \leqslant \nu, \\ y_0 = N_B\left(\sum_{n=0}^{\nu} \xi_B^n\right)^{-1}; \end{gathered} \tag{2.3}$$

$$\begin{gathered} \xi_B = C_2/D_2, \\ C_2 = P_{10}(B)\,e^{-\theta_B} + N_B Q_{10}^{01}(BB)\,\alpha_B + N_A Q_{10}^{01}(AB)\,\alpha_A, \\ D_2 = P_{10}(B) + N_B Q_{10}^{01}(BB)\,(1+\alpha_B) + N_A Q_{10}^{01}(AB)\,e^{\Delta}(1+\alpha_A). \end{gathered} \tag{2.4}$$

If we introduce into the analysis the vibrational temperatures $T_{\text{vib}}^{(A)}$ and $T_{\text{vib}}^{(B)}$ of each component, determining them from the equations

$$\vartheta_A = \hbar\omega_A/kT_{\text{vib}}^{(A)}, \quad \vartheta_B = \hbar\omega_B/kT_{\text{vib}}^{(B)}, \quad e^{-\vartheta_A} = \alpha_A/(1+\alpha_A),$$

and $e^{-\vartheta_B} = \alpha_B/(1+\alpha_B)$, and the "effective" temperatures $T_{\text{eff}}^{(A)}$ and $T_{\text{eff}}^{(B)}$: $\Theta_A = \hbar\omega_A/kT_{\text{eff}}^{(A)}$, $\Theta_B = \hbar\omega_B/kT_{\text{eff}}^{(B)}$, $\xi_A = e^{-\Theta_A}$, and $\xi_B = e^{-\Theta_B}$, then the distribution functions (2.1) and (2.3) can be represented in the form

$$\begin{aligned} x_n &= N_A F_n e^{-n\Theta_A}, & 0 &\leqslant n \leqslant k, \\ x_n &= N_A F_k e^{-n\Theta_A}, & 1 + k &\leqslant n \leqslant \mu; \\ y_n &= N_B G e^{-n\Theta_B}, & 0 &\leqslant n \leqslant \nu, \end{aligned}$$

where the form of the functions F_n (characterizing the degree of distortion of the Boltzmann distribution by the optical pumping) and G is clear from (2.1) and (2.3).

In the absence of pumping, as is easy to see from (2.2) and (2.4), $\xi_A = e^{-\theta_A}$ and $\xi_B = e^{-\theta_B}$, and Eqs. (2.1) and (2.3) are changed into

$$x_n = N_A^{(0)}\left(1-e^{-\theta_A}\right)e^{-n\theta_A}, \quad 0\leqslant n\leqslant \mu;$$
$$y_n = N_B^{(0)}\left(1-e^{-\theta_B}\right)e^{-n\theta_B}, \quad 0\leqslant n\leqslant \nu.$$

respectively, where $N_A^{(0)}$ and $N_B^{(0)}$ are the equilibrium concentrations.

It is seen from (2.1) that when $W_{k0}/D_1 \gg 1$ (strong pumping) the level populations x_n cease to depend on the optical pumping intensity; i.e., the molecular system reaches saturation conditions. The saturation effect is connected with the fact that there exists a so-called "bottleneck," determined by the quantity D_1, which limits the rate of introduction of radiant energy into the system of oscillators.

From the equations presented above it is seen that optical pumping causes the separation of the vibrational temperatures $T_{\text{vib}}^{(A)}$ and $T_{\text{vib}}^{(B)}$ from the translational temperature T, distorting the Boltzmann distribution in levels $n\leqslant k$ in the component A. However, the vibrational distribution function retains the Boltzmann form for all the levels of component B and for the levels $n > k$.

If we are confined to the case of a low translational temperature ($e^{-\theta_A}$, $e^{-\theta_B} \ll 1$), then we can obtain explicit expressions for the distribution function in the limiting cases of high and low concentrations of the product atoms.

<ins>1. N_A, $N_B \gg N_a$, N_b.</ins> In accordance with (1.4) we must set $N_A \approx N_A^0$ and $N_B \approx N_B^0$ in all the equations. A further simplification is connected with the estimation of ξ_A and ξ_B. The quantities ξ_A and ξ_B can be estimated as follows. From Eqs. (2.2) and (2.4) it is seen that $\xi_A \approx \alpha_A/(1 + \alpha_A)$ when $N_A^0 \gg N_B^0$ and $\xi_A < \alpha_A/(1 + \alpha_A)$ when $N_A^0 \ll N_B^0$. Therefore,

$$e^{-\theta_A}\leqslant\xi_A\leqslant\alpha_A/(1+\alpha_A) \tag{2.5}$$

and similarly,

$$e^{-\theta_B}\leqslant\xi_B\leqslant\alpha_A e^{-\Delta}/(1+\alpha_A). \tag{2.6}$$

The relations (2.5) and (2.6) lead in a natural way to the analysis of the limiting cases $\xi \ll 1$, $\alpha \ll 1$; $\xi \ll 1$, $\alpha < 1$; $\xi \leqslant 1$, $\alpha > 1$:

a) ξ_A, $\xi_B \ll 1$, in which case the distribution functions of the molecules by vibrational levels take the form

$$x_0 = N_A^0\frac{1+\frac{W_{k0}}{D_1}\frac{1}{k}}{1+\frac{W_{k0}}{D_1}\left(\frac{1}{k}+\sum_{r=1}^{k}\frac{1}{r}\right)},$$

$$x_n = N_A^0\frac{1+\frac{W_{k0}}{D_1}\frac{1}{n\xi_A^n}}{1+\frac{W_{k0}}{D_1}\left(\frac{1}{k}+\sum_{r=1}^{k}\frac{1}{r}\right)}\xi_A^n, \quad 1\leqslant n\leqslant k, \tag{2.7}$$

$$x_n = N_A^0\frac{1+\frac{W_{k0}}{D_1}\frac{1}{k\xi_A^k}}{1+\frac{W_{k0}}{D_1}\left(\frac{1}{k}+\sum_{r=1}^{k}\frac{1}{r}\right)}\xi_A^n, \quad 1+k\leqslant n\leqslant\mu;$$

$$y_n = N_B^0\xi_B^n, \quad 0\leqslant n\leqslant\nu. \tag{2.8}$$

It follows from (2.7) that in the levels $1 \leqslant n \leqslant k$ the distortion of the Boltzmann distribution for molecules A follows a 1/n law. For weak pumping, i.e., when $W_{k0}/D_1 \ll 1$, the populations of the levels depend linearly on W_{k0}. For strong pumping ($W_{k0}/D_1 \gg 1$) the populations of the levels no longer depend on W_{k0} (i.e., the molecular system reaches saturation conditions):

$$\begin{aligned} x_0 &= N_A^0 \frac{1}{1+k\sum\limits_{r=1}^{k}\frac{1}{r}}, \\ x_n &= N_A^0 \frac{1}{\frac{1}{k}+\sum\limits_{r=1}^{k}\frac{1}{r}}\frac{1}{n}, \quad 1 \leqslant n \leqslant k; \\ x_n &= N_A^0 \frac{1}{\left(1+k\sum\limits_{r=1}^{k}\frac{1}{r}\right)\xi_A^k}\xi_A^n, \quad 1+k \leqslant n \leqslant \mu. \end{aligned} \tag{2.9}$$

Under saturation conditions, as seen from (2.9), the distribution function in levels $1 \leqslant n \leqslant k$ differs strongly from a Boltzmann distribution and varies with the number of the level as 1/n; in levels $1 + k \leqslant n \leqslant \mu$ the distribution function becomes a Boltzmann distribution (with an effective number of particles). Such behavior of the distribution function suggests a steady distribution in a system of anharmonic oscillators, which was studied in [7].

b) $\xi_A, \xi_B \leqslant 1$, in which case the approximations (2.1) and (2.3) of the distribution take the form

$$\begin{aligned} x_0 &= N_A^0 (1-\xi_A)\frac{1+\frac{W_{k0}}{D_1}\sum\limits_{r=1}^{k}\frac{1}{r}}{1+\frac{W_{k0}}{D_1}\xi_A\sum\limits_{r=1}^{k}\frac{1}{r}}; \\ x_n &= N_A^0 (1-\xi_A)\frac{\xi_A^n+\frac{W_{k0}}{D_1}\left[\xi_A^n\sum\limits_{r=1}^{k}\frac{1}{r}+(1-\xi_A^k)\sum\limits_{r=1}^{n}\frac{1}{r}\right]}{1+\frac{W_{k0}}{D_1}\xi_A\sum\limits_{r=1}^{k}\frac{1}{r}}, \quad 1 \leqslant n \leqslant k; \\ x_n &= N_A^0 (1-\xi_A)\frac{1+\frac{W_{k0}}{D_1}\frac{1}{\xi_A^k}\sum\limits_{r=1}^{k}\frac{1}{r}}{1+\frac{W_{k0}}{D_1}\xi_A\sum\limits_{r=1}^{k}\frac{1}{r}}\xi_A^n, \quad 1+k \leqslant n \leqslant \mu; \end{aligned} \tag{2.10}$$

$$y_n = N_B^0 (1-\xi_B)\xi_B^n, \quad 0 \leqslant n \leqslant \nu. \tag{2.11}$$

[The sums entering into (2.10) and (2.11) were estimated in the approximation $k \ll \mu, \nu$.]

Under the conditions of weak and strong optical pumping the function (2.10) is reduced to the expressions

$$\begin{aligned} &\frac{W_{k0}}{D_1} \ll 1: \quad x_n = N_A^0 (1-\xi_A)\xi_A^n, \quad 0 \leqslant n \leqslant \mu; \\ &\frac{W_{k0}}{D_1} \gg 1: \quad x_0 = N_A^0 \frac{1-\xi_A}{\xi_A}; \\ &x_n = N_A^0 \frac{1-\xi_A}{\xi_A}\frac{\xi_A^n\sum\limits_{r=1}^{k}\frac{1}{r}+(1-\xi_A^k)\sum\limits_{r=1}^{n}\frac{1}{r}}{\sum\limits_{r=1}^{k}\frac{1}{r}}, \quad 1 \leqslant n \leqslant k; \\ &x_n = N_A^0 \frac{1-\xi_A}{\xi_A^{k+1}}\xi_A^n, \quad 1+k \leqslant n \leqslant \mu. \end{aligned} \tag{2.12}$$

Under saturation conditions, as follows from (2.12), the distribution has the character of a plateau (in levels $0 \leqslant n \leqslant k$), which changes into a Boltzmann distribution for $1 + k \leqslant n \leqslant \mu$. The difference between the forms of the distribution in cases a) and b) is explained by the fact that when $\xi \ll 1$ the effect of distortion of the Boltzmann distribution by laser pumping plays the main role, while when $\xi \leqslant 1$ the effect of an increase in the vibrational temperature plays the main role.

2. Let N_α, $N_b \gg N_A$, N_B. Then, in accordance with (1.4), $N_\alpha \gg 2N_A^0$ and $N_b \approx 2N_B^0$. We will also assume that

$$P_{10}(A)\,e^{-\theta_A} \gg N_A Q_{10}^{01}(AA)\,\alpha_A, \quad N_B Q_{10}^{01}(AB)\,e^{\Delta}\alpha_B;$$
$$P_{10}(B)\,e^{-\theta_B} \gg N_B Q_{10}^{01}(AB)\,\alpha_B, \quad N_A Q_{10}^{01}(AB)\,\alpha_A.$$

In this case for low translational temperatures the distribution functions of the molecules over the vibrational levels will have the form of (2.7) and (2.8) where now $\xi_A \approx e^{-\theta_A}$, $\xi_B \approx e^{-\theta_B}$, $D_1 \approx 2N_A^0 P_{10}(A\alpha) + 2N_B^0 P_{10}(Ab)$, and N_A^0 will be replaced by N_A, which can be found from the law of mass action under the nonequilibrium conditions being considered.

3. Let us find the dependence of the supply of vibrational quanta α_A and α_B on the probability of optical pumping. In the steady case being considered the equations for α_A and α_B have the form

$$\frac{\alpha_A - \alpha_A^{(0)}}{\tau_{VT}^{(A)}} - \frac{(1+\alpha_A)\,\alpha_B e^{\Delta} - (1+\alpha_B)\,\alpha_A}{\tau_{VV'}^{(AB)}} =$$
$$= kW_{k0}\frac{x_0}{N_A}\,\frac{1-\xi_A^k}{1+\dfrac{W_{k0}}{D_1}\sum\limits_{r=1}^{k}\dfrac{1}{r}\,\xi_A^{k-r}}; \tag{3.1}$$
$$\frac{\alpha_B - \alpha_B^{(0)}}{\tau_{VT}^{(B)}} + \frac{(1+\alpha_A)\,\alpha_B e^{\Delta} - (1+\alpha_B)\,\alpha_A}{N_B/N_A\tau_{VV'}^{(AB)}} = 0.$$

It is seen from the equations that when $(N_B/N_A)\tau_{VV'}^{(AB)} \ll \tau_{VT}^{(B)}$ vibrational "quasiequilibrium" [8] is established between the components, determined by the equation

$$\alpha_A/(1+\alpha_A) = \alpha_B e^{\Delta}/(1+\alpha_B), \tag{3.2}$$

where α_A and α_B depend on W_{k0}.

When $W_{k0} = 0$ the system (3.1) has a unique solution corresponding to the state of total statistical equilibrium.

Let us investigate the dependence of α on W_{k0}.

1. Let N_A, $N_B \gg N_\alpha$, N_b.

a) ξ_A, $\xi_B \ll 1$, and in the case of α_A, $\alpha_B \ll 1$ we obtain from the system of equations (3.1)

$$\alpha_A = \alpha_A^{(0)} + \frac{k\overline{W}_{k0}}{P_{10}(A)}\,\frac{1+\varphi_1 e^{\Delta}}{1+\varphi_2}; \tag{3.3}$$
$$\alpha_B = \alpha_B^{(0)} + \frac{k\overline{W}_{k0}}{P_{10}(A)}\,\frac{\varphi_1}{1+\varphi_2}, \tag{3.4}$$

where

$$\overline{W}_{k0} = \frac{W_{k0}}{1+\dfrac{W_{k0}}{D_1}\left(\dfrac{1}{k}+\sum\limits_{r=1}^{k}\dfrac{1}{r}\right)};$$

$$\varphi_1 = \frac{N_A^0 Q_{10}^{01}(AB)}{P_{10}(B)}; \quad \varphi_2 = \varphi_1 e^{\Delta} + \frac{N_B^0 Q_{10}^{01}(AB)}{P_{10}(A)}; \quad D_1 = N_A^0 Q_{10}^{01}(AA) + N_B^0 Q_{10}^{01}(AB).$$

When $W_{k0}/D_1 \gg 1$ one can obtain from (2.7) and (2.8) approximate expressions for the supply of vibrational quanta:

$$\alpha_A = \frac{1}{N_A^0} \sum_{n=0}^{\mu} n x_n \approx \frac{kW_{k0}/D_1}{1 + \frac{W_{k0}}{D_1}\left(\frac{1}{k} + \sum_{r=1}^{k} \frac{1}{r}\right)}, \tag{3.5}$$

and similarly,

$$\alpha_B = \frac{p}{2}\left(\sqrt{1 + \frac{4q}{p^2}} - 1\right), \tag{3.6}$$

where

$$p = \frac{N_B^0 P_{10}(BB) + N_A^0 Q_{10}^{01}(AB)\, e^{\Delta}(1 + \alpha_A)}{N_B^0 Q_{10}^{01}(BB)}; \quad q = \frac{N_A^0 Q_{10}^{01}(AB)}{N_B^0 Q_{10}^{01}(BB)} \alpha_A.$$

It follows from (3.5) that at high pumping rates ($W_{k0}/D_1 \gg 1$) the supply of vibrational quanta does not depend on W_{k0} (saturation conditions) and equals

$$\alpha_A \approx k\left(\frac{1}{k} + \sum_{r=1}^{k} \frac{1}{r}\right)^{-1}. \tag{3.7}$$

b) $\xi_A, \xi_B \approx 1$, in which case using (2.1) and (2.3) one can obtain $\alpha_A^{\max} \approx \mu/2$ and $\alpha_B^{\max} \leqslant \nu/2$. It should be emphasized that such values of α_A and α_B and the corresponding vibrational temperature $T_{\text{vib}}^{\max} \approx \hbar\omega/k \ln (1 + \alpha^{\max})/\alpha^{\max}$ represent an upper estimate and evidently are not attainable in practice.

2. Let N_a, $N_b \gg N_A$, N_B. In the case of $N_a P_{10}(Aa) + N_b P_{10}(Ab) \approx N_A Q_{10}^{01}(AA)(1 + \alpha_A) + N_B Q_{10}^{01}(AB)(1 + \alpha_B)$ and $\xi \ll 1$, the expressions for the average supply of vibrational quanta will have the form (3.3)-(3.7), where N_A^0 and N_B^0 must be replaced by $N_A \approx 2N_A^0 P_{10}(Aa)/Q_{10}^{01}(AA)$ and $N_B \approx 2N_B^0 P_{10}(Ab)/Q_{10}^{01}(AB)$.

If $\xi_A \approx e^{-\theta_A}$ and $\xi_B \approx e^{-\theta_B}$, then from (3.1) we obtain

$$\alpha_A \approx \alpha_A^{(0)} + \frac{kW_{k0}/D_1}{1 + \frac{W_{k0}}{D_1}\left(\frac{1}{k} + \sum_{r=1}^{k} \frac{1}{r}\right)}; \quad \alpha_B \approx \alpha_B^{(0)}, \tag{3.8}$$

where $D_1 \approx 2N_A^0 P_{10}(Aa) + 2N_B^0 P_{10}(Ab)$.

It follows from (3.8) that when $W_{k0}/D_1 \gg 1$ we have

$$\alpha_A \approx k\left(\frac{1}{k} + \sum_{r=1}^{k} \frac{1}{r}\right)^{-1}.$$

By comparing this value with (3.7), we see that under saturation conditions the average supply of vibrational quanta per molecule in component A reaches its maximum value, which does not depend on the degree of dissociation of the molecular gas.

3. The dependences of α_A and α_B on the dimensionless probability of optical pumping $W_{k0}/N_A^0 Q_{10}^{01}(AA)$ calculated from Eqs. (3.3)-(3.7) are presented in Fig. 1a, b [a: curve 1 describes a one-component system and curves 2-4 correspond to the values $N_B^0/N_A^0 = 1$, 10^2, and 10^4 and $k = 1$; b: curves 1 (for α_A) and 2 (for α_B) correspond to the value $N_B^0/N_A^0 = 10^4$ while 3 (for α_A) and 4 (for α_B) correspond to $N_B^0/N_A^0 = 10^6$; $k = 1$]. The following values of the

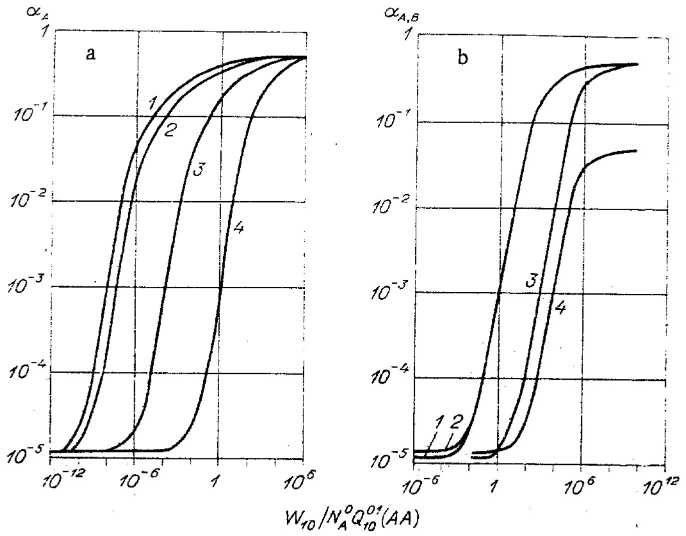

Fig. 1

molecular parameters were used in the calculations:

$$P_{10}(AA) \approx P_{10}(BB) \approx P_{10}(AB);\ Q_{10}^{01}(AA) \approx Q_{10}^{01}(BB) \approx Q_{10}^{01}(AB);$$
$$Q_{10}^{01}(AA)/P_{10}(AA) = 10^5;\ P_{10}(Aa) \approx P_{10}(Ab) \approx P_{10}(Ba) \approx P_{10}(Bb);$$
$$Q_{10}^{01}(AA)/P_{10}(Aa) = 2\cdot 10^3;$$

$\mu = \nu = 25$; $\hbar\omega_A = 2359.6\ \text{cm}^{-1}$; $\Delta = -0.1$; $T = 300°K$. These molecular parameters correspond to a mixture of the isotope molecules $^{28}N_2$ (type A) and $^{29}N_2$ (type B). It should be noted that because of the absence of an intrinsic dipole moment the direct excitation of homonuclear molecules in a laser radiation field is extremely inefficient. It is known, however, that such molecules are active in the generation of combination scattering (with the condition that $\omega_A = \omega_{las} - \omega_s$, where ω_A and ω_s are the frequencies of the molecular vibrations and of the scattered quantum, respectively). This process can lead to the selective heating of the vibrational mode with the frequency ω_A. Such a possibility was demonstrated experimentally in [9] on the example of the initiation of the nitrogen oxidation reaction.

From Fig. 1a, b and Eqs. (3.3) and (3.5) it is seen that for small values of the probability of optical pumping the behavior of α_A is characterized by a linear dependence on $W_{k_0}/N_A^0 Q_{10}^{01}(AA)$. With an increase in W_{k_0} the dependence $\alpha = \alpha(W_{k_0})$ becomes nonlinear, and with a further increase in the pumping rate saturation conditions are reached. Figure 1a, b also illustrates the effect of the ratio N_B^0/N_A^0 of concentrations of the components on the dependence $\alpha = \alpha(W_{k_0})$. The peeling off of curves 2-4 in Fig. 1a from curve 1 which describes a one component system is explained by the fact that in proportion to the dilution of gas A by gas B (this corresponds to an increase in the parameter N_B^0/N_A^0 when $N_A^0 = \text{const}$) with a fixed pumping intensity the supply of vibrational quanta α_A decreases because of dissipation by V—T processes and the transfer of vibrational energy from component A to B due to V—V' processes.

From Fig. 1b and Eqs. (3.1) and (3.2) it is seen that for values of N_B^0/N_A^0 satisfying the relation $N_B^0 P_{10}(BB) \gtrsim N_A^0 Q_{10}^{01}(AB)$ the condition (3.2) is violated starting with a certain pumping intensity: α_A becomes greater than α_B; i.e., the oscillators with the larger quanta are more strongly "heated."

Thus, as shown by the calculations conducted, the presence of laser pumping under steady conditions leads to distortion of the equilibrium distribution function of molecules of type A by vibrational levels (for $1 \leqslant n \leqslant k$), leaving the vibrational distribution function of molecules of type B undistorted, and to separation of the vibrational temperature in both components from the translational temperature, and for certain concentration ratios it can also cause the violation of the condition of quasiequilibrium between the components defined by Eq. (3.2).

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CALCULATION OF CHEMICAL- AND VIBRATIONAL-NONEQUILIBRIUM FLOW OF A MULTICOMPONENT GAS THROUGH A NOZZLE

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INTRODUCTION

The calculation of the flow of a multicomponent gas mixture under certain conditions requires the joint allowance for the kinetics of the chemical reactions and the processes of vibrational energy exchange. Until now, however, such calculations have not been made in a sufficiently general formulation, and this is explained both by the complexity of the mathematical solution and by difficulties connected with the systematic formulation of the problem and the absence of data on many of the kinetic characteristics, particularly those describing the interaction of the processes of chemical and vibrational kinetics.

In practice one usually assumes that the separation of these processes is possible. Under specific conditions this can actually be justified. For example, for nozzles of relatively large diameters and with high reservoir temperatures ($T_0 \sim 3000$°K), such as in application to the calculation of the flow parameters in rocket engine nozzles (see the review in [1], for example), it is sufficient to allow for only the chemical nonequilibrium, assuming in this case that the vibrational degrees of freedom of the molecules are in equilibrium with the translational degrees of freedom. The soundness of such an approach is due both to the

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