

1. Introduction. Currently, the most effective method of selective excitation of the vibrational degrees of freedom in molecular gases is direct absorption of resonant IR radiation [1]. A fundamentally different method of selective excitation of molecular vibrations has been proposed [2], based on multiquanta resonant transfer of vibrational energy to impurity molecules from reservoir molecules where the latter have a nonequilibrium (non-Boltzmann) distribution of vibrational energies. From the theoretical analysis in [2] it is assumed that in collisions of impurity molecules A (which are modeled as harmonic oscillators) with reservoir molecules B,  $q$  vibrational quanta of B transform into  $p$  quanta of A. Hence in each oscillator A, transitions only occur between vibrational levels  $m$  and  $n$  whose difference  $m - n$  is a multiple of  $p$ , and the whole system of harmonic oscillators splits up into  $p$  groups. The number of molecules in each group is determined by the initial conditions and in the stationary case a Boltzmann distribution is established in each group

$$z_{r+lp} = C_r \exp\left(-\frac{\hbar\omega_a}{kT_v^a}(r+lp)\right), \quad r=0,1,\dots,p-1, \quad l=0,1,\dots \quad (1.1)$$

with the temperature  $T_v^a$  defined by the relation

$$p \frac{\hbar\omega_a}{kT_v^a} - q \frac{\hbar\omega_b}{kT_v^{b*}} = \frac{p\hbar\omega_a - q\hbar\omega_b}{kT}$$

Here  $\omega_a$  and  $\omega_b$  are the frequencies of oscillators A and B;  $T$  is the temperature of the translational degrees of freedom (the gas temperature). The effective vibrational temperature  $T_v^{b*}$  is determined by the nonequilibrium distribution  $y_n$  of vibrational energies of the molecules according to the formula

$$q \frac{\hbar\omega_b}{kT_v^{b*}} = \ln \frac{\sum_{n=0}^{\infty} \frac{(n+q)!}{n!} y_n}{\sum_{n=q}^{\infty} \frac{n!}{(n-q)!} y_n}$$

Intense chemical reactions, IR radiation, and other types of selective excitation of the reservoir molecules can strongly disturb their equilibrium distribution, without directly affecting the other components of the mixture. Under these conditions when  $q > 1$  the value of  $T_v^{b*}$  (and hence also  $T_v^a$ ) can differ significantly from the kinetic vibrational temperature determined from the average stored vibrational energy [2]. In this way, redistribution of vibrational energies in the reservoir (i.e., changes in the  $y_n$ ) can widely change the vibrational temperature  $T_v^a$  of the impurity. This leads to a new method of exciting molecular gases, without direct absorption of IR radiation. We point out that the case of most practical interest is a three-quanta resonant transition  $p = 1, q = 2$  which is realized (within an error of less than 1%) in collisions between such abundant molecules as OH-NO, N<sub>2</sub>-SO, SO-Cl<sub>2</sub>, OH-O<sub>2</sub>, H<sub>2</sub>-CO.

In the present paper we discuss how chemical reactions in the impurity can be speeded up by a distortion of the equilibrium vibrational distribution in the reservoir. Specific calculations for the dissociation of diatomic molecules (modeled as anharmonic oscillators) are carried out.

2. Stationary Vibrational Distribution. We study the stationary vibrational distribution of the harmonic oscillators A in a non-Boltzmann reservoir of B molecules. The following processes are taken into account in the analysis: (V-V') exchange from A-B collisions

(p quanta of A transform into q quanta of B), (V-T) processes from A-B collisions, and also (V-V) processes from A-A collisions.

The kinetic equation for the population density of the vibrational levels  $x_n(t)$  of the A molecules has the form

$$\frac{dx_n}{dt} = L_{VV'} + L, \quad (2.1)$$

where  $L_{VV'}$  is the collision integral for multiquanta (V-V') exchange [2]:

$$L_{VV'} = z_{ab} Q_{p0} \left\{ \frac{(n+p)!}{n!} x_{n+p} - \left[ \frac{(n+p)!}{n!} e^{-\theta p} + \frac{n!}{(n-p)!} \right] x_n + \frac{n!}{(n-p)!} e^{-\theta p} x_{n-p} \right\}, \quad (2.2)$$

$$\theta = \frac{\hbar \omega_a}{kT \alpha}, \quad Q_{p0} = \frac{Q_{p0}^{0q}}{p!q!} \sum_{s=0}^{\infty} \frac{(s+q)!}{s!} y_s.$$

$Q_{p0}^{0q}$  is the probability of a (V-V') process



in a single collision,  $z_{ab}$  is the collision frequency of a single A molecule with B molecules, and L is the collision integral corresponding to the slower processes of (V-T) exchange in collisions of A with B and (V-V) exchange in collisions of A molecules with each other. We ignore (V-T) exchanges in A-A collisions since the concentration of A molecules is taken to be small. Hence

$$L = L_{VT} + L_{VV}, \quad (2.3)$$

where

$$L_{VT} = z_{ab} P_{10} \{ (n+1)x_{n+1} - [(n+1)e^{-\theta} + n]x_n + ne^{-\theta} x_{n-1} \} \quad (2.4)$$

is the collision integral for (V-T) exchange [3],  $\theta = \hbar \omega_a / kT$ , and  $P_{10}$  is the probability of the single-quantum (V-T) transition  $n = 1 \rightarrow n = 0$ . Finally

$$L_{VV} = z_{aa} Q_{10}^{VV} \{ (n+1)(1+\alpha)x_{n+1} - [(n+1)\alpha + n(1+\alpha)]x_n + n\alpha x_{n-1} \} \quad (2.5)$$

is the collision integral for (V-V) exchange [3],  $\alpha = \sum_{n=0}^{\infty} nx_n$  is the average number of vibra-

tional quanta per A molecule. An exact solution of (2.1) with (2.2)-(2.5) would be difficult. However, the problem can be simplified considerably if it is realized that (V-T) and (V-V) processes proceed much more slowly than (V-V') exchange ( $(z_{ab}Q_{p0})^{-1} \ll (z_{ab}P_{10})^{-1}$ ,  $(z_{aa}Q_{10}^{VV})^{-1}$ ). The vibrational relaxation can then be treated as proceeding in two stages. In the first stage, after a time of order  $\tau_{VV} = (z_{ab}Q_{p0})^{-1}$  the distribution (1.1) is established; the factors  $C_r(0)$  are determined by the relative numbers of particles in each group at the initial instant of time:

$$C_r(0) = (1 - e^{-\theta p}) e^{\theta r} \sum_{l=0}^{\infty} x_{n+lp}(0).$$

The next relaxation stage is characterized by the time  $\tau_{VT} = (z_{ab}P_{10})^{-1}$  or  $\tau_{VV} = (z_{aa}Q_{10}^{VV})^{-1}$ . In this stage the slower (V-T) and (V-V) processes will result in a stationary distribution of molecules according to groups  $\{C_r(\infty)\}$ . We study only the vibrational relaxation in the second stage. Substitute the distribution (1.1) into (2.1). After summation of (2.1) within each group (i.e., over  $l$ ) we obtain a set of kinetic equations for the distribution of particles according to group  $\{C_r(t)\}$ :

$$dC_r/dt = I_{VT} + I_{VV}, \quad r = 0, 1, \dots, p-1; \quad (2.6)$$

$$I_{VT} = z_{ab} P_{10} \{ (r+1 + p/(e^{\theta p} - 1))e^{-\theta} C_{r+1} - [(r+1 + p/(e^{\theta p} - 1))e^{-\theta} + r + p/(e^{\theta p} - 1)]C_r + (r + p/(e^{\theta p} - 1))e^{\theta - \theta} C_{r-1} \}; \quad (2.7)$$

$$I_{VV} = z_{aa} Q_{10}^{VV} \{ (r+1 + p/(e^{\theta p} - 1))(1+\alpha)e^{-\theta} C_{r+1} - [(r+1 + p/(e^{\theta p} - 1))\alpha + (r + p/(e^{\theta p} - 1))(1+\alpha)]C_r + (r + p/(e^{\theta p} - 1))\alpha e^{\theta} C_{r-1} \}, \quad (2.8)$$

where one must put  $C_{-1} = C_{p-1}$ ,  $C_p = C_0$ . Equation (2.6) conserves the total number of A particles so that

$$\sum_{r=0}^{p-1} \frac{e^{-\theta r}}{1 - e^{-\theta p}} C_r = 1.$$

For very small concentrations of impurity A molecules ( $z_{ab}P_{10} \gg z_{aa}Q_{10}^{VV}$ ), when one may ignore collisions among themselves, the distribution  $\{C_r(t)\}$  is formed by (V-T) processes after the characteristic time  $\tau_{VT}$ . In this case the stationary distribution  $\{C_r^{VT}(\infty)\}$ , which is the solution of the equation  $1_{VT} = 0$ , can differ strongly from the Boltzmann distribution when  $\theta \neq \theta$  at temperature  $T_V^{\alpha}$ :

$$C_r^{(0)}(\infty) = 1 - e^{-\theta}. \quad (2.9)$$

For higher concentrations of the impurity A molecules ( $\tau_{VV} \ll \tau_{VT}$ ) the (V-V) processes will equalize all of the coefficients  $C_r$ , thereby forming a stationary distribution equivalent to (2.9) after the characteristic time  $\tau_{VV}$ .

In the case of most practical interest,  $p = 2$ , Eq. (2.6) with the help of (2.7) and (2.8) takes the form

$$\begin{aligned} dC_0/dt &= \tau_{VT}^{*-1} [C_0^{VT}(\infty) - C_0] + (2\tau_{VV}^*)^{-1} [(C_0 - 1)^2 - e^{-2\theta}] e^{\theta}, \\ C_0 + C_1 e^{-\theta} &= 1 - e^{-2\theta}, \end{aligned} \quad (2.10)$$

where

$$\begin{aligned} \tau_{VT}^* &= \tau_{VT} \frac{e^{2\theta} - 1}{3 + 3e^{-\theta}e^{2\theta} + e^{2\theta} + e^{-\theta}}; \\ \tau_{VV}^* &= \tau_{VV} \frac{(1 - e^{-2\theta})^2}{8(1 + e^{-2\theta})} e^{\theta}; \\ C_0^{VT}(\infty) &= \frac{(e^{\theta} - e^{-\theta})(e^{\theta} + e^{-\theta} + 2e^{-\theta}e^{\theta})}{3 + e^{-\theta} + 3e^{2\theta}e^{-\theta} + e^{2\theta}}. \end{aligned} \quad (2.11)$$

The solution of (2.10) has the form

$$C_0(t) = 1 + a - b \frac{[C_0(0) - (1+a) - b] + [C_0(0) - (1+a) + b] e^{-t/\tau^*}}{[C_0(0) - (1+a) - b] - [C_0(0) - (1+a) + b] e^{-t/\tau^*}},$$

where

$$\begin{aligned} a &= (\tau_{VV}^*/\tau_{VT}^*) e^{-\theta}; \quad b = \sqrt{2a[1 - C_0^{VT}(\infty)] + a^2 + e^{-2\theta}}; \\ \tau^* &= (\tau_{VV}^*/b) e^{-\theta}. \end{aligned}$$

Note that  $C_0(\infty) = 1 + a - b$ ; in the limiting cases  $a \ll 1$  and  $a \gg 1$ ,  $C_0(\infty)$  takes the forms (2.9) and (2.11), respectively.

**3. Dissociation in a Non-Boltzmann Reservoir.** The nonequilibrium vibrational distribution of the impurity molecules in the non-Boltzmann reservoir will significantly affect the rate of dissociation. We first consider the case when only single-quantum transitions occur in the system of A oscillators. The kinetic equation for the vibrational population densities  $x_n$  in the quasistationary regime (it is assumed that the rate of dissociation is slower than the rate of vibrational relaxation) has the form

$$\begin{aligned} -K_d x_n &= z_{ab} \{P_{n+1,n}^* x_{n+1} - (P_{n,n+1}^* + P_{n,n-1}^*) x_n + P_{n-1,n}^* x_{n-1}\}, \\ n &= 0, 1, \dots, s-1, \\ -K_d x_s &= z_{ab} \{P_{s-1,s}^* x_{s-1} - (P_{s,s+1}^* + P_{s,s-1}^*) x_s\}, \end{aligned} \quad (3.1)$$

where  $K_d = -(1/N_a) dN_a/dt$  is the dissociation rate constant (DRC) and  $P_{n,n\pm 1}^*$  are the probabilities of single-quantum vibrational transitions (V-T) and (V-V') exchanges. It is also assumed that dissociation occurs as a result of transitions from the last vibrational level  $s$  to the continuum of vibrational energies with probability  $P_{S,S+1}^*$  in a single collision. We ignore recombination processes, i.e., dissociation is considered only in the initial stages. The methodology of solving equations of the type (3.1) is well known [3]; within small terms of order  $\sim (1/z_{ab})K_d$  included we can write

$$x_n = x_n^{(0)} - K_d \sum_{j=0}^{n-1} x_j^{(0)} \sum_{i=j}^{n-1} \frac{\Pi_{i+2}^n}{z_{ab} P_{i+1,i}^*}; \quad (3.2)$$

$$K_d = \frac{x_0^{(0)} \Pi_1^s}{\sum_{j=0}^{s-1} x_j^{(0)} \sum_{i=j}^s \frac{\Pi_{i+2}^s}{z_{ab} P_{i+1,i}^*}}; \quad (3.3)$$

where

$$\Pi_i^j = \prod_{l=i}^j \frac{P_{l-1,l}^*}{P_{l,l-1}^*}, \quad i \leq j, \quad \Pi_i^i = 1, \quad i > j; \quad (3.4)$$

$x_n^{(0)} = x_0 \Pi_1^n$  is the stationary, unperturbed vibrational distribution. In the equilibrium reservoir the condition of detailed balance is satisfied

$$P_{ij}^*/P_{ji}^* = \exp[-(E_i - E_j)/kT], \quad (3.5)$$

where  $E_i$  is the vibrational energy of the A molecules in state  $i$ . Then  $\Pi_1^j = \exp[-(E_j - E_{j-1})/kT]$  and (3.2), (3.3) can be transformed into expressions for the population density of the vibrational levels and the thermal DRC familiar from the theory of thermal dissociation [3].

In the case of a non-Boltzmann reservoir, the condition of detailed balance (3.5) is not satisfied in general, however (3.4) can be calculated, using the following reasoning. We break up the vibrational spectrum of the molecule into two regions. We will assume that in the low-level region ( $n \leq m$ ), resonant (V-V') exchange ( $p = 1, q > 1$ ) plays the dominant role ((V-V) exchange is insignificant in this region because it does not alter the Boltzmann distribution established by the (V-V') exchange). In the high-level region ( $n \geq m$ ), (V-T) exchange is dominant. Thus, the following relations are valid

$$P_{n-1,n}^* = Q_{n-1,n} \sigma_{n,m} + P_{n-1,n}, \quad \sigma_{n,m} = \begin{cases} 1, & n \leq m, \\ 0, & n > m, \end{cases}$$

$$Q_{n-1,n}/Q_{n,n-1} = e^{-\vartheta}, \quad P_{n-1,n}/P_{n,n-1} = \exp[-(E_n - E_{n-1})/kT].$$

Using the inequality  $Q_{n,n-1} \gg P_{n,n-1}$  we obtain

$$\Pi_i^j = \begin{cases} \exp[-\vartheta(j+1-i)], & i, j < m, \\ \exp[-(E_j - E_m)/kT - \vartheta(m-i+1)], & i < m < j, \\ \exp[-(E_j - E_{i-1})/kT], & i, j > m. \end{cases}$$

For the stationary unperturbed vibrational distribution we have

$$x_n^{(0)} = \begin{cases} N_a z_V^{-1} \exp(-\vartheta n), & n \leq m, \\ N_a z_V^{-1} \exp\left(-\vartheta m + \Theta m - \frac{E_n}{kT}\right), & n > m, \end{cases} \quad (3.6)$$

where  $z_V = \frac{1}{N_a} \sum_{n=0}^{\infty} x_n^{(0)}$ . With the help of the inequality  $e^{-\vartheta m} \ll 1$  the following is valid

$$z_V \approx \sum_{n=0}^s e^{-\vartheta n} = z_V(T_v^a).$$

In the inner summation over  $i$  in (3.3) it is possible to carry out the summation from  $i = 0$  without introducing large errors; the important contributions in  $\sum_{i=0}^s (z_{ab} P_{i+1,i}^*)^{-1} \Pi_{i+2}^i$  involve terms with  $i > m$ . We then obtain

$$K_d = e^{\Theta m(1-T/T_v^a)} \left/ \left[ z_V(T_v^a) \sum_{i=0}^s (z_{ab} P_{i+1,i})^{-1} e^{E_{i+1}/kT} \right] \right. \quad (3.7)$$

In this same approximation, the DRC in the equilibrium reservoir with temperature  $T$  has the form

$$K_d^{(0)} = 1 \left/ \left[ z_V(T) \sum_{i=0}^s (z_{ab} P_{i+1,i})^{-1} e^{E_{i+1}/kT} \right] \right. \quad (3.8)$$

The ratio of the DRC for the non-Boltzmann reservoir (3.7) to the equilibrium DRC (3.8) is

$$K_d/K_d^{(0)} = (z_V(T)/z_V(T_v^a)) e^{\Theta m(1-T/T_v^a)}. \quad (3.9)$$

From (3.9) it is clear that  $K_d/K_d^{(0)} \gg 1$  even when  $T_v^a$  only slightly exceeds  $T$ .

Formulas like (3.9) were first obtained by Losev [4] and Kuznetsov [5] in the treatment of the kinetics of thermal dissociation under conditions when the vibrational temperature differs from the gas temperature.

The case of multiquanta resonant (V-V') transitions ( $p > 1$ ) is not different in principle from the single-quantum case ( $p = 1$ ). Dissociation hardly distorts the distribution in the  $n < m$  region, therefore one can regard intense single-quantum (V-V') exchange together with (V-T) and (V-V) exchanges as forming a stationary distribution of the type (1.1) for the low level region, and thus the relative population density  $x_m$  of level  $m$  will be fixed. It is convenient to write the DRC in this case as

$$K_d = x_m^{(0)} e^{E_m/kT} / \left[ \sum_{i=0}^s (z_{ab} P_{i+1,i}^*)^{-1} \exp(E_{i+1}/kT) \right].$$

The population density  $x_m^{(0)}$  according to (1.1) is determined not only by the vibrational temperature  $T_v^a$ , but also by the number of particles in the group of levels into which level  $m$  falls. For sufficiently high concentration of A molecules, (V-V) processes lead to the Boltzmann distribution, as was shown above. The resulting quasistationary distribution (unperturbed by dissociations) is equivalent to (3.6). In this case the ratio (3.9) of the DRC in the non-Boltzmann reservoir to the equilibrium DRC remains valid. For arbitrary concentration of the impurity A molecules

$$K_d/K_d^{(0)} = z_v(T) C_r e^{\theta_m(1-T/T_v^a)} \quad (3.10)$$

Using the fact that  $C_r > C_0 e^{-\theta(p-r)}$  (this follows from the monotonicity of the distribution (1.1)) the ratio (3.10), as well as (3.9), can exceed unity by several orders of magnitude.

Finally, we note that the increase in the dissociation rate due to resonant (V-V') exchange in the low vibrational levels of the impurity molecules allows in principle chemical reactions to be conducted in the non-Boltzmann reservoir at very low gas temperatures; in general these reactions would not proceed under normal conditions at these temperatures.

#### LITERATURE CITED

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