

VIBRATIONAL RELAXATION OF DIATOMIC
MOLECULES - ANHARMONIC OSCILLATIONS
IN A BOLTZMANN RESERVOIR.
TWO-COMPONENT SYSTEM

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In the general case of a binary mixture of diatomic molecules, relaxation of the initial nonequilibrium vibrational energy distribution is accomplished by way of various elementary processes (see, for example, [1]): vibration-vibration (V-V) exchange between molecules of the same kind, vibration-vibration (V-V') exchange between molecules of different kinds, and vibrational-translation (V-T) exchange. The solution of the kinetic problem, formulated in quantum statistics, is extremely difficult even with the help of powerful modern computational devices because of the necessity of including multiquanta transitions, and in the case of a mixture of molecules with different principal vibrational frequencies, these transitions can be dominant.

In [2] a diffusion description of vibrational relaxation is given for a two-component system of anharmonic oscillators with the fundamental vibrational frequencies of the components of the mixture being arbitrary. The solution of a kinetic equation, i.e., a rigorous kinetic analysis, is not carried out in [2].

The kinetic problem is simplified considerably, while still retaining all of the basic features of the process, in the case of relaxation of a dilute mixture of nonequilibrium impurity molecules of one kind in a reservoir of molecules of another kind. This system turns out to be convenient for comparing the roles of V-V', V-V, and V-T exchange processes for different values of the ratio of the fundamental vibrational frequencies $W = \omega_{02}/\omega_{01}$ and different values of the adiabatic parameter $\xi_0 = \omega_{01}\tau_{int}$ (ω_{01}, ω_{02} are the principal vibrational frequencies of the impurity molecules and reservoir molecules, respectively; τ_{int} is the characteristic interaction time of the molecules). This type of nonequilibrium system is realized in practice either under the action of a source of excited molecules (optical or chemical excitation), or in a mixture of a small amount of heated (cooled) gas with another cooled (heated) gas serving as the reservoir.

In the present paper, which is an extension of [2, 3], we study the relative importance of V-V' and V-T exchange processes as dependent on the parameters W and ξ_0 . The kinetic mechanisms of vibrational relaxation are considered for a dilute mixture of a nonequilibrium impurity gas in a Boltzmann reservoir for $W \neq 1$ (i.e., a two-component system) over a wide range of values of W .

1. Kinetic Equation. The process of vibrational relaxation in a two-component system of classical oscillators is described by the following pair of equations [2]:

$$\frac{\partial f_i}{\partial t} = \int d\varepsilon' \left[\frac{\partial}{\partial \varepsilon} \left(f_i^0(\varepsilon) f_1^0(\varepsilon') B_{11}^{i1} \frac{\partial \varphi_{i1}}{\partial \varepsilon} + f_i^0(\varepsilon) f_1^0(\varepsilon') B_{12}^{i1} \frac{\partial \varphi_{i1}}{\partial \varepsilon'} \right) + \frac{\partial}{\partial \varepsilon} \left(f_i^0(\varepsilon) f_2^0(\varepsilon') B_{11}^{i2} \frac{\partial \varphi_{i2}}{\partial \varepsilon} + f_i^0(\varepsilon) f_2^0(\varepsilon') B_{12}^{i2} \frac{\partial \varphi_{i2}}{\partial \varepsilon'} \right) \right] (i = 1, 2), \quad (1.1)$$

where t is the time, ε is the vibrational energy, f_i^0 is the equilibrium distribution function; $\varphi_{ij}(\varepsilon, \varepsilon', t) = f_i(\varepsilon, t) f_j(\varepsilon', t) / f_i^0(\varepsilon) f_j^0(\varepsilon')$; $B_{11}^{ij} = \frac{\langle \Delta^2 \rangle}{2\tau_p}$; $B_{12}^{ij} = \frac{\langle \Delta \Delta' \rangle}{2\tau_p}$; Δ, Δ' are the changes in the vibrational energies ε and ε' of the first and second collision partners; $\langle \dots \rangle$ denotes an average with respect to all collision parameters; τ_p is the time of a mean free path for molecules of type i in an atmosphere of molecules of type j . Equation (1.1) must be supplemented by the following boundary conditions derived from the constancy of the number of particles

$$\left[f_i^0(\varepsilon) f_j^0(\varepsilon') B_{11}^{ij} \frac{\partial \varphi_{ij}}{\partial \varepsilon} + f_i^0(\varepsilon) f_j^0(\varepsilon') B_{12}^{ij} \frac{\partial \varphi_{ij}}{\partial \varepsilon'} \right] \Big|_{\substack{\varepsilon=\varepsilon'=0, \\ \varepsilon=D_1(D_2), \\ \varepsilon'=D_2(D_1)}} = 0$$

and also the initial conditions $f_i(\varepsilon, 0) = \Psi_i(\varepsilon)$. Here D_i is the dissociation energy of the i -th components.

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In (1.1) terms with $i=j$ describe interactions of molecules of a single kind with each other (V-V and V-T exchanges), while terms with $i \neq j$ refer to interactions between molecules of different kinds (V-V' and V-T exchanges).

If the molecules of type 1 are out of equilibrium with respect to vibrational energy and form a weak impurity in a reservoir of molecules of type 2 ($f_2(\varepsilon', t) \equiv f^0(\varepsilon')$), then the second equation in (1.1) reduces to an identity and the first, after ingetration with respect to ε' takes the form

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial \varepsilon} \left[B(\varepsilon) f^0(\varepsilon) \frac{\partial}{\partial \varepsilon} (f/f^0) \right] \quad (1.2)$$

where the index 1 is omitted. The function $B(\varepsilon)$ denotes an average of the coefficient $B_{11}^{12}(\varepsilon, \varepsilon')$ with respect to the nonequilibrium distribution of the reservoir

$$B(\varepsilon) = \int_0^{D_2} B_{11}^{12}(\varepsilon, \varepsilon') f_2^0(\varepsilon') d\varepsilon'. \quad (1.3)$$

The boundary conditions take the form

$$\left[B(\varepsilon) f^0(\varepsilon) \frac{\partial}{\partial \varepsilon} (f/f^0) \right] \Big|_{\substack{\varepsilon=0 \\ \varepsilon=D_1}} = 0. \quad (1.4)$$

We consider initial conditions of two different types: (1) a Boltzmann distribution with temperature T_0 ; and (2) a strong inversion distribution of the form $f(\varepsilon, 0) = C \exp[-p(\varepsilon - \varepsilon_{\max})^2]$, where ε_{\max} defines the maximum of the distribution and p and C are constants.

2. System of Harmonic Oscillators. In a two-component system of harmonic oscillators, it is necessary to take into account with multiquanta V-V' exchange processes, as these can play an important role when $W \neq 1$. It can be shown [4] that in a system of harmonic oscillators with multiquanta transitions, the kinetic coefficient B has the form

$$B(x) = D_1^2 \sum_{n \geq 1} \frac{x^n}{\tau_n} \quad (x = \varepsilon/D_1). \quad (2.1)$$

Here we let τ_m be the characteristic times of n -quanta vibrational exchange, such that for $n=1$ we have $1/\tau_1 = 1/\tau_1^{VT} + 1/\tau_1^{VV}$, where the characteristic times of single-quantum V-T exchange and n -quanta V-V' exchange are determined from the relations:

$$\frac{1}{\tau_1^{VT}} = \frac{2M\Lambda_1\Phi(\xi_0)}{a\mu_1\tau_p\sqrt{2\pi}(4\sqrt{2}/e-1)},$$

$$\frac{1}{\tau_n^{VV'}} = \sum_{m \geq 1} \frac{\sqrt{2\pi m} 16M\beta_1^2 \left(\frac{m}{ea}\right)^m}{a^2\mu_1\alpha^2\tau_p f(n,m)} \left(\frac{\Lambda_1\alpha^2}{4\beta_1^2}\right)^n \left(\frac{\Lambda_2\alpha^2}{4\beta_2^2}\right)^m \frac{nm}{(n!m!)^2} \Phi(\xi_0 | n - mW |),$$

$$f(n,m) = 2\pi m^{m+1/2} e^{-m} [(n+1)^{n+3/2} e^{-(n+1)} - n^{n+3/2} e^{-n}],$$

Here n and m are the numbers of quanta received or transmitted by the impurity and reservoir molecules, respectively. We have introduced the following notation; τ_p , time of a mean free path (collision time) for the impurity molecules; M , reduced mass of the colliding molecules; μ_i , reduced mass of molecules of the i -th kind; $a = D_2/kT$; k , Boltzmann constant, T , equilibrium temperature; $\beta_i = \omega_{0i}/\sqrt{\mu_i/2D_i}$; m_{1i} , m_{2i} , masses of the atoms comprising a molecule of the i -th kind; $\Lambda_i = (m_{1i}^2 + m_{2i}^2)/(m_{1i} + m_{2i})^2$; $1/\alpha$, characteristic interaction range of the intermolecular potential. Finally the function Φ is given by

$$\Phi(y) = y^2 \int_0^\infty e^{-z} \operatorname{csch}^2(y/\sqrt{z}) dz \simeq \begin{cases} 8\sqrt{\frac{\pi}{3}} y^{7/3} \exp(-3y^{2/3}), & y \gg 1, \\ \frac{1}{2}(3 - e^{-2y/3}) e^{-2y/3}, & 0 \leq y \leq 20. \end{cases}$$

Equation (1.2) with the coefficient B given by (2.1) does not have the property of canonical invariance because of the presence of nonlinear terms in x in (2.1) from multiquanta V-V' exchange processes. The relaxation process of the average energy cannot be described by a single relaxation time. It can be shown, however, that in the near-equilibrium stages of the process, i.e., when $t \rightarrow \infty$, the system relaxes according to an exponential law with a relaxation time determined by the following relation [4]:

$$\frac{1}{\tau_h} = \sum_{n \geq 1} \frac{n!}{a^{n-2}\tau_n}.$$

Relations between the relaxation times of the different vibrational exchange process (V-T and n-quanta V-V') are determined by the values of W and ξ_0 . The importance of V-V' exchange increases with increasing ξ_0 and the range of values of W for which V-V' exchange dominates expands. We analyze the following cases for determining the relative importance of the various elementary processes as dependent upon the values of W and ξ_0 : for arbitrary W and $\xi_0 < 5$, and also for $W < 1/3$ or $W > 3$ and arbitrary ξ_0 , V-T exchange is dominant with respect to rate, i.e., $\tau^{VT} < \tau^{VV'}$ and $\tau_h \approx \tau^{VT}$; for $1/3 \leq W \leq 3$ with $\xi_0 \geq 10$, V-V' exchange dominates, while for $1/3 \leq W \leq 3/2$ the fastest of the V-V' exchange processes is single-quantum exchange, i.e., $\tau_1^{VV'} < \tau^{VT}$, $\tau_n^{VV'}$ and $\tau_h \approx \tau_1^{VV'}$.

3. System of Anharmonic Oscillators. Dependence of B(x). In [2] formulas for the kinetic coefficients B_{12}^{ij} are given for the general case of arbitrary intermolecular and intramolecular potentials. In the case of an exponential repulsive intermolecular potential and a Morse intramolecular potential, after performing the integration indicated in (1.3) and averaging over different orientations of all colinear collisions we have

$$B(x, \xi_0, W) = B_{VT}(x, \xi_0) + B_{VV'}(x, \xi_0, W) \cong \quad (3.1)$$

$$\cong 16D_1^2/\tau_h \sigma (1-x) \left[2 \left(\frac{\beta_2}{\alpha} \right)^2 \frac{1}{\Lambda_2} \sum_{n \geq 1} \left(\frac{1-\sqrt{1-x}}{\sqrt{x}} \right)^{2n} \Phi(n\xi_0 \sqrt{1-x}) + \sum_{n, m \geq 1} \left(\frac{1-\sqrt{1-x}}{\sqrt{x}} \right)^{2n} F_{n,m}(x, \xi_0, W), \right]$$

where

$$F_{n,m} = \frac{A(T)}{m^2} \int_0^1 \Phi(\xi_0 | n\sqrt{1-x} - mW\sqrt{1-x'} |) \left(\frac{1-\sqrt{1-x'}}{\sqrt{x'}} \right)^{2m} dx';$$

$$x' = \frac{\epsilon}{D_2}, \quad \xi = \xi_0 \sqrt{1-x}; \quad A(T) = \left(\int_0^1 \frac{e^{-D_2 x' / kT} dx'}{\sqrt{1-x'}} \right)^{-1}; \quad \sigma = \frac{\tau_h}{\tau^{VV'}};$$

and $\tau^{VV} = \mu_1 \tau_h D_2 \beta_2^2 / \Lambda_1 \Lambda_2 M k T \alpha^2$ is of order of the characteristic time of V-V exchange of the impurity oscillators. In the case of a single component system we have $W=1$, $\tau_h = \tau_1$, $\tau^{VV} = \tau_1^{VV}$, $\sigma = \tau_1^{VT} / (\tau_1^{VT} + \tau_1^{VV})$ and (3.1) reduces to the corresponding result in [3].

The first and second terms in (3.1) describe V-T and V-V' exchange processes. The indices n and m refer to the number of quanta received or transmitted as a result of collisions by the impurity and reservoir oscillators, respectively. When $D_2/kT \gg 1$ the factor $\exp(-D_2 x'/kT)$ is rapidly falling with increasing x and we can therefore calculate F_{nm} approximately for values $x' \ll 1$. Expanding $\sqrt{1-x'}$ in a power series in x' and cutting off the series at the first term, and also using the approximate expression for Φ we obtain after integration

$$F_{nm} \cong \frac{D_2}{kT} \sqrt{\frac{\pi}{2}} m^{-3/2} \left(\frac{m}{4e} \right)^m \left[\frac{3}{(m\xi_0 W/3 + a)^{m+1}} - \frac{\exp\left(-\frac{2}{3}\xi_0 |n\sqrt{1-x} - mW|\right)}{(2m\xi_0 W/3 + a)^{m+1}} \right] \exp\left(-\frac{2}{3}\xi_0 |n\sqrt{1-x} - mW|\right) \quad (3.2)$$

for $0 \leq \frac{2}{3}\xi_0 |n\sqrt{1-x} - mW| \leq 20$ and

$$F_{nm} \cong (D_2/kT) 8 \sqrt{\frac{2}{3}} \pi m^{-3/2} (\xi_0 |n - mW|)^{7/3} \left(\frac{m}{4e} \right)^m \frac{\exp[-3(\xi_0 |n - mW|)^{2/3}]}{[a + m\xi_0 W/(\xi_0 |n - mW|)^{1/3}]^{m+1}} \quad (3.3)$$

for $\xi_0 |n\sqrt{1-x} - mW| \gg 1$.

With study of the dependence of the coefficient B(x, ξ_0 , W) one can make some qualitative deductions on the influence of anharmonicity on the kinetics of vibrational relaxation without directly solving (1.2).

The nature of the interaction of the impurity and reservoir molecules is mainly determined by the adiabatic parameter ξ_0 and the value of W. There exists a relation between ξ_0 and a: $\xi_0 = \xi_0^0 \sqrt{a_x}$, $\xi_0^0 = \frac{\pi \beta_1}{\alpha} \sqrt{M/\mu_1}$. The values of W and ξ_0^0 depend on the specific system; their values for some actual mixtures are given in Table 1.

The effectiveness of V-T exchange depends weakly on the nature of the reservoir and is mainly determined by the value of ξ_0 . It falls rapidly with increasing ξ_0 , while for fixed ξ_0 it increases (more strongly as ξ_0 increases) with increasing molecular excitation x.

TABLE 1

X_1-X_2	$W = \frac{\xi_0 \xi_1}{0.01}$	ξ_0^0	X_1-X_2	$W = \frac{\xi_0 \xi_1}{0.01}$	ξ_0^0
I ₂ -N ₂	11	0,60	N ₂ -HF	1,75	1,75
Cl ₂ -N ₂	4,175	1,39	F ₂ -O ₂	1,71	2,6
O ₂ -HF	2,62	1,47	NO-HCl	1,57	2,41
F ₂ -N ₂	2,55	1,86	O ₂ -N ₂	1,49	2,12
NO-HF	2,17	1,63	NO-N ₂	1,24	2,25
O ₂ -HCl	1,9	2,19	CO-N ₂	1,09	2,13
CO-HF	1,9	1,57	HF-N ₂	0,57	5,00

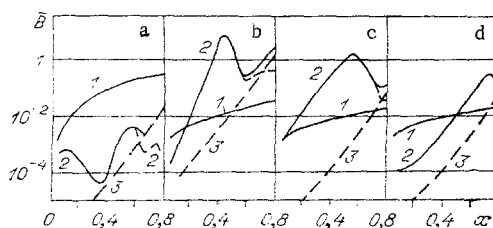


Fig. 1

It follows from (3.2) that $V-V'$ exchange reaches resonance when the condition

$$n\sqrt{1-x} - mW = 0, \quad (3.4)$$

is satisfied, and this determines what energy ranges play a part in resonant $V-V'$ transitions. From (3.4) it follows that for low enough reservoir temperatures ($D_2/kT \gg 1$), anharmonic vibrations of the reservoir molecules are not significant. It can be shown that $V-V'$ exchange of n quanta of an impurity molecule by m quanta of a reservoir molecule is nearly resonant in a certain neighborhood of the point $x_{\max} = 1 - (mW/n)^2$ and the width of this neighborhood is determined by the formula $\delta = 6mW/n^2 \xi_0$, from which it follows that the width of the resonant peak of the function $B_{VV'}$, is inversely proportional to the square of the number of quanta transmitted by an impurity molecule and directly proportional to the change in the number of quanta of reservoir molecules; the larger the value of ξ_0 , the narrower the resonant peak of $B_{VV'}$. From (3.1) to (3.3) it follows that the effectiveness of $V-V'$ transitions (accompanied by the exchange of n quanta of the impurity for m quanta of the reservoir) falls much more rapidly with increasing m than with increasing n .

The importance of anharmonicity in $V-V'$ exchange increases with increasing ξ_0 and strongly depends on W . In Fig. 1a-1d we have plotted the behavior of $\bar{B}(x) = B(x)\bar{n}_h/D_1^2$ with $\xi_0 = 30$ and $W = 2, 3/2, 2/3, 1/2$. The curves labeled 1 correspond to harmonic oscillations, curves labeled 2 ($B_{VV'}$) and 3 (\bar{B}_{VT}) correspond to anharmonic oscillations. For integral values of $W = 1, 2, \dots$ the exchange is exactly resonant in the case of harmonic oscillators because (3.4) is satisfied for $m = 1$ and $n = 1, 2, \dots$ in this case ($x \ll 1$). Anharmonic molecular vibrations for integral W lead to violation of the resonance condition (3.4) and to a decrease in the effectiveness of $V-V'$ exchange which becomes more pronounced the less closely (3.4) is satisfied (see curves 1 and 2 in Fig. 1a). In the case of nonintegral values of W , the $V-V'$ exchange for harmonic oscillations can be strongly nonresonant. The anharmonicity in this case leads to a range of values of x for which the resonant condition will be satisfied and thus $V-V'$ exchange for anharmonic oscillations will be more effective than $V-V'$ exchange for harmonic oscillations (see curves 1 and 2 of Fig. 1b-d).

We now compare the importance of $V-T$ and $V-V'$ exchange in a system of anharmonic oscillators for specific values of W and ξ_0 : 1) for arbitrary W and $\xi_0 \gg 10$ and also for $W < 1/3$ or $W > 3$ and arbitrary ξ_0 , $V-T$ exchange is dominant according to rate; 2) for $1/3 \leq W \leq 3$ and $\xi_0 \gg 10$ it is always possible to partition the energy into ranges where either $V-T$ or $V-V'$ exchange dominates. For $1/3 \leq W < 1$ (see Fig. 1c, d) single-quantum $V-V'$ exchange dominates for practically all values of x . When $W > 1$, $V-T$ exchange dominates $V-V'$ exchange by only an order of magnitude in the region of high vibrational excitation (see Fig. 1a, b). With increasing ξ_0 the importance of $V-V'$ exchange increases and its influence extends in the direction of increasingly higher values of the excitation energy.

We also point out that when the nonequilibrium gas is a weak impurity, multiquanta $V-V'$ exchange becomes very important for $W > 1$. For example when $W = 2$ (see Fig. 1a) it is necessary to include the exchanges 2-1 (2 quanta of the impurity for 1 quanta of the reservoir) and 3-1. When $W < 1$ the exchange 1-1 dominates other $V-V'$ exchanges.

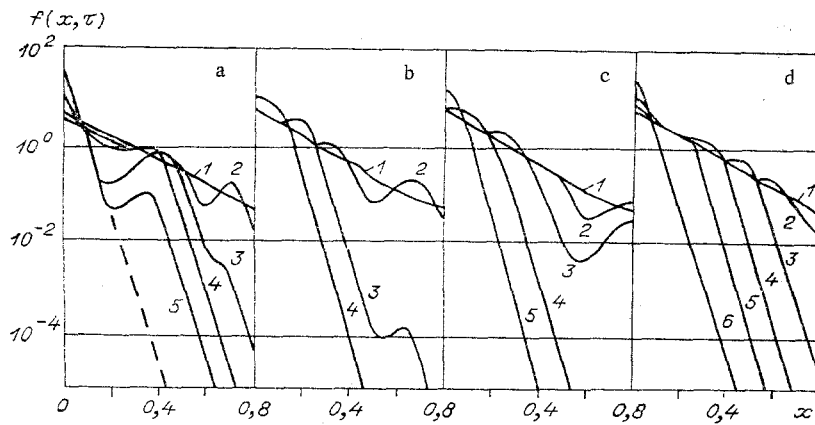


Fig. 2

Relaxation of the Distribution Function. The kinetic equation (1.2) with the boundary conditions (1.4) was solved numerically over wide ranges of values of W and ξ_0 . Particular attention was devoted to the ranges $1/3 \leq W \leq 3$, $\xi_0 \geq 10$, where $V-V'$ exchange is either significant or dominating. $V-V$ exchange ($w=1$, a single-component system) has been studied in detail in [3]; $V-T$ exchange has been studied in [5]. As a time scale for the process, we use τ_h (the relaxation time of the average energy in a system of harmonic oscillators). This time scale is convenient for studying the effect of anharmonicity on the kinetics of the process. In appropriate limiting cases, τ_h reduces to τ_i used in [3, 5].

In Figs. 2 and 3 we plot the molecular vibrational energy distribution function $f(x, \tau)$ where $\tau = t/\tau_h$ and the vibrational temperature

$$T_V(x, \tau) = -D_1/k[\partial \ln f(x, \tau)/\partial x]^{-1}$$

for $\xi_0 = 30$, $D_1/kT_0 = 7$ and $D_1/kT = 40$ at different times during decay of the initial Boltzmann distribution. Figure 1a refers to $W=2$, curves 1-5 refer to the following values of τ : $2.3 \cdot 10^{-3}$, $2.4 \cdot 10^{-2}$, 4.8 ; $2.4 \cdot 10^1$, $1.25 \cdot 10^2$. Figure 1b refers to $W=3/2$ with curves 1-4 labeling the following values of τ : 10^{-4} ; 10^{-3} ; 10^{-2} ; 2 . Figure 1c refers to $W=2/3$ with curves 1-4 referring to the following values of τ : $3 \cdot 10^{-4}$; $3 \cdot 10^{-3}$; $3 \cdot 10^{-2}$; $3 \cdot 10^{-1}$. Finally Fig. 1d refers to $W=1/2$ with curves 1-6 labeling the following values of τ : $2.5 \cdot 10^{-3}$; $2.5 \cdot 10^{-2}$; 2.5 ; $1.25 \cdot 10^1$; $6.25 \cdot 10^1$; $6.5 \cdot 10^1$.

Relaxation of the distribution function for different values of W have some common features. In the cases of the most effective vibrational exchange (near-resonant $V-V'$ exchange and $V-T$ exchange for large x), after a time of order of the characteristic time for these processes, a quasi-Boltzmann distribution with $T_V \approx T$ is established; however the population density exceeds that in the equilibrium case.

For example, with $W=2$ (see Fig. 2a, 3a) the various vibrational exchange processes can be arranged in order of decreasing rate as follows: For $x \geq 0.7$ the fastest process is $V-T$ exchange so that after a time $\tau \sim 2 \cdot 10^{-2}$ a quasi-Boltzmann distribution is established with $T_V \approx T$ (curves 2-5). The next fastest process is near-resonant $V-V'$ exchange 3-1 (3 impurity quanta for 1 reservoir quantum) so that for $0.5 \leq x \leq 0.6$ a quasi-Boltzmann distribution is formed with $T_V \approx T$ after a time of order $\tau \sim 2 \cdot 10^{-1}$. Then follow two processes with practically the same rates; nonresonant $V-V'$ exchange of type 3-1 and $V-T$ exchange for $0.6 \leq x \leq 0.7$ in which excess molecules with upper repopulated levels "diffuse" into lower energy ranges with a relaxation time of order $\tau \sim 20$ (curve 4). During a time of about the same order $\tau \sim 25$, near-resonant $V-V'$ exchange of type 2-1 causes a quasi-Boltzmann distribution to be established in the low-energy region ($x < 0.15$). The slowest process is that of nonresonant $V-V'$ exchange of types 3-1 and 2-1 for $0.15 \leq x \leq 0.35$ and these determine the time $\tau > 10^2$ to establish complete equilibrium (curve 5).

For $W=3/2$ (see Fig. 2b, 3b) the fastest process is $V-T$ exchange for $x > 0.7$ and near-resonant $V-V'$ (2-1) exchange for $0.3 \leq x \leq 0.5$ and as a result of a quasi-Boltzmann distribution is formed in these energy ranges after a time of order $\tau \sim 10^{-2}$. Next in order of decreasing rate are the near-resonant $V-V'$ exchanges of types 2-1 and 3-1 and $V-T$ exchange for $0.5 \leq x \leq 0.7$ with the relaxation time $\tau \sim 2 \cdot 10^{-1}$. The slowest process in this case is that of strongly nonresonant $V-V'$ exchange of type 2-1 for $x \leq 0.2$ with characteristic time $\tau > 2$.

For $1/3 \leq W < 1$ the most important of the $V-V'$ processes is single-quantum 1-1 exchange, along with it a greater or lesser role (depending on the specific values of W and ξ_0) is played by $V-T$ exchange. For example, when $W=2/3$ (see Fig. 2c, 3c) after a time of order $\tau \leq 3 \cdot 10^{-2}$ in the region $0.4 \leq x \leq 0.6$ (near-resonant

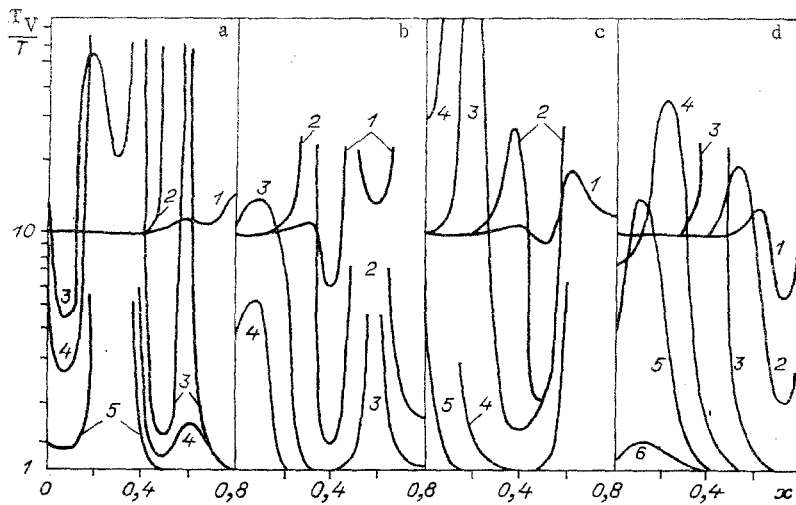


Fig. 3

$V-V'$ exchange of type 1-1) and $x \gtrsim 0.8$ ($V-T$ exchange) a quasi-Boltzmann distribution is established with temperature T ; the time to establish complete equilibrium ($\sim 3 \cdot 10^{-1}$) is determined by nonresonant $V-V'$ exchange for small x and also $V-T$ exchange for $x \approx 0.6$. With increasing W the region where single-quantum exchange is important is shifted toward larger x . For example, when $W=1/2$ (see Fig. 2c, 3d) single-quantum $V-V'$ exchange results in a quasi-Boltzmann distribution with temperature T for $x > 0.5$ after a time of order $\tau \sim 2.5$; as the time increases this range is widened in the direction of increasingly lower energies.

The relaxation process of the distribution function for an initial inversion distribution in the case $W=1$ (single-component system) has been worked out in [3]. When $W \neq 1$ this process occurs in an analogous fashion; the relaxation mechanisms are determined principally by the value of x_{\min} at which $B(x)$ reaches a minimum (or minima) and also the value x_{\max} which defines the maximum of the initial distribution $x_{\max} = \varepsilon_{\max}/D$.

Application of our results to the case of a completely nonequilibrium binary mixture, i.e., when the nonequilibrium component of the mixture cannot now be treated as a weak impurity allows one to make some qualitative conclusions. In this system the following cases can occur, depending on the actual values of W and ξ_0 : 1) $\tau_{VV}^1, \tau_{VV}^2 \ll \tau_{VV'} \ll \tau_{VT}$ (τ_{VV}^i is the characteristic time of single-quantum $V-V$ exchange for the i -th component). In this case in the low energy range, after a time of order $\tau \lesssim 10$ [3] Trinorov distributions are established for each of the components. Then after a time of order $\tau_{VV'}$ "mixing" of quanta between the components occurs [1]. For $W=3/2$, $\xi_0=30$ and in the low energy region ($\tau_{VV'} \sim \tau_{VT}$) the "mixing" occurs so slowly that each of the components will have its own Trinorov distribution until complete equilibrium is established; 2) $\tau_{VV}^1 \sim \tau_{VV}^2 \sim \tau_{VV'}$. In the general case of multiquanta $V-V'$ exchange the Trinorov distribution of each of the components will not occur because of nonconservation of the number of quanta. For the example $W=2$ in the low energy region, as a result of cooperative action of these three processes, after a time of order $\tau \sim 25$ quasi-Boltzmann distributions with $T_V \approx T$ will be established for each of the components at low energy.

Relaxation of the Average Energy. As in the case of a single-component system [3] (see also [5]) we define the time-dependent relaxation time of the average energy as

$$\tau_e = -\{d \ln [E(t) - E(\infty)]/dt\}^{-1}.$$

In order to describe the effect of anharmonic molecular vibrations on the relaxation of $E(t)$ we define $g(t) = \tau_e(t)/\tau_h$.

If $V-T$ exchange dominates with respect to rate ($\xi_0 < 10$ and arbitrary W , or $W < 1/3$, $W > 3$ and arbitrary ξ_0), then the behavior of $g(t)$ is qualitatively determined by the same mechanisms as in the case of dilute mixture of diatomic molecules in an inert gas medium; this has been studied in detail [5].

For $1/3 \lesssim W \lesssim 3$ and $\xi_0 \gtrsim 10$, i.e., when vibration-vibration exchange processes are important, the presence of a minimum (minima) in $B(x)$ leads to radical complication of the behavior of $g(t)$ as a function of ξ_0 , W , and the initial conditions. In particular, g depends on the initial conditions (the initial population density of the region $x \gtrsim x_{\min}$) during practically the entire relaxation process. Figure 4 shows the dependence of g on $\tau = t/\tau_h$ for fixed initial conditions (an initial Boltzmann distribution with $D_1/kT_0 = 7$, $\xi_0 = 30$, $D_1/kT = 40$) and for different values of W within $1/3 \lesssim W \lesssim 3$ ($W=2, 3/2, 2/3, 1/2, 1$ correspond to curves 1-5, respectively). The

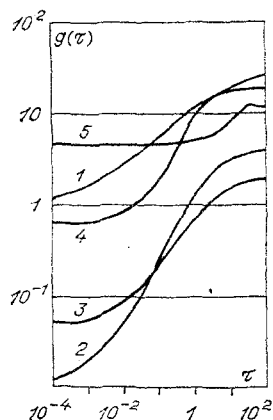


Fig. 4

effect of anharmonicity is seen in the strong dependence of g on τ ; in all cases considered g increases monotonically and changes by one or two orders of magnitude during the relaxation process. It is clear from Fig. 4 that, depending on W and the degree of deviation of the system from equilibrium, both the case $\tau_e < \tau_h$ (anharmonicity leads to an acceleration of the process) and $\tau_e > \tau_h$ (anharmonicity leads to a slowing of the process) can occur. For integral values of W such as $W=2$ (curve 1) and $W=1$ (curve 5), $\tau_e > \tau_h$ during the entire process. But when $W=3/2$, $2/3$ and $1/2$ (curves 2, 3, 4, respectively) we have $\tau_e < \tau_h$ initially when the high-energy region is significantly populated and $B > B_h$; as time increases to the point where most of the molecules are now found in the low-energy region with $B < B_h$, the relaxation process is slowed and $\tau_e > \tau_h$.

We estimate the relaxation time of the average energy in the limit $\tau \rightarrow \infty$. Because the relaxing system is close to equilibrium, we can use the approximation

$$f(\epsilon, t) = [1/E(t)] \exp[-\epsilon/E(t)]. \quad (3.5)$$

Substituting (3.5) into (1.2), we obtain an equation which describes the relaxation of the average vibrational energy of the nonequilibrium impurity in the limit $\tau \rightarrow \infty$:

$$dE(t)/dt = (kT - E(t))/\tau_e(\infty),$$

where

$$\tau_e(\infty) = (kT)^2 \int_0^{D_1} B(\epsilon) f^0(\epsilon) d\epsilon. \quad (3.6)$$

Equation (3.6) correctly describes the behavior of $\tau_e(\infty)$ as a function of W and ξ_0 .

In conclusion, we summarize the basic features of the effect of anharmonicity on the kinetics of vibrational relaxation in a binary mixture of diatomic molecules. The effect of anharmonicity is determined principally by the values of the adiabatic parameter ξ_0 and the ratio of fundamental frequencies W . For arbitrary W and $\xi_0 \ll 10$ or for $W < 1/3$, $W > 3$ and arbitrary ξ_0 , $V-T$ exchange dominates with respect to rate. For $1/3 \lesssim W \lesssim 3$ and $\xi_0 \gtrsim 10$, vibration-vibration exchange becomes important (depending on the excitation energy) and here the effect of anharmonicity increases with increasing ξ_0 and depends on W (for integral values of W the anharmonicity leads to a decrease in the effectiveness of vibration-vibration exchange, fractional values of W lead to an increase). The time-dependent relaxation time τ_e of the average energy can change during the relaxation process by one to two orders of magnitude.

LITERATURE CITED

1. E. E. Nikitin and A. I. Osipov, "Vibrational relaxation in gases," *VINITI, Kinet. Katal.*, **4** (1977).
2. V. M. Volokhov, M. N. Safaryan, and O. V. Skrebkov, "Diffusion description of vibrational relaxation of anharmonic oscillators - two-dimensional system," *Teor. Eksp. Khim.*, **14**, No. 4 (1978).
3. V. M. Volokhov and O. V. Skrebkov, "Vibrational relaxation of diatomic molecules - anharmonic oscillations in a Boltzmann reservoir. Single-component system," *Fiz. Goreniya Vzryva*, **17**, No. 4 (1981).
4. V. M. Volokhov and O. V. Skrebkov, "Diffusion description of vibrational relaxation in a binary mixture of diatomic molecules - harmonic oscillations," Preprint T-10812, Chernogolovka, OIKhF, Academy of Sciences of the USSR (1981).

5. M. N. Safaryan and O. V. Skrebkov, "Kinetics of vibrational-translational exchange of diatomic molecules - anharmonic oscillations in an inert gas medium," *Fiz. Goreniya Vzryva*, **11**, No. 4 (1975).

DEPENDENCE OF THE EFFICIENCY OF A CO₂
GASDYNAMIC LASER (GDL) RESONATOR
ON THE LASING MIXTURE PARAMETERS

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Carbon dioxide gasdynamic lasers are widely studied at this time [1]. Numerous methods for analyzing the GDL characteristics have been developed, starting with approximate analytical formulas permitting execution of some estimates, to numerical methods of solving complex systems of differential equations describing diverse physical processes. Nevertheless, perfecting the analytical formulas remains urgent. This is related to the ongoing search to raise GDL efficiency by application and development of new methods to obtain an active medium, which is related, in turn, to the need to optimize many parameters.

An analytic dependence is obtained in this paper for the limit value of the resonator efficiency (understood here to be the ratio between the number of radiation quanta which have emerged from the resonator and the number of vibrational quanta accumulated at the upper lasing level and in the nitrogen molecules) as a function of the characteristics of the active medium at the resonator input with relaxation losses taken into account in its cavity and without thermodynamic equilibrium between the vibrational modes (a four-temperature model). The conditions of equality of the total radiation losses and the total amplification for a constant intensity in the whole resonator volume [2]

$$2\langle k \rangle d = \ln(1/r), \quad (1)$$

is used in the derivation, where $\langle k \rangle = (1/S) \int k dS$; k is the gain coefficient, S is the area of the generation zone, r is the effective coefficient of resonator reflection taking into account the losses associated with absorption in the mirrors and the radiation yield, and d is the thickness of the active medium along the optical axis. An explicit expression for the power being generated is obtained in [2] within the framework of the two-temperature model. Analysis of this expression and optimization of certain resonator parameters permit limit values to be obtained for the parameter efficiency σ for a given ratio η between the gain of the active medium $k_0 d$ at the resonator input and the absorption coefficient δ of the mirrors:

$$\sigma = 1 - (1 + \ln \eta)/\eta. \quad (2)$$

However, the formula presented in [2] does not correctly indicate the nature of the dependence of the power of the radiation being generated on the composition of the lasing mixture (for instance, its maximal value is obtained in the absence of water vapor), and on the length of the generation zone, for which the power grows continuously, according to [2], as it diminishes. This is a result of using the two-temperature model which is not applicable for large values of the radiation intensity in the resonator and a small relaxation rate of the lower lasing level, which takes place for a deficiency of vapors. All this results in the need to consider the four-temperature model. Linearized equations describing a system in conformity with this model are represented in [2], and the means to solve the problem are noted. In this paper the solution is executed to an explicit expression for σ and it is analyzed. A system of linear equations analogous to [2] is used

$$\begin{aligned} de/d\xi &= Ae + B, \\ e &= (e_1, e_2, e_3), \quad B = (K_1 e_{1*}, 0, 0), \\ A &= \begin{pmatrix} -(K_1 + \beta_1 I + \beta_2^2 K_{1,2}) & \beta_1 I + \beta_2 K_{1,2} & 0 \\ \beta I + K_{1,2} \beta_2 & -(x_N + \beta I + K_{1,2}) & x_N \\ 0 & x_C & -(x_C + x_H K_3) \end{pmatrix}, \end{aligned} \quad (3)$$

where $\xi = x_i v \tau_{ex}$; $\beta = K_0 \tau_{ex} [x_C N(e_2(0) - c_1(0)) h \nu]^{-1}$; $K_i = \tau_{ex} / \tau_i$; $\beta_1 = 2\beta \sqrt{e_{1*}}$; $\beta_2 = \sqrt{e_{1*}}$. Here e_3, e_2, e_1 are the populations of the vibrational modes of nitrogen, the upper and lower lasing levels in the computation per molecule of the appropriate species, x_C, x_H, x_N are the carbon dioxide gas, water vapor, and nitrogen con-

Moscow. Translated from *Zhurnal Prikladnoi Mekhaniki Tekhnicheskoi Fiziki*, No. 5, pp. 11-14, September-October, 1982. Original article submitted August 11, 1981.