APPROXIMATE ANALYTICAL DESCRIPTION OF VIBRATION RELAXATION OF WEAKLY ANHARMONIC OSCILLATORS

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The finding of analytical solutions of the relaxation equations for a mixture of weakly anharmonic oscillators is of current interest in the qualitative and quantitative analysis of the role of anharmonic effects in the theory of lasers [1], chemical kinetics [2], in the calculation of kinetic coefficients for slow relaxation [3], in the theory of absorption and dispersion of sound, etc. This problem has been solved numerically [4-6] and analytically [7] using the single-quantum approximation or diffusion approximation, where V—T transitions are taken into account and model expressions for the rate coefficients are used. A quasistationary solution has been worked out when V—T, V—V, and V—V' processes are considered simultaneously for special initial conditions on the number of quanta [8-9]. Relaxation processes in systems with sources of vibrationally excited molecules are exhaustively treated (in the harmonic approximation) in [10]. In the present paper, we use the single-quantum approximation to obtain new analytical solutions of vibrational relaxation problems in a system of weakly anharmonic oscillations for arbitrary forms of the rate constants and a non-Boltzmann heat reservoir. The condition that the ratio of two successive population densities is a smooth function of the number of levels is assumed. The analysis shows that this approximation is realized under gasdynamical conditions where the diffusion approximation is inapplicable since it requires that the distribution function itself be smooth for transitions between levels, and on the other hand, many-quanta processes are still unimportant and can be taken into account in integral form (e.g., in terms of many-quantum diffusion coefficients). Starting from the conventional formulation of the problem [2, 8], we ignore the coupling of vibrations and rotations; this coupling can be significant in the presence of vibrational—rotational resonances and requires a special treatment.

1. Distribution Function for V—T Relaxation for a Non-Boltzmann Heat Reservoir. We first consider the vibrational relaxation of a weak solution of diatomic molecules (modeled as anharmonic oscillators) in an inert gas. The system of relaxation equations in the single-quantum transition approximation has the following form in this case [8]:

$$\dot{x}_n = K_{n+1,\,n}x_{n+1} - K_{n,\,n+1}x_n - K_{n,\,n-1}x_n + K_{n-1,\,n}x_{n-1} \equiv \mathrm{K}_n(x), \tag{1.1}$$

where x_n is the population density of the n-th vibrational level, and the K_{mn} are rate coefficients which do not necessarily satisfy the principle of detailed balance (i.e., we have a non-Boltzmann heat reservoir).

The ratio of two successive population densities can be written in the form

$$x_{n+1}(t)/x_n(t) = a_n \exp\left(-\varphi_n(t)\right), \tag{1.2}$$

where the function $\varphi_n(t)$ is to be determined. We choose the coefficients a_n in the form $a_n = [(n+1)K_{n,n-1}]/[nK_{n+1,n}]$ such that we obtain the correct limiting expression $(K_{n+1,n} = (n+1)K_{10},\ a_n = 1)$ for the case of harmonic oscillators and also the correct limiting expression for the case where the effect of anharmonicity on the transition probabilities is taken into account only through the magnitude of the adiabatic factor [2] $(K_{n+1,n} = (n+1)K_{10}\gamma^n,\ a_n = \gamma^{-1})$. The coefficients a_n and functions φ_n are assumed to depend smoothly on n. With the use of (1.2), the system (1.1) can be rewritten in the form

$$\dot{x}_n/x_n = [K_{n+1,n}a_n \exp(-\varphi_n) - K_{n,n-1}]\left[1 - R_{n,n+1}a_n^{-1}\exp(\varphi_n)\right] + \varepsilon_n, \tag{1.3}$$
$$\varepsilon_n \equiv K_{n,n-1}\left[R_{n-1,n}a_{n-1}^{-1}\exp(\varphi_{n-1}) - R_{n,n+1}a_n^{-1}\exp(\varphi_n)\right], \quad R_{nm} \equiv K_{nm}/K_{mn}.$$

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When a_n and φ_n depend smoothly on n, it follows that $\varepsilon_n(t)$ is small for all values of t ($\varepsilon_n(t) \ll 1$). We look for an approximate solution of (1.3) in the form

$$x_n \simeq z_n = C_n\left(\frac{K_{n,n-1}}{n} - a_n \frac{K_{n+1,n}}{n+1} e^{-\varphi_n}\right) e^{-n\varphi_n}, \tag{1.4}$$

where the C_n are arbitrary constants. Substituting (1.4) in (1.3) and ignoring ε_n, we find an equation for φ_n, which can be solved explicitly

$$e^{\varphi_n(t)} = \left[e^{-t/\tau_n}\left(1 - a_n R_{n+1,n} e^{-\varphi_n^0}\right) - a_n R_{n+1,n}\left(1 - e^{-\varphi_n^0}\right)\right] \times$$
$$\times \left[e^{-t/\tau_n}\left(1 - a_n R_{n+1,n} e^{-\varphi_n^0}\right) - \left(1 - e^{-\varphi_n^0}\right)\right]^{-1}, \quad \varphi_n^0 \equiv \varphi_n(0); \tag{1.5}$$

$$\tau_n^{-1} = n^{-1} K_{n,n-1}\left(1 - a_n^{-1} R_{n,n+1}\right). \tag{1.6}$$

Equation (1.6) obviously gives the relaxation time for level n. The constant of integration φ_n^0 is found from the initial condition $\varphi_n^0 = \ln\,[a_n x_n(0)/x_{n+1}(0)]$, and must be determined so that a_n and φ_n depend smoothly on n. It is easy to see that for the weakly anharmonic case, the Boltzmann, Trinor, and Gordiets distributions satisfy this condition.

To find the correction due to the inclusion of ε_n, we write the solution of (1.3) in the form

$$x_n(t) = z_n(t)/u_n(t). \tag{1.7}$$

Substituting (1.7) in (1.3) we obtain the equation $\dot{u}_n + \varepsilon_n u_n = 0$ and thus

$$u_n(t) = \exp\left\{-n\left[\ln\frac{\exp(\varphi_n) - 1}{a_n R_{n+1,n} - 1} - a_{n-1}^{-1} \ln\frac{\exp(\varphi_{n-1}) - 1}{a_{n-1} R_{n,n-1} - 1}\right]\right\}. \tag{1.8}$$

We consider the properties of this solution. For a Boltzmann distribution of harmonic oscillators at t = 0 $a_n = 1$, $u_n(t) = 1$, $K_{n+1,n} = (n+1)K_{10}$, $\tau_n^{-1} = \tau_\Gamma^{-1} = K_{10} - K_{01}$, $C_n = N_A/K_{10}$, $\varphi_n(t) = \vartheta(t) = \hbar\omega/kT_V(t)$ and (1.4) gives the well-known harmonic oscillator solution $z_n(t) = N_A\,(1 - \exp(-\vartheta)) \exp(-n\vartheta)$, which is canonically invariant. When $t \gg \tau_n$

$$e^{\varphi_n} \to a_n R_{n+1,n},\ u_n \to 1,\ x_n(t) \to C_n a_n^{-n}\,[K_{n,n-1}/n - K_{n,n+1}/(n+1)]\,R_{n,n+1}^n.$$

Substituting the calculated value of x_n into the quasistationary distribution condition $x_{n+1}/x_n = R_{n,n+1}$ and also using the normalization relation $\sum\limits_n x_n = N_A$, the coefficients C_n can be determined and thus the quasistationary distribution function can be found for the case of a non-Boltzmann heat reservoir. In particular, for a Morse oscillator in a Boltzmann heat reservoir

$$R_{n,n+1} = \exp\,[-(E_{n+1} - E_n)/kT],\ E_n = nE_1 - n(n-1)\Delta E,$$
$$E_{n+1} - E_n = E_1 - 2n\Delta E,\ E_1 = \hbar(\omega - 2\omega x_e), \quad \Delta E = \hbar\omega x_e \tag{1.9}$$

we obtain the Boltzmann distribution

$$x_n = N_A Q^{-1} \exp(-E_n/kT), \quad Q = \sum_{n=0}^{n_0} \exp(-E_n/kT), \tag{1.10}$$

if the C_n are chosen in the form $C_n = N_A Q^{-1} a_n^n \delta^{-n(n-1)}\,[K_{n,n-1}/n - K_{n,n+1}/(n+1)]^{-1}$, $\delta \equiv \exp(\Delta E/kT)$.

The approximate solution (1.4) for anharmonic oscillators does not have the property of canonical invariance characteristic for harmonic oscillators.

2. Equation for the Vibrational Energy.

We determine the average vibrational energy per unit volume of the gas

$$E_V(t) = \sum_{n=0}^{n_0} E_n x_n(t). \tag{2.1}$$

We write K_{mn} in a form such that the factor characteristic for the rate coefficients of the harmonic oscillator case is separated out

$$K_{n+1,n} = (n+1)K_{10}A_n,\ K_{n,n+1} = (n+1)K_{01}B_n. \tag{2.2}$$

Differentiating (2.1) with respect to t and using (1.1), (1.9), and (2.2), we obtain

$$\dot{E}_V = -\sum_{n=0}^{n_0} x_n E_n (K_{10}A_{n-1} - K_{01}B_n) + K_{01}E_1 \sum_{n=0}^{n_0} B_n x_n + \\ + \Delta E \sum_{n=0}^{n_0} [K_{10}A_{n-1}x_n n (n-1) - K_{01}B_n x_n n (n+3)]. \tag{2.3}$$

Introducing the notation

$$\tau^{-1} \equiv \sum_{n=0}^{n_0} x_n E_n (K_{10}A_{n-1} - K_{01}B_n) \Big/ \sum_{n=0}^{n_0} x_n E_n, \\ E_V^0 \equiv \tau \sum_{n=0}^{n_0} x_n \left\{ E_1 K_{01} B_n + \Delta E \left[(n-1) K_{n,n-1} - \frac{n(n+3)}{n+1} K_{n,n+1} \right] \right\}, \tag{2.4}$$

relation (2.3) can be written in the form

$$\dot{E}_V(t) = -\frac{E_V(t) - E_V^0(t)}{\tau(t)}. \tag{2.5}$$

When the quantities τ and E_V^0 depend weakly on time, this equation describes "fast" relaxation of the instantaneous value of the vibrational energy density to a quasiequilibrium value. In this case the relaxation time τ and the quasiequilibrium energy density E_V^0 can be determined by simpler approximate equations. We consider some examples.

A. For harmonic oscillators we have $\Delta E = 0$, $A_n = B_n = 1$, and (2.5) reduces to the Landau–Teller equation [2, 8] $\dot{E}_V = -(E_V - E_\Gamma^0)/\tau_\Gamma$, $\tau_\Gamma^{-1} = K_{10} - K_{01}$, $E_\Gamma^0 = E_1 \tau_\Gamma K_{01} N_A$.

B. We take into account the effect of anharmonicity in the rate coefficients only through the magnitude of the adiabatic factor ($A_n = B_n = \gamma^n$) and ignore the nonuniformity of the spectrum ($E_n \simeq nE_1$) and also ignore the deviation of x_n from the Boltzmann distribution (1.10). We then obtain an approximation for the energy relaxation time

$$\tau^{-1} = K_{10}(1 - \gamma e^{-\theta}) \left(\frac{1 - e^{-\vartheta}}{1 - \gamma e^{-\vartheta}} \right)^2, \quad \vartheta = \frac{\hbar\omega}{kT_V}, \quad \theta = \frac{\hbar\omega}{kT}, \tag{2.6}$$

which differs from the analogous expression in [11] only by the factor γ in front of $e^{-\theta}$.

C. Substituting (2.2) into (1.6), we obtain the following compact formula for the relaxation time of level n:

$$\tau_n^{-1} = K_{10}A_{n-1} - K_{01}B_n, \tag{2.7}$$

showing that the anharmonic corrections alone determine the difference between the relaxation time of level n and the energy relaxation time in the Landau–Teller model. In particular, when $A_{n-1} \simeq B_n \simeq \gamma^n$, we can write $\tau_n = \tau_\Gamma \gamma^{-n}$. Taking into account (2.7) and (2.4) we obtain

$$\tau^{-1} = \sum_{n=0}^{n_0} \tau_n^{-1} x_n E_n \Big/ \sum_{n=0}^{n_0} x_n E_n, \tag{2.8}$$

i.e., the reciprocal of the energy relaxation time in a system of anharmonic oscillators is a weighted average of the reciprocals of the relaxation times of the separate levels. In the approximation $A_{n-1} \simeq B_n \simeq \gamma^n$ we obtain from (2.8) the formula $\tau_\alpha = \tau_\Gamma/\Gamma$, $\Gamma \equiv \Sigma\gamma^n x_n E_n / \Sigma x_n E_n$, which, unlike (2.6), is independent of assumptions on the nature of the spectrum. One can use the following expression for the E_V^0: $E_V^0 \simeq E_\Gamma^0/\tilde{\Gamma} + \Delta E L/\Gamma \equiv E_a^0$, $\tilde{\Gamma} = \Gamma/\overline{B}$, where L is chosen so that the sum is most closely approximated. Then (2.5) can be written in the form

$$\dot{E}_V = -\frac{E_V - E_a^0}{\tau_a}. \tag{2.9}$$

Equation (2.9) shows that for a pulse excitation, the system of anharmonic oscillators relaxes faster and can store more vibrational energy than a system of harmonic oscillators.

3. V–T Relaxation in a System of Anharmonic Oscillators with a Positive Source of Vibrationally Excited Molecules. We consider now the system of equations describing V–T relaxation in a weak solution of diatomic molecules (anharmonic oscillators) in a non-Boltzmann heat reservoir with a positive source of strength η of vibrationally excited molecules with energy E_m:

$$\dot{x}_n = \mathbf{K}_n(x) + \eta\delta_{nm}, \tag{3.1}$$

where $K_n(x)$ has the same form as in (1.1). An approximate solution of (3.1) can be worked out in analogy with [10] for times $0 \leqslant t \leqslant \tau^*$ (where τ^* is the action time of the source) when the initial distribution is sufficiently smooth

$$x_n(t) \simeq z_n(t)/u_n(t) + t\eta x_n^0 + g_n(t). \tag{3.2}$$

Here z_n and u_n are given by (1.4), (1.5), (1.6), and (1.8); x_n^0 is the quasistationary distribution normalized to unity and determined from the condition

$$\mathbf{K}_n(x) = 0, \tag{3.3}$$

and the $g_n(t)$ are excitation functions satisfying the normalization relation $\sum\limits_n g_n(t) = 0$. The first term in (3.2) describes relaxation of the initial distribution due to V–T processes; the second term shows that an increase in the population density of the vibrational levels due to the source comes from multiple scattering of molecules having a quasistationary distribution; the excitation function describes a redistribution of molecular levels due to the combined effects of the source and the V–T processes.

For times much larger than the V–T relaxation time (the quasistationary case) the solution (3.2) becomes

$$x_n(t) = [N_A(0) + \eta t]\, x_n^0 + g_n \equiv \eta t x_n^0 + f_n, \tag{3.4}$$

where f_n does not depend on time and is normalized as follows:

$$\sum_n f_n = N_A(0). \tag{3.5}$$

The f_n are determined by a system of algebraic equations which is obtained by substituting (3.4) into (3.1) with the use of condition (3.3), where $K_n(f) = \eta x_n^0 - \eta\delta_{nm}$. This system can be rewritten in the form

$$f_n = R_{n-1,n} f_{n-1} + \eta\,(Q_{n-1} - \zeta_{nm})/K_{n,n-1}, \tag{3.6}$$
$$Q_n = \sum_{l=0}^{n} x_l^0, \quad \zeta_{nm} = \begin{cases} 0, & n \leqslant m, \\ 1, & n > m. \end{cases}$$

The solution of (3.6) can be written in the following form:

$$f_n = f_0 x_n^0/x_0^0 + \sum_{l=1}^{n} b_{l-1} x_n^0/x_l^0 - \eta\zeta_{nm} \sum_{l=m+1}^{n} K_{l,l-1}^{-1} x_n^0/x_l^0, \tag{3.7}$$

where $b_l = \eta Q_l/K_{l+1,l}$, and f_0 is determined from the normalization condition (3.5):

$$f_0 = \left[N_A(0) - \sum_{n=1}^{n_0} \sum_{m=1}^{n} b_{m-1} x_n^0/x_m^0 + \eta \sum_{n=m+1}^{n_0} \sum_{l=m+1}^{n} K_{l,l-1}^{-1} x_n^0/x_l^0 \right] \Big/ x_0^0. \tag{3.8}$$

We note that for low gas temperatures $R_{n-1,n} \ll 1$ for all n and the solution (3.7), (3.8) takes the form

$$f_n \simeq \eta/K_{n,n-1},\ n \leqslant m;\ f_n \approx \eta K^{-1}_{m,m-1} x^0_n / x^0_m \equiv B(m)\, x^0_n, \quad n > m,$$

i.e., as in a system of harmonic oscillators [12], the monoenergy source disturbs the quasistationary vibrational distribution such that the excitation function f_n is quasistationary in form for n > m (with a fictitious total number of particles B(m)) and markedly differs from the quasistationary distribution for $n \leqslant m$.

The equation for the vibrational energy in a system of anharmonic oscillators with a delta-function source has the form (2.5), with the only difference being the term ηE_m on the right hand side, where in (2.4) it is necessary to use the distribution function (3.2) or the quasistationary distribution (3.4). We note that a single-component system of anharmonic oscillators, unlike a weak solution of molecules in an inert gas, is characterized by a stronger time dependence of the relaxation time, since in this case $\tau^{-1}(t) \sim N_A(t) = N_A(0) + \eta t$.

4. Vibrational Relaxation in a Binary Mixture of Anharmonic Oscillators. We will denote the population densities of vibrational levels of oscillators A and B by x and y, respectively. Then in the approximation of single-quantum processes the system of relaxation equations for the A oscillators has the form [8]

$$\dot{x}_n = K^*_{n+1,n} x_{n+1} - K^*_{n,n+1} x_n - K^*_{n,n-1} x_n + K^*_{n-1,n} x_{n-1}, \tag{4.1}$$

where

$$\begin{gathered} K^*_{n+1,n} = K_{n+1,n}(A) + \sum_m \left[K^{m,m+1}_{n+1,n}(A, A)\, x_m + K^{m,m+1}_{n+1,n}(A, B)\, y_m\right], \\ K^*_{n,n+1} = K_{n,n+1}(A) + \sum_m \left[K^{m+1,m}_{n,n+1}(A, A)\, x_{m+1} + K^{m+1,m}_{n,n+1}(A, B)\, y_{m+1}\right]. \end{gathered} \tag{4.2}$$

The corresponding relations for the B oscillators are obtained from (4.1) and (4.2) by replacing x by y and A by B.

We write the rate coefficients for V—V and V—V' processes in a form analogous to (2.2) where the appropriate harmonic factors are separated out

$$K^{m,m+1}_{n+1,n}(A, A) = (n+1)(m+1) K^{01}_{10}(A, A)\, C^m_n, \ K^{m+1,m}_{n,n+1}(A, A) = (n+1)(m+1) K^{10}_{01}(A, A)\, D^m_n, \tag{4.3}$$

$$K^{m,m+1}_{n+1,n}(A, B) = (n+1)(m+1) K^{01}_{10}(A, B)\, E^m_n, \quad K^{m+1,m}_{n,n+1}(A, B) = (n+1)(m+1) K^{10}_{01}(A, B)\, F^m_n.$$

We determine the higher-order moments of the distribution function:

$$M^{AA}_n \equiv K^{01}_{10}(A, A) \sum_m (m+1)\, C^m_n x_m, \quad N^{AA}_n \equiv K^{10}_{01}(A, A) \sum_m (m+1)\, D^m_n x_{m+1}, \tag{4.4}$$

$$M^{AB}_n \equiv K^{01}_{10}(A, B) \sum_m (m+1)\, E^m_n y_m, \quad N^{AB}_n \equiv K^{10}_{01}(A, B) \sum_m (m+1)\, F^m_n y_{m+1}.$$

Recall that in the harmonic approximation all coefficients C — F = 1 and the moments M, N are proportional to $\alpha_{A,B}$ which can be thought of as the average numbers of quanta in molecules A and B. With the help of (4.2)-(4.4), the system (4.1) can be written in the form

$$\dot{x}_n = (n+1)\, x_{n+1} G^A_n - n x_n G^A_{n-1} - (n+1)\, x_n H^A_n + n x_{n-1} H^A_{n-1}, \tag{4.5}$$

where

$$G^A_n = K_{10}(A)\, A_n + M^{AA}_n + M^{AB}_n, \quad H^A_n = K_{01}(A)\, B_n + N^{AA}_n + N^{AB}_n. \tag{4.6}$$

The equation for the y_n is similar.

Note that for a system of harmonic oscillators (4.6) reduces to

$$G_n^A \to G^A \equiv K_{10}(A) + K_{10}^{01}(A, A)\,N_A(1+\alpha_A) + K_{10}^{01}(A, B)\,N_B(1+\alpha_B),$$
$$H_n^A \to H^A \equiv K_{01}(A) + K_{01}^{10}(A, A)\,N_A\alpha_A + K_{01}^{10}(A, B)\,N_B\alpha_B$$

with similar expressions for G_n^B and H_n^B. In the harmonic approximation, it is not difficult to obtain from (4.5) the following nonlinear equations for α_B:

$$\dot{\alpha}_A = -G^A\alpha_A + H^A(1+\alpha_A), \qquad (4.7)$$
$$\dot{\alpha}_B = -G^B\alpha_B + H^B(1+\alpha_B),$$

which can be reduced to the form in [2, 8]. In particular, it follows from these equations that when $\tau_{VV} \ll \tau_{VV'} \ll \tau_{VT}$ and for $t \approx \tau_{VV}$, we have $\dot{\alpha}_A = \dot{\alpha}_B = 0$, i.e., the average number of quanta turn out to be constants of the motion.

We assume now that in the anharmonic approximation the moments $G_n^{A,B}$ and $H_n^{A,B}$ can be considered as slow variables. Then in analogy with Sec. 1, for a weak deviation from equilibrium (i.e, when a_n and φ_n depend smoothly on n), we find the following solution of (4.5):

$$x_n = z_n/u_n, \quad a_n = G_{n-1}^A/G_n^A, \quad z_n = C_n G_{n-1}^A\left(1-e^{-\varphi_n^A}\right)e^{-n\varphi_n^A}, \qquad (4.8)$$
$$u_n = \exp\left\{-n\left[\ln\frac{\exp(\varphi_n^A)-1}{G_{n-1}^A/H_n^A-1} - a_{n-1}^{-1}\ln\frac{\exp(\varphi_{n-1}^A)-1}{G_{n-2}^A/H_{n-1}^A-1}\right]\right\};$$
$$\varphi_n^A = \ln\left\{\frac{e^{-t/\tau_n^A}\left(1-G_{n-1}^A/H_n^A e^{-\varphi_n^{0A}}\right) - G_{n-1}^A/H_n^A\left(1-e^{-\varphi_n^{0A}}\right)}{e^{-t/\tau_n^A}\left(1-G_{n-1}^A/H_n^A e^{-\varphi_n^{0A}}\right) - \left(1-e^{-\varphi_n^{0A}}\right)}\right\}, \qquad (4.9)$$
$$\tau_n^A = \left(G_{n-1}^A - H_n^A\right)^{-1}.$$

Using the notation introduced above, we obtain

$$\left(\tau_n^A\right)^{-1} = [K_{10}(A)A_{n-1} - K_{01}(A)B_n] + \left[M_{n-1}^{AA} - N_n^{AA}\right] + \qquad (4.10)$$
$$+\left[M_{n-1}^{AB} - N_N^{AB}\right] \equiv \left(\tau_{nVT}^A\right)^{-1} + \left(\tau_{nVV}^A\right)^{-1} + \left(\tau_{nVV'}^A\right)^{-1},$$

so that in this approximation the reciprocal of the total relaxation time is the sum of the reciprocals of the relaxation times for V—T, V—V, and V—V' processes, which is plausible. Taking into account that the moments G_n^A and G_n^B depend on the time as slow variables, we obtain the complete system of equations for the calculation of the distribution function

$$x_n = \Phi\left(G_n^A, G_{n-1}^A; H_n^A, H_{n-1}^A\right),\ y_n = \Phi\left(G_n^B, G_{n-1}^B; H_n^B, H_{n-1}^B\right), \qquad (4.11)$$
$$\dot{G}_n^A = \varphi\left(G^A\right), \quad \dot{G}_n^B = \varphi\left(G^B\right),$$

where the form of Φ is given by (4.8) and (4.9), and the function $\varphi(G)$ is determined from (4.4) through (4.6). We note that the solution (4.8) and (4.9) is only valid when the moments $G_n^{A,B}$ are slowly varying in comparison to the population densities themselves. These functions can be found from (4.11).

When $t \ll \tau_n$ we have from (4.8) and (4.9)

$$e^{\varphi_n^A} \to G_{n-1}^A/H_n^A, \ \frac{x_{n+1}}{x_n} \to \frac{H_n^A}{G_n^A} = \frac{K_{01}(A)B_n + N_n^{AA} + N_n^{AB}}{K_{10}(A)A_n + M_n^{AA} + M_n^{AB}} \equiv \frac{K_{n,n+1}^*(A)}{K_{n+1,n}^*(A)} \equiv \frac{x_{n+1}^0}{x_n^0}, \qquad (4.12)$$

which determines the general form of the quasistationary distribution function x_n° which is realized for $t \gg \tau_n$ [8, 9]. If V—T processes are dominant such that $G_n^A \simeq K_{n+1,n}(A)$, $H_n(A) \simeq K_{n,n+1}(A)$, then we obtain from (4.12) the Boltzmann distribution

$$x_n^0 = x_n^B = x_0^0 \exp(-E_n/kT), \tag{4.13}$$

correct for $n > n^{**}(T)$ [2]. If $G_n^A \simeq M_n^{AA}$, $H_n^A \simeq N_n^{AA}$, so that V–V processes are dominant, then we obtain from (4.12) the Trinor distribution [2]

$$x_n^0 = x_0^0 \exp(-\varkappa n - E_n/kT), \tag{4.14}$$

in which the quantities $\varkappa$ and x_0^o are determined from the normalization condition and from the total number of vibrational quanta at the initial instant of time. For a system of harmonic oscillators we obtain in this case a relation determining the vibrational temperature T_V^A of the gas [8]:

$$\exp\left(-\frac{\hbar\omega_A}{kT_V^A}\right) = \frac{\alpha_A}{1+\alpha_A}. \tag{4.15}$$

Relations analogous to (4.13) through (4.15) can be written for the B oscillators. When V–V, V–V', and V–T processes are all taken into account, we obtain from (4.12) in the anharmonic case a more complicated distribution of the Gordiets type [2], and in the harmonic case we obtain a relation determining the relaxation of the vibrational temperatures of the separate subsystems; this is not discussed here.

We note that according to (4.10), the relaxation time of level n is now determined by the smallest of the times τ_{nVT}, τ_{nVV}, $\tau_{nVV'}$; after a time of this order the quasistationary distribution given by (4.12) is realized. Our treatment will obviously be valid when the moments $G_n^{A,B}$ and $H_n^{A,B}$ change only slightly in this time interval. This will be true for a small initial number of quanta; in this case the change in the number of quanta can be described approximately by (4.7). In the case where the moments $G_n^{A,B}$ and $H_n^{A,B}$ cannot be considered as slow variables, nonstationary solutions are more difficult to obtain.

Thus in the approximation of single-quantum processes, one can follow the time evolution of a smooth initial distribution for arbitrary forms of the rate coefficients. The solution can be used directly to form the dynamical equations of molecular gases for the case of slow relaxation. The ideas used here apparently also apply for the treatment of rotational relaxation; however in this case it is necessary to know the nature of the dependence of the rotational excitation rate constants on quantum number.

The analysis given here is one method of treating energy level kinetics in the diffusion approximation formulated in general form in [3]. The combination of these two approaches expands the analytical methods available for studying relaxation phenomena in molecular gases.

Addendum. After preparation of the manuscript, we obtained a more accurate solution of the system (1.1) using the ideas of Sec. 1. If we write the ratio of two successive levels in the form

$$x_{n+1}(t)/x_n(t) = (K_{n,n+1}/K_{n+1,n})f_n(t) = b_n f_n(t), \tag{A.1}$$

where the functions f_n are to be determined, and substitute (A.1) into (1.1), we obtain

$$b_{n-1}(f_{n-1}\dot{x}_{n-1} + x_{n-1}\dot{f}_{n-1}) = [K_{n+1,n}b_n b_{n-1}f_n f_{n-1} - (K_{n,n+1} + K_{n,n-1})b_{n-1}f_{n-1} + K_{n-1,n}]x_{n-1}.$$

From (1.1) we have $\dot{x}_{n-1} = K_{n-1}(x)$. Therefore, using (1.1) and (A.1), we can derive the following system of equations for the f_n:

$$\begin{gathered}\dot{f}_n = (K_{n+1,n+2} - K_{n,n+1})(f_n - 1)(f_n - \beta_n) + \varepsilon_n,\\ \varepsilon_n(t) = K_{n,n-1}(1 - f_n/f_{n-1}) - K_{n+1,n+2}f_n^2(1 - f_{n+1}/f_n),\\ \beta_n = (K_{n+1,n} - K_{n,n-1})/(K_{n+1,n+2} - K_{n,n+1}).\end{gathered} \tag{A.2}$$

When the f_n depend smoothly on n, the quantity $\varepsilon_n(t)$ is small for all t. Ignoring this quantity, we find the explicit solution of (A.2)

$$f_n(t)=\frac{e^{-t/\tau_n}\left(1-f_n^0\right)\beta_n+f_n^0-\beta_n}{e^{-t/\tau_n}\left(1-f_n^0\right)+f_n^0-\beta_n}, \tag{A.3}$$

$$\tau_n^{-1}=K_{n+1,n}-K_{n+1,n+2}+K_{n,n+1}-K_{n,n-1}.$$

The constants of integration f_n^o are determined in terms of the initial conditions with the help of (A.1) as $b_n f_n^o = x_{n+1}(0)/x_n(0)$.

The population densities x_n can be expressed in terms of the f_n with the help of n applications of (A.1):

$$x_n(t)=x_0(t)\prod_{k=0}^{n-1} b_k f_k(t), \quad x_0(t)=N\left[1+\sum_{n=1}^{n_0}\prod_{k=0}^{n-1} b_k f_k(t)\right]^{-1}. \tag{A.4}$$

It is easy to see that the solution (A.4) has all of the properties of the solution (1.5) to (1.8), but is also applicable for less smooth distributions. It can be used in Secs. 2 through 4.

LITERATURE CITED

1. K. Smith and R. Thomson, Numerical Modeling of Gas Lasers [Russian translation], Mir, Moscow (1981).
2. B. F. Gordiets, A. I. Osipov, and L. A. Shelepin, Kinetic Processes in Gas and Molecular Lasers [in Russian], Nauka, Moscow (1980).
3. G. V. Dubrovskii, "Simplified kinetic approach to the dynamics of a structurally relaxing gas" [in Russian], Zh. Tekh. Fiz., 52, No. 10 (1982).
4. N. A. Generalov, B. V. Kuksenko, et al., "Simultaneous treatment of the vibrational relaxation and thermal dissociation of diatomic molecules" [in Russian], Teor. Eksp. Khim., 4, No. 3 (1968).
5. C. T. Hsu and F. H. Maillie, "Vibrational relaxation of anharmonic oscillators with vibration–vibration and vibration–translation energy exchanges," J. Chem. Phys. 52, No. 4 (1970).
6. N. M. Safaryan and O. V. Skrebkov, "On classical and quantum methods of calculating the kinetics of VT exchange and the radiative deactivation of diatomic molecules" [in Russian], Preprint No. 56, Inst. of Mechanics, Academy of Sciences of the USSR, Moscow (1975).
7. G. V. Naidie, "Vibration–translation relaxation of anharmonic oscillators at low temperatures" [in Russian], Zh. Prikl. Mekh. Tekh. Fiz., No. 2 (1976).
8. E. E. Nikitin and A. I. Osipov, "Vibrational relaxation in gases," in: Summaries of Science and Technology [in Russian], Ser. Kinetika i Kataliz., Vol. 4, VINITI, Moscow (1977).
9. M. B. Zheleznyak and G. V. Naidie, "Distribution of vibrational levels, vibrational relaxation rates, and the dissociation of diatomic molecules in nonequilibrium conditions" [in Russian], Zh. Prikl. Mekh. Tekh. Fiz., No. 1 (1976).
10. T. Z. Kalanov, A. I. Osipov, V. Ya. Panchenko, and P. K. Khabibullaev, Vibrational Relaxation in Gas Systems with Sources of Vibrationally Excited Molecules [in Russian], FAN, Tashkent (1981).
11. S. A. Losev, O. P. Shatalov, and M. S. Yalovik, "On the effect of anharmonicity on the relaxation time for adiabatic excitation and deactivation of molecular vibrations" [in Russian], Dokl. Akad. Nauk SSSR, 195, No. 3 (1970).
12. A. I. Osipov, "On the transition probability of the vibrational energy of oxygen for collisions with nitrogen oxide molecules" [in Russian], Dokl. Akad. Nauk SSSR, 139, No. 2 (1961).