

VIBRATIONAL DISTRIBUTION FUNCTIONS  
AND RELAXATION RATE IN ANHARMONIC-  
OSCILLATOR SYSTEMS

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Analytical expressions were derived for the vibrational distribution function in a system of anharmonic oscillators under conditions where the supply of vibrational energy considerably exceeded the equilibrium value. Distribution was found by considering the effect of vibrational-vibrational and vibrational-translational energy exchange, as well as spontaneous radiative transitions. Analytical expressions were also obtained for the relaxation rate of vibrational energy. It was shown that where there is a strong deviation from equilibrium this rate can significantly exceed the corresponding value for a model of harmonic oscillators and is determined by the probability of vibrational-vibrational exchange in the molecules.

In recent years, the vibrational relaxation of molecules patterned after anharmonic oscillators has attracted considerable attention (see, e.g., [1]). The effect of anharmonicity on the vibrational distribution function and energy relaxation rate can be very substantial, especially in strong disequilibrium where the vibrational energy store greatly exceeds the equilibrium value. Such conditions occur in electric discharge, exothermic chemical reactions, the escape of gases from holes and jets, and the effect of infrared resonance radiation on the molecules, and are of practical interest in potential applications of radiation in influencing chemical reactions and studying the operative mechanisms of several molecular lasers (the CO laser and hydrogen-halide lasers).

The distribution of vibrational level populations within an anharmonic-oscillator system was first discovered for disequilibrium conditions by Treanor, Rich, and Rehm [2]. This equilibrium in real systems occurs only for low-level groups because it holds in the assumption that vibrational-vibrational energy exchange (V-V processes) is the sole molecular process involved. However, in view of the physical problems mentioned above, it is of interest to know the distribution function for highly excited states, where vibrational-translational energy exchange (V-T processes) and radiative transitions (for emitting molecules) begin to play an important role in the population of levels. In this case the vibrational distribution function should be found from the solution of the nonlinear system made up of a large number of equations for the balance of the populations. The accurate solution of such a system requires cumbersome numerical calculations and has presently been done only for some concrete molecular gas mixtures with fixed parametric values [3-9]. Approximate analytical expressions for the distribution function were found in [10, 14]; however, only individual cases are described. Thus, the distribution function found in [10-12] describes only the case of a slight deviation in the value of the vibrational energy from the equilibrium value, when nonresonance vibrational-vibrational exchange with lower-lying quanta plays a basic role in V-V processes (i.e., in V-V processes where highly excited molecules collide with molecules that occur at lower-lying vibrational levels). In [13-14], the problem is considered in a diffusion approximation, and a continuous vibrational energy spectrum is hypothesized. The distribution equations and functions derived in these papers, while describing the conditions appropriate for a large store of vibrational energy, are nevertheless unsuitable for the practically important case of low gas temperatures  $T \ll E_1$  ( $E_1$  is the energy of a low-energy vibrational quantum from the oscillator, expressed in °K).

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The concrete form of the distribution function is determined by the deviation of the molecular vibrational energy from the equilibrium value. In a system of anharmonic oscillators the relaxation rate of the vibrational energy can differ significantly from the values supplied by the Landau–Teller theory for the harmonic model. An accurate calculation of the relaxation rate, just as of the distribution function, is very tedious and has been done up to now only for individual partial cases [3] and [4]. The analytical expressions obtained in [15] are purely qualitative in nature and can be used practically only for the case of weak disequilibrium.

## 1. VIBRATIONAL DISTRIBUTION FUNCTION

To find the distribution of populations of vibrational levels in conditions of disequilibrium we will, in accordance with [13, 14], use the diffusion approximation and assume a smooth variation in populations during the transition from level to level. However, when deriving the equation from the appropriate vibrational distribution function, we will start out from the ordinary system of balance equations in the populations  $N_n$  of vibrational levels  $n$ :

$$\begin{aligned} \frac{dN_n}{dt} = & \frac{1}{N} \sum_m (Q_{n+1, n}^{m, m+1} N_m N_{n+1} - Q_{n, n+1}^{m+1, m} N_{m+1} N_n) - \\ & - \frac{1}{N} \sum_m (Q_{n, n-1}^{m, m+1} N_m N_n - Q_{n-1, n}^{m+1, m} N_{m+1} N_{n-1}) + (P_{n+1, n} N_{n+1} - \\ & - P_{n, n+1} N_n) - (P_{n, n-1} N_n - P_{n-1, n} N_{n-1}) + A_{n+1, n} N_{n+1} - A_n N_n + F_n, \quad n = 0, 1, 2, \dots, k \end{aligned} \quad (1.1)$$

Here  $N$  is the molecular density,  $Q_{i, j}^{p, q}$  is the probability in  $\text{sec}^{-1}$  of vibrational–vibrational exchange when, as a result of collisions of molecules situated at levels  $p$  and  $i$ , there occurs a transition at levels  $q$  and  $j$ ;  $P_{i, j}$  and  $A_{i, j}$  are the probabilities in  $\text{sec}^{-1}$  of collisional and spontaneous radiative transition  $i \rightarrow j$ ;  $F_n$  is the term which describes the change in the population of the  $n$ -th level due to external effects; and  $k$  is the general number of vibrational levels of the molecules. In writing out Eq. (1.1), account was taken only of single-quantum transitions which ordinarily play a basic role in population levels.

Transferring  $F_n$  into the left side of Eq. (1.1) and summing with respect to  $n$  from 0 to  $i$ , we obtain

$$\sum_{n=0}^i \left( \frac{dN_n}{dt} - F_n \right) = \frac{1}{N} \sum_m Q_{i+1, i}^{m, m+1} N_m N_{i+1} - Q_{i, i+1}^{m+1, m} N_{m+1} N_i + P_{i+1, i} N_{i+1} - P_{i, i+1} N_i + A_{i+1, i} N_{i+1} \quad (1.2)$$

The physical concept of Eq. (1.2) is very simple: in energy space it determines the ordinary flow of molecules through an arbitrary cross section between energy levels  $i+1$  and  $i$ . The probabilities of direct and reverse transitions in Eq. (1.1) and Eq. (1.2) are associated with the common relations

$$Q_{i, i+1}^{m+1, m} = Q_{i+1, i}^{m, m+1} \exp \{ -2\Delta E (m - i) / T \} \quad (1.3)$$

$$P_{i, i+1} = P_{i+1, i} \exp \{ - (E_1 - 2\Delta E i) / T \} \quad (1.4)$$

Here  $T$  is the gas temperature in  $^\circ\text{K}$ ,  $E_1$  and  $\Delta E$  are, respectively, the lower vibrational quantum of the molecule and its anharmonicity in  $^\circ\text{K}$ .

We will consider from now on the gas temperature as substantially less than characteristic (i.e.,  $T \ll E_1$ ) and be concerned with population levels  $i$  such that

$$E_1 - 2\Delta E i \gg T \quad (1.5)$$

Furthermore, we will assume that exchange with vibrational quanta can affect the level populations only in cases where the resonance defect  $2\Delta E(m-i)$  is such that

$$2\Delta E |m - i| \ll T \quad (1.6)$$

If the populations slowly change with a variation in level number, then the term  $P_{i, i+1} N_i$  in Eq. (1.2) can be ignored when Eq. (1.5) is satisfied. We will also note that the condition (1.6) is not rigid and is ordinarily satisfied within a wide range of temperatures.

It is now convenient to pass from Eq. (1.2) to the diffusion approximation. Considering the conditions as quasistationary for the sake of simplicity and that external disturbances take place only for the lowest levels, it is possible to make the left side of Eq. (1.2) equal to zero. Then we introduce the continuous vibrational distribution function  $f(i)$  such that

$$N_i = N f(i), \quad N_{i+1} = N f(i) [1 + d \ln f(i) / di] \quad (1.7)$$

The writing of Eq. (1.7) presupposes a smooth variation in populations as one goes from level to level, i.e., satisfying the relation

$$d \ln f(i) / di \ll 1 \quad (1.8)$$

Expanding the exponent in Eq. (1.3) into a series and substituting Eqs. (1.3) and (1.7) in Eq. (1.2), after the replacement of summation with integration

$$\int Q_{i+1,i}^{m,m+1} f(m) \left[ \frac{d \ln f(i)}{di} - \frac{d \ln f(m)}{dm} + \frac{2\Delta E}{T} (m-i) \right] dm + P_{i+1,i} + A_{i+1,i} = 0 \quad (1.9)$$

The relation (1.9) is an integrodifferential equation for the vibrational distribution function  $f(i)$  in quasistationary conditions and is valid when satisfying the relations (1.5), (1.6), and (1.8), i.e., under the examined conditions where there is a strong deviation from equilibrium. The main difference of Eq. (1.9) from analogous equations [13, 14] consists in the expression for the term which describes vibrational-translational relaxation, because when it was written in Eq. (1.9), the relations (1.4), (1.5), and (1.8) were taken into account. If one puts into Eq. (1.9)  $P_{i+1,i} = A_{i+1,i} = 0$ , then its solution is, as indeed should be expected, a Treanor distribution function [2]:

$$\begin{aligned} f_{Tr} &= f_0 \exp \{ -i (E_1/T_1 - \Delta E (i-1)/T) \}, \\ T_1 &= E_1 / \ln (f_0/f_1) \end{aligned} \quad (1.10)$$

where  $T_1$  is the vibrational temperature of the first level, determined by the overall nonequilibrium store of vibrational energy in the system.

To solve Eq. (1.9) it is necessary to know the probability dependence from the number of the vibrational level. For simplicity we will in the following text basically use probabilities in which the anharmonic effects are considered only when calculating exponential factors which give the most substantial dependence on the energy and, consequently, on the anharmonicity  $\Delta E$ . In this case we have

$$\begin{aligned} Q_{i+1,i}^{m,m+1} &\approx Q_{10} (i+1) (m+1) e^{-\delta_{VV} |i-m|} (3/2 - 1/2 e^{-\delta_{VV} |i-m|}) \\ P_{i+1,i} &\approx P_{10} (i+1) e^{\delta_{VT} i}, \quad A_{i+1,i} \approx A_{10} (i+1), \\ \delta_{VV} &= (0.427/\alpha) \sqrt{\mu/T} \Delta E \end{aligned} \quad (1.11)$$

where  $\mu$  is the reduced mass of colliding particles in atomic units (amu);  $\alpha$  is a constant in the exponential potential of the intermolecular interaction in  $\text{\AA}^{-1}$ . The expression is analogous for  $\delta_{VT}$ , although  $\mu$  and  $\alpha$  can be different if the V-T processes are determined by collisions with an extrinsic gas.

It is possible to obtain an analytical solution of Eq. (1.9), with consideration given to the last two sums, only if several approximations are made. We will examine these approximations converting Eq. (1.9) into the differential form.

We will first assume that collisions with molecules in lower vibrational states comprise the main V-V processes for highly excited molecules. (This case is analogous to the one investigated in [10-12] in a discrete approximation.) In this connection the basic contribution to the integral in Eq. (1.9) will be made by terms with low  $m$ . Therefore, substituting the function (1.10) in place of  $f(m)$  as the zeroth approximation and integrating approximately, we obtain for  $f(i)$  the differential equation

$$\frac{1}{f} \frac{df}{di} \approx - \left[ \frac{E_1}{T_1} - \frac{2\Delta E i}{T} + \frac{\Delta E}{T} \right] - \frac{2}{3f_0} \left( \frac{E_1}{T_1} - \delta_{VV} \right)^2 \left[ \frac{P_{10}}{Q_{10}} e^{(\delta_{VV} + \delta_{VT}) i} + \frac{A_{10}}{Q_{10}} e^{\delta_{VV} i} \right] \quad (1.12)$$

This equation has the simple solution

$$f(i) = f_0 \exp \left\{ -i \left( \frac{E_1}{T_1} - \frac{\Delta E (i-1)}{T} \right) - \frac{2}{3f_0} \left( \frac{E_1}{T_1} - \delta_{VV} \right)^2 \left[ \frac{P_{10} (e^{(\delta_{VV} + \delta_{VT}) i} - 1)}{Q_{10} (\delta_{VV} + \delta_{VT})} + \frac{A_{10}}{Q_{10} \delta_{VV}} (e^{\delta_{VV} i} - 1) \right] \right\} \quad (1.13)$$

It can be shown that  $f_0 \approx E_1/T_1$  occurs when Eqs. (1.12) and (1.13) are applicable. At lower levels due to the small values of  $P_{10}/Q_{10}$  and  $A_{10}/Q_{10}$ , expression (1.13) is, as one should expect, nearly the same as Eq. (1.10). We will note that in distribution (1.13) at some values of the parameters  $T$ ,  $T_1$ ,  $P_{10}$ ,  $Q_{10}$ , and  $A_{10}$  it is possible to have an absolutely inverse population of vibrational levels. This inversion can exist only for states above the level which corresponds to the minimum in function (1.10). The number  $n^*$  of this level is

$$n^* = \frac{E_1}{2\Delta E} \frac{T}{T_1} + \frac{1}{2} \quad (1.14)$$

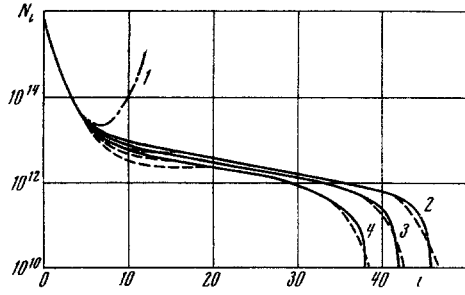


Fig. 1

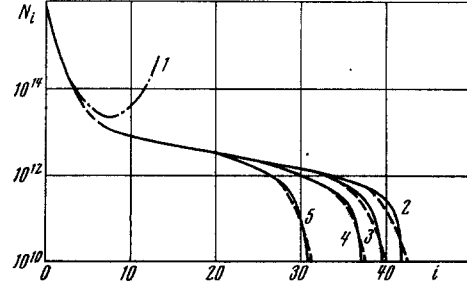


Fig. 2

It is necessary, however, to bear in mind that if the terms containing  $P_{10}$  and  $A_{10}$  in Eq. (1.13) remain very much smaller than the first term in the exponent when  $i > n^*$ , then Eq. (1.13) cannot be used to figure out the distribution function. Actually, in this case, due to the important absolute inversion, the populations at levels  $i > n^*$  will be comparable to those in lower energy states, and the principal role in the V-V processes will not be played by exchange with lower vibrational quanta [which was supposed in deducing Eq. (1.13)], but rather by the collision of two highly excited molecules with a low resonance defect in the presence of quantum exchange. This situation ordinarily takes place in the strongest disequilibrium of vibrational energy, i.e., at low gas temperatures and high values of  $T_1$ .

Eq. (1.12) is invalid for the given case, and Eq. (1.9) can in any case be transformed to the differential form, taking into account that at low gas temperatures the parameter  $\delta_{VV}$  [see Eq. (1.11)] is such that the probability of an exchange  $Q_{i+1, i}^{m, m+1}$  has a sharp maximum when  $m=i$ . This indicates that the principal contribution to the integral in Eq. (1.9) comes from the vicinity of point  $i$  where the function  $f(m)$  can be expressed by  $f(i)$  using a power series expansion of  $(m-i)$  [13]:

$$f(m) \approx f(i) + \frac{df(i)}{di}(m-i) + \frac{1}{2} \frac{d^2f(i)}{di^2}(m-i)^2 + \dots \quad (1.15)$$

Substituting Eqs. (1.11) and (1.15) in Eq. (1.9) and integrating with respect to  $m$ , we obtain still one more form of differential equation for the vibrational distribution function:

$$\frac{3Q_{10}}{\delta_{VV}^3} \frac{d}{di} \left\{ (i+1)^2 f^2 \left( \frac{2\Delta E}{T} - \frac{d^2 \ln f}{di^2} \right) \right\} + P_{10}(i+1) e^{\delta_{VT}i} f + A_{10}(i+1) f = 0 \quad (1.16)$$

The approximate analytical solution of Eq. (1.16) for the levels  $i > n^*$  can be obtained, assuming that  $d^2 \ln f / di^2 = \text{const}$ . A comparison with accurate numerical calculations shows that for a broad range of parameters for  $T$ ,  $T_1$ ,  $Q_{10}$ ,  $P_{10}$ , and  $A_{10}$  in the domain of  $i > n^*$ , the best results are obtained if it is assumed

$$d^2 \ln f / di^2 \approx \text{const} \approx -4\Delta E/T \quad (1.17)$$

Providing that Eq. (1.17) is true, the solution of Eq. (1.16) takes the form:

$$f(i) = \frac{C}{i+1} - \frac{P_{10}}{Q_{10}} \frac{T\delta_{VV}^3}{36\Delta E\delta_{VT}} \frac{e^{\delta_{VT}i}}{i+1} - \frac{A_{10}}{Q_{10}} \frac{T\delta_{VV}^3}{36\Delta E}, \quad i \geq n^* \quad (1.18)$$

Following [13] we determine the integration constant  $C$  from the boundary condition at point  $i=n^*$ :

$$f(n^*) = e^{-1/2} f_0 \exp \left\{ -n^* \left[ \frac{E_1}{T_1} - (n^*-1) \frac{\Delta E}{T} \right] \right\} = f_0 \exp \left\{ -(n^*)^2 \frac{\Delta E}{T} - \frac{1}{2} \right\} \quad (1.19)$$

In this connection, it can be assumed with good accuracy that the distribution function at levels of  $i < n^*$  takes the form of Eq. (1.10). It is only within the narrow vicinity of point  $n^*$  when  $1 < n^*$  that an accurate solution of Eq. (1.16) will differ from Treanor's solution Eq. (1.10) and smoothly turn into Eq. (1.18).

Probabilities are often used in calculations besides Eq. (1.11), in which the anharmonic effects are approximately accounted for, and in calculating preexponential factors. In this case the probabilities  $Q_{i+1, i}^{m, m+1}$ ,  $P_{i+1, i}$ , and  $A_{i+1, i}$  in Eq. (1.11) must also be multiplied by the factors corresponding to

$$\left(1 - \frac{\Delta E}{E_1} i\right)^{-1} \left(1 - \frac{\Delta E}{E_1} m\right)^{-1}, \quad \left(1 - \frac{\Delta E}{E_1} i\right)^{-1}, \quad \left(1 - \frac{2\Delta E}{E_1} i\right)^3 \left(1 - \frac{\Delta E}{E_1} i\right)^{-1}$$

Equations (1.12) and (1.16) are modified in a corresponding manner, and the solution, instead of Eq. (1.18) assumes the form

$$f(i) = C \frac{1 - (\Delta E/E_1)i}{i+1} - \frac{P_{10}}{Q_{10}} \frac{T\delta_{VV}^3}{36\Delta E\delta_{VT}} \frac{e^{\delta_{VT}i}}{i+1} \left(1 - \frac{\Delta E}{E_1}i\right) + \frac{A_{10}}{Q_{10}} \frac{T\delta_{VV}^3}{36\Delta E} \frac{E_1}{8\Delta E} \left(1 - \frac{2\Delta E}{E_1}i\right) \frac{1 - (\Delta E/E_1)i}{i+1}, \quad i \geq n^* \quad (1.20)$$

It is apparent from the appearance of solutions (1.18) and (1.20) that they do not have any physical meaning for the group of levels where  $f(i) < 0$ . This limitation in the scope of the solution is connected with the use of correlation (1.17) in the presence of the deduction of Eqs. (1.8) and (1.20), as well as with the same equation (1.16) being true only for levels where Eq. (1.5) is satisfied. However, we will note that the populations of levels for which Eqs. (1.18) and (1.20) yield negative values of  $f(i)$  are very small and do not contribute to the overall store of vibrational energy in disequilibrium.

Figures 1 and 2 compare the distribution functions for CO calculated according to Eqs. (1.10), (1.19), and (1.20) (solid lines) with the accurate calculations performed in [5] by the numerical solution of 80 balance equations for a CO + He mixture with an electron concentration of  $2.5 \cdot 10^9 \text{ cm}^{-3}$ . Curves 2, 3, and 4 in Fig. 1 correspond to the distribution function (0.2 mm Hg for CO + 6 mm Hg for He) at a gas temperature of 150, 175, and 200°K, while curve 1 is Treanor's distribution [2] at  $T_1 = 1950^\circ\text{K}$ ,  $T = 150^\circ\text{K}$ . Curves 2, 3, 4, and 5 in Fig. 2 represent helium pressures of 6, 10, 20, and 50 mm Hg in a mixture at 0.2 mm Hg for CO + p mm Hg for He at  $T = 175^\circ\text{K}$ , and curve 1 is Treanor's distribution at  $T_1 = 2050^\circ\text{K}$ , and  $T = 175^\circ\text{K}$ .

It is obvious from these figures that the fit for a large group of levels is excellent. The distribution for levels  $i < n^*$  is Treanor's equation (1.10), while for  $i > n^*$  the absolute inversion of vibrational levels does not arise, and the distribution has the shape of a slanting plateau, connected with the leading role of the first term in Eqs. (1.18) and (1.20). With an increase in  $i$  an even greater part is played by the second term in Eqs. (1.18) and (1.20), which causes in the final reckoning a sharp decrease in populations. Level number  $n^{**}$ , which corresponds to this sharp inflection in the distribution function can be approximately determined from the condition  $f(n^{**}) = 0$ . For nonradiating oscillators we have

$$e^{\delta_{VT}n^{**}} = C \frac{Q_{10}}{P_{10}} \frac{36\Delta E\delta_{VT}}{T\delta_{VV}^3} \approx e^{\delta_{VT}n^*} + \frac{Q_{10}}{P_{10}} \frac{36\Delta E\delta_{VT}}{T\delta_{VV}^3} (n^* + 1) f_0 \exp\left\{- (n^*)^2 \frac{\Delta E}{T} - \frac{1}{2}\right\} \quad (1.21)$$

A knowledge of the inflection point  $n^{**}$  is important in determining the relaxation rate in vibrational energy under conditions of strong disequilibrium.

## 2. RELAXATION RATE OF VIBRATIONAL ENERGY

Multiplying Eq. (1.1) by  $n/N$  and summing up for all  $n$ , we obtain the equation for the rate of variation of an average store of quanta  $\varepsilon$  per single molecule:

$$\frac{d\varepsilon}{dt} = -\frac{1}{N} \sum_{n=0}^k P_{n+1, n} N_{n+1} + \frac{1}{N} \sum_{n=0}^k P_{n, n+1} N_n - \frac{1}{N} \sum_{n=0}^k A_{n+1, n} N_{n+1} + \frac{1}{N} \sum_{n=0}^k n F_n, \quad \varepsilon = \frac{1}{N} \sum_{n=0}^k n N_n \quad (2.1)$$

We will not concern ourselves in the future with the last term in Eq. (2.1), which describes energy pumping to a vibrational degree of freedom by external actions. Instead, we will examine only the variation in the store of quanta due to vibrational-translational energy exchange (the first two terms) and spontaneous radiative transitions (the third term).

For a harmonic oscillator, relation (2.1) after summation takes on the appearance of the Landau-Teller equation. For low gas temperatures of  $T \ll E_1$  and large deviations from equilibrium in this case, we have

$$d\varepsilon / dt = -\varepsilon/\tau_H - A_{10}\varepsilon, \quad \tau_H = 1/P_{10} \quad (2.2)$$

For the anharmonic oscillator when the probabilities are selected in the form of Eq. (1.11), the radiative relaxation  $\varepsilon$ , as may readily be seen from Eq. (2.1), does not depend on the form of the distribution function and, as in the case of the harmonic model, is described by the second term in Eq. (2.2). Nevertheless, the rate of the vibrational-translational energy exchange can depend heavily on the form of the vibrational distribution function and considerably exceed (up to several orders of magnitude) the value given in Eq. (2.2). To find this relaxation rate, we will start out from the distribution function in Eqs. (1.10) and (1.18). Turning in Eq. (2.1) from summation to integration and taking into account the relation (1.5), we obtain

$$\frac{d\varepsilon}{dt} \approx -P_{10} \int_0^k i e^{\delta_{VT}i} f(i) di \approx -P_{10} \left[ \int_0^{n^*} i e^{\delta_{VT}i} f_{T,i}(i) di + f(n^*) (n^*/\delta_{VT}) (e^{\delta_{VT}n^{**}} - e^{\delta_{VT}n^*}) \right] \quad (2.3)$$

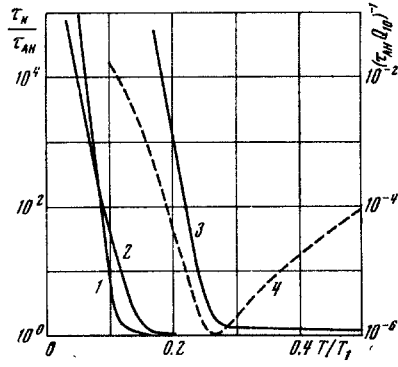


Fig. 3

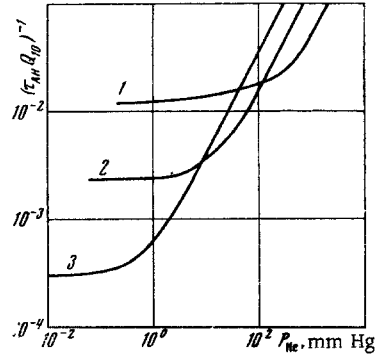


Fig. 4

where  $f_{Tr}(i)$ ,  $n^*$ ,  $f(n^*)$ , and  $n^{**}$  are determined in Eqs. (1.10), (1.14), (1.19), and (1.21). It was taken into consideration when writing Eq. (2.3) that, according to what was said above, the populations at levels of  $i > n^{**}$  are small and do not affect the relaxation rate.

In order to represent the relaxation rate  $\varepsilon$  in the form of Eq. (2.2), we will also compute the value

$$\varepsilon = \frac{1}{N} \sum_{n=0}^k n N_n \approx \int_0^{n^{**}} i f(i) di \approx \int_0^{n^*} i f_{Tr}(i) di + f(n^*)(n^{**} - n^*) \quad (2.4)$$

It is convenient to make further transformations associated with calculating the integrals in Eqs. (2.3) and (2.4) for different values of the parameter

$$\sqrt{\Delta E/T} |n^* - 1 + \delta_{VT} T / (2\Delta E)|$$

Ordinarily, this parameter is greater than unity. In this case  $f_0 \approx E_1/T_1$ , and the approximate integration in Eq. (2.4) yields

$$\varepsilon \approx (T_1^2 / E_1^2) f_0 + f(n^*) n^* (n^{**} - n^*) \quad (2.5)$$

Now calculating the integral in Eq. (2.3) and using Eq. (2.5), we obtain the general expression for the relaxation rate:

$$\begin{aligned} \frac{d\varepsilon}{dt} &= -\frac{\varepsilon}{\tau_{AH}} \\ \frac{1}{\tau_{AH}} &\approx P_{10} \left\{ \left( \frac{E_1}{T_1} - \delta_{VT} \right)^{-2} + \exp \left\{ - (n^*)^2 \frac{\Delta E}{T} - \frac{1}{2} \right\} \times \right. \\ &\times \left[ \frac{T}{2\Delta E} (1 + \delta_{VT} n^*) e^{\delta_{VT} n^{**+1/2}} + \frac{n^*}{\delta_{VT}} (e^{\delta_{VT} n^{**}} - e^{\delta_{VT} n^*}) \right] \left[ \frac{T_1^2}{E_1^2} + n^* (n^{**} - n^*) \exp \left\{ - (n^*)^2 \frac{\Delta E}{T} - \frac{1}{2} \right\} \right]^{-1} \end{aligned} \quad (2.6)$$

Figure 3 represents the calculation of values of  $\tau_H/\tau_{AH}$  carried out in accordance with Eq. (2.6) for pure CO gas (curve 3) and a mixture of 3.2% CO + 96.8% He (curves 1 and 2) for different parameters of  $T_1$  and  $T$  (curve 1 -  $T_1 = 1850^\circ\text{K}$ , curves 2 and 3 -  $T_1 = 3000^\circ\text{K}$ ). It is evident that with a reduction in  $T/T_1$  the relaxation rate  $\varepsilon$  for the anharmonic model with some moment will begin substantially to exceed the corresponding value for the harmonic model.

The expression (2.6) can be significantly simplified by examining the different relations that exist between the supply of vibrational quanta at the levels where  $i \leq n^*$  and  $n^* \leq i \leq n^{**}$ . If  $T_1$  and  $T$  are such that all energy is basically concentrated at levels  $n^* \leq i \leq n^{**}$  (the case of maximum deviation from equilibrium), then the first term in Eq. (2.5) and in the factors in Eq. (2.6) can be ignored, and for  $\tau_{AH}$  we have

$$\tau_{AH}^{-1} = P_{10} (e^{\delta_{VT} n^{**}} - e^{\delta_{VT} n^*}) [\delta_{VT} (n^{**} - n^*)]^{-1} \quad (2.7)$$

When  $\delta_{VT} (n^{**} - n^*) \gg 1$ , considering Eqs. (1.14) and (1.21) and assuming  $f_0 \approx E_1/T_1$ , we obtain

$$\frac{1}{\tau_{AH}} \approx P_{10} \frac{e^{\delta_{VT} n^{**}}}{\delta_{VT} (n^{**} - n^*)} \approx Q_{10} \frac{36\Delta E}{T\delta_{VT}^3} \frac{E_1}{T_1} \frac{n^*}{n^{**} - n^*} \exp \left\{ - (n^*)^2 \frac{\Delta E}{T} - \frac{1}{2} \right\} \quad (2.8)$$

where  $n^*$  and  $n^{**}$  are determined by expressions (1.14) and (1.21).

Equations (2.7) and (2.8) distinctly illustrate the fact that, where there is strong disequilibrium, the vibrational-translational energy exchange in a system of anharmonic oscillators is realized principally through levels near the level of  $n^{**}$ , where the populations are still comparatively large, and the prob-

abilities are significantly [for level  $n^{**}$  by  $\exp(\delta_{VT}n^{**})$  times] over the corresponding values for the harmonic model. It is also apparent from Eq. (2.8) that at the boundary the relaxation rate cannot be determined by the value of  $P_{10}$ , but rather by the probability of a vibrational energy exchange  $Q_{10}$ . It is explained physically by the fact that with fast deactivation in the levels near  $n^{**}$  the transition rate of vibrational energy converting to translational degrees of freedom is limited by the conversion rate of the molecules at these levels, which produces the vibrational exchange. It is interesting to note that in this case the dependence of  $\tau_{AH}$  on the gas temperature  $T$  can sharply differ from the conventional law  $\tau \sim \exp\{A/T^{1/3}\}$  and is of a nonmonotonic nature. This fact is illustrated in Fig. 3 by the dependence of  $(\tau_{AH}Q_{10})^{-1}$  (curve 4) on  $T/T_1$ , calculated for pure CO at  $T_1=300^\circ\text{K}$ . The dependence on gas pressure must also be singular. Thus, in a gas mixture, where the probability  $P_{10}$  in the gas being studied is determined by collisions in the extrinsic gas (e.g., in typical laser mixtures of CO+He), the time  $\tau_{AH}$  might nevertheless not follow the law of inverse proportionality of the dependence on concentration of this mixture and vary only slightly [see Eq. (2.8)]. The dependence of  $\tau_{AH}$  on the pressure of the extrinsic gas in strong disequilibrium is illustrated in Fig. 4, which shows the dependences of  $(\tau_{AH}Q_{10})^{-1}$  on the pressure of He in a mixture at 0.2 mm Hg for CO + p mm Hg for He, calculated with  $T_1=3000^\circ\text{K}$  and at different temperatures  $T$ :  $300^\circ\text{K}$  (curve 1),  $400^\circ\text{K}$  (curve 2), and  $500^\circ\text{K}$  (curve 3). Expression (2.6) is also simplified in the case where the vibrational energy is concentrated at low levels of  $i < n^*$ . If a fundamental role is taken by the second term in the right side of the relaxation equation (2.3), then we obtain for  $\tau_{AH}$

$$\frac{1}{\tau_{AH}} \approx P_{10} \frac{E_1^3}{T_1^3} \frac{T}{2\Delta E} \frac{1}{\delta_{VT}} (e^{\delta_{VT}n^{**}} - e^{\delta_{VT}n^*}) \exp\left\{-\frac{(n^*)^2}{T} - \frac{1}{2}\right\} \quad (2.9)$$

Finally, in the case where the vibrational-translational energy exchange occurs at levels of  $i \leq n^*$ , we have

$$\frac{1}{\tau_{AH}} \approx P_{10} \left[ \left(1 - \delta_{VT} \frac{T_1}{E_1}\right)^{-2} + (n^*)^2 \frac{2\Delta E}{T} (1 + \delta_{VT}n^*) \exp\left\{-\frac{(n^*)^2}{T} + \delta_{VT}n^*\right\} \right] \quad (2.10)$$

In many practical instances the second term in Eq. (2.10) can be ignored. Then Eq. (2.10) will coincide with the expression found in [15]. The relation (2.10) can be used to calculate the relaxation rate also in the case where the distribution function has the form of Eq. (1.13).

We will note in conclusion that if the parameter  $\sqrt{\Delta E/T} |n^* - 1 - \delta_{VT}T/(2\Delta E)| < 1$ , then practically all energy will be concentrated at levels  $i > n^*$ . Therefore, Eqs. (2.7) and (2.8) can be used in this case to calculate the relaxation rate, remembering however that  $f_0$  is no longer equal to  $E_1/T_1$ , but determined by the relation

$$f_0 \approx [n^* e^{-1/2} \ln(n^{**}/n^*)]^{-1}$$

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