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 $\text{K}$).
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:

\[
\frac{dN_n}{dt} = \frac{1}{N} \sum_m \left( Q_{m,n}^{m+1,n} N_m N_{m+1} - Q_{m+1,n}^{m,n} N_{m+1} N_m \right) - \frac{P_{n,n} N_n}{N} (P_{n,n+1} N_n - P_{n+1,n} N_{n+1}) + (P_{n+1,n} N_n - P_{n,n+1} N_{n+1}) + A_{n+1,n} N_{n+1} - A_n N_n + F_n, \quad n = 0, 1, 2, \ldots, k
\]

(1.1)

Here \(N\) is the molecular density, \(Q_{i,j}^{k,l}\) is the probability in 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 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 1, we obtain

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

(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

\[
Q_{m,n}^{m+1,n} = Q_{m+1,n}^{m,n} \exp \left\{ -2\Delta E (m - i) / T \right\}
\]

\[
P_{i+1,i} = P_{i,i+1} \exp \left\{ -(E_i - 2\Delta E) / T \right\}
\]

(1.3)

Here \(T\) is the gas temperature in \(\text{K}\), \(E_i\) and \(\Delta E\) are, respectively, the lower vibrational quantum of the molecule and its anharmonicity in \(\text{K}\).

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

\[
E_1 - 2\Delta E i \gg T
\]

(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

\[
2\Delta E |m - i| \ll T
\]

(1.6)

If the populations slowly change with a variation in level number, then the term \(P_{i+1,i} N_i\) 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 \(f(l)\) such that

\[
N_i = Nf(i), \quad N_{i+1} = Nf(i) \left[ 1 + d \ln f(i) / dl \right]
\]

(1.7)