

INTRODUCTION

The investigation of the vibrational relaxation of diatomic molecules at high vibrational temperature and low gas temperature is due to the development of certain types of lasers (in particular, CO lasers). The distributions of molecules over the vibrational levels and the rates of vibrational relaxation have been computed numerically in a number of studies (review [1]). In the presence of strong vibrational excitation the distribution over the levels contains a slowly decaying part (plateau). An analytical description of a distribution with a plateau is given in [2], which is based on the classical oscillator model. Later, the vibrational relaxation of diatomic molecules under the conditions of existence of a plateau was investigated in [3, 4], where analytical expressions for the rate of change of the number of quanta were derived. In [3, 4] the rate of dissipation of the vibrational energy was determined by summing the contributions from the vibrational-translational exchange processes (V-T process) in each vibrational level.

The upper vibrational levels, where the rates of vibrational-translational and vibrational-vibrational exchanges (V-V process) become comparable (end of the plateau), make the main contribution. Thus, the direct summation requires a rather accurate computation of the distribution in the region where V-V processes are important; this presents a complex problem that does not have a universal solution. However, in the case where the rate of V-T relaxation is determined by the upper vibrational levels, there is no need for an explicit computation of the vibrational distribution in this region, since the rate of relaxation can be related to the magnitude of the upward flux of quanta along the vibrational levels [2]. This approach has been used in [5] for deriving the formula for the rate of dissipation of the vibrational energy in polyatomic molecules. In the present work the quantum flux is computed in the discrete space of vibrational numbers, which gives a more exact formula in the case of a steep dependence of the rate of V-V exchange on the energy defect. The results are compared with earlier known formulas and with experiment. The analytical results are compared with the numerical solution.

1. Equation of Vibrational Energy. We introduce a quantum flux in section k of the axis of vibrational numbers, given by the formula

$$\Pi_k = \sum_{m \geq 1} \sum_{u=k}^{k+m-1} S_{um},$$

where the number of quanta transferred from transition $(u-m) - (u-m+1)$ to transition $(u) - (u+1)$ is

$$S_{um} = \begin{cases} Q_{um}(N_u N_{u-m+1} - e^{-2bm} N_{u+1} N_{u-m}), & u \geq m, \\ 0, & u < m. \end{cases}$$

Here Q_{um} is the rate constant of the V-V process $(u) + (u-m+1) \rightarrow (u+1) + (u-m)$; $b = \Delta E/T$; ΔE is the anharmonicity; T is the gas temperature; and N_u is the population of the u -th level. The difference of the quantum fluxes in adjacent sections is

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$$\Pi_k - \Pi_{k+1} = \sum_{m \geq 1} (S_{km} - S_{k+m,m}) = \sum_m S_{km}. \quad (1.1)$$

In the last equation we have made use of the fact that

$$S_{k,-m} = -S_{k+m,m}$$

and the summation is extended over negative values of m . The expression on the right-hand side of (1.1) represents the particle flux between adjacent levels (the difference in the numbers of direct and inverse transitions) due to V-V processes.

Let us consider the case of stationary excitation of molecules by electrons (V-E processes) in an electrical discharge. In the absence of dissipation, the total particle flux between the levels; which is composed of V-V, V-T, and V-E fluxes, is equal to zero. Then Eq. (1.1) shows that the difference of the quantum fluxes in adjacent sections is equal (but of opposite sign) to the particle flux caused by V-E and V-T processes. Thus, V-E and V-T processes are the sources of the quanta.

The excitation by electrons is related mainly to the lower vibrational levels. On the other hand, for strong vibrational excitation quenching occurs at upper levels where the rate of V-T processes is large. Therefore, the distributed sources may be replaced by some effective sources acting at the boundary of the investigated range of vibrational numbers. In this case the equation of the vibrational energy has the following form:

$$dE/dt = W - \omega\Pi, \quad (1.2)$$

where E is the vibrational energy, W is the pumping, and $\omega\Pi$ is the flux of vibrational energy associated with the quantum flux.

Taking the distribution [2] (corresponding to constant quantum flux)

$$N_k = N_0 \exp(-b\alpha^2 - 1/2)(\alpha/k)$$

in the region of the plateau, for large k we have

$$\Pi = Q_{00} N_0^2 \alpha^2 \sum_{m \geq 1} m (1 - e^{-2bm}) f(m). \quad (1.3)$$

In the expression for N , $\alpha = 1/2 + \omega T / 2T_1 \Delta E$ is the number of the level corresponding to the minimum of Treanor distribution, ω is the vibrational quantum, and T_1 is the excitation temperature of the first level. In (1.3) we have made use of the representation of the V-V exchange constant in the form

$$Q_{um} = Q_{00}(u+1)(u-m+1)f(m), \quad 0 \leq m \leq u, \quad (1.4)$$

where Q_{00} is the rate constant of defectless exchange $(0) + (1) \rightarrow (1) + (0)$.

For exchange in the presence of short-range interaction the factor $f(m)$ is of the form [1]

$$f(m) = e^{-\delta m}. \quad (1.5)$$

Sometimes (1.5) can be used also for V-V exchange in the case of long-range interaction. In particular, according to the experimental data [6, 7] for CO, the dependence on the energy defect in the region, giving the main contribution to the sum over m in (1.3), can be taken as exponential with a reasonable accuracy. Using (1.5), we have

$$\Pi = Q_{00} N_0^2 \alpha^2 \left[\frac{e^\delta}{(e^\delta - 1)^2} - \frac{e^{\delta+2b}}{(e^{\delta+2b} - 1)^2} \right]. \quad (1.6)$$

Formula (1.6) is more universal than that of [4] describing the vibrational relaxation only in the one-component gas of diatomic homonucleus molecules. Computations show that the rates of vibrational relaxation, determined from (1.6) and from the formula from [4], are in satisfactory agreement within the limits of applicability of the latter. In the range of small b and δ the expression for the energy flux becomes

TABLE 1

Variant	T, °K	T ₁ ^{exp} , °K	$\frac{W_p}{W}/\text{cm}^3$	T ₁ ^{calc} , °K
1	149	2400	0,15	2400
2	132	2450	0,12	2700
3	230	3400 (4000)	0,18	4300
4	230	3300 (3900)	0,25	4200

$$\omega\Pi = \omega Q_{00} N_{\alpha}^2 \alpha^2 \cdot 4b/\delta^3. \quad (1.7)$$

We note that (1.7) is similar in form to the corresponding expression from [3]; however, the numerical factor in [3] is 10 times larger (this difference is in part — by a factor of 1.5 — due to the fact that a slightly different dependence $f(m)$ is used in [3]).

According to (1.6), the magnitude of the quantum flux is determined by the population of the level corresponding to the Treanor minimum. In the presence of distributed quenching (for example, diffusion, emission) leading to a decrease of the quantum flux with the increase of the vibrational number, the slope at the plateau increases. However, the population at the Treanor minimum does not change significantly. Therefore, formula (1.6) describes approximately the magnitude of the quantum flux in the neighborhood of the Treanor minimum and in the presence of quenching at the plateau. The quenching in the Treanor region must be taken into consideration directly in the energy equation. In this case, in (1.2) W must be taken as the difference between the pumping W_p and quenching W_q at the Treanor minimum. Equation (1.2) offers the possibility of determining the temperature T_1 corresponding to the vibrational distribution from the known value of the vibrational pumping.

The available information enables us to make a comparison with the experiment. In [8] the vibrational distribution in CO has been measured in a wide range of conditions from the amplification factor at rotational-vibrational transitions. For known electron density and temperature the vibrational pumping is found from the data of [9]. The electron density at the axis of the discharge is determined from the current and the elastic scattering constant of electrons in helium (it is assumed that the electron density profile along the radius of the tube is of Bessel type), while the electron temperature is found from the energy balance. Under the conditions of the experiment [8] quenching at the Treanor minimum is significant only at low pressures ($p = 3$ mm Hg) and is due to the diffusion of the excited molecules to the walls. The experimental data from [10] show that under such conditions the characteristic quenching period due to diffusion is independent of the accommodation coefficient and is equal to $R^2/6D$, where R is the radius of the tube and D is the diffusion coefficient. The constants Q_{00} and δ were determined from the experimental data of [6]. For variants 1 and 2, $Q_{00} = 3.4 \cdot 10^{-12}$ cm³/sec and $\delta^{-1} = 1.5$; for variants 3 and 4, $Q_{00} = 9.1 \cdot 10^{-12}$ cm³/sec and $\delta^{-1} = 1.5$, which corresponds to the data of [6] for $T = 100$ and 250°K . A comparison of the experimental and computed values of T_1 is shown in Table 1. In variants 3 and 4 the values of the vibrational temperature, computed with the total width of the spectral line taken into consideration, are shown in parentheses (in [8] only the impact width is considered for these variants). Considering the approximate nature of the comparison, on the whole the agreement should be regarded as satisfactory.

2. Vibrational Relaxation. The case of relaxation of the vibrational distribution in time requires special investigation, since here there is a downward particle flux through the vibrational levels and the magnitude of this flux is proportional to the rate of relaxation. The presence of this flux leads (in the absence of distributed quenching) to a change of the quantum flux along the plateau, which, in turn, causes a change in the rate of quenching at the end of the plateau. Thus, it becomes necessary to consider the backlash effect of the distribution relaxation rate on the distribution itself, i.e., to introduce a correction to the basic quasistationary approximation.

In the quasistationary stage the plateau relaxes as a whole. In this case we have

$$d \ln N_k / dt = -\gamma \quad (k > \alpha), \quad (2.1)$$

where

$$\gamma = -(d \ln N_k / d\alpha)(d\alpha/dQ)(dQ/dt) = \Pi/NQ^{(p)} (1 + a); \quad (2.2)$$

$$a = (dQ^{(t)} / d\alpha) / (dQ^{(p)} / d\alpha) \simeq Q^{(t)} / Q^{(p)} \alpha (1 - e^{-2b\alpha}). \quad (2.3)$$

Here $Q = Q(t) + Q(p)$, $Q(t) \simeq (e^{2b\alpha} - 1)^{-1}$, and $Q(p) \simeq \alpha N_\alpha (n - \alpha) / N$ are, respectively, the total number of quanta, the number of quanta in the Treanor region, and the number of quanta at the plateau per molecule; N is the density of the molecules. In (2.2) we have made use of the equation $NdQ/dt = -\Pi$. The coordinate of the end of the plateau is $n = \delta_{V-T}^{-1} \ln(8bQ_{00} \times \alpha N_\alpha \delta_{V-T} / P_{10} \delta^3)$, where the probability of $V - T$ quenching is

$$P_{k+1, k} = P_{10}(k + 1)e^{\delta_{V-T} k}. \quad (2.4)$$

Only the basic exponential dependence is taken into consideration in differentiation with respect to α in (2.2). The quasistationarity results from the fact that the relaxation time of the population of the k -th level $\sim N_k / \Pi$ is much smaller than γ^{-1} .

From the balance equation

$$dN_k/dt = j_{k-1, k} - j_{k, k+1}, \quad (2.5)$$

where $j_{k-1, k}$, $j_{k, k+1}$ is the particle flux in the $(k - 1) - k$ transition, we get

$$j_{k-1, k} = -\gamma \sum_k^n N_k. \quad (2.6)$$

In deriving (2.6) we have taken into consideration that the flux $j_{n-1, n}$ is small due to rapid decay of the distribution for $k > n$. Expressing the particle flux in the form of the divergence of the quantum flux, we get

$$\Pi d/dk = \gamma \int_k^n N_k dk \quad (k > \alpha). \quad (2.7)$$

For $k = \alpha$ the magnitude of the flux is given by formula (1.6). It is evident from (2.7) that the quantum flux increases toward the end of the plateau, which causes an enhancement of the relaxation. The main change in the quantum flux occurs in some neighborhood of the Treanor minimum. Integrating (2.7), we get

$$\Pi_n = \Pi_\alpha + \gamma(NQ^{(p)} - \alpha N^{(p)}), \quad (2.8)$$

where

$$Q^{(p)} = (1/N) \int_\alpha^n k N_k dk; \quad N^{(p)} = \int_\alpha^n N_k dk. \quad (2.9)$$

We introduce a function $\kappa_k = \Pi_k / \Pi_\alpha$. Since on the plateau $\Pi_k \sim k^2 N_k^2$, we have $N_k = (\alpha N_\alpha / k) \times \sqrt{\kappa_k}$. The consideration of the enhancement of the relaxation amounts to a replacement of π by $\kappa \Pi_\alpha$ in (2.2), where $\kappa = \kappa_n$. Substituting (2.2) into (2.8), we obtain the equation for κ , from which we get

$$\kappa = (1 + a) / (\alpha N^{(p)} / NQ^{(p)} + a). \quad (2.10)$$

The main change in the function $\sqrt{\kappa_k}$ occurs in the neighborhood of $k = \alpha$, giving a small contribution to the integral in (2.9). Therefore, a correction factor $\sqrt{\kappa}$ appears in the expressions for $Q(p)$ and $N(p)$ (in comparison with the standard case). Taking this fact into consideration, for small values of α from (2.10) we get

$$\kappa = (n/\alpha - 1) / \ln(n/\alpha). \quad (2.11)$$

An explicit form of the distribution can be obtained by substituting the unperturbed distribution into the integral on the right-hand side of (2.7) as a first approximation. For small values of α we have

$$N_k = (\alpha N_\alpha / k) \sqrt{[(k/\alpha)(\ln(n/k) + 1) - 1] / \ln(n/\alpha)}, \quad (\alpha < k < n). \quad (2.12)$$

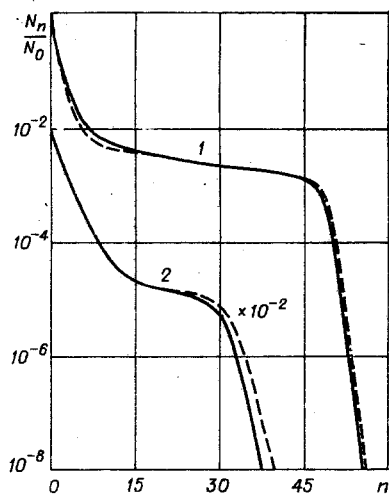


Fig. 1

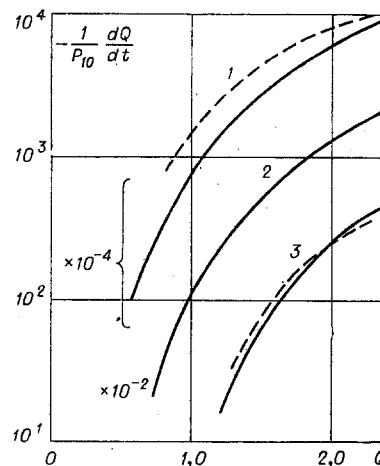


Fig. 2

It is evident from (2.10) that κ differs from unity noticeably only in the case of small α when the change in the number of quanta with time is associated mainly with the plateau. For small α the correction factor for the quantum flux may reach a few times unity, i.e., for a given vibrational temperature T_1 , the rate of dissipation of the vibrational energy may be several times larger than in the stationary case. On the other hand, if the quantum flux is expressed in terms of $Q(p)$, then since $\Pi \sim [Q(p)]^2$, the correction factors for the flux and the number of quanta on the plateau mutually cancel out, i.e., the rate of dissipation does not change in comparison with the stationary case for the same number of quanta on the plateau.

3. Numerical Computation of Relaxation. We present the results of a numerical solution of the temporal problem of vibrational relaxation of nitrogen molecules at a constant gas temperature. The system of equations for the populations of the vibrational levels was solved considering single-quantum V-V and V-T processes. The probabilities were specified in the form (1.4), (1.5), (2.4) for $\delta v_{-T} = \delta$. The molecule was modeled by a Morse oscillator; the magnitude of anharmonicity was determined from the formula $\Delta E = \omega^2/4D_0$; the experimental values of the vibrational quantum ω and the dissociation energy D_0 were used in this formula. The computations were carried out for two values of $T = 0.03$ and 0.1 eV. The initial distribution over the vibrational levels was taken to be the Boltzmann distribution with temperature T_0 , whose value was varied.

The time-dependence of the distribution over the levels and the rate of change of the average number of quanta dQ/dt were determined. Examples of distributions are shown in Fig. 1 by the dashed curves for two variants of computation corresponding to $T = 0.03$ eV, $Q = 2.15$ (curve 1) and $T = 0.1$ eV, $Q = 1.45$ (curve 2) ($T_0 = 0.8$ eV in both variants). The continuous curves in this figure show the stationary distributions computed for the same T and Q in accordance with the formulas from [4]. It is evident that the distributions obtained from the numerical computation decay more slowly in the region of the plateau than the stationary distributions, which is in agreement with the results of Sec. 2. Thus, the stationary curve 1 decreases from the beginning to the end of the plateau 1.5 times more than the relaxation curve, whereas formula (2.12) gives a value of 1.6 for the corresponding factor.

In the computations with different T_0 but with the same T and Q the distributions and the values of dQ/dt are similar. This fact indicates the establishment of a quasistationary distribution over the vibrational levels. The time for the establishment of the quasistationary distribution is small compared to the characteristic time of vibrational relaxation $Q(dQ/dt)^{-1}$, where Q and dQ/dt correspond to the stationary distribution with the number of quanta equal to the initial number. After this time, the average number of quanta does not change significantly.

The dependence of the rate of relaxation on the average number of quanta, obtained from the numerical computation for two values of T with $T_0 = 0.8$ eV, is shown in Fig. 2 (dashed curves). The values of the relaxation rate, computed from the formula from [4], are shown by the continuous curves (in the investigated range of conditions the difference in the

values of dQ/dt determined from the formula from [4] and from (1.6) does not exceed 30%). Curve 1 corresponds to $T = 0.03$, curve 2 to $T = 0.05$, and curve 3 to $T = 0.1$ eV. It is evident that there is a satisfactory agreement.

Thus, the analytical description of the vibrational relaxation agrees satisfactorily with the experiment and numerical computations.

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VIBRATIONAL RELAXATION IN AN ISOTHERMAL SYSTEM WITH A δ -FUNCTION SOURCE OF MOLECULES

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UDC 536.48+539.194+539.196

§1. In the intensive investigations being conducted into the properties of molecular lasers, and the mechanism and kinetics of gas-phase reactions, there is at present a great deal of interest in studying the nonequilibrium distribution function of molecules over the vibrational energy levels in systems with sources of particles [1]. Vibrationally excited molecules can arise, for example, in the pulsed photolysis of gas mixtures, in the recombination of atoms and radicals, in combination and exchange reactions [2], and in electrical discharges, optical excitation, etc.

The problem of determining the populations of the levels is most simply formulated in the case when the molecules introduced into the system are characterized by vibrational energy E_v (pulsed photolysis), and so the source is a δ -function. This situation was studied in [3, 4], where the quasistationary distribution function was obtained corresponding to the times $\tau_1 \ll t \ll \tau_0$ (τ_1 is the progressive vibrational relaxation time, and τ_0 is the time

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