EFFECT OF THE PUMPING LEVEL ON THE DYNAMICS OF ESTABLISHING THE DISTRIBUTION OF DIATOMIC MOLECULES OVER VIBRATIONAL LEVELS

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Strong vibrational nonuniformity is achieved relatively easily for a number of molecules, for example, in a gas discharge or in the case of optical excitation. This nonuniformity can be used in molecular lasers (for example, a CO laser) as well as for carrying out chemical reactions. The problem of finding a vibrational distribution function under conditions of strong excitation has been solved in many papers (for example, see the review [1]) in large part numerically. An approximate analytic theory which permits finding the steady distribution function was constructed in [2-4]. Approximate analytic solutions of the problem of establishing the vibrational distribution function under conditions of variable pumping have been found in [5], and the applicability of the solutions obtained for the description of physical reality in the case of sufficiently powerful pumping is demonstrated. The purpose of this paper is to clarify the lower limit with respect to pumping power of the applicability of the theory of [5]. The evolution of the distribution function over the vibrational levels in nitrogen is considered as an example.

The complete set of nonsteady kinetic equations for the populations of individual vibrational levels has been solved numerically. The processes of vibrational exchange (V—V), energy relaxation into translational degrees of freedom (V—T processes), and excitation by an external source were taken into account (it was assumed that electrons excite the discharge). The approximation ($v > v'$)

$$Q_{v+1,v}^{v',v'+1} = Q_{10}(v+1)(v'+1)\exp(-\delta_{VV}|v-v'|), \tag{1}$$

was used for the rate constant of V—V-exchange, and

$$P_{v+1,v} = P_{10}(v+1)\exp(\delta_{VT}v),$$

was used for the rate of V—T-relaxation, where Q_{10} and P_{10} are the constants for the first level, which depend on the gas temperature, and δ_{VV} and δ_{VT} are the temperature-dependent constants which characterize the dependence of V—V- and V—T-processes on the energy defect upon collision.

Two classes of solutions are considered separately. The first class describes the establishment of the distribution function f(v) for rapid switching on of powerful pumping, and the second one describes the evolution of the distribution function after a brief pulsed excitation. The gas temperature was fixed in the numerical calculations, which can be easily justified in the region of relatively small pumpings of interest to us. The vibrational distribution function obtained numerically was illustrated graphically in the coordinates in which the theoretical expression of [5] predicted a linear dependence. It was discovered that the regularities which follow from [5] give a good description of the total distribution function in some interval of vibrational numbers (Figs. 1 and 2).

Analysis of the computational results will start from the case of the switching on of pumping which is constant in time. The final state asymptotically attained at long times is known [2-4]. A plateau of the distribution function in the range of vibrational numbers $v^* \leqslant v \leqslant v^{**}$,

$$f(v) = c/(v+1), \tag{2}$$

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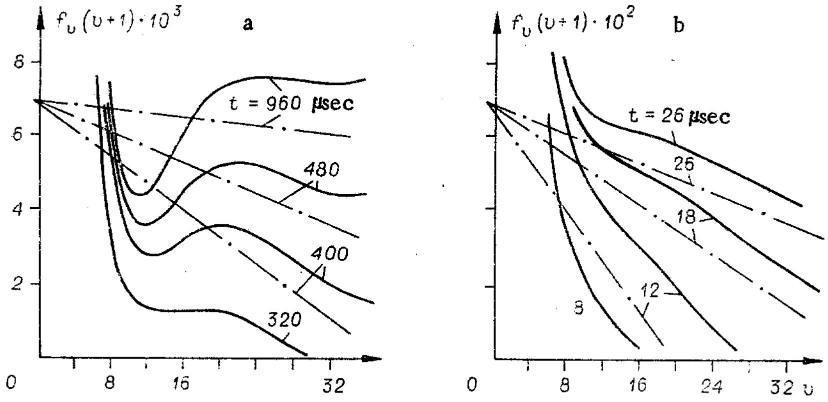

Fig. 1

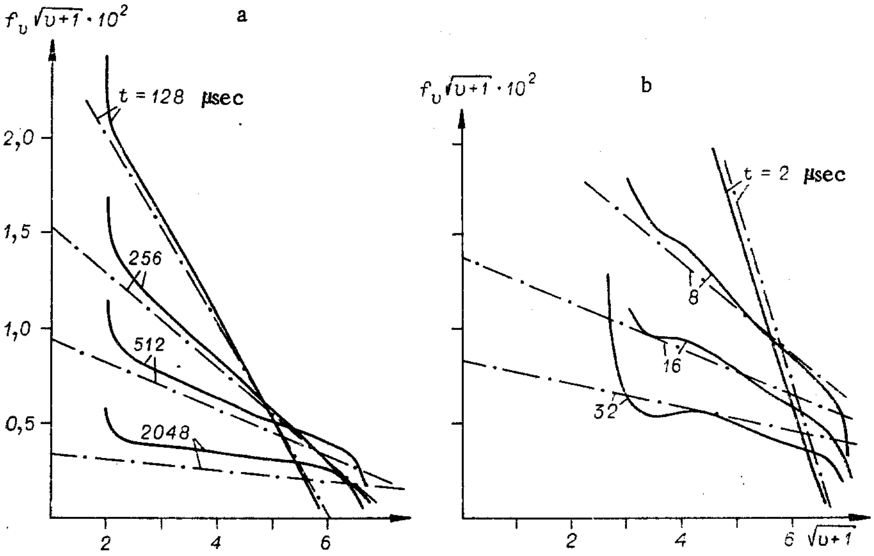

Fig. 2

characterizes it, where $v^* = \frac{E_1}{2\Delta E}\frac{T}{T_1} + \frac{1}{2}$ (the so-called Treanor number), E_1 is the energy of the first vibrational quantum, ΔE is the anharmonicity energy, T is the gas temperature, T_1 is the effective temperature of the first excited level, $c = \sqrt{W/\nu}$, W is the pumping power per single molecule, ν is the effective frequency of quasiresonant V—V-exchange (see [2-4]), which in the case of the approximation (1) is of the form

$$\nu = \frac{4\Delta E}{T}\delta_{VV}^{-3}Q_{10}\left[\frac{1}{2} + \frac{1}{2}\left(1 - \frac{2\Delta E}{T\delta_{VV}}\right)^{-3}\right],$$

and v** is the number of the vibrational level for which the rate of V—V-exchange is comparable to the rate of V—T-relaxation [3]:

$$v^{**} = \delta_{VT}^{-1}\ln\frac{2c\nu\delta_{VT}}{P_{10}}.$$

In the region before the plateau ($v < v^{**}$) the distribution function is close to a "Treanor" one with vibrational temperature T_1, i.e., $f(v < v^*) \simeq f_{\mathrm{Tr}}(v)$. The relation of the value of T_1 to the pumping power W is determined from the equation [2-4] $c = (v^* + 1)\exp\times\left[-\frac{\Delta E}{T}(v^*)^2 - \frac{1}{2}\right]$.

As has been found in [5], the steady state (2) is established according to the law

$$f(v)=\frac{c}{v+1}-\frac{1}{2\nu(t-t_0)}, \tag{3}$$

upon the switching on of pumping, where t_0 is some constant which is not determinable within the framework of the theory [5]. Evidently, at small times while the reserve of quanta in the lower vibrational levels is small, the evolution of the distribution function is determined mainly by V—V-exchange in the lower levels, the population of the high levels is negligible, and the role of quasiresonant exchange is small. The effects of anharmonicity in V—V-exchange and quasiresonant exchange become appreciable when the reserve of quanta per molecule approaches unity. Thus one can expect that $t_0 \simeq 1/W$. Interpretation of the results of numerical calculations for the complete system of equations [see Fig. 1, $N = 10^{19}$ cm^{-3}, T = 300°K, a) WN = 570 W/cm^3, b) NW = 57 kW/cm^3; the dashed curve is for Eq. (3)] permits obtaining an expression for t_0 which is valid with good accuracy:

$$t_0 = n_B(T_1)/W, \tag{4}$$

where $n_B(T_1) = (e^{E_1/T_1} - 1)^{-1}$. The establishment of the distribution function occurs in two stages. For $t \leqslant t_0$ the effective vibrational temperature of the lower levels increases, and there is no plateau. After establishment of the temperature of the lower levels, which is approximately equal to T_1, an excitation wave described by the law (3) propagates (for the adopted values of the parameters $v^*/2\nu c \ll n_B(T_1)/W$). The limiting reserve of quanta per molecule attainable in the steady state is equal [3, 4] (in the limit of weak pumping) to

$$n_{st} \simeq c(v^{**} - v^*) + n_B(T_1).$$

If $c(v^{**} - v^*) \leqslant n_B(T_1)$, then the first stage of energy accumulation in the lower levels occupies most of the time, and the propagation of the excitation wave described by (3) occurs relatively rapidly. Naturally, the role of the plateau in the energetics of the molecule also turns out to be dominant. For the parameters of nitrogen ($Q_{10}/N = 2.5\cdot 10^{-13}$, $\delta_{VV} = 6.8/\sqrt{T}$) the power at which $cv^{**} \simeq n_B(T_1)$ in the case of T = 300°K and a gas density $N = 10^{19}$ cm^{-3} is equal to 600 W/cm^3. The possibility of dividing the establishment process into two stages is due to the pronounced dependence of the plateau level on the vibrational temperature of the lower levels $c(T_1)$. In addition to the distribution function over the vibrational levels, the rate of heating of the gas, which is related to the liberation of the defect energy in the process of V—V-exchange in the translational degree of freedom, was also found in the numerical calculation. An approximate explicit expression for the indicated heating rate

$$\frac{q_{VV}}{E_1\dot{n}}=\frac{4}{3}\frac{\Delta E}{E_1}cv(t-t_0) \tag{5}$$

has been derived in [5].

Equation (5) is applicable as long as the excitation wave does not reach v^{**}, where V—T-relaxation starts to play an important role. Comparison of the results of a numerical calculation with the law (5) [Fig. 3, NW = 5.7 kW/cm^3, T = 300°K, 1) $Q_{10} = \tilde{Q}_{10}$, $\delta_{VV} = \tilde{\delta}_{VV}$, 2) $Q_{10} = 10\tilde{Q}_{10}$, $\delta_{VV} = 10^{1/3}\tilde{\delta}_{VV}$, $\tilde{Q}_{10} = 2.5N\left(\frac{T}{300}\right)^{3/2}10^{-13}$ (c^{-1}), $\tilde{\delta}_{VV} = 6.8/\sqrt{T}$, and dashed curves — theory [5]] shows very good quantitative agreement between them for t_0 defined by Eq. (4).

It is also evident from Fig. 3 that heating of the gas due to V—V-exchange starts to occur somewhat earlier when $t \leqslant t_0$. It also follows from the form of the distribution functions over the vibrational levels (see Fig. 1a) that the situation is more complicated than outlined above in the case of a low pumping power. One should recall here that an approximation of quasiresonant exchange has been taken as the basis of the analytic theory [2-5] in which "distant" exchange is neglected, in particular, the exchange of highly excited particles with weakly excited ones. The criterion of this approximation for the steady state is of the form [4]

$$Q_{10}\exp(-\delta_{VV}v^* - E_1/T_1) \ll \nu c/v^*. \tag{6}$$

An analytic theory of a steady distribution has been constructed in [6] for cases in which condition (6) is violated. The principal conclusion of this paper consists of the prediction of a dip in the distribution function f(v) at $v \simeq v^*$. Absolute inversion of the popu-

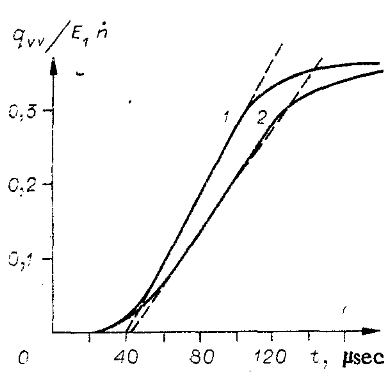

Fig. 3

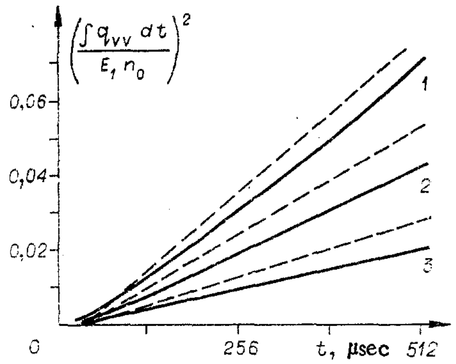

Fig. 4

lations of the vibrational levels occurs in the interval $v^* \leqslant v \leqslant v_0$. The results of our numerical calculation are in qualitative agreement with the conclusions of [6]; however, the estimate of v_0 according to the equations of [6] gives somewhat smaller values than in our calculation. Thus for a low degree of excitation nonresonant exchange can exert a significant effect on the populations of vibrational levels with $v \leqslant v_0$. Since the rate of quasiresonant exchange is proportional to the plateau level, an interval of time always exists in which the population in the end level increases mainly due to nonresonant exchange. The liberation of the energy defect during the exchange in this stage leads to the fact that $q_{VV} \neq 0$ for $t \leqslant t_0$ (see Fig. 3). However, since v_0 differs little from v^*, nonresonant exchange makes a small contribution to q_{VV} and is rapidly replaced for $v \geqslant v_0$ by quasiresonant exchange when Eq. (3) proves to be valid.

Let us proceed to the analysis of the results of numerical calculations of the evolution of the distribution function after pulsed excitation. A self-similar solution describing the evolution of the average part of the distribution function over the vibrational levels and corresponding to a supply of quanta n_0 has been obtained in [5]:

$$f(v) = \frac{1}{2\nu(t-t_0)}\left(\frac{[12n_0\nu(t-t_0)]^{1/4}}{\sqrt{v+1}} - 1\right). \tag{7}$$

The quantity t_0 is indeterminable within the framework of the theory [5], just as in the preceding problem. The solution (7) describes an excitation wave propagating from the direction of small v and attenuating due to outflow of the initial reserve of quanta n_0 through many vibrational levels. Evidently, it is necessary for the validity of (7) that the reserve of quanta in a developed plateau be appreciably greater than the supply of quanta which remains frozen in the lower levels after the passage of the wave. The time t_0 is physically due to V–V-exchange in the lower levels and the formation on this account of an excess population with respect to the Boltzmann one (it is assumed initially that there is a Boltzmann distribution with a temperature corresponding to the supply of quanta n_0). The task of our analysis is to determine t_0 and the residual supply of quanta, which determines the late stage of evolution of the distribution function, during which Eq. (7) loses its validity. The numerical calculation shows that the dependence f(v) predicted by (7) is well justified at the specified time [see Fig. 2, $N = 10^{19}$ cm^{-3}, a) $n_0 = 1.06$, $T = 50$°K, $Q_{10} = 10\tilde{Q}_{10}$, $\delta_{VV} = 10^{1/3}\tilde{\delta}_{VV}$; b) $n_0 = 3.26$, $T = 300$°K, $Q_{10} = \tilde{Q}_{10}$, $\delta_{VV} = \tilde{\delta}_{VV}$]. We note the rapid establishment of the lower level v* characterizing the region of applicability of (7). The value of v* is practically constant in time. Assuming for the number v* found in this way that the distribution is close to a Treanor one for $v \leqslant v^*$, one can recover the value of the vibrational temperature T_{1V} which characterizes the residual supply of quanta. The dependence of v* on the parameters can be estimated by joining the Treanor distribution

$$f_{\mathrm{Tr}}(v) \sim \exp\left[-\frac{\Delta E}{T}(v^*)^2 - \frac{1}{2}\right]$$

to the function (7), from which we obtain

$$v^* = a\sqrt{T/\Delta E}, \tag{8}$$

where a is a numerical constant. Numerous calculations with variation of n_0, T, ΔE, Q_{10}, and δ_{VV} have shown that the coefficient a in (8) does not depend on the indicated parameters and $a \approx 2.3$. Using this value of the constant, we find the value of $T_{1V}\left(v^* \simeq \frac{E_1}{2\Delta E}\frac{T}{T_{1V}}\right)$ as follows:

$$E_1/T_{1V} = 4.6\sqrt{\Delta E/T}$$

and the residual supply of quanta

$$n_V = [\exp(4.6\sqrt{\Delta E/T}) - 1]^{-1}.$$

It is evident that the applicability of the analytic theory [5] is limited from the direction of small degrees of excitation by the inequality $n_0 > n_V$. Numerical calculations confirm the conclusions drawn.

Just as in the previous problem, a quantity which is important for applications was also found numerically — the fraction of energy liberated as heat in the process of evolution f(v) due to the defect associated with V—V-exchange. In [5] the formula

$$\frac{1}{E_1 n_0}\int_0^t q_{VV}dt = \frac{4}{5}\frac{\Delta E}{E_1}(3n_0)^{1/2}[\nu(t-t_0)]^{1,2} \tag{9}$$

has been derived for this fraction. A comparison of the value found numerically $\left(\int q_{VV}dt\right)^2$ with that obtained from Eq. (9) shows [Fig. 4, N = 10^{19} cm^{-3}, T = 50°K, $Q_{10} = 10\tilde{Q}_{10}$, $\delta_{VV} = 10^{1/3}\tilde{\delta}_{VV}$, 1) $n_0 = 3.26$, 2) $n_0 = 1.97$, and 3) $n_0 = 1.06$; the dashed curve refers to the calculation according to (9) and (10)] that the temporal dependence (9) is satisfied with good accuracy. The time t) can be estimated from the formula

$$t_0 \simeq v^*/2\nu n_V. \tag{10}$$

whose validity was checked by us by varying such parameters as T, n_0, Q_{10}, and δ_{VV}. The numerical factor differs from that found from (9) (with the replacement $n_0 \to n_0 - n_V$ taken into account) by approximately 15-20%.

Thus the difference between the analytic solution for heat liberation and the exact solution proves to be greater in the case of pulsed excitation than in the problem of switching on of the source. The discrepancy can be decreased by changing the value of ν, but the principles by which it is necessary to change it are not clear to us.

We note in conclusion that detailed numerical calculations of the evolution of the vibrational distribution function after switching on of the excitation source or after pulsed excitation have permitted formulating quantitative criteria for the applicability of the analytic theory of [5]. The true expression has been found for the delay time t_0 starting from which the analytic solutions (3) and (7) are applicable. The residual supply of quanta frozen in the lower vibrational levels has been determined. It does not restrict the applicability of the approximate theory from the side of weak excitation.

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