Nonequilibrium vibrational kinetics of molecules in the presence of the field of resonant laser emission

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The vibrational kinetics of molecules under nonequilibrium conditions produced by resonant laser emission is considered within the framework of the harmonic-oscillator model. An approach is developed, with which it is possible to investigate the response of the system to the action of an external field whose frequency coincides with the frequency of one of the vibrational levels (resonance of arbitrary multiplicity). The nonequilibrium distribution function is calculated in the stationary and quasistationary regime. The dependences of the vibrational energy and of the decay rate of the system on the external parameters are determined. The limiting characteristics are determined. Similar questions are examined in the case of nonequilibrium conditions considered by resonant emission via the cascade mechanism of populating the vibrational levels.

INTRODUCTION

With further progress in laser technology (increased radiation power, broadband frequency tuning) the number of problems connected with the action of laser radiation on the internal structure of microscopic objects (atoms, ions, molecular complexes, etc.) becomes larger.

These problems can be divided into two classes. The first includes the determination of the cross sections of the elementary acts and questions in the kinetics of an isolated system (outside the statistical ensemble) in the presence of the field. There have been theoretical[1] and experimental[2] investigations of multiphoton transitions of atoms under the influence of a strong field. The study of elementary processes stimulated by laser radiation, and of those causing changes in the intramolecular structure, is the subject of[3-5].

The second class of problems covers the investigation of the behavior of an ensemble of interacting particles in the presence of a resonance-radiation field, namely: redistribution of the energy among particles, exchange between different degrees of freedom, realignment of energy bonds, etc. The study of these problems is of particular importance in connection with the developing possibility of initiating and controlling chemical reactions with the aid of infrared (IR) lasers with tunable frequency.

A number of recent papers report experiments on the stimulation of chemical reactions (of the substitution type) in the field of a resonant IR source[6-10]. We note also work on selective laser excitation of high vibrational levels of molecules[11], initiation of dissociation[12,13], and the two-step dissociation method[14,15]. Theoretical investigations of these topics have been reported in[16-19,8]. Even during the early discussions of laser stimulation of chemical reaction[20] it became clear that to determine beforehand the course of the reaction it is necessary to realize a "fast adiabatic passage" of a selected vibrational mode of the molecule, i.e., a rapid (without energy losses) filling of the high vibrational levels. Artamonova, Platonenko, and Khokhlov[16] obtained a number of important results, namely, they determined the conditions for selective "heating" of the vibrational mode of the molecule, and estimated the corresponding parameters of the (IR) laser radiation. A theoretical analysis of the excitation of molecule oscillations in the diffuse approximation was carried out in[8,17]. The influence of rotational relaxation on the process of laser excitation of oscillations was considered in[19] 1).

The present paper is devoted to a study of vibrational kinetics of a molecular gas under nonequilibrium conditions produced by resonant multiphoton laser pumping (resonance of arbitrary multiplicity), and also by laser radiation via cascade population of the vibrational levels. The approach developed below is free of the limitations connected with the diffusion model, and makes it possible to take full account of the principal processes that bring about the nonequilibrium distribution over the vibrational levels.

I. EXCITATION OF MOLECULE VIBRATIONS BY LASER RADIATION AT A RESONANCE OF ARBITRARY MULTIPLICITY

1. Formulation of Problem

The action of resonant radiation on a selected vibrational mode initiates migration of the molecules to the upper branch of the mode spectrum, owing to exchange of vibrational energy between the colliding partners. An investigation of vibrational kinetics under conditions of nonequilibrium excitation reduces to a determination of distribution function of the particles over the vibrational levels. Solution of this problem provides the answer to questions of practical importance, concerning the reserve of vibrational energy, the rate of decay of the system, etc.

Taking into account multiquantum field-induced transitions $0 \rightleftarrows m$ (transition rate W_m), vibrational exchange processes (characteristic time τ_{VV}), vibrational-translational relaxation (time τ_{VT}), single-quantum spontaneous transitions (Einstein coefficient A_{10}), and the decay of the p-th level (rate k_p), we write down, within the framework of the model of cut-off harmonic oscillator, a system of kinetic equations for the populations of the vibrational levels in the form[22,23]

$$\begin{aligned}\frac{dy_n}{dt} &= \eta(y_0-y_m)(\delta_{nm}-\delta_{n0})+\xi(1-e^{-\Theta})^{-1}\{(n+1)y_{n+1}(1-\delta_{np})\\ &-[n+(n+1)e^{-\Theta}(1-\delta_{np})]y_n+ne^{-\Theta}y_{n-1}\}+\{(n+1)(\varepsilon+1)y_{n+1}(1-\delta_{np})\\ &-[(n+1)\varepsilon(1-\delta_{np})+n(\varepsilon+1)]y_n+n\varepsilon y_{n-1}\}-\delta y_n\delta_{np}-\frac{y_n}{c}\frac{dc}{dt},\\ & n=0,\ 1,\ 2,\ \ldots, \qquad p>m \qquad (p=D/h\nu),\end{aligned} \tag{1.1}$$

where the time and the characteristic time-dependent constants are normalized to τ_{VV}, $\xi = \tau_{VV}(\tau_{VT}^{-1} + A_{10})$, $\eta = W_m\tau_{VV}$, $\delta = k_p\tau_{VV}$, $y_n = x_n(t)/N(t)$ (x_n is the density of the molecules at the n-th level, N(t) is the total density), $c = N(t)/N(0)$, $\epsilon = \Sigma n y_n(t)$ is the average number of quanta (per oscillator), δ_{ik} is the Kronecker symbol, $\Theta = h\nu/kT$ (T is the gas temperature and $h\nu$ is the vibrational quantum), and D is the activation (in particular, dissociation) energy[2].

The standard procedure makes it possible to obtain with the aid of (1.1) equations for the decay rate and for the energy of the system

$$w=\frac{1}{c}\frac{dc}{dt}=-\delta y_p(t), \tag{1.2}$$

$$\frac{d\varepsilon}{dt}=-\xi(\varepsilon-\varepsilon_0)+m\eta(y_0-y_m)+(p-\varepsilon)w, \tag{1.3}$$

where ϵ_0 is the equilibrium vibrational-energy reserve ($p \gg 1$).

We solve the initial nonlinear system by the generating-function method[24,25], which is valid, strictly speaking, for a system with an infinite number of equidistant levels. The system (1.1) is therefore supplemented formally to form an infinite system with "inclusion" of the coupling between the levels p and p + 1. This approach, obviously, introduces a certain error in the calculation of the populations $y_n(t)$, the largest deviation taking place for the populations of the levels numbered $n \approx p$. At sufficiently large p-level decay rates, the accuracy of the solution is greatly increased, this being due physically to the weakening of the coupling between the levels p and p + 1. For the model of "instantaneous" decay of the p level (formally $\delta \to \infty$), the employed method is exact. It should be noted, however, that even at moderate values of δ the errors incurred in the calculation of y_p are relatively small[3]. Generally speaking, in the case of the collision mechanism the decay rate depends on the physical parameters of the system. Inasmuch as δ is arbitrary in the present problem, it follows naturally that the value of δ corresponding to this dependence is included here as a particular case. It should be noted here that: 1) if the system decay is due to chemical reactions (via an excited complex), then the decay rate k_p can greatly exceed the rate of exchange for the activation level ($\delta \gg p$); 2) in real conditions the anharmonicity of the oscillations leads to a condensation of the levels near the dissociation threshold D, making it necessary to consider multiquantum exchange processes and to take into account the decay of the levels adjacent to the level p in the range ~kT; 3) the kinetics of the decay of "hot" molecules should take into account the rather important process of the transition of the rotation energy of the nondissociating molecules into vibrations of the dissociating molecules[28,22]. The latter circumstances introduce into the decay probability within the framework of the cut-off harmonic oscillator, an uncertainty that is obviously retained even in the most consistent investigations of the kinetics of thermal dissociation[22].

Regarding the energy reserve ϵ and the system decay rate w as functions of the time, we can easily obtain for the generating function $G(z, t) = \sum_n z^n y_n(t)$ the equation

$$\begin{gathered}\frac{\partial G}{\partial t}=\left(\frac{\partial G}{\partial t}\right)_0+\left(\frac{\partial G}{\partial t}\right)_m+\left(\frac{\partial G}{\partial t}\right)_p,\\ \left(\frac{\partial G}{\partial t}\right)_0=\left[\varepsilon(z-1)^2-(z-1)\left(1+\xi\frac{1-ze^{-\Theta}}{1-e^{-\Theta}}\right)\right]\frac{\partial G}{\partial z}+(z-1)(\varepsilon+\xi\varepsilon_0)G,\\ \left(\frac{\partial G}{\partial t}\right)_m=(z^m-1)\eta(y_0-y_m),\qquad \left(\frac{\partial G}{\partial t}\right)_p=w(z^p-G).\end{gathered} \tag{1.4}$$

The terms in the right-hand side of (1.4) are due respectively to relaxation processes, multiphoton laser pumping, and the decay process. The method of characteristics makes it possible to obtain from (1.4) an integral representation of the function G(z, t):

$$\begin{gathered}G(z,t)=G_0+G_m+G_p,\\ G_0=\frac{e^{qt}}{c(t)}\frac{1}{e^{qt}-(z-1)[\varepsilon_0+H(0,t)]},\\ G_m=\frac{\eta e^{qt}}{c(t)}\int_0^t\frac{c(t')[y_0(t')-y_m(t')]dt'}{e^{qt}-(z-1)H(t',t)}\left\{\left[1+\frac{(z-1)e^{qt'}}{e^{qt}-(z-1)H(t',t)}\right]^m-1\right\},\\ G_p=\frac{e^{qt}}{c(t)}\int_0^t\frac{c(t')w(t')dt'}{e^{qt}-(z-1)H(t',t)}\left[1+\frac{(z-1)e^{qt'}}{e^{qt}-(z-1)H(t',t)}\right]^p,\end{gathered} \tag{1.5}$$

where $q = 1 + \xi$,

$$H(t',t)=\int_{t'}e^{qt''}[\varepsilon(t'')+\xi\varepsilon_0]dt'';$$

(1.5) corresponds to an initial Boltzmann distribution. Recognizing that

$$y_n(t)=\frac{1}{n!}\frac{\partial^n G}{\partial z^n}\bigg|_{z=0},$$

we obtain with the aid of (1.5) the following relation for the distribution function:

$$\begin{gathered}y_n(t)=y_n^{(0)}(t)+y_n^{(m)}(t)+y_n^{(p)}(t),\\ y_n^{(0)}=\frac{e^{qt}[\varepsilon_0+H(0,t)]^n}{c(t)[e^{qt}+\varepsilon_0+H(0,t)]^{n+1}}\\ y_n^{(p)}=\frac{e^{qt}}{n!\,c(t)}\left[\sum_{k=0}^{n}\sum_{r=n-k}^{n}(-1)^{k-n+r}C_p^kC_n^rA_{k+r}^n\Phi_{kr}(t)\right.\\ \left.+\sum_{k=n+1}^{p}\sum_{r=0}^{n}(-1)^{k-n+r}C_p^kC_n^rA_{k+r}^n\Phi_{kr}(t)\right],\\ y_n^{(m)}=\frac{\eta e^{qt}}{n!\,c(t)}\sum_{k=1}^{m}\sum_{r=n-k}^{n}(-1)^{k-n+r}C_m^kC_n^rA_{k+r}^nI_{kr}(t),\qquad n\geqslant m,\\ y_n^{(m)}=\frac{\eta e^{qt}}{n!\,c(t)}\left[\sum_{k=1}^{n}\sum_{r=n-k}^{n}(-1)^{k-n+r}C_m^kC_n^rA_{k+r}^nI_{kr}(t)\right.\\ \left.+\sum_{k=n+1}^{m}\sum_{r=0}^{n}(-1)^{k-n+r}C_m^kC_n^rA_{k+r}^nI_{kr}(t)\right],\qquad n\leqslant m,\end{gathered} \tag{1.6}$$

where

$$C_j^i=j!/i!(j-i)!,\qquad A_j^i=j!/(j-i)!,$$

$$I_{kr}(t)=\int_0^t c(t')(y_0-y_m)e^{kqt'}\frac{H^r(t',t)dt'}{[e^{qt}+H(t',t)]^{k+r+1}},$$

$$\Phi_{kr}(t)=\int_0\frac{c(t')w(t')e^{kqt'}H^r(t',t)dt'}{[e^{qt}+H(t',t)]^{k+r+1}}.$$

Thus, the obtained relations (1.6) yield an integral representation of the distribution function $y_n(t)$. The derived expressions contain $\epsilon(t)$ and w(t). To determine the latter it is necessary to turn to (1.2) and (1.3), where (1.6) must be taken into account. This procedure enables us to find, in particular, an equation in closed form for the reserve of vibrational energy $\epsilon(t)$. For example, in the absence of a decay process and in the case of single-quantum pumping (m = 1) the equation for the vibrational energy is

$$\frac{d\varepsilon}{dt}+\xi(\varepsilon-\varepsilon_0)=\eta e^{2qt}\left\{[e^{qt}+H(0,t)]^{-2}\right.$$
$$\left.-2\int_0^t e^{qt'}\left[\frac{d\varepsilon}{dt'}+\xi(\varepsilon(t')-\varepsilon_0)\right][e^{qt}+H(t',t)]^{-3}dt'\right\}.$$

In the general case, the determination of $\epsilon(t)$ is a complicated problem even in the case of single-quantum pumping. The relations obtained in this section will be used later on to determine the distribution functions in the stationary and quasistationary cases.

2. Quasistationary Regime

If there is no p-level decay, then the system admits of a solution corresponding to the stationary regime ($\dot{y}_n = 0$). This regime corresponds physically to cancellation of the effects due, on the one hand, to laser pumping, and on the other to v—T relaxation and spontaneous transitions. The stationary distribution function can be determined rigorously as the asymptotic form of the function $y_n(t,\epsilon)|_{t\to\infty}$. In the presence of decay processes, this transition to the limits is no longer correct, for in this case, as shown by an analysis (see also [26,27,29]), it is impossible in principle to realize exactly the condition $\dot{y}_n = 0$ as $t \to \infty$. In addition, it must be recognized that when the concentration c(t) differs noticeably from unity, the vibrational-exchange time τ_{VV} increases, and consequently the parameters ξ, η, and δ cannot be regarded as constant. If the condition $|c^{-1}dc/dt| \ll 1$ is satisfied, then the initial system admits of a solution corresponding to the quasistationary regime. Assuming that this regime is established at large but finite values $qt \gg 1$, we write down for the distribution function

$$y_n(\varepsilon, t)|_{qt\gg1} \approx y_n(\varepsilon) = y_n^{(0)} + y_n^{(m)} + y_n^{(p)}.$$

In the quasistationary regime, the form of the function (1.6) becomes noticeably simpler. Calculating, for example, $y_n^{(0)}(\epsilon)$, we represent the integral in the corresponding formula in the form

$$H(0,t) = \int_0^{t_1} e^{qt'}(\varepsilon+\xi\varepsilon_0)\,dt' + \int_{t_1}^{t} e^{qt'}(\varepsilon+\xi\varepsilon_0)\,dt'.$$

The value of t_1 is chosen here large enough to be able to put $\epsilon(t) \approx \text{const}$ at $t' > t_1$; then

$$H(0,t) \approx \text{const} + \frac{\varepsilon+\xi\varepsilon_0}{q}(e^{qt}-e^{qt_1}),$$

and consequently, for times $t \gg t_1$ we have

$$H(0,t) \approx \frac{\varepsilon+\xi\varepsilon_0}{q} e^{qt}[1+O(e^{-qt})].$$

Thus, the quasistationary expression for $y_n^{(0)}$ takes the form

$$y_n^{(0)} = q(\varepsilon+\xi\varepsilon_0)^n/(q+\varepsilon+\xi\varepsilon_0)^{n+1}.$$

A similar procedure is used in the calculation of $y_n^{(m)}$ and $y_n^{(p)}$. Carrying out the corresponding summation operations in (1.6) and taking into account the identity

$$\sum_{k=1}^{n} k^{-1}\{1+C_n^k x^k-(1+x)^k\}=0,$$

we obtain a complete expression for the quasistationary distribution function

$$y_n = y_n^{(0)} + y_n^{(m)} + y_n^{(p)},$$
$$y_n^{(0)} = \frac{qa^n}{b^{n+1}}, \quad y_n^{(m)} = \frac{a^n}{b^{n+1}}\eta(y_0-y_m)(L_s-R_m), \tag{2.1}$$
$$y_n^{(p)} = \frac{a^n}{b^{n+1}} w(L_n-R_p),$$

where

$$a \equiv a(\varepsilon) = \varepsilon+\xi\varepsilon_0, \quad b \equiv b(\varepsilon) = q+\varepsilon+\xi\varepsilon_0, \quad R_r = \sum_{k=1}^{r} k^{-1},$$
$$L_s \equiv L_s\left(\frac{a}{b}\right) = \sum_{k=1}^{s} k^{-1}\left(\frac{a}{b}\right)^{-k} \quad s = \begin{cases} n, & n \leqslant m \\ m, & n \geqslant m \end{cases}.$$

We note that in the absence of laser pumping ($\eta = 0$) and in the absence of decay ($\delta = 0$) expression (2.1) describes the Boltzmann distribution $y_n = \epsilon_0^n/(\epsilon_0 + 1)^{n+1}$. For the populations y_0, y_m, and y_p we get from (2.1)

$$y_0 = [q-\eta(y_0-y_m)R_m - wR_p]b^{-1},$$
$$y_m = [q+\eta(y_0-y_m)(L_m-R_m)+w(L_m-R_p)]a^m b^{-m-1}, \tag{2.2}$$
$$y_p = \left[q+\frac{\xi}{m}(\varepsilon-\varepsilon_0)(L_m-R_m)\right]a^p b^{-p-1}$$
$$\times\left\{1+\delta(\varepsilon+\xi\varepsilon_0)^{-1}\left(\frac{a}{b}\right)^{p+1}\left[L_p-R_p-\frac{p-\varepsilon}{m}(L_m-R_m)\right]\right\}^{-1}.$$

The expression for y_p takes into account (1.2) and the energy equation (1.3) expressed in the stationary ($\dot{\epsilon} = 0$) form:

$$\eta(y_0-y_m) = \frac{1}{m}[\xi(\varepsilon-\varepsilon_0)+\delta y_p(p-\varepsilon)]. \tag{2.3}$$

Relations (2.2) and (2.3) yield an algebraic equation for the reserve of vibrational energy ϵ. It can be shown that the sought value of ϵ is the smallest positive root of this equation. Let us consider separately some particular cases.

a) Single-photon pumping. At m = 1 it is easy to obtain from the general relations of the present section, assuming the initial energy reserve to be $\epsilon_0 = 0$, the following equation for ϵ:

$$\xi\varepsilon(q+\varepsilon)^2 = \eta[(q+\varepsilon)(q-\xi\varepsilon)-q^2\varepsilon] - \delta y_p\Big\{(q+\varepsilon)^2(p-\varepsilon)$$
$$+\eta\Big[(q+\varepsilon)\Big(p-\varepsilon-\sum_{k=1}^{p}k^{-1}\Big)+q(p-\varepsilon-1)+\varepsilon\sum_{k=2}^{p}k^{-1}\Big]\Big\}, \tag{2.4}$$

where

$$y_p = \frac{q^2\varepsilon^p}{(q+\varepsilon)^{p+1}}\left\{1+\delta\frac{\varepsilon^p}{(q+\varepsilon)^{p+1}}\left[\sum_{k=1}^{p}k^{-1}\left(\frac{q+\varepsilon}{\varepsilon}\right)^k-\sum_{k=1}^{p}k^{-1}-q\frac{p-\varepsilon}{\varepsilon}\right]\right\}^{-1}$$

At relatively small δ, from approximately 1 to 10, the perturbation of the distribution function as a result of the p-level decay is small. In the case $p \gg 1$, $\xi = 0$, and $\eta \to \infty$, it is easy to obtain from (2.4) a relation that permits an estimate of the reserve of vibrational energy:

$$\left(\frac{\varepsilon}{\varepsilon+1}\right)^{p+1} \approx \delta^{-1}\Big\{p+[(\delta p)^{1/(p+1)}-1](2p-1-\ln p-C_0)$$
$$-\left(3+\frac{1}{(\delta p)^{1/(p+1)}-1}\right)\Big\}^{-1}$$

($C_0 \approx 0.677$ is the Euler constant).

At large pump intensities $\eta \to \infty$ (saturation regime) and at $\xi = 0$, in the case of absolute "transparency" of the potential barrier ($\delta \to \infty$) we have

$$1-|w|_{max}\Big\{(2+\varepsilon)(p-\varepsilon)-\varepsilon-1-\sum_{k=1}^{p}k^{-1}\Big\}=0,$$

where

$$|w|_{max} = \delta y_p|_{\delta\to\infty} = \left[1+\sum_{k=2}^{p}C_p^k k^{-1}\varepsilon^{-k}\right]^{-1}$$
$$= \left\{1+\sum_{k=1}^{p}k^{-1}(1+\varepsilon^{-1})^k - p\varepsilon^{-1} - \sum_{k=1}^{p}k^{-1}\right\}^{-1}. \tag{2.5}$$

The last formula gives the limiting value of the decay rate of the system in the case of single-quantum pumping. It is easy to obtain from (2.5) an equation for the reserve of the vibrational energy in the limiting regime:

$$\sum_{k=1} k^{-1}(1+\varepsilon^{-1})^k + (\varepsilon+2)(\varepsilon+1-p) - p\varepsilon^{-1} = 0.$$

The relations obtained in this section were used to calculate different variants for a sufficiently wide range

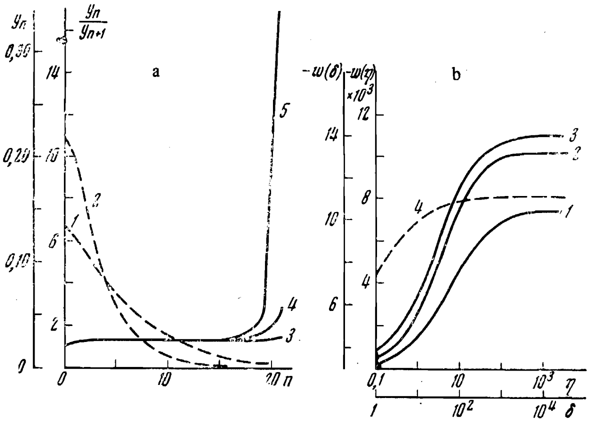

FIG. 1. Distribution function y_n and dependence of the system decay rate w for different parameters (single-photon pumping, m = 1; quasi-stationary regime): a—curves 1, 2—for $y_n(\xi = 10^{-3})$, curves 3 to 5—for y_n/y_{n+1} ($\xi = 10^{-4}$); p = 22, η = 10; 1—δ = 1, 2—δ = 10^3, 3—δ = 10, 4—δ = 10^2, 5—δ = 10^3; b) curves 1 to 3—for w(η), curve 4—for w(δ); p = 22, $\xi = 10^{-4}$; 1—δ = 1, 2—δ = 10, 3—δ = 10^2, 4—η = 10^3.

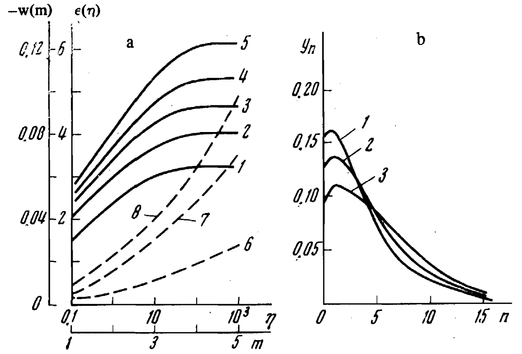

FIG. 2. Dependence of ε and w on the system parameters and form of the distribution function y_n in the quasistationary regime (multiphoton pumping): a) $\xi = 10^{-2}$, δ = 10^2, p = 22; 1—m = 1, 2—m = 2, 3—m = 3, 4—m = 4, 5—m = 5, 6—η = 1, 7—η = 10, 8—η = 100 (variants 1 to 5—for ε(η)), variants 6 to 8—for w(m)); b) $\xi = 10^{-2}$, p = 22, δ = η = 100; 1—m = 2, 2—m = 3, 3—m = 5.

of external parameters. Figure 1a illustrates the influence of the decay rate of the activation level on the form of the distribution function of the molecules with respect to the vibrational levels. An increase of the degree of "transparency" of the potential barrier (δ ≥ 100) affects significantly the form of the distribution in the vibrational-spectrum region close to the threshold value; at the same time, as expected, for large δ the dependence of the decay rate w(δ) is quite weak (Fig. 1b). At $\xi \ll 1$, a change of δ in the interval 10—10^4 corresponds to an increase of approximately 10% in the decay rate. The saturation effect (Fig. 1b) is connected with the increase of the rate η of the (0 → 1) induced transitions. At $\xi \ll 1$, the characteristic value η_{sat} of the saturation parameter is ~10^2. Notice should be taken of the rather weak dependence of the reserve of vibration energy on the degree of transparency of the barrier in the region of large δ; thus, at $\xi \ll 1$ in the saturation regime ($\eta \gg 1$), a change of δ ranging from 10 to 10^3 corresponds to an energy increment $\Delta\epsilon \lesssim 1$. The limiting characteristics ($\delta \to \infty$) in the case of single-photon pumping are shown in Fig. 6b below. On the basis of the obtained data we can easily verify that the stationarity condition $|w_{\max}| \ll 1$ is satisfied. The influence of the spontaneous and vibrational-translational relaxation on the quasistationary characteristics of the system is reflected in Fig. 6a.

b) Multiphoton pumping. The calculations in the case of multiquantum pumping of the vibrational mode were carried out with the aid of the general relations (2.1)—(2.3). It follows from the performed analysis that at relatively weak laser pumping ($\eta \lesssim 1$) of even high multiplicity (m ~ 10) the decay-rate constant w is small and satisfies well the condition $|w| \ll 1$. On the other hand, if η is large (at small and moderate values of the potential barrier, p < 20—30), then high decay rates (|w| ~ 1) are readily attained at large m; obviously, under these conditions the quasistationary analysis no longer holds.

Figure 2 contains information that gives an idea of the singularities of the quasistationary regime under conditions of multiphoton laser pumping. Figure 2a shows the form of the dependence of the reserve of vibrational energy on the pump level for a number of values of m from 1 to 5. We see that no fundamental difference from the case of single-photon pumping is observed here; we note only that the growth of the vibrational energy slows down with increasing multiplicity m. The plots of w(m), which are also shown in Fig. 2a, make it possible to estimate the decay rates at different pump values. The form of the quasistationary distribution function (a regime close to saturation) is illustrated in Fig. 2b. We note the singularities in the behavior of the distribution function, which becomes manifest at the first two levels of the vibrational spectrum, namely an intense multiphoton pumping leads to inversion of the 1 → 0 transition. Of course, at high pump levels and at relatively short times, an inversion is realized also with respect to the transitions n → n − 1 (n ≤ m), but in the transition regime the inversion for 2 ≤ n ≤ m becomes "dissolved" and remains in the quasistationary regime only for the 1 → 0 transition. This circumstance is connected with the fact that with increasing number of the level n the collision processes in which molecules take part become more intense.

3. Stationary Regime

If the decay rate is negligibly small (δ → 0), then a stationary regime is realized. In this case the form of the distribution function (2.1) becomes much simpler (we assume for simplicity $\epsilon_0 = 0$)[4)]

$$y_n(\varepsilon)=\frac{\varepsilon^n}{(q+\varepsilon)^{n+1}}\begin{cases} q+\dfrac{\xi\varepsilon}{m}\left[\sum\limits_{k=1}^{n}k^{-1}\left(\dfrac{\varepsilon}{q+\varepsilon}\right)^{-k}-\sum\limits_{k=1}^{m}k^{-1}\right], & n\leqslant m \\ q+\dfrac{\xi\varepsilon}{m}\left[\sum\limits_{k=1}^{m}k^{-1}\left(\dfrac{\varepsilon}{q+\varepsilon}\right)^{-k}-\sum\limits_{k=1}^{m}k^{-1}\right], & n\geqslant m \end{cases} \qquad (3.1)$$

If the rate of the inhibition processes is small ($\xi \ll 1$), then in the saturation regime ($\eta \to \infty$), in the case of arbitrary pump multiplicity, the populations of the zeroth and m-th levels, which are coupled by the laser field, correspond to the relations

$$y_0=\frac{q}{q+\varepsilon}\left(1-\frac{\xi\varepsilon}{mq}\sum_{k=1}^{m}k^{-1}\right),\quad y_m\approx q^2\varepsilon^m(q+\varepsilon)^{-m-1},$$

while the equation for the energy takes the form

$$q(q+\varepsilon)^m-\xi\varepsilon(q+\varepsilon)^m\frac{1}{m}\sum_{k=1}k^{-1}-q^2\varepsilon^m=0.$$

It is easy to obtain from this equation the limiting value of the energy (for not too large m)

$$\varepsilon \approx m\left(\xi \sum_{k=1}^{\bar{m}} k^{-1}\right)^{-1/2}. \qquad (3.2)$$

The results obtained in this section generalize the results of[16], where the stationary regime at m = 1 is considered.

Figure 3 illustrates the influence of different parameters on the characteristics of the stationary regime. The qualitative behavior of the curves is understandable. We note only the singularity in the case of multiquantum pumping ($m \gtrsim 2$), namely, at sufficiently high rate of the induced processes ($\eta \gg 1$) population inversion sets in with respect to the transition $1 \to 0$ (Fig. 3b), i.e., this singularity is retained also in the stationary regime (see Sec. 2).

II. VIBRATIONAL KINETICS OF MOLECULES IN THE CASCADE EXCITATION MECHANISM

4. Possibility of Cascade Excitation Mechanism

In this section we investigate the vibrational kinetics of molecules under nonequilibrium conditions produced by resonant laser radiation as a result of the cascade mechanism of population of the vibrational levels[13,20]. The study of the kinetic processes under these conditions is of undoubted interest, since the cascade mechanism, from the point of view of selective excitation of high sections of the vibrational spectrum of the molecule, has obvious advantages, since it permits rapid excitation of a single-out vibrational branch without energy loss to the excitation of other degrees of freedom of the molecules.

Cascade population can be realized in principle by using multifrequency radiation produced, for example, with several lasers with tunable frequency[20]. Such a system makes it possible to overcome in natural fashion the difficulties due to anharmonicity of the molecule vibrations. A practical realization of this method, however, is difficult because, in particular, the question of producing an effective tunable laser in the IR band is presently only in the speculative state[30,31].

In the case of single-frequency laser radiation, the realization of the cascade mechanism imposes definite conditions on the spectroscopic properties of the resonant molecules and on the irradiated gas mixture as a whole. Let us formulate these conditions: 1) the vibrational-rotational absorption lines of the selected mode must overlap, so as to enable the field to "capture" resonantly several lower vibrational bands. 2) The rate of excitation of the vibrations should exceed the rate of energy dissipation into other degrees of freedom, thereby ensuring selectivity of the excitation of the given mode.

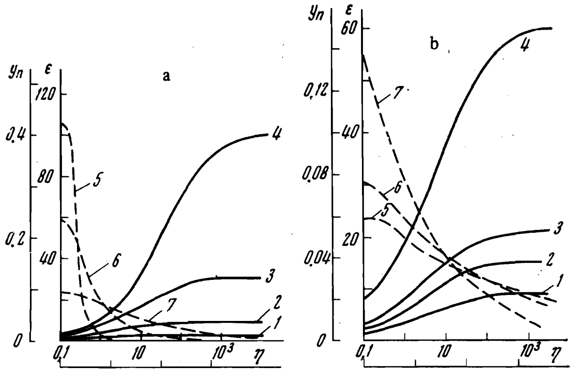

FIG. 3. Dependence of the reserve of vibrational energy $\varepsilon(\eta)$ and form of the distribution function y_n in the stationary regime ($\delta = 0$) at different system parameters: a) singlequantum pumping ($m = 1$); curves 1 to 4—for $\varepsilon(\eta)$; 1—$\xi = 10^{-1}$, 2—$\xi = 10^{-2}$, 3—$\xi = 10^{-3}$, 4—$\xi = 10^{-4}$; curves 5 to 7—for y_n at $\eta = 100$; 5—$\xi = 1$, 6—$\xi = 10^{-1}$, 7—$\xi = 10^{-2}$; b) multiquantum pumping; curves 1 to 4—for $\xi(\eta)$ at $\xi = 10^{-2}$; 1—m = 1, 2—m = 2, 3—m = 3, 4—m = 10; curves 5 to 7 for y_n at m = 2; 5—η = 100, 6—η = 10, 7—η = 1.

From the point of view of satisfying the first condition, it is preferable to use molecules with sufficiently weak anharmonicity and with low values of the rotational constant. Such properties are possessed by many heavy polyatomic molecules. For example, for the molecules C_4H_4S, OsO_4, $H_2C_2O_2$, $(CH_3)_2CO$, the minimum value of the rotational constant B_e [in cm^{-1}] are respectively 0.10, 0.11, 0.14, and 0.16, and the anharmonicity amounts to $\omega_e x_e \sim 1.5\ cm^{-2}$[32]. If the impact broadening is $\Delta\nu \sim 5 \times 10^9$ Hz/atm, then at $B_e \sim 10^{-1}\ cm^{-1}$ the lines begin to overlap at a pressure $p \sim B_e c/\Delta\nu \sim 0.5$ atm[5)]. It should be noted that overlap of the vibrational-rotational lines can be achieved at moderate pressures by using a mixture that is rich in different isotopes of the irradiated molecule; thus, for example, at $p \sim 1$ atm, for the CO_2 molecule, which has 18 isotopic formations, the width of the overlap region is $\sim kT \sim 200\ cm^{-1}$[31]. The second condition corresponds to molecules having a relatively low probability of deactivation of the vibrational excitation ($P_{10} \sim 10^{-3}-10^{-5}$).

Several theoretical papers published to date[8,17,19] deal with certain questions connected with the cascade excitation of molecule vibrations. In particular, the nonstationary process of populating vibrational levels is investigated in[19] on the basis of a certain simplified model. A quasistationary excitation regime is considered in[8,17] within the framework of the diffusion approximation.

It should be noted that in the general case vibrational-kinetic problems reduce in essence to a determination of a discrete distribution function, the evolution of which explains the features of the excitation process itself under various conditions. The diffuse model, on the other hand, yields a certain averaged picture. In this part we use three regimes of laser excitation of vibrational degrees of freedom under conditions of cascade population: nonstationary, stationary, and quasistationary.

5. General Relations. Nonstationary Regime

The competition between the cascade population of vibrational levels and different relaxation processes that tend to bring the system into thermodynamic equilibrium predetermines the resultant distribution function of the molecules over the spectrum of the selected vibrational branch. In the case of multiphoton pumping, the evolution of the distribution function y_n is described by the system (1.1). In the case of cascade population, all that changes in this system is the term corresponding to the specific features of the pumping (it is assumed that the laser radiation "captures" m lower vibrational levels):

$$\begin{gathered}\left(\frac{dy_n}{dt}\right) = (n+1)\left[y_{n+1}\eta_{n,J(n)}^{n+1,J(n+1)} - y_n\eta_{n+1,J(n+1)}^{n,J(n)}\right](1-\delta_{nm}) \\ -n\left[y_n\eta_{n-1,J(n-1)}^{n,J(n)} - y_{n-1}\eta_{n,J(n)}^{n-1,J(n-1)}\right], \quad n \leqslant m, \\ \eta_{n,J(n)}^{n+1,J(n+1)} = \frac{g_{n,J(n)}f_{n+1,J(n+1)}}{f_{n,J(n)}g_{n+1,J(n+1)}}\eta_{n+1,J(n+1)}^{n,J(n)} = \tau_{vv}\frac{c^2IA_{10}}{8\pi^2h\Delta\nu\nu_0^3}f_{n+1,J(n+1)}g(\nu),\end{gathered} \qquad (5.1)$$

$$g(\nu)\equiv g(\nu_0-\nu_{n,J(n)}^{n+1,J(n+1)})=\Delta\nu^2\{\Delta\nu^2+[\nu_0-\nu_{n,J(n)}^{n+1,J(n+1)}]^2\}^{-1},$$

where $f_{kJ(k)}$ is the relative fraction of the molecules on the J-th vibrational sublevel of the k-th vibrational level (it is assumed that only two rotational sublevels of each of the captured bands are coupled by the resonant radiation and that the equilibrium with respect to rotation sets in instantaneously), $g_{k,J(k)}$ is the degeneracy factor, I [erg/cm^{2}sec] is the intensity, $\Delta\nu$ is the impact half-width of the lines, $g(\nu)$ is the form factor, ν_0 is the laser frequency, and $\nu_{n,J(n)}^{n+1,J(n+1)}$ is the frequency of the vibrational-rotational lines. If the interaction of the laser radiation with the rotational substructure of each of the vibrational bands is spelled out concretely, the problem becomes quite cumbersome (although straightforward in principle). To simplify the analysis and to clarify the principal features of the cascade excitation mechanism, we shall assume henceforth that $\eta_{i,J(i)}^{k,J(k)}\equiv\eta$.

In this case, the equation for the average energy reserve, with allowance for (5.1), takes the form

$$\frac{d\varepsilon}{dt}=-\xi(\varepsilon-\varepsilon_0)+\eta\left[\sum_{i=0}^{m-1}y_i-my_m\right]+(p-\varepsilon)w. \tag{5.2}$$

The cascade excitation mechanism introduces into (1.4) and (1.5) the following changes:

$$\left(\frac{\partial G}{\partial t}\right)_m=\eta(z-1)\sum_{i=0}^{m-1}(i+1)z^i(y_i-y_{i+1}),$$

$$G_m(z,t)=\frac{\eta e^{qt}}{c(t)}\sum_{i=0}^{m-1}(i+1)\sum_{k=1}^{i+1}C_i^{k-1}\int_0^t\frac{c(t')(y_i-y_{i+1})(z-1)^ke^{kqt'}dt'}{[e^{qt}-(z-1)H(t',t)]^{k+1}} \tag{5.3}$$

A chemical reaction stimulated by laser emission has a selective character if the condition of rapid population of the levels of the selected molecule vibration mode is satisfied. From the practical point of view, therefore, the question of the rate of excitation of the vibrations is one of the most important ones. Obviously, the most favorable possibilities in this sense is a system in which the radiation extends over all the levels. If we neglect the decay process in (5.2) (w = 0) and let m → ∞, then we can easily obtain the law governing the variation of the average energy ϵ with time:

$$\varepsilon(t)=\varepsilon_0+\frac{\eta}{\xi}(1-e^{-\xi t}), \tag{5.4}$$

where ϵ_0 is the initial energy reserve. From (5.4) at $t\to\infty$ we obtain $\epsilon_\infty=\epsilon_0+\eta/\xi$, i.e., the stationary energy reserve in the considered idealized case is directly proportional to the rate of induced transitions and is inversely proportional on the rate of the inhibiting processes. If the rates of spontaneous transitions and of the v–T relaxation are small, then $\epsilon(t)$ is a linear function:

$$\varepsilon(t)\approx\varepsilon_0+\eta t,\quad \xi t\ll1.$$

This relation characterizes the maximum possible rate of laser excitation of the molecule vibrations ($\dot{\epsilon}=\eta$). It is easy to obtain the nonstationary distribution function in explicit form. The equation for the generating function simplifies as m → ∞, and when (5.3) is taken into account it can be expressed in the form

$$\frac{\partial G}{\partial t}=\left\{(\varepsilon+\eta)(z-1)^2+(z-1)\left[1+\xi\frac{1-ze^{-\theta}}{1-\rho^{-\theta}}\right]\right\}\frac{\partial G}{\partial z}+(z-1)(\varepsilon+\eta+\xi\varepsilon_0)G.$$

This equation is easy to solve (the initial distribution coincides with the equilibrium distribution):

$$G(z,t)=e^{qt}\left\{e^{qt}-(z-1)\left[\varepsilon_0+\int_0^t e^{qt'}(\varepsilon+\eta+\xi\varepsilon_0)dt'\right]\right\}^{-1}.$$

The standard procedure[24,25] with allowance for the explicit form of the generating function yields for the distribution function the expression

$$y_n(t)=\varepsilon^n(t)/[1+\varepsilon(t)]^{n+1},$$

where $\epsilon(t)$ is determined by (5.4). Thus, if the radiation extends over the entire vibrational mode, then the distribution of the molecules over the levels retains its Boltzmann character in the course of time ($y_n(0)=\epsilon_0^n/(1+\epsilon_0)^{n+1}$). For the limiting value of the effective vibrational temperature ($t\to\infty$, $\epsilon_0\approx0$), we can write down the expression

$$T_{vib,\infty}=\frac{h\nu}{k}\left[\ln\left(1+\frac{\xi}{\eta}\right)\right]^{-1},$$

and at $\xi\sim\eta$ we obtain $T_{vib}\sim h\nu/k$.

6. Quasistationary Regime

The form of the quasistationary distribution function can be obtained with the aid of the method used in Sec. I. In this case we shall use a simple approach. From the initial system of kinetic equations, with allowance for (5.1), it is easy to obtain in the quasistationary regime ($|w|\ll1$) the following recurrence relations:

$$\begin{aligned} y_n&=\frac{d}{c}y_{n+1}-\frac{w}{(n+1)c},\quad n\leqslant m-1,\\ y_n&=\frac{b}{a}y_{n+1}-\frac{w}{(n+1)a},\quad m\leqslant n\leqslant p-1,\end{aligned} \tag{6.1}$$

where we have introduced the additional notation

$$c\equiv c(\varepsilon)=\varepsilon+\eta+\xi\varepsilon_0,\quad d\equiv d(\varepsilon)=q+\varepsilon+\eta+\xi\varepsilon_0.$$

Using the explicit form of the generating function G(z, t) (see (1.5) and (5.3)), and taking into account the relation $y_0(\epsilon, t) = G(0, t)$, we easily find the asymptotic form of $y_0(\epsilon)$:

$$y_0(\varepsilon)=\left[q-\eta(y_0-y_m)-w\sum_{k=1}^{p}k^{-1}\right](q+\varepsilon+\xi\varepsilon_0)^{-1}.$$

The last relation in (6.1) enables us to find the distribution function

$$\begin{aligned} y_n&=\frac{c^nd^{m-n}}{d^{m+1}-\eta c^m}\left\{q+w\left[-R_p+\frac{\eta}{d}\sum_{k=1}^{m}k^{-1}\left(\frac{c}{d}\right)^{m-k}\right]\right\}\\ &\quad+\frac{w}{d}\sum_{k=1}^{n}k^{-1}\left(\frac{c}{d}\right)^{n-k},\quad n\leqslant m,\\ y_n&=\frac{c^m(ab^{-1})^{n-m}}{d^{m+1}-\eta c^m}\left\{q+w\left[-R_p+\frac{\eta}{d}\sum_{k=1}^{m}k^{-1}\left(\frac{c}{d}\right)^{m-k}\right]\right\}\\ &\quad+\frac{w}{d}\left(\frac{a}{b}\right)^{n-m}\sum_{k=1}^{m}k^{-1}\left(\frac{c}{d}\right)^{m-k}+\frac{w}{b}\sum_{k=m+1}^{n}k^{-1}\left(\frac{a}{b}\right)^{n-k},\quad n\geqslant m.\end{aligned} \tag{6.2}$$

Using (1.2) and (6.2), we obtain for the system decay rate

$$\begin{aligned} w=-\delta qa^{p-m}c^m\Bigg\{&b^{p-m}(d^{m+1}-\eta c^m)\left[1+\frac{\delta}{b}\sum_{k=m+1}^{p}k^{-1}\left(\frac{a}{b}\right)^{p-k}\right.\\ &\left.+\delta a^{p-m}\left[d^m\sum_{k=1}^{m}k^{-1}\left(\frac{c}{d}\right)^{m-k}-b^mR_p\right]\right]\Bigg\}^{-1}.\end{aligned} \tag{6.3}$$

If the potential barrier is absolutely "transparent" ($\delta\to\infty$), i.e., the molecules decay instantaneously after reaching the activation-energy level, then the expression for the decay rate of the system (6.3) takes the form

$$\begin{aligned} w(\delta\to\infty)=-qc^m\Bigg\{&\frac{1}{b}\left(\frac{b}{a}\right)^{p-m}(d^{m+1}-\eta c^m)\sum_{k=m+1}^{p}k^{-1}\left(\frac{a}{b}\right)^{p-k}\\ &+d^m\sum_{k=1}^{m}k^{-1}\left(\frac{c}{d}\right)^{m-k}-b^mR_p\Bigg\}^{-1}.\end{aligned}$$

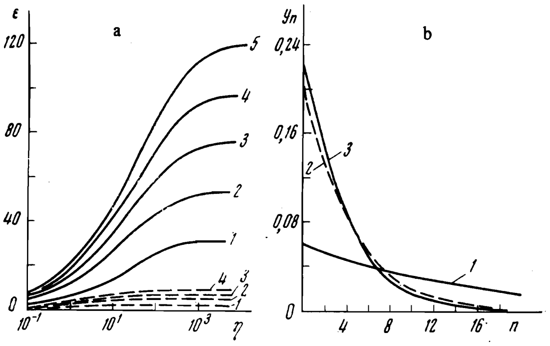

FIG. 4. a) Dependence of the reserve of vibrational energy in the stationary regime ($\delta = 0$) on the excitation level η at different m and ξ (cascade population): 1—m = 1, 2—m = 2, 3—m = 3, 4—m = 4, 5—m = 5, solid lines—$\xi = 10^{-3}$, dashed—$\xi = 10^{-1}$; b) stationary and quasistationary distribution functions y_n at $\xi = 10^{-3}$, $\eta = 1$, p = 22, and m = 3 (cascade population); 1—$\delta = 0$, 2—$\delta = 10$, 3—$\delta = \infty$.

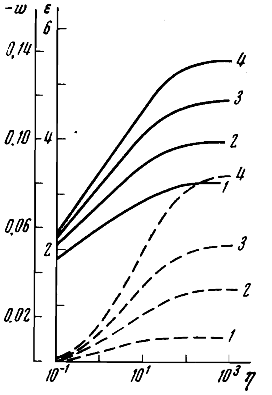

FIG. 5. Vibrational energy and system decay rates vs. pump level η for different m in the case of instantaneous decay of the p level ($\delta = \infty$), $\xi = 10^{-3}$, p = 22, solid lines—$\epsilon(\eta)$, dashed—$w(\eta)$; 1—m = 1, 2—m = 2, 3—m = 3, 4—m = 4 (cascade population).

It is easy to verify that in the case of single-cascade excitation the relations obtained in this section coincided identically with the relations corresponding to the particular situation m = 1 of Chap. I.

If we add to (6.2) and (6.3) the energy equation (5.2), expressed in the stationary form ($\dot{\epsilon} = 0$)

$$\xi(\varepsilon-\varepsilon_0)=\eta\left(\sum_{i=0}^{m-1} y_i-my_m\right)+w(p-\varepsilon),$$

then the problem of determining the character of the quasistationary nonequilibrium distribution function and of the principal parameters of the system becomes closed. It is clear that a solution of this problem can be obtained in the general case only by numerical methods.

Under the conditions of cascade population, the quasistationary distribution function decreases monotonically with increasing number of the vibrational level (compare with the multiquantum pumping in the saturation regime, $\eta \gg 1$). With increasing degree of transparency of the potential barrier ($\delta \gg 1$), the "tail" of the distribution becomes significantly deformed ($\delta \to \infty$, $y_{p-1}/y_p \to \infty$). With decreasing rate of decay of the activation level, the distribution function acquires a more gently sloping character (Fig. 4b).

Figure 5 shows plots of the margin of the vibrational energy ϵ and of the decay-rate constant w on the laser-pumping level η in the case of absolute transparency of the potential barrier (the number of cascades is m = 1—4). As follows from the foregoing calculation that at not too large m and small ξ, the saturation regime is reached at $\eta \gtrsim 10^2$ ($p \lesssim 40$). An increase of the number of cascades to m = 4 increases the average vibrational energy by ~2—3 quanta (per oscillator). Attention is called to the strong dependence of the system decay rate |w| on the pump level in the range of relatively small η, and this dependence becomes stronger with increasing number of vibrational bands captured by the field (for example, for m = 4, the rate changes by a factor of 10 in the range of η from 0.1 to 1, and by a factor 1.5—2 in the range from 10 to 10^2). The reason is that far from saturation the system decay rate is quite sensitive to the total reserve of vibrational energy.

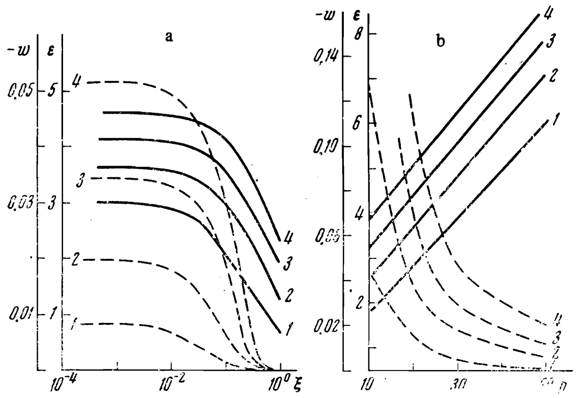

FIG. 6. Dependence of the reserve of vibrational energy and of the system decay rate on the rate ξ of inhibition processes and on the number p of the activation level for different values of m at $\delta = \infty$; 1—m = 1, 2—m = 2, 3—m = 3, 4—m = 4: a—$\epsilon(\xi)$ (solid lines) and $w(\xi)$ (dashed) for p = 22 and $\eta = 10$; b) $\epsilon(p)$ (solid lines) and w(p) (dashed) for $\xi = 10^{-3}$ and $\eta = 10^2$.

Figure 6a gives an idea of the influence of the inhibition processes (spontaneous decay, v—T relaxation) on the parameters of the excited system. As follows from the calculations, this influence comes into play for inhibition rates $\xi \gtrsim 10^{-2}$ and becomes appreciable at $\xi \sim 10^{-1}$. Of course, at sufficiently large v—T relaxation rates, the analysis must take into account thermal effects that lead to an increase in the total temperature "background."

Figure 6b contains information on the dependence of the vibrational energy and of the system decay rate on the activation energy. Although the quasistationary energy reserve increases with increasing potential barrier, the rate of decay of the system decreases. As seen from the figure, the function $\epsilon(p)$ is practically linear, and at small p the decay rate increases sharply. It should be noted that inasmuch as the existence of the quasistationary regime calls for satisfaction of the condition $|w| \ll 1$, in the case of large rates ($|w| \sim 0.3$), the analysis within the framework of the assumed model becomes in general less rigorous.

7. Stationary Regime

Neglecting the system decay process ($\delta = 0$), let us find the characteristics of the stationary excitation regime under conditions of cascade population of the vibrational levels. In this case, the form of the distribution function (6.2) becomes much simpler:

$$\begin{aligned} y_n&=qc^nd^{m-n}(d^{m+1}-\eta c^m)^{-1}, \quad n\leq m,\\ y_n&=qc^m(a/b)^{n-m}(d^{m+1}-\eta c^m)^{-1}, \quad n\geq m. \end{aligned} \tag{7.1}$$

Neglecting the initial energy reserve ($\epsilon_0 \approx 0$), we express the equation for the vibrational-energy reserve in the form

$$\frac{\xi\varepsilon}{\eta q}[(q+\varepsilon+\eta)^{m+1}-\eta(\varepsilon+\eta)^m]=\sum_{k=0}^{m-1}(\varepsilon+\eta)^k(q+\varepsilon+\eta)^{m-k}-m(\varepsilon+\eta)^m \tag{7.2}$$

It is easy to obtain the solution of this equation in the saturation regime, when $\eta \to \infty$ and $\xi \ll 1$. In this case Eq. (7.2) becomes simpler and takes the following form (the number of cascades m is not too large, and $\epsilon \gg 1$)

$$\xi\varepsilon^2+\xi(m+1)\varepsilon-{}^1\!/_2qm(m+1)=0,$$

whence

$$\varepsilon_{max}\approx\frac{m+1}{2}\left\{\left[1+\frac{2qm}{\xi(m+1)}\right]^{1/2}-1\right\}.$$

If the rate of the inhibition processes is small ($\xi \ll 1$), then

$$\varepsilon_{max}\approx\sqrt{m(m+1)/2\xi}.$$

This result demonstrates the advantages of the m-cascade pumping over m-photon excitation (cf. (3.2)). If the laser radiation covers the entire vibrational mode ($m \to \infty$) then, as can be easily shown, solution of (7.2) yields for the maximum stationary energy reserve the value $\epsilon_{max} = \epsilon_\infty = \eta/\xi$, which coincides with the result obtained in Sec. 5.

Figure 4a illustrates the dependence of the average vibrational energies stored by the molecule in the laser field on the excitation level η in the case when several cascades are captured (m = 1—5) at different rates of the inhibition processes. An increase in the number of cascades leads to an increase of ϵ (for values of η in the interval $1-10^2$, a change of m from 1 to 5 corresponds to an increase in the energy reserve by approximately three times). An increase in the inhibition rate ξ decreases the reserve appreciably (by one order of magnitude in the saturation regime when ξ varies in the interval $10^{-3}-10^{-1}$). Figure 4b shows the distribution function of the molecules with respect to the vibrational spectrum in the case of three-cascade pumping (for comparison, we present several quasistationary distributions).

CONCLUSION

The foregoing analysis of the nonequilibrium vibrational kinetics of molecules in the presence of a resonant laser field was based on a number of assumptions (see Sec. 1), which naturally limit the applicability of its results. Nonetheless, the analysis developed above explains the specific features of the kinetics under conditions of nonequilibrium decay. It should be noted that modern theory of chemical reactions (regardless of how they are initiated) is considerably model-dependent. The primary reason is lack of exact knowledge of the multidimensional surface potential energy of the interaction of the system particles, and lack of knowledge of the mechanism of the energy-exchange processes between the vibrationally-excited polyatomic molecules. In the latter case, the situation becomes greatly complicated by the anharmonicity of the molecules. The anharmonicity leads to interaction of the normal modes, and exchange interaction becomes particularly strongly manifest in the case when the energy defect ΔE between the fundamental tone (or overtone) of one mode in the overtone of another mode is small enough ($\Delta E/kT < 1$). Allowance for anharmonicity should include the multiphoton (generally of the Raman type) energy-exchange processes.

Letokhov and Makarov [19] called attention to the question of the role of rotational relaxation in the process of saturation of a vibrational transition acted upon by a laser field. It is clear from general considerations that if the frequency of the laser radiation coincides with one of the rotational-vibrational lines of the vibrational band, then at sufficiently high radiation intensity the rate of filling of the rotational spectrum of the upper vibrational level is limited by the rate of rotational relaxation[6]. Allowance for the influence of the rotational relaxation calls for a correct analysis of the corresponding kinetics responsible for the redistribution of the molecules over the rotational sublevels. Unfortunately the theory has made very little progress so far in this direction.

A theory free of the indicated limitations is of undisputed interest. In addition, research connected with different modifications of the considered excitation methods is worthy of attention. In particular, one of the possible modifications of the cascade excitation mechanism was pointed out in [13]. If a polyatomic molecule has multiple frequencies, then levels of different vibrational modes can be made to participate in the excitation process (owing to the combined effect due, on the one hand, to the induced transitions and on the other hand to resonant v-v energy exchange between these modes).

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[1] After this paper sent to press, an article dealing with some analogous problems was published by Gordiets, Osipova, and Panchenko [21].

[2] In this paper we do not take into account the process inverse to the p-level decay, the processes of v-v exchange of energy between a given oscillation mode and others, thermal effects, and effects connected with relaxation of the vibrational sublevels. The latter, generally speaking, are negligible in the case of multifrequency pumping. On the other hand, if the laser frequency is tuned to a single vibrational-rotational line of the 0 → m band, then it is assumed that the rate of the induced transitions (0J → mJ′) is smaller than the rotational-relaxation rate (in the case $W_m = \sigma_{0J}{}^{mJ'}If(J')$, where f(J′) is the equilibrium fraction of the molecules at the vibrational sublevel J′, $\sigma_{0J}{}^{mJ'}$ is the cross section of the induced transition, and I is the intensity).

[3] We note that, in any approach, the calculation of the distribution function y_n in the quasistationary regime entails in principle a definite error due to the specifics of the regime itself [26,27].

[4] We recall that formulas (2.1) yield the exact stationary distribution function for an infinite system of kinetic equations.

[5] In principle, the anharmonicity can be cancelled out by broadening the levels with a sufficiently strong field [7]. In this case the necessary fields E are determined from the relation $\mu E/h \sim 2\omega_e x_e v$, where μ is the dipole moment and v is the number of the vibrational level. If v = 5 and we assume that $\mu = 5 \times 10^{-19}$ cgs esu, then we get $E \sim 10^5-10^6$ V/cm for $\omega_e x_e \sim 1-10$ cm^{-1}. Many other processes become important in such fields (for example, breakdown in gas).

[6] Obviously, optimal conditions for multiphoton pumping are obtained by tuning the laser to the frequency of the transition between the rotational sublevels with maximum relative population, i.e., with $J_{max} \approx \sqrt{T/2\Theta_{rot}}$ (Θ_{rot} is the characteristic rotational temperature). Within the framework of the model of [19], the rotational quantum number J_{max} corresponds to a vibrational-transition saturation time $\sim\tau_{rot}/f(J_{max})$ (case of large pump intensities).

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