# KINETICS OF EXCITATION OF MOLECULAR VIBRATIONS BY INFRARED LASER RADIATION

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Excitation of a selected vibrational degree of freedom by infrared laser radiation is considered. Expressions for nonequilibrium distribution functions corresponding to various excitation models are obtained. It is shown that the rate of introduction of vibrational energy E into the molecular system as a result of resonance interaction with the laser radiation in the most general case is restricted by the relation $(\hbar\omega)^{-1} dE/dt < q/2\tau_{rot}$, where q is the fraction of molecules involved in the absorption, $\tau_{rot}$ is the rotational relaxation time, and $\hbar\omega$ is the transition energy. It is concluded that the restriction on rate of excitation of molecular vibrations impedes the vibrational heating of the molecules before vibrational-translational relaxation sets in.

## 1. INTRODUCTION

SELECTIVE excitation of molecule vibrations by laser radiation is an important potential capability of laser technology, already noted during its first years of development. Prior to the appearance of powerful infrared lasers, this possibility was not investigated experimentally. In 1966, Borde and co-workers[1] observed dissociation of ammonia molecules in the field of monochromatic radiation of a powerful cw $CO_2$ laser, the frequency of a number of lines of which coincides with the vibrational band $\nu_2$ of the $NH_3$ molecule[1]. Although the mechanism of the ammonia-molecule idssociation in such experiments is thermal[1,3], i.e., perfectly nonselective, this investigation stimulated the study of the possibility of selective heating of a definite vibration of the molecule[2]. In particular, this possibility was discussed in[2]. A theoretical analysis of the excitation of high vibrational levels of a molecule by laser radiation under conditions of predominant vibrational-vibrational relaxation was carried out in[5,6].

It was assumed in the known theoretical papers that all the molecules int he ground and first-excited vibrational states take part in the induced transitions. Actually, monochromatic laser radiation is absorbed only by one or several vibrational-rotational transitions of the entire band. It is intuitively clear that such an approach can be valid if the following condition is satisfied

$$W\tau_{rot} \ll 1, \tag{1.1}$$

where W is the probability of the induced transitions

between the corresponding vibrational-rotational states and $\tau_{rot}$ is the time of rotational relaxation. Relation (1.1) is certainly valid for interactions between absorbing molecules and continuous laser radiation. However, this condition may not be satisfied in interaction with powerful pulses. Physically this corresponds to the fact that the molecules at the rotational levels of the ground and excited vibrational states, which are strongly coupled by the resonant fields, do not have time to relax over the remaining rotational levels.

As shown in Sec. 2 below, this effect limits the rate of transfer of the molecules to the excited state, and in the case of high power ($W\tau_{rot} \gg 1$) the time to excite half the molecules even to the first level cannot be shorter than $\tau_{rot}/q$, where q is the relative fraction of the molecules at one rotational level. The "bottleneck" effect plays an important role in the limitation of the regular excitation of high vibrational levels both in the model of cascade excitation of high vibrational levels by radiation (Sec. 3) and in the model of their excitation in the process of vibrational-vibrational exchange of energy (Sec. 4). In the conclusion (Sec. 6), it is shown that an analysis of the kinetics of the excitation of vibrational levels with allowance for the rotational relaxation is important for the interpretation of experiments on the dissociation of molecules by pulsed infrared radiation[7,8], since it makes it possible to reject the mechanism of selective vibrational heating of the molecule by the field[8]. The calculated upper bound of the excitation rate of the molecule vibrations is a serious obstacle to vibrational heating of the molecule prior to relaxation of the vibrations to translational motion.

## 2. "BOTTLENECK" EFFECT IN THE SATURATION OF A VIBRATIONAL TRANSITION OF A MOLECULE

We consider the kinetics of the saturation of a vibrational transition of molecules under the influence of monochromatic laser radiation with a frequency that coincides with the frequency of some particular vibra-

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[1] A similar experiment with the $BCl_3$ molecule was subsequently performed in [2].

[2] It was demonstrated recently by direct spectral measurements of the populations of the excited vibrational levels that the mechanism for the excitation of the vibrations of the $NH_3$ molecule at a pressure above approximately 10 Torr by continuous emission from an infrared laser is purely thermal even below the threshold of dissociation and visible glow [4].

tional-rotational transition of the band. We are interested in the dependence of the rate of excitation of the molecules on the ratio of the rate of induced transitions W to the time of rotational relaxation $\tau_{rot}$. It is natural in this case to neglect the slower vibrational and radiative relaxation processes, and to assume that the parameter of the lower and upper levels (the statistical weights and the times of rotational relaxations) are identical and that the gas pressure is such that the absorption-line broadening is homogeneous.

Under such assumptions, the equations describing the population of the rotational sublevels of the lower and upper vibrational states $n_0'$ and $n_1'$ can be written in the form

$$\frac{dn_0'}{dt} = -W(n_0' - n_1') + \frac{q_0 n_0 - n_0'}{\tau_{rot}},$$
$$\frac{dn_1'}{dt} = W(n_0' - n_1') + \frac{q_1 n_1 - n_1'}{\tau_{rot}}$$

(2.1)

where $n_0$ and $n_1$ are the total populations of the lower and upper vibrational levels; $q_0$ and $q_1$ are the factors of the populations of the working rotational sublevels, which are expressed in terms of the partition function of the rotational states $Z_i^{rot}$, the degeneracy of the sublevel $g_i$, and the energy of the corresponding rotational sublevel $E_i$;

$$q_i = (Z_i^{rot})^{-1} g_i \exp(-E_i / kT).$$

(2.2)

We assume henceforth that $q_0 = q_1 = q$.

Taking into account the obvious relation

$$\frac{dn_0}{dt} = -W(n_0' - n_1') = -\frac{dn_1}{dt}$$

(2.3)

and assuming the initial conditions

$$n_0|_{t=0} = N_0, \quad n_1|_{t=0} = 0,$$

(2.4)

we obtain as a result the following expression for $n_0$ and $n_1$:

$$n_0 = \frac{N_0}{2} + N_0 q W \left[ \frac{A_1}{p_1} \exp(-p_1 t) + \frac{A_2}{p_2} \exp(-p_2 t) \right],$$

(2.5)

$$n_1 = \frac{N_0}{2} - N_0 q W \left[ \frac{A_1}{p_1} \exp(-p_1 t) + \frac{A_2}{p_2} \exp(-p_2 t) \right];$$

(2.6)

$$p_{1,2} = W + \frac{1}{2\tau_{rot}} \pm \left[ \left( W + \frac{1}{2\tau_{rot}} \right)^2 - \frac{2qW}{\tau_{rot}} \right]^{1/2},$$

(2.7)

$$A_{1,2} = \frac{1}{2} \left\{ \left[ \left( W + \frac{1}{2\tau_{rot}} \right)^2 - \frac{2qW}{\tau_{rot}} \right]^{1/2} \pm \left( W - \frac{1}{2\tau_{rot}} \right) \right\}$$
$$\times \left[ \left( W + \frac{1}{2\tau_{rot}} \right)^2 - \frac{2qW}{\tau_{rot}} \right]^{-1/2}.$$

(2.8)

When $q \ll 1$, i.e., when a small fraction of the molecules takes part in the absorption, expressions (2.5) and (2.6) become much simpler:

$$n_0 \approx \tfrac{1}{2} N_0 (1 + e^{-2bt}), \quad n_1 \approx \tfrac{1}{2} N_0 (1 - e^{-2bt});$$

(2.9)

$$b = \frac{qW}{2\tau_{rot}(W + 1/2\tau_{rot})}.$$

(2.10)

It is seen from (2.10) that at $q \ll 1$ the quantities $n_0$ and $n_1$ satisfy approximately the following differential equations:

$$dn_0 / dt = -b(n_0 - n_1),$$

(2.11)

$$dn_1 / dt = b(n_0 - n_1).$$

(2.12)

The quantity $(2b)^{-1}$ is the characteristic saturation time of the vibrational transition. It is seen from (2.10) that $b$ increases with increasing $W$ and at $W\tau_{rot} \gg 1$

it tends to the maximum value

$$b_{max} = q / 2\tau_{rot}.$$

(2.13)

Thus, the characteristic time of saturation of the vibrational transition cannot be smaller than $\tau_{rot}/q^{3)}$.

The validity of Eqs. (2.11) and (2.12) for the case $W\tau_{rot} \gg 1$, which will be used subsequently, can be illustrated by the following considerations. At $W\tau_{rot} \gg 1$, the working transition is saturated at all times, i.e., $n_0' \approx n_1' \approx n'$. Since $q \ll 1$, it follows that $n_0 \gg n_0'$ and $n_1 \gg n_1'$, and consequently, the following relaxation equations hold true for $n_0$ and $n_1$

$$\frac{dn_0}{dt} = \frac{n' - qn_0}{\tau_{rot}}$$

(2.14)

$$\frac{dn_1}{dt} = \frac{n' - qn_1}{\tau_{rot}}.$$

(2.15)

But since $n_0 + n_1 = N_0$, it follows that $d(n_0 + n_1)/dt = 0$, whence $n' = q(n_0 + n_1)/2$, which leads to the equations

$$\frac{dn_0}{dt} = -\frac{q}{2\tau_{rot}}(n_0 - n_1),$$

(2.16)

$$\frac{dn_1}{dt} = \frac{q}{2\tau_{rot}}(n_0 - n_1),$$

(2.17)

which coincides with (2.11) and (2.12) at $W\tau_{rot} \gg 1$.

Equation (2.12) (or (2.17)) imposes significant limitations on the rate of change of the vibrational energy that a molecular system can acquire through action of a field on one rotational-vibrational transition. The rate of excitation of molecules to the first vibrational level satisfies the relation

$$\frac{1}{N_0} \frac{dn_1}{dt} \leqslant \frac{q}{2\tau_{rot}}.$$

(2.18)

Regardless of the mechanism that excites the succeeding vibrational levels, the growth rate of the vibrational energy of the molecule also satisfies relation (2.18).

We consider now two possible mechanisms of the excitation of the two higher molecular levels, cascade excitation by radiation and excitation by collision.

## 3. CASCADE EXCITATION OF VIBRATIONAL LEVELS BY RADIATION

To understand the possible role of radiation in the excitation of high vibrational levels, we consider a situation in which the radiation is at resonance not only with some rotational-vibrational transition of the band $0 \rightarrow 1$, but also with succeeding bands $1 \rightarrow 2$, $2 \rightarrow 3$, etc. Naturally, the rotational sublevels of the vibrational state, from which up and down transitions take place, do not coincide, and the process requires participation of rotational relaxation (Fig. 1). We shall show that even in this case, which is seemingly ideal for excitation, rotational relaxation greatly limits the rate of acquisition of vibrational energy by the molecular system.

In practice, cascade excitation to successive transitions of the molecules can be realized only under the following conditions: 1) the anharmonicity is much smaller than the width of the vibrational band, 2) the frequency of the laser radiation lies near the long-

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[3] The fact that the absorption saturation rate of a molecular system dependes on the factor q can be used for an experimental determination of its value. This question was recently considered in [9].
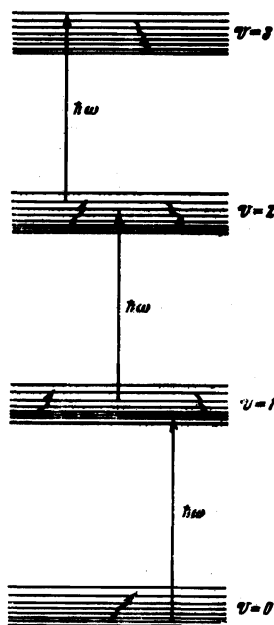
FIG. 1. Scheme of cascade excitation of vibrational levels of a molecule by monochromatic radiation ($\omega$ is the radiation frequency, v is the number of the vibrational level).

wave edge of the $0 \to 1$ band, 3) the broadening of the lines of individual rotational-vibrational transitions, due to pressure or to a strong field, is comparable with the distance between neighboring lines of the band, so that the coincidence of the frequency with successive transitions is not random in character. We note that the possible role of cascade excitation of vibrational levels of a molecule was pointed out in[2].

We shall neglect the slower vibrational-rotational and vibrational-translational relaxation processes. For simplicity we assume that the population factor q is the same for all sublevels participating in the induced transitions. If $W\tau_{rot} \gg 1$, then we can write for the populations of the vibrational levels a chain of equations analogous to (2.16) and (2.17):

$$\frac{dn_0}{dt} = -\frac{q}{2\tau_{rot}}(n_0 - n_1),$$

$$\frac{dn_1}{dt} = \frac{q}{2\tau_{rot}}[(n_0 - n_1) - (n_1 - n_2)],$$

$$\cdots \cdots \cdots \cdots \cdots \cdots$$ (3.1)

$$\frac{dn_v}{dt} = \frac{q}{2\tau_{rot}}[(n_{v-1} - n_v) - (n_v - n_{v+1})]$$

$$\cdots \cdots \cdots \cdots \cdots \cdots \cdots$$

From (3.1) we easily find that for such a model the rate of growth of the number of vibrational quanta in the system, i.e., of the quantity defined by the relation

$$\alpha = \frac{1}{N_0}\sum vn_v,$$ (3.2)

is given by

$$\frac{d\alpha}{dt} = \frac{q}{2\tau_{rot}}\frac{n_0}{N_0}$$ (3.3)

Thus, the "bottleneck" effect imposes the bound (2.8) on the growth rate of the vibrational energy for such a scheme, too.

We consider the kinetics of the population of the vibrational levels in cascade excitation. We change from (3.1) to an equation for a continuous distribution, following the well-known Fokker-Planck method (see,

for example,[10]). Of course, such a transition is possible for $\alpha \gtrsim 1$, i.e., when the vibrational energy of the molecular system is of the order of the energy of the vibrational quantum, and is certainly not correct for small $\alpha$. This is perfectly applicable when the kinetics of the excitation is considered. As a result we obtain a diffusion equation for the distribution function over the vibrational level $u(x, t)$:

$$\frac{\partial u}{\partial t} = \frac{q}{2\tau_{rot}}\frac{\partial^2 u}{\partial x^2}$$ (3.4)

The physical meaning of this equation is quite clear. The transitions of the vibrationally-excited molecule to neighboring vibrational states as a result of the interaction with the radiation field are analogous to the "random walk" process, since the probabilities of the downward and upward transitions are equal.

The solution of equation (3.4) with the initial condition $u|_{t=0} = N_0\delta(x)$ is given by[4]

$$u(x, t) = N_0(2\tau_{rot}/\pi qt)^{1/2}\exp(-\tau_{rot}x^2/2qt),$$ (3.5)

i.e., the characteristic time of population of the m-th vibrational level is determined by the expression

$$t_m^{char} \sim \tau_{rot}m^2/2q.$$ (3.6)

On going from the discrete distribution to the continuous one for $\alpha$, we can use the formula

$$\alpha = \frac{1}{N}\int_0^\infty xu\,dx.$$ (3.7)

We therefore obtain from (3.5)

$$\alpha = (2qt/\pi\tau_{rot})^{1/2}.$$ (3.8)

Thus, the rate of the cascade excitation of the high vibrational levels by radiation is low not only because the factor $q/\tau_{rot}$ is small, i.e., the "bottleneck" effect, but also because the energy depends on the time like $t^{1/2}$. For example, for a molecule with $q \approx 10^{-2}$ the time required to excite the vibrational level m = 10 ($\alpha \approx 10$) would be $t \approx 10^4\tau_{rot}$.

We proceed to consider the mechanism of excitation of high vibrational levels via vibrational-vibrational V-V exchange in collisions.

## 4. THE KINETICS OF EXCITATION OF VIBRATIONAL LEVELS IN VIBRATIONAL-VIBRATIONAL EXCHANGE IN THE QUASISTATIONARY APPROXIMATION

We ascertain first the kinetics of the relaxation of vibrational levels in V-V exchange, and then examine in greater detail the so-called quasistationary case, when the rate of growth of the vibrational energy of the molecule is less than the rate of the vibrational-vibrational relaxation. The equations describing the relaxation of the singled-out vibrational degree of freedom of the molecular system in the harmonic approximation are (see, for example,[11])

$$\frac{dn_v}{dt} = \frac{1}{\tau}\{(v+1)[(1+\alpha)n_{v+1} - \alpha n_v] - v[(1+\alpha)n_v - \alpha n_{v-1}]\},$$ (4.1)

where $\alpha$ is defined by (3.2) and $\tau_0$ is the time of vibra-

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[4]Here and below the $\delta$-function and its derivatives are assumed to be normalized to a semi-infinite straight line.

tional-vibrational relaxation within the singled-out degree of freedom, i.e., a quantity reciprocal to the probability of the process $M_{V=0} + M_{V=1} \rightarrow M_{V=1} + M_{V=0}$. To simplify the formulas, we shall henceforth use $\tau_0$ as the unit of time.

As noted above, at $\alpha \gtrsim 1$ we can change over from (4.1) to an equation for the continuous distribution

$$\frac{\partial u}{\partial t} = \alpha x \frac{\partial^2 u}{\partial x^2} + (\alpha + x)\frac{\partial u}{\partial x} + u \qquad (4.2)$$

with $\alpha$ defined by (3.7). For a semi-infinite line ($x \geq 0$), this equation has a solution that tends to infinity, in the form

$$u(x,t) = \sum_{k=0}^{\infty} a_k \exp\left[-\left(kt + \frac{x}{\alpha}\right)\right] F\left(-k, 1, \frac{x}{\alpha}\right), \qquad (4.3)$$

where F is the confluent hypergeometric function, which reduces to polynomials for integer k. For example,

$$F\left(0, 1, \frac{x}{\alpha}\right) = 1, \qquad F\left(-1, 1, \frac{x}{\alpha}\right) = 1 - \frac{x}{\alpha}.$$

$$F\left(-2, 1, \frac{x}{\alpha}\right) = 1 - 2\frac{x}{\alpha} + \frac{1}{2}\left(\frac{x}{\alpha}\right)^2,$$

$$F\left(-3, 1, \frac{x}{\alpha}\right) = 1 - 3\frac{x}{\alpha} + \frac{3}{2}\left(\frac{x}{\alpha}\right)^2 - \frac{1}{6}\left(\frac{x}{\alpha}\right)^3 \quad \text{etc.} \qquad (4.4)$$

The coefficients $a_k$ are determined by expanding the initial non-equilibrium distribution in terms of the corresponding hypergeometric polynomials with weight $e^{-x/\alpha}$. For any initial condition we have $a_0 = N_0/\alpha$, as follows from the normalization condition

$$\int_0^\infty u\, dx = N_0.$$

It can be stated that a Boltzmann distribution is established within a time on the order of $\tau_0$. Let us see how the mean-squared distribution function

$$\langle x^2 \rangle = \int_0^\infty x^2 u\, dx \qquad (4.5)$$

changes during the relaxation process. This can be established directly from (4.2) by multiplying the left and right-hand sides of (4.2) by $x^2$ and integrating along the semi-infinite line. As a result we get

$$\frac{1}{N_0^2}\frac{d}{dt}\langle x^2 \rangle = 4\alpha^2 - \frac{2}{N_0^2}\langle x^2 \rangle. \qquad (4.6)$$

Integrating (4.6) with the initial condition

$$\langle x^2 \rangle|_{t=0} = \langle x^2 \rangle_0,$$

we obtain

$$\frac{1}{N_0^2}\langle x^2 \rangle = \frac{1}{N_0^2}\langle x^2 \rangle_0 e^{-2t} + 2\alpha^2(1 - e^{-2t}). \qquad (4.7)$$

Thus, the mean-squared distribution function $\langle x^2 \rangle^{1/2}/N_0$ approaches the stationary function $\sqrt{2}\alpha$, which is proportional to the number of vibrational quanta in the molecular systems, within the characteristic time $\tau_0$ of the vibrational-vibrational exchange.

The quantity $\alpha$ (3.2) is conserved in the considered relaxation process. If we consider a process in which, in addition to the vibrational-vibrational relaxation, induced transitions occur under the influence of the radiation, then $\alpha$ is no longer a conserved quantity. In the general case, the law governing the variation of $\alpha$ can be obtained only by solving for the level popula-

tions a system of equations that take into account both induced transitions and vibrational-vibrational relaxation. However, as shown above, the growth rate of $\alpha$ is essentially limited by the "bottleneck" effect both in the case when the radiation acts only on the $0 \rightarrow 1$ transition and in the case of the cascade mechanism of level excitation, namely:

$$d\alpha/dt \leq q/2\tau_{\text{rot}}, \qquad (4.8)$$

where q is the relative fraction of the molecules that take part in the induced transitions upon interaction with the monochromatic radiation. Usually for molecules with three and more atoms $q \approx 10^{-2} - 10^{-3}$ and $\tau_{\text{rot}} \approx 10^{-1}\tau_0$, so that the following condition is satisfied

$$q/2\tau_{\text{rot}} \ll 1/\tau_0. \qquad (4.9)$$

It follows from (4.8) and (4.9) that in a typical case the molecule distribution function over the vibrational levels changes in a quasistationary fashion, and coincides at each instant of time with Boltzmann distribution having a definite value of $\alpha$. The law governing the variation of $\alpha$ can be obtained for each concrete excitation scheme. For example, if the radiation acts only on the $0 \rightarrow 1$ transition and the condition $W\tau_{\text{rot}} \gg 1$ is satisfied, then

$$\frac{d\alpha}{dt} \approx \frac{q}{2\tau_{\text{rot}}} \frac{n_0(\alpha) - n_1(\alpha)}{N_0}, \qquad (4.10)$$

where $n_0(\alpha)$ and $n_1(\alpha)$ are the corresponding equilibrium populations corresponding to the instantaneous value of $\alpha$:

$$n_0(\alpha) = \frac{N_0}{1+\alpha}, \qquad n_1(\alpha) = \frac{N_0\alpha}{(1+\alpha)^2}. \qquad (4.11)$$

Substituting (4.11) in (4.10) and integrating with the initial condition $\alpha|_{t=0} = 0$, we obtain

$$\alpha \approx (1 + 3qt/2\tau_{\text{rot}})^{1/4} - 1. \qquad (4.12)$$

The population of the m-th vibrational level ($m \gg 1$) corresponds to a value $\alpha \approx m$, from which we obtain with the aid of (4.12) the characteristic time of population of the m-th level when the transition $0 \rightarrow 1$ is pumped:

$$t_m^{\text{char}} \sim 2\tau_{\text{rot}}m^3/3q. \qquad (4.13)$$

We now turn to the idealized model of cascade excitation of the levels by irradiation on the successive transition $0 \rightarrow 1$, $1 \rightarrow 2$, etc, which we considered in Sec. 3. According to (4.9), for real molecules it is necessary to take into account the vibrational-vibrational relaxation. According to (4.8) and (4.9), the quasistationary approximation is valid also in this case, and the cascade mechanism for the excitation of the levels by radiation can be taken into account in the law that governs the variation of $\alpha$ in accordance with (3.3):

$$\frac{d\alpha}{dt} \approx \frac{q}{2\tau_{\text{rot}}} \frac{n_0(\alpha)}{N_0} \qquad (4.14)$$

Substituting (4.9) in (4.14) and integrating with the initial condition $\alpha|_{t=0} = 0$, we obtain

$$\alpha \approx (1 + qt/\tau_{\text{rot}})^{1/2} - 1. \qquad (4.15)$$

The characteristic time of population of the m-th level in the cascade-excitation model is equal to

$$t_m^{\text{char}} \sim \tau_{\text{rot}}m^2/q, \qquad (4.16)$$

i.e., is much shorter than in the case of pumping of only one vibrational transition $0 \to 1$.

## 5. KINETICS OF THE EXCITATION OF HIGH VIBRATIONAL LEVELS IN V-V EXCHANGE AND ACTION OF RADIATION ON THE $0 \to 1$ TRANSITION

We consider a more general case of excitation of high vibrational levels as a result of V-V exchange in the case when the radiation acts only on the $0 \to 1$ transition, but the ratio of the growth rate of the vibrational energy $q/2\tau_{rot}$ ($W\tau_{rot} \gg 1$) and the rate of the vibrational-vibrational exchange $1/\tau_0$ is arbitrary.

An exact solution of such a problem cannot be found, but a good approximation can be obtained by adding a "source" of vibrational excitations located at the origin to the right-hand side of the relaxation equation (4.2) for the continuous distribution function. This corresponds to the action of the radiation on the $0 \to 1$ transition. Such a source is conveniently represented in the form

$$-N_0\gamma\delta'(x). \tag{5.1}$$

Then the equation for the continuous distribution function takes the form

$$\frac{\partial u}{\partial t} = ax\frac{\partial^2 u}{\partial x^2} + (a+x)\frac{\partial u}{\partial x} + u - N_0\gamma\delta'(x). \tag{5.2}$$

Multiplying the left- and right-hand sides by $x$ and integrating along the semi-infinite line $(0 \le x < \infty)$, we obtain

$$\frac{da}{dt} = \gamma(t) \quad \text{or} \quad a(t) = \int_0^t \gamma(t')dt'. \tag{5.3}$$

we see therefore that $\gamma$ has the meaning of the number of vibrational excitations obtained by the molecular system under the influence of radiation during the time $\tau_0$ of the vibrational-vibrational exchange.

The form of $\gamma(t)$ is determined by the character of the saturation of the transition. At $W\tau_{rot} \gg 1$, according to (2.17), the number of vibrational excitations obtained per unit time by the molecular system is equal to

$$\frac{da}{dt} = \frac{1}{N_0}\frac{dn_1}{dt} = \frac{q\tau_0}{2\tau_{rot}}\frac{n_0 - n_1}{N_0} \tag{5.4}$$

where $\tau_0$ appears on going from the dimensional to the dimensionless time. The difference of the populations of the vibrational levels 0 and 1 can be approximately expressed in terms of $\partial u/\partial x$ at the point $x = 0$. We find finally that the "source" term in (5.2) is given by

$$-N_0\gamma\delta'(x) = \frac{q\tau_0}{2\tau_{rot}}\frac{\partial u}{\partial x}\delta'(x) = \beta\frac{\partial u}{\partial x}\delta'(x), \tag{5.5}$$

where $\beta = q\tau_0/2\tau_{rot}$. Thus, the quantity $\gamma(t)$ in the general case depends on the saturation of the transition.

We confine ourselves henceforth to the particular case when $a$ does not depend on the time:

$$\gamma(t) = -\frac{\beta}{N_0}\frac{\partial u(x,t)}{\partial x}\bigg|_{x=0} = \gamma. \tag{5.6}$$

We are interested in a solution of this equation with initial condition $u(x, 0) = N_0\delta(x)$. If we make in the corresponding homogeneous equation the change of variables $y = xe^t$, then the variables separate, and the
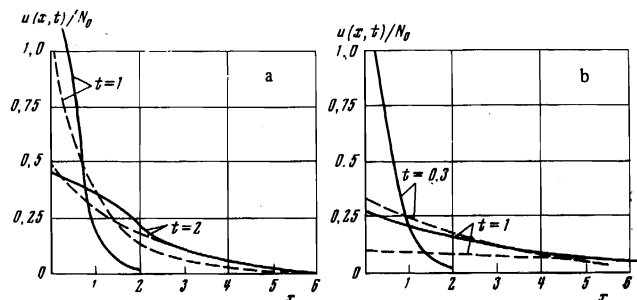
corresponding Sturm-Liouville problem will have eigenfunctions that are bounded as $y \to 0$ in the form of zero-order Bessel functions $J_0(2\sqrt{\lambda y})$, where $\lambda$ is the separation parameter. It is convenient to seek the solution of (5.2) in the form

$$u(x,t) = \int_0^\infty f(\lambda, t)\exp\{t - \lambda\gamma[(t-1)e^t + 1]\}J_0(2\sqrt{\lambda xe^t})d\lambda. \tag{5.7}$$

Substituting (5.7) in the initial equation we obtain

$$\int_0^\infty \frac{\partial f}{\partial t}\exp\{t - \lambda\gamma[(t-1)e^t + 1]\}J_0(2\sqrt{\lambda xe^t})d\lambda = -N_0\gamma\delta'(x). \tag{5.8}$$

Since

$$\delta'(x) = \int_0^\infty \lambda J_0(2\sqrt{\lambda x})d\lambda, \quad \delta'(x) = a^2\delta'(ax),$$

we get

$$\frac{\partial f}{\partial t} = -N_0\gamma\lambda\exp\{t + \lambda\gamma[(t-1)e^t + 1]\}. \tag{5.9}$$

The integration constant must be taken from the initial condition $u(x, y) = N_0\delta(x)$. Since

$$\delta(x) = \int_0^\infty J_0(2\sqrt{\lambda x})d\lambda,$$

it follows that

$$f(\lambda, 0) = N_0. \tag{5.10}$$

Substituting the integral of (5.9) with allowance for (5.10) in (5.7) and integrating with respect to $\lambda$, we obtain ultimately

$$u(x,t) = \frac{N_0}{\gamma(t-1+e^{-t})}\exp\left[-\frac{x}{\gamma(t-1+e^{-t})}\right]$$

$$+ \frac{N_0}{\gamma}\int_0^t \frac{e^{\tau-t}}{[(t-1)-(\tau-1)e^{\tau-t}]^2}\left\{\frac{x}{\gamma[(t-1)-(\tau-1)e^{\tau-t}]} - 1\right\}$$

$$\times \exp\left\{-\frac{x}{\gamma[(t-1)-(\tau-1)e^{\tau-t}]}\right\}d\tau. \tag{5.11}$$

It follows from (5.11) that at $t \gg 1$ (i.e., $t \gg \tau_0$) the distribution function has a Boltzmann form:

$$u(x,t) \approx \frac{N_0}{\gamma t}\exp\left(-\frac{x}{\gamma t}\right). \tag{5.12}$$

For arbitrary $t$, the tail of the distribution is determined mainly by the first term. The second term makes an appreciable contribution for those $x$ for which the integrand is non-negative at $\tau = 0$ and goes through a maximum when $\tau$ changes from zero to $t$, i.e., for



FIG. 2. Dependence of the distribution function u(x, t) (continuous curves) on x for different t and at $\gamma = 1$ (Fig. 2a) and $\gamma = 10$ (Fig. 2b). The dashed curves show the corresponding instantaneous Boltzmann distributions $e^{-x/\gamma t}/\gamma t$.

$$x \sim (1 - 2)\gamma(t - 1 + e^{-t}). \tag{5.13}$$

Figure 2 shows the dependence of the distribution function on x for different t at $\gamma = 1$ (Fig. 2a) and $\gamma = 10$ (Fig. 2b). A noticeable deviation of the distribution function from the Boltzmann form is observed at $\gamma \gg 1$.

In conclusion, we present the dependence of the mean-squared distribution of (5.11) on the time:

$$\langle x^2 \rangle / N_0^2 = \gamma^2(2t^2 - 2t + 1 - e^{-2t}). \tag{5.14}$$

For $t \ll 1$ (i.e., at $t \ll \tau_0$) we get

$$\langle x^2 \rangle / N_0^2 \approx {}^2/_3 \gamma^2 t^3. \tag{5.15}$$

## 6. DISCUSSION

We have shown that the rate of introduction of vibrational energy in to a molecular system by interaction with monochromatic radiation does not exceed $q/2\tau_{rot}$. This leads to the conclusion that selective heating of a selected vibrational degree of freedom is possible in principle only under the condition

$$^1/_2 q P_{rot} \gg P_{vib}, \tag{6.1}$$

where $P_{rot}$ is the probability of rotational relaxation per collision and $P_{vib}$ is the probability of deactivation of the vibrationally-excited states with transfer of energy to other degrees of freedom by collision. For polyatomic molecules usually $q \sim 10^{-2}-10^{-3}$, $P_{rot} \sim 1-10^{-1}$, and $P_{vib} \sim 10^{-2}-10^{-4}$ (see, for example,[12]). This means that for most molecules the condition (6.1) is apparently not satisfied, and the possibility in principle of selective heating of a singled-out vibrational degree of freedom by monochromatic radiation is more readily an exception than the rule for molecules. This is a serious obstacle to the realization of selective chemical reactions under the influence of monochromatic infrared laser radiation.

This situation can be alleviated in part by surrounding the excited molecules with a buffer gas with a higher pressure. An inert buffer gas will not decrease $P_{rot}$ noticeably, but can greatly lower the probability of excitation transfer to molecules of a different sort, which it is not desirable to excite.

Owing to the limitations imposed by the "bottleneck" effect, the vibrational energy, which can be introduced into the molecular system during the time of the laser pulse, does not exceed at any rate the value $qt_p \hbar\omega/2\tau_{rot}$, where $t_p$ is the duration of the laser pulse and $\hbar\omega$ is the energy of the vibrational quantum; during the time of the pulse it is possible to excite levels whose number does not exceed $m_{max} \sim qt_p/2\tau_{rot}$. These estimates are important for the interpretation of the results of[7,8], in which the influence of optical breakdown in $C_2F_3Cl$ gas that absorbs the radiation of a pulsed $CO_2$ laser was investigated. The breakdown was observed at gas pressures $\sim 10-100$ Torr at a laser pulse duration $10^{-6}$ sec. If it is assumed that the fraction of the $C_2F_3Cl$ molecules interacting with the

powerful radiation and participating in the absorption does not exceed $10^{-2}$, then for the experimental conditions of[8] we have $qt_p/2\tau_{rot} < 1$, which enables us to refute the role of selective excitation of vibrational levels in the optical breakdown phenomenon.

There is, of course, no "bottleneck" effect when the radiation acts on the $0 \to 1$ transition if the radiation is not monochromatic, so that it acts on all the filled rotational sublevels of the lower vibrational state. In principle, such a situation can arise also for single-frequency radiation if the rotational-vibrational lines of the band overlap. In practice, for the transitions of the P and R branch this can be reached at pressures of several atmospheres and above, which are of no interest for the problem in question, owing to the rapid relaxation of the vibrational excitation into translational degrees of freedom. An exception is perhaps the case when the radiation acts on the Q branch, in which the density of the lines is high, and the case of sufficiently moderate broadening of the lines by pressure or by strong resonant field for the interaction of all the molecules with radiation.

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