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

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

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

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

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

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during which the δ-function source of constant power acts). The aim of the present paper is to analyze the distribution of molecules over the vibrational levels for an arbitrary relation of the times τ_1 and τ_0 (nonstationary problem), as well as the behavior of vibrational energy. We shall consider a small amount of impurity, in the form of diatomic molecules modelled by harmonic oscillators, in an inert gas (thermostat). Vibrational relaxation is described by the following system of kinetic equations for the populations x_n of the levels:

$$dx_n/dt = ZP_{10}\{(n+1)x_{n+1} - [(n+1)e^{-\theta} + n]x_n + ne^{-\theta}x_{n-1}\} + \eta\delta_{nv},\ n = 0, 1, 2, \ldots, \tag{1.1}$$

where P_{10} is the probability of the vibrational transition 1 → 0, calculated for one collision; Z is the number of collisions per second between molecules and atoms of the reservoir, as calculated from gas-kinetics; η is the source power, i.e., the number of vibrationally excited molecules with energy E_v arising per unit volume per unit time; δ_{nv} is the Kronecker delta; and $\theta = \hbar\omega/kT$. The coefficients in Eq. (1.1) are independent of time. Equations for the number of molecules $N(t) = \sum\limits_{n=0}^{\infty} x_n(t)$ and vibrational energy $E(t) = \hbar\omega \sum\limits_{n=0}^{\infty} nx_n(t)$ per unit volume can be obtained from the system of equations (1.1) without solving it. Standard methods give

$$dN(t)/dt = \eta; \tag{1.2}$$

$$\frac{dE(t)}{dt} = -\frac{E(t) - \hbar\omega\,[e^{-\theta}/(1-e^{-\theta})]\,N(t)}{\tau_1} + \eta v\hbar\omega, \tag{1.3}$$

where $\tau_1 = [ZP_{10}(1-e^{-\theta})]^{-1}$.

The linear equations (1.2), (1.3) have the following respective solutions:

$$N(t) = N_0 + \eta t; \tag{1.4}$$

$$E(t) = E^0 + [E(0) - E^0]\,e^{-t/\tau_1} + \frac{\eta}{N_0}E^0 t + \frac{\eta\tau_1}{N_0}(N_0E_v - E^0)\left(1 - e^{-t/\tau_1}\right), \tag{1.5}$$

where N_0 is the number density of molecules in the system before the source is switched on; $E^0 = \hbar\omega\left[e^{-\theta}/(1-e^{-\theta})\right] N_0$ is the equilibrium value of vibrational energy; and $E_v = v\hbar\omega$. [In the second term of Eq. (1.5), $0 \leqslant t < \infty$, while $0 \leqslant t \leqslant \tau_0$ in subsequent terms.] The first two terms in Eq. (1.5) describe the relaxation of vibrational energy due to the initial nonequilibrium value of E(0). The third term shows that the increase in stored equilibrium energy occurs due to the linear increase in the number of molecules in the system. The fourth term describes the increase in vibrational energy due to the difference between the equilibrium (E^0) and nonequilibrium (N_0E_v) values of energy. Thus, the action of a δ-function source leads to the appearance of stored nonequilibrium vibrational energy in the system, which increases with time from zero to a constant value. However, it should be noted that the type of source affects only the magnitude and not the structure of the last term in Eq. (1.5).

§2. We shall construct the general solution of the inhomogeneous system of equations (1.1) using the fundamental matrix of solutions of a system of homogeneous equations (cf. [5], for example). The general solution of the system of homogeneous equations corresponding to Eq. (1.1) has the form [6]

$$x_n(t) = \sum_{m=0}^{\infty} \alpha_m G_n(m)\,e^{-mt/\tau_1}, \tag{2.1}$$

where $G_n(m) = e^{-n\theta}\sum\limits_{i=0}^{\infty}(1-e^{\theta})^i\binom{n}{i}\binom{m}{i}$ are the Gottlieb polynomials, and α_m are coefficients determined by the initial conditions. We shall find the fundamental matrix. The set of functions

$$x_{nm}(t, t_0) = G_n(m)e^{-mt/\tau_1} \tag{2.2}$$

for each value of m = 0, 1, 2, . . . is a particular solution of the system of homogeneous equations, bounded with respect to the norm, and satisfying certain initial conditions for $t = t_0$. Since any (bounded) solution $x_n(t)$ of such a system can be represented in the form of Eq. (2.1), the system of functions $x_{nm}(t, t_0)$ is a fundamental system of solutions. We normalize the matrix

$$\Phi(t) = \{x_{nm}(t, t_0)\}$$

of the fundamental system of solutions at the point $t = \tau$ (τ is an arbitrary time):

$$\Phi^*(t) = \Phi(t)\Phi^{-1}(\tau).$$

At $t = \tau$ the fundamental matrix $\Phi^*(t)$ becomes a unit matrix. Using the orthogonalization and normalization conditions for the Gottlieb polynomials,

$$\sum_{m=0}^{\infty} e^{-m\theta} G_n(m) G_s(m) e^{s\theta}(1 - e^{-\theta}) = \delta_{ns} \tag{2.3}$$

(δ_{ns} is the Kronecker delta), we find the constant matrix $\Phi^{-1}(\tau)$:

$$\Phi^{-1}(\tau) = \{x_{ms}(\tau, t_0)\} = \{e^{-m\theta} G_s(m) e^{m\tau/\tau_1} e^{s\theta}(1 - e^{-\theta})\}. \tag{2.4}$$

When Eqs. (2.2), (2.4) are taken into account, the matrix $\Phi^*(t)$ takes the following form:

$$x_{ns}(t, \tau) = \sum_{m=0}^{\infty} G_n(m) e^{-mt/\tau_1} G_s(m) e^{m\tau/\tau_1} e^{-m\theta} e^{s\theta}(1 - e^{-\theta}).$$

The general solution of the system of inhomogeneous equations (1.1) is written as follows, with the help of the fundamental matrix $\Phi^*(t)$:

$$x_n(t) = \sum_{m=0}^{\infty} \alpha_m G_n(m) e^{-mt/\tau_1} + \int_0^t \sum_{\substack{m=0,\\ s=0}}^{\infty} \eta \delta_{sv} G_n(m) e^{-mt/\tau_1} G_s(m) e^{m\tau/\tau_1} e^{-m\theta} e^{s\theta}(1 - e^{-\theta})\, d\tau, \tag{2.5}$$

where we have set $t_0 = 0$ for simplicity, i.e., the source is switched on at zero time.

Carrying out the integrations and summations in Eq. (2.5) with respect to s, we obtain the distribution function of molecules over the vibrational levels:

$$x_n(t) = \sum_{m=0}^{\infty} \alpha_m G_n(m) e^{-mt/\tau_1} + \eta t e^{-n\theta}(1 - e^{-\theta}) + \frac{\eta e^{v\theta}}{ZP_{10}} \sum_{m=1}^{\infty} G_n(m) G_v(m) \frac{e^{-m\theta}}{m}(1 - e^{-mt/\tau_1}). \tag{2.6}$$

As in the case of Eqs. (1.4), (1.5), the first term here describes the relaxation of the initial state of the system. The second term results from the well-known fact [3, 4] that molecules in the vibrational levels are replenished only at the expense of the "old" molecules with a Boltzmann distribution. The third term (which, following the terminology of [3, 4], we shall call the "perturbation function") describes the redistribution of molecules over the levels caused by the source. (We note that in the first term $0 \leqslant t < \infty$, while $0 \leqslant t \leqslant \tau_0$ in the second and third.)

§3. The perturbation function in Eq. (2.6) has a fairly complex form. We shall thus restrict ourselves to treating extreme cases.

1) Let $t/\tau_1 \ll 1$. Then, expanding the time factor in Eq. (2.6) in a Maclaurin series and using the property (2.3), we have, in the linear approximation,

$$x_n(t) = \sum_{m=0}^{\infty} \alpha_m G_n(m) e^{-mt/\tau_1} + \eta t \delta_{nv}. \tag{3.1}$$

It follows from Eq. (3.1) that for $t \ll \tau_1$ the action of the source leads to a linear growth of population of the level v only. This explains the appearance of population inversion of the levels v and v − 1. Setting $x_n(0) = N_0(1 - e^{-\theta})e^{-n\theta}$ for simplicity, the inversion condition $x_v/x_{v-1} > 1$ for the case $e^{-\theta} \ll 1$ (low temperatures), which is important in practice, can lead to the inequality

$$v > 1 + (1/\theta)\ln(N_0/\eta t).$$

It is clear from this that as the power of the source increases, population inversion can be achieved for lower v levels.

2) If $\tau_1 \ll t \ll \tau_0$ (quasistationary case), the solution (2.6) passes to the expression

$$x_n(t) = N_0(1 - e^{-\theta})e^{-n\theta} + \eta t(1 - e^{-\theta})e^{-n\theta} + \frac{\eta e^{v\theta}}{ZP_{10}}\sum_{m=1}^{\infty} G_n(m)G_v(m)\frac{e^{-m\theta}}{m}. \tag{3.2}$$

The infinite sum on the right-hand side of Eq. (3.2) can be represented as follows. Introducing the symbol

$$f_n = \frac{\eta e^{v\theta}}{ZP_{10}}\sum_{m=1}^{\infty} G_n(m)G_v(m)\frac{e^{-m\theta}}{m}$$

and setting

$$x_n(t) = N_0(1 - e^{-\theta})e^{-n\theta} + \eta t(1 - e^{-\theta})e^{-n\theta} + f_n$$

in the initial equation (1.1), we obtain a system of algebraic equations for f_n. This system of algebraic equations can be solved fairly simply, and the solution has the form [3, 4]

$$f_n = \left\{\frac{\eta}{ZP_{10}}\left[\sum_{m=1}^{n}\frac{e^{m\theta}-1}{m} - \sum_{m=1}^{n}\frac{e^{m\theta}}{m}\sum_{l=1}^{m}\delta_{l-1,v}\right] + f_0\right\}e^{-n\theta}, \tag{3.3}$$

where the constant f_0 is determined from the condition $\sum_{n=0}^{\infty} f_n = 0$ in accordance with Eq. (1.4). The behavior of the perturbation function (3.3) is analyzed in [3, 4] for the case $e^{-\theta} \ll 1$. We note that the population condition $x_v/x_{v-1} > 1$ is not satisfied in the quasistationary regime.

3) We shall consider the case of low gas temperatures T, important in practice. The presence of the binomial coefficients $\binom{n}{i}$ and $\binom{v}{i}$ in the sum (2.6) allows the whole system of vibrational levels to be separated naturally into the two regions $n \leqslant v$ and $n > v$. Using this fact to calculate the sum in Eq. (2.6), we obtain the following expressions for the perturbation function in the case $e^{-\theta} \ll 1$:

$$f_0(t) = \frac{\eta}{ZP_{10}}\left[e^{-\theta}(1 - e^{-t/\tau_1}) + \sum_{m=1}^{v}(-1)^m\binom{v}{m}\frac{1}{m}(1 - e^{-mt/\tau_1})\right]; \tag{3.4}$$

$$f_n(t) = \frac{\eta}{ZP_{10}}\binom{v}{n}\sum_{m=n}^{v}(-1)^{m+n}\frac{1}{m}\binom{v-n}{v-m}(1 - e^{-mt/\tau_1}), \quad 0 < n \leqslant v; \tag{3.5}$$

$$f_n(t) = \frac{\eta}{ZP_{10}}e^{-n\theta}\sum_{m=1}^{n}(-1)^m\frac{1}{m}\binom{n}{m}(1 - e^{-mt/\tau_1}), \quad n > 0, \quad v = 0; \tag{3.6}$$

$$f_n(t) = \frac{\eta e^{v\theta}}{ZP_{10}}e^{-n\theta}\binom{n}{v}\sum_{m=v}^{n}(-1)^{m+v}\frac{1}{m}\binom{n-v}{n-m}(1 - e^{-mt/\tau_1}), \; 0 < v < n. \tag{3.7}$$

For times $t > \tau_1$, Eqs. (3.4)-(3.7), describing the complex process of redistribution of molecules over the levels, simplify considerably and assume the form

$$f_0(t) = \frac{\eta}{ZP_{10}}e^{-\theta}(1 - e^{-t/\tau_1}), \quad n = v = 0; \tag{3.8}$$

$$f_0(t)=-\frac{\eta}{ZP_{10}}\sum_{m=1}^{v}\frac{1}{m}\left(1-e^{-t/\tau_1}\right),\quad n=0,\quad v>0; \tag{3.9}$$

$$f_n(t)=\frac{\eta}{ZP_{10}}\frac{1}{n}\left(1-\mathrm{e}^{-nt/\tau_1}\right),\quad 0<n\leqslant v; \tag{3.10}$$

$$f_n(t)=-\frac{\eta}{ZP_{10}}\sum_{m=1}^{n}\frac{1}{m}\,\mathrm{e}^{-n\theta}\left(1-\mathrm{e}^{-t/\tau_1}\right),\quad n>0,\quad v=0; \tag{3.11}$$

$$f_n(t)=\frac{\eta}{ZP_{10}}\frac{\mathrm{e}^{v\theta}}{v}\,\mathrm{e}^{-n\theta}\left(1-\mathrm{e}^{-vt/\tau_1}\right),\quad 0<v<n. \tag{3.12}$$

It follows from Eqs. (3.8)-(3.12) that in the present approximation the perturbation function $f_n(t)$, which has an exponential dependence on time, has the form of a Boltzmann distribution in the region $n > v$, while in the region $n \leqslant v$ it behaves like $1/n$. For levels with $n \leqslant v$ this distribution is attained at a rate which depends on n, while for levels with $n > v$ it is attained simultaneously. In the case $t/\tau_1 \gg 1$, Eqs. (3.8)-(3.12) coincide with the results of [3, 4]. It is interesting to note that the perturbation of the distribution function of molecules over the vibrational levels in the present case is of a similar nature to that introduced by multiquantum laser pumping.

The solution obtained above — Eq. (2.6) — is valid only for a δ-function source. In the case of an arbitrary source the distribution function for the molecules can be represented in the form of a superposition of solutions (2.6).

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