KINETICS OF THE DEACTIVATION OF THE VIBRATIONS OF HIGHLY EXCITED OSCILLATORS IN AN INERT GAS MEDIUM, TAKING ACCOUNT OF SPONTANEOUS RADIATION

M. H. Safaryan

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In the diffusion approximation, the article discusses the kinetics of the process of deactivation of the vibrations of radiating anharmonic and harmonic oscillators in an inert gas medium. Limiting solutions are given for the purely radiational deactivation of a classical Morse oscillator and of a harmonic oscillator. It is shown that, with an increase in the effect of spontaneous radiation, the role of the anharmonic character of the vibrations in the process of deactivation increases; the initial (or arbitrary) distribution relaxes more slowly the higher its energy level, i.e., the greater the effect of the anharmonic character of the vibrations. The results are of importance for systems with a considerable population of the upper vibrational levels of the molecules, which may arise as a result of a chemical reaction or by the optical pumping of a gas.

Taking account of the anharmonic character of the vibrations in the description of the vibrational relaxation of diatomic molecules without taking account of radiation has shown that, in an inert gas medium, deactivation of the vibrations of anharmonic oscillators, in comparison to harmonic oscillators, takes place with a considerable overpopulation of the upper levels [1], while in a purely molecular gas the quasi-steady-state distribution is inverse in the upper levels [2]. In what follows it is shown that the inverse effect in pure gases, connected with the anharmonic character of the vibrations, decreases (and disappears) due both to vibrational-translational and to radiational transitions with the upper levels [3-5]. It is also of interest to evaluate the effect of the factor of the anharmonic character of the vibrations on the relaxation of the vibrations of the molecules in a medium of inert gas in the presence of radiation, as well as the overall effect of radiation on the deactivation process of the vibrations in the case when there is no exchange of vibrational quanta. Below this is done qualitatively, without setting up an actual model of the molecule.

We consider a system of diatomic molecule–Morse oscillators (and of harmonic oscillators) in an inert gas medium, playing the role of a thermostat with the temperature T. At the initial moment of time, the vibrational energy of the oscillators considerably exceeds the value of kT.

An oscillator may lose energy due to collisions with particles of the thermostat and as the result of radiational transitions. To describe the kinetics of the change in the distribution functions of the molecules $f(\varepsilon, t)$ with respect to the vibrational energy ε, the possibility of using the diffusion theory has been proposed; in the theory of thermal relaxation, in addition to the usual conditions (see below), the deactivation of highly excited oscillators, $v \gg 1$ (v is the number of the vibrational level), must also be considered.

The kinetic equation for $f(\varepsilon, t)$ consists of terms describing the thermal [1] and radiational deactivation of the vibrations of the molecules; it has the following form:

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial \varepsilon}\left\{B\left(\frac{\partial f}{\partial \varepsilon} - f\frac{\partial \ln f^{\circ}}{\partial \varepsilon}\right)\right\} + \frac{\partial}{\partial \varepsilon}\{Jf\} \quad \left(B = \frac{\langle(\Delta\varepsilon)^2\rangle}{2\tau_*}\right) \tag{1}$$

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Here J is the intensity of the radiation of a molecule; $f^{\circ}(\varepsilon)$ is the equilibrium function of the distribution, corresponding to the temperature T; B is the "diffusion" constant in the space ε; τ_* is the free-flight time of the molecules; $\langle(\Delta\varepsilon)^2\rangle$ is the square of the change in the energy resulting from a collision between a molecule and a particle of the thermostat, averaged over all the collisions in unit time; the diffusion approximation holds if $\langle(\Delta\varepsilon)^2\rangle \ll \varepsilon_*^2$ [ε_* is the region of change in $f(\varepsilon, t)$].

Let us obtain the value of J for a classical Morse oscillator.*

The intensity of dipole radiation is equal to

$$J = \frac{2e}{3c^3}\langle\ddot{r}^2\rangle \tag{2}$$

Here c is the velocity of light; e is the charge of an electron; r is the interatomic distance; the angular brackets denote averaging with respect to all values of r with a given value of the vibrational energy ε; the dots denote differentiation with respect to the time.

The trajectory of the intramolecular motion r(t) is determined from the equation

$$\dot{r} = \sqrt{\frac{2}{\mu}(\varepsilon - V(r))}$$

where μ is the reduced mass of a molecule; V(r) is the intramolecular potential. In the case of a Morse oscillator

$$V(r) = D(1 - e^{-\beta(r-r_e)})^2$$

where D is the dissociation energy of a molecule, we have

$$r(t) = r_e + \frac{1}{\beta}\ln\frac{1-\sqrt{x}\cos\omega t}{1-x} \tag{3}$$
$$\omega = \omega_0\sqrt{1-x}, \quad \omega_0 = \beta\sqrt{2D/\mu}, \quad x = \varepsilon/D$$

Hence

$$\ddot{r}(t) = \frac{\omega_0^2}{\beta}\frac{(1-x)\sqrt{x}}{(1-\sqrt{x}\cos\omega t)^2}(\cos\omega t - \sqrt{x}) \tag{4}$$

By definition

$$\langle\ddot{r}^2\rangle = \frac{1}{2\pi}\int_0^{2\pi}\ddot{r}^2 d(\omega t)$$

Averaging (4), we have

$$\langle\ddot{r}^2\rangle = \frac{\omega_0^4}{\beta^2}(1-x)^2\frac{1}{\pi}\int_0^{\pi}\frac{(x-\sqrt{x}\cos y)^2}{(1-\sqrt{x}\cos y)^4}dy \tag{5}$$

Substituting the result of integration of (5) into (2), we obtain the intensity of the radiation of a dipole Morse oscillator

$$J = \frac{e^2\omega_0^4}{3c^3\beta^2}x\sqrt{1-x} = \frac{e^2}{3c^3}\beta^2\left(\frac{2D}{\mu}\right)^2 x\sqrt{1-x} \tag{6}$$

With $\varepsilon/D \ll 1$, the Morse oscillator is equivalent to a harmonic oscillator; in this case, (6) goes over into the usual expression for the intensity of the radiation of a harmonic oscillator:

$$J = \frac{2}{3}\frac{\omega_0^2}{\mu c^3}\varepsilon \equiv A_0\varepsilon = A_0\hbar\omega_0\frac{\varepsilon}{\hbar\omega_0} \tag{7}$$

where A_0 is the Einstein coefficient for spontaneous radiation.

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*We note that the approximation of a classical Morse oscillator is particularly useful with application to the deactivation of the upper levels, since it permits taking account also of multiquantum transitions.

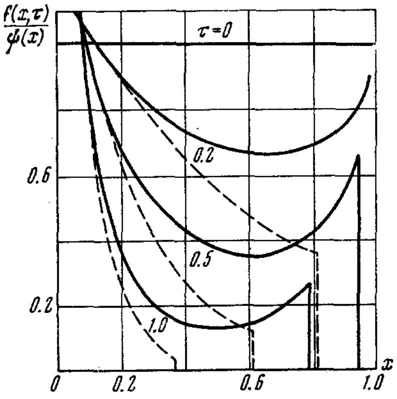

Fig. 1

Taking account of (7), formula (6) is conveniently represented in the form

$$J = \frac{1}{\tau_0}\varepsilon\sqrt{1-\varepsilon/D} = \frac{1}{\tau_0}\frac{\varepsilon}{\hbar\omega_0}\hbar\omega(\varepsilon) \tag{8}$$

Here $\tau_0 = A_0^{-1}$ is the lifetime of the lower vibrational level of a Morse oscillator; $\omega(\varepsilon)$ is the frequency corresponding to the energy ε.

The effect of radiation on the deactivation process depends on the relationship of the terms in the right-hand part of Eq. (1), i.e., on the relationship between $B/\varepsilon_* \approx B/D$ and J.

Let us consider the limiting case $JD \gg B$, when the thermal relaxation can be neglected; this case allows of a simple analytical solution, and permits bringing out the difference in the processes of radiational deactivation of Morse oscillators and harmonic oscillators, i.e., determining the role of the anharmonic character of the vibrations for the process of radiational relaxation. We have

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial \varepsilon}\{Jf\} \tag{9}$$

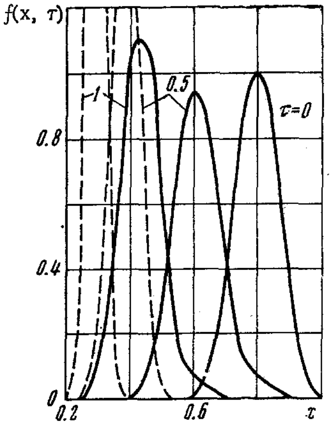

Fig. 2

The solutions of Eq. (9) differing from zero, under the condition of conservation of the total number of particles, and taking account of (8) and (7), for Morse oscillators (f_1) and harmonic oscillators (f_2) have, respectively, the following form:

$$f_1(x,\tau) = \frac{x_0\sqrt{1-x_0}}{x\sqrt{1-x}}\psi(x_0)$$

$$x_0 = \frac{4ye^{\tau}}{(1+ye^{\tau})^2}, \quad y = \frac{1-\sqrt{1-x}}{1+\sqrt{1-x}}, \quad ye^{\tau} < 1 \tag{10}$$

$$f_2(x,\tau) = e^{\tau}\psi(xe^{\tau}), \quad xe^{\tau} < 1 \tag{11}$$

Here $\tau = t/\tau_0$; $x = \varepsilon/D$; $\psi(x)$ is the initial distribution function $[\psi(x) = f(x, 0)]$.

From a comparison of (10) and (11) it can be seen that the time change in the distribution functions of anharmonic and harmonic oscillators as a result of radiational deactivation differs considerably. This change is also appreciable at $x \ll 1$, if $e^{\tau} \gg 1$, and especially appreciable in the remaining region of values of x at any arbitrary values of τ; in particular, the limits for the reversion to zero of the functions f_2 and f_1 are shifted considerably: $f_2 = 0$ when $x \geq x_1 = e^{-\tau}$, while $f_1 = 0$ only at $x \geq x_2 = 4e^{-\tau}(1+e^{-\tau})^{-2} > x_1$. The anharmonic character of the vibrations also has an effect on the character of the change in the form of the initial distribution, since the derivatives $\partial f_1/\partial x$ and $\partial f_2/\partial x$ also differ considerably; for example, with time, the table-shaped form of the initial distribution for f_2, shifting along x, is mainly simply constricted and rises, while for f_1 there is an appreciable amount of distortion and of washing out of the boundary from the side of large values of x.

What has been said above is illustrated by Figs. 1 and 2, on which is shown the relaxation of the two initial distributions for Morse oscillators (solid curves) and harmonic oscillators (dotted curves). Figure 1 corresponds to an initial Boltzmann distribution with the temperature T_0, $a_0 = D/kT_0 = 7$; the figure shows the function $f(x, \tau)/\psi(x)$ at different moments of time $\tau = t/\tau_0$; it is evident that, in the region $x_1 < x < x_2$, where $f_2 = 0$, a considerable part of the initial population of the Morse oscillators is still retained. Figure 2 illustrates the change in the initial distribution, having a sharp maximum at x = 0.8; this is an evident difference in the change of the value and form of the distribution function (with given values of x, τ) for anharmonic and harmonic oscillators.

Under actual conditions, it is difficult to completely exclude thermal relaxation.

In the general case, the analytical description of the process admits of a model of harmonic oscillators; we give the corresponding solution.

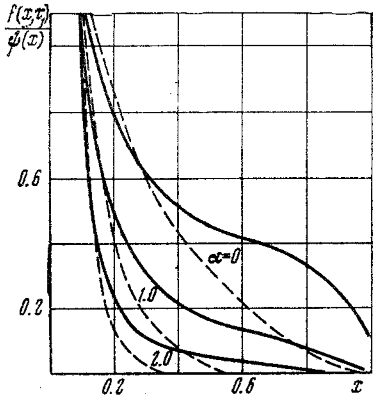

Fig. 3

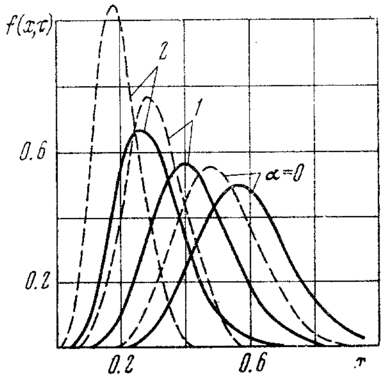

Fig. 4

For this model, the coefficient B is equal to

$$B = kT\tau_v^{-1}\varepsilon \tag{12}$$

where τ_v is the time of vibrational (thermal) relaxation in the system.

Taking account of (12) and (7), Eq. (1) is written in the form

$$a\frac{\partial f}{\partial \tau_1} = x\frac{\partial^2 f}{\partial x^2} + (a(1+\alpha)x+1)\frac{\partial f}{\partial x} + a(1+\alpha)f \tag{13}$$

Here

$$\alpha = \tau_v/\tau_0, \quad \tau_1 = t/\tau_v, \quad a = D/kT$$

In Eq. (13) we formally replace the quantity a by $a' = a(1+\alpha)$ and τ_1 by $\tau_1' = (1+\alpha)\tau_1$; we then arrive at the usual equation for the thermal relaxation of harmonic oscillators in the absence of radiation ($\alpha = 0$), whose solution is known in the approximation $\psi(1) \approx 0$ (see, for example [6]).

In particular, for the initial value of δ, the functions

$$\begin{gathered}\psi = \delta(x - x_0)\\ f(x,\tau_1) = \frac{a(1+\alpha)e^{-a(1+\alpha)x}}{1-g}\exp\left\{-\frac{a(1+\alpha)(x+x_0)g}{1-g}\right\}I_0\left(\frac{2a(1+\alpha)\sqrt{x_0xg}}{1-g}\right)\\ g = \exp\{-(1+\alpha)\tau_1\}\end{gathered} \tag{14}$$

[$I_0(z)$ is a modified Bessel function of zero order], and the initial Boltzmann distribution relaxes in accordance with the law

$$\begin{gathered}f(x,\tau_1) = a_*e^{-a_*x}\\ \frac{1}{a_*} = \frac{1}{a(1+\alpha)} + \left(\frac{1}{a_0} - \frac{1}{a(1+\alpha)}\right)e^{-(1+\alpha)\tau_1}\end{gathered} \tag{15}$$

Consequently, a system of radiating oscillators relaxes in an inert gas medium with retention of the form of a Boltzmann distribution whose temperature depends on the time in accordance with formula (17).

With $\alpha \gg 1$, $(a\alpha)^{-1} \to 0$, (15) goes over into (11); with $\alpha \to 0$, (16) and (17) describe the thermal relaxation [6].

For Morse oscillators, no general expression is known for the coefficient B. With deactivation of the upper levels, the following expression, used in [1], may be used as an approximation:

$$B \simeq 2D_kT\tau_0^{-1}\sqrt{1-x}\,(1-\sqrt{1-x}) \tag{16}$$

We note that the above approximation holds if the dependence of $\langle(\Delta\varepsilon)^2\rangle$ on ε is determined on the basis of the value of $\langle\dot{r}^2\rangle$; this occurs with a nonadiabatic interaction between the oscillators and particles of the thermostat, in particular, in systems of the type ICl + He or CO + H (the mass of each atom of a molecule considerably exceeds the mass of a particle) and of the type HBr + Ar (the mass of a particle is much greater than the mass of the light atom of the molecule).

A solution of Eq. (1) with (8), (16) can be obtained numerically, with a boundary condition corresponding to conservation of the total number of oscillators. However, certain qualitative estimates of the effect of radiation on the relaxation of Morse oscillators can be made on the basis of the equation itself. This equation has a simpler form if it is written for the function $\Phi = f\sqrt{1-x}$, that is

$$a\frac{\partial\Phi}{\partial\tau_1} = 2\sqrt{1-x}\,(1-\sqrt{1-x})\,\frac{\partial^2\Phi}{\partial x^2} + [a(2\sqrt{1-x}\,(1-\sqrt{1-x}) + \\ + \alpha\sqrt{1-x}x) + 1]\,\frac{\partial\Phi}{\partial x} + a(1 + a\sqrt{1-x})\Phi \tag{17}$$

With $\alpha \gg 1$, at the limit, (17) goes over into (9), with (8), whose solution is (10); with $\alpha \to 0$, (17) describes the thermal relaxation [1]. With $\alpha \neq 0$, it follows from (17) that, formally, the increase in the values of a and τ_1 [compare (13)] due to radiation is here nonlinear with respect to x; actually, in place of α we have the quantity $\alpha\sqrt{1-x}$; therefore, at $x \ll 1$ the effect of radiation will be close to that for harmonic oscillators, while at large values of x, $x \sim 1$, it will be substantially less.

Figures 3 and 4 give the results of a numerical calculation for the initial distributions used above (Figs. 2 and 3) (the temperature of the thermostat corresponds the value $a = 30$); the functions $f(x, \tau_1)/\psi(x)$ (Fig. 3) and $f(x, \tau_1)$ (Fig. 4) are shown at the moment of time $\tau_1 = t/\tau_v = 0.5$, for several values of the parameter $\alpha = \tau_v/\tau_0$. With an increase in the value of α (as well as of τ_1), the difference between the relaxations of Morse oscillators and harmonic oscillators increases, approaching the limiting case with $\alpha \gg 1$ (Figs. 1 and 2); to compare Figs. 1 and 2 with Figs. 3 and 4, it must be taken into account that $\tau = \alpha\tau_1$. On Figs. 3 and 4 the solid lines also relate to Morse oscillators, and the dotted curves to harmonic oscillators.

It follows from the above considerations that the effect of radiation on the process of the deactivation of the vibrations of oscillators in an inert gas medium depends on the value of the ratio of the time of vibrational relaxation to the radiational lifetime of the ground level, i.e., τ_v/τ_0. At $\tau_v/\tau_0 \gg 1$, the deactivation of classical oscillators is described by formulas (10) and (11); these formulas make it possible to exhibit the limiting tendency of the effect of the factor of the anharmonic character of the vibrations, with the presence of radiation. For a system of harmonic oscillators, the effect of radiation is equivalent to a formal decrease in the temperature of the thermostat and of the time scale of the process by $(1 + \tau_v)/\tau_0$ times. For Morse oscillators, this effect depends on the region of the deactivation energy; with $\varepsilon \ll D$, it is analogous to harmonic oscillators; with $\varepsilon \sim D$, it is substantially less. The anharmonic character of the vibrations slows down considerably the deactivation of the vibrations of the upper levels of radiating oscillators. On the whole, radiation reinforces the relative redistribution of the population of the upper levels of Morse oscillators relaxing in an inert gas medium.

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