Effect of nonlinear interaction of molecules on their emission

V.N. Ivanov

Omsk State Technical University

The effect of nonlinear interaction of molecules on the intensity of radiation emitted by them at transitions between vibrational levels is studied theoretically. For this purpose, the solution of a nonlinear Schrödinger equation describing the state of interacting diatomic molecules is analyzed. It is shown that in the case that the kinetic degree of freedom of molecules can be considered as a heat bath, the population of vibrational levels is close to the Boltzmann distribution in a broad range of temperatures. However, when the energy of heat motion becomes less than some critical limit, rather fast destruction of excited levels should occur. Such a behavior of the population density of quantum states should result (as the temperature of a molecular ensemble drops down below some limit) in practically complete disappearance of spontaneous and stimulated emission.

Molecular gases are a thoroughly studied object. In particular, it is known that in a broad range of temperatures the population of quantum levels of gas molecules obeys the Boltzmann distribution. Nevertheless, experiments on determination of gas heat capacity show that at the temperature below some critical values this distribution can be violated for rotational and vibrational degrees of freedom.

As it is well-known, as the temperature decreases, the dependence of gas heat capacity on the internal degrees of freedom disappears instantly first for the vibrational degrees of freedom of a molecule and then for the rotational ones.[1] Such a behavior of heat capacity shows that gas molecules at the temperature below some critical value are at low energy levels. This phenomenon is usually explained by the translational kinetic energy insufficient for efficient collisional excitation. This explanation has a purely qualitative character and does not answer a lot of questions, in particular, why the efficiency of vibrational and rotational excitation at the temperature below some critical value is practically independent of the Maxwell distribution wing corresponding to high translational velocities of molecules. Besides, there is no answer to the question what is the character of emission at the temperature below this critical limit.

This paper gives one of possible explanations for such a behavior of the population of vibrational levels of diatomic gas molecules. It is shown that it is mostly caused by molecular interaction, due to which the molecular ensemble becomes a nonlinear system with some equilibrium states. At the temperature below some limit, population of excited states becomes impossible, and this leads to the absence of spontaneous and stimulated emission.

In our experiments, an oscillator was used as a model of an individual molecule. Such modeling allows the actual molecular structure to be ignored.

To take into account the effect of the environment on the individual quantum system, we selected the method proposed in Refs. 2 and 3. In this method, the state of the studied object is described by such a wave function that the mean values calculated with it coincide, in some approximation, with the values obtained using the formalism of the density matrix. For this purpose, the Feynman method is used.[4] The effect of the environment on the considered subsystem is taken into account through the corresponding definition of the Feynman propagator.

In Ref. 5 it was shown that reasonably universal form of the Hamiltonian for interacting molecules in the stationary state is the following:

$$\hat{H} = \hat{H}_0 + \lambda \hat{A} \, \langle \psi | \hat{B} | \psi \rangle. \qquad (1)$$

In Eq. (1) $\hat{H}_0$ is the unperturbed Hamiltonian of an isolated molecule; $\hat{A}$ and $\hat{B}$ are the operators describing the model interaction of the molecule with the environment; λ is the parameter characterizing the interaction intensity.

As is well-known, in the Feynman method, to determine the amplitude of probability of quantum system transition from one state to another, the method of functional integration is used. The contributions to the amplitude of all possible alternative ways from the initial to the final states of the quantum system are summed up, and the contribution of one trajectory is represented as a phase factor of the following form:

$$\varphi = \text{const} \cdot \exp \left[i S(\mathbf{r}, \mathbf{r}_1) / \hbar \right], \qquad (2)$$

where $S(\mathbf{r}, \mathbf{r}_1)$ is a classical operation calculated along this way from the point $\mathbf{r}_1$ to $\mathbf{r}$. Finally, we have a propagator meeting the following group multiplication rules:

$$K(\mathbf{r}, \mathbf{r}_1) = \int_{-\infty}^{\infty} K(\mathbf{r}, \mathbf{r}_2) \, K(\mathbf{r}_2, \mathbf{r}_1) \, d\mathbf{r}_2. \qquad (3)$$

Using Eq. (3) and comparing the probability amplitude at two close instants, we can easily obtain

the Schrödinger equation.[4] Having written the Lagrangian accounting for nonlinearity of the molecular ensemble, using the functional of the wave function, and having averaged the propagator over collisional perturbations, after some transformations we can write the equation valid in the dipole approximation:

$$i\hbar \frac{\partial \psi}{\partial t} = \frac{1}{1 + i\alpha} [\hat{T} + \chi] \psi + U\psi +$$
$$+ \Phi(\psi) \psi - (\mathbf{E} \cdot \mathbf{d}) \psi. \qquad (4)$$

In Eq. (4) $\hat{T}$ is the kinetic operator, U is the potential energy operator of an oscillator; the parameters α and χ are some positive values connected with the environment density and temperature (it can be shown that the higher the environment density, the higher α; and χ increases with the increasing temperature (see below)); $\mathbf{E}$ is the external electric field, and $\mathbf{d}$ is the dipole moment. In the simplest case, the functional of the wave function describing, in essence, the self-action of the considered system through the environment has the following form:

$$\Phi(\psi) = \lambda \hat{A} \langle \psi | \hat{B} | \psi \rangle = \frac{i\alpha}{1 + \alpha^2} \langle \psi | \hat{T} + \chi | \psi \rangle. \qquad (5)$$

In the case that the self-action through the environment is negligible, it follows from Eq. (4) that:

$$i\hbar \frac{\partial \widetilde{\psi}}{\partial t} = \frac{1}{1 + i\alpha} (\hat{T} + \chi) \widetilde{\psi} + U\widetilde{\psi} - (\mathbf{E} \cdot \mathbf{d}) \widetilde{\psi}. \qquad (6)$$

A peculiarity of this equation is that all perturbations having a collisional character are considered with the help of only one parameter α. The value of this parameter depends on the environmental density. If we pass from Eq. (6) to the Neumann equation for the statistical operator

$$\widetilde{\rho} = | \widetilde{\psi} \rangle \langle \widetilde{\psi} |, \qquad (7)$$

then, accurate to values of the higher order of smallness with respect to α, we can write:

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H}_0, \hat{\rho}] + [\hat{V}, \hat{\rho}] - i\alpha \{\hat{T}, \hat{\rho}\} - i2\alpha\chi\hat{\rho}. \qquad (8)$$

Here, as in Eq. (1), $\hat{H}_0$ is the Hamiltonian of the isolated subsystem. Besides, the operator of the kinetic energy of the subsystem $\hat{T}$ and the operator of external time-regular perturbation $\hat{V}$ are introduced in Eq. (8). Square brackets denote the commutator, and braces denote the anticommutator of the operators.

In Ref. 6 it was shown that reduction of the Neumann equation of a complex system to the equation of the separated subsystem by the Lax method[7] yields the equation of the similar form:

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H}_0, \hat{\rho}] + [\langle \hat{V} \rangle, \hat{\rho}] - i\beta \{\hat{T}, \hat{\rho}\} - i\gamma\hat{\rho}. \qquad (9)$$

Equation (9) takes place, when the environment of the subsystem under study can be considered as a heat bath. Here β and γ are constants. Angle brackets in Eq. (9) denote averaging of the perturbation operator over the states of the heat bath. Similarity of Eqs. (8) and (9) indicates that the method proposed for description of subsystem states in the heat bath with the use of effective wave functions is rather valid.

A simple substitution shows that the wave function meeting Eq. (4) is connected with the solution of Eq. (6) as follows:

$$\psi = \widetilde{\psi} / \sqrt{\langle \widetilde{\psi} | \widetilde{\psi} \rangle}. \qquad (10)$$

Equation (10) points to one of simple methods to find some of possible solutions of nonlinear equation (4). For this purpose, it is sufficient to solve Eq. (6) and then re-normalize the wave function using Eq. (10). This method is especially convenient in the case of time-regular perturbation. However, since Eq. (4) is nonlinear, its solution has some singularities, which do not show themselves in the solution of Eq. (6). Let us consider them.

In view of Eq. (10) and assuming the validity of the superposition principle for wave functions, the solution of Eq. (4) in the general case should have the following form:

$$\psi(\mathbf{r},t) = \sum_n C_n(t)\psi_n(\mathbf{r}), \qquad (11)$$

where $C_n(t)$ are some functions of time; $\psi_n(\mathbf{r})$ are eigenfunctions of the stationary Schrödinger equation following from Eq. (6):

$$E_n \psi_n = \frac{1}{1 + i\alpha} (\hat{T} + \chi) \psi_n + U\psi_n. \qquad (12)$$

In Eq. (12) the separation constant E_n can take complex values.

Because of nonlinearity of the initial equations, the coefficients $C_n(t)$ can be complex functions of time. Their phase part carries the information about the effect of external fields on the considered subsystem, and it can turn out to be very important at solution of some problems. However, within the framework of the formulated problems, the coefficients $|C_n(t)|$ are of our particular interest. Just these parameters determine the probability of finding a quantum system in some or other state disturbed by collisions. To reveal the regularities of the sought parameters, let us pass to their squares for convenience

$$P_n(t) = |C_n(t)|^2. \qquad (13)$$

Since in the presence of the time-regular perturbations there are no principal problems in solution of the nonlinear Schrödinger equation in view of Eq. (10), assume that the value of $\mathbf{E}(t)$ is close to zero, that is, we will analyze the behavior of an oscillator under the effect of stochastic perturbation. It is assumed that at fluctuations of the density of perturbing

V.N. Ivanov

Vol. 15, No. 3 / March 2002/ Atmos. Oceanic Opt. 247

particles near the considered subsystem, the value of the parameter α characterizing these perturbations may change adiabatically.

Substitution of Eq. (11) into Eq. (4) gives the following:

$$\sum_n \left(i\hbar \frac{\partial C_n}{\partial t} - E_n C_n - \frac{i\alpha}{1+\alpha^2} C_n \sum_{k,l} C_k^* C_l \tilde{T}_{kl} \right) \times$$

$$\times \psi_n(\mathbf{r}) = 0, \qquad (14)$$

which should be fulfilled at any $\mathbf{r}$. This is possible only if the parenthesis is zero. Finally, after some simple transformations, we have the system of equations:

$$\frac{\partial P_n}{\partial t} = \frac{2\alpha}{\hbar(1+\alpha^2)} \times$$

$$\times P_n \left(-\tilde{T}_{nn} + \sum_k P_k \tilde{T}_{kk} + \sum_{\substack{k,l \\ l \neq k}} \sqrt{P_k P_l} \left| \tilde{T}_{kl} \right| \cos(\beta_{kl}) \right) \quad (15)$$

$$(n = 1, 2, 3, \ldots).$$

In Eqs. (14) and (15) the matrix elements

$$\tilde{T}_{kl} = \langle \psi_k | \hat{T} + \chi | \psi_l \rangle \qquad (16)$$

are introduced.

The cosine argument in Eq. (15) is a phase of a complex parameter $C_k^*(t) C_l(t) \tilde{T}_{kl}$:

$$\cos(\beta_{k,l}) = \frac{C_k^*(t)C_l(t)\tilde{T}_{kl} + C_k(t)C_l^*(t)\tilde{T}_{lk}}{2|C_k(t)||C_l(t)||\tilde{T}_{kl}|}. \qquad (17)$$

Unlike the states of an isolated system ($\alpha = 0$), for which

$$\frac{\partial P_n}{\partial t} = 0, \qquad (18)$$

and within the framework of the condition

$$\sum_n P_n = 1 \qquad (19)$$

all P_n are equiprobable. The situation is different for the subsystem interacting with the environment. For such a system more and less probable states exist. First, let us find what $P_n(t)$ are most probable. For this purpose, equate the time derivatives in Eq. (15) to zero. Finally, we have the nonlinear system of equations:

$$P_n \left(-\tilde{T}_{nn} + \sum_k P_k \tilde{T}_{kk} + \sum_{\substack{k,l \\ l \neq k}} \sqrt{P_k P_l} \left| \tilde{T}_{kl} \right| \cos(\beta_{kl}) \right) = 0 \quad (20)$$

$$(n = 1, 2, 3, \ldots).$$

It can be easily seen that this system of equations allows only discrete solutions of the following form:

$$P_n = \begin{cases} 1 \\ 0 \end{cases}. \qquad (21)$$

Only one constant can be equal to unity, while all other constants are equal to zero, that is, the condition (19) fulfills for the population of quantum levels. In other words, the interaction of oscillators (molecules) leads to the situation that the number of most probable vibrational states becomes a countable set. Note that in this case the most probable states of the perturbed oscillator are ψ-eigenfunctions of the Hamiltonian in Eq. (12).

It follows from the obtained results that the molecule most probably is in one of its vibrational eigenstates. The question arises: whether these equilibrium states are stable and what is their dynamics. To answer this question, we can use the methods of solution of nonlinear equations.[8–10]

As was already mentioned, vibrations of diatomic gas molecules can be modeled with sufficient accuracy by a one-dimensional oscillator. Consequently, to reveal the stability of molecular vibrational states, one should know eigenvalues and eigenfunctions of the Hamiltonian of an oscillator subject to collisional perturbations.

In the one-dimensional approximation, the corresponding stationary Schrödinger equation has the form

$$\frac{\partial^2 \psi_n}{\partial x^2} + \frac{2m}{\hbar^2}(1+i\alpha)\left(\tilde{E}_n - \frac{m\omega^2 x^2}{2} \right)\psi_n = 0, \quad (22)$$

where m is the oscillator mass; ω is the frequency of vibrations. The constant $\tilde{E}_n$ is

$$\tilde{E}_n = E_n - \chi / (1 + i\alpha). \qquad (23)$$

The standard method of solution of such equations gives the following results:

$$\tilde{E}_n = \frac{1}{\sqrt{(1+i\alpha)}}\left(n + \frac{1}{2} \right)\hbar\omega \qquad (24)$$

and

$$\psi_n(\xi) = A_n \exp\left(-\sqrt{(1+i\alpha)}\,\xi^2 / 2 \right)H_n(\xi). \qquad (25)$$

In Eq. (25) A_n is the normalization constant; ξ is a dimensionless variable:

$$\xi = x\sqrt{m\omega / \hbar} ; \qquad (26)$$

$H_n(\xi)$ are Hermitian polynomials of a complex variable:

$$H_n(\xi) = (-1)^n xp\left(\sqrt{1+i\alpha}\,\xi^2 \right)\frac{\mathrm{d}^n}{\mathrm{d}\xi^n}\exp\left(-\sqrt{1+i\alpha}\,\xi^2 \right). (27)$$

As is seen from Eqs. (23)–(27), although the stationary states of the oscillator subject to collisional

perturbations are close to the states of a harmonic oscillator, but still differ from them. Coincidence is observed at $\alpha = 0$.

Due to nonlinearity of the initial equation, all oscillator states turn out to be interrelated. Therefore, when analyzing the dynamics of a populated level $(\,|C_n(t)| = 1)$, it is necessary to follow simultaneously the behavior of all unpopulated states. For this purpose, let us notice that near the equilibrium for the unpopulated oscillator quantum states $(P_l = 0)$ the constant $C_l(t)$ meets the equation

$$\frac{\partial C_l}{\partial t} = -\frac{i+\alpha}{(1+\alpha^2)\hbar}(T_{ll}+\chi)C_l - \frac{i}{\hbar}U_{ll}\,C_l +$$

$$+\frac{\alpha}{(1+\alpha^2)\hbar}(T_{ll}+\chi)|C_l|^2\,C_l, \qquad (28)$$

where T_{ll} and U_{ll} are matrix elements of the kinetic and potential energy operators.

In the form, this equation coincides with the well-known equation describing a single-parameter family of vector fields on a plane:

$$\frac{\mathrm{d}z}{\mathrm{d}t} = z(i\omega + \varepsilon + kz\bar{z}), \qquad (29)$$

the peculiarities of whose solution are thoroughly studied.[8,11] In Eq. (29) z is a complex coordinate; ω and k are real nonzero constants; ε is a real parameter. In the considered case

$$z = C_l; \quad \omega = -\frac{1}{(1+\alpha^2)\hbar}(T_{ll}+\chi) - \frac{U_{ll}}{\hbar};$$

$$\varepsilon = -k = -\frac{\alpha}{(1+\alpha^2)\hbar}(T_{ll}+\chi). \qquad (30)$$

At any ε the point $z = 0$ in Eq. (29) is the equilibrium position of the focus type, and the focus is stable at $\varepsilon < 0$. Consequently, if the environmental density is high (α is far from zero), then even in the presence of weak time-regular perturbations $(\mathbf{E}(t) \neq 0)$, the oscillator cannot transit to any unpopulated level. In this case, in the absence of strong time-regular perturbations, it is in some eigenstate for infinitely long time, that is, the found equilibrium states are stable. Recall a common postulation that a quantum system is in one of the states being a solution of the stationary Schrödinger equation. This condition automatically appears when taking the interaction into account. According to the obtained equations, for an oscillator to transit from one equilibrium state to another, either a marked time-regular perturbation or a vanishing parameter α is needed (as known, at $k > 0$, if $\varepsilon = 0$, the focuses $z = 0$ loss their stability). This circumstance allows us to study the regularities of transition from one equilibrium state to another.

In the considered case, the following is valid for the parameter ε

$$\varepsilon = -\frac{\alpha}{(1+\alpha^2)\hbar}(T_{nn}+\chi). \qquad (31)$$

In Refs. 8, 11, and 12 it was shown that since Eq. (29) has a fold-type singularity, as ε approaches zero from the negative side at some small but nonzero value $|\varepsilon| = \delta$, the existing perturbations can disturb the system equilibrium. In this case, the system transits to another remote equilibrium state or some limiting cycle or another more complex attracting set. A "catastrophe" occurs. This circumstance seems to be important. For an oscillator it means that at α less than some critical value, at which the Schrödinger equation is still nonlinear, stepwise changes in the population of quantum level are possible.

Such a stepwise disturbance of the equilibrium state of an unpopulated energy level is possible only under the condition $|\varepsilon| \leq \delta$. Taking into account Eq. (31) and the fact that the diagonal matrix elements of the kinetic energy operator are real

$$\tilde{T}_{kk} = \frac{1}{2}\left(k+\frac{1}{2}\right)\hbar\omega + \chi \qquad (32)$$

(Eq. (32) is valid accurate to the square parameter α), we can conclude that this behavior is possible for the unpopulated mth level, if α meets the inequality

$$\alpha \leq \alpha_m = 2\hbar\delta \left/\left[\left(m+\frac{1}{2}\right)\hbar\omega + 2\chi\right]\right. . \qquad (33)$$

Consequently, the probability of change of the state $C_l = 0$ is proportional to the probability that α is in the interval from zero to α_m due to fluctuations of the environmental density:

$$F(\alpha_m) = \int\limits_0^{\alpha_m} f(\alpha)\mathrm{d}\alpha, \qquad (34)$$

where $f(\alpha)$ is the probability density of realization of this value of α.

To find the explicit form of $F(\alpha_m)$, one should know the dependence $f(\alpha)$. However, within the framework of the considered problem, this is not an obligatory condition because of the smallness of α_m. Actually, because of the smallness of α_m and the condition $f(0) = 0$ (recall that the starting point was the assumption on impossibility of existence of isolated quantum subsystems), for $F(\alpha)$ we can write approximately:

$$F(\alpha_m) \approx C\alpha_m + O(\alpha^2), \qquad (35)$$

where C is some constant.

Then, according to Eq. (33), the probability of excitation of the unpopulated lth oscillator level is inversely proportional to the energy of this state. However, such excitation not always can lead finally to re-distribution of the population of oscillator levels, in particular, if transition to another attractive set takes place. Let us determine in what cases this is possible. The corresponding estimate can be obtained in the two-level approximation.

Let us separate two "stationary" states of the quantum system: $\psi_n(\mathbf{r}, t)$ and $\psi_m(\mathbf{r}, t)$, one of which is populated. Assume for certainty that the system initially is in the equilibrium state: $P_{n0} = 1$, $P_{m0} = 0$. All other P_{k0} are assumed identically equal to zero. Then the system of equations (15) takes the form

$$\frac{\partial P_n}{\partial t} = \frac{2\alpha}{\hbar \left(1 + \alpha^2\right)} P_n \left[-\tilde{T}_{nn} + P_n \tilde{T}_{nn} + P_m \tilde{T}_{mm} + \right.$$

$$\left. + 2\sqrt{P_n P_m} \left| \tilde{T}_{nm} \right| \cos(\beta_{nm})\right] = F(P_n, P_m),$$

$$\frac{\partial P_m}{\partial t} = \frac{2\alpha}{\hbar \left(1 + \alpha^2\right)} P_m \left[-\tilde{T}_{mm} + P_n \tilde{T}_{nn} + P_m \tilde{T}_{mm} + \right. \tag{36}$$

$$\left. + 2\sqrt{P_n P_m} \left| \tilde{T}_{nm} \right| \cos(\beta_{nm})\right] = \Phi(P_n, P_m).$$

According to the general properties of nonlinear systems on a plane,[10] the stability of a stationary point depends on the behavior of the right-hand side of the system of equations (36).

One of the necessary conditions for absence of other neighboring equilibrium points is a nonzero Jackobian:

$$\Delta = \begin{vmatrix} F'_{P_n}(P_{n0}, P_{m0}) & F'_{P_m}(P_{n0}, P_{m0}) \\ \Phi'_{P_n}(P_{n0}, P_{m0}) & \Phi'_{P_m}(P_{n0}, P_{m0}) \end{vmatrix} \neq 0. \tag{37}$$

One more parameter determining whether this equilibrium state is stable or not is

$$\sigma = F'_{P_n}(P_{n0}, P_{m0}) + \Phi'_{P_m}(P_{n0}, P_{m0}). \tag{38}$$

Depending on the values of Δ and σ, the equilibrium states of the considered two-level subsystem are nodes, focuses, or saddles.

If $\Delta > 0$ and $\sigma \neq 0$, then it is a node. At $\Delta > 0$ and $\sigma = 0$ the equilibrium state is a focus. At $\Delta < 0$ it is a saddle.

For the perturbed oscillator, the values of Δ and σ near the equilibrium points depend on the values of diagonal matrix elements $\tilde{T}_{nn}$, $\tilde{T}_{mm}$ and α. Taking into account Eq. (32), accurate to the second order of smallness with respect to α, we can write:

$$\Delta = (\alpha\omega)^2 \left(n + \frac{1}{2} + \frac{\chi}{\hbar\omega}\right)(n - m), \tag{39}$$

$$\sigma = \alpha\omega \left(2n - m + \frac{1}{2} + \frac{2\chi}{\hbar\omega}\right). \tag{40}$$

The obtained equations allow studying the dynamics of variation of the equilibrium state.

First, consider the case that the quantum number n corresponds to the upper layer. In this case Δ and σ exceed zero. Such an equilibrium point turns out to be unstable.[10] If the oscillator is disturbed from this point so that its final state is a superposition of the initial wavefunctions, then, according to Eq. (12), the following equation is valid for this superposition:

$$\psi(x,t) =$$

$$= \left[C_n \exp\left(-i\frac{E_n t}{\hbar}\right)\psi_n(x) + C_m \exp\left(-i\frac{E_m t}{\hbar}\right)\psi_m(x)\right] /$$

$$/ \left\{ |C_n|^2 \exp\left(-i\frac{(E_n - E_n^*)t}{\hbar}\right) + \right.$$

$$+ |C_m|^2 \exp\left[-i\frac{(E_m - E_m^*)t}{\hbar}\right] +$$

$$\left. + 2\operatorname{Re}\left[C_n C_m^* \exp\left(-i\frac{(E_n - E_n^*)t}{\hbar}\right)\langle\psi_n | \psi_m\rangle\right]\right\}^{\frac{1}{2}}. \tag{41}$$

It follows from Eq. (41) that with time, because of the exponentially decreasing factors, the wavefunction of a two-level subsystem tends to the lower-state wavefunction keeping normalization in time. In other words, the oscillator relaxes to the lower energy state.

This means that in the case that there arise conditions for a catastrophe, the equilibrium state of the oscillator being at the higher energy level is to change stepwise. No closed trajectories are formed. It is natural to interpret such a change in the oscillator equilibrium state as a quantum jump.

Consider the next variant: $n < m$. The equilibrium point in this case is a saddle. This point is also unstable. This means that the population P_n of the lower level, as well as at $n > m$, can change stepwise. However, this case has a significant difference. Such changes are not always possible. Actually, if the oscillator is disturbed from the equilibrium state so that its new state is described by the superposition (41), then with time the oscillator comes back to the initial state. In other words, a loop passing through the equilibrium point is possible here. The stability of this point depends on the sign of σ (Ref. 10). The loop is stable if this parameter is negative at the equilibrium point and unstable if it is positive. Consequently, the stepwise change of the oscillator equilibrium position is possible only at $\sigma > 0$. Otherwise, even if prerequisites for a quantum jump exist, the oscillator returns to the initial state after disturbance. This means that the upper state remains unpopulated. It follows from Eq. (40) that the oscillator cannot change the equilibrium state stepwise at

$$m > 2n + \frac{2\chi}{\hbar\omega} + \frac{1}{2}. \tag{42}$$

This inequality (42) depends not only on quantum numbers, but also on χ. In spite of the fact that mechanistic identification of realization of an alternative trajectory and Brownian motion of an actual particle is likely conditional, we would like to note some important circumstance here. At ordinary Brownian motion of a particle in a heat bath, this parameter is equal to the energy per one degree of freedom[3]:

$$\chi = k_B T / 2 \tag{43}$$

(k_{B} is the Boltzmann constant; T is the temperature). If χ has just this physical meaning, then we can assert that quantum jumps from the lower level to the upper one are possible only at a certain temperature:

$$k_{\mathrm{B}}T > \hbar\omega\left(m+\frac{1}{2}\right) - 2\hbar\omega\left(n+\frac{1}{2}\right). \qquad (44)$$

It follows from Eq. (44) that at

$$T < \hbar\omega/(2k_{\mathrm{B}}) \qquad (45)$$

stepwise transitions from the ground level ($n = 0$) to upper levels are impossible. In other words, at the temperature below the limit determined by Eq. (45), the oscillator, finding itself in the lower equilibrium state, cannot leave it without strong external disturbance. Consequently, if we consider an ensemble of oscillators, then only the lower energy state is populated in them at the temperature below some critical limit. At the temperature below the value determined by Eq. (45), vibrational degrees of freedom are "frozen." Note that at the temperature above the critical limit, the distribution of the population probability of energy levels is close to Boltzmann distribution (the materials of the corresponding investigation are sent for publication) and, consequently, emission of a molecular ensemble is to obey the Plank formula.

"Freezing" of vibrational degrees of freedom must apparently lead to a change in the character of emission. As the temperature drops down below the limit determined by Eq. (45), both spontaneous and stimulated emissions from a molecular ensemble are to be absent. The disappearance of emission is caused by the nonlinear character of molecular interaction. The same effect seemingly shows itself in heat capacity of gases.

References

1. D.V. Sivukhin, *General Course of Physics*. (Nauka, Moscow, 1975), Vol. 2. 551 pp.
2. V.N. Ivanov, *"Scattering of unstable particles,"* Dep. VINITI, No. 8176-V86 (1986), 13 pp.
3. V.N. Ivanov, Izv. Vyssh. Uchebn. Zaved., Ser. Fiz. **39**, No. 2, 7–13 (1996).
4. R.P. Feynman and A.R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw Hill, New York, 1965).
5. P.R. Surian and J. Angyan, Phys. Rev. A **28**, No. 1, 45–48 (1983).
6. V.N. Ivanov, Izv. Vyssh. Uchebn. Zaved., Ser. Fiz. **41**, No. 7, 64–68 (1998).
7. M. Lax, *Fluctuation and Coherence Phenomena in Classical and Quantum Physics* (Gordon and Breach, New York, 1968).
8. V.I. Arnold, *Additional Chapters on the Theory of Ordinary Differential Equations* (Nauka, Moscow, 1978), 304 pp.
9. G. Iooss and D.D. Joseph, *Elementary Stability and Bifurcation Theory* (Springer-Verlag, New York, 1980).
10. A.A. Andronov, E.A. Leontovich, I.I. Gordon, and A.G. Maier, *Bifurcation Theory of Dynamic Systems on a Plane* (Nauka, Moscow, 1967), 487 pp.
11. G.M. Zaslavskii and R.Z. Sagdeev, *Introduction to Nonlinear Physics* (Nauka, Moscow, 1988), 368 pp.
12. V.I. Arnold, *Theory of Catastrophes* (Nauka, Moscow, 1990), 127 pp.