Role of coherent effects in the excitation of high vibrational molecular levels

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Several methods of exciting the high vibrational levels of molecules located in an electromagnetic field are proposed and considered. These methods are: 1) the action of a set of phased pulses (an analog of Veksler's phase-stability method for relativistic charged particles), 2) periodic radiation-frequency modulation (the modulation frequency is equal to the frequency of the anharmonic shift), 3) amplitude-frequency modulation. The considered methods allow the neutralization of the anharmonicity of the molecules and ensure the feasibility of high vibrational level excitation. It is shown that an important role in this may be played by the coherent effects of the interaction between the field and the medium. The conditions under which the molecule distribution over the vibrational levels can be inverted as a whole (overexcited state) are investigated. In each of the cases considered, the solutions to the problems are presented in a closed analytic form.

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1. INTRODUCTION

The problem of laser application in chemistry has attracted the attention of researchers for a relatively long time [1-5]. During the last five-year period an intense development of this field has taken place (see the reviews [6-10]). Laser separation of the isotopes of a number of molecules has already been accomplished with an exceptionally high enrichment factor $\beta \sim 10^2-10^3$ [11,12]. The experimental successes achieved were foreordained, in the first place, by the feasibility of selective excitation of a chosen vibrational branch of molecules by resonance infrared laser radiation and the high spectral density of the radiation.

The theoretical problems connected with the vibrational kinetics of molecules under nonequilibrium conditions created by resonance laser radiation have been studied in quite a number of papers [1,13-23]. The analysis carried out in the majority of these papers [12-20] is based on the solution to a set of equations of the balance type for the population of the vibrational levels (i.e., for the diagonal elements of the density matrix). Also, traditional methods were used [24-26]. The approach based on the balance equations is clearly valid if the relaxation time T_2 is shorter than the duration of the radiation pulse.

Some distinctive features of the coherent interaction of radiation with a gaseous medium were considered in [1,22,23]. Askar'yan in his paper [1] estimates on the basis of the harmonic-oscillator model the amplitude and buildup time of the vibrations of isolated molecules located in high-intensity resonance fields. In the paper [22] by one of the present authors and Savva, the kinetics of the excitation of an anharmonic oscillator under conditions when the electric field is in resonance with the frequency of some transition of the molecule is investigated. Goodman, Stone, and Thiele [23] have considered the quasi-stationary regime of excitation and decay of molecules stimulated by "truncated" harmonic oscillators. In [22,23], numerical methods were used.

One of the main obstacles to the selective action of laser radiation on a chosen vibrational degree of freedom of a molecule is the molecule's anharmonicity, which does not allow a sufficiently efficient excitation of the high vibrational levels. In this connection, the choice by experimenters of the molecules BCl_3 and SF_6 as suitable objects in which to realize selective oscillation pumping [12,27-31] is not accidental. The point is that molecules of this type[1)] possess anomalously low anharmonicities (according to [28], the anharmonicity of the ν_3 mode of BCl_3 is 1.6 cm^{-1}). Furthermore, these molecules are characterized by a high density of the rotational lines ($\sim 10^3$ lines/cm [32]). High-intensity fields ($\sim 10^7-10^9$ W/cm^2) considerably broaden the rotational lines (up to ~ 1 cm^{-1}), allow us to "shut off" the anharmonicity and, thus, force a significant fraction of the molecules in the lower states to participate in the absorption of the laser radiation. It is precisely these factors that characterize the experiments on the separation of the isotopes of boron [30] and sulfur [12].

In the usual cases the anharmonicity is high ($2\omega_e x_e \gtrsim 10$ cm^{-1}; $\gtrsim 100$ cm^{-1} for bonds with light atoms), and the tendency towards selective oscillation excitation meets with serious difficulties. Therefore, the proposition of new methods that allow the "neutralization" of anharmonicity as a negative factor is a matter of great urgency. In this connection, let us mention Lugovoĭ and Strel'tsov's paper [33], in which, for the purposes indicated, a method of adiabatic scanning of the laser-radiation frequency is proposed[2)].

In the present paper we propose and consider several methods for the selective excitation of the high vibrational levels of molecules by resonance laser radiation: 1) the action of a set of "π-pulses" (Sec. 3), 2) frequency modulation (Sec. 4), and 3) amplitude-frequency modulation (Sec. 6). In all the indicated case, under certain conditions, an important role is played by the coherence effects of the field-molecule interaction. The solution to the pertinent problems is representable in a closed analytic form. Furthermore, we present exact solutions to the problem of the excitation of a harmonic oscillator in the presence of relaxation (Sec. 2) and a problem whose formulation is based on the balance equations in the case of arbitrary field modulation (Sec. 5).

2. EXCITATION OF A HARMONIC OSCILLATOR BY RESONANCE RADIATION

Let us consider the simplest system: a harmonic oscillator of photon energy $\hbar\omega_0$, excited by the resonance electric field $E = E_0 \cos \omega t$. The Hamiltonian can be written in the form

$$\hat{H}=\hbar\omega_0\hat{\varepsilon}-E(t)\hat{\mu},$$

where $\hat{\mu}$ is the operator of projection of the dipole moment of the molecule along the direction of the field, $\hbar\omega_0\hat{\epsilon}$ is the Hamiltonian of the isolated harmonic oscillator, and to the operator $\hat{\epsilon}$ corresponds a matrix with elements $\epsilon_{ik} = (i-1)\delta_{ik}$ (i, k = 1, 2, ...). It is assumed that the field induces a high-frequency polarization only between neighboring pairs of vibrational levels.

The equation of motion for the dipole-moment operator can be derived in the conventional manner[34]:

$$\frac{d^2\hat{\mu}}{dt^2}+\frac{2}{T_2}\frac{d\hat{\mu}}{dt}+\left(\omega_0^2+\frac{1}{T_2^2}\right)\hat{\mu}=\frac{\omega_0}{\hbar}E(t)[[\hat{\mu}\varepsilon]\hat{\mu}],$$

where T_2 is a phenomenologically introduced phase-relaxation time and the square brackets correspond to commutation operations. Taking into account the connection between the squares of the matrix elements, $\mu_{k+1,k}^2 = k\mu_{21}^2$, and the relation $\mathrm{Sp}(\hat{\rho}[[\hat{\mu}\hat{\epsilon}]\hat{\mu}]) = 2\mu_{21}^2$, we obtain for the observable quantity

$$p=\mathrm{Sp}(\hat{\rho}\hat{\mu})=\sum_{m=1}^{\infty}(\mu_{m+1,m}\rho_{m,m+1}+\mu_{m,m+1}\rho_{m+1,m})$$

the equation

$$\ddot{p}+\frac{2}{T_2}\dot{p}+\left(\omega_0^2+\frac{1}{T_2^2}\right)p=2\mu_{21}\omega_0\Omega\cos\omega t, \tag{2.1}$$

where $\Omega = \mu_{21}E_0/\hbar$ is the Rabi frequency. For the operator $\hat{\epsilon}$ it is not difficult to obtain the equation

$$\frac{d\hat{\varepsilon}}{dt}+\frac{\hat{\varepsilon}}{T_1}=\frac{E(t)}{\hbar\omega_0}\left(\frac{d\hat{\mu}}{dt}+\frac{\hat{\mu}}{T_2}\right),$$

so that for the mean number of vibrational quanta $\epsilon = \mathrm{Sp}(\hat{\rho}\hat{\epsilon})$, we have

$$\dot{\varepsilon}+\frac{\varepsilon}{T_1}=\frac{E_0}{\hbar\omega_0}\cos\omega t\left(\dot{p}+\frac{p}{T_2}\right), \tag{2.2}$$

where T_1 is the energy-relaxation time.

In the case of small detunings $|\Delta|/\omega_0 \ll 1$, but under the condition $T_2^2\omega_0|\Delta| \gg 1$, from (2.1) and (2.2) we find for the energy of the harmonic oscillator the expression ($\epsilon(0) = 0$)

$$\varepsilon=\frac{\Omega^2}{2(\Delta^2+T_2^{-2})}\left\{\frac{T_1}{T_2}(1-e^{-t/T_1})+\left[\frac{\Delta^2+(T_2\tau_{12})^{-1}}{\Delta^2+\tau_{12}^{-2}}\right]e^{-t/T_1}\right. \tag{2.3}$$
$$\left.-e^{-t/T_2}(\Delta^2+\tau_{12}^{-2})^{-1}[(\Delta^2+T_2^{-1}\tau_{12}^{-1})\cos\Delta t+\Delta(T_2^{-1}-\tau_{12}^{-1})\sin\Delta t]\right\},$$

where $\Delta = \omega_0 - \omega$ and $\tau_{12}^{-1} = T_1^{-1} - T_2^{-1}$.

In the particular case when $T_2 \ll t$ and $T_2 \ll T_1$, the expression for the energy assumes a form obtainable from an analysis in which the coherence effects are neglected[16]:

$$\varepsilon=\frac{1}{2}\frac{T_1}{T_2}\frac{\Omega^2}{(\Delta^2+T_2^{-2})}(1-e^{-t/T_1}).$$

It can be seen from this that the energy in time reaches the steady-state level; at small t the energy $\epsilon \sim t$.

In the opposite limiting case, when T_1^{-1} and $T_2^{-1} \to 0$, from (2.3) we have

$$\varepsilon=\frac{1}{2}\frac{\Omega^2}{\Delta^2}(1-\cos\Delta t),$$

i.e., the vibrational-energy reserve varies periodically with the optical-beat frequency (see[35]); at small t the energy $\epsilon \sim t^2$.

3. EXCITATION OF A HARMONIC OSCILLATOR BY A SET OF PHASED PULSES

For the excitation of the upper vibrational levels of molecules by resonance laser radiation, we can use a method based on the well-known principle of phase stability. The principle of phase stability (autophasing) first put forward by Veksler[36] as a means of maintaining indefinitely the resonance between charged particles and a high-frequency field in an accelerator of the cyclotron type.

A modification of this method in the case of the excitation of anharmonic molecules by an electric field consists in the following. If the frequency of the light pulse $E = E_0\cos\omega t$ coincides with the transition frequency for the lowest pair of levels 1 and 2 ($\omega = \omega_{21}$), then, in the absence of relaxation, the populations of these levels will vary periodically in time with the Rabi frequency $\Omega_{21} = E_0\mu_{21}/\hbar$[34]. At moments of time $t = \tau_1$ such that $\Omega_{21}\tau_1 = (2n+1)\pi$ (n = 0, 1, ...), the system is completely inverted, i.e., all the molecules are in the upper level 2. Let us now assume that at the moment τ_1 the radiation frequency changed discontinuously and became equal to the transition frequency ω_{32} for the higher-lying pair of levels. The molecules "trapped" in the resonance by the pulse will again begin to oscillate, but now between the levels 3 and 2 with frequency $\Omega_{32} = E_0\mu_{32}/\hbar$. The choice of the phase value at which the next pulse is switched on in accordance with the condition $\Omega_{32}\tau_2 = \pi(2n+1)$ transfers the molecules to a still higher level, etc. Thus, a set of phased pulses with frequencies $\omega_{21}, \omega_{32}, \omega_{43}, \ldots$ allows, in principle, the excitation of high vibrational levels.

Let us determine what fraction of the molecules can get into the upper levels of the vibrational mode. Let the external influence consist of a set of successively switched-on pulses. For the k-th pulse of duration $\tau_{k+1,k}$, let us write

$$E_k(t)=E_{k0}\cos\omega_{k+1,k}t, \quad k=1,2,\ldots,$$
$$t_{k-1}<t<t_k, \quad t_k=\sum_{i=0}^{k}\tau_i, \quad \tau_0=t_0=0.$$

In the interval $t_{k-1} < t < t_k$ the population difference $W_k = \rho_{k+1,k+1} - \rho_{k,k}$ and the population sum $V_k = \rho_{k+1,k+1} + \rho_{k,k}$ satisfy respectively the equations:

$$\begin{gathered}\ddot{W}_k+\frac{2}{T_{12}}\dot{W}+\left(\Omega_k^2+\frac{1}{T_1T_2}\right)W_k+\frac{1}{T_1T_2}\delta_{1k}=0,\\ \dot{V}_k+\frac{1}{T_1}V_k=\frac{1}{T_1}\delta_{1k}, \quad k=1,2,\ldots\\ W_k(t_{k-1})=-\rho_{kk}(t_{k-1}), \quad \dot{W}_k(t_{k-1})=0, \quad V_k(t_{k-1})=\rho_{kk}(t_{k-1}),\\ \Omega_k=\frac{E_{0k}\mu_{k+1,k}}{\hbar}, \quad \frac{1}{T_{12}}=\frac{1}{2}\left(\frac{1}{T_1}+\frac{1}{T_2}\right).\end{gathered} \tag{3.1}$$

It is assumed that the inequalities

$$2\left(\Omega_k^2+\frac{1}{T_1T_2}\right)^{1/2}>\frac{1}{T_1}+\frac{1}{T_2}.$$

are fulfilled. The conditions for the coherent phasing of the radiation pulses allow us to determine their durations:

$$\Omega_k'\tau_k=2\,\mathrm{arc\,tg}\,(T_{12}\Omega_k')+2\pi n_k, \quad n_k=0,1,\ldots,$$
$$\Omega_k'^2=\Omega_k^2-\frac{1}{4}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)^2.$$

For the fraction of the molecules populating the k-th vibrational level at the moment of time

$$t_{k-1}=\sum_{j=1}^{k-1}\tau_j,$$

we obtain the expression

$$\rho_{kk}=2^{1-k}T_1T_2\Omega_{21}^2(1+T_1T_2\Omega_{21}^2)^{-1}(1+\exp\{-\tau_1/T_{12}\})$$
$$\times\exp\left\{-\sum_{i=2}^{k-1}\tau_i/2T_1\right\}\prod_{j=2}^{k-1}(\exp\{-\tau_j/2T_1\}+\exp\{-\tau_j/2T_2\}).$$

In the particular case when $T_1 = T_2 = T$ (which is typical for experiments[37]) and $\Omega_j \equiv \Omega$, this expression assumes the form ($n_k = 0$)

$$\rho_{kk}=\frac{x^2}{1+x^2}\operatorname{ch} y e^{-(2k-3)y} \quad (k\geqslant 2),$$
$$t_{k-1}=2T(k-1)y, \quad x=\Omega T, \quad y=\operatorname{arc\,tg} x/x.$$

For $x = 10^2$, the characteristic time of occupation of, for example, the 10-th level $\approx 0.3T$ and the fraction of the excited molecules in this level $\approx e^{-0.25}$.

4. PERIODIC PHASE MODULATION AS A METHOD FOR REALIZING THE CASCADE POPULATION MECHANISM

Let us consider the second method of exciting molecules by laser radiation, which allows the neutralization of the effect of anharmonicity.

Let us label the levels of the anharmonic oscillator as follows: 1, 2, 3, ..., N, N + 1; the energy of the (N + 1)-st level coincides with the energy of dissociation. The one-photon transition frequencies of such an oscillator can be written in the form

$$\omega_{m+1,m}=\omega_{21}-(m-1)\Delta\omega \quad (m=1,2,\ldots,N), \tag{4.1}$$

where ω_{21} is the frequency of the transition between the first excited and the ground vibrational levels and $\Delta\omega$ is the anharmonic shift ($\Delta\omega/\omega_{21} \ll 1$). The characteristic property of the anharmonic oscillator in the approximation when the relation (4.1) is valid consists in the following: The difference between the frequencies of the transitions between neighboring pairs of levels does not depend on the number, and coincides with the frequency of the anharmonic shift

$$\omega_{m,m-1}-\omega_{m+1,m}=\Delta\omega.$$

To within the same degree of accuracy is valid the expression for the periods:

$$T_{m+1,m}-T_{m,m-1}=\Delta T=2\pi/\Delta\omega. \tag{4.2}$$

Notice that Veksler's idea is, in essence, based on the relation (4.2). This follows if $T_{m+1,m}$ is taken in[36] to be the time of the m-th cycle in the revolution of a charged relativistic particle around the magnetic field, so that (4.2) physically implies that the difference between the times of two consecutive cycles remains a constant quantity, not depending on the particle energy, i.e., on m.

Let us consider the oscillations of the anharmonic oscillator in an electric field whose intensity is given in the form

$$E(t)={}^1/{}_2E_0(e^{i(\omega t+\Phi(t))}+\text{c.c.}), \tag{4.3}$$

where the carrier frequency ω coincides with the frequency of one of the transitions (e.g., for the lowest pair of levels 2 – 1), while the phase $\Phi(t)$ periodically varies in time, the frequency of variation being equal to the frequency, $\Delta\omega$, of the anharmonic shift. Then, clearly, the oscillation spectrum of the field will contain the frequencies of all the one-photon transitions of the molecule. Thus, the periodic modulation of the phase at the anharmonicity frequency allows the realization of the cascade mechanism of population of the levels of the anharmonic oscillator. Let us write (4.3) in the Fourier representation

$$E(t)=\frac{E_0}{2}\Big(\sum_{n=-\infty}^{\infty} C_n e^{i(\omega+n\Delta\omega)t}+\text{c.c.}\Big),$$

$$C_n=\frac{\Delta\omega}{2\pi}\int\limits_0^{2\pi/\Delta\omega} dt\exp[i(\Phi(t)-n\Delta\omega t)]. \tag{4.4}$$

In the particular case when the modulation is sinusoidal, i.e., when $\Phi(t) = \delta \sin\Delta\omega t$, for the spectral amplitudes we have: $C_n = J_n(\delta)$, where J_n is a Bessel function.

The process of excitation of molecular vibrations in the presence of a field is described by the equation for the density matrix

$$i\hbar\left(\frac{\partial\hat\rho}{\partial t}+\frac{\hat\rho-\hat\rho_0}{T}\right)=[\hat H\hat\rho], \tag{4.5}$$

where the Hamiltonian operator in the dipole approximation has the form

$$\hat H=\hat H_0-E(t)\hat\mu,$$

the eigenvalues of the Hamiltonian H_0 being the energies of the levels of the anharmonic oscillator; $\hat\rho_0$ is the equilibrium density matrix; and T is a phenomenologically introduced relaxation time (for the diagonal elements $T = T_1$, while for the off-diagonal elements $T = T_2$). For simplicity, we shall assume that each individual transition ($m + 1 \rightleftarrows m$) is affected only by the resonance spectral component from the expansion (4.4):

$$E_{m+1,m}(t)={}^1/{}_2E_0C_m(\exp\{i\omega_{m+1,m}t\}+\text{c.c.}).$$

Then to the Boltzmann equation (4.5) will be equivalent the following system (we are considering one-photon transitions):

$$\begin{gathered}
i\hbar(\dot\rho_{mm}+(\rho_{mm}-\delta_{1m})/T_1)=E_{m+1,m}(t)A_{m+1,m}-E_{m,m-1}(t)A_{m,m-1}(1-\delta_{1m}),\\
i\hbar(\dot\rho_{m,m+1}+\rho_{m,m+1}/T_2)=-\hbar\omega_{m+1,m}\rho_{m,m+1}-E_{m+1,m}(t)\mu_{m,m+1}(\rho_{m+1,m+1}-\rho_{mm}),\\
i\hbar(\dot\rho_{m+1,m}+\rho_{m+1,m}/T_2)=\hbar\omega_{m+1,m}\rho_{m+1,m}+E_{m+1,m}(t)\mu_{m+1,m}(\rho_{m+1,m+1}-\rho_{mm}),\\
A_{m+1,m}=\mu_{m+1,m}\rho_{m,m+1}-\mu_{m,m+1}\rho_{m+1,m},\\
\sum_{m=1}^{N+1}\rho_{mm}=1, \qquad m=1,2,\ldots,N.
\end{gathered} \tag{4.6}$$

The system (4.6) is of order 2N; it is assumed that the equilibrium value of the diagonal element ρ_{11} of the density matrix is equal to unity, while the equilibrium values of the remaining elements are equal to zero. If in (4.6) we set $E_{m+1,m}(t) = E_0(t)$, then this system describes, in particular, the excitation of a truncated harmonic oscillator.

It is convenient to carry out the subsequent analysis for a renormalized density matrix. Let us introduce the quantities

$$y_m=1-\sum_{j=1}^{m}\rho_{jj}(t), \qquad m=1,2,\ldots,N.$$

The quantity y_m has a simple physical meaning: It is the fraction of the molecules populating the levels starting from the (m + 1)-th to the (N + 1)-th (i.e., up to the dissociation level).

It is not difficult to show that the system (4.6) can be reduced to the following system (in the computations the second harmonics $\exp(2i\omega_{m+1,m}t)$ were naturally[34] neglected):

$$\begin{gathered}
\ddot y_m+\left(\frac{1}{T_1}+\frac{1}{T_2}\right)\dot y_m+\frac{1}{T_1T_2}y_m=\frac{\Omega_m^2}{2}(\delta_{1m}+y_{m-1}-2y_m+y_{m+1}),\\
m=1,\ldots,N; \quad y_m(0)=\dot y_m(0)=0; \quad y_0=y_{N+1}=0;\\
\Omega_m=E_0C_m\mu_{m+1,m}/\hbar.
\end{gathered} \tag{4.7}$$

The system (4.7), which describes the oscillations of N coupled oscillators, is often encountered in physics, and the methods for its solution have been well studied.

In the present paper we restrict ourselves to the case when $\Omega_m \equiv \Omega_0$3). Following the well-known methods (see, for example, [38]), let us introduce the "collective coordinates"

$$z_k=\left(\frac{2}{N+1}\right)^{1/2}\sum_{m=1}^{N} y_m \sin\frac{mk\pi}{N+1}, \quad k=1,2,\dots,N, \tag{4.8}$$

with

$$y_m=\left(\frac{2}{N+1}\right)^{1/2}\sum_{k=1}^{N} z_k \sin\frac{mk\pi}{N+1}, \quad m=1,2,\dots,N. \tag{4.9}$$

Then we obtain for the z_k the set of decoupled equations:

$$\ddot{z}_k+\left(\frac{1}{T_1}+\frac{1}{T_2}\right)\dot{z}_k+\left(\nu_k^2+\frac{1}{T_1T_2}\right)z_k=\frac{\Omega_0^2}{2}f_k,$$
$$z_k(0)=\dot{z}_k(0)=0, \quad k=1,2,\dots,N. \tag{4.10}$$

Here we have introduced the notation

$$\nu_k=2^{1/2}\Omega_0\sin\frac{k\pi}{2(N+1)}, \quad f_k=\left(\frac{2}{N+1}\right)^{1/2}\sin\frac{k\pi}{N+1}. \tag{4.11}$$

Solving (4.10), and substituting the result into (4.9), we obtain

$$y_m=\frac{1}{N+1}\sum_{k=1}^{N}\sin\frac{mk\pi}{N+1}\sin\frac{k\pi}{N+1}\left(\frac{\Omega_0}{\omega_k'}\right)^2F_k(t),$$
$$F_k(t)=1-\frac{\omega_k'}{\omega_k}\exp\left[-\frac{t}{2}\left(\frac{1}{T_1}+\frac{1}{T_2}\right)\right]\cos(\omega_kt+\varphi_k), \tag{4.12}$$
$$\omega_k^2=\nu_k^2-\frac{1}{4}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)^2; \quad \omega_k'^2=\nu_k^2+\frac{1}{T_1T_2}, \quad \cos\varphi_k=\omega_k/\omega_k',$$
$$k=1,2,\dots,N.$$

The diagonal elements of the density matrix, ρ_{mm}, are determined by the relation

$$\rho_{mm}=y_{m-1}-y_m=\frac{1}{N+1}\sum_{k=1}^{N}\left(\sin\frac{(m-1)k\pi}{N+1}-\sin\frac{mk\pi}{N+1}\right)$$
$$\times\sin\frac{k\pi}{N+1}\left(\frac{\Omega_0}{\omega_k'}\right)^2F_k(t) \quad (m=1,2,\dots,N+1). \tag{4.13}$$

For the mean number of vibrational quanta (per oscillator), we have

$$\varepsilon=\sum_{m=1}^{N+1}(m-1)\rho_{mm}=\sum_{m=1}^{N}y_m=\frac{1}{N+1}\sum_{k=1}^{N}(1-(-1)^k)\cos\frac{k\pi}{2(N+1)}\left(\frac{\Omega_0}{\omega'_k}\right)^2F_k(t). \tag{4.14}$$

The physical structure of the found relations is clear: The formulas (4.12)—(4.14) are superpositions of the eigensolutions of the problem. If the condition $\omega_k' > \frac{1}{2}(1/T_1 + 1/T_2)$ is fulfilled, then the solutions have the character of damped oscillations. The latter are due to the coherent mechanism of interaction between the field and the medium. The spectrum of the pulsations is given by the formula for ω_k ($k = 1, 2, \dots, N$). In the particular case when $T_1 = T_2$, the frequencies $\omega_k = \nu_k$ (see (4.11)).

As $t \to \infty$, the amplitudes of the pulsations decrease, and the solutions reach the steady-state level. Using the conventional techniques of operational calculus, we can show that the steady-state values of the corresponding quantities have the form

$$y_{m,0}=\frac{\operatorname{sh}(N+1-m)\alpha}{\operatorname{sh}(N+1)\alpha}, \quad \rho_{mm,0}=2\frac{\operatorname{sh}(\alpha/2)}{\operatorname{sh}(N+1)\alpha}\operatorname{ch}\left(N+\frac{3}{2}-m\right)\alpha,$$
$$m=1,\dots,N+1, \tag{4.15}$$
$$\varepsilon_0=\frac{1}{2}\frac{\operatorname{sh}(N\alpha/2)}{\operatorname{sh}(\alpha/2)\operatorname{ch}((N+1)\alpha/2)}, \quad \operatorname{ch}\alpha=1+\frac{1}{\Omega_0^2T_1T_2}.$$

For strong fields, for which $\beta = \Omega_0^2T_1T_2 \gg 1$ ($\alpha \to 0$), we have

$$y_{m,0}=(N+1-m)(N+1)^{-1}, \quad \rho_{mm,0}=(N+1)^{-1}, \quad \varepsilon_0=2^{-1}N, \tag{4.16}$$

i.e., the saturation regime, in which the oscillator-level occupation probabilities are equal, is realized.

For weak fields, for which $\beta \ll 1$, the dependences have the character of power functions:

$$y_{m,0}\approx(\beta/2)^m, \quad \rho_{mm,0}\approx(\beta/2)^{m-1}, \quad \varepsilon_0\approx\beta/2.$$

In the purely coherent case, when $\nu_k^2 \gg 1/T_1T_2$ and $t \ll T_2 < T_1$ (the phase and field relaxation times are large), the oscillator-level occupation probabilities and the mean number of quanta are determined by the relations

$$\Delta\rho_{mm}=\sum_{k=1}^{N}U_{mk}\cos\nu_kt, \quad \Delta\varepsilon=\sum_{k=1}^{N}V_k\cos\nu_kt, \tag{4.17}$$

where we have introduced the notation

$$\Delta\rho_{mm}=\rho_{mm}(t)-(N+1)^{-1}, \quad \Delta\varepsilon=\varepsilon(t)-2^{-1}N,$$
$$U_{mk}=\frac{1}{N+1}\left(\cos\frac{mk\pi}{N+1}+\cos\frac{(m-1)k\pi}{N+1}\right), \tag{4.18}$$
$$V_k=\frac{1}{2(N+1)}[(-1)^k-1]\operatorname{ctg}^2\frac{k\pi}{2(N+1)}.$$

The first relation in (4.7) generalizes the well-known solution, given in Landau and Lifshitz's book [34], for a two-level system (exact resonance) to the case of an arbitrary finite number of levels. It can be seen from (4.17) and (4.18) that the probabilities ρ_{mm} oscillate about the value $(N + 1)^{-1}$, while the number of quanta oscillates about the value $2^{-1}N$. Notice that the spectrum of the pulsations in the mean reserve of quanta contains frequencies with only odd indices.

In the opposite limiting case,

$$4(T_2^2\nu_k^2+T_2/T_1)\ll1, \quad T_2\ll1, \tag{4.19}$$

the role of the coherence effects are not important. In this case the function $F_k(t)$ in (4.12)—(4.14) assumes the form

$$F_k(t)=1-\exp[-T_1^{-1}t(1+T_1T_2\nu_k^2)]. \tag{4.20}$$

In the following section we show that the relation (4.20) is immediately obtainable from the usual balance equations for the diagonal matrix elements of the density matrix. Consequently, the conditions (4.19) are the conditions of applicability of these equations (for a constant field amplitude).

5. APPROACH BASED ON EQUATIONS OF THE BALANCE TYPE

The balance equations for the probabilities of occupation of the oscillator levels, $\rho_m = \rho_{mm}$, are usually written in the form

$$\dot\rho_m+T_1^{-1}(\rho_m-\delta_{m1})=\sigma_mI_m(\rho_{m+1}-\rho_m)-\sigma_{m-1}I_{m-1}(\rho_m-\rho_{m-1}),$$
$$m=1,2,\dots,N, \quad \sum_{m=1}^{N+1}\rho_m=1, \quad \rho_m(0)=\delta_{m1}. \tag{5.1}$$

For the stimulated-transition cross sections, $\sigma_m = \sigma_{m+1,m}$ (exact resonance), and the spectral intensities, $I_m = I_{m+1,m}$, we have the relations

$$\sigma_m=4\pi T_2\omega_{m+1,m}\frac{\mu_{m+1,m}^2}{\hbar c}, \quad I_m=\frac{c}{8\pi}\frac{E_{m+1,m}^2}{\hbar\omega_{m+1,m}}, \quad \sigma_mI_m=\frac{T_2}{2}\left(\frac{E_{m+1,m}\mu_{m+1,m}}{\hbar}\right)^2.$$

Let us solve the system (5.1) in the general case, when the spectral amplitudes of the field depend on the time:

$$E_{m+1,m}(t)=E_{m0}g(t).$$

Introducing, as in Sec. 4, the quantities y_m, we obtain from (5.1) the set of equations:

$$\dot{y}_m+\frac{1}{T_1}y_m=\frac{1}{2}\Omega_m^2T_2g^2(t)[\delta_{1m}+y_{m-1}-2y_m+y_{m+1}], \quad m=1,2,\dots,N. \tag{5.2}$$

Let us restrict ourselves to the case when Ω_m

$= E_{m0}\mu_{m+1,m}/\hbar \equiv \Omega_0$. Then the solution to the system (5.2) is formally given by the expression (4.9), the collective coordinates z_k satisfying the equations

$$\dot{z}_k + \frac{z_k}{T_1}(1+\nu_k^2 T_1 T_2 g^2(t)) = \frac{\Omega_0^2 T_2}{2} f_k g^2(t),$$
$$z_k(0)=0, \quad k=1,\ldots,N. \tag{5.3}$$

Let us recall that ν_k and f_k are defined in (4.11). The Eqs. (5.3) can easily be solved; substituting $z_k(t)$ into (4.9), we find the dependence of y_m on the time. This dependence has the form (4.12), where for $F_k(t)$ we should set

$$F_k(t) = T_1^{-1}(1+\nu_k^2 T_1 T_2)\exp\{-\psi_k(t)\}\int_0^t dt'\, g^2(t')\exp\{\psi_k(t')\},$$
$$\psi_k(t) = T_1^{-1}\left(t+\nu_k^2 T_1 T_2 \int_0^t g^2(t')\,dt'\right). \tag{5.4}$$

The forms of the expressions for the probabilities ρ_{mm} and the mean number, ϵ, of oscillator quanta are similar to (4.13) and (4.14), but under $F_k(t)$ we mean (5.4).

In the particular case when $g(t) = 1$, (5.4) coincides with the relation (4.20), obtained upon going over to the incoherent case.

If the spectral amplitudes of the field vary periodically in time, i.e., if $g(t) = \cos \nu t$, then, in the absence of collisional relaxation ($T_1 \to \infty$), we have

$$\Delta\rho_{mm} = \sum_{k=1}^{N} U_{mk}\exp\{-\gamma_k(t)\}, \quad \Delta\varepsilon = \sum_{k=1}^{N} V_k \exp\{-\gamma_k(t)\},$$
$$\gamma_k(t) = \frac{1}{2}\nu_k^2 T_2 t\left(1+\frac{\sin 2\nu t}{2\nu t}\right). \tag{5.5}$$

It follows from the second relation in (5.5) that an approach that does not take the coherence effects into account gives for the vibrational-quanta reserve ϵ a value $< 2^{-1}N$, since $V_k < 0$ (see (4.18)). This means that at any moment of time the probability of occupation of the lower half of all the levels exceeds the occupation probability for the upper half. In the following section we show that in the case of the periodic amplitude modulation the coherence interaction mechanism can play an important role even for sufficiently large times ($t \gg T_1, T_2$). There then arise effects that, in principle, cannot be described in the framework of velocity equations.

6. THE COHERENCE EFFECT OF INVERSION OF THE DISTRIBUTION OVER THE LEVELS OF THE ANHARMONIC OSCILLATOR

It follows from the analysis carried out in Sec. 4 that, in the interaction of an anharmonic oscillator with a field whose frequency is periodically modulated in time (see (4.4)), the maximum attainable photon reserve is equal to N/2. In the coherent case this is the mean value about which the oscillator energy pulsates. If the coherence effects are not important, then $\epsilon \to N/2$ for high-intensity fields (i.e., we have a saturation regime).

The question arises whether we can, in principle, create conditions under which the mean number of quanta will exceed N/2. In this case we have in mind the overexcited state of the quantum oscillator; to such a state corresponds an inverted distribution over its levels. It is a priori clear that the coherence field-medium interaction mechanism should be the basis of the method for the possible realization of the corresponding conditions.

The coherence effects manifest themselves in, in particular, the fact that the variation of the level-occupation probabilities has a pulsating character. In the case of a two-level system the pulsation frequency coincides with the Rabi frequency of the given transition; in a multilevel scheme there appears a pulsation spectrum. The idea underlying the proposed method of inverting the distribution over the oscillator levels consists in the following. Let us assume that the amplitude of the field (4.4) varies periodically in time with the frequency ν:

$$E(t) = {}^1\!/_2 E_0 g(t)\left(\sum_{n=-\infty}^{\infty} C_n e^{i(\omega+n\Delta\omega)t} + \text{c.c.}\right). \tag{6.1}$$

Then the Rabi frequencies corresponding to the various transitions of the anharmonic oscillator will be modulated with the same frequency. By choosing in some manner the frequency and depth of the modulation, we can effect a parametric excitation of the oscillator. The situation here is entirely analogous to, for example, the process of oscillation buildup by a pendulum with a pulsating point of suspension (the Kapitza pendulum[39]): The appropriate set of modulation frequencies stabilizes the new (dynamical) equilibrium state of the pendulum. In the case of the coherent excitation of the oscillator by the field the analog is the overexcited state.

In the presence of the amplitude modulation (6.1), the set of equations similar to (4.7) assumes the form

$$\ddot{y}_m + \left(\frac{1}{T_1}+\frac{1}{T_2}-\frac{\dot{g}(t)}{g(t)}\right)\dot{y}_m + \frac{1}{T_1}\left(\frac{1}{T_2}-\frac{\dot{g}(t)}{g(t)}\right)y_m$$
$$= \frac{\Omega_0^2}{2} g^2(t)\,(\delta_{1m}+y_{m-1}-2y_m+y_{m+1}). \tag{6.2}$$

Notice that the variation of the amplitude of the electric-field intensity leads not only to the modulation of the Rabi frequency, but also to the modulation of the "coefficient of friction."

The solution to the system (6.2) can be written in the form (4.9), the z_k satisfying the equations

$$\ddot{z}_k + \left(\frac{1}{T_1}+\frac{1}{T_2}-\frac{\dot{g}}{g}\right)\dot{z}_k + \left[\frac{1}{T_1}\left(\frac{1}{T_2}-\frac{\dot{g}}{g}\right)+\nu_k^2 g^2(t)\right]z_k = \frac{\Omega_0^2}{2} f_k g^2(t). \tag{6.3}$$

Below we consider the case when $T_1 = T_2 = T$. It can be shown that the system (6.3) then admits of an exact solution for an arbitrary function g(t):

$$z_k = \alpha_k[1-G_k(t)], \quad k=1,2,\ldots,N,$$

$$G_k(t) = e^{-t/T}\cos\tau_k(t) + \frac{e^{-t/T}}{T}\int_0^t \cos[\tau_k(t)-\tau_k(t')]e^{t'/T}\,dt', \tag{6.4}$$

$$\tau_k(t) = \nu_k\int_0^t g(t')\,dt', \quad \alpha_k = \frac{1}{2}\left(\frac{2}{N+1}\right)^{1/2}\operatorname{ctg}\frac{k\pi}{2(N+1)}.$$

Using the found $z_k(t)$, we can determine $y_m(t)$ from (4.9), so that for $\Delta\rho_{mm}$ and $\Delta\epsilon$ we can write the expressions

$$\Delta\rho_{mm} = \sum_{k=1}^{N} U_{mk}G_k(t), \quad \Delta\varepsilon = \sum_{k=1}^{N} V_k G_k(t). \tag{6.5}$$

Let us now consider the case of the periodic modulation of the amplitude of the field intensity, $g(t) = \cos \nu t$. If the period of the modulation $T_\nu = 2\pi/\nu$ is shorter than the relaxation time, i.e., if $T_\nu \ll T$, then for the times $T_\nu \ll t \ll T$ the averaging of (6.5) over the period T_ν yields

$$\langle\rho_{mm}\rangle = (N+1)^{-1} + \sum_{k=1}^{N} U_{mk}J_0\left(\frac{\nu_k}{\nu}\right),$$
$$\langle\varepsilon\rangle = 2^{-1}N + \sum_{k=1}^{N} V_k J_0\left(\frac{\nu_k}{\nu}\right). \tag{6.6}$$

For example, for a two-level medium (N = 1) we have

$$\langle\rho_{11}\rangle=\frac{1}{2}\left[1+J_0\left(\frac{\Omega_0}{\nu}\right)\right],\quad\langle\rho_{22}\rangle=\frac{1}{2}\left[1-J_0\left(\frac{\Omega_0}{\nu}\right)\right],$$

from which it can be seen that in certain amplitude-modulation frequency ranges where the Bessel function J_0 is negative the occupation probability for the upper state exceeds ½. A similar situation for N = 5 and N = 10 is illustrated by Figs. 1 and 2: The overexcited state of the oscillator (the mean number of quanta $>2^{-1}N$) is realizable in certain intervals of $q = \Omega_0/\nu$.

For large times, $t \gg T$, the function $G_k(t)$ entering into (6.5) and (6.6) has the form

$$G_k(t)=P_k(t)\cos\left(\frac{\nu_k}{\nu}\sin\nu t\right)+Q_k(t)\sin\left(\frac{\nu_k}{\nu}\sin\nu t\right),$$

$$P_k(t)=\sum_{n=-\infty}^{\infty}\frac{J_{2n}(\nu_k/\nu)}{[1+(2n\nu T)^2]}(\cos 2n\nu t+2n\nu T\sin 2\nu T),\qquad(6.7)$$

$$Q_k(t)=2\sum_{n=0}^{\infty}\frac{J_{2n+1}(\nu_k/\nu)}{[1+((2n+1)\nu T)^2]}[\sin(2n+1)\nu t-(2n+1)\nu T\cos(2n+1)\nu t].$$

Thus, the coherence interaction mechanism gives rise to undamped oscillations in the diagonal elements of the density matrix for times t exceeding the relaxation time of the system (cf. the result of Sec. 4), the pulsation frequencies being multiples of the modulation frequency ν.

Averaging (6.7) over the period T_ν, we obtain

$$\langle G_k(t)\rangle=\sum_{n=-\infty}^{+\infty}\frac{J_n(\nu_k/\nu)}{[1+(n\nu T)^2]}=\frac{\pi x}{\operatorname{sh}\pi x}J_{ix}\left(\frac{\nu_k}{\nu}\right)J_{-ix}\left(\frac{\nu_k}{\nu}\right),\qquad(6.8)$$

where $x = (\nu T)^{-1}$ and i is the imaginary unit. In the particular case when the modulation period is shorter than the relaxation time, i.e., for $x \ll 1$, (6.5) reduces to the form

$$\langle\rho_{mm}(\infty)\rangle=(N+1)^{-1}+\sum_{k=1}^{N}U_{mk}J_0^2\left(\frac{\nu_k}{\nu}\right),$$

$$\langle\varepsilon(\infty)\rangle=2^{-1}N+\sum_{k=1}^{N}V_kJ_0^2\left(\frac{\nu_k}{\nu}\right).\qquad(6.9)$$

It follows from (6.9) that $\langle\epsilon(\infty)\rangle$ is less than $2^{-1}N$.

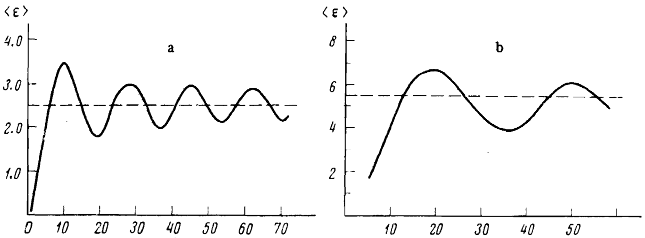

FIG. 1. Dependence of the vibrational-photon reserve per oscillator, $\langle\epsilon\rangle$, averaged over the pulsation period of the field, on the parameter $q = \Omega_0/\nu$ ($T_1 = T_2 = \infty$; the case when $\Omega_m = \Omega_0$): a) N = 5; b) N = 10. The dashed lines correspond to an energy level $\langle\epsilon\rangle = 2^{-1}N$.

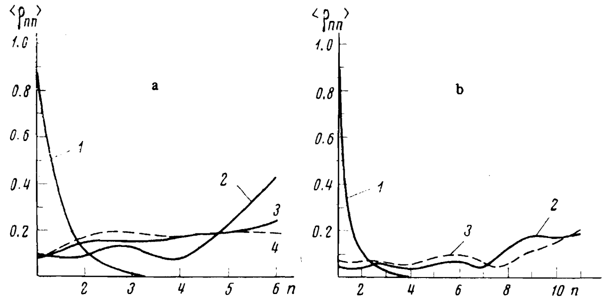

FIG. 2. Distribution function over the vibrational anharmonic-oscillator levels, $\langle\rho_{nn}\rangle$, averaged over the field-pulsation period, for different values of the parameter $q = \Omega_0/\nu$ ($T_1 = T_2 = \infty$; the case when $\Omega_m = \Omega_0$). (a) N = 5: 1) q = 1, 2) q = 10, 3) q = 30, 4) q = 60; (b) N = 10: 1) q = 1, 2) q = 20, 3) q = 50.

If the modulation law is given by the relation

$$g(t)=1+\gamma\cos\nu t,$$

then, for the function $G_k(t)$ entering into (6.5), it is not difficult to derive the expression ($T_\nu = 2\pi/\nu \ll t \ll T$)

$$G_k(t)=\sum_{n=-\infty}^{\infty}J_n\left(\gamma\frac{\nu_k}{\nu}\right)\cos(\nu_k-n\nu)t.\qquad(6.10)$$

Thus, in the case under consideration the spectrum of the pulsations consists of the combination frequencies $\nu_{kn} = \nu_k \pm n$ (k = 1, ..., N; n = 0, 1, 2, ...). Let us assume that for certain n and k the condition $\nu_k = n\nu$ is fulfilled, i.e., that

$$q_{nk}^{-1}=\frac{\nu}{\Omega_0}=\frac{\sqrt{2}}{n}\sin\frac{k\pi}{2(N+1)},\qquad(6.11)$$

then, as follows from (6.10), the constant component for the probabilities ρ_{mm} and the number ϵ of quanta shifts. To the dynamical equilibrium state then correspond the quantities

$$\bar\rho_{mm}=(N+1)^{-1}+(N+1)^{-1}J_n(n\gamma)\times\left(\cos\frac{mk\pi}{N+1}+\cos\frac{(m-1)k\pi}{N+1}\right),$$

$$\bar\varepsilon=2^{-1}N+2^{-1}(N+1)^{-1}\times((-1)^k-1)J_n(n\gamma)\operatorname{ctg}^2\frac{k\pi}{2(N+1)}.\qquad(6.12)$$

It can be seen from the second equality that for even k the number of quanta $\bar\epsilon = 2^{-1}N$. If k = 1, 3, 5, ... ($k \le N$) and the modulation-depth parameter γ lies in a range where the Bessel function $J_n(n\gamma)$ is negative, then $\bar\epsilon > 2^{-1}N$ and, thus, the overexcited state is realized. In Fig. 3 we schematically show the regions of the modulation-amplitude parameters (γ, Ω_0/ν) where such a state arises.

7. CONCLUSION

In the present paper we have considered a number of methods of exciting the high vibrational levels of molecules: a set of phased pulses (an analog of Veksler's phase-stability method), the periodic modulation of the electromagnetic-field frequency, and amplitude-frequency modulation. Under certain conditions, the coherence effects of the field-medium interaction may play an important role in all these cases. In particular, the amplitude-frequency modulation method allows, on account of the coherence mechanism, the production of an anomalous state of the oscillator, when the distribution over the os-

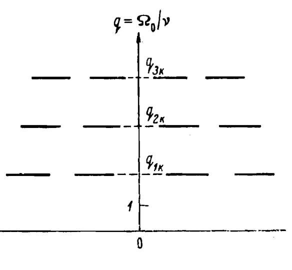

FIG. 3. Schematic representation of the regions of the field-amplitude-modulation parameters (γ, Ω_0/ν) where the overexcited oscillator state is realizable; $q_{nk}^{-1} = \frac{\sqrt{2}}{n}\sin\frac{k\pi}{2(N+1)}$, n = 1, 2, 3, ...; k = 1, 3, 5, ... ($k \leqslant N$).

cillator levels turns out to be as a whole inverted. The methods proposed in this paper are unified by one quality—the possibility of neutralizing with their aid the oscillator anharmonicity and, consequently, by the feasibility of the excitation of high vibrational levels.

In conclusion, let us note that consideration has been given in this paper only to the fundamental aspect of the problems. A more complete analysis should take into account a number of effects connected, in particular, with rotational relaxation, level degeneracy, etc.

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[1] In [16] attention is drawn to quite a number of other molecules possessing low anharmonicities ($\omega_e x_e \sim 1$ cm^{-1}) and low values of the rotational constant ($B_e \sim 0.1$ cm^{-1}).

[2] Let us also mention the paper presented by Askar'yan and Namiot at the joint seminar of the Oscillation and Quantum-Radiophysics Laboratories of the P. N. Lebedev Physics Institute of the USSR Academy of Sciences in April 1975. In this paper the cascade mechanism of excitation of a multilevel system was studied.

[3] The solution to the problem for arbitrary Ω_m is extremely unwieldy and, therefore, it is not given here.

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