Excitation of molecular vibrations by laser radiation in the dynamic resonance regime: nonlinear classical-oscillator model

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The excitation of a nonlinear oscillator by an external force with a varying frequency is considered. The use of classical formalism allows the excitation energy to be expressed as a function of the frequency of the external force for arbitrary potential and arbitrary level of excitation. The final result is expressed in terms of the dependence of the amplitude of the eigenfunctions on their frequency. This dependence takes a simple analytical form in the case of the Morse potential. The behavior of the limiting value of the oscillation amplitude is investigated in the presence of relaxation, and similarity expressions are found close to resonance. It is shown that an external force with varying frequency is very effective in exciting nonlinear oscillations, and the effect of the time dependence on the excitation process is studied. © *1995 American Institute of Physics.*

1. INTRODUCTION

The efficiency with which an oscillatory mode can be excited by an external force sharply decreases away from resonance, which explains the considerable difference in the behavior of harmonic and anharmonic oscillators undergoing excitation. In the latter case increasing the shift away from resonance means that energy can no longer be transferred efficiently to the oscillator. Hence it is important to study the problem of excitation of molecular vibrations by an external force whose frequency sweeps over a region of nonlinear resonances, as a result of which a consistent excitation level and external force frequency are reached.

Two factors account for the importance of this problem in applications. First, the excitation of molecular vibrations is a means of dissociating molecules, ionizing them, producing selective desorption, and controlling chemical reactions.[1–3] The efficiency of such processes frequently rises considerably when they are acted on by multiple frequencies.[4–8] Secondly, the substantial progress which has been made in developing free electron lasers (FELs) eliminates the question of finding a source of radiation with a tunable frequency.

The International Center of Photochemical Research which will be established in Novosibirsk will use FELs with the following parameters: mean power 10 kW, pulse repetition rate 45–180 MHz, peak power 10 MW, and individual pulse length 10–100 ns. The radiation frequency of this laser will span the region of vibrational transitions for practically all existing molecules.

Radiation is generated in an FEL when an electron beam passes through a wiggler, a structure in which the direction of the magnetic field is alternating. The wavelength generated in the wiggler has a strong dependence on the electron energy ($\lambda \propto d/\gamma^2$, where d is the wiggler period and γ is the relativistic electron energy), so fairly short wavelengths can be generated with moderate electron energies. Thus, for the Novosibirsk FEL with $d \sim 10$ cm and $\gamma \sim 100$ we have $\lambda \sim 10$ μm.

In principal, wigglers with shorter periods allow the beam electron energy to be reduced below the threshold for photonuclear reactions, which is advantageous both as regards the choice of the type of electron accelerator on which the FEL is based and in order to avoid radiation hazards.

Thus, Baryshnikov[9] proposed a way of producing radiation inside a cavity with arbitrary frequency dependence and the possibility of operational control of the radiation parameters. Essentially, the idea is that the parameters of the electron pulses injected into the wiggler and the optical cavity vary periodically, which allows optical modes to be accumulated in the cavity with the requisite frequency and time properties. The electron energy can be varied, e.g., using an auxiliary accelerating section of the *hf* cavity or by varying the phase of the electron injection into the underlying accelerator.

Let us say a few words about the classical approximation used in the present work. It is well known[10] that the problem of exciting a harmonic oscillator with a resonant force can be solved exactly both in the classical and the quantum formalisms, where the two are closely related. In particular, the average values of the momentum and position and of their squares are the same in the two approaches. The probability of exciting a particular quantum state is expressed in terms of the classical work done by the external force. The correspondence principle,[11] which holds in the general case for large values of the vibrational quantum number $n \gg 1$, holds here for arbitrary n. Finally, as a result of the action of the resonant force the excitation "climbs up the staircase" of vibrational states as a compact packet, whose relative width decreases with n.

In the case of an anharmonic oscillator for small values of n, when the deviation from a harmonic oscillator is still small, we can use the above arguments in favor of the classical treatment (see, e.g., Refs. 12–15, where the excitation of a nonlinear oscillator by a resonant force with constant frequency is treated classically). The classical treatment allows one to determine the field required to excite a given

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level and shows that for a specified field the value of $n = n_{\max}$ which is reached is bounded.

The question of the correspondence between the quantum and classical approaches in the problem of exciting a nonlinear oscillator with an external force of constant frequency was addressed directly in Ref. 15. By solving the corresponding equations numerically for the Morse potential[16] they were above to show that the classical and quantum solutions coincide with the exception of narrow frequency ranges in which multiple resonance occur. These considerations along with (naturally) the difficulty of the quantum treatment are decisive in our choice of the classical approach for solving this problem.

Note that for weak anharmonicity or small values of n the solution of this problem is well known (see, e.g., Ref. 17). It follows in particular that when the frequency of the external force changes, considerably higher states can be excited than in the case of a fixed frequency. Here, however, we arrive at a certain contradiction, since when n grows the power-series expansion of the oscillatory potential usually employed is no longer valid. In the present work we have derived a solution for arbitrary potentials, including the Morse potential, and for arbitrary levels of excitation.

We also show that this problem is very close to that treated by Gorchakov and Savonov,[13] in which the excitation of a nonlinear oscillating rotator by a circularly polarized wave was treated classically. The rotator is turned by the circular wave, as a result of which the anharmonic shift from the resonance in the problem is balanced by rotational transitions whose frequency increases with the rotational quantum number. In the case of arbitrary polarization this effect naturally does not arise. In the present work rotation of the molecule is disregarded, and the deviation from resonance is balanced by the change in the frequency of the external force.

2. THE NONLINEAR CLASSICAL OSCILLATOR MODEL

We assumed that a molecule represented by the one-dimensional classical nonlinear oscillator with mass M, potential $U(x)$, and rotating force $f(x) = -\partial U/\partial x$ is acted on by the external force $F \cos \Omega t$, where Ω can vary slowly on the scale of the molecular oscillations. In the case of homeopolar molecules this force is the result of the interaction of dipoles induced by the laser radiation, while in the case of heteropolar molecules we are concerned with the effect of the external field on the effective molecular charges.[1] Note that in Ref. 1 different forms of excitation of the molecular oscillations were proposed, among them the version with a time-dependent frequency discussed below. We will neglect the rotation of the molecule and the interaction with nearby vibrational modes, assuming that this is small because the oscillations have different symmetry or because the frequency difference is large.

The equation of the oscillations takes the form

$$M\ddot{x} + f(x) = F \cos \Omega t. \tag{1}$$

To lowest order in the external force F in Eq. (1) only the first harmonic of the frequency Ω is important, and we can use a procedure equivalent to linearization (Ref. 18; see also Ref. 19). If we are not interested in frequency-doubling effects, then we need only retain the first harmonic in Eq. (1), which yields a new linear equation with coefficients that depend on the amplitude a of the oscillation:

$$\ddot{x} + 2\gamma\dot{x} + \omega^2(a)x = \frac{F}{M} \cos \psi, \tag{2}$$

where $\dot{\psi} = \Omega$ and we have formally introduced the term $2\gamma\dot{x}$ to take into account the possible relaxation of the excitation through various processes. In accordance with the linearization procedure we have for $\omega(a)$

$$\omega^2(a) = \frac{1}{\pi a} \int_0^{2\pi} f(a \cos \psi) \cos \psi \, d\psi. \tag{3}$$

As shown by Magnus,[20] this procedure turns out to be unexpectedly accurate even in the case of very nonlinear oscillations. Thus, the error in determining the eigenfrequency and the amplitude of the oscillations of a ball in an angular groove (with a discontinuity in the rotating force)[20] is a few percent. But if we use for the frequency $\omega(a)$ not the approximate formulate (3) but the exact classical expression

$$\frac{2\pi}{\omega} = \sqrt{2M} \int \frac{dx}{\sqrt{E - U(x)}}, \tag{4}$$

where the integral is taken between the turning points and E is the energy of the oscillations, then the solution of the linearized equation for this example coincides with the exact solution.

In what follows we will need the amplitude $a(\omega)$ as a function of the eigenfrequency. This dependence can be determined either from (3) or from (4). In the latter case, using the first integral of the linearized equation and assuming that the relaxation is small, we can write

$$a(\omega) = \sqrt{\frac{2E(\omega)}{M\omega^2}}, \tag{5}$$

where $E(\omega)$ is the dependence given by Eq. (4).

We will look for a solution of Eq. (2) in the form $x = a \sin \varphi$, where $\varphi = \psi + \vartheta$. Then, neglecting second derivatives and assuming $\gamma/\Omega \ll 1$, we find[19]

$$\dot{a} + \gamma a = \frac{F}{2M\Omega} \cos \vartheta,$$

$$\dot{\vartheta} = \omega - \Omega - \frac{F}{Ma(\omega + \Omega)}. \tag{6}$$

It is easy to find a stationary solution of Eqs. (6), corresponding to a slow variation in the frequency of the external force for which the excitation can be adjusted by means of this variation. Since in real molecular systems relaxation of the excitation requires passing through the resonance region fairly fast, one must raise the question as to whether it is possible to use the time-independent solution when the external force changes rapidly. It is clear qualitatively that if the eigenfrequency of the oscillation does not exceed the frequency of the external force, the oscillator goes out of dynamic resonance and the effective exchange of energy with the external force ceases. In fact, when we estimate this effect we arrive at the problem of exciting a single resonance with an external force having variable frequency. This problem was investigated numerically by Mitropol'skii,[19] who showed that when the frequency of the external force varies sufficiently slowly the system is described well by the time-independent equations, where the efficiency of excitation decreases as a function of the speed with which the resonance is passed through. Most of the energy is transferred to the system near the resonance, and the faster the system passes through this region the less energy it can get from the external source. Below we will show that $\vartheta\approx 0$ holds near resonance in the quasisteady limit. If ϑ begins to vary due to the time dependence of the frequency, the efficiency with which energy is transferred from the exciting force changes accordingly. Let us estimate the magnitude of this change from the second of Eqs. (6). For estimating purposes we set $\vartheta\approx 0$, drop the first term, and assumed that the frequency difference is a linear function of time, i.e., $\Omega-\omega\approx\kappa t$. As a result we find $\vartheta\approx\kappa t^2/2$. Setting $\vartheta\sim 1$, for the time δt required to pass through the resonance and the frequency width $\delta\omega$ we find

$$\delta t\propto\sqrt{\kappa},\quad \delta\omega\propto\sqrt{\kappa}. \tag{7}$$

If $a(\Omega)$ is the time-independent solution of Eqs. (6), then in order for the time-dependent solution to be tuned to the steady or slowly varying frequency we must have

$$\frac{da(\Omega)}{d\Omega}\dot{\kappa}\lesssim\dot{a}\approx\frac{F}{2M\Omega}, \tag{8}$$

where $da/d\Omega$ must be estimated in the region determined by (7) and $\dot{a}$ is determined from (6).

Let us write down the time-independent solution of Eqs. (6). Setting $\dot{a}=0$, $\dot{\vartheta}=0$ we find

$$a^2[(\omega^2-\Omega^2)^2+4\gamma^2\Omega^2]=\left(\frac{F}{M}\right)^2,$$

$$\tan\vartheta=\frac{\omega^2-\Omega^2}{2\gamma\Omega}. \tag{9}$$

Solving Eq. (9) for Ω^2 we have

$$\Omega^2=\omega(a)^2-2\gamma^2\pm\sqrt{4\gamma^4+\left(\frac{F}{Ma}\right)^2-4\gamma^2\omega^2(a)}. \tag{10}$$

Expression (10) determines the amplitude of the steady oscillations as a function of the frequency of the external force, $a=a(\Omega)$. Let us rewrite Eq. (10) in a form more convenient for analysis. We introduce the dimensionless variables $y=(\Omega/\omega_0)^2, x=(\omega/\omega_0)^2$, $\Gamma=2(\gamma/\omega_0)^2$, $b=(\alpha a)^2$, $\varepsilon=\alpha F/M\omega_0{}^2$, $\alpha=\sqrt{k/2D}$, where $\omega=\omega(a)$, $\omega_0=\omega(0)$, α^{-1} is the characteristic dimension of the potential well, and D is the dissociation energy. By virtue of the above assumptions we omit a term $4\gamma^4$ from (10) and obtain

$$y=x-\Gamma\pm\sqrt{\frac{\varepsilon^2}{b(x)}-2\Gamma x}. \tag{11}$$

The function $\omega(a)$ is generally monotonic, so $b(x)$ is a single-valued function of x. From (11) we can obtain useful results without specifying the form of the potential or the function $b(x)$.

3. GENERAL RESULTS

Equation (11) explicitly determines the dependence of the amplitude of the forced oscillations as a function of the frequency of the applied force for arbitrary potential and arbitrary level of excitation. The details of a specific function enter only through $b(x)$, which is what makes this form of the solution convenient. By following the usual quantization procedure[15] we can easily find the probability of exciting particular quantum states; here, however, we restrict ourselves to analyzing the classical expressions.

The multivalued behavior of the function (11) is typical for nonlinear oscillations excited by an external force.[1] In the limit of small excitation force there are two branches of the solution of (11) close to the so-called skeleton curve,[18] $y=x$ and $\omega(a)=\Omega$. For large relaxation it follows from (11) that the value of x cannot be arbitrarily small, i.e., the amplitude of the oscillation is bounded. As we move away from the limiting point the role of damping decreases, and in the limit $\Gamma=0$ for $x\approx y\simeq 1$ a similarity formula follows from (11) close to resonance. We will prove these assertions.

The restriction on the amplitude when relaxation is taken into account arises from the condition $xb(x)\geqslant\varepsilon^2/2\Gamma$. Since we have $xb(x)=E/D$, we find that the maximum excitation energy E^* is determined by the relation

$$\frac{E^*}{D}=\frac{\varepsilon^2}{2\Gamma}. \tag{12}$$

Under the condition $\varepsilon^2/2\Gamma>1$ this restriction naturally no longer holds. Condition (12) in ordinary units acquires a clear physical meaning:

$$E^*=\frac{F^2}{8M\gamma^2}, \tag{13}$$

i.e., under resonant conditions in the presence of damping the external force interacts with the oscillator only over an effective time γ^{-1}.

Let us determine the behavior of the function (11) near $E=E^*$ (or $x=x^*$). We expand $xb(x)=\varepsilon^2/2\Gamma+(xb)'(x-x^*)$ and find from (11)

$$y=x-\Gamma\pm\sqrt{\left(-\frac{2\Gamma(xb)'}{b}\right)}\sqrt{x-x^*}, \tag{14}$$

where the expression in parentheses is evaluated at $x=x^*$. Equation (14) determines the behavior of the excitation function near the maximum of the amplitude. It follows from (11) that for small excitation energy the role of the damping decreases. Consequently, the relaxation, which has a critical value near $x=x^*$, can be omitted when we treat the region $x\approx y\approx 1$ near resonance.

Let us show that in this region under the conditions $\varepsilon^2\ll 1$ and $\Gamma=0$ expression (11) can be rewritten in the form of a similarity formula. Near resonance ($x\approx 1$) from $xb(x)=E/D$ we find $b(x)\approx E/D$. We assume that E/D approaches zero near $x=1$ as $C(1-x)^m$, where C and m are constants determined by the form of the potential. We introduce new variables

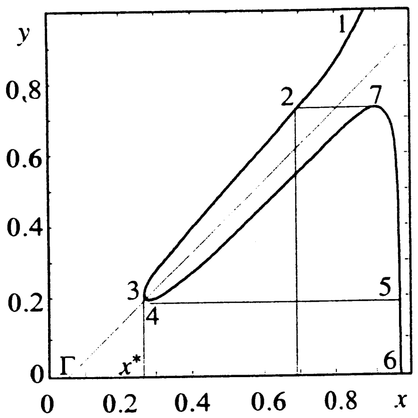

FIG. 1.

$$X=\frac{1-x}{\chi},\quad Y=\frac{1-y}{\chi},\quad \text{where } \chi=\left(\frac{\varepsilon^2}{4C}\right)^{1/(m+2)}$$

It follows that Eq. (11) can be rewritten in parameter-free form as

$$Y=X\mp\frac{2}{X^{m/2}}. \tag{15}$$

The upper and lower signs in (15) correspond to those in (11). Equation (15) is noteworthy not only because of its universality and simplicity but because it gives a complete description of the excitation by a resonant force with constant frequency. Equations (14) and (15) are useful in the limits of small and large excitation. Figure 1 shows the qualitative behavior of $y(x)$. For constant frequency the point 2 corresponds to maximum excitation. The point which represents the state of the system as a function of frequency moves along the curve 12756. When the frequency varies the phase point moves along the curve 123456, reaching maximum excitations at point 3. The reverse motion follows the route 65721. Under the conditions $\varepsilon^2\gtrsim 2\Gamma$ and $\varepsilon^2\ll 1$ the excitation at point 3 is considerably greater than that at point 2, which is responsible for the practical interest in this excitation regime.

4. THE MORSE POTENTIAL

The Morse potential[16] is widely used to describe molecular vibrations.[11] It takes the form

$$U(x)=D(1-e^{-\alpha x})^2. \tag{16}$$

Using (4) we find the frequency as a function of the excitation energy E:

$$\omega^2=\omega_0^2\left(1-\frac{E}{D}\right), \tag{17}$$

where $\omega_0^2=2D\alpha^2/M$. The amplitude of the oscillations and the excitation energy are expressed in terms of x as follows:

$$\alpha a=\sqrt{\left(\frac{\omega_0}{\omega}\right)^2-1}=\sqrt{\frac{1}{x}-1},\quad E=D(1-x). \tag{18}$$

The general expression (11) can be written in the form

$$y=x-\Gamma\pm\sqrt{\frac{\varepsilon^2 x}{1-x}-2\Gamma x}. \tag{19}$$

Following (8) we can estimate the allowable rate of change of the frequency:

$$\dot{\kappa}\lesssim\left(\frac{\alpha F}{M\sqrt{\Omega}}\right)^{4/3} \tag{20}$$

From $xb(x)=\varepsilon^2/2\Gamma$ we find the maximum values of x^*:

$$x^*=1-\frac{\varepsilon^2}{2\Gamma}. \tag{21}$$

There is no restriction on the amplitude due to relaxation of the excitation in the case $\varepsilon^2/2\Gamma>1$, or

$$\gamma\lesssim\frac{F}{\sqrt{8MD}}. \tag{22}$$

In the region where the amplitude is restricted we find from (14)

$$y=x-\Gamma\pm\sqrt{\frac{2\Gamma(2\Gamma-\varepsilon^2)}{\varepsilon^2}}\sqrt{x-x^*}. \tag{23}$$

Near resonance in (15) we have $m=C=1$ and the characteristic parameter is $\xi=(\varepsilon/2)^{2/3}$, for which the similarity formula can be written in the form

$$Y=X\mp\frac{2}{\sqrt{X}}. \tag{24}$$

Near the phase point $Z=(X,Y)$ we find in accordance with Fig. 1

$$Z_1=(2^{2/3},0),\quad Z_2=(4,3),\quad Z_7=(1,3).$$

5. DISCUSSION

Let us apply these results to estimate the excitation of molecular vibrations. We will start with the following typical values of the molecular constants (see, e.g., Ref. 5): $\omega_0\approx\Omega\approx 10^3\ \text{cm}^{-1}$, $\gamma\approx 10^{-3}$–$10^{-1}\ \text{cm}^{-1}$ in the range of pressures from 1 to 100 torr, where the resonance defect for neighboring levels is $\Delta\approx 10\ \text{cm}^{-1}$. For the dissociation energy we take $D\approx 3\cdot 10^4\ \text{cm}^{-1}$. We will assume that $\alpha\approx 10^8\ \text{cm}^{-1}$ holds, which corresponds to the atomic length scale. We have $\varepsilon=\alpha F/M\omega_0^2=E_{\text{L}}/E_{\text{M}}$, where E_{L} is the strength of the laser field and $E_{\text{M}}=2D\alpha/e\approx 10^9$ V/cm is the typical intramolecular field. For comparison we will estimate the field necessary to excite the level $N\sim 3$ when the frequency is constant (see the analogous estimates in Refs. 5 and 12). For a fixed frequency the excitation of large N requires extremely large laser fields, so we use the time-independent approach, which is probably applicable only to multiatomic molecules for which a quasicontinuum of molecular states is adjacent to the low-lying levels. Using (24) we find

$$E_{\text{L}}\approx 2E_{\text{M}}\left(\frac{N\Delta}{2\omega_0}\right)^{3/2}\approx 10^7\ \text{V/cm}. \tag{27}$$

Such fields are typical for collisionless dissociation of multiatomic molecules by a laser field.

Returning to the dynamical resonance regime, we start by considering the double inequality which determines the allowable range for the rate of change of the frequency $\dot{\varkappa}$ [cf. Eq. (20)]:

$$\frac{N\gamma\Delta}{\omega_0^2} \lesssim \frac{\dot{\kappa}}{\omega_0^2} \lesssim \varepsilon^{4/3}. \tag{28}$$

The dynamical range for $\dot{\kappa}$ broadens as the parameter $\mu=\varepsilon^{4/3}\omega_0^2/N\gamma\Delta$ increases. Setting $\mu\sim 1$ we find the maximum field strength for which the time-independent regime applies. For purposes of obtaining an estimate we assume $N\sim 5-10$, i.e., we treat molecules with few atoms:

$$E_L=E_M\left(\frac{N\gamma\Delta}{\omega_0^2}\right)^{3/4} \approx 10^4-10^5 \text{ V/cm},$$

which is much smaller than (27).

It is useful to directly compare the maximum oscillation amplitudes a_d and a_s in the dynamic and static regimes. We estimate a_s from the similarity formulas (24) and a_d from the expression for x^*, Eq. (21). We include the fact that if $\varepsilon^2>2\Gamma$ holds then a_d and a_d/a_s both diverge. But if $\varepsilon^2<2\Gamma$ holds, then

$$\frac{a_d}{a_s} \sim \frac{\varepsilon^2/2\Gamma}{\varepsilon^{2/3}} \sim \frac{\varepsilon^{4/3}}{\Gamma}.$$

For realistic parameters it can easily be shown that this expression is much larger than unity.

Let us estimate the time $t\approx N\Delta/\dot{\kappa}$ over which the excitation process takes place. For the estimate we used the inequality (28) and find

$$\frac{N\Delta\varepsilon^{-4/3}}{\omega_0^2} \lesssim t \lesssim \gamma^{-1}. \tag{29}$$

For moderate fields $E_L\sim 10^5-10^6$ V/cm it follows from (29) that

$$10^{-11}-10^{-10} \lesssim t[c] \lesssim 10^{-10}-10^{-8}. \tag{30}$$

As can be seen from (30) there is a broad range of durations which satisfy the condition for optimum dynamical excitation. This fact is significant when specific accelerators and free-electron lasers are used with a specified electron or light-pulse length. Note that the typical pulse lengths in microtron accelerators, which are regarded as very promising for use in FELs, lie in the range defined by (30).

In conclusion we briefly discuss some particular questions which are important for practical applications.

Why have we chosen the regime in which nonlinear resonances are encountered in succession? The reason is that, first, the nonlinear resonances are quite closely spaced and can easily be swept over with a relatively small frequency change. The typical value of the anharmonic detuning amounts to ~1% (Ref. 5). The operational frequency tuning range for FEL radiation can be considerably larger than this value, and depending on the type of tuning and accelerator may reach a value of 5–10%. The range over which the frequency varies should not, however, include neighboring vibrational modes, so as not to reduce the excitation efficiency.

The quality of the excitation resonance in this case is determined by the change in the frequency, not the strength of the laser field, which allows one to use moderate laser field strengths.

Competitors with this regime include: a) multifrequency excitation with constant-frequency fields;[1,3] b) excitation through several levels; c) direct excitation above a threshold, e.g., dissociation.

In regime a) it is necessary to determine the energy of the vibrational states with greater accuracy than in the present case or to correct for the possible detuning from the resonance due to field broadening, i.e., large laser fields. In regime b) for intramode excitation the dipole moment is small, and hence large laser field strengths are again required. For arbitrary excitation in the general case it is difficult to achieve resonance of the excitation within the limits of available FEL tuning. In regime c) excimer lasers or discharges of various types are ordinarily used, which have a low energy efficiency. In principle an FEL can also generate fairly short wavelengths, but for various reasons the efficiency is low except in the IR region.

There is one more question which is important in practice: To what extent does the time-independent nature of excitation by realistic laser pulses actually affect the quasistationary results of this work? It is clear that the excitation must be relatively fast so that relaxation cannot take place. On the other hand, the rate of change of the frequency cannot be arbitrarily large because the excitation level and the frequency of real lasers would be inconsistent [see Eq. (29)]. If the laser pulse length is greater than the value determined by the inequality (29), then the temporal profile of the pulse can be taken into account in the quasisteady approximation. In the opposite case, as can be seen from (29), the excitation efficiency decreases.

The question of the role of rotation in real molecules in the process of exciting vibrations is not out of place. In the case of a circularly polarized wave, as shown in Ref. 13, the molecule can become "unspun," which gives rise to qualitatively new effects which were not mentioned above. For linear polarization this unspinning does not occur, but here also rotational effects can prove important.

The rotational broadening $\Delta\omega_r$ itself probably does not affect the excitation, since it is generally smaller than the typical anharmonic shifts (see, e.g., Ref. 5) and even more because it is smaller than the range of variation of the frequency. An important role may be played by collisional relaxation of rotational states, which leads to loss of coherence of the energy. The necessary condition for effective excitation of a molecule is $\gamma_r t \ll 1$, where t is the excitation time determined by (29) and γ_r is the rotational relaxation constant. In the opposite limit $\gamma_r t \gtrsim 1$ we must have $t\Delta\omega_r \lesssim 1$ in order to preserve the coherence of the excitation; this is generally incompatible with the previous inequality. From the information given in Ref. 5 we can make the following estimates: $\Delta\omega_r \approx 5$ cm^{-1}, $\gamma_r\sim 10^{-3}-10^{-1}$ cm^{-1} in the pressure range from 1 to 100 torr. For this value of γ_r we find from the condition $\gamma_r t\sim 1$ the typical time $t\sim 10^{-8}-10^{-10}$ s, which agrees with one of the limiting values in (30).

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