Vibrational-rotational spectra and the process of excitation of a molecule in the field of an intense resonance wave

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The conditions under which the problem of excitation of a molecule in the field of a resonance wave reduces to the problem of an effective anharmonic oscillator are found. Solutions to such a problem are found for the asymptotic case of a strong field. It is shown that the quasienergy vibrational-rotational levels become equidistant in this limit. The molecule distribution over the vibrational-rotational levels that arises under the action of an intense field is found under the assumption of adiabatic switching on of the interaction, an assumption which is valid for nanosecond and longer pulses. It is shown that the number, v_0, of the most efficiently excitable level increases with increasing intensity, F_0, of the resonance wave like $F_0^{2/3}$.

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1. INTRODUCTION

Of late the problem of the resonance interaction of molecules with intense electromagnetic (EM) radiation of the infrared band has been attracting quite considerable attention, which undoubtedly is connected primarily with the discovery of the phenomenon of collisionless dissociation of molecules of the type BCl_3, SiF_4, SF_6, etc.[1–5] According to the current viewpoint, this process can be conditionally divided into a number of stages. First, there occurs the excitation of several low-lying vibrational levels of the molecule, after which follow stages in which the excitation of many vibrational modes of the molecule and the subsequent transformation of the excitation energy into the energy of the electron detachment term. However, from the theoretical point of view even the investigation of the simplest first phase of the process can hardly be considered to have been accomplished, since all the existing theoretical approaches either are based on various model concepts, or have the character of qualitative estimations. In diatomic molecules, which possess a single vibrational mode, the excitation process is confined to the first phase. Owing to anharmonicity, a significant excitation of the vibrations of a diatomic molecule is possible only under those conditions when there occurs under the action of the EM field a considerable rearrangement of its quasienergy levels (the resonance Stark effect[6]).

In the present paper we investigate the feasibility of an analytic description of the process of excitation of the vibrational-rotational degrees of freedom of a diatomic molecule under the action of an intense resonance EM field of the infrared band. As will be shown below, in the two cases corresponding to a high and a low rotational energy of the molecule, the quantum-mechanical equations of motion reduce to steady-state equations for some effective anharmonic oscillator located in a constant uniform electric field. The analytic solutions found for these equations in the asymptotic limit of a high resonance-field intensity contain information about the character of the quasienergy vibrational-rotational spectra of the molecule, and allow us to describe the molecule-excitation process. It may be surmised that results similar to those obtained here describe the initial phase of the process of excitation in multiatomic molecules.

2. GENERAL EQUATIONS

The Hamiltonian describing the vibrational-rotational motion of a diatomic molecule interacting with an EM wave, $\mathbf{F}(t)$, has the form

$$H=H_v+B(r)\hat{J}^2-\mathbf{d}\mathbf{F}(t), \tag{1}$$

where H_v is the Hamiltonian of the vibrational motion in the absence of an external wave, $\hat{J}$ is the angular-momentum operator, $\mathbf{d}$ is the molecule's dipole moment operator averaged over the electron wave function and, in the case of the Σ term, directed along the axis of the molecule, $B(r)=\frac{1}{2}Mr^2$ (we set $\hbar=1$), M being the reduced mass of the nuclei and r, the internuclear distance. The vibrational-rotational wave function, Ψ, of the molecule can be expanded in terms of the products of the vibrational (φ_v) and rotational ($\chi_J e^{im\varphi}$) functions of the free molecule,[7] which functions satisfy the equations

$$H_v\varphi_v=E_v\varphi_v, \quad \hat{J}^2(\chi_J e^{im\varphi})=J(J+1)\chi_J e^{im\varphi}.$$

With allowance for the smallness of the parameter μ/M (μ is the electron mass), we can, as usual, set

$$B(r)\approx B(r_e)\equiv B_e. \quad E_v=\omega_e(v+{}^1/_2)-x_e\omega_e(v+{}^1/_2)^2,$$

where r_e is the equilibrium distance between the nuclei, B_e is the rotational constant; ω_e and $x_e\omega_e$ are respectively the vibrational frequency and the anharmonicity constant; $v, J, m=0, 1, 2, \ldots, m\leq J$, m being the component of the angular momentum of the molecule along the z axis in the laboratory system of coordinates; and φ is the azimuthal angle.

In the case of a linearly polarized monochromatic wave

$$\mathbf{F}(t)=\mathbf{F}_0\cos\omega t, \quad \mathbf{d}\mathbf{F}_0=d(r)F_0\cos\theta,$$

where θ is the angle between the axis $z \parallel \mathbf{F}_0$ and the axis of the molecule. Since the interaction energy in this case does not depend on the azimuthal angle φ, the expansion of the wave function Ψ can be represented in the form

$$\Psi = e^{-iEt} e^{im\varphi} \sum_{Jv} C_{J,v} \varphi_v(r) \chi_J(\theta) e^{-i\omega(v+1/2)t} . \tag{2}$$

As is easy to verify, in the resonance approximation, which is valid for $|\omega - \omega_e| \ll \omega_e$, $d_0F_0 \ll \omega_e (d_0 \equiv \langle \varphi_v | d(r) | \times \varphi_v \rangle \approx \text{const})$, the coefficients C_{Jv} can be assumed to be independent of the time, and the constant E in this case has the meaning of quasienergy of the molecule in the periodic field. The equations for the C_{Jv}'s, which follow in the resonance approximation from the Schrödinger equation $i\partial\Psi/\partial t = H\Psi$, have the form

$$\begin{aligned}\left[E - E_{Jv} + \omega\left(v + \frac{1}{2}\right)\right] C_{Jv} = -\frac{F_0}{2} \Bigg\{ d_{v,v-1} \Bigg[\left(\frac{J^2 - m^2}{4J^2 - 1}\right)^{1/2} C_{J-1,v-1} \\ + \left(\frac{(J+1)^2 - m^2}{4(J+1)^2 - 1}\right)^{1/2} C_{J+1,v-1} \Bigg] + d_{v,v+1} \Bigg[\left(\frac{J^2 - m^2}{4J^2 - 1}\right)^{1/2} C_{J-1,v+1} \\ + \left(\frac{(J+1)^2 - m^2}{4(J+1)^2 - 1}\right)^{1/2} C_{J+1,v+1} \Bigg] \Bigg\},\end{aligned} \tag{3}$$

where $E_{Jv} = E_v + B_v J(J+1)$.

In the coordinate representation, with respect to the angular variable θ, the equations for the functions

$$A_v(\theta) = \sum_J C_{Jv} \chi_J(\theta),$$

that are equivalent to the system (3), evidently have the form

$$\begin{aligned}\left[E - \frac{B_e}{\sin\theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) - E_v + \omega\left(v + \frac{1}{2}\right)\right] A_v \\ = -\frac{d_1 F_0 \cos\theta}{2} [v^{1/2} A_{v-1} + (v+1)^{1/2} A_{v+1}].\end{aligned} \tag{4}$$

In the general case, only a numerical solution of Eqs. (3) and (4) is, apparently, possible. An analytical solution of these equations turns out to be possible only in the asymptotic cases of low and high rotational energy of the molecule. If the rotational energy is small in comparison with the energy responsible for the anharmonicity $x_e\omega_e$, then according to Ref. 6, Eq. (4) can be solved in the adiabatic approximation, which is equivalent to the neglect in this equation at the first stage of the operator

$$-\frac{B_e}{\sin\theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right).$$

The then resulting system of equations

$$[E - E_v + \omega(v + 1/2)] A_v = -1/2\, d_1 F_0 \cos\theta [v^{1/2} A_{v-1} + (v+1)^{1/2} A_{v+1}] \tag{5}$$

determines the correct vibrational functions of the molecule in the external resonance field. The eigenvalues, $E_p(\theta)$, of the system (5), which depend parametrically on the angle θ, has the meaning of potential energy of the molecule in the field $F(t)$.[6]

It is convenient to consider the other limiting case, which corresponds to a high rotational energy, on the basis of the matrix equations (3). These equations relate the probability amplitudes for finding the molecule in states with the quantum numbers (J, v) and $(J+1, v \pm 1)$, $(J-1, v \pm 1)$. The differences between the energies of the corresponding transitions are

$$\begin{aligned} &Jv \to J-1.v-1; \quad E_{Jv} - E_{J-1,v-1} - \omega = \omega_e - \omega - 2vx_e\omega_e + 2JB_e, \\ &Jv \to J+1.v+1: \quad E_{Jv} - E_{J+1,v+1} + \omega = \omega - \omega_e + 2(v+1)x_e\omega_e - 2(J+1)B_e; \end{aligned} \tag{6}$$

$$\begin{aligned} &Jv \to J-1.v+1: \quad E_{Jv} - E_{J-1,v+1} + \omega = \omega - \omega_e + 2(v+1)x_e\omega_e + 2JB_e, \\ &Jv \to J+1.v-1: \quad E_{Jv} - E_{J+1.v-1} - \omega = \omega_e - \omega - 2vx_e\omega_e - 2(J+1)B_e. \end{aligned} \tag{7}$$

If the rotational quantum number is, on the average, large, i.e., if $J \gg 1$, then the resonance conditions for the two groups of transitions (6) and (7) differ considerably from each other. For a not too high intensity F_0, the frequency ω can be chosen such that the conditions for resonance are fulfilled only for one of these groups of transitions. For example, if for all the levels substantially perturbed by the field we have fulfilled the conditions

$$\begin{aligned} |\omega - \omega_e + 2vx_e\omega_e - 2JB_e| \ll 2(2J+1)B_e. \\ d_1F_0 \ll 2(2J+1)B_e. \end{aligned} \tag{8}$$

then the group of transitions (7) are off-resonance transitions, and the coefficients $C_{J+1,v-1}$ and $C_{J-1,v+1}$ in Eqs. (3) can be dropped:

$$\begin{aligned}\left[E - E_{Jv} + \omega\left(v + \frac{1}{2}\right)\right] C_{Jv} \\ = -\frac{d_1F_0}{2} \left\{ \left(v \frac{J^2 - m^2}{4J^2 - 1}\right)^{1/2} C_{J-1,v-1} + \left((v+1) \frac{(J+1)^2 - m^2}{4(J+1)^2 - 1}\right)^{1/2} C_{J+1,v+1} \right\}.\end{aligned} \tag{9}$$

In this case if $d_1F_0 \gtrsim 2|x_e\omega_e - B_e|$, then both transitions in (6) are resonance transitions.

The inequalities (8) can be assumed to be fulfilled for all (J, v) if the rotational quantum number J significantly exceeds the number of vibrational levels effectively perturbable by the external field, i.e., if $J \gg v \gtrsim 1$. This condition allows us to neglect the variation of J in the coefficients of Eqs. (9). (If, furthermore, the numbers J and m are not too close, then $J \pm m \gg v$.) Setting $C_{Jv} = C_{J_0+v,v} \equiv a_v$, we obtain, as a result,

$$\left[E - E_{J_0+v,v} + \omega\left(v + \frac{1}{2}\right)\right] a_v = -\frac{d_1F_0}{4} \frac{(J_0^2 - m^2)^{1/2}}{J_0} \left\{v^{1/2} a_{v-1} + (v+1)^{1/2} a_{v+1}\right\} \tag{10}$$

$$\Psi_{J_0mE} = e^{-i(Et - m\varphi)} \sum_v a_v \varphi_v(r) \chi_{J_0+v}(\theta) e^{-i\omega(v+1/2)t}, \tag{11}$$

where $J = J_0 + v$, the number J_0 (together with E and m) is one of the quantum numbers characterizing the wave function of the molecule in the external field.

The limitation imposed on the intensity F_0 by the second of the inequalities (8) assumes, when $J_0 \gg v$, the form

$$d_1F_0 \ll 4J_0B_e. \tag{12}$$

As will be shown below, the external field most efficiently excites the levels with numbers $v \sim [d_1F_0/|x_e\omega_e - B_e|]^{2/3}$ and the condition $J_0 \gg v$ yields

$$d_1F_0 \ll 2^{3/2} J_0^{3/2} |x_e\omega_e - B_e|. \tag{13}$$

The inequalities (12) and (13) are a quantitative formulation of the assumption that the rotational energy is high. Below it will be shown that, for certain molecules, even at not too high temperatures the corresponding limitations on the magnitude, F_0, of the intensity are not very rigid and allow us to follow the transition to the asymptotic case of high fields.

In the case of the action on the molecule of a circularly polarized resonance wave,

$$\mathbf{F}(t) = F_0(\mathbf{e}_x \cos\omega t \pm i\mathbf{e}_y \sin\omega t)$$

($\mathbf{e}_x$ and $\mathbf{e}_y$ are unit vectors along the x and y axes), the expansions, (2) and (11), of the wave function are replaced by

$$\Psi = e^{-iEt+im\varphi} \sum_{J,v} C_{J,v}\varphi_v(r)\chi_J(\theta) e^{-i\omega(v+1/2)t \pm iv\varphi} \tag{14}$$

and

$$\Psi_{J_0mE} = e^{-iEt+im\varphi} \sum_{v} a_v\varphi_v(r)\chi_{J_0+v}(\theta) e^{-i\omega(v+1/2)t \pm iv\varphi}. \tag{15}$$

The matrix elements in Eqs. (3) get somewhat modified,[7] which leads to the substitution $\cos\theta \to \sin\theta$ in Eqs. (4) and (5) and to the substitution $(J_0^2 - m^2)^{1/2} \to J_0 \pm m$ in Eqs. (10).

Thus, in both the case of low, and the case of high, rotational energies, the equations for the vibrational-rotational wave function of the molecule in the presence of a resonance EM wave reduce to a system of equations for some effective anharmonic oscillator located in an external uniform constant electric field. The effective oscillator frequency, equal to $\omega_e - \omega$ in the case of slow rotations and $\omega_e - \omega + 2J_0B_e$ in the case of high rotational energies, can be arbitrarily low under near-resonance conditions. Therefore, the effective anharmonicity in Eqs. (5) and (10), which is determined by the constants $x_e\omega_e$ and $x_e\omega_e - B_e$, respectively, is strong.[1]

Let us write down Eqs. (5) and (10) in a more convenient dimensionless form:

$$[\varepsilon - \alpha(2v+1) + (2v+1)^2]a_v = -2^{3/2}\xi[v^{1/2}a_{v-1} + (v+1)^{1/2}a_{v+1}], \tag{16}$$

where, for example, in the case of high rotational energies

$$\varepsilon = \frac{4(E - J_0^2B_e) + B_e}{x_e\omega_e - B_e} \qquad \alpha = \frac{2(2J_0B_e + \omega_e - \omega)}{x_e\omega_e - B_e}$$
$$\xi = \frac{d_1F_0}{2^{1/2}(x_e\omega_e - B_e)}\left(1 - \frac{m^2}{J_0^2}\right)^{1/2}.$$

The determination of the quasienergy ε and the coefficients a_v with the aid of Eqs. (16) in the general form is difficult.[9] Equations of this type have been considered before for $\xi \ll 1$, $|\alpha - 4| \ll 1$ in the two-level approximation and numerically for $\xi \gtrsim 1$.[6] Below we shall propose a procedure that allows us to find the analytic solutions of Eqs. (16) for large values of $|\varepsilon|$, including the asymptotic case of strong fields, i.e., for $\xi \gg 1$. In this case instead of the system (16) we shall consider the equivalent differential equation for the function

$$\psi(x) = \sum_v a_v\varphi_v^{(0)}(x), \tag{17}$$
$$\varphi_v^{(0)}(x) = (2^v\pi^{1/2}v!)^{-1/2}\exp(-x^2/2)H_v(x),$$

the $H_v(x)$ are Hermite polynomials and x is some auxiliary dimensionless variable.

Multiplying (16) by $\varphi_v^{(0)}(x)$, and summing over v, we find

$$[(x^2 - d^2/dx^2)^2 + \alpha(d^2/dx^2 - x^2) + \varepsilon + 4\xi x]\psi(x) = 0. \tag{18}$$

If the function $\psi(x)$ is normalized to unity, then the coefficients of the expansion (11) are defined as

$$a_v = \int_{-\infty}^{+\infty} dx\, \psi(x)\varphi_v^{(0)}(x). \tag{19}$$

3. QUASICLASSICAL SOLUTIONS

The fourth-order equation (18) can hardly be solved in the general case. However, if one of the parameters ε and ξ is large, then the solution to the equation can be sought in the quasiclassical form:

$$\psi(x) = e^{iS(x)}.$$

Let us substitute this expression into (18) and, assuming the mean values of the "coordinate" x and the "momentum" d/dx to be large, neglect in the zeroth order the higher derivatives of the function $S_0(x)$ and retain in the equation for $S_0(x)$ only the leading (fourth-order)—with respect to x and d/dx—terms together with the energy $\varepsilon + 4\xi x$. Allowance for the neglected terms allows us to find the correction to $S_0(x)$, which yields

$$S = S_0 + S_1 + \dots$$
$$S_0(x) = \pm\int dx[(-\varepsilon - 4\xi x)^{1/2} - x^2]^{1/2},$$
$$S_1(x) = \frac{\alpha}{2}\int\frac{dx}{S_0'(x)} + \frac{i}{2}\ln[S_0'(-\varepsilon - 4\xi x)^{1/2}]. \tag{20}$$

The reversal points x_1 and x_2 ($x_1 < x_2$), which define the boundaries of the classically accessible region for the x motion, are solutions to the equation

$$x^2 = (-\varepsilon - 4\xi x)^{1/2}. \tag{21}$$

In all the cases considered below the branch point, $x_3 = -\varepsilon/4\xi$, of the function $(-\varepsilon - 4\xi x)^{1/2}$ is located at a considerable distance from the reversal point x_2, i.e., $x_3 - x_2 \gg 1$, and therefore can be ignored in the determination by the conventional method of the phase of the function $\psi(x)$ by bypassing the reversal points in the complex x plane.[7] The quasiclassical solution to Eq.

(18) and the quantization conditions found with its aid have the form

$$\psi(x)=C(-\varepsilon-4\xi x)^{-1/2}[(-\varepsilon-4\xi x)^{1/2}-x^2]^{-1/4}\sin\left\{\frac{\pi}{4}+\int_{x_1}^{x}dx[(-\varepsilon-4\xi x)^{1/2}\right.$$

$$\left.-x^2]^{1/2}+\frac{\alpha}{2}\int_{x_1}^{x}dx[(-\varepsilon-4\xi x)^{1/2}-x^2]^{-1/2}\right\}, \tag{22}$$

$$\int_{x_1}^{x_2}dx[(-\varepsilon-4\xi x)^{1/2}-x^2]^{1/2}+\frac{\alpha}{2}\int_{x_1}dx[(-\varepsilon-4\xi x)^{1/2}-x^2]^{-1/2}=\pi\left(n+\frac{1}{2}\right)$$

$$n=0,\ 1,\ 2,\ldots, \tag{23}$$

where C is a normalization constant.

In the expounded derivation we did not consider two more solutions of the quasiclassical equations corresponding to the negative sign in front of the root $(-\varepsilon-4\xi x)^{1/2}$ in the formulas (20). This is connected with the fact that for these solutions there does not exist a region in which the motion with respect to the variable x is classical, i.e., where the action $S_0(x)$ would be real. For this reason, each of the discarded solutions increases exponentially as $x\rightarrow\infty$ or $x\rightarrow-\infty$ and, consequently, cannot be normalized.

The quantization conditions (23) in the case of weak fields, i.e., for $\xi\ll 1$ (but for $|\varepsilon|\gg 1$) lead, as was to be expected, to asymptotic expressions for the energies of the high-lying levels of the anharmonic oscillator:

$$S_0(x_2)=\pm\frac{\pi(-\varepsilon)^{1/2}}{2},\quad \int_{x_1}^{x_2}\frac{dx}{S_0'}=\pm\pi,$$

$$E=-(x_e\omega_e-B_e)n^2+(\omega_e-\omega+2J_0B_e)n+\ldots,\quad n\gg 1. \tag{24}$$

Let us consider further the strong-field region, which is defined by the condition $\xi\gg 1$, and which is the most interesting region. The function $S_0(x)$, (20), can be real, and the classically accessible region (with respect to the variable x) is nonvanishing if the quantity ε is not too large. The conditions for the appearance of a classically accessible region of motion can be found from Eq. (21) together with the requirement that the derivatives of the functions x^2 and $(-\varepsilon-4\xi x)^{1/2}$ should be equal, which yields

$$x_0=-\xi^{1/3},\quad \varepsilon_0=3/4\,\xi^{4/3}. \tag{25}$$

The x region of classical motion arises when the energy $(\varepsilon<\varepsilon_0)$ is decreased in the vicinity of the point $x=x_0$. Setting $x=x_0+y$, $\varepsilon=\varepsilon_0-\Delta$, and assuming that $|y|\ll|x_0|$, $\Delta\ll\varepsilon_0$, we obtain

$$y_{1,2}=-\frac{\Delta^{1/2}}{6^{1/2}\xi^{1/3}},\quad S_0(x_2)=\pm\frac{\pi\Delta}{4\sqrt{3}\xi^{2/3}},\ \int_{x_1}^{x_2}\frac{dx}{S_0'(x)}=\pm\frac{\pi}{\sqrt{3}}, \tag{26}$$

which allows us to find a set of quasienergy levels near the threshold for the appearance of a region of classical motion:

$$\mathcal{E}_n=(x_e\omega_e-B_e)\left[\frac{3}{4}\xi^{4/3}-3^{1/2}\xi^{2/3}\left(n+\frac{1}{2}-\frac{\alpha}{2\sqrt{3}}\right)\right],\quad n=0,1,2,\ldots \tag{27}$$

The condition $\varepsilon_0\gg\Delta$ and the quasiclassicality condition lead respectively to the limitations on the value of the quantum number n:

$$n\ll\xi^{2/3},\quad n\gg 1. \tag{28}$$

The quasiclassical solution, $\psi(x)$, to Eq. (18) in the region $x_0+y_1<x<x_0+y_2$ in the considered case assumes the form

$$\psi_n(x_0+y)=\frac{C}{(y_0^2-y^2)^{1/2}}\sin\left\{\frac{\pi}{4}+\frac{\sqrt{3}}{2}y(y_0^2-y^2)^{1/2}\right.$$

$$\left.+\frac{1}{2}\left(3^{1/2}y_0^2+\frac{\alpha}{\sqrt{3}}\right)\left(\frac{\pi}{2}+\arcsin\frac{y}{y_0}\right)\right\}.\quad y_0^2=\frac{2}{\sqrt{3}}\left(n+\frac{1}{2}-\frac{\alpha}{2\sqrt{3}}\right) \tag{29}$$

Equation (27) shows that for high EM-wave intensities, i.e., for $\xi\gg 1$, the magnitude of the quasienergy of each of the levels increases like $\xi^{4/3}\sim F_0^{4/3}$; the difference between neighboring levels (the transition frequency) increases like $\xi^{2/3}\sim F_0^{2/3}$; the levels for large ξ and for fixed values of the quantum numbers J_0, m become equidistant. These conclusions are illustrated also by the results of numerical computations (see Fig. 2 of Ref. 6).

4. THE OSCILLATOR SOLUTIONS AND THE PROCESS OF MOLECULE EXCITATION

The quasiclassical solutions (29) are not too convenient for the computation of the overlap integrals with the functions $\varphi_v^{(0)}$, (19). Also burdensome is the limitation $n\gg 1$, since in the course of excitation the molecules can substantially populate the levels corresponding to small n. At the same time the appearance of the set of equidistant levels (27) may be an indication of the fact that, for $\xi\gg 1$, near the threshold for the appearance of a classically accessible region of motion $(n\ll\xi^{2/3})$, Eq. (18) possesses solutions of the oscillator type. Treating in Eq. (18) the sum

$$U(x)=x^4-2\alpha x^2+4\xi x$$

as a potential energy, we find that for $\xi\gg|\alpha|^{3/2}$ the equilibrium position coincides with the point $x=x_0=-\xi^{1/3}$, in the vicinity of which

$$U(x)\approx-\varepsilon_0+6\xi^{2/3}(x-x_0)^2-2\alpha x_0^2.$$

The substitution $x=x_0+y$, $\varepsilon=\varepsilon_0-\Delta$ allows us, when $\xi\gg 1$, to separate in Eq. (18) the dominant and correction terms if we take into account the fact that, according to the uncertainty relation for the states localized in the vicinity of the point $y=0$, $d^n/dy^n\sim y^{-n}$ near the threshold for the appearance of a region of classical motion. An elementary evaluation allows us to estimate the dimension of the region of localization: $y\sim 1$, and shows that the dominant terms in Eq. (18) are the energy $\varepsilon+U(x)$ and the term $-2x_0^2d^2/dy^2\sim\xi^{2/3}$, whereas $x_0d/dy\sim x_0yd^2/dy^2\sim\xi^{1/3}$ and $d^4/dy^4\sim y^2d^2/dy^2\sim yd/dy\sim d^2/dy^2\sim 1$. The corrections due to these terms, as well as those due to the anharmonicity of the function $U(x)$, have relative orders of smallness $\xi^{-1/3}$ and $\xi^{-2/3}$. Equation (18) in the lowest order in $\xi^{-1/3}$ assumes the form of an equation for the harmonic oscillator:

$$\left[-2x_0^2\frac{d^2}{dy^2}+6\xi^{2/3}y^2-\Delta-2\alpha x_0^2\right]\psi(x_0+y)=0. \tag{30}$$

From this again follows the expression (27) for the quasienergy values E_n, while for the function $\psi_n(x)$ we have in place of (29) the expression

$$\psi_n(x)=3^{1/8}\varphi_n^{(0)}\left[3^{1/4}(x+\xi^{1/3})\right],\quad n=0,1,2,\dots \tag{31}$$

The condition of applicability of these results is determined by only the first of the inequalities (28), and is connected with the possibility of a series expansion of the potential energy $U(x)$ and the neglect of the terms discarded in Eq. (18).

The found quasienergy solutions (27), (31) of Eq. (18) allow us to investigate the problem of the excitation of the vibrational-rotational motion of a molecule under the action of a resonance EM field pulse. Such a problem has been considered before without allowance for the rotations of the molecule on the basis of one or another model approach,[10-11] which, generally speaking, is not justified by the presence of a small parameter, as well as numerically[12] under the assumption that the interaction is switched on instantaneously, an assumption which is usually not fulfilled. It follows from the analysis carried out in the present paper that the characteristic distance between the molecule's quasienergy levels, (27), is determined by the effective-anharmonicity parameter $x_e\omega_e - B_e$, or it exceeds this quantity when $\xi \gg 1$. Therefore, the interaction switching-on process should be considered to be adiabatic if the pulse duration, τ, satisfies the condition

$$\tau\gg|x_e\omega_e-B_e|^{-1}\sim10^{-11}-10^{-12}\,\text{sec},$$

which is fulfilled for nanosecond and longer laser pulses. The general criterion for adiabaticity is similar to the condition of applicability of the quasiclassical approximation,[7] and has the form

$$\left|\frac{d}{dt}(E_0-E_1)^{-1}\right|\ll1$$

(for all t), where $E_{0,1}$ are the quasienergy values for the levels 0, 1, which depend parametrically on t through the slowly varying amplitude $F_0(t)$. In the regions $d_1F_0 \ll x_e\omega_e - B_e$ and $d_1F_0 \gg x_e\omega_e - B_e$ we have respectively

$$E_1-E_0\sim x_e\omega_e-B_e+\beta\frac{d_1^2F_0^2}{x_e\omega_e-B_e}\ (\beta=\text{const}\sim1).\qquad E_1-E_0\sim\frac{(x_e\omega_e-B_e)^{1/3}}{(d_1F_0)^{2/3}}$$

(formula (27)). If we assume that $dF_0/dt\sim F_0(t)\tau^{-1}$, then the adiabaticity condition in these cases assumes the form $\tau(x_e\omega_e - B_e)^3 \gg (d_1F_0)^2$ and $\tau(x_e\omega_e - B_e)^{1/3}(d_1F_0)^{2/3} \gg 1$. The limitation on the rate of change of $F_0(t)$ in the region $d_1F_0 \sim x_e\omega_e - B_e$ is the most rigid, and is determined by the given inequality, which can thus be regarded as a sufficient condition for the switching on of the interaction to be adiabatic.

The adiabaticity of the switching-on process and the condition of non-intersection of the terms[7] allow us to assert that, as the intensity F_0 is increased, each of the levels $E^{(0)}_{J_0v} \equiv E_{J_0+v,v} - \omega(v+\frac{1}{2})$ goes over into the level E_n, (27), corresponding to the initial values of the quantum numbers J_0, m if we stipulate that the number n numbers the levels $E^{(0)}_{J_0}$ in their decreasing order. The relative arrangement of the levels $E^{(0)}_{J_0v}$ depends on the magnitude, determined by the parameter α, of the detuning of the resonance. Let us, for concreteness, consider the case $\alpha<4$, when the frequency ω is higher than the frequency of the first vibrational transition,

$$\omega_{10}=\omega_e-2x_e\omega_e+2B_e(J_0+1),$$

and the initially populated level $E^{(0)}_{J_00}$ is the uppermost level in the system of levels $E^{(0)}_{J_0v}$. This means that the solution to Eq. (18) that arises in the course of the adiabatic switching on of the interaction is given by the function $\psi_0(x)$, (31), which allows us to find with the aid of the formula (19) the coefficients, a_v, of the expansion of the wave function Ψ in terms of the vibrational-rotational states of the free molecule:

$$|a_v|^2=\frac{2\cdot3^{1/4}}{1+3^{1/2}}\frac{1}{v!}\left(\frac{1}{2}\frac{3^{1/2}-1}{3^{1/2}+1}\right)^v\exp\left(-\frac{3^{1/2}}{1+3^{1/2}}\xi^{2/3}\right)H_v^2\left(\left(\frac{3}{2}\right)^{1/2}\xi^{1/3}\right). \tag{32}$$

The distribution of the molecules over the vibrational levels, (32), generally speaking, differs significantly from the Poisson distribution, which arises in the framework of the model—the so-called semiquantum—theory.[12]

The probability of excitation of the vibrational-rotational levels (v,J_0+v), (30), is maximum at $v=v_0\sim\xi^{2/3}$, i.e., the field with intensity F_0 most efficiently excites the vibrational level with the number

$$v=\left(\frac{d_1F_0}{2^{3/2}(x_c\omega_e-B_e)}\right)^{2/3}. \tag{33}$$

On the other hand, for the most efficient excitation of the vibrational level with the number v, it is necessary to use a field of intensity

$$F_0\sim2^{3/2}v^{3/2}(x_e\omega_e-B_e)/d_1. \tag{34}$$

Formulas similar to the expression (32) can be obtained for another arrangement of the levels $E^{(0)}_{J_0v}$. The condition for an adiabatic switching on of the interaction is fulfilled at all t if the level spacing for all the levels $E^{(0)}_{J_0v}$ exceeds $1/\tau$. This requirement is not fulfilled at exact resonance in, for example, the $\alpha=4$ case, when $\omega=\omega_{10}$ and $E^{(0)}_{J_00}=E^{(0)}_{J_01}$. However, we can also find in this case a distribution of the molecules over the levels that is of the type (32) if we take into account the fact that the initial phase of the excitation can be described in terms of a two-level system,[13] after which we can again use the concept of adiabatically slow growth of the interaction in a multilevel system. The solution to Eq. (18) arising as a result of such a process is determined by the superposition $2^{-1/2}(\psi_0+\psi_1)$, (31), which allows us also in this case to find with the aid of Eq. (19) a probability distribution $|a_v|^2$ that is qualitatively similar to the distribution (32).

For the investigation of the frequency dependence of the excitation process and for a comparison with the classical description of the nonlinear oscillator in a resonance field, it is convenient to consider not the distribution over the levels, but the mean-square deviation from the equilibrium configuration, which, in the state characterized by the solution $\psi_n(x)$ of Eq. (18), has the form

$$\overline{b^2}=\langle (r-r_e)^2\rangle=\frac{1}{2\cdot 3^{1/4}M\omega_e}\left[\xi^{2/3}+\frac{4}{\sqrt{3}}\left(n+\frac{1}{2}\right)\right]. \qquad (35)$$

If the interaction is switched on adiabatically and the molecule is initially at the level $E^{(0)}_{J_0 0}$, then, by definition, the number n is connected in the following way with the frequency ω:

$$n=\left[\frac{\omega_e-\omega+2J_0B_e}{x_e\omega_e-B_e}-1\right]=\left[\frac{\alpha}{2}-1\right] \quad \text{for } \alpha>2 \qquad (36)$$
$$n=0 \quad \text{for } \alpha\leqslant 2,$$

where the square brackets denote the integral part of the number.

The formula (35) describes the discontinuous increase of the amplitude of the forced vibrations when the frequency is decreased. For a finite pulse duration τ, the region of the discontinuities is finite and has a width $\sim 1/\tau$. If we neglect the unevenness of the function $n(\omega)$ by dropping the sign denoting the integral part in the formula (36), then the character of the dependence of $\overline{b^2}$ on the intensity F_0 and on the frequency ω, as well as the orders of magnitude of all the coefficients coincide with the corresponding classical results.[14] In this case it is necessary to take into account the fact that in the approximation under consideration the natural level width (damping) is neglected and that on account of the condition $\xi \gg |\alpha|^{3/2}$ the detuning $\omega-\omega_{10}$ is small.

Consequently, in the asymptotic limit of a strong resonance field, the behavior of the quantum anharmonic oscillator is similar to the classical oscillator. The quantum-mechanical characteristics manifest themselves only in the stepwise dependence of $\overline{b^2}$ on ω, the amplitude of the jumps being small in comparison with the first term in the formula (35) when $\xi \gg 1$.

5. CONCLUSIONS AND DISCUSSION

Thus, for molecules with small and large rotational energies, the problem of the resonance excitation of the vibrational-rotational levels under the action of an intense EM wave reduces to the problem of an effective anharmonic oscillator in a constant electric field. The found asymptotic solutions of this problem allow us to follow the evolution of the vibrational-rotational spectra and the process of excitation of a molecule as the field is increased. The main spectral characteristic of molecules in a strong resonance EM field is the equidistance of the levels described by Eq. (27). The laws governing the excitation process characterizable by Eqs. (32)–(34) allow us to establish a relation between the field intensity F_0 and the most efficiently excitable vibrational levels.

The conditions of applicability of the assumption that the rotational energy is small compared to $x_e\omega_e$ and of the adiabatic approximation considered in Ref. 6 can be fulfilled on account of the numerical smallness of the constant B_e in comparison with $x_e\omega_e$ (for many diatomic molecules $x_e\omega_e \sim 10B_e$[15]). However, under normal conditions (at room temperature) the fraction of such molecules in a gas is quite small. At the same time the conditions of applicability of the assumption that the rotational energy is large, (13), are fulfilled simultaneously with the condition of applicability of the asymptotic form for a strong field if

$$1\ll\xi\ll\lambda\equiv 2^{1/2}J_0B_e/(x_e\omega_e-B_e),\, J_0^{3/2}, \qquad (37)$$

where, at a temperature T, $J_0 \sim (kT/B_e)^{1/2}$ for the majority of molecules. One of the necessary conditions, $J_0^{3/2} \gg 1$, that follow from the inequalities (37) is well fulfilled even at room temperature for virtually all diatomic molecules. As for the parameter λ, its magnitude under normal conditions cannot be too large. This circumstance is unimportant from the point of view of the investigation of the quasienergy spectra of molecules, an investigation which can be carried out at any temperature, owing to which we can always find that temperature range in which $\lambda \gg 1$. However, the investigation of the process of excitation of a molecule under the action of a resonance EM field is, apparently, justified only when $kT \lesssim \hbar\omega_e$, since for $kT \gg \hbar\omega_e$ a substantial population of the high vibrational levels is realized even by heating the molecules.

For many diatomic molecules $\lambda \sim 3-5$ when $kT \sim \hbar\omega_e$, which indicates the limited applicability of the widely used[10–12] equivalent-anharmonic-oscillator approximation (for $\xi > \lambda$ it is necessary to use the general equations (3), exactly taking into account the dependence of the matrix elements on the rotational quantum number J). However, for a number of other molecules the region of applicability of the obtained results can be fairly wide. Let us give as an example the molecules InCl, which exist in the gaseous phase at $T > T_{\text{vap}} = 882$ K, and which possess the following parameters: $\omega_e = 317.4$ cm^{-1}, $B_e = 0.117$ cm^{-1}, and $x_e\omega_e = 1.01$ cm^{-1}.[15] The parameter λ, computed for

$$J_0=(kT_{\text{vap}}/B_e)^{1/2}\approx 72$$

is equal to $10.8 \gg 1$. For $\xi = \lambda$, the fifth vibrational level is most efficiently excited. The distribution then arising with the maximum at $v = 5$ differs significantly from the equilibrium distribution for $T = T_{\text{vap}} \approx 2\hbar\omega_e/k$, which can, in principle, be experimentally detected. One of the possible schemes for verification is the investigation of the dissociation of the molecules under the action of a resonance wave and another field of frequency Ω: $D - v_0\omega_e < \Omega < D - (v_0 - 1)\omega_e$, where D is the energy of dissociation of the molecule and v_0 is the number of the level under investigation. In the absence of a resonance field such a process is impossible, and the probability of dissociation of a molecule during its excitation is proportional to the probability of finding the molecule at levels with numbers $v \geqslant v_0$.

Notice, finally, that an elementary estimate yields $\lambda \sim (M/\mu)^{1/4}$ for $J_0 \sim (\omega_e/B_e)^{1/2}$, on account of which we can, apparently, expect a broadening of the region of applicability of the effective-anharmonic-oscillator approximation when we go over to polyatomic molecules, at least for some vibrational modes.

1) An effect of partial rotational compensation of the anharmonicity was noted in Ref. 8, where an attempt was made to describe classically the excitation of diatomic molecules by a resonance field.

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Primary ionization of noble gases by relativistic electrons

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The specific primary ionization produced by ~2-MeV relativistic electrons in the noble gases helium, neon, argon, krypton and xenon, and also in henogal, is measured with a low pressure wire spark chamber. It is shown that the results of the measurements of the specific primary ionization, carried out under the most favorable conditions, with a streamer chamber and with a low-pressure wire spark chamber, are in agreement with the theoretical predictions, in which the contribution of rapid secondary processes in the gas is taken into account.

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1. INTRODUCTION

While the specific primary ionization of gases under the action of nonrelativistic gases has been studied in sufficient detail, the primary ionization brought about by charged particles of high energy has been measured only for a small number of gases and in the restricted range of values of the Lorentz factor $\gamma = E/mc^2$.[1–12]1) The existing theoretical calculations of the primary ionization by relativistic particles[13–16] also call for verification.

In addition, the data on the primary ionization is of interest for plasma physics, upper atmosphere physics, astrophysics and high energy physics. In the present work, we give the results of measurements of the specific primary ionization of noble gases by relativistic electrons in the region of minimum ionization at $\gamma \approx 4$. The measurements were carried out by means of a spark chamber—a pulsed gas-discharge detector, widely used in high energy physics for the determination of the coordinates of charged particles. As has been pointed out previously,[17–19] the effectiveness of the spark chamber, i.e., the probability of the generation in it of a spark discharge by the passage of a charged particle, should depend on the specific primary ionization. It can therefore be used for the measurement of the latter, similar to what was done in the low-efficiency Geiger–Müller counters. In spite of the obviousness of this idea, attempts at its realization have been undertaken only recently.[11,12]

The spark chamber method has a potential advantage over the other methods of measurement of the primary ionization. Thus, for example, in contrast with the low-efficiency Geiger–Müller counters,[1,2] and also the Wilson chamber[3,4] or the diffusion chamber,[5] where the presence of impurities in the working gas is a condition for the normal operation of the apparatus, the spark chamber can be used with the pure gas. The spark chamber method is much simpler than that with the streamer chamber,[6–10] where electron-optical amplification of the light of the streamers is necessary, and, as will be shown below, it allows us to make the

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