with the experimental result given above.

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Rotational spectrum of diatomic molecules in the field of an intense electromagnetic wave

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Rotational spectra of diatomic heteronuclear molecules in the field of an external electromagnetic wave are investigated. Explicit expressions are obtained for the dynamic Stark effect in the vibrational-rotational levels of the molecule in a nonresonance field. A discussion is given of the resonance Stark effect, in which the frequency of the wave is close to the frequency of a vibrational transition. It is shown that in a resonance field with a field strength $F_0 \sim (10^5–10^6)$ V/cm a radical restructuring of the rotational spectra of the molecule occurs. It is found that in still more intense fields there is an orientation of the molecules (as the result of the resonance Stark effect) in directions perpendicular to the field F_0.

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1. INTRODUCTION

It is well known that the action of a weak constant or alternating (nonresonance) electric field on a molecule produces only small shifts of the vibrational-rotational levels. The magnitude of these shifts can be determined by means of the usual formulas of the static[1-4] or dynamic[3-5] Stark effects in terms of perturbation theory.

Explicit expressions for the quadratic Stark shift of molecular levels in an alternating field due to the vibrational and rotational motions of the nuclei in the molecule were obtained recently by Braun and Petelin.[5] In Sec. 2 of the present article we discuss the dynamic Stark effect in second-order perturbation theory with inclusion of the electronic motion in addition to the vibrational and rotational motions.

The most interesting case is that in which the external field cannot be considered small, i.e., when the Stark shift becomes comparable with the distance between the rotational sublevels. The restructuring of the rotational spectrum in a strong constant field has been discussed by several authors.[6-9] In the case of an alternating field, in the nonresonance case the interaction ceases to be small at $d_0 F_0 \sim \hbar\omega_e$, where d_0 is the characteristic value of the dipole moment of an electronic transition, F_0 is the electric field strength, and ω_e is the vibrational frequency. In the resonance case $\omega \approx \omega_e$, a substantial rearrangement of the rotational spectrum arises at much lower fields, when $V_0 \equiv d_1 F_0 \sim B_e$, where d_1 is the characteristic value of the dipole moment of a vibrational transition ($d_1 \sim (m/M)^{1/4} d_0$, m is the electron mass, and M is the reduced mass of the nuclei) and B_e is the rotational constant of the molecule.

In Sec. 3 we discuss the problem of the rotational spectrum of a diatomic heteronuclear molecule in a linearly polarized electromagnetic wave of not too high

intensity with frequency ω close to the frequency of the first vibrational transition: $\omega \approx \omega_{10}$, $\omega_{10} = \omega_e(1 - 2x_e)$, $V_0 \ll 2\hbar x_e \omega_e$, where x_e is the anharmonicity constant. It is shown that in this case a radical restructuring of the rotational spectrum of the molecule occurs and rotational frequencies arise which do not have an analog in the case of a free molecule. In Sec. 4 we present the result of a similar calculation for the case of circular polarization of the wave. In Sec. 5 we discuss the rotational spectrum of diatomic heteronuclear molecules in the field of an intense wave, when $V_0 \gtrsim \hbar x_e \omega_e$. The frequencies of the rotational motion are determined and the question of orientation of the molecules in such fields is investigated.

2. THE STARK EFFECT IN A WEAK NONRESONANCE FIELD

The shift of an energy level (more accurately, the quasienergy[10,11]) of an arbitrary quantum-mechanical system in the field of a linearly polarized wave $\mathbf{F} = \mathbf{F}_0 \cos \omega t$ is determined by well known formulas[3,11] which, when the z axis is chosen along the field $\mathbf{F}_0$, can be written in the form

$$\Delta E_i = -\frac{1}{2} \alpha^{(i)}(\omega) \overline{F^2}, \tag{2.1}$$

$$\alpha^{(i)}(\omega) \equiv \alpha_{zz}^{(i)}(\omega) = \frac{2}{\hbar} \sum_{i'} \frac{|d_{i'i}^z|^2 \omega_{i'i}}{\omega_{i'i}^2 - \omega^2}$$

Here $\alpha_{jk}^{(i)}(\omega)$ is the dynamic polarizability tensor of a system in the i-th state, [12] $\mathbf{d}$ is its dipole-moment operator, $\omega_{ii'}$ are the transition frequencies, and $\overline{F^2} = F_0^2/2$.

In diatomic molecules $|i\rangle = |JM_J v\Lambda\rangle$, where J and M_J are the quantum numbers of the angular momentum and its projection on the z axis, v is the vibrational quantum number, and Λ designates a set of quantum numbers which determine the electronic states of the molecule. [2]

In the present work we limit ourselves to discussion of the most common type of diatomic molecule, in which the electronic ground state is a $^1\Sigma$ term. The polarizability of the molecule in the state $|JM_J v0\rangle$ of the electronic ground-state term is conveniently written in the form

$$\alpha(\omega;\, JM_J v0) = \alpha'(\omega;\, JM_J v0) + \alpha''(\omega;\, JM_J v0), \tag{2.2}$$

where α' contains a summation over all intermediate vibrational-rotational states of the ground-state electronic term and α'' contains a summation over all intermediate vibrational-rotational states of all terms except the ground-state.

For frequencies ω far from the frequencies of the electronic transitions (i.e., for $|\omega - \omega_{\Lambda 0}| \sim \omega_{\Lambda 0}$), the polarizability α'' is defined as the electronic polarizability of a given nuclear configuration. [12] By means of the usual transformations[2,12] it is easy to express α'' in terms of the longitudinal electronic polarizability $\alpha_{\parallel}$ and the transverse electronic polarizability $\alpha_{\perp}$ (with respect to the molecule axis) for the equilibrium inter-

nuclear distance $r = r_e$:

$$\alpha''(\omega;\, JM_J 0) = \frac{\alpha_{\parallel}(\omega) + 2\alpha_{\perp}(\omega)}{3} + \frac{2}{3}[\alpha_{\parallel}(\omega) - \alpha_{\perp}(\omega)]\frac{J(J+1) - 3M_J^2}{(2J+3)(2J-1)}, \tag{2.3}$$

$$\alpha_{\parallel,\perp}(\omega) = \frac{2}{\hbar} \sum_{\Lambda} \frac{|d_{0\Lambda}^{\parallel,\perp}|^2 \omega_{\Lambda 0}}{\omega_{\Lambda 0}^2 - \omega^2}, \tag{2.4}$$

where $d^{\parallel}$ and $d^{\perp}$ are the projection of the dipole moment on the axis of the molecule and on one of the directions perpendicular to the axis.

The polarizability $\alpha'(\omega;\, JM_J v0)$ is determined by the dipole moment of the molecule averaged over the electronic ground state, $\overline{\mathbf{d}}(r) = d(r)\mathbf{n}$, where $\mathbf{n} = [\sin\theta \cos\varphi, \sin\theta \sin\varphi, \cos\theta]$ is a unit vector along the axis of the molecule. In the lower orders in the parameter $\sim (m/M)^{1/4}$ the matrix elements are

$$d_{vv'} = \int \phi_v(r) d(r) \phi_{v'}(r) r^2\, dr = d_0 \delta_{vv'} + d_1(v^{1/2}\delta_{v',v-1} + (v+1)^{1/2}\delta_{v',v+1}), \tag{2.5}$$

where $\phi_v(r)$ are the vibrational wave functions of the molecule (in the absence of an external field) with the corresponding energies

$$\varepsilon_v = \hbar\omega_e(v + 1/2) - \hbar\omega_e x_e(v + 1/2)^2, \quad v = 0, 1, 2, \ldots. \tag{2.6}$$

As we can easily see, the anharmonic corrections to the matrix elements of each of the transitions d_{vv} and $d_{v,v+1}$ in Eq. (2.5) have a relative order of smallness $v\sqrt{m/M}$. The remaining matrix elements are also small: $d_{v,v+k} \sim d_0(mv^2/M)^{k/4}$. This also determines the condition of applicability of the expressions (2.5): $v \ll \sqrt{M/m}$. Inclusion of anharmonic corrections to the energies ε_v may be necessary in principle in the resonance case (Secs. 3–5), when the principal term $\hbar\omega_e$ in the energies of the transitions $v \to v+1$ partly or completely is compensated by the magnitude of the resonance field quantum $\hbar\omega$.

In the nonresonance case, i.e., for frequencies ω sufficiently far from ω_e and rotational transition frequencies $B_e J/\hbar$, by using the well known formulas for the matrix elements of the vectors, [2] it is easy to obtain the following expression for the polarization α':

$$\alpha'(\omega;\, JM_J 0) = -\frac{4B_e d_0^2}{(\hbar\omega)^2}\frac{J^2 + J - 1 + M_J^2}{(2J+3)(2J-1)} - \frac{2d_1^2 \omega_e}{\hbar(\omega^2 - \omega_e^2)}\frac{2J^2 + 2J - 1 - 2M_J^2}{(2J+3)(2J-1)} \tag{2.7}$$

Note that in the approximation adopted here, i.e., in the lowest order in the parameter $(mv^2/M)^{1/2}$, α' and α'' do not depend on the vibrational quantum number v.

Equations (2.2), (2.3), and (2.7) determine the Stark shift of the vibrational-rotational level $|JM_J v0\rangle$ of the ground-state electronic term:

$$\Delta E_{JM_J} = E_{JM_J v} - E_{JM_J v}^{(0)} = -\frac{1}{4}[\alpha'(\omega;\, JM_J 0) + \alpha''(\omega;\, JM_J 0)]F_0^2. \tag{2.8}$$

In the case of optical frequencies ω, the main contribution to the Stark shift is from the electronic polarizability α''. In the infrared region, where $|\omega - \omega_e| \sim \omega_e$, the two terms in α' (2.7) are of the same order and $\alpha' \sim \alpha''$. Only for frequencies $\omega \ll \omega_e$ or near a resonance where $|\omega - \omega_e| \ll \omega_e$ is the Stark shift deter-

mined by the first or second term, respectively, in the vibrational-rotational polarizability[1] α'.

For sufficiently large fields, when the Stark shift ΔE_{JM_J} becomes comparable with the distance B_e between the lower rotational levels ($\alpha F_0^2 \sim B_e \ll \hbar\omega_e$, where $d_0 F_0 \sim \hbar\omega_e$ or $V_0 \sim \sqrt{\hbar\omega_e B_e}$), it is necessary to take into account the perturbation matrix elements nondiagonal in J, which leads to replacement of the polarizability tensor $\alpha_{jk}(\omega; JM_J v0)$ by the scattering tensor $C_{jk}(\omega; JM_J v0; J'M_J v0)$.[12] Values of the quasienergy $E_{M_J v}$ are determined here, as usual,[2,11] from the secular equation

$$\det |(E_{M_J v} - E_{JM_J v}^{(0)})\delta_{JJ'} + \tfrac{1}{4} F_0^2 C_{zz}(\omega; JM_J v0, J'M_J v0)| = 0. \quad (2.9)$$

Under these conditions (i.e., for $V_0 \sim \sqrt{\hbar\omega_e B_e}$) there can arise important changes in the rotational quasienergy spectrum of molecules similar to what occurs in a strong constant field.[6-9]

The approach to resonance obviously increases the sensitivity of the molecules to external action. Therefore the effect of a radical restructuring of the rotational spectrum of the molecules in a resonance electromagnetic field in the infrared region ($\omega \approx \omega_e$) occurs at lower fields, namely when $V_0 \sim B_e$. This question is discussed in the next section.

3. ROTATIONAL SPECTRUM OF A MOLECULE IN A RESONANCE FIELD

In the case when the frequency of the electromagnetic field is close to a vibrational frequency ω_e and the field is not too large: $V_0 \ll \hbar\omega_e$ (i.e., up to fields $F_0 \sim 10^8$ V/cm), the resonance interaction is stronger than the quadratic Stark effect due to the electronic polarizability α'' (2.3) and the rotational polarizability (the first term in α' (2.7)), and the latter can be neglected. In terms of one (ground-state) electronic term the motion of the molecule in a field $\mathbf{F}(t)$ is described by the Schrödinger equation:

$$i\hbar \frac{\partial \Phi}{\partial t} = (H_0 + V)\Phi, \quad H_0 = H_{\text{vib}} + \frac{\hbar^2 J^2}{2Mr^2};$$
$$(3.1)$$

$$V = -d(r)F_0 \cos\theta \cos\omega t,$$

where $H_{\text{vib}}(r)$ is the Hamiltonian of the vibrational motion in the absence of an external field and $\mathbf{J}$ is the angular momentum operator of the molecule.

The rotational motion is slow in comparison with the vibrational motion. In the sense of the adiabatic approximation[2] a convenient basis for expansion of the nuclear wave function $\Phi(r, \theta, \varphi, t)$ is the set of solutions of the purely vibrational problem (for fixed values of the angle variables θ and φ). Here, however, if the energy of interaction with the field $V_0 \gtrsim B_e$, then the time of molecular motion induced by the field, $\tau \sim \hbar/V_0$, can be small in comparison with the characteristic time of the rotational motion $\tau_{\text{rot}} \sim \hbar/B_0$. This leads to the necessity of taking into account the interaction with the field V simultaneously with solution of the vibrational problem[2]:

$$i\hbar \frac{\partial \Psi}{\partial t} = (H_{\text{vib}} + V)\Psi. \quad (3.2)$$

In the resonance approximation $\hbar|\omega - \omega_e|$, $V_0 \ll \hbar\omega_e$ the solutions of Eq. (3.2) can be represented in the form

$$\Psi(r, t; \theta) = e^{-i\gamma(\theta)t/\hbar}\psi(r, t; \theta), \quad (3.3)$$
$$\psi(r, t; \theta) = \sum_v A_v(\theta) e^{-i(v-1)\omega t}\phi_v(r).$$

As a result of the resonance approximation, i.e., with accuracy to small corrections $\sim V_0/\hbar\omega_e$, Eq. (3.2) already leads to a system of equations which connect just the coefficients A_v corresponding to neighboring vibrational levels, i.e., A_v and A_{v+1}. If in addition the resonance interaction does not involve too many levels, so that $v \ll \sqrt{M/m}$, then the expressions for the matrix elements $d_{v,v\pm 1}$ from Eq. (2.5) can be used. Under these conditions the coefficients $A_v(\theta)$, together with the quasienergy $\gamma(\theta)$ of the vibrational motion, are determined from the equations

$$[\gamma(\theta) + \hbar(v-1)\omega - \varepsilon_v]A_v(\theta) + \tfrac{1}{2}V(\theta)[(v+1)^{\frac{1}{2}}A_{v+1}(\theta) \\ + v^{\frac{1}{2}}A_{v-1}(\theta)] = 0, \quad (3.4)$$

where $V(\theta) \equiv V_0 \cos\theta$. We will denote by the index p the various quasienergy levels $\gamma(\theta)$ and the functions $A_v(\theta)$ and $\psi(r, t; \theta)$ corresponding to them. If these functions are found, then the solution of Eq. (3.1) corresponding to the total quasienergy E_{M_J} of the molecule and the projection of the angular momentum on the direction of the field M_J has the form

$$\Phi_{M_J}(r, \theta, \varphi, t) = \exp\{-iE_{M_J}t/\hbar\}\frac{\exp\{iM_J\varphi\}}{(2\pi \sin\theta)^{\frac{1}{2}}}\sum_p \chi_p(\theta)\psi_p(r, t; \theta). \quad (3.5)$$

Without taking into account the small vibrational-rotational interaction which exists in the presence of an external field (i.e., for $\hbar^2/2Mr^2 \to \hbar^2/2Mr_e^2 \equiv B_e$), the rotational wave functions $\chi_p(\theta)$ satisfy the following equations:

$$-B_e \frac{\partial^2 \chi_p}{\partial\theta^2} + (U_p - E_{M_J})\chi_p = B_e \sum_{p'(\neq p)} \sum_v A_v^{(p)}\left(\frac{\partial^2 A_v^{(p')}}{\partial\theta^2} + 2\frac{\partial A_v^{(p')}}{\partial\theta}\frac{\partial}{\partial\theta}\right)\chi_{p'}, \quad (3.6)$$

where

$$U_p(\theta) = \gamma_p(\theta) + B_e\left(\frac{M_J^2 - \tfrac{1}{4}}{\sin^2\theta} - \frac{1}{4}\right) - B_e \sum_v A_v^{(p)}(\theta)\frac{\partial^2 A_v^{(p)}(\theta)}{\partial\theta^2}. \quad (3.7)$$

If the nonadiabatic terms (i.e., the right-hand side) of Eq. (3.6) can be neglected, then Eq. (6) takes the form of the one-dimensional Schrödinger equation with an effective potential energy $U_p(\theta)$.

In the general case only numerical solution of Eq. (3.4) is possible (see Sec. 5). Here we shall discuss the special case in which it is possible to obtain an analytic solution of Eqs. (3.4) and (3.6). Let the frequency ω be close to the frequency of the first vibrational transition ω_{10} and let the field F_0 be sufficiently weak:

$$|\Delta| \ll 2\hbar\omega_e x_e, \quad 2B_e \lesssim V_0 \ll 2\hbar\omega_e x_e,$$
$$\Delta \equiv \hbar(\omega - \omega_{10}), \quad \omega_{10} = \omega_e(1 - 2x_e). \quad (3.8)$$
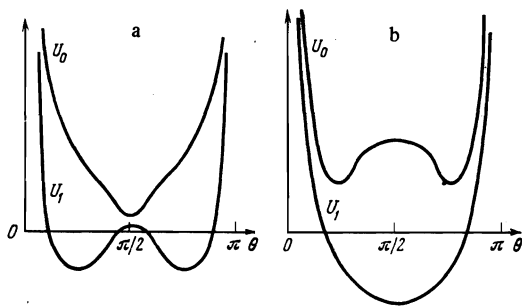
FIG. 1. Qualitative dependence of the effective potential energy $U_0(\theta)$ and $U_1(\theta)$ in the case of linear (a) and circular (b) polarization of the external wave.

(Note that for many diatomic molecules $\hbar\omega_e x_e/B_e$ ≈ 10.)[14] In this case the equations in (3.4) with $v = 0$ and 1 are split off from the remaining equations and the vibrational problem for the levels $v = 0$ and 1 becomes equivalent to the problem of a two-level system in a resonance field.[2] As a result we obtain

$$\gamma_{e,1} = \frac{\varepsilon_0 + \varepsilon_1 + \hbar\omega}{2} \pm \frac{1}{2}[\Delta^2 + V^2(\theta)]^{1/2},$$

$$\psi_{0,1}(r, t; \theta) = \left[\frac{1 \mp \sin\delta}{2}\right]^{1/2} e^{i\omega t}\phi_0(r) \mp \left[\frac{1 \pm \sin\delta}{2}\right]^{1/2}\phi_1(r), \quad (3.9)$$

$$A_0^{(0)} = A_1^{(1)} = \left[\frac{1 - \sin\delta}{2}\right]^{1/2}, \quad A_1^{(0)} = -A_0^{(1)} = -\left[\frac{1 + \sin\delta}{2}\right]^{1/2}, \quad \delta = \text{arctg}\frac{\Delta}{V(\theta)}.$$

The remaining vibrational levels $(v = p = 2, 3, \dots)$ can be obtained by means of perturbation theory:

$$\gamma_v(\theta) = \varepsilon_v - \hbar\omega(v-1) - V^2(\theta)[8\hbar x_e \omega_e v(v-1)]^{-1}. \quad (3.10)$$

The potential energy $U_1(\theta)$ (see Fig. 1a) for $V_0 \gg B_e$, $|\Delta|$, has narrow minima near the values $\theta = 0$ and π. The equation for $\chi_1(\theta)$ when the terms proportional to B_e/V_0 and $|\Delta|/V_0$ are neglected is identical to the equation for a two-dimensional isotropic oscillator.[3] Thus, the wave functions and energies of the lower rotational levels are obtained in the form

$$\chi_1^{(nM_J)}(\theta) = \left[\frac{2n!}{(n + |M_J|)!}\right]^{1/2}\exp\left(-\frac{\beta}{2}\theta^2\right)\theta^{|M_J|+1/2}\beta^{(|M_J|+1)/2}L_n^{|M_J|}(\beta\theta^2), \quad (3.11)$$

$$\beta = \frac{1}{2}\left(\frac{V_0}{B_e}\right)^{1/2}, \quad E_{nM_J}^{(1)} = \frac{1}{2}(\varepsilon_0 + \varepsilon_1 + \hbar\omega - V_0) + (B_e V_0)^{1/2}(2n - |M_J| + 1),$$

$$n = |M_J|, \; |M_J| + 1, \dots,$$

where $L_n^m(x)$ are Laguerre polynomials. The same formulas are valid for states $\chi_1(\theta)$ localized near $\theta = \pi$; it is necessary only to replace θ by $\pi - \theta$ in Eq. (3.11).

The potential energy $U_0(\theta)$ has a narrow minimum at $\theta = \pi/2$. For $V_0 \gg |\Delta| \gg (B_e V_0^2)^{1/3}$ the equation for $\chi_0(\theta)$ is identical to the equation for an ordinary oscillator and as a result we obtain

$$\chi_0^{(n)}(\theta) = \varphi_n\left(\left[\frac{V_0}{2\pi(|\Delta|B_e)^{1/2}}\right]^{1/2}\left(\theta - \frac{\pi}{2}\right)\right),$$

$$E_n^{(0)} = \frac{\varepsilon_0 + \varepsilon_1 + \hbar\omega + |\Delta|}{2} + V_0\left[\frac{B_e}{|\Delta|}\right]^{1/2}\left(n + \frac{1}{2}\right), \quad n = 0, 1, \dots, \quad (3.12)$$

where the oscillator functions[2] have the form

$$\varphi_n(x) = (2^n n! \pi^{1/2})^{-1/2} e^{-x^2/2}H_n(x). \quad (3.13)$$

Note that under the conditions (3.8) the resonance field can also have an appreciable effect on the rotational spectrum of the vibrational levels with $v = 2, 3, \dots$. In fact, if the field is sufficiently strong, so that $[V_0^2/8B_e \hbar x_e \omega_e v(v-1)] \gg 1$, the rotational motion in the vibrational levels $v = 2, 3, \dots$ becomes localized near the directions $\theta = 0$ and $\theta = \pi$.

4. CIRCULAR POLARIZATION

In the case of interaction of molecules with a circularly polarized electromagnetic field, the separation of the vibrational and rotational motions can be carried out for the most part in the same way as was done above for linearly polarized radiation. Here, however, some specific features arise.

The interaction energy of the molecule with the field V in Eqs. (3.1) and (3.2) in the case of circular polarization takes the form $V = -d(r)F_0\sin\theta\cos(\omega t \pm \varphi)$, where θ and φ are spherical angles which determine the orientation of the molecule in a coordinate system with z axis along the direction of propagation of the wave, and the upper and lower signs refer respectively to the cases of left-hand and right-hand polarization. Instead of Eq. (3.3) we now have

$$\Psi(r, t; \theta, \varphi) = \exp\{-i\gamma(\theta)t/\hbar\}\psi(r, t; \theta, \varphi),$$

$$\psi(r, t; \theta, \varphi) = \sum_v A_v(\theta)\exp\{-i(v-1)(\omega t \pm \varphi)\}\phi_v(r). \quad (4.1)$$

The expansion coefficients A_v satisfy the former equation (3.4), where, however, $V(\theta) = V_0\sin\theta$.

Equation (3.6) remains in effect (with the dependence of ψ_p on φ taken into account), and the equations for the rotational angular functions $\chi_p(\theta)$ take the form

$$-B_e\frac{\partial^2 \chi_p}{\partial\theta^2} + (U_p - E_{M_J})\chi_p = B_e \sum_{p'(\neq p)} \sum_v A_v^{(p)}\left[\frac{\partial^2 A_v^{(p')}}{\partial\theta^2} + 2\frac{\partial A_v^{(p')}}{\partial\theta}\frac{\partial}{\partial\theta}\right.$$
$$\left. - \frac{(v-1)\mp 2M_J}{\sin^2\theta}(v-1)A_v^{(p')}\right]\chi_{p'},$$

$$U_p(\theta) = \gamma_p(\theta) + B_e\left(\frac{M_J^2 - 1/4}{\sin^2\theta} - \frac{1}{4}\right) \quad (4.2)$$

$$-B_e\sum_v A_v^{(p)}\left[\frac{\partial^2 A_v}{\partial\theta^2} - \frac{(v-1)\mp 2M_J}{\sin^2\theta}(v-1)A_v^{(p)}\right].$$

In terms of the two-level approximation (the conditions (3.8)) the vibrational wave functions in a circularly polarized field take the form

$$\psi_{0,1}(r, t; \theta, \varphi) = \left[\frac{1 \mp \sin\delta}{2}\right]^{1/2}e^{i(\omega t \pm \varphi)}\phi_0(r) \mp \left[\frac{1 \pm \sin\delta}{2}\right]^{1/2}\phi_1(r), \quad (4.3)$$

while the remaining equations (3.9) remain in force provided that the new definition of $V(\theta)$ is taken into account.

The effective potential energies for rotations in these vibrational states $U_{0,1}(\theta)$ are qualitatively illustrated in Fig. 1b.

For $V_0 \gg B_e$ the curve $U_0(\theta)$ has two narrow minima

near the values $\theta = 0$ and $\theta = \pi$. In the range of detunings $V_0 \gg |\Delta| \gg (B_e V_0^2)^{1/3}$ the lower quasienergy levels of the state ψ_0 are determined by the expression

$$E_{nM_J}^{(0)} = \frac{\varepsilon_0 + \varepsilon_1 + \hbar\omega + |\Delta|}{2} + V_0 \left(\frac{B_e}{|\Delta|}\right)^{1/2} (2n - |M_J| + 1),$$

$$n = |M_J|, \ |M_J| + 1, \ldots \tag{4.4}$$

The corresponding wave functions $\chi_0^{(nM_J)}(\theta)$ are determined from the first formula in Eq. (3.11), in which now $\beta = V_0/(4|\Delta|B_e)^{1/2}$.

The potential curve $U_1(\theta)$ has one minimum at $\theta = \pi/2$ and near this value can be approximated by a parabola. The wave functions $\chi_1(\theta)$ and the quasienergy levels $E^{(1)}$ near the bottom of the well are determined by the corresponding expressions for a one-dimensional oscillator:

$$E_n^{(1)} = \frac{\varepsilon_0 + \varepsilon_1 + \hbar\omega - V_0}{2} + (V_0 B_e)^{1/2}\left(n + \frac{1}{2}\right),$$

$$\chi_1(\theta) = \varphi_n\left[\left(\frac{V_0}{B_e}\right)^{1/4} \frac{\theta - \pi/2}{\sqrt{2}}\right], \quad n = 0, 1, \ldots \tag{4.5}$$

For higher vibrational levels ($v = 2, 3, \ldots$) under the conditions of (3.8), the solutions of the vibrational problem are given by Eqs. (3.10), in which it is necessary to take into account that $V(\theta) = V_0 \sin\theta$. As before, for $V_0 \gg [8\hbar\omega_e x_e B_e v(v-1)]^{1/2}$ the structure of the lower rotational sublevels of the vibrational level with number v differs substantially from the usual structure. The corresponding quasienergy levels and wave functions are determined by expressions (4.5), where it is necessary to replace V_0 by $V_0^2/2\hbar\omega_e x_e v(v-1)$.

Thus, the behavior of a molecule in resonance circularly polarized field is somewhat different from the case of linear polarization. We can, however, distinguish the following general regularities. Under conditions determined by the inequalities (3.8), the resonance field substantially changes the spectrum and the rotational functions of the resonance states ($v = 0$ and $v = 1$) and possibly also some of the next vibrational states. The corresponding rotational functions of the lower quasienergy levels turn out to be localized in the variable θ. In the vibrational state ψ_0 the rotational wave functions are localized near directions perpendicular to the direction of $\mathbf{F}_0$. In the rotational state ψ_1 (and also in other states ψ_p, $p > 1$, if they are sufficiently strongly perturbed by the field $V_0^2 \gg 8\hbar\omega_e x_e B_e v \times (v-1)$) the region of localization adjoins the direction "along" the field (the direction of the vector $\mathbf{F}_0$ in the case of linear polarization and the (x, y) plane in the case of a circularly polarized wave). As will be shown below, the latter result is specific for the range of external field strength F_0 defined by the inequalities (3.8), and changes substantially in the transition to higher fields.

5. STRONG FIELD

It was noted above for many diatomic molecules $\hbar\omega_e x_e \approx 10 B_e$.[14] As a result of this the inequalities (3.8) can be satisfied for certain values of V_0. Under

these conditions the interaction of the molecule with the field is not weak, but can be described in terms of two resonance vibrational levels. However, these limitations on V_0 (3.8) are extremely rigid and burdensome. In addition, as a consequence of the limited range of the parameter V_0/B_e the potential wells shown in Fig. 1 turn out to be not too deep, which is the cause of strong anharmonicity. In essence, in terms of the limitations (3.8) we can speak only of certain levels described by Eqs. (3.11), (3.12), (4.4), and (4.5). We note, finally, that the field strength F_0 defined by the inequalities (3.8) is not too large ($F_0 \approx (10^5 - 10^6)$ V/cm). All of these circumstances make it desirable to extend the results obtained to the case of a stronger field, where we have

$$\hbar\omega_e \gg V_0 \gg \hbar\omega_e x_e > B_e. \tag{5.1}$$

It is evident that in this range of interaction energies first of all the two-level approximation to the vibrational problem is violated. Giving up the two-level model on taking into account the anharmonicity of the vibrational levels makes analytic solution of the equation impossible. It is possible, however, to carry out a separation of variables and to find rotational quasienergy spectra of the molecule by using the adiabatic and resonance approximations and numerically solving the multilevel vibrational problem.

The system of Eqs. (3.4) and the secular equation corresponding to them can be solved if we limit ourselves to a certain finite number of vibrational levels. Such a cutoff of the chain of equations is permissible, since with increasing level number the detuning increases and actually under the conditions (5.1) the resonance interaction always encompasses a finite number of levels. Diagonalization of the matrix corresponding to the cut-off chain of equations (3.4) has been carried out by us numerically in the case of exact resonance $\Delta = 0$ with inclusion of 20 vibrational levels.[4] The single dimensionless parameter $\xi \equiv V(\theta)/2\hbar\omega_e x_e$ characterizing these equations was varied in the internal from 1 to 10.

The results of the calculations confirmed the assumption made above that the resonance interaction actually encompasses a finite number of levels. With increase of V_0 the number of these levels increases. For the maximum value of the parameter ($\xi = 10$) the results of the calculations agree with calculations according to the formulas of perturbation theory for levels with $8 \leq v \leq 13$. The six quasienergy values corresponding to levels with $v = 0, 1, \ldots, 5$, differ substantially from the perturbation theory results, which indicates the strong interaction of these levels with the field. The difference from perturbation theory at large v is due to the effect of cutting off the chain of equations. The correctness of this procedure for description of states strongly interacting with the field is confirmed by the presence of a group of intermediate levels (at all ξ) rather far from the region of strong interaction and from the final level at which the perturbation theory results are valid.

As a result of the numerical calculations the eigen-

values of the diagonalized matrix

$$\lambda_p = \frac{\gamma_p}{\hbar\omega_e x_e} - \frac{3}{2x_e} + \frac{9}{4}$$

are determined as a function of the parameter ξ. Knowledge of the functions $\lambda_p(\xi)$ permits determination of vibrational-quasienergy corrections to the effective potential energy $U_p(\theta)$ for any diatomic heteronuclear molecules. For this purpose it is necessary to carry out a reparametrization of the quantities $\lambda_p(\xi)\hbar\omega_e x_e$ in accordance with the dependence $\xi = V(\theta)/2\hbar\omega_e x_e$. We note finally that in cases in which the region of localization of the rotational function χ_p is not too close to the region of small interactions ($\theta \approx \pi/2$ or $\theta \approx 0$ and π in the case of circular or linear polarization), the dependence of the coefficients A_v on θ is weak and terms with $\partial^2 A_v/\partial\theta^2$ in the potential energy (3.7) and (4.2) can be neglected. Under these conditions the results of the numerical calculations completely determine the form of $U_p(\theta)$ and the characteristic frequencies of oscillations in localized rotational states in the range of fields (5.1).

In Fig. 2 we have shown the results of the calculations of $\lambda_p(\xi)$ for $p = 0$, 1, 2, and 3; $\lambda_p(-\xi) = \lambda_p(\xi)$. The region of applicability of the two-level approximation corresponds to small ξ, for which $\lambda_{0,1}(\xi)$ are linear functions, and the remaining $\lambda_p(\xi)$ are not very different from $\lambda_p(0) = -p(p-1)$. The function $\lambda_0(\xi)$ increases monotonically with increase of $|\xi|$ and reaches a minimum value at $\xi = 0$, $\lambda_0(0) = 0$. All the remaining functions $\lambda_p(\xi)$ have a minimum at $\xi = \xi_p$: $\xi_1 \approx 0.83$, $\xi_2 \approx 2.22$, $\xi_3 \approx 4.0$, and so forth.

The effective potential energies $U_p(\theta)$ can be obtained as the result of the reparametrization procedure described above, which in the case of linear polarization reduces to the following results.

The potential energy $U_0(\theta)$ is similar to the curve $U_0(\theta)$ in Fig. 1a and consequently the transition to strong fields does not qualitatively change the rotational motion in the state ψ_0.
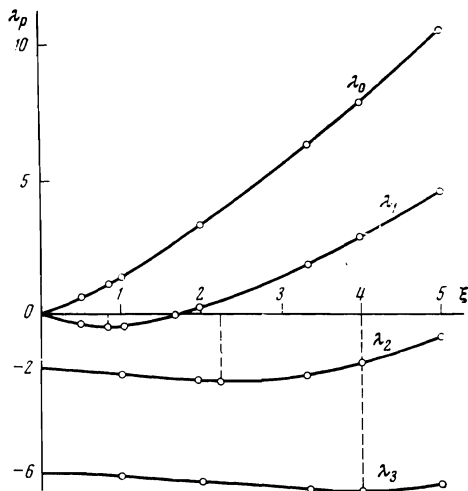

FIG. 2. Dependence (in dimensionless units) of the values of the vibrational quasienergy λ_p on the energy of interaction with the field ξ.
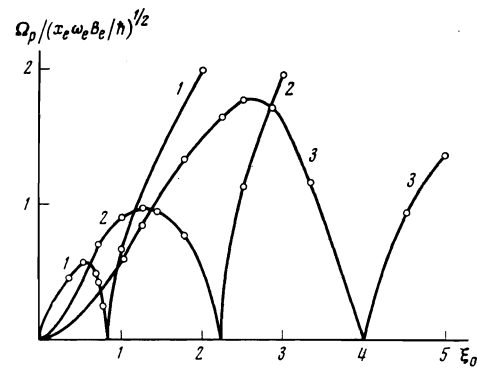

FIG. 3. Frequency of oscillations Ω_p in the angle variable θ in vibrational states ψ_p.

The remaining potential curves $U_p(\theta)$ at interaction energies $V_0 < V_p \equiv 2x_0\hbar\omega_e\xi_p$ appear similar to the curve $U_1(\theta)$ in Fig. 1a. However, with increase of V_0 each of these curves becomes flatter, which leads to a decrease of the corresponding frequencies Ω_p of oscillations in the angle θ. For $V_0 > V_p$ the quasienergy $\gamma_p(\theta)$ has minima at $\theta \neq 0$ and π, and with increase of V_0 the position of these minima approaches $\theta = \pi/2$. This indicates localization of the rotational wave functions χ_p near certain intermediate values of θ_p and $\pi - \theta_p$ corresponding to the points of the minimum of $\gamma_p(\theta)$, where $\theta_p \to \pi/2$ as $V_0 \to \infty$. The potential wells which determine the localization of these states become narrower with increase of V_0, which leads to an increase of the frequencies Ω_p. For example, the function $\Omega_1(V_0)$ for $V_0 > V_1$ is determined by the equation

$$\Omega_1 \approx 1.1\,(x_e\omega_e B_e/\hbar)^{1/2}\,(\xi_0^2 - 0.7)^{1/4}, \quad \xi_0 \equiv V_0/2\hbar\omega_e x_e. \tag{5.2}$$

In Fig. 3 we have shown the functions $\Omega_p(\xi_0)/(x_e\omega_e B_e/\hbar)^{1/2}$ obtained as the result of numerical calculations in the region $V_0 < V_p$ and determined by formulas similar to (5.2) in the region $V_0 > V_p$ (the coefficients in these formulas also were determined by means of numerical calculations).

Thus, with increase of the field F_0 the resonance interaction encompasses more and more vibrational levels. For each of these levels the effective potential energy $U_p(\theta; V_0)$ behaves in such a way that for sufficiently large fields $(V_0 > V_p)$ in each of the states ψ_p, the molecules attempt to align themselves in a plane perpendicular to F_0.[5]

Similar results are obtained also in the case of circular polarization of the radiation. The potential curve U_0 in this case is similar to the curve U_0 in Fig. 1b (with increase of V_0 its maximum value at the point $\theta = \pi/2$ increases). The remaining curves $U_p(\theta)$ for $V_0 < V_p$ are similar to $U_1(\theta)$ in Fig. 1b. Here, however, with increase of V_0 the minimum value $U_p(\pi/2)$ increases, and for $V_0 > V_p$ a maximum appears at the point $\theta = \pi/2$. In this case two stable equilibrium locations arise at the points θ_p and $\pi - \theta_p$, where $\theta_p \to 0$ as $V_0 \to \infty$, i.e., the equilibrium values of the angle variable θ approach 0 and π with increase of the field. This means that in a strong resonance field of circular polarization, the molecules attempt to align themselves

along and opposite the direction of the wave vector. Consequently, both in the case of linear polarization and circular polarization, the main tendency is that an intense resonance field draws the axis of the molecule out of the region of localization of its intensity.

6. CONCLUSION

The experimental observation of the phenomena discussed can be accomplished, for example, by investigation of the absorption spectra of molecules in the radiofrequency region[3,4] under the action of intense resonance radiation. Such experiments can provide direct information on the change of states between rotational levels of molecules under the influence of external action. Another effect accessible to observation is the preferred orientation of molecules in various directions in a resonance field of various polarizations. We note, finally, that a strong distortion of the rotational wave functions can lead to removal of the forbiddenness of transitions between different molecular states. As a result of this, more efficient absorption of radiation by molecules is possible in the strong field, both at the resonance frequency itself and in other frequency regions.

[1] In the formula for $\Delta E_{J M_J}$ in Ref. 5 corrections are also given which have a relative order of smallness $\sim B_e / \hbar |\omega - \omega_e|$ $\sim (m/M)^{1/4} \omega_e / |\omega_e - \omega|$. Corrections of the same order of smallness $\sim x_e \omega_e / |\omega - \omega_e| \sim (m/M)^{1/4} \omega_e / |\omega - \omega_e|$ arise also in taking into account anharmonicity in the energy of the vibrational levels (2.6).

[2] Similarly under conditions of electronic resonance at somewhat higher fields $d_0 F_0 \gtrsim \hbar \omega_e$ the characteristic time $\hbar / d_0 F_0$ becomes less than the period of vibrations of the molecule $1/\omega_e$, which leads to the necessity of taking into account the interaction with the field already in the electronic Hamiltonian. This question has been discussed in Ref. 13, where it is shown that under such conditions both the procedure for separating the nuclear and electronic motions and the vibrational spectrum of the molecule change substantially.

[3] In a sufficiently strong constant electric field F the behavior of a diatomic molecule with a constant dipole moment d also is equivalent to the free motion of a two-dimensional isotropic oscillator near the direction of a field with frequency equal to $(2 B_e dF)^{1/2}$ (Ref. 8). An additional twofold degeneracy (in comparison with the case of a constant field) of the levels $E^{(1)}$ corresponding to the motion near $\theta = 0$ or $\theta = \pi$ is, of course, a specific property of an alternating field. States $\chi_0(\theta)$ localized near $\theta = \pi/2$ also are a specific property of an alternating field.

[4] We emphasize again that the initial equations Eqs. (3.4) are valid for the condition $v \ll \sqrt{M/m}$. The numerical calculation results given below show that the resonance interaction up to extremely intense fields actually encompasses a comparatively small number of vibrational levels with $v \ll \sqrt{M/m}$.

[5] For the CO molecule, for example, the fields F_0 corresponding to energies $V_0 = 2 B_e$ and $V_0 = V_1$ are respectively 6×10^5 V/cm and 3.5×10^6 V/cm.

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