Quantum chaos in a diatomic molecule interacting with a resonant field

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We investigate the dynamics of a diatomic molecule acted on by circularly and linearly polarized IR radiation of high intensity (10–100 GW/cm^2). The analysis is carried out in a two-dimensional approximation, so that account can be taken of the effect of the rotational degree of freedom on the dynamics of the vibrational transitions. The spectrum of the molecule quasi-energies is analyzed in the case of circularly polarized radiation. It is shown that quantum chaos is produced by linearly polarized irradiation. In particular, the change of the polarization with time is quasi-random leading to a quasi-continuous spectrum of the proper radiation of the molecule. The quantum-mechanical analysis of the system is preceded by a classical one.

1. INTRODUCTION

The last decades have seen considerable progress in the understanding and analysis of the dynamics of nonlinear classical systems. It has been found that the system dynamics can have a random character, and no special conditions need be met to realize motion of this type. In particular, chaotic motion can occur even in a one-dimensional system acted upon by an external periodic perturbation. The onset of chaotic dynamics can be roughly described as follows: An external field leads to formation of a system of primary nonlinear resonances at frequencies that are multiples of the external frequency. The influence of the nonlinear resonances on one another produces secondary nonlinear resonances and stochastic layers in the vicinity of the resonance separatrices. If the field amplitude exceeds a certain critical value the various stochastic layers coalesce, and this leads to global stochasticity in the system.[1]

Obviously, the specific features of the dynamics of a classical nonlinear system should be manifested also in the quantum approach. Recent research in this field (named "quantum chaos") has shown that for a quantum nonlinear system in an external filed to reflect features of a classical system it is necessary to satisfy the requirement $V/\gamma \gg 1$, where V is the interaction of the field with the quantum system and γ is the nonlinearity parameter.[2,3] In the opposite case $V/\gamma \ll 1$ the nonlinear quantum resonances degenerate into two-level systems and the dynamics of the object has a quantum character.

From among the simplest objects of quantum mechanics, the condition $V/\gamma \gg 1$ can be met by a highly excited atom of hydrogen (or of an alkali metal) in a microwave field, and by a diatomic molecule in an IR field. The behavior of highly excited atoms is theoretically analyzed in Refs. 4 and 5. One of their main results is the determination of the external magnetic field's critical amplitude above which a regime of overlapping resonances is realized in the system. This brings about a situation in which an electron "diffuses" as a result of a sequence of many transitions into a region of lower-lying levels, all the way down to the ionization limit.

In contrast to the hydrogen atom, the dynamics of a diatomic molecule acted upon by IR radiation has a different character. In fact, in the one-dimensional approximation the vibrational degree of freedom of a diatomic molecule corresponds to a nonlinear oscillator with a weakly nonequidistant spectrum. At high radiation intensity the matrix element of a transition between nearest vibrational levels exceeds the anharmonicity of the spectrum, so that many levels participation thus right away in the dynamics of the transition. The ensuing specific dynamics of the system has been named quantum nonlinear resonance (QNR). According to the results of Refs. 2 and 6, in the QNR regime the molecule polarization oscillates at the characteristic frequency of the phase oscillations, $\Omega_{\text{ph}} \propto (V\gamma)^{1/2}$, where V is proportional to the external-field strength. The square-root dependence of the phase-oscillation frequency on the external-field amplitude, and its insensitivity to variation (within the limits of the spectrum anharmonicity) of the radiation frequency, make it possible to treat this frequency on a par with the Rabi frequency and with other fundamental nonlinear-optics frequencies. Note that no experimental observation of the phase-oscillation frequency Ω_{ph} has as yet been reported for quatum systems.

Our present purpose is an investigation of the dynamics of a diatomic molecule acted upon by intense IR radiation in a two-dimensional approximation that allows for the rotational degree of freedom of the molecule. This question was first considered in a classical approximation in Ref. 7, where it was shown that interaction of a molecule with a circularly polarized field produces in the latter an isolated nonlinear-resonance regime. The system reduces in this case to one-dimensional, with a nonlinearity $\gamma = x\hbar\Omega - B$ (the notation is defined in Sec. 2). In Secs. 3 and 6 we investigate in detail, by a quantum approach, the structure of the nonlinear-resonance phase-space and the structure of the system's quasi-energy spectrum.

The dynamics of the molecule is fundamentally different if the radiation is linearly polarized. A regime of two interacting QNR is realized then in the system, and the molecule motion (in the classical approach) is chaotic (Sec. 4). The results, given in Sec. 7, of a numerical analysis of the system show that the molecule dynamics is qualitatively altered also in the quantum case if the radiation field is linearly polarized. In particular, the time variation of the polarization is quasi-random, leading to a quasi-continuous spectrum of the molecule's proper radiation. We discuss the possibility of observing quantum chaos in this system under conditions of a real experiment.

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2. CLASSICAL MODEL

In the classical approach, a diatomic molecule in a Σ state can be set in correspondence with a system of two point masses m_1 and m_2 in an interaction potential $U(r)$ having a minimum at $r = r_0$. In "action–angle" variables, the unperturbed motion of the molecule corresponds to a Hamiltonian $H_0 = H_0(I, L^2)$, where I is indicative of the vibrational motion of the nuclei ($I = 0$ corresponds to the absence of oscillations), and the variable L coincides with the torque. We shall designate the variables conjugate to I and L by θ and φ respectively (φ is the angle between the x axis and the molecule axis). We confine ourselves hereafter to small values of I and L ($H_0(I,L^2) \ll |U(r_0)|$). Expanding H_0 up to quadratic terms, we have

$$H_0 = \hbar\Omega n - x\hbar\Omega n^2 + Bl^2, \tag{2.1}$$

$$r = r_0 + (2\hbar n/\Omega M)^{1/2} \cos\theta. \tag{2.2}$$

We have changed in (2.1) to the dimensionless action variables $n = I/\hbar$ and $l = L/\hbar$, and have used standard notation for the harmonic-oscillation frequencies $\Omega = dH_0/dI$, the anharmonicity $x = \hbar(d^2H_0/dI^2)/\Omega$, the moment of inertia $B = \hbar^2 dH_0/d(L^2)$ and the reduced molecule mass $M = m_1 m_2/(m_1 + m_2)$.

Consider the interaction of a molecule with a circularly polarized electric field $\mathbf{E}(t)$ ($E_x = E\cos\omega t$, $E_y = E\sin\omega t$). Let the dipole moment of the molecule be $\mathbf{d} = e_{\text{eff}}\mathbf{r}$, where e_{eff} is the effective charge of the atoms and d_0 the dipole moment in the absence of the field. The Hamiltonian of the interaction of the molecule with the radiation is then

$$H_{int} = \mathbf{E}\mathbf{d} = Ee_{\text{eff}}\, r\cos(\omega t - \varphi).$$

Substituting r from (2.2) and retaining only terms responsible for the resonance interaction, we have

$$H_{int} = \frac{Wn^{1/2}}{2}\cos(\theta - \omega t + \varphi), \quad W = e_{\text{eff}} E\left(\frac{2\hbar}{\Omega M}\right)^{1/2}, \tag{2.3}$$

where W is the parameter of the interaction of the IR with the molecule. We shall relate hereafter the value of the field E to the radiation intensity $S = cE^2/8\pi$. For r_0 in Å, d_0 in D, $\hbar\Omega$ in cm^{-1}, M in a.u., and S in GW/cm^2 we have

$$W[\text{cm}^{-1}] = 120.3\frac{d_0}{r_0}\left(\frac{S}{M\hbar\Omega}\right)^{1/2}.$$

For example, for the GeO molecule parameters $\hbar\Omega = 985.8$ cm^{-1}, $x\hbar\Omega = 4.2$ cm^{-1}, $B = 0.48$ cm^{-1}, $d_0 = 3.28$ D, $r_0 = 1.62$ Å, $M = 13.11$ amu and radiation intensities $S = 2.5$–25 GW/cm^2 the parameter W is 3.39–10.72 cm^{-1}.

We conclude this section by noting that for three-dimensional space the Hamiltonian $H = H_0 + H_{\text{int}}$ [Eqs. (2.1) and (2.3)] correspond to a molecule with an orbital angular momentum parallel to the radiation vector.

3. ISOLATED NONLINEAR RESONANCE

We proceed to analyze the vibrational–rotational motion of a molecule on the basis of the Hamiltonian (2.1) and (2.3). We make a canonical change of variables:

$$(n, l) \to (n, k), \qquad (\varphi, \theta) \to (\vartheta, \tilde{\vartheta}),$$

where $k = l - n$, $\vartheta = \theta - \omega t + \varphi$ is the slow phase and $\tilde{\vartheta}$ is the variable conjugate to k. The Hamiltonian takes then the form

$$\begin{gathered} H = \Delta(k)n - Bk^2 + {}^1/_2 Wn^{1/2}\cos\vartheta = H_{\text{eff}}(n, \vartheta) + Bk^2, \\ \Delta(k) = \hbar(\Omega - \omega) + 2Bk, \qquad \gamma = x\hbar\Omega - B. \end{gathered} \tag{3.1}$$

It is seen from (3.1) that k is an integral of the motion, so that the problem has been reduced to an analysis of a one-dimensional system with a Hamiltonian

$$H_{\text{eff}}(n, \vartheta) = \Delta(k)n - \gamma n^2 + {}^1/_2 Wn^{1/2}\cos\vartheta,$$

where k assumes the role of a parameter.

Let us draw the portrait of the system (3.1) for different values of the parameters k. The equation for the immobile points is

$$\dot{n} = \frac{Wn^{1/2}}{2}\sin\vartheta = 0, \quad \dot{\vartheta} = \Delta(k) - 2\gamma n + \frac{W}{4n^{1/2}}\cos\vartheta = 0. \tag{3.2}$$

We obtain from (3.2) five immobile points with the following coordinates: hyperbolic points $n = 0$, $\vartheta = \pm\pi/2$; elliptic point $n = n_1$, $\vartheta = \pm\pi$; hyperbolic point $n = n_2$, $\vartheta = \pm\pi$; elliptic point $n = n_3$, $\vartheta = 0$ ($0 < n_1 \leqslant n_2 < n_3$). The actual values of $n_{1,2,3}$ are obtained by solving a cubic equation that follows directly from (3.2), where the points (n_1, π) and (n_2, π) occur only under the condition

$$k \geqslant k_1 = [3\gamma(W/\gamma)^{2/3} - 4\hbar(\Omega - \omega)]/8B.$$

By way of example, Fig. 1 shows, for the parameters of the GeO molecule ($S = 25$ GW/cm^2, $\hbar(\Omega - \omega) = 15$ cm^{-1}), the positions of the points $n_{1,2,3}$ as functions of the parameter k. Corresponding to a specific value of the integral of motion k is the straight line $l - n = k$ along which the system moves in fact in the case of a circularly polarized field.

Knowing the positions of the immobile points, it is easy to draw a qualitative phase portrait of the system (3.1) for different values of k. It can be shown, in particular, that for

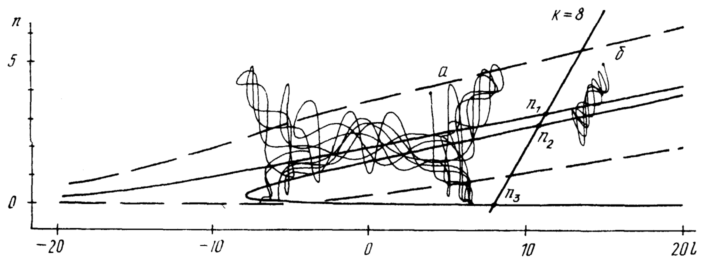

FIG. 1. Positions of immobile points n_1, n_2, and n_3 (thick solid curves) and of the separatrix of the principal nonlinear resonance (dashed lines). The parameter values are: $\hbar(\Omega - \omega) = 15$ cm^{-1}, $x\hbar\Omega = 4.2$ cm^{-1}, $B = 0.48$ cm^{-1}, $S = 25$ GW/cm^2 ($W = 10.72$ cm^{-1}). The figure shows also the projections, on the nl plane, of the phase trajectory of the molecule in the case of linearly polarized radiation, for two initial conditions: a—$n(0) = l(0) = 4, \varphi(0) = \vartheta(0) = 0$, trajectory duration 10^{-10} s; b—$n(0) = 5$, $l(0) = 15$, $\varphi(0) = \vartheta(0) = 0$, trajectory duration 10^{-11} s. In the case of circularly polarized radiation the system moves (on the nl) plane along the line $k = l - n = \text{const}$. The positions of the points n_1 and n_3 should be interchanged.

$k > k_1$ there takes place in the system a principal nonlinear resonance in the vicinity of the elliptic point $(n_3, 0)$ and an "accompanying" resonance in the viciniy of the elliptic point (n_1, π). At radiation intensities $S < 25$ GW/cm^2, however, the real dimensions of the accompanying resonance are small for most diatomic molecules, and its influence on the system dynamics can be neglected.

If the system locks-in with the principal nonlinear resonance, the molecule motion constitutes periodic changes of the vibrational state $n(t)$ [which are accompanied by changes of the rotational state $l(t) = n(t) + k$], with a characteristic frequency

$$\Omega_{\rm Ph} \sim (\gamma V)^{1/2}/\hbar = (\gamma W n_3^{1/2})^{1/2}/\hbar \sim 10^{12}\ \mathrm{s}.$$

The maximum and minimum possible values of $n(t)$ are determined in this case by the position of the separatrix of the principal nonlinear resonance. Figure 1 shows dashed the position of the principal-resonance separatrix for selected values of the parameters.

4. INTERACTION OF NONLINEAR RESONANCES

As shown in the preceding section, nonlinear resonance is produced in the molecule in the case of a circularly polarized field. Roughly speaking, the region of the influence of the nonlinear resonance is bounded by the dashed lines in Fig. 1. When the field-rotation direction is reversed, the region of influence of the resonance is symmetric about the ordinate axis to that shown in Fig. 1. The molecule dynamics has a fundamentally different character in the case of linearly polarized radiation. The regions of influence of the right- and left polarized radiation components overlap in this case. It is common knowledge that if the influence regions of the nonlinear resonances overlap, the dynamics of the system has (in this region) a chaotic character.

In the resonance approximation, the dynamics of the vibrational-rotational motion of a molecule in a linearly polarized field is described by the effective Hamiltonian

$$H_{\rm eff} = \hbar(\Omega - \omega) n - x\hbar\Omega n^2 + Bl^2 + W n^{1/2} \cos\vartheta \cos\varphi, \qquad \vartheta = \theta - \omega t. \tag{4.1}$$

The system (4.1) has no global integrals of motion other than the energy, so that the integral $k = l + n$ can be approximately conserved only in regions where the influence of the the resonances is substantially weaker than that of the other. Figure 1 shows examples of the projections of the trajectories of the GeO molecule [calculated on the basis of (4.1)] for two initial conditions. Evidently, in the second case the value $k = 10$ is approximately conserved. For initial conditions pertaining to the common region of the influence of the nonlinear resonances (case *a*), the trajectory is chaotic. The durations of the given trajectories in real time are 10^{-10} and 10^{-11} s, respectively.

5. QUANTUM MODEL

We proceed to analyze the dynamics of a diatomic molecule exposed to IR radiation in the quantum case. We confine ourselves, as before, to small values of the quantum numbers n and l. For low-energy states, the energy eigenvalues and the wave functions of diatomic molecule take in the two-dimensional approximation the form

$$\begin{aligned} &E_{n,l} = \hbar\Omega(n + 1/2) - x\hbar\Omega n^2 + Bl^2, \\ &\psi_{n,l}(r, \varphi) = (2\pi)^{-1/2} e^{il\varphi} \rho_n(r - r_0), \end{aligned} \tag{5.1}$$

where the function ρ_n is close to a Hermite polynomial. Using the operators $\hat{a}$ and $\hat{a}^+$ ($\hat{a}\rho_n = n^{1/2}\rho_{n-1}$), we can represent the Hamiltonian of a molecule interacting with a circularly polarized field by

$$\hat{H} = \hbar\Omega(\hat{a}^+\hat{a} + 1/2) - x\hbar\Omega(\hat{a}^+\hat{a})^2 - B\partial^2/\partial\varphi^2 + \hat{H}_{int}, \tag{5.2}$$

$$\hat{H}_{int} = E\left[d_0 + \frac{d_0}{r_0}\left(\frac{2\hbar}{M\Omega}\right)^{1/2} \frac{\hat{a}^+ + \hat{a}}{2}\right] \cos(\omega t - \varphi). \tag{5.3}$$

Note that, just as in the classical case, the Hamiltonian (5.2) and (5.3) describes approximately the dynamics of the molecule in the three-dimensional case, when the orbital momentum of the molecule is perpendicular to the field. In fact, in the three-dimensional case the wave eigenfunction of the molecule is given by $\psi_{n,L,m} = \rho_n \Phi_{L,m}$, where $\Phi_{L,m}$ is a spherical harmonic ($|m| \leqslant L$). We choose the quantization axis parallel to the vector of the radiation whose interaction is defined by the Hamiltonian $\hat{H}_{\rm int} = \mathbf{E}(t)\hat{\mathbf{d}}$. Let $m \approx L \gg 1$, i.e., the oribital-momentum vector is directed along the radiation vector. By virtue of the properties of spherical harmonics, the matrix elements that differ from zero are $\langle \Phi_{L,m} | \hat{H}_{\rm int} | \Phi_{L',m'} \rangle$, and satisfy the selection rules $L' = L \pm 1$ and $m' = m \pm 1$, while under the condition $m \approx L \gg 1$ we have

$$|\langle \Phi_{L,m} | \hat{H}_{int} | \Phi_{L\pm1,\, m\pm1} \rangle| \approx 1/2, \qquad |\langle \Phi_{L,m} | \hat{H}_{int} | \Phi_{L\pm1,\, m\mp1} \rangle| \sim 1/L.$$

The transitions $L, m \to L + 1, m - 1$; $L, m \to L - 1, m + 1$ can thus be neglected and consequently the rotational state of the molecule can be characterized by only one quantum number, which is tantamount to a transition to the two-dimensional case.

6. ISOLATED QUANTUM NONLINEAR RESONANCE

Let us construct the quasi-energy eigenstates of the system (5.2) and (5.3). We represent the system wave function in the form

$$\psi(t, r, \varphi) = \sum_{n=0}^{\infty} \sum_{l=-\infty}^{\infty} c_{n,l}(t) e^{-i\omega n t} (2\pi)^{-1/2} e^{il\varphi} \rho_n(r - r_0). \tag{6.1}$$

We substitute (6.1) in a Schrödinger equation with a Hamiltonian (5.2). Discarding the nonresonant terms, we obtain the following equation for the coefficients $c_{n,l}(t)$:

$$\begin{aligned} &i\hbar\dot{c}_{n,l} = [\hbar(\Omega - \omega)n - x\hbar\Omega n^2 + Bl^2] c_{n,l} \\ &+ 1/4\, W[(n+1)^{1/2} c_{n+1,\, l+1} + n^{1/2} c_{n-1,\, i-1}]. \end{aligned} \tag{6.2}$$

It is clear from (6.2) that only the amplitudes with constant $n - l$ are directly coupled to one another. We introduce $B_n^{(k)} = c_{n,n+k}$. Equation (6.2) goes over then into the equation for the vector $\mathbf{B}^{(k)}(t)$, where the superscript k acts as a parameter. Putting

$$\mathbf{B}^{(k)}(t) = \exp(-i\varepsilon^{(k)} t/\hbar) \mathbf{B}^{(k)},$$

we obtain an equation for the system quasi-energy $\varepsilon^{(k)}$:

$$[\Delta(k)n-\gamma n^2+Bk^2]B_n^{(k)}$$

$$+{}^1/_4W[(n+1)^{1/2}B_{n+1}^{(k)}+n^{1/2}B_{n-1}^{(k)}]=\varepsilon_p^{(k)}B_n^{(k)}, \qquad (6.3)$$

where the parameters $\Delta(k)=\hbar(\Omega-\omega)+2Bk$, $\gamma=x\hbar\Omega-B$ and W coincide with those defined in Secs. 2 and 3 above. Note that Eq. (6.3) can be obtained by direct quantization of the Hamiltonian (3.1) of the classical nonlinear resonance. Notice should be taken here of Ref. 8, where a quasiclassical method of obtaining the quasi-energy levels of a diatomic molecule in the field of an IR laser was proposed for the first time ever on the basis of (3.1). Actually, however, the conditions $W/\gamma\gg 1$ for the validity of the quasiclassical approach (which corresponds for most diatomic molecules to very high external-field intensities) are difficult to meet. It is therefore necessary to calculate the molecule quasi-energy spectrum at the considered intensities $S\sim$ 10–100 GW/cm^2 directly on the basis of Eq. (6.3).

We have computed numerically the quasi-energy spectrum of the system for the parameters of the GeO molecule at $\hbar(\Omega-\omega)=15$ cm^{-1} and for different values of $k(-20\leqslant k\leqslant 20)$. It was found that the distance between the first two quasi-energy levels is constant already at $S=25$ GW/cm^2 (W = 10.72 cm^{-1}), i.e., it is independent of k and of the detuning variation $\hbar(\Omega-\omega)$ (within the spectrum-anharmonicity range). The frequnecy $\Omega_{\rm ph}$ of the transition between these quasi-energy levels is determined exclusively by the interaction W and by the nonlinearity γ. In the case of an external field that is at resonance with the transition $n\leftrightarrow n+1$, where $n\gg 1$, we have $\Omega_{\rm ph}\propto(Wn^{1/2}\gamma)^{1/2}$ (Refs. 2 and 7). For $n\sim 1$, according to Ref. 9, $\Omega_{\rm ph}\propto\gamma(W^2)^{1/3}$.

7. REGIME OF INTERACTING RESONANCES

The molecule dynamics in the case of linearly polarized radiation was investigated numerically. The fourth-order Runge–Kutta method was used to integrate the following system of equations:

$$i\hbar\dot{c}_{n,l}=[\hbar(\Omega-\omega)n-x\hbar\Omega n^2+Bl^2]c_{n,l}$$

$$+{}^1/_4W(n+1)^{1/2}(c_{n+1,\,l+1}+c_{n+1,\,l-1})+{}^1/_4Wn^{1/2}(c_{n-1,\,l+1}+c_{n-1,\,l-1}). \qquad (7.1)$$

The computation accuracy was monitored against the normalization conservation $\Sigma_{n,l}|c_{n,l}|^2=1$. The system dynamics in the case of circularly polarized radiation was calculated in accordance with the system of equations (6.2). The parameter values were the same as before: $\hbar(\Omega-\omega)=15$ cm^{-1}, $x\hbar\Omega=4.2$ cm^{-1}, $B=0.48$ cm^{-1}, $W=10.72$ cm^{-1}. The initial condition was chosen to be a ground-state population ($|c_{0,0}|=1$). In this case only amplitudes with $n=l$ can differ from zero. Integration has shown that at the chosen values of the parameters and of the intial population, in the case of an isolated QNR (circularly polarized field), six or seven vibrational-rotational levels become involved in the dynamics of the transition. (On the average, the population of the sixth level $|c_{6,6}|^2$, was 10%, that of the seventh (1%), and that of the eighth (0.1%). It is seen from Fig. 1 that this is in full agreement with the classical estimate of the vibrational levels that are captured into nonlinear resonance (the size of the region bounded by the separatrix). In the case of linearly polarized radiation, 7–8 levels with n and 21–25 levels with l were captured into resonance, i.e., altogether 200 vibrational–rotational levels.

It is convenient to choose as the observable quantity that characterizes the molecule motion the high-frequency component of the molecule polarization:

$$P_x(t)=\tilde{P}_x^{(s)}(t)\sin\omega t+\tilde{P}_x^{(c)}(t)\cos\omega t,$$
$$P_y(t)=\tilde{P}_y^{(s)}(t)\sin\omega t+\tilde{P}_y^{(c)}(t)\cos\omega t, \qquad (7.2)$$

where

$$\tilde{P}_{x,y}^{(s)}(t)=\frac{1}{T}\int_0^T\langle\psi(t)|\hat{d}_{x,y}|\psi(t)\rangle\sin\omega t\,dt,\qquad T=\frac{2\pi}{\omega}$$

and an analogous expression for $\tilde{P}_{x,y}^{(c)}$, with $\sin\omega t$ replaced by $\cos\omega t$. Since the radiation intensity is proportional to the second derivative of the polarization, the frequency spectrum of $\tilde{P}(t)$ determines the spectral composition of the proper high-frequency radiation of the molecule. Using the expansion (6.1) of the wave function, we have following expressions for $\tilde{P}(T)$ in terms of the coefficients $c_{n,l}(t)$:

$$\tilde{P}_x^{(s)}\sim\operatorname{Im}\left(\frac{\tilde{P}^++\tilde{P}^-}{2}\right),\qquad \tilde{P}_y^{(s)}\sim\operatorname{Re}\left(\frac{\tilde{P}^+-\tilde{P}^-}{2}\right),$$
$$\tilde{P}_x^{(c)}\sim\operatorname{Re}\left(\frac{\tilde{P}^++\tilde{P}^-}{2}\right),\qquad \tilde{P}_y^{(c)}\sim\operatorname{Im}\left(\frac{\tilde{P}^+-\tilde{P}^-}{2}\right). \qquad (7.3)$$

where

$$\tilde{P}^\pm(t)=\frac{1}{2}\sum_l\sum_n n^{1/2}c^*_{n-1,l\pm1}(t)c_{n,l}(t). \qquad (7.4)$$

Note that in the case of an isolated resonance, if the initial condition is chosen in the form of the population of a single level we have $\tilde{P}^+(t)\equiv 0$, and thus $\tilde{P}_y^{(s)}=-\tilde{P}_x^{(c)}$ and $\tilde{P}_y^{(c)}=-\tilde{P}_x^{(s)}$. In addition, in the case of a linearly polarized field, for a symmetric initial condition (in particular, when the ground state is populated), we have by virtue of the symmetry of the solution $\tilde{P}_y^{(c,s)}(t)\equiv 0$.

Figure 2 shows the time dependences of $\tilde{P}_x^{(c)}$ and their frequency spectrum

$$\tilde{P}(\nu)=\langle\tilde{P}(t)e^{-i\nu t}\rangle$$

(the angle brackets denote averaging over the time) in the case of perpendicularly (b) and linearly (a) polarized radiation. For convenience, the polarization is normalized to the intensity of the field interaction with the molecule, corresponding to replacement of the approximation symbol in (7.3) by an equal sign. The corresponding plots for $\tilde{P}_x^{(s)}$ are similar in form. It is clear from Fig. 2 that in the isolated QNR regime the proper spectrum $\tilde{P}(\nu)$ is a set of a small number of well-resolved lines. In the interacting QNR regime, on the contrary, the molecule polarization $\tilde{P}(t)$ constitutes a very complicated quasi-periodic process with a nearly continuous spectrum. This result agrees with the conclusion that quasi-chaos is present in the system of the quasi-interacting QNR obtained earlier in Ref. 2 on the basis of a model Hamiltonian. Note that according to Ref. 2 the qualitative differences between the two regimes increase when the external-field intensity is increased.

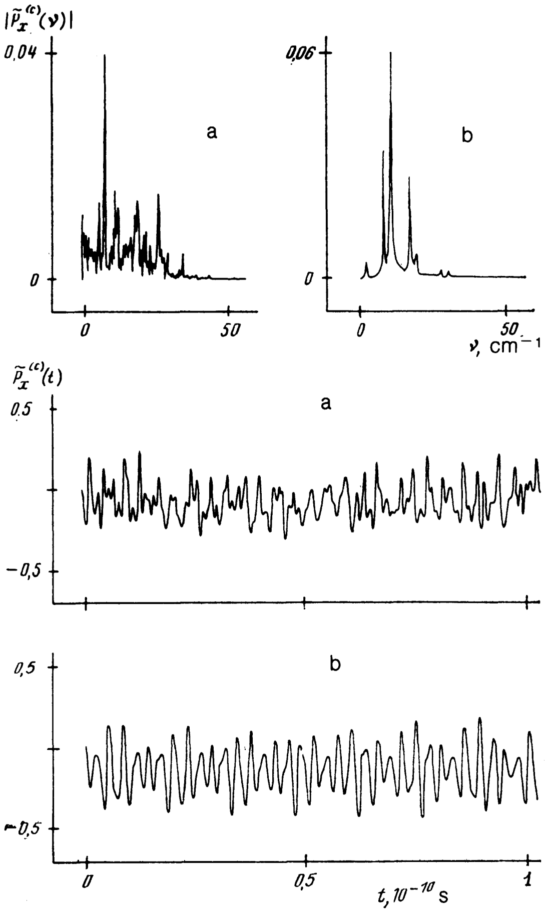

FIG. 2. Time dependence of the polarization $\tilde{P}(t)$ (7.2) of a diatomic molecule and its Fourier spectrum in linearly (a) and circularly (b) polarized fields. The polarization is normalized to the interaction of the field with the molecule. The Fourier spectrum is shown only for positive values of ν, the plot being symmetric for negative ν. The numerical calculation is based on (6.2), (7.3), and (7.4) for the parameters of Fig. 1. The initial condition was chosen to be a population $|c_{0,0}(0)| = 1$ of the ground state of the molecule.

8. CONCLUSION

The results above show that a diatomic molecule in an intense IR field is a promising object for the investigation of quantum stochasticity. An advantage of this system over a Rydberg atom in a microwave field is that quantum chaos can be realized without a preliminary selective excitation into the region of high-lying levels.

We have confined ourselves in this paper to a two-dimensional case. The reason is that the two-dimensional case, on the one hand, is much more illustrative, and on the other it makes it possible to take into account the main effects connected with the influence of the rotational degree of freedom on the dynamics of the vibrational transitions. A change to the three-dimensional case entails allowance for $(2L+1)$-fold degeneracy of the rotational state of the molecule with respect to the magnetic quantum number. In principle (at least from the standpoint of computer experiments) allowance for degeneracy of the rotational levels does not raise unsurmountable difficulties.

We conclude by considering one more question, not directly connected with our results, namely the problem of the onset of a quasi-continuum in complex molecule systems. It is common knowledge that an external field can be regarded as an additional degree of freedom. In this sense the situation investigated above is close to the problem of determining the eigenspectrum of a conservative system with three degrees of freedom (e.g., a triatomic molecule). Drawing an analogy between the quasi-energy spectrum of a diatomic molecule and the radiation field in the energy spectrum of a polyatomic molecule, we can assume that the stochastic mechanism connected with the QNR interaction is one of the possible ways that a quasi-continuous spectrum can be produced in complex systems with a large number of degrees of freedom.

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