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Nonlinear resonance and dynamical chaos in a diatomic molecule driven by a resonant ir field

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We consider the transition from regular motion to dynamical chaos in a classical model of a diatomic molecule which is driven by a circularly polarized resonant ir field. Under the conditions of a nearly two-dimensional case, the Hamiltonian reduces to that for the nonintegrable motion of a charged particle in an electromagnetic wave [A. J. Lichtenberg and M. A. Lieberman, *Regular and Stochastic Motion* (Springer-Verlag, City, 1983)]. In the general case, the transition to chaos is connected with the overlapping of vibrational-rotational nonlinear resonances and appears even at rather low radiation field intensity, $S \gtrsim 1$ GW/cm^2. We also discuss the possibility of experimentally observing this transition.

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I. INTRODUCTION

The theoretical and experimental investigation of dynamical chaos in atomic and molecular, mesoscopic systems, and, in particle, physics, is of considerable current interest (see [1–17] and references therein). Under certain conditions, such systems can be described by model Hamiltonians possessing only a few degrees of freedom. In this low-dimensional situation, the conditions of transition to dynamical chaos are well understood at the classical level [1,18,19]. At the quantum level of description, such systems are usually considered in the quasiclassical region of parameters [2–12]. Quantum motion in parameter regions for which classically chaotic behavior occurs is called "quantum chaos." For example, in quantum nonlinear optics, a transition from "regularity" to "quantum chaos" is often invoked to describe the dynamical and spectral properties of Rydberg states of atoms and molecules interacting with an external resonant field, or taking into account the interactions among various internal degrees of freedom [2–12].

We consider the problem of investigating nonintegrable optical systems that are initially populated in the ground state, or are weakly excited. In this case, one does not need to prepare atoms or molecules in a Rydberg state. This approach is also used (see, for example [12,13]), in studying the interaction of weakly excited molecules with a resonant external field.

In the present paper we determine the conditions for transition from regular motion to dynamical chaos in a system consisting of a diatomic molecule driven by a circularly polarized resonant ir field. We describe the molecule's dynamics at the classical level. The quantum description will be considered separately. The transition to dynamical chaos in this system is found to be due to the overlapping of vibrational-rotational nonlinear resonances (NR's), under rather moderate intensity of the external radiation. Moreover, in this system the transition to chaos appears at rather small molecular excitation energy. Thus, there is no need to prepare the diatomic molecule in a Rydberg state. The model we consider consists of a diatomic molecule with one vibrational and two rotational degrees of freedom. This molecule has a dipole interaction with an external resonant ir electric field, which is taken to be circularly polarized. Thus, the system we consider has 3.5 degrees of freedom. In this system, nonlinear resonance occurs between the external resonant ir field and the vibrational degree of freedom. The appearance of such NR's in nonlinear classical Hamiltonian systems interacting with an external resonant field is discussed in detail in, e.g. [1,18,19]. The quantum analog of NR was introduced in [20], and studied for various quantum systems in [13,17,19,21] (see also references therein). Different aspects of nonlinear dynamics of vibrational-rotational degrees of freedom in diatomic molecule, interacting with the external resonant field, are also considered in [22–24].

A NR is usually characterized by two main parameters [18]: its width in action $(\Delta n)_{\max}$, and the frequency of slow phase oscillations near its center, ω_{ph}. We assume that the value of the constant of interaction W of the molecule with the external field is sufficiently small that the condition $\omega_{\mathrm{ph}} \ll \omega$ is satisfied, where ω is the frequency of the resonant ir field. At the same time, the following conditions also can be satisfied: $\omega_{\mathrm{ph}} \sim \dot{\theta} \sim \dot{\varphi}$, where θ and φ are the angles of the molecule's rotation. In this case, vibrational-rotational NR's appear. These NR's are well isolated at $W < W_{\mathrm{cr}}$, where W_{cr} is a certain critical value of W. In this paper we show that W_{cr} corresponds to the value of the intensity of the external ir field at which $S_{\mathrm{cr}} \equiv cE_0^2/8\pi \sim 1$ GW/cm^2. For $W > W_{\mathrm{cr}}$, the NR's overlap significantly, and the dynamics of the molecule become chaotic over most of its phase space volume. It is important to note that when considering Rydberg states of diatomic molecules, the electron degrees of freedom can also be involved in the resonant dynamics even at small amplitudes of an external field. Actually, at the field intensities of the order 1 GW/cm^2, even nonresonant interaction can perturb significantly the electronic states of a diatomic molecule. We shall consider these two problems elsewhere.

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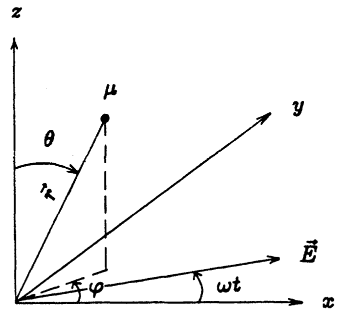

FIG. 1. Diatomic molecule in the spherical system of coordinates $(\vec{r},\theta,\varphi)$. The resonant ir electric field is circularly polarized in the (x,y) plane; ωt is the phase of the electric field.

One of the main results of this paper is the following. We show that the transition to chaos due to overlapping of the vibrational-rotational NR's appears in a diatomic molecule even for the ground state in the case of a circularly polarized resonant ir field and at rather moderate field intensity. We believe this circumstance suggests considering the system (diatomic molecule)+(circularly polarized resonant ir field) as a promising candidate for investigating the transition to dynamical chaos in molecular systems under weak initial excitation.

In Sec. II we describe the model and introduce the Hamiltonian, which describes its slow resonant dynamics. Sec. III is devoted to the analytical consideration of the resonant dynamics, which is nearly two dimensional. We show that the initial Hamiltonian reduces in this case to the Hamiltonian for the motion of a charged particle driven by an electromagnetic wave [1]. Section IV considers an isolated NR. Section V concludes with the results of numerical calculations on the transition from regular motion to dynamical chaos and discusses the possibility of experimental observation of this transition.

II. DESCRIPTION OF THE MODEL

To describe the dynamics of a diatomic molecule driven by a resonant ir field, we shall use a basis model that consists of two point masses m_1 and m_2 interacting through the potential $U(\vec{r})$, where $\vec{r}=\vec{r}_1-\vec{r}_2$ is a radius vector connecting masses m_1 and m_2. The potential $U(\vec{r})$ depends only on the modulus of the radius-vector $r\equiv|\vec{r}|$, and has a minimum at the point $r=r_0$. It is natural to describe the dynamics of the molecule in the center-of-mass reference system with radius-vector $\vec{R}=(m_1\vec{r}_1+m_2\vec{r}_2)/(m_1+m_2)$. It is known that in this system of reference $(\vec{R}=0)$ a diatomic molecule can be described effectively as a single particle with a reduced mass $\mu=m_1m_2/(m_1+m_2)$. Then, in a spherical system of reference, a diatomic molecule is characterized by two angles θ and φ, and by $r=|\vec{r}_1-\vec{r}_2|$ (see Fig. 1).

The vibrations of the molecule along the $\vec{r}$ direction are described by using the action I and phase ϑ. The rotational motion in angles θ and φ is described using the angular momentum L. In this case, the unperturbed Hamiltonian has the form

$$H_0(I,L^2)=\left(\frac{dH_0}{dI}\right)I+\frac{1}{2}\left(\frac{d^2H_0}{dI^2}\right)I^2+\left(\frac{dH_0}{dL^2}\right)L^2. \tag{2.1}$$

It is convenient to introduce the following dimensionless variables

$$n=I/\hbar, \quad l=L/\hbar, \tag{2.2}$$

$$x_e=\hbar|(d^2H_0/dI^2)|/2\omega_e, \quad B=\hbar^2(dH_0/dL^2),$$

$$(\omega_e=dH_0/dI).$$

In this paper we shall consider only the classical dynamics of a diatomic molecule driven by a resonant ir field. In spite of this, the variables (2.2) are useful for comparison with the corresponding quantum dynamics, which will be considered in a separate paper. In dimensionless variables (2.2), the unperturbed Hamiltonian (2.1) takes the form

$$H_0(n,l^2)=\hbar\omega_e n-\hbar x_e\omega_e n^2+Bl^2. \tag{2.3}$$

To construct the interaction Hamiltonian, we introduce the vector of the dipole moment $\vec{d}$ of the molecule, and the vector of the external resonant electric field $\vec{E}(t)$, given by

$$\vec{d}=d(r)(\sin\theta\cos\varphi,\sin\theta\sin\varphi,\cos\theta), \tag{2.4}$$

$$\vec{E}(t)=(E_x(t),E_y(t),E_z(t)). \tag{2.5}$$

It follows from (2.4) that the dipole moment of the molecule depends on the value of r. We express r in the form

$$r=r_0+\sqrt{\frac{2\hbar n}{\mu\omega_e}}\cos\vartheta, \tag{2.6}$$

where ϑ is the phase of the molecule's vibrational oscillations along the radius $\vec{r}$, and is canonically conjugate to the action I. Using (2.6), we express the dipole moment $d(r)$ as follows

$$d(r)=e_{\text{eff}}r=d_0+e_{\text{eff}}\sqrt{\frac{2\hbar n}{\mu\omega_e}}\cos\vartheta, \tag{2.7}$$

where $d_0\equiv e_{\text{eff}}r_0$.

Using Eqs (2.4) and (2.5) allows us to express the Hamiltonian for the interaction of the molecule with the resonant field $\vec{E}(t)$ in the form

$$\begin{aligned}H_{\text{int}}=&-(\vec{d},\vec{E})=-(\vec{d}_0,\vec{E})-e_{\text{eff}}\sqrt{\frac{2\hbar n}{\mu\omega_e}}\\&\times\cos\vartheta[E_x(t)\sin\theta\cos\varphi\\&+E_y(t)\sin\theta\sin\varphi+E_z(t)\cos\theta].\end{aligned} \tag{2.8}$$

The unperturbed Hamiltonian, which describes the one-dimensional oscillations and two-dimensional rotations of the molecule, is expressed as

$$H_0(I,\vartheta;p_\theta,\theta;p_\varphi,\varphi)=\omega_e I-\tilde{x}_e\omega_e I^2+\frac{1}{2\mu r_0^2}\left(p_\theta^2+\frac{p_\varphi^2}{\sin\theta^2}\right)$$

$$\equiv H_0^{(\mathrm{os})}+H_0^{(\mathrm{rot})}, \tag{2.9}$$

where $p_\theta=\mu r_0^2\dot{\theta}$, $p_\varphi=\mu r_0^2\sin^2\theta\dot{\varphi}$, and $x_e=\hbar\tilde{x}_e$.

The rotational part of the unperturbed Hamiltonian in (2.9) can be written in the form

$$H_0^{(\mathrm{rot})}=L^2/2\mu\ r_0^2, \qquad \text{with} \quad L^2=\mu^2 r_0^4(\dot{\theta}^2+\sin^2\theta\dot{\varphi}^2). \tag{2.10}$$

In what follows, we consider only the case of a circularly polarized electric field $\vec{E}(t)$, which rotates in the plane (x,y)

$$\vec{E}(t)=E_0(\cos\omega t,\sin\omega t), \quad E_z(t)=0. \tag{2.11}$$

Next, we introduce the resonant Hamiltonian, which describes the dynamics of the molecule on a time scale large compared to $1/\omega$. This Hamiltonian corresponds to neglecting rapidly oscillating terms $\sim\exp(\pm 2i\omega t)$. We assume that the frequency of the external field ω is resonant with the molecule's oscillation frequency ω_e ($\omega\approx\omega_e$) and significantly exceeds the rotational frequencies with respect to θ and φ, that is,

$$\omega\approx\omega_e\gg|\dot{\varphi}|,|\dot{\theta}|. \tag{2.12}$$

In this case, the resonant Hamiltonian takes the form

$$H=\omega_e I-\tilde{x}_e\omega_e I^2+\frac{1}{2\mu r_0^2}\left(p_\theta^2+\frac{p_\varphi^2}{\sin^2\theta}\right)$$

$$-\frac{e_{\mathrm{eff}}E_0}{2}\sqrt{\frac{2I}{\mu\omega_e}}\sin\theta\cos(\vartheta+\varphi-\omega t). \tag{2.13}$$

The Hamiltonian (2.13) implies the following equations of motion

$$\dot{I}=-\frac{\partial H}{\partial\vartheta}=-\frac{e_{\mathrm{eff}}E_0}{2}\sqrt{\frac{2I}{\mu\omega_e}}\sin\theta\sin(\vartheta+\varphi-\omega t), \tag{2.14}$$

$$\dot{\vartheta}=\frac{\partial H}{\partial I}=\omega_e-2\tilde{x}_e\omega_e I-\frac{e_{\mathrm{eff}}E_0}{2}\sqrt{\frac{1}{2\mu\omega_e I}}$$

$$\times\sin\theta\cos(\vartheta+\varphi-\omega t),$$

$$\dot{p}_\theta=-\frac{\partial H}{\partial\theta}=\frac{p_\varphi^2\cos\theta}{\mu r_0^2\sin^3\theta}+\frac{e_{\mathrm{eff}}E_0}{2}\sqrt{\frac{2I}{\mu\omega_e}}$$

$$\times\cos\theta\cos(\vartheta+\varphi-\omega t),$$

$$\dot{\theta}=\frac{\partial H}{\partial p_\theta}=\frac{p_\theta}{\mu r_0^2},$$

$$\dot{p}_\varphi=-\frac{\partial H}{\partial\varphi}=-\frac{e_{\mathrm{eff}}E_0}{2}\sqrt{\frac{2I}{\mu\omega_e}}\sin\theta\sin(\vartheta+\varphi-\omega t),$$

$$\dot{\varphi}=\frac{\partial H}{\partial p_\varphi}=\frac{p_\varphi}{\mu r_0^2\sin^2\theta}.$$

These equations possess the integral of motion

$$p_\varphi-I=\mathrm{const}=\hbar k, \tag{2.15}$$

which has a simple physical meaning. Namely, in the *resonant* approximation, the photons of a circurlaly polarized external ir field simultaneously excite both a vibrational and a rotational degree of freedom with the same number of quanta. In the quantum case, the integral (2.15) corresponds to the operator $\hat{Q}=\hat{L}_z-\hbar\hat{a}^\dagger\hat{a}$, where $\hat{L}_z=-i\hbar\partial/\partial\varphi$, and $\hat{a}^\dagger$ and $\hat{a}$ are the vibrational creation and annihilation operators, respectively. So, the quantum case obeys the following selection rules: $\Delta l=1$, $\Delta m=1$, $\Delta n=1$, where l, m, are rotational quantum numbers, and n is a vibrational quantum number. Using the integral (2.15) allows us to introduce a new effective resonant Hamiltonian which depends on the following canonically conjugate variables:

$$\psi=\vartheta+\varphi-\omega t, \quad n=I/\hbar; \quad \text{and} \quad \theta, \quad p=p_\theta/\hbar. \tag{2.16}$$

In the variables (2.16), the Hamiltonian (2.13) takes the form

$$H_{\mathrm{eff}}=\frac{\hbar(\omega_e-\omega)n}{\hbar\Omega}-\frac{\hbar x_e\omega_e n^2}{\hbar\Omega}+\frac{Bp^2}{\hbar\Omega}+\frac{B(k+n)^2}{\hbar\Omega\sin^2\theta}$$

$$-\frac{W}{2\hbar\Omega}\sqrt{n}\sin\theta\cos\psi. \tag{2.17}$$

In writing the effective Hamiltonian (2.17), we have introduced the following dimensionless notations

$$\tau=\Omega t, \quad W=e_{\mathrm{eff}}E_0\sqrt{\frac{2\hbar}{\mu\omega_e}}, \tag{2.18}$$

where $\hbar\Omega$ is a normalization energy. The Hamiltonian (2.17) describes the slow (resonant) dynamics of a diatomic molecule driven by a resonant circularly polarized electric field.

III. RESONANT PERTURBATION THEORY

For convenience, we choose the normalization energy in (2.17) as

$$\hbar\Omega=1\ \mathrm{cm}^{-1}. \tag{3.1}$$

This choice of $\hbar\Omega$ corresponds to an energy ≈ 1 K, which is a characteristic excitation energy of the rotational degrees of freedom.

Small oscillations in θ

The case of small oscillations in θ in the vicinity of $\theta=\pi/2$ can be considered analytically. Then, the motion of a molecule is close to the two-dimensional (2D) case on the (x,y) plane considered in [12]. We shall show that in the case of small oscillations in θ, the effective Hamiltonian (2.17) can be reduced to the Hamiltonian for the dynamics of a charged particle driven by a sinusoidal electromagnetic wave [1].

Consider $\theta=\pi/2+\varepsilon$ ($|\varepsilon|\ll 1$). Then, an approximate expression for $H_{\rm eff}$ follows from (2.17). Namely,

$$H_{\rm eff}=\hbar(\omega_e-\omega)n-\hbar x_e\omega_e n^2+B(k+n)^2+Bp^2 +B(k+n_0)^2\varepsilon^2-\frac{W\sqrt{n_0}}{4}[\cos(\psi+\varepsilon)+\cos(\psi-\varepsilon)]. \tag{3.2}$$

The variation of n is assumed to be small in the vicinity of n_0 (In the following n_0 is a number less then, say, ten).

We introduce new canonical variables J and ϕ for the rotational motion in θ, as

$$\Omega_* J=Bp^2+B(k+n_0)^2\varepsilon^2, \tag{3.3}$$

where

$$\Omega_*=2B|k+n_0|. \tag{3.4}$$

The variable ϕ canonically conjugate to the action J, is related to ε by

$$\varepsilon=\sqrt{\frac{2J}{|k+n_0|}}\sin\phi. \tag{3.5}$$

It is easy to see that $|\partial(p,\varepsilon)/\partial(J,\phi)|=1$, so the transformation to J and ϕ is canonical. The Hamiltonian $H_{\rm eff}$ (3.2) is expressible in the new variables as

$$H_{\rm eff}=\hbar(\omega_e-\omega)n-\hbar x_e\omega_e n^2+B(k+n)^2+\Omega_* J -\frac{W\sqrt{n_0}}{4}\left\{\cos\left(\psi+\sqrt{\frac{2J}{|k+n_0|}}\sin\phi\right) +\cos\left(\psi-\sqrt{\frac{2J}{|k+n_0|}}\sin\phi\right)\right\}. \tag{3.6}$$

Using the formula

$$e^{i(\psi+z\sin\phi)}=\sum_{m=-\infty}^{\infty}J_m(z)e^{i(\psi+m\phi)}, \tag{3.7}$$

we derive from (3.6) for $H_{\rm eff}$

$$H_{\rm eff}=[\hbar(\omega_e-\omega)+2Bk]n-(\hbar x_e\omega-B)n^2+\Omega_* J -\frac{W\sqrt{n_0}}{2}\sum_{l=-\infty}^{\infty}J_{2l}(z)\cos(\psi-2l\phi),$$
$$z=\sqrt{2J/|k+n_0|}. \tag{3.8}$$

The substitutions

$$\bar\psi=\psi+\pi/2,\quad \bar\omega=\hbar(\omega_e-\omega)+2Bk,\quad \varepsilon e\Phi_0=W\sqrt{n_0}/2, \tag{3.9}$$
$$k_z^2/2M=\hbar x_e\omega_e-B,\quad k_\perp=\sqrt{2BM},\quad \rho=\sqrt{2J/M\Omega_*},$$

reduce the Hamiltonian (3.8) to the same form as the Hamiltonian for the motion of a charged particle in a sinusoidal electromagnetic wave [1], namely,

$$-H_{\rm eff}=\frac{k_z^2}{2M}n^2-\bar\omega n-\Omega_* J+\varepsilon e\Phi_0 \times\sum_{l=-\infty}^{\infty}J_{2l}(k_\perp\rho)\sin(\bar\psi-2l\phi). \tag{3.10}$$

The canonically conjugate variables in the Hamiltonian (3.10) are $(n,\bar\psi)$ and (J,ϕ).

IV. AN ISOLATED NONLINEAR RESONANCE

Following [1], we introduce a slow phase $\tilde\psi$ and an action $\tilde J$, given by

$$\tilde\psi=\bar\psi-2l_0\phi-\pi/2,\quad \tilde J=J+2l_0 n, \tag{4.1}$$

where $(n,\tilde\psi)$ and $(\tilde J,\phi)$ are new canonically conjugate variables. The number $l=l_0$ specifies a given resonance. The substitution (4.1) transforms the expression for $H_{\rm eff}$ in (3.10) into

$$-H_{\rm eff}=\frac{k_z^2}{2M}n^2-\bar\omega n-\Omega_*(\tilde J-2l_0 n) +\varepsilon e\Phi_0\sum_{l=-\infty}^{\infty}J_{2l}(k_\perp\rho)\cos[\tilde\psi-2(l-l_0)\phi], \tag{4.2}$$

where

$$\rho=\sqrt{2(\tilde J-2l_0 n)/M\Omega_*}. \tag{4.3}$$

Averaging over the fast phase ϕ gives an effective Hamiltonian, which describes the dynamics in the vicinity of an isolated nonlinear resonance associated with the number $l=l_0$

$$\langle -H_{\rm eff}^{(l_0)}\rangle=\frac{k_z^2}{2M}n^2-\bar\omega n-\Omega_*(\tilde J-2l_0 n) +\varepsilon e\Phi_0 J_{2l_0}(k_\perp\rho)\cos\tilde\psi. \tag{4.4}$$

It follows from (4.4) that the value

$$\tilde J=J+2l_0 n \tag{4.5}$$

is an integral of motion. We estimate the parameters of the l_0th resonance. For this, we expand the expression in (4.4) in the vicinity of the nonlinear resonance, which is defined by the equations

$$\frac{k_z^2}{M}n_0+2l_0\Omega_*-\bar\omega=0,\quad J=J_0,\quad \rho=\rho_0\equiv\sqrt{\frac{2J_0}{M\Omega_*}}. \tag{4.6}$$

Using (4.5) and (4.6), we have from (4.4) the resonant Hamiltonian, which coincides with the Hamiltonian describing the dynamics of the pendulum,

$$\langle -H_{\rm eff}^{(l_0)}\rangle=\frac{k_z^2}{2M}(\Delta n)^2+\varepsilon e\Phi_0 J_{2l_0}(k_\perp\rho_0)\cos\tilde\psi, \tag{4.7}$$

where $\Delta n = n - n_0$. Thus, the resonant dynamics described by the Hamiltonian (4.7) is effectively one dimensional and integrable. The stable stationary point is $\tilde{\psi} = \pi$. The unstable hyperbolic stationary point corresponds to $\tilde{\psi} = 0$ (or 2π). The frequency of slow phase oscillations in the vicinity of this stationary point is given by the expression

$$\omega_{\mathrm{ph}} = |\varepsilon e \Phi_0 J_{2l_0}(k_\perp \rho) k_z^2 / M|^{1/2}. \tag{4.8}$$

The width $(\Delta n)_{\max}$ of the nonlinear resonance is usually defined as the distance between two separatrixes [1,18]. For the Hamiltonian (4.7), we have

$$(\Delta n)_{\max} = 4\omega_{\mathrm{ph}} M / k_z^2. \tag{4.9}$$

Now we derive the conditions under which the l_0th nonlinear resonance described by the Hamiltonian (4.7) can be regarded as isolated. First, we estimate the distance δn between neighboring resonances associated with the numbers l_0 and $l_0 \pm 1$. We have from (4.4) and (4.6)

$$\delta n = 2M\Omega_* / k_z^2. \tag{4.10}$$

Using (4.9) and (4.10), we find the Chirikov's criterion for resonances to overlap [18]:

$$K = \frac{(\Delta n)_{\max}}{\delta n} = \frac{2\omega_{\mathrm{ph}}}{\Omega_*} > 1. \tag{4.11}$$

When $K \ll 1$, the resonances with $l = l_0$ and $l = l_0 \pm 1$ interact weakly and they can be considered as isolated. We may now present the main resonance parameters in the original notation. The frequency of phase oscillations is given by

$$\omega_{\mathrm{ph}} = \sqrt{W\sqrt{n_0}|J_{2l_0}(2\sqrt{BJ_0/\Omega_*})(\hbar x_e \omega_e - B)|}. \tag{4.12}$$

The width of l_0th resonance according to (4.9), is given by the expression

$$(\Delta n)_{\max} = \frac{2\omega_{\mathrm{ph}}}{\hbar x_e \omega_e - B}. \tag{4.13}$$

Using (3.9), the expression (4.10) can be written in the form

$$\delta n = \frac{\Omega_*}{\hbar x_e \omega_e - B}. \tag{4.14}$$

In deriving these expressions, we have used the condition,

$$(\Delta n)_{\max} \ll n_0.$$

In this section, the oscillations in angle θ in the vicinity of $\theta = \pi/2$ are assumed to be small ($|\varepsilon| \ll 1$). According to (3.5), this assumption leads to the following restriction on J

$$2J \ll |k + n_0|. \tag{4.15}$$

In addition, the conservation law (4.5) implies

$$(\Delta J)_{\max} \approx 2l_0 (\Delta n)_{\max}. \tag{4.16}$$

The approximation considered in this section $\rho \approx \rho_0$ (4.6) also requires the following condition to be satisfied: $(\Delta J)_{\max} \ll J$.

V. RESULTS OF NUMERICAL CALCULATIONS

As an example to illustrate the theory developed above, we consider here the diatomic molecule GeO, which has the following parameters [12]:

$$\begin{gathered} \hbar\omega_e = 985.8 \ \mathrm{cm}^{-1}, \ \hbar(\omega_e - \omega) = 15 \ \mathrm{cm}^{-1}, \\ \hbar x_e \omega_e = 4.2 \ \mathrm{cm}^{-1}, \\ B = 0.48 \ \mathrm{cm}^{-1}, \ d_0 = 3.28 \ \mathrm{D}, \ r_0 = 1.62 \ \text{Å}, \\ \mu = 13.1 \ \mathrm{amu}, \end{gathered} \tag{5.1}$$

driven by a resonant ir field of intensity:

$$S \equiv cE^2/8\pi = 2.5 - 25 \ \mathrm{GW/cm^2},$$

which corresponds to $W = 3.39 - 10.72 \ \mathrm{cm}^{-1}$.

Using the results of the previous section, we derive the following estimates (in the approximation of isolated nonlinear resonances) for the primary resonance with $l_0 = 0$, and for two secondary resonances, with $l_0 = \pm 1$. As an example, we take the integral $k = 8$ in (2.15). We have in this case, for $l_0 = 0$, $k = 8$,

$$\begin{gathered} n_0^{(0)} = 3.0483, \quad \omega_{\mathrm{ph}}^{(0)} = 2.549\sqrt{W}, \ (\Delta n)_{\max}^{(0)} = 1.37\sqrt{W}, \\ \Omega_* = 10.606. \end{gathered} \tag{5.2}$$

for $l_0 = 1$, $k = 8$,

$$\begin{gathered} n_0^{(1)} = 0.782, \quad \omega_{\mathrm{ph}}^{(1)} = 0.306\sqrt{WJ_0}, \quad (\Delta n)_{\max}^{(1)} = 0.164\sqrt{WJ_0}, \\ (\Delta J)_{\max}^{(1)} = 0.33\sqrt{WJ_0}, \quad \Omega_* = 8.43. \end{gathered} \tag{5.3}$$

for $l_0 = -1$, $k = 8$,

$$\begin{gathered} n_0^{(-1)} = 6.86, \quad \omega_{\mathrm{ph}}^{(-1)} = 0.404\sqrt{WJ_0}, \\ (\Delta n)_{\max}^{(-1)} = 0.217\sqrt{WJ_0}. \end{gathered} \tag{5.4}$$

In a numerical experiment we constructed the Poincaré map by plotting the points of the dynamical trajectory at the moments of time when they cross the plane $\theta = \pi/2$ with positive velocity, $\dot{\theta} > 0$. As follows from the Hamiltonian (4.7), and from the formulas

$$\tilde{\psi} = \psi - 2l_0\phi, \quad \theta - \pi/2 \approx \sqrt{2J/|k + n_0|}\sin\phi, \tag{5.5}$$

under the conditions of an isolated nonlinear resonance, the crossing points of a dynamical trajectory with the plane $\theta = \pi/2$ are described by the equation

$$H_{\mathrm{eff}}^{(l_0)}(\Delta n, \tilde{\psi}) = \mathrm{const} \tag{5.6}$$

and form an invariant curve. In the numerical experiment, the equations of motion were solved corresponding to the Hamiltonian (2.17). Figures 2(a) and 2(b) show the Poincaré map for the cases (5.2) and (5.3), respectively. According to Figs. 2(a) and 2(b), the motion at the chosen parameters shows satisfactory agreement between the theoretical estimates (5.2) and (5.3), based on the isolated resonance ap-

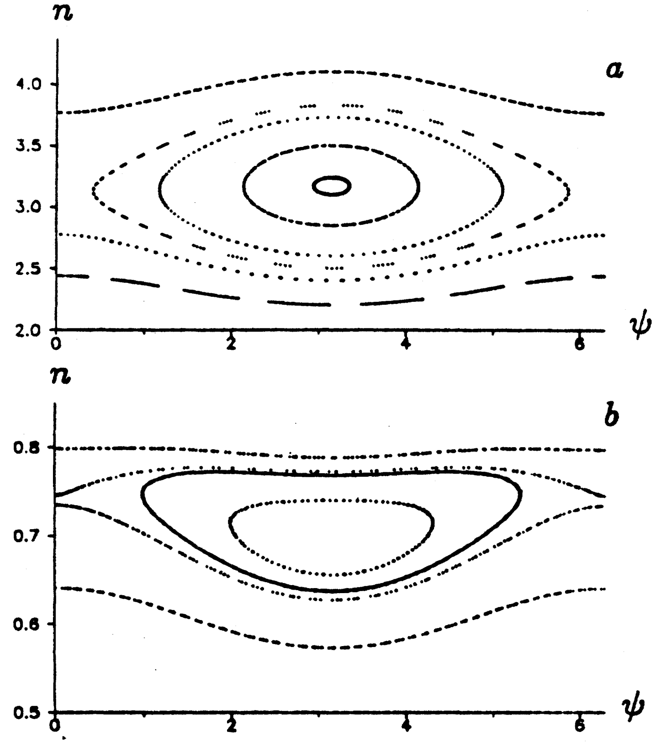

FIG. 2. Regular dynamics. The Poincaré map on the plane (n,ψ) of the dynamical trajectories corresponding to the Hamiltonian (2.17), upon crossing the plane $\theta=\pi/2$ with positive $\dot{\theta}$. Parameters are given in (5.1); $W=1$, $k=8$, $p_\theta(0)=0$, and $\theta(0)=1.2$; (a) the primary resonance $(l_0=0)$; (b) The secondary resonance $(l_0=1)$.

proximation, and the results of the numerical calculations. Figures 3(a) and 3(b) show the dependences $\theta(t)$ and $p_\theta(t)$ for the regular dynamics, at the center of the primary resonance. As one can see, the approximation of small oscillations $(\varepsilon\ll 1)$ is violated in this case.

Note that there exists a significant difference in the description of a diatomic molecule interacting with a circularly polarized resonant ir field using the 2D approach [12] (when $\theta=\pi/2$), and the 3D approach considered above. Indeed, using the variables $(I,\vartheta;p_\varphi,\varphi)$, when a circularly polarized resonant field is applied to a diatomic molecule one sees that only the primary nonlinear resonance with $l_0=0$ can be realized in the 2D approach (see [12]). In the 3D approach considered above, additional nonlinear resonances with $l_0=0$ appear in the system, which are connected with oscillations in the θ degree of freedom. As will be shown below, overlapping of the resonances with $l_0=0,\pm 1$ can lead under the condition $S\gtrsim S_{\mathrm{cr}}\sim 1$ GW/cm^2 to chaotic dynamics of the molecule in the classical description.

We now present the results of numerical calculations under the conditions for transition to the dynamical chaos to occur in the system of "(diatomic molecule)+(resonant circularly polarized ir field)." In Fig 4(a), the primary resonance with $l_0=0$ and the biggest secondary resonance with $l_0=1$ are shown at $k=0$. In this case, the interaction constant W is rather small $(W=0.05)$, and the resonances essentially do not interact. As W increases, the interaction between the resonances becomes more significant. Figure 4(b) shows that for $W=0.5$, the resonances presented in Fig. 4(a) are partly destroyed, and a portion of phase space is filled with a chaotic trajectory. The transition to fully developed dynamical chaos is demonstrated in Figs. 4(c) and 4(d), for $W\geqslant 1$.

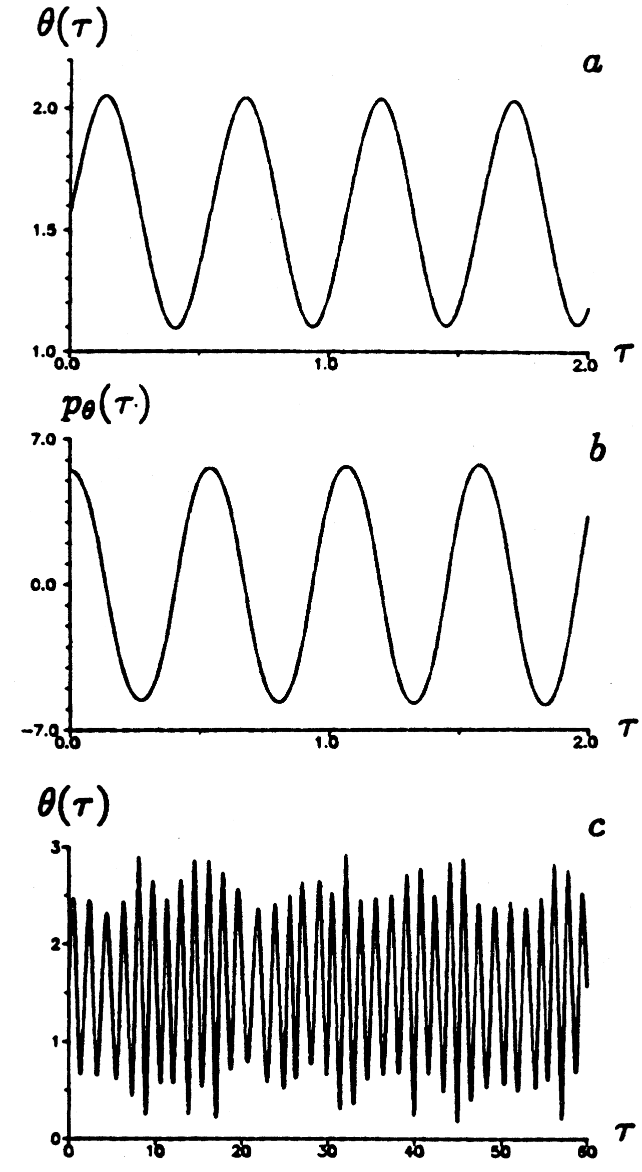

FIG. 3. Dependences of $\theta(\tau)$ and $p_\theta(\tau)$ for regular dynamics, at the center of the primary resonance, (a),(b) $W=1$, $k=8$, (c) dependence $\theta(\tau)$ for one of the chaotic trajectories, $W=1$, $k=0$. Parameters are given in (5.1).

In conclusion, the results of the numerical calculations show that the critical value of the intensity of the external resonant ir field (at which the transition to the dynamical chaos should be expected), is of the order $S_{\mathrm{cr}}\approx 1$ GW/cm^2. When $S\gtrsim S_{\mathrm{cr}}$, the resonances are significantly destroyed and most of the motion in the phase space is chaotic. As shown in [12], if a diatomic molecule is approximated by a 2D model, the transition to the dynamical chaos due to in-

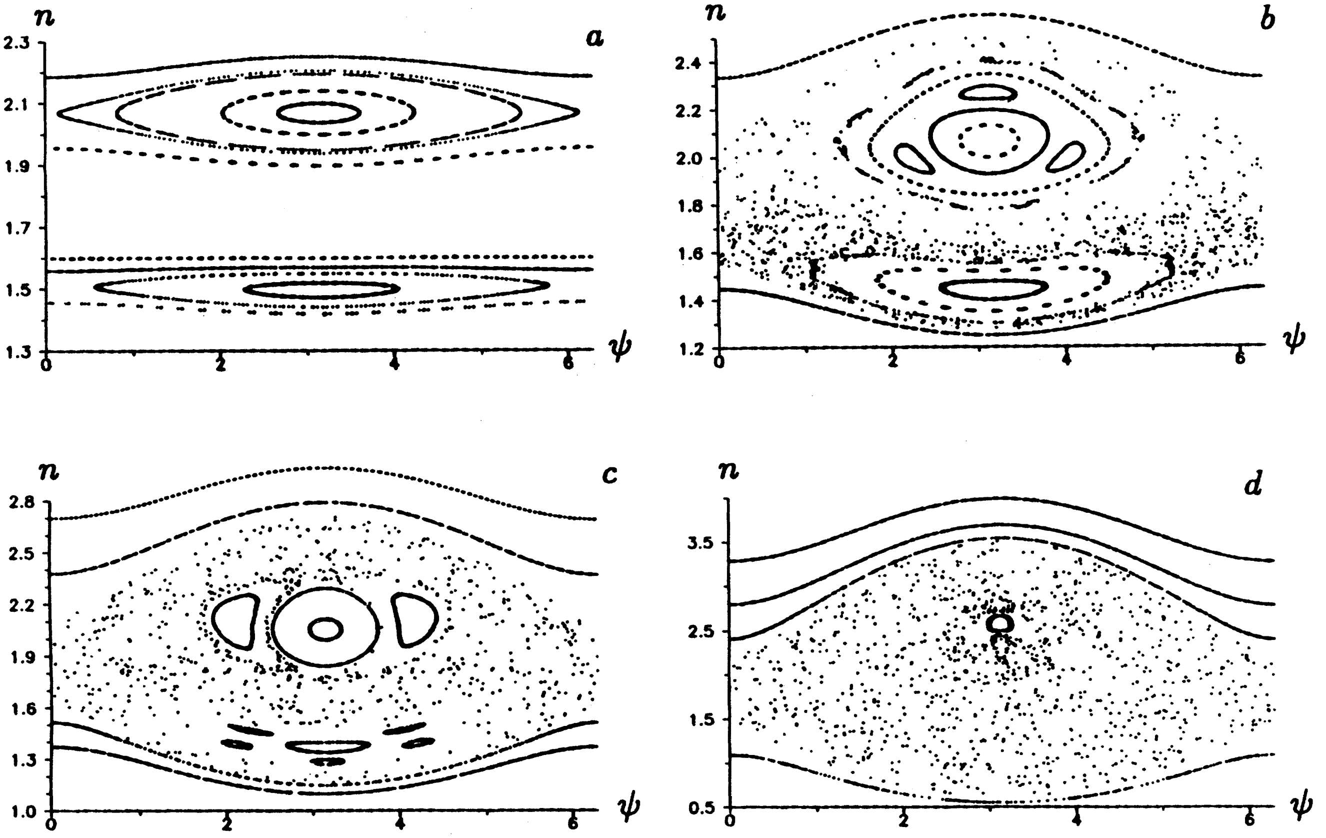

FIG. 4. Transition to dynamical chaos upon overlapping of nonlinear resonances. The Poincaré map is shown in the plane (n,ψ) of the trajectories corresponding to the Hamiltonian (2.17), upon crossing the plane $\theta=\pi/2$ with positive $\dot{\theta}$. Parameters are given in (5.1); $k=0$; (a) $W=0.05$; (b) $W=0.5$; (c) $W=1$; (d) $W=4$.

teraction of vibrational-rotational resonances can be expected only in the case of a linearly polarized resonant ir field, and at rather large resonant ir field intensities of ≈ 25 GW/cm^2. In the 3D diatomic molecule model considered in this paper, the transition to chaos arises for the circularly polarized ir field even at rather small values of the initial population. Thus, this system has an advantage over Rydberg atoms and molecules driven by a microwave field in that the transition to dynamical chaos can be realized without a preliminary excitation into the region of high-lying energy levels. These circumstances allow one to consider the system "(diatomic molecule)+(resonant ir field)" as a promising candidate for investigating the transition to dynamical chaos in molecular systems interacting with coherent radiation. One possibility for observing the transition to chaos experimentally could be to study the frequency spectrum of radiation of the system "(diatomic molecule)+(circularly polarized resonant ir field." In the region of $S\sim S_{\rm cr}$ a qualitative modification of the frequency spectrum should be observed. Namely, for $S<S_{\rm cr}$ the frequency spectrum will have well resolved lines. However, for $S>S_{\rm cr}$, the frequency spectrum should broaden, thereby indicating the transition of the system to dynamical chaos.

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[1] A.J. Lichtenberg and M.A. Lieberman, *Regular and Stochastic Motion* (Springer-Verlag, Berlin, 1983).
[2] J.E. Bayfield and P.M. Koch, Phys. Rev. Lett. **33**, 258 (1974)
[3] P. M. Koch in *Rydberg States of Atoms and Molecules*, edited by R.F. Stebling and F.B. Dunning (Cambridge University Press, New York, 1983).
[4] G. Casati, B.V. Chirikov, D.L. Shepelyansky, and I. Guarnery, Phys. Rep. **154**, 77 (1987).

[5] G.P. Berman, E.N. Bulgakov, and D.D. Holm, *Crossover-Time in Quantum Boson and Spin Systems* (Springer-Verlag, Berlin, 1994).

[6] E.V. Shuryak, Zh. Eksp. Teor. Fiz. **71**, 2039 (1976) [Sov. Phys. JETP **44**, 1070 (1976)].

[7] P. Labastie, M.C. Bordas, B. Tribollet, and M. Broyer, Phys. Rev. Lett. **52**, 1681 (1984).

[8] J. Chevaleyre, C. Bordas, M. Broyer, and P. Labastie, Phys. Rev. Lett. **57**, 3027 (1986).

[9] C. Bordas, P.F. Brevet, M. Broyer, J. Chevaleyre, P. Labastie, and J.P. Perrot, Phys. Rev. Lett. **60**, 917 (1988).

[10] M. Lombardi, P. Labastie, M.C. Bordas, and M. Broyer, J. Chem. Phys. **89**, 3479 (1988).

[11] M. Lombardi and T.H. Seligman, Phys. Rev. A **47**, 3571 (1993).

[12] G.P. Berman and A.R. Kolovsky, Zh. Eksp. Teor Fiz. **95**, 1552 (1989) [Sov. Phys. JETP **68**, 898 (1989)].

[13] G.P. Berman and A.R. Kolovsky, Usp. Fiz. Nauk **162**, 95 (1992) [Sov. Phys. Usp. **35**, 303 (1992)].

[14] K.N. Alekseev, G.P. Berman, and D.K. Campbell, Phys. Lett. A, **193**, 54 (1994).

[15] M.S. Sherwin, in *Quantum Chaos*, edited by G. Casati and B.V. Chirikov (Cambridge University Press, Cambridge, England, 1995), p. 209.

[16] G.P. Berman, E.N. Bulgakov, D.D. Holm, and Y. Kluger, Phys. Lett. A **194**, 251 (1994)

[17] M. Holthaus, Prog. Theor. Phys. **116**, 417 (1994).

[18] B.V. Chirikov, Phys. Rep. **52**, 263 (1979).

[19] L.E. Reichl, *The Transition to Chaos* (Springer-Verlag, Berlin, 1992).

[20] G.P. Berman and G.M. Zaslavsky, Physica A **61**, 295 (1977).

[21] G.P. Berman, E.N. Bulgakov, and D.D. Holm, Physica D **83**, 55 (1995).

[22] P.S. Dardi and S.K. Gray, J. Chem. Phys. **77**, 1345 (1982).

[23] P.S. Dardi and S.K. Gray, J. Chem. Phys. **80**, 4738 (1984).

[24] R.P. Parson, J. Chem. Phys. **88**, 3655 (1987).