Rovibrational dynamics of the RbCs molecule in static electric fields. Classical study

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We study the classical dynamics of the RbCs molecule in the presence of a static electric field. Under the Born–Oppenheimer approximation, we perform a rovibrational investigation which includes the interaction of the field with the molecular polarizability. The stability of the equilibrium points and the phase space structure of the system are explored in detail. We find that, for strong electric fields or for energies close to the dissociation threshold, the molecular polarizability causes relevant effects on the system dynamics.

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1. Introduction

Since the pioneering works of Langevin [1] and Debye [2] to nowadays, the manipulation of the spatial direction (rotational orientation and alignment) of molecules by means of external fields has been a permanent “hot topic” in Chemical Physics (see [3] to get an overall vision of the state of the art).

For polar dimers, the simplest experimental technique that allows to control the molecular orientation is provided by an static electric field [4,5]. On the other hand, molecular alignment is obtained by means of nonresonant laser fields [6]. The theoretical investigations following these experiments have been focused on the impact of the field in the molecular structure, mainly on the rotational dynamics [5–7]. The major effect for strong fields is the appearance of pendular states [7] for which the molecule is oriented and/or aligned along the electric field axis. Friedrich and Herschbach [8] and Cai et al. [9] proposed the combination of static electric and nonresonant laser fields to enhance the molecular orientation and to gain versatility in the manipulation procedure. The predicted properties of this combined configuration have been successfully tested at the laboratory [10].

In general, the theoretical description of the nuclear dynamics of diatomic molecules exposed to electric fields has been based on the rigid rotor approximation. Under this approximation, the coupling between the vibrational and rotational motion is neglected, and the dipole moment and the polarizabilities of the dimer take constant values [11]. However, for strong field strengths and within certain energy regions, recent theoretical studies showed that the rigid rotor model fails because the vibrational motion is also affected by the external fields [12]. Then a full quantum rovibrational treatment is needed.

From the classical point of view, molecular systems are in general nonlinear dynamical systems with a few degrees of freedom. Then, invariant objects as periodic orbits, act as organizing structures for the quantum mechanical eigenstates and their identification is needed for the spectral assignment of highly excited levels [13,14]. In other words, molecular systems, in particular diatomic molecules in external fields, are perfect systems to follow the tracks of the classical phase space structure in the quantum spectra. In this sense, the classical rovibrational dynamics of the LiCs dimer in the presence of a static homogeneous electric field has been investigated [15]. For the case of a dimer exposed to parallel static and nonresonant laser fields, the analysis of the stability of the equilibrium points, their bifurcation and the evolution of the phase flow have provided a detailed picture of the classical dynamics and, in particular, of the influence on the orientation of the quantum states [16]. For the general case of tilted fields, the phase space structure, the degree of classical chaos, the classical-quantum correspondence for the non-integrable case, and the phenomenon of monodromy [17] have been investigated [14]. When the rotational dynamics of a diatomic molecule in the presence of ac fields was considered, these studies revealed a close correspondence between the classically chaotic dynamics and the corresponding quantum time evolution [18]. Furthermore, when
the dissociation threshold is studied in Section 4. The conclusions
of section. Special attention is paid to the bifurcations that suffer
the long range potential energy curve can be expressed as
in an anomalous stable way parallel
to the field. However, this region is small and appears close to the
dissociation threshold to represent a new dynamical situation.
be more important than on the LiCs.
The Letter is organized as follows. In Section 2, the two-
dimensional Hamiltonian used to describe the dynamics of the
dimer and the corresponding classical equations of motion
are presented. The classification of the equilibrium points of
the potential energy surface of the system as a function of the field
strength is also provided. Section 3 is devoted to the analysis
of the phase space structure. The dynamics of the dimer close to
the dissociation threshold is studied in Section 4. The conclusions
and outlook are provided in Section 5. Atomic units will be used throughout.

2. Classical Hamiltonian, equations of motion and equilibrium
points

We employ the Born–Oppenheimer approximation to describe
the dynamics of the RbCs dimer in its $^1\Sigma^+$ electronic ground
state in the presence of a homogeneous static electric field of
strength $F$. We restrict our study to a non-relativistic treatment
and we take into account that the interaction of the field with
the molecule is via its dipole moment and its polarizability. The
electric field is assumed to be oriented parallel to the $z$-axis of an
inertial reference frame with the origin at the center of mass of
the nuclei. Using spherical coordinates $(R, \theta, \phi)$, the classical Hamiltonian
governing the nuclear motion is given by:

$$\mathcal{H} = \frac{p_R^2}{2\mu} + \frac{p_\theta^2}{2\mu R^2} + V_{ef}(R, \theta), \quad (1)$$

$$V_{ef}(R, \theta) = \frac{p_\phi^2}{2\mu R^2 \sin^2 \theta} + \varepsilon(R) - F D\cos \theta$$

$\frac{F^2}{2}[\left(\alpha_{||}(R) - \alpha_{\perp}(R)\right) \cos^2 \theta + \alpha_{\perp}(R)]$, \quad (2)

where $\mu$ is the reduced mass of the nuclei and $p_R$, $p_\theta$ and $p_\phi$ are the corresponding classical conjugate momenta. $V_{ef}(R, \theta)$ is
the effective potential energy surface composed by the centrifugal
term depending on $p_\phi$, the field-free adiabatic electronic potential
energy curve $\varepsilon(R)$, and the interaction of the static electric
field with both the electronic dipole moment function $D(R)$
and the parallel and the perpendicular molecular polarizabilities
$\alpha_{||}(R)$ and $\alpha_{\perp}(R)$ [22]. These functions are plotted in Fig. 1.
In order to manage an analytical representation for the potential
energy surface $V_{ef}(R, \theta)$, we have fitted the numerical data of
$\varepsilon(R)$, $D(R)$, $\alpha_{||}(R)$ and $\alpha_{\perp}(R)$ to four different appropriate functional
forms. Besides, the fitting functions have been built in such a
way that they satisfy the correct long range behavior. In this
sense, the long range potential energy curve can be expressed as
$\varepsilon(R) = C_6/R^6 + C_8/R^8 + C_{10}/R^{10}$. For the $^1\Sigma^+$ RbCs these coefficients can be found in the literature [23]. For the dipole moment function $D(R)$ we fitted the large $R$ values to the well known expression $D(R) = C_2/R^2$. Finally, the asymptotic behavior of the polarizabilities $\alpha_{||}(R)$ and $\alpha_{\perp}(R)$ have been fitted to the corresponding Silberstein expressions [24].

Owing to the axial symmetry, the $z$-component $P_\phi$ of the angular
momentum is conserved. Hence, the expression (1) defines the classical Hamiltonian of a system with two degrees of freedom
$(R, \theta)$. The Hamiltonian equations of motion read as

$$\dot{\mathbf{R}} = \frac{\mathbf{P}_R}{\mu}, \quad \dot{\theta} = \frac{p_\theta}{\mu R^2};$$

$$\dot{P}_R = \frac{p_\phi^2}{\mu R^3} + \frac{p_\phi}{\mu R^2 \sin^2 \theta} - \frac{\partial \varepsilon}{\partial R} + \frac{F \partial D}{\partial R} \cos \theta$$

$$+ \frac{F^2}{2} \left[\frac{\partial \Delta \alpha_{||}(R)}{\partial R} \cos^2 \theta + \frac{\partial \alpha_{\perp}}{\partial R}\right];$$

$$\dot{P}_\theta = \frac{p_\phi \cos \theta}{\mu R^2 \sin^2 \theta} - \left[FD(R) + F^2 \Delta \alpha_{||}(R) \cos \theta\right] \sin \theta, \quad (3)$$

where $\Delta \alpha_{||}(R) = (\alpha_{||}(R) - \alpha_{\perp}(R))$. Besides $P_\phi$, the classical dynamics of this system depends on the energy $E = \mathcal{H}$ and on the external parameter $F$.

A previous way to see how the external field $F$ modify the
dynamics of the molecule is to study the shape of the potential
energy surface $V_{ef}(R, \theta)$ as $F$ varies. The shape of $V_{ef}(R, \theta)$ is
we obtain the three equations or a (relative) maximum, respectively. The results of this numerical investigation are illustrated by the diagram in Fig. 2. In this diagram it is shown the evolution of the energy of the critical points as a function of the field strength $F$. For $F < 0.0011156$ a.u., there are three critical points: the (relative) minimum $P_1$, the saddle point $P_2$ and the (relative) maximum $P_3$ (see Fig. 3). The contour plot of $V_{ef}(R, \theta)$ for $F = 10^{-3}$ a.u. is depicted in Fig. 3(a), where depending on the value of the energy, two different regions of motion are distinguished. For illustrative purposes, these contour figures have been plotted for $\theta = 0$, $\theta = \pi$, and not only in the interval of definition of the polar angle $[0, \pi]$. When the energy $E$ is below $E_2$, the energy of the saddle point $P_2$, the molecule is trapped into the potential energy well around $\theta = \pi$, in such way that the field prevents the molecule from describing complete rotations. Thence, the molecule can eventually be oriented along the opposite electric field direction, as it corresponds to the pendular states of dimers with a negative electric dipole moment. Note that, as $F$ increases, the depth of the potential well increases. When the energy surpasses the energy of $P_2$, the electric field is not able to trap the molecule and full rotations are allowed. Moreover, the polarizability creates an “energy hill” (the maximum $P_3$, see Fig. 3(a)) which, in fact, prevents the molecular bond $R$ from reaching large values unless through two narrow channels located along the $\theta = 0$ and $\theta = \pi$ directions. As we shall see, these directions will allow us to define the dissociation threshold of the dimer.

2.1. Critical points: Case $P_\phi = 0$

By substituting $P_\phi = 0 = P_R = P_\theta = 0$ in the Hamiltonian flux (3) and equating to zero, it yields

$$\frac{\partial \varepsilon}{\partial \mathbf{R}} - F \frac{\partial D}{\partial \mathbf{R}} \cos \theta = \frac{F^2}{2} \left[ \frac{\Delta \alpha(R)}{\partial R} \cos^2 \theta + \frac{\partial \alpha}{\partial R} \right] = 0. \quad (4)$$

$$\frac{1}{2} F \frac{\partial}{\partial \mathbf{R}} \gamma(\mathbf{R}) + \frac{F^2}{2} \left[ \frac{\partial \Delta \alpha}{\partial R} \gamma(\mathbf{R})^2 + \frac{\partial \alpha}{\partial R} \right] = 0. \quad (5)$$

From Eq. (5), it is clear that the critical points, when they exist, appear at $\theta_1 = 0$, $\theta_2 = \pi$, and $\cos \theta_3 = \gamma(\mathbf{R}) = \left[ \frac{\partial D(\mathbf{R})}{\partial \mathbf{R}} \right] \leq 1$. Whereas the critical points associated to $\theta_1 = 0$ and $\theta_2 = \pi$ are due to the interaction of the field with the molecular dipole moment, those arising from $\cos \theta_3 = \gamma(\mathbf{R})$ are due to the molecular polarizability. As a direct consequence, the dimer presents this anomalous molecular orientation parallel to the field direction, i.e., opposite to the orientation due to the interaction with the dipole moment. When $P_\phi \neq 0$, the centrifugal barrier in $V_{ef}(R, \theta)$ prevents the molecule to pass through $\theta = 0$ and $\theta = \pi$, i.e. complete rotations are not allowed. Then, the critical points when they exist are located in the interior of the interval $(0, \pi)$ and they are the roots of the equations

$$\frac{p_\phi^2}{\mu R^3 \sin^2 \theta} - \frac{\partial \varepsilon}{\partial \mathbf{R}} + F \frac{\partial D}{\partial \mathbf{R}} \cos \theta$$

$$+ \frac{F^2}{2} \left[ \frac{\partial \Delta \alpha(R)}{\partial R} \cos^2 \theta + \frac{\partial \alpha}{\partial R} \right] = 0. \quad (9)$$
maximum or a (relative) maximum, respectively. In the saddle-node bifurcation, the reader is referred to the web version of this Letter.)

As expected, the main qualitative effect of the centrifugal term in the effective potential is that the saddle point of motion of the molecule.

Now, besides the roots of the system (9) and (10) depending on the value of \( P_0 \). Following the same procedure as in the case \( P_0 = 0 \), we determine numerically the roots of this system as a function of \( F \) for a constant value of \( P_0 \). In diagram of Fig. 4 it is shown the evolution of the energy of the critical points for \( P_0 = 2 \) a.u. We observe in this diagram that for \( F \leq 0.00252 \) there are two critical points: a minimum and a maximum. Because these critical points would correspond to the minimum \( P_1 \) and the maximum \( P_3 \) in the case \( P_0 = 0 \), we call them \( P_1 \) and \( P_3 \) as well. The contour plot of \( V_{eff}(\theta, R) \) for \( F = 0.001 \) a.u. in Fig. 5(a) shows that there is only one region of motion in such way that, the greater the value of \( F \), the wider the amplitude of the rotation of the molecule. As expected, the main qualitative effect of the centrifugal term in the shape of the effective potential is that the saddle point \( P_2 \) does not exist.

For \( F_e \approx 0.001257 \) a.u. a saddle-node bifurcation takes place. This bifurcation is denoted by SN in Fig. 4. From this bifurcation, there appear two new critical points: a saddle point and a minimum named as \( P_4 \) and \( P_2 \), respectively (see Fig. 5(b)). This structure remains unchanged for increasing \( F \). As in the \( P_0 = 0 \) case, there appears a new oscillatory region of motion due to the polarizability interaction.

A general feature of the dynamics is that, due to the large value of \( \mu \), the dynamics is only affected by the centrifugal term when the angle \( \theta \) tends to 0 or \( \pi \).

It is interesting to note that these kind of bifurcations with similar consequences also appear in the classical study of rigid diatomic molecules in the presence of combined electrostatic and nonresonant polarized laser fields [16]. Because for both \( P_0 = 0 \) and \( P_0 \neq 0 \) the system shows a similar dynamical behavior, hereafter we reduce to the case \( P_0 = 0 \).

3. Evolution of the phase space

In this section we study the phase space structure of the system (for \( P_0 = 0 \)) by using Poincaré surfaces of section [25]. We define the surface of section by the intersection of the phase trajectories with the \((\theta, P_\theta)\)-plane for \( P_R = 0 \). With this selection we ensure that all the orbits (both rotational and oscillatory) will cross it at any time, i.e., it is guaranteed that this surface of section is transverse to the Hamiltonian flux [26]. They are generated by the numerical integration of the Hamiltonian equations of motion (3) using an explicit Runge–Kutta algorithm of eighth order with step size control and dense output [27].

Using Hamiltonian (1) for \( P_\theta = 0 \), the region in the \((\theta, P_\theta)\)-plane defining the Poincaré surface of section for \( P_R = 0 \) is determined by those values of \( P_\theta \) satisfying

\[
P_\theta = \pm \sqrt{\frac{2}{\mu} R^2} E - F D(\theta) \cos \theta + F^2 \frac{\Delta \alpha(R)}{2} \cos^2 \theta + \frac{\cos \theta}{2 \mu} \left( \frac{\alpha_1(R) - \alpha_\perp(R) \cos \theta}{\alpha_\perp(R)} \right) \right)^{1/2}.
\]

(11)

Therefore, the limit of the surface of section corresponds to the maximum and minimum values of \( P_\theta \) satisfying the above equation. The initial conditions have been chosen inside the region limited by these extreme points, which were computed numerically. Note that, to get a better visualization of the different phase space structures, the surfaces of section have been plotted for \( 0 \leq \theta \leq 2 \pi \), and not only in the interval of definition of the polar angle [0, \( \pi \)]. A complementary vision of the phase space structure is provided by the surface of section in the \((R, P_R)\)-plane for \( \theta = \pi \). In this case, the allowed region is limited by the equation

\[
P_R = \pm \sqrt{2 \mu} E - V_{eff}(R, \pi).
\]

(12)

In order to study the evolution of the phase space structure, we fix the electric field value \( F = 5 \times 10^{-4} \) a.u. while we vary the energy \( E \). This value of \( F \) is well below the critical bifurcation field \( F_e \approx 0.0011156 \) a.u. and the potential energy surface has similar structure to the case discussed in Fig. 3(a). The value of the saddle point energy is \( E_2 \approx -0.01751 \) a.u. We restrict our study to this dynamical region because the required electric field values in this regime are experimentally more accessible than in the regime for \( F > 0.0011156 \) a.u.

When the energy of the molecule is below the saddle point energy \( E_2 \), the surfaces of section in the planes \((\theta, P_\theta)\) and \((R, P_R)\) (see Fig. 6(a)-(b)) show that all orbits are ordered forming invariant KAM tori around two stable fixed points (periodic orbits) \( O_{V_1} \) and \( O_R \) respectively. As can be analytically checked in (3), \( O_{V_1} \) corresponds to a pure vibrational rectilinear periodic orbit along the negative z-axis (\( \theta = \pi \)). On the other hand, the fixed point \( O_R \) corresponds to an arch-like oscillatory periodic motion.
These periodic orbits as well as representative quasiperiodic orbits around them are presented in Fig. 6(c).

When the energy of the system is above the energy \( E_2 \) of the saddle point \( P_2 \), the molecule is not trapped into the potential well of the minimum \( P_1 \) and it can, eventually, describe complete rotations. We observe this behavior in Fig. 6(d)–(e) where the surfaces of section in the planes \( (\theta, P_\theta) \) and \( (R, P_R) \) for an energy \( E = -0.015 \) a.u. slightly above the energy of the saddle are shown.

Comparing to the previously discussed case, the \( (R, P_R) \) surface of section shows a similar structure to the one presented in Fig. 6(b). However, in the \( (\theta, P_\theta) \) surface of section significant modifications are encountered. In the present dynamics, two unstable fixed points appear located at \( (\theta, P_\theta) = (0, 0) \) and \( (\theta, P_\theta) = (2\pi, 0) \). They correspond to another pure vibrational rectilinear \( (\theta = 0) \) periodic orbit \( O_{V2} \) along the positive z-axis, which can also be analytically checked in Eq. (3). These two unstable fixed points are connected by a separatrix that encloses quasiperiodic oscillatory motions. Outside this separatrix, there are two families of curves which sweep out the \( \theta \) angle from 0 to \( 2\pi \), which correspond to complete (quasiperiodic) molecular rotations in opposite directions. To obtain a global vision of the different motions that characterize in this regime the dynamics of this system, the periodic orbits \( O_{V1}, O_{V2} \) and \( O_R \), as well as two representative quasiperiodic orbits, are depicted in Fig. 6(f). Finally, note that the surfaces of section in Fig. 6 show regular behavior which indicates that the system is still near integrable.

We have seen that, for an energy slightly above the saddle point energy \( E_2 \), the structure of the phase space is characterized by the periodic orbits \( O_{V1}, O_{V2} \) and \( O_R \). An efficient tool that allows one to detect the possible changes in this basic structure is the numerical continuation of the families of periodic orbits generated by the variations of the system’s parameters and the computation of the stability parameter of the families.

As it is well known, the linear stability of a periodic orbit is determined from the eigenvalues of the monodromy matrix. Since we are dealing with a two degrees of freedom Hamiltonian system, the four eigenvalues \( (\lambda_1, \lambda_2, \lambda_3, \lambda_4) \) appear in reciprocal pairs. As a consequence of the invariance of the Hamiltonians equations of motion, we have two trivial eigenvalues \( \lambda_1 = \lambda_2 = 1 \). Thus, we just have to study the remaining two eigenvalues \( (\lambda_3, \lambda_4) \) as they are complex conjugate and reciprocal, they are on the unit circle in the complex plane or on the real axis. In other words, \( \lambda = \lambda_3 = 1/\lambda_4 \). In order to have a stable periodic orbit, the two eigenvalues have to be on the unit circle [28]. If \( \lambda_3 \) and \( \lambda_4 \) are real the orbit is unstable. At the critical cases \( \lambda_3 = \lambda_4 = \pm 1 \) the stability may change. Following Barrio [29] the stability index \( k \) defined as

\[
k = \lambda + 1/\lambda.
\]
is normally used, where $k$ is real and $|k| < 2$ applies for linear stability, and the critical value $k = \pm 2$ means that a new family of periodic orbits has likely bifurcated from the original one. Therefore, numerical continuation of periodic orbits and stability diagrams, where the $k$ is plotted versus the parameter generator of the family, are useful tools in nonlinear studies (see for instance [29,30]).

At this point, we proceed as follows. For the fixed value $F = 5 \times 10^{-4}$ a.u. and by using the software AUTO [31], we carry out the numerical continuation of the families of the periodic orbits $O_{V1}$ and $O_{V2}$ that emanate from these solutions. Because we fix the electric field strength, in our system the only parameter for the continuation procedure is the energy. The stability diagram of each family as a function of the energy $E$ is also computed. From this diagram, we can detect values of the energy for which possible bifurcations take place. Bifurcations produce qualitative changes in the phase space structure. When a bifurcation is found, we illustrate its effect by calculating the surfaces of section when the energy is slightly less and slightly larger than its value at the bifurcation.

The stability diagram of the families of the periodic orbits $O_{V1}$ and $O_{V2}$ is shown in Fig. 7. This diagram gives the stability parameter $k$ of each family in the interval $-0.01751 < E \leq -0.001$ a.u. We call each family with same name as the corresponding periodic orbit. In this interval the family $O_{V1}$ is always stable. However, we see in this diagram that at $E_b \approx -0.003$ a.u. the family $O_{V2}$ suffers a bifurcation because its stability index reaches at that energy $E_b$ the critical value $k = 2$. As we can visualize in the surfaces of section in Fig. 8, it is a pitchfork bifurcation: when the energy crosses the value $E_b$, from the fixed point $O_{V2}$ (which becomes stable) emanate two new unstable fixed points (periodic orbits). These two new families, named $O_{V3}$, have the same stability index, and thus in the diagram in Fig. 7 are represented by the same blue dashed line. These new periodic motions $O_{V3}$ consist of two unstable asymmetric stretchings whose projection in the $(R, \theta)$-plane joins the corresponding equipotential curves (see Fig. 9). As the energy increases, they migrate away from the stable fixed point $O_{V2}$.

The separatrix passing through these new unstable fixed points in the surface of section Fig. 8(b) surrounds new oscillatory (pendular) motions around $O_{V2}$. Note that in these new pendular orbits the molecule is mainly aligned along the electric field direction, that is, around the positive $z$-axis. In Fig. 9 it is shown one of these anomalously pendular orbits. It is important to realize that the origin of this new alignment region is completely dynamical, due to the influence of the polarizability and that cannot be inferred from the potential energy surface structure, which in fact remains the same in the considered energy interval.

As the energy increases, the size of the anomalously pendular region $O_{V2}$ increases (see the surface of section in Fig. 10(a) for $E = -1.7 \times 10^{-4}$ a.u.), in such way that it becomes comparable in size to the $O_{V1}$ pendular region. It is important to note that even for this quite high energy, for which the size of the molecule is larger than $R = 20$ a.u. (see Fig. 10(b)), the phase space still presents a regular KAM tori structure.

4. Dynamics close to the dissociation threshold

After having studied the evolution with energy of the fundamental structures of phase space, in this section we focus on dynamics of the dimer in an energy range close to the dissociation energy threshold $E_d$. The existence of the aforementioned dissociation channels along $\theta = 0, \pi$, together with the threshold dissociation conditions $R \to \infty$, $P_R \to 0$ and $P_\theta \to 0$, allow us to get an analytical estimation of $E_d$. Under the condition $R \to \infty$, $P_R \to 0$ and $P_\theta \to 0$, allow us to get an analytical estimation of $E_d$. Under the condition $R \to \infty$,
functions $\varepsilon(R)$ and $D(R)$ both tend to 0, and $\alpha_\| (\infty) = \alpha_\perp (\infty) = \alpha_\infty = \alpha_{\text{C}} + \alpha_{\text{Rb}}$. Indeed, the approximate value for the dissociation energy is given by

$$
\mathcal{H} = E_d \approx - \frac{F^2}{2} \alpha(\infty) = - \frac{F^2}{2} (\alpha_{\text{Rb}} + \alpha_{\text{C}}).
$$

(13)

Thus, the atomic polarizabilities lead to decrease the dissociation energy to a nonzero negative value, which depends on the electric field strength $F$ as well as on the polarizabilities of the atoms. For example, for the value $F = 5 \times 10^{-4}$ a.u., we obtain that $E_d = -8.965 \times 10^{-5}$ a.u.

In Fig. 11 it is shown a gallery of surfaces of section for a fixed electric field $F = 5 \times 10^{-4}$ a.u. and for increasing energies values in the interval $-9.576 \times 10^{-5}$ a.u. $\leq E \leq -8.96 \times 10^{-5}$ a.u. When the $E = -9.576 \times 10^{-5}$ a.u. the separatrix passing through $O_{V_1}$ has been replaced by a thin stochastic layer of chaotic motions, see Fig. 11(a). In this small layer, the motion of the molecule alternates randomly between complete rotations in both directions and oscillations of large amplitude around both directions of the $z$-axis. Moreover, chains of resonant island appear in both the rotational and the pendular $O_{V_1}$ regions. For a higher energy (see Fig. 11(b)), the width of the chaotic layer grows and, in general, the phase space structure becomes more complex. As the energy is further increased, this trend to a more complex dynamics continues (see Fig. 11(c)-(d)-(e)) until the dissociation threshold is reached, see Fig. 11(f). It is interesting to note that the first orbits to dissociate are the rectilinear motions $O_{V_1}$, $O_{V_2}$ and the nearest quasiperiodic orbits surrounding them because they are strongly oriented to the dissociation channels in $\theta = 0, \pi$. This is why Fig. 11(f) presents empty regions around $O_{V_1}$ and $O_{V_2}$.
Finally, it is worth to note that the molecule can persist bounded in rotational or even in oscillatory states for energies above the dissociation threshold, see Fig. 11(f).

5. Conclusions

In this work we have studied the classical rovibrational dynamics of the alkali polar dimer RbCs in its electronic ground state under the action of a strong static homogeneous electric field. In the framework of the Born–Oppenheimer approximation, we have considered the interaction of the molecule with the field due to both, the permanent electric dipole moment of the dimer and its molecular polarizability. Owing to the axial symmetry of the system, the component $P_{\theta}$ of the angular momentum of the dimer along the direction of the field is conserved and thus, the system has two degrees of freedom. This study is focused on the case $P_{\phi} = 0$, that is, a zero magnetic quantum number.

The shape of the potential energy surface $V(R, \theta)$ and its critical points are studied depending on the electric field strength $F$. This study shows that, due to a pitchfork bifurcation, above a certain critical value of $F$, the typical pendular structure of $V(R, \theta)$ is replaced by a new structure where the molecule can be aligned parallel to the electric field. This orientation is anomalous because the RbCs dimer has a negative electric dipole moment function.

By means of appropriate Poincaré surfaces of section, the evolution of the phase space structure as a function of the energy has also been analyzed. For small energy values, the phase space exhibits a regular structure with quasiperiodic motions organized on invariant KAM tori around three periodic orbits: two of them, $O_{V1}$ and $O_{V2}$, are pure vibrational rectilinear motions parallel to the electric field ($O_{V1}$ is stable in the opposite direction of the field, and $O_{V2}$ is unstable in the same direction of the field), and the third one is an oscillatory orbit $O_{g}$. For larger energies, $O_{g}$ develops into a periodic complete rotation.

In order to detect relevant changes in the phase space structure, we have performed the numerical continuation of the vibrational periodic motions $O_{V1}$ and $O_{V2}$ as a function of the energy for a fixed electric field strength. The stability diagrams of the families of $O_{V1}$ and $O_{V2}$ revealed that the unstable motion $O_{V2}$ suffers a pitchfork bifurcation becoming stable. From this bifurcation two new unstable periodic asymmetric stretchings $O_{V3}$ arise. As the energy increases, new quasiperiodic oscillatory motions appear surrounding the rectilinear vibrational motion $O_{V2}$ that becomes stable. In these new oscillatory (pendular) orbits the molecule is mainly aligned in the electric field direction. The amplitude of these “anomalous” oscillatory motions increase with the energy becoming comparable to the amplitude of the pendular oscillations aligned opposite to the direction of the field. The origin of this new aligned region is completely dynamical, due to the influence of the polarizability and it cannot be inferred from the potential energy surface structure.

For energy values close to the dissociation threshold, the system loses regularity and the phase space structure is more complex. An stochastic layer appears in the neighborhood of the separatrix which keeps apart the oscillatory motions from the complete rotations. In this chaotic region, the dimer alternates randomly complete rotations in both directions with oscillations of great amplitude.

With respect to the dissociation of the molecule, there exist two dissociation channels located along the direction of the electric field, as the first orbits to dissociate are the two periodic vibrational rectilinear motions $O_{V1}$ and $O_{V2}$ and the quasiperiodic orbits surrounding them. On the other hand, the molecular polarizability leads to decrease the dissociation threshold to a nonzero negative energy value, which depends not only on the electric field strength, but also on the polarizabilities of the atoms.

An interesting direction for a future study is the investigation of the impact of these classical results in the quantum counterpart. Work along this line is now under consideration.

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