Bifurcations of the normal modes of the Ne···Br₂ complex

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Abstract

We study the classical dynamics of the rare gas-dihalogen Ne···Br₂ complex in its ground electronic state. By considering the dihalogen bond frozen at its equilibrium distance, the system has two degrees of freedom and its potential energy surface presents linear and T-shape isomers. We find the nonlinear normal modes of both isomers that determine the phase space structure of the system. By means of surfaces of section and applying the numerical continuation of families of periodic orbits, we detect and identify the different bifurcations suffered by the normal modes as a function of the system energy. Finally, using the Orthogonal Fast Lyapunov Indicator (OFLI), we study the evolution of the fraction of the phase space volume occupied by regular motions.

1. Introduction

It is well known that nonlinear classical and semiclassical mechanics have proven to be very useful for interpreting the quantum dynamics of real atomic and molecular systems, even when the classical dynamics is chaotic and the quantum dynamics is strongly mixed [1]. Due to the simplicity of the model, the hydrogen atom in the presence of external fields is the keystone system on which all nonlinear classical tools have been successfully applied [2]. In particular, the studies of the periodic orbits and the corresponding phase space structure provide a very useful information that can be compared with the behavior of the corresponding quantum system and with the experiments [1,3]. Since the pioneering work of Gutzwiller [4], many authors (see, e.g., Ref. [5] and references therein) have stated a clear relation between classical periodic orbits and quantum eigenfunctions.

In relation to molecules, and in spite of the difficulties of dealing with in general more complex systems, a wide variety of molecular systems have been studied by using periodic orbit theory. In this sense, among a plethora of works, we refer the reader to those of Elstathiou and Contopoulous [6], Farantos [7] and Ezra [8].

A nice example where classical dynamics is playing an important role are the rare gas-dihalogen van der Walls molecules. These molecules are simple systems where several phenomena can be studied by combining classical and quantal studies. In particular, much effort has been paid to the study of the vibrational predissociation [5,10] and photodissociation [11] of these molecules. In these processes, nonlinear dynamics is particularly useful to understand the decay of the complex due to the energy transfer from the dihalogen bond to the weak van der Waals bond. However, not much attention has been paid to the vibrational dynamics of the rare gas around the dihalogen dimer. With this kind of study, widely applied in the LiCN and HCP molecules [12], it is possible to determine the structure of the phase space. As it is well known, periodic orbits are the backbone of the phase space. Moreover, they play an important role because they are essential to understand some quantum features as the localization of quantum states along unstable periodic orbits [13].

With this in mind, here we focus on the evolution of the phase space structure of one of these rare gas-dihalogen complexes: the Ne···Br₂ complex in its ground electronic state. This study is based on a systematic searching of periodic orbits by using numerical continuation of families of periodic orbits. The Letter is organized as follows. In Section 2 we describe the potential energy surface and the Hamiltonian we used in the study. We find the basic periodic orbits (normal modes) that determine the fundamental phase space structure in Section 3. In Section 4 we detect and classify by numerical continuation the different bifurcations that determine the evolution of the phase space. In Section 5 we study the evolution of the fraction of the phase space volume occupied by regular motions as a function of the energy. Finally, in Section 6 the main results are summarized.
2. The Hamiltonian

We consider the motion of a Ne atom around a Br$_2$ molecule which bond coordinate $r$ is frozen at its equilibrium distance $r_e \approx 2.281$ Å. By considering that the total angular momentum of the molecule is zero, the dynamics of the Ne atom around the Br$_2$ dimer is described by the two-dimensional Hamiltonian [14]

$$\mathcal{H} = \frac{p_R^2}{2\mu_2} + \frac{1}{2} \left( \frac{1}{\mu_2 r^2} + \frac{1}{\mu_1 r^2} \right) p_{\theta}^2 + V(R, \theta, r_e).$$  \hspace{1cm} (1)

In Hamiltonian (1), $R$ is the distance of the Ne atom to the Br–Br center of mass, $\theta$ is the angle between $R$ and $r_e$, $(p_R, p_\theta)$ are the canonical momenta conjugated of $R$ and $\theta$ and $\mu_1^{-1} = m_{Br}^{-1} + m_{Ne}^{-1}$ and $\mu_2^{-1} = m_{Br}^{-1} + (2m_{Br})^{-1}$ are the diatomic and triatomic reduced masses. Finally, $V(R, \theta, r_e)$ is the potential energy surface describing the interaction of the Ne atom with the Br$_2$ molecule. Throughout the Letter atomic units are used.

In order to perform classical calculations, an analytical potential energy surface (PES) is the most suitable choice. We built the PES as an expansion in Legendre polynomials $P_n(\cos \theta)$ allowing one to write the PES as

$$V(R, \theta, r_e) = \sum_\lambda \left\{ \sum_{i=1}^5 \alpha_{i\lambda} [e^{-2\delta_i(R-r_e)} - 2e^{-\delta_i(R-r_e)}] - \frac{\delta_\lambda}{R^6} \sin \theta \right\} \frac{\eta_\lambda}{R^8},$$  \hspace{1cm} (2)

where the parameters are listed in Table II of Ref. [10]. Note that as for $\lambda = 0, 2, 4, 6, 8$ the Legendre polynomials are periodic functions of period $\pi$, the potential energy surface $V(R, \theta, r_e)$ and the Hamiltonian $\mathcal{H}$ are also periodic functions of the same period in the $\theta$ angle.

In Fig. 1 the equipotential curves of (2) are shown. At $R = 8.479433$ a.u. and $\theta = 0$ and $\theta = \pi$ the PES has two equivalent minima $P_L$ of energy $E_L = -0.000427$ a.u. These minima correspond to the linear isomer of the molecule. At $R = 6.798360$ a.u. and $\theta = \pi/2$ and $\theta = 3\pi/2$ the potential energy surface $V(R, \theta, r_e)$ presents two additional minima $P_T$ of $E_T = -0.000388$ a.u. which correspond to the so-called T-shape isomer. The linear and T-shape potential wells are kept apart by a separatrix passing through four saddle points $P_S$ of energy $E_S = -0.000219$ a.u. located at $R = 8.383587$ a.u. and $\theta = 0.876222, \theta = 2.265371, \theta = 4.017815$ and $\theta = 5.406964$.

From the shape of $V(R, \theta, r_e)$ we deduce that the Ne atom can move in different regions of motion. There is one region of rotational orbits for energies above the isomerization barrier $E_S$ and four regions of vibrational orbits for energies below $E_S$. When the energy $E$ of the atom is below $E_S$, the atom is in a vibrational mode because it always confined inside one of the four potential wells. In other words, the Ne atom is mainly aligned along the linear or the T-shape configurations and cannot reach large values of $R$. When in a rotational mode (energy bigger than the isomerization barrier $E_S$), the atom can travel from one potential well to other and, depending on the energy and initial conditions, can reach large values of $R$.

The Hamiltonian equations of motion read

$$\dot{R} = \frac{p_R}{\mu_2}, \hspace{1cm} \dot{\theta} = \frac{1}{\mu_2 R^2} \left\{ \frac{1}{2} \frac{1}{\mu_1 R^2} - \frac{1}{\mu_2 R^2} \right\} p_\theta,$$

$$\dot{p}_R = -\frac{\partial V(R, \theta, r_e)}{\partial R}, \hspace{1cm} \dot{p}_\theta = -\frac{\partial V(R, \theta, r_e)}{\partial \theta}. \hspace{1cm} (3)$$

The equilibrium points of the above Hamiltonian flow are the critical points of the PES $V(R, \theta, r_e)$ together with the conditions $p_R = p_\theta = 0$. Moreover, if we consider initial conditions $p_\theta = 0$ and $\theta = 0, \pi/2, \pi$ or $3\pi/2$ it is straightforward to see that in the above equations we obtain $\dot{\theta} = \dot{p}_\theta = 0$, which corresponds to pure analytic vibrational rectilinear periodic orbits passing through each of the critical points $P_L$ and $P_T$ of $V(R, \theta, r_e)$. We name these rectilinear orbits as $L_1$ and $T_1$, respectively.

3. Phase space structure

The computation of Poincaré surfaces of section is a common way to illustrate the structure and evolution of the phase space of a two-degrees Hamiltonian dynamical system. The construction of a surface of section is a delicate task because it should be transverse to the flow [15]. In our problem a good choice is to define the surfaces of section as the intersection of the phase trajectories with the $(\theta, p_\theta)$ plane for $p_R = 0$. We choose this surface of...
section because all the orbits (both rotational and vibrational) will cross it at any time, e.g., we can guarantee that this surface of section is transverse to the Hamiltonian flux.

The surface of section is generated by numerical integration of the Hamiltonian equations of motion (3). These equations are solved by means of an explicit eight order Runge–Kutta algorithm with stepsize control and dense output [16].

Under the conditions of this surface of section and taking into account the Hamiltonian (1), the available region in the plane \((\theta, P_\theta)\) of the surface of section is determined by the possible values of the momentum \(P_\theta\) that are given by the equation

\[
P_\theta = \pm \sqrt{\frac{2 \mu_2 \mu_1 R^2}{\mu_2 R^2 + \mu_1 I_2^2} \left( E - V(R, \theta, r_e) \right)}.
\]

In Fig. 2a we show the surface of section for an energy \(E = -0.00039\) a.u. This energy is above the energy \(E_L\) of the linear minimum \(P_L\) and below the energy \(E_T\) of the T-shape minima \(P_T\). Due to the symmetry of the Hamiltonian, the complete surface of section for this energy presents two equal disjoint regions around \(\theta = 0\) and \(\theta = \pi\) that correspond to “trapped” motions inside each of the two potential wells of the linear isomer (for simplicity we only show in Fig. 2a the region around \(\theta = \pi\)). In this surface of section all the orbits are ordered defining invariant closed curves around two stable fixed points (periodic orbits) located at \((0, 0)\) and \((\pi, 0)\) respectively. These fixed points correspond to the vibrational rectilinear orbits \(L_1\) (see Fig. 3a). In Fig. 2a is also shown a zoom of the upper and lower parts of the surface of section. In these zooms there appear two more stable fixed points which correspond to the same arch-like periodic orbit named as \(L_2\) (see Fig. 3a). A complementary vision of the phase space structure is given by computing the surface of section \(\theta = \pi\) in the \((R, P_R)\) plane. In this case, the limit of the available region in the \((R, P_R)\) plane is given by the equation

\[
P_R = \pm \sqrt{2 \mu_2 \left( E - V(R, \pi, r_e) \right)}.
\]

It is worth noting that the rectilinear orbit \(L_1\) is tangent to the flux in this Poincaré map and it corresponds to the curves (5). When this surface of section is computed for the same value of \(E\) (see Fig. 2b) we observe a similar phase space structure as in Fig. 2a, being the central fixed point the periodic orbit \(L_2\).

From the phase plots of Fig. 2, we deduce that the phase space in the linear potential energy well is organized around the periodic orbits \(L_1\) and \(L_2\). Then, the nearer a quasiperiodic orbit is to \(L_1\) the greater its orientation is along this periodic orbit. On the other
hand, the quasiperiodic orbits near $L_2$ show an arch-like shape. In Fig. 3a examples of these two kinds of motions are shown.

In fact, it is worth noting that the periodic orbits $L_1$ and $L_2$ are, respectively, the radial and the angular nonlinear normal modes of the linear isomer.

When the energy $E$ is above $E_T$ and below $E_L$, the Ne atom can live trapped inside any of the four potential wells of $V(R, \theta, \phi)$. In this energy interval, surfaces of section will show four disjoint regions of motion. The surfaces of section in Fig. 4 correspond to an energy value $E = -0.00037$ a.u. slightly above $E_T$. For this energy, the linear and the T-shape phase space regions show regular motion. For simplicity we only show the surfaces of section of the T-shape $\theta = \pi/2$ isomer (Fig. 4a) and the linear $\theta = \pi$ isomer (Fig. 4b–c). The dynamics in the T-shape isomer regions (Fig. 4a) is organized around three fixed stable points located at the axis which are the nonlinear normal modes of the T-shape isomer. Indeed, the central fixed point is the vibrational rectilinear orbit $T_1$ while the other two stable fixed points correspond to the same periodic orbit. This periodic, named as $T_2$, is again an arch-like periodic orbit. In Fig. 3b are depicted the periodic orbits $T_1$ and $T_2$ as well as two representative quasiperiodic orbits.

In the linear isomer regions, Fig. 4b–c shows that, besides the appearance of two islands of resonances, the phase space shows a similar structure as in Fig. 2.

4. Evolution of the nonlinear normal modes

From the above study we have determined the four normal modes of the system. These normal modes are the fundamental families of periodic orbits of the system because their numerical continuation generated by the variations of the energy $E$ and the computation of the stability parameter of each family will help us in understanding the dynamics of the problem.

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 Hamiltonian problem, the eigenvalues appear in reciprocal pairs, and as a consequence of the invariance of the Hamiltonian equations of motion we have one trivial eigenvalue $\lambda_0 = 1$ with multiplicity 2. Then, the stability index

$$k = \lambda + 1/\lambda$$

is normally used [17], where the condition $k$ real and $|k| < 2$ applies for linear stability, and the critical values $k = \pm 2$ mean that a new family of periodic orbits has likely bifurcated from the original one. Therefore, stability diagrams where the stability index is presented versus the parameter generator of the family are commonly used.

At this point, we proceed as follows. By using the numerical software AUTO [18] we carry out the numerical continuation of the families of the four normal modes that emanate from these solutions. The stability diagram of every periodic orbit 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. In the present study, when a bifurcation is found, we calculated the surfaces of section when energy is slightly less and slightly larger than its value at bifurcation, in order to illustrate the effect of bifurcation.

4.1. Linear configuration

We begin considering the linear isomer and its angular nonlinear normal mode. The diagram in Fig. 5 shows the evolution of the stability index of the family of the periodic orbits corresponding to this normal mode. This diagram gives the stability parameter $k$ of this family in the interval $-4 \times 10^{-4}$ a.u. $\leq E \leq -1.2 \times 10^{-4}$ a.u. We call this family with the same name as the corresponding periodic orbit $L_2$. The evolution of this family is depicted in blue in Fig. 5. As it can be seen in the figure, this family $L_2$ suffers four different bifurcations, and it is always stable until the last bifurcation which takes place at $E \approx -1.9 \times 10^{-4}$ a.u. The first bifurcation occurs for $E \approx -3.86 \times 10^{-4}$ a.u. when the stability index reaches the critical value $k = 2$ in a tangential way (without crossing it). This is a double pitchfork bifurcation [19] in which four new periodic families (two stable ones and two unstable ones) emanate from the $L_2$ family. The two new stable families have the same stability index values, and thus, both branches are represented in Fig. 5 by the same continuous red line. The same occurs with the two new unstable families (dashed red line).

The bifurcation is visualized in Fig. 6 by means of surfaces of section for $\theta = \pi$. In Fig. 6a, when $E = -3.9 \times 10^{-4}$ a.u., the SOS only exhibits one fixed center point corresponding to the angular normal mode $L_2$. This periodic motion is depicted in blue in the $(\theta, R)$ plane in Fig. 6c–d. After the bifurcation, for $E = -3.82 \times 10^{-4}$ a.u., two new center points and two saddle points arise in the SOS emanating from $L_2$, see Fig. 6b. The two new stable periodic motions are drawn in red in the $(\theta, R)$ plane in Fig. 6d. The orbits of both motions have the same shape in this plane but they are traveled in opposite directions.

The second bifurcation takes place for $E \approx -3.08 \times 10^{-4}$ a.u. when the stability index reaches the critical value $k = -2$. This is a double period-doubling bifurcation [19] in which four new periodic families (two stable ones and two unstable ones) emerge from the normal mode $L_2$. All these new periodic orbits have double period of $L_2$ and, therefore, have a periodicity $m = 2$ [19]. The two new stable families have the same stability index values, and therefore, both branches are represented in Fig. 5 by the same continuous clear green line. The same happens with the two new un-
Fig. 5. Stability diagram of the families of the periodic orbits emanating from the angular nonlinear normal mode of the linear isomer as a function of the energy $E$. Dashed lines stand for unstable periodic orbits. (For interpretation of the colours in this figure, the reader is referred to the web version of this Letter.)

Fig. 6. First bifurcation of the angular nonlinear normal mode family in the linear isomer. Surfaces of section for $\theta = \pi$ before (a) and after (b) the double pitchfork bifurcation. Stable periodic orbits before (c) and after (d) bifurcation. Red line represents the new stable periodic orbits arisen from the bifurcation. (For interpretation of the colours in this figure, the reader is referred to the web version of this Letter.)

stable families (dashed clear green lines). Fig. 7 represents the evolution of the surface of section $\theta = \pi$ through this bifurcation, as well as the stable periodic motions involved in it. The orbit in the $(\theta, R)$ plane of this periodic motion is shown in blue in Fig. 7c–d.
After bifurcation occurs, see Fig. 7b for $E = -3.06 \times 10^{-4}$ a.u., four new center points and four new saddle points appear in the SOS emerged form $L_2$. Each pair of the four new center points corresponds to each one of the two new stable periodic motions. Fig. 7d shows as a red line the orbit of these two new stable motions plotted in the $(\theta, R)$ plane. The orbit shape of these two motions are the same, but they are traveled in opposite directions.

The third bifurcation occurs for $E \approx -2.46 \times 10^{-4}$ a.u., it is also a double period-doubling one and, thus it is very similar to the previous bifurcation. Two new stable periodic families and two new unstable ones arise from the angular normal mode $L_2$, see Fig. 5. All these new families have twice the period of $L_2$, that is, they have multiplicity $m = 2$. As it can be seen in Fig. 8a–b, the surfaces of section $\theta = \pi$ show that a region of chaotic motions surrounding these periodic motion has already appeared for this energy range. This chaotic region increases quickly after the bifurcation. The orbit of the angular normal mode $L_2$ has taken a W-like shape in the $(\theta, R)$ plane for this energy, see the blue line in Fig. 8c–d. The orbits of the two new stable periodic motions emerged from this bifurcation are shown as red and orange lines in Fig. 8d. It is important to note that, unlike all the previous stable periodic motions, the shapes of these new ones are not symmetric with respect to the $\theta = \pi$ axis in the $(\theta, R)$ plane, but they are as mirror reflections one each other.

The last bifurcation in the angular normal mode $L_2$ of the linear isomer takes place for $E \approx -1.9 \times 10^{-4}$ a.u., when the stability index crosses the critical value $k = 2$, see Fig. 5. This is a pitchfork bifurcation in which the angular mode $L_2$ changes its stability becoming an unstable periodic motion ($k > 2$). At the same time, two new periodic stable motions with the same period of $L_2$ arise from it. For this energy range, Fig. 9a–b shows that most of the surface of section is filled by chaotic motions. The center fixed point corresponding to $L_2$ before bifurcation, transforms after it into a saddle point and two nearby center points corresponding to the two new stable periodic motions. The orbits of these two new stable motions plotted in the $(\theta, R)$ plane are shown as red and orange lines in Fig. 9d. As it happens in the previous bifurcation, the shapes of these new periodic motions are not symmetric with respect to the $\theta = \pi$ axis in the $(\theta, R)$ plane, but they are as mirror reflections one each other. As this energy range is above the isomerization energy barrier $E_5$, the equipotential curves of Fig. 9c–d are not closed because the potential wells of both isomers are connected in these situations. Nevertheless, the periodic motions involved in this bifurcation are confined in the potential well of the linear isomer.

On the other hand, the radial nonlinear normal mode of the linear isomer follows a much simpler evolution with the energy. Fig. 10a shows the stability diagram of the family of the periodic orbits corresponding to this normal mode. This diagram gives the stability parameter $k$ of this family in the interval $-4 \times 10^{-4} \leq E \leq -0.5 \times 10^{-4}$ a.u. We call this family with the same name as the corresponding periodic orbit $L_1$. The evolution of this family is depicted in blue in Fig. 10a. This family $L_1$ only suffers one bifurcation, as it can be seen in that figure. This bifurcation occurs for $E \approx -2.16 \times 10^{-4}$ a.u., when the stability index crosses the critical value $k = -2$. This is a period-doubling bifurcation in which the normal mode $L_1$ changes its stability becoming unstable.
Fig. 8. Third bifurcation of the angular nonlinear normal mode family in the linear isomer. Surfaces of section for $\theta = \pi$ before (a) and after (b) the double period-doubling bifurcation. Stable periodic orbits before (c) and after (d) bifurcation. Red and orange lines represent the two new stable periodic orbits arisen from the bifurcation. (For interpretation of the colours in this figure, the reader is referred to the web version of this Letter.)

Fig. 9. Fourth bifurcation of the angular nonlinear normal mode family in the linear isomer. Surfaces of section for $\theta = \pi$ before (a) and after (b) the pitchfork bifurcation. Periodic orbits before (c) and after (d) bifurcation. Red and orange lines represent the two new stable periodic orbits arisen from the bifurcation. (For interpretation of the colours in this figure, the reader is referred to the web version of this Letter.)
and simultaneously a new periodic stable motion emerges from $L_1$, represented as a red line in Fig. 10a. This new stable motion has twice the period of $L_1$, and thus a multiplicity $m = 2$.

In order to visualize this bifurcation in a clearer way, we have made use of surfaces of section for $P_R = 0$ instead of the previous one $\theta = \pi$, because in the last one, the radial normal mode $L_1$ appears as the limit of the SOS. Fig. 10b–c shows the SOS $P_R = 0$ before (b) and after (c) the bifurcation takes place. In these figures it can be seen how the fixed center point corresponding to $L_1$ becomes a saddle point and two new center points along the $P_R = 0$ axis. These two new center points correspond to the new stable periodic motion of multiplicity $m = 2$. For this energy range, great part of the SOS is covered by chaotic motions. Fig. 10d–e shows as a green line the orbit of the radial mode $L_1$ plotted in the $(\theta, R)$ plane, as well as the orbit of the new stable periodic motion (red line) arisen from the bifurcation. As the energy considered after the bifurcation, $E = -2 \times 10^{-4}$ a.u., is above the isomerization energy barrier $E_S$, the SOS of Fig. 10c and the equipotential curve of Fig. 10e are not closed because in that case, the potential wells of both isomers are connected. However, the periodic motions involved in this bifurcation remain confined in the well of the linear configuration. Moreover, around the periodic orbits involved in this bifurcations there exist islands of regular motion confined in the well of the linear configuration.

4.2. T-shape configuration

With regards to the T-shape isomer, we also begin considering the angular nonlinear normal mode. Fig. 11a shows the stability diagram of the family of the periodic orbits corresponding to this normal mode. This diagram gives the stability parameter $k$ of this family in the interval $-3.8 \times 10^{-4}$ a.u. $\leq E \leq -2.2 \times 10^{-4}$ a.u. We call this family with the same name as the corresponding periodic orbit $T_2$. As it can be seen in this figure, the evolution of the $T_2$ family with the energy, represented by a blue line, is only affected by a bifurcation, that takes place for $E \approx -2.75 \times 10^{-4}$ a.u., when the stability index crosses the critical value $k = 2$. This is a pitchfork bifurcation in which the normal mode $T_2$ changes its stability becoming unstable, and simultaneously two new periodic stable motions emerge from $T_2$. Both new stable periodic motions have the same stability index values, and thus, they are represented with the same red line in Fig. 11a.

As we are considering now the T-shape configuration whose potential well is centered at $\theta = \pi/2$, this bifurcation is better visualized in Fig. 11b–c making use of surfaces of section for $\theta = \pi/2$. The angular normal mode $T_2$, that appears before the bifurcation as a fixed center point located at the $P_R = 0$ axis (Fig. 11b), transforms after bifurcation into a saddle point and two new center points situated symmetrically with respect to the $P_R = 0$ axis (Fig. 11c). Each one of these new center points corresponds to one of the two new stable periodic motions emerged from this bifurcation. As it also can be seen in these figures, most of the SOS is filled by chaotic motions for this energy range. It is important to note that in the T-shape configurations chaotic motions appear more quickly than in the linear one. In Fig. 11d–e the orbit of the normal mode $T_2$ is plotted in the $(\theta, R)$ plane as a blue line. The orbits of the two new stable periodic motions are also represented by red and orange lines in Fig. 11e. It is interesting to note that, unlike the normal mode $T_2$, the shapes of these new periodic motions are not symmetric with respect to the $\theta = \pi/2$ axis, but they are as mirror reflections one each other.

On the other hand, Fig. 12a shows the stability diagram in the interval $-4 \times 10^{-4}$ a.u. $\leq E \leq -1.5 \times 10^{-4}$ a.u. of the family of the periodic orbits $T_1$ corresponding to the radial nonlinear normal mode of the T-shape isomer. The evolution of this family with the energy, that is represented in this figure by the blue line, is only affected by a bifurcation for $E \approx -2.65 \times 10^{-4}$ a.u., when the stability index crosses the critical value $k = -2$. This is a period-doubling bifurcation in which the radial normal mode $T_1$ changes its stability becoming unstable, and at the same time a new periodic stable motion emerges from $T_1$. This new stable family,

*Fig. 10. Bifurcation of the radial nonlinear normal mode family in the linear isomer. (a) Stability diagram of the family of the periodic orbits as a function of the energy $E$. Surfaces of section for $P_R = 0$ before (b) and after (c) the period-doubling bifurcation. Periodic orbits before (d) and after (e) bifurcation. Red line represents the new stable periodic orbit arisen from the bifurcation. (For interpretation of the colours in this figure, the reader is referred to the web version of this Letter.*)
Fig. 11. Bifurcation of the angular nonlinear normal mode family in the T-shape isomer. (a) Stability diagram of the family of the periodic orbits as a function of the energy $E$. Surfaces of section for $\theta = \pi/2$ before (b) and after (c) the pitchfork bifurcation. Periodic orbits before (d) and after (e) bifurcation. Red and orange lines represent the two new stable periodic orbits arisen from the bifurcation. (For interpretation of the colours in this figure, the reader is referred to the web version of this Letter.)

plotted as a red line in Fig. 12a, has twice the period of $T_1$ and a multiplicity $m=2$.

This bifurcation is portrayed in Fig. 12b–c by means of surfaces of section for $P_R = 0$. The new center points correspond to the new stable periodic motion of multiplicity $m=2$. For these energy values, similar to those of the previous bifurcation of the angular mode, great part of the SOS is covered by chaotic motions. Fig. 12d–e shows as a green line the orbit of the radial normal mode $T_1$ plotted in the $(\theta, R)$ plane, as well as the orbit of the new stable periodic motion (red line) emerged from the bifurcation.

Fig. 12. Bifurcation of the radial nonlinear normal mode family in the T-shape isomer. (a) Stability diagram of the family of the periodic orbits as a function of the energy $E$. Surfaces of section for $P_R = 0$ before (b) and after (c) the period-doubling bifurcation. Periodic orbits before (d) and after (e) bifurcation. Red line represents the new stable periodic orbit arisen from the bifurcation. (For interpretation of the colours in this figure, the reader is referred to the web version of this Letter.)
5. Chaotic behavior

As we observe in the gallery of surfaces of section throughout the Letter, as the energy increases, the regions of stochasticity grow in size. A clear way to illustrate this fact is to measure the fraction \( f \) of the phase space volume occupied by regular trajectories in the accessible linear (green line) and T-shape phase space volumes as a function of the energy \( E < E_S \). (b) Evolution of the fraction \( f \) for energy \( E > E_S \). (For interpretation of the colours in this figure, the reader is referred to the web version of this Letter.)

6. Conclusions

In the present work, we have studied the classical dynamics of the rare gas-dihalogen Ne···Br\(_2\) complex in its ground electronic state. Owing to the fact that the van der Waals bond between the Ne atom and the Br\(_2\) dimer is much weaker than the dihalogen bond, we have considered this bond frozen at its equilibrium distance, and therefore we have treated this molecular complex as a system of two degrees of freedom. We have also restricted our study to the case in which the total angular momentum of the complex is taken to be zero.

Under these assumptions, the potential energy surface of the system has two pairs of minima: one pair corresponds to the two equivalent linear configurations of the complex, and the other pair corresponds to the T-shape configurations. These four potential wells are separated by four saddle points.

By direct inspection of the equations of motion and using suitable Poincaré surfaces of section, we have found four stable basic periodic orbits that determine the phase space structure of the system. These basic periodic motions are the nonlinear normal modes of both linear and T-shape isomers. Each one of both configurations has one radial normal mode and one angular mode. Moreover, by means of the surfaces of section and applying the numerical continuation of families of periodic orbits, we have studied the evolution the normal modes of both isomers as a function of the system energy.

We have detected and identified the different bifurcations suffered by the normal modes, as well as the new periodic orbits emanated from the bifurcations. For increasing values of the energy, the angular mode of the linear isomer undergoes a sequence of four bifurcations: a double pitchfork one, two consecutive double period-doubling ones, and at last a simple pitchfork one, in which this normal mode becomes unstable. Each one of the other normal modes only suffers one bifurcation: either a pitchfork one or a period-doubling one, in which they turn into unstable periodic motions.
Although some of the detected bifurcations take place for energy values above the isomerization energy barrier, we have found that the orbits of the normal modes and the new periodic motions involved in the bifurcations remain confined in the potential well of the corresponding isomer. On the other hand, even though the shape of the orbits of the normal modes are always symmetric with respect to the angular coordinate for all considered energy values, we have detected that in some of the bifurcations, the new arisen periodic orbits lose this kind of symmetry in their shapes.

With respect to the evolution of the phase space, for small values of energy, the phase space presents quite regular structure with quasiperiodic motions organized around the normal modes of both configurations. Nevertheless, for increasing values of the energy, the regularity of the system dynamics decrease because the phase space begins to be filled by growing regions of chaotic motions. By means of the Orthogonal Fast Lyapunov Indicator (OFLI), we have studied the evolution of the fraction of the phase space volume occupied by regular motions. In this way, we have found that the dynamics of the T-shape isomer loses its regularity much more quickly than the linear isomer dynamics. For energy values above the isomerization energy barrier the system dynamics is almost completely dominated by chaotic motions.

There are some potential directions for future studies. In particular, the extension of this study when the total angular momentum of the complex is not zero is now under consideration.

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