

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

Fernando Blesa^a, Jorge Mahecha^b, J. Pablo Salas^c, Manuel Iñarraea^{c,*}

^a Departamento de Física Aplicada, Universidad de Zaragoza, Zaragoza, Spain

^b Instituto de Física, Universidad de Antioquia, Medellín, Colombia

^c Área de Física Aplicada, Universidad de La Rioja, Logroño, Spain

ARTICLE INFO

Article history:

Received 23 June 2009

Received in revised form 14 September 2009

Accepted 16 October 2009

Available online 24 October 2009

Communicated by A.P. Fordy

PACS:

05.45.-a

45.20.jj

34.10.+x

31.15.xv

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.

© 2009 Elsevier B.V. All rights reserved.

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 Efsthathiou and Contopoulos [6], Farantos [7] and Ezra [8].

A nice example where classical dynamics is playing an important role are the rare gas-dihalogen van der Waals 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 [9,10] 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 the 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.

* Corresponding author.

E-mail address: manuel.inarraea@unirioja.es (M. Iñarraea).

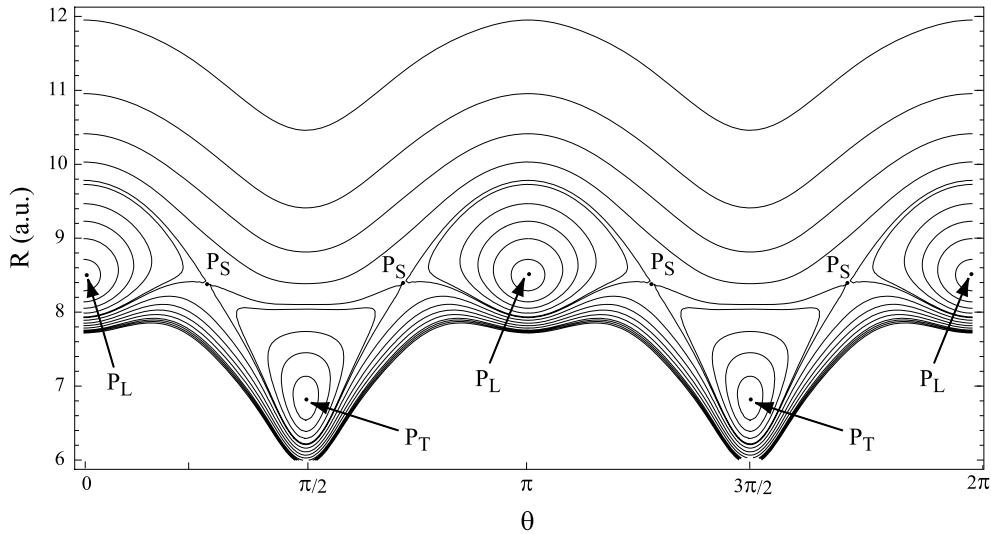


Fig. 1. Equipotential curves of the potential energy surface $V(R, \theta, r_e)$.

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 $r_e \approx 2.281 \text{ \AA}$. 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]

$$\mathcal{H} = \frac{P_R^2}{2\mu_2} + \frac{1}{2} \left(\frac{1}{\mu_2 R^2} + \frac{1}{\mu_1 r_e^2} \right) P_\theta^2 + V(R, \theta, r_e). \quad (1)$$

In Hamiltonian (1), R is the distance of the Ne atom to the $\text{Br}-\text{Br}$ center of mass, θ is the angle between R and r_e , (P_R, P_θ) are the canonical momenta conjugated of R and θ and $\mu_1^{-1} = m_{\text{Br}}^{-1} + m_{\text{Br}}^{-1}$ and $\mu_2^{-1} = m_{\text{Ne}}^{-1} + (2m_{\text{Br}})^{-1}$ 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 from the *ab initio* data calculated in [10]. Using these data and following the collocation procedure also reported in Ref. [10], an expansion in Legendre polynomials $P_\lambda(\cos\theta)$ allows one to write the PES as

$$\begin{aligned} V(R, \theta, r_e) &= \sum_{\lambda} \left\{ \sum_{i=1}^5 \alpha_{i\lambda} [e^{-2\beta_i(R-\gamma_i)} - 2e^{-\beta_i(R-\gamma_i)}] - \frac{\delta_\lambda}{R^6} - \frac{\eta_\lambda}{R^8} \right\} \\ &\times P_\lambda(\cos\theta), \quad \lambda = 0, 2, 4, 6, 8, \end{aligned} \quad (2)$$

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 π , the potential energy surface $V(R, \theta, r_e)$ and the Hamiltonian \mathcal{H} are also periodic functions of the same period in the θ angle.

In Fig. 1 the equipotential curves of (2) are shown. At $R = 8.479433 \text{ a.u.}$ and $\theta = 0$ and $\theta = \pi$ the PES has two equivalent minima P_L of energy $E_L = -0.000427 \text{ a.u.}$ These minima correspond to the linear isomer of the molecule. At $R = 6.798360 \text{ a.u.}$ 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 $E_T = -0.000388 \text{ a.u.}$ 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 $E_S = -0.000219 \text{ a.u.}$ located at

$R = 8.383587 \text{ a.u.}$ 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 is 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

$$\begin{aligned} \dot{\theta} &= \left(\frac{1}{\mu_2 R^2} + \frac{1}{\mu_1 r_e^2} \right) P_\theta, \\ \dot{P}_\theta &= -\frac{\partial V(R, \theta, r_e)}{\partial \theta}, \\ \dot{R} &= \frac{P_R}{\mu_2}, \\ \dot{P}_R &= \frac{P_\theta^2}{\mu_2 R^3} - \frac{\partial V(R, \theta, r_e)}{\partial R}. \end{aligned} \quad (3)$$

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 (θ, P_θ) plane for $P_R = 0$. We choose this surface of

Download English Version:

<https://daneshyari.com/en/article/1861788>

Download Persian Version:

<https://daneshyari.com/article/1861788>

[Daneshyari.com](https://daneshyari.com)