A periodic orbit analysis of the vibrationally highly excited LiNC/LiCN: a comparison with quantum mechanics

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Abstract

By constructing continuation/bifurcation diagrams of families of periodic orbits of LiNC/LiCN system the spectroscopy and dynamics for this species are deduced and compared with accurate quantum mechanical calculations up to 13000 cm^{-1}. The interesting phenomenon of the appearance of *gaps* in the continuation diagram of the principal family that corresponds to the bend motion is shown to occur in both isomers, LiNC and LiCN. Through semiclassical quantization a one to one correspondence of specific periodic orbits to certain eigenstates is demonstrated. One interesting example is the case of periodic orbits that are generated from a saddle-node bifurcation and describe rotations of Li^+ ion around the CN^- fragment. The correspondence of these periodic orbits to regular rotating type eigenfunctions is shown, thus, demonstrating in a clear way the importance of the saddle-node bifurcations in locating localized wavefunctions in highly energized molecules.

1 Introduction

The spectroscopy of vibrationally highly excited small polyatomic molecules is currently a challenging area of research, both for theory and experiment.[1,2] The vibrational spectra reveal the nonlinear dynamical properties of the molecule, and thus, they can provide information for understanding quantum chaos.[3]

In spite of the significant progress in theory and experiment of the last decade, accurate measurements and calculations exist only for a few triatomic and tetratomic molecules and for limited energy ranges. For example, quantum mechanical calculation are available for acetylene,[4] with the full six dimensional (6-D) potential energy surface, but for a significantly smaller energy range than that covered in Stimulated Emission Pumping (SEP) spectra.[5]

It is well known that quantum calculations depend on the current state of the computer technology, which does not allow at present one to compute vibrational levels at very high energies. Therefore, it is quite common to use classical mechanics to investigate the spectroscopy and dynamics of polyatomic molecules.[1] Moreover, we are interested in vibrationally excited molecules, and thus, it is necessary to use techniques of nonlinear mechanics.[2]

A method that we have developed in the last years for studying the spectroscopy and the dynamics of polyatomic molecules is based on locating families of periodic orbits in order to deduce the structure of molecular phase space, and then, we associate this structure with the spectra through classical, semiclassical or even time dependent quantum mechanical calculations.[2] We have applied this methodology in several molecules, such as, HCN,[6] O_3,[7,8] SO_2,[9] and recently in HCCH.[10] By locating periodic orbits and following their evolution with the total energy of the molecule, we construct continuation/bifurcation diagrams that portray the dynamics of the molecule at particular regions of phase space. Thus, we can trace the regions where the dynamics is regular or chaotic, and the regions where interesting localization effects occur.

In the previous applications it was necessary to compare the Periodic Orbit Method (POM) either with experimental spectra or limited quantum mechanical calculations, available mainly for the low energy vibrational levels. Now, the LiNC/LiCN molecular system offers the opportunity to carry out a direct comparison of the Periodic Orbit Method with quantum mechanics. The reasonable assumption to consider the CN^- bond frozen, and thus, to reduce the dimensionality of the system to two degrees of freedom, has allowed the calculation of a large number (900) well converged quantum levels[11,12] that cover an energy interval of about 13000 cm^{-1}.

The LiNC/LiCN species has attracted a lot of interest in the past, because of the low energy barrier to isomerization that makes the molecule floppy at the excited vibrational states. Initially, Farantos and Tennyson[13,14] carried out both classical and quantum calculations in order to study the dynamical behavior of this system at high energies where nonlinear effects are important. By applying techniques of nonlinear mechanics a relatively early onset of chaos was detected. Several diagnostics of quantum chaos were tested, such as level spacing statistics, the complexity of the nodal structures of eigenfunctions, sensitivity of the eigenvalues to small perturbations in the hamiltonian, and overlapping of the avoided crossings in energy levels,[13] and all these revealed a generally good correspondence with classical mechanics. An interesting result of the above studies was the discovery of localized eigenfunctions in the configuration space, and that in spite of the high level of excitation.

Later on, Light and Bacic[15,16] used the Discrete Variable Representation (DVR) to compute 131 vibrational levels, thus, pioneering in the field of theoretical vibrational spectroscopy. Henderson and Tennyson[12] extended the above record by obtaining 900 vibrational states of the rotationless LiNC/LiCN system using the DVR method as well. Again, nodal structure analysis of the eigenfunctions in high lying energies has shown, that most of them are irregular, but there is a number of eigenstates which can be assigned with normal mode quantum numbers or as rotating type states. The latter means, that the Li^+ ion can rotate around the CN^- fragment. The distribution of the differences of the adjacent energy levels indicated a chaotic behavior for the system at energies above the barrier of isomerization.

Benito et al.[11] recalculated the 900 eigenfunctions of LiNC/LiCN and obtained the Husimi transforms of them. The latter is a representation of the eigenfunctions in phase space (coordinates and momenta), and that in some cases reveals better the correspondence of the eigenfunctions to classical mechanical objects, such as periodic orbits.[17]

In a recent paper, Neuhauser[18] applied time dependent methods and a filtering diagonalization scheme to calculate 146 vibrational energy levels. All the above calculations are based on a 2-D SCF potential energy surface of Essers et. al.[19] in which the CN^- bond is frozen at the equilibrium bond length.

The amount of the previous work on LiNC/LiCN system makes this molecule a prototype for vibrational calculations. Particularly, the large number of the quantum mechanical eigenlevels now available, poses for a classical mechanical analysis and comparison with quantum mechanics.

The purpose of this paper is to carry out such a comparison with the Periodic Orbit Method. The importance of a particular class of periodic orbits, the saddle-nodes, emphasized before,[20] can now be examined by direct comparison with exact quantum calculations at high energies. The paper is organized as follows: In Section 2 we introduce the Hamiltonian and the Periodic Orbit Method. In section 3 we present the continuation/bifurcation diagrams of periodic orbits, and in Section 4 we show the correspondence of particular families of periodic orbits, semiclassically quantized, to the eigenfunctions. Finally, a discussion and conclusions are given in Section 5.

2 The Hamiltonian and the Periodic Orbit Method

We use the SCF potential energy surface of Essers et. al.[19] (the same potential was used in all quantum mechanical calculations) for the two dimensional vibrational problem with fixed the CN^- bond. The hamiltonian is expressed in Jacobi coordinates, (R, θ), where R is the distance of Li^+ from the center of mass of CN^-, and θ is the angle between R and the bond length of CN^-, r, which is fixed at 2.186 a_o.

The Hamiltonian has the form:

$$H = \frac{P_R^2}{2\mu_1} + (\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2})\frac{P_\theta^2}{2} + V(R,\theta), \tag{1}$$

where $\mu_1^{-1} = m_{Li}^{-1} + (m_C + m_N)^{-1}, \quad \mu_2^{-1} = m_C^{-1} + m_N^{-1}$ are the reduced masses, and m_C, m_N, m_{Li} are the atomic masses.

The potential surface, $V(R,\theta)$, has two minima with linear geometries: the absolute minimum is for LiNC at (R=4.3487 a_o, θ=π), and the relative minimum is for LiCN at (R=4.7947 a_o, θ=0) with energy 2281 cm^{-1} above the LiNC minimum. The barrier of isomerization between these two minima is at 3455.5 cm^{-1} and with the geometry (R =4.2197 a_o, θ=0.91799). Also, there is a plateau in the LiNC well at 1207 cm^{-1} above the absolute minimum, and with geometry (R =3.65 a_o, θ=1.92).

A new ab initio potential energy surface has been produced that includes the electron correlation at MP2[21] and MP4[22] level. Although the geometries of the linear minima are in close agreement in the two potential functions, there are significant differences in their relative energies. The most important difference is the appearance of a new T-shaped minimum in the place of the plateau observed in the Essers. et al. potential surface.[19] Both potentials predict that the LiNC isomer is the absolute minimum, with harmonic vibrational frequencies in good agreement with the experimental results obtained from microwave spectroscopy[23] and infrared spectra in inert gas matrices.[24] There is no experimental manifestation of the the T-shaped minimum.

In the traditional approach of molecular spectroscopy, a normal mode description of the system is used to assign the low vibrational levels. However, this formulation is generally considered inappropriate for the high levels. Still, to our surprise, vibrational spectra of some highly energized molecules are successfully assigned with normal mode quantum numbers.[5]

The use of periodic orbits (nonlinear objects) for the assignment of the vibrational spectra can explain the validity of the normal mode assignment at high energies. The periodic orbits that originate from a minimum of the potential function are closely related to the normal modes of the molecule. As energy increases the coupling and nonlinearities of the potential deforms the periodic orbits, but still they keep a lot of the normal mode morphologies. Localization of the eigenfunctions around these periodic orbits will result in spectra which show progressions of a particular normal mode.

Thus, we start searching for periodic orbits from the stationary points of the potential from where the principal families originate.[25,26] Then, by carrying out continuations of these periodic orbits with the energy of the molecule or the period of the periodic orbit, we find bifurcating families. Finally, saddle-node bifurcations that give rise to families of periodic orbits suddenly in phase space, are investigated. These bifurcations are difficult to locate in general, but we have found a category of them to emerge systematically above barriers of isomerizations.[20] They mainly connect the regions of the two minima of the potential.

To locate the periodic solutions of Hamilton's equations of motion we must solve the nonlinear equations:

$$\vec{x}[T; \vec{x}(0)] - \vec{x}(0) = 0, \tag{2}$$

where $\vec{x}$ is the vector that contains the coordinates and their conjugated momenta, and T is the period of periodic orbit. To solve Eq. (2) the Newton-Raphson method is employed in conjunction to multiple shooting techniques.[27] The latter requires the integration of the variational equations:

$$\Delta\dot{\vec{x}}(t) = A(t)\Delta\vec{x}(0). \tag{3}$$

$\Delta\vec{x}(t)$ is the deviation from the reference trajectory $\vec{x}(t)$, and $A(t)$ is a matrix with the second derivatives of the hamiltonian, $A(t) = J\partial H^2[x(t)]$, calculated at $\vec{x}(t)$. J is a symplectic matrix expressed with the zero and unit matrices of order N, the number of degrees of freedom,

$$J = \begin{pmatrix} 0_N & I_N \\ -I_N & 0_N \end{pmatrix}. \tag{4}$$

Details of the method have been given in previous publications.[2,20]

For a periodic orbit the matrix $A(T)$ is called monodromy matrix. The eigenvalues of the monodromy matrix determine the stability of periodic orbit.[28] The evolution of periodic orbits with the total energy of the molecule (or the period) and their stability analysis give a portrait of the phase space structure. For the LiNC/LiCN molecule we have found the principal periodic orbits and the most important bifurcating families. The results are presented with continuation/bifurcation diagrams, that is, plots of the initial conditions of periodic orbits as functions of the total energy of the system.

3 Continuation/Bifurcation Diagrams of Periodic Orbits

In Figure 1 we show the projection of the continuation/bifurcation diagram constructed for LiNC on the (E, R) plane. In Table I we give initial conditions for one periodic orbit of each family found, and Fig. 2 shows the morphologies of representative periodic orbits. In the continuation scheme we kept the angle coordinate θ equal to π.

The two principal families of periodic orbits that emanate from the minimum of LiNC are related to the normal modes of the molecule, and thus, we label them with S for the stretch mode and with B for the bend mode. Solid lines denote stable periodic orbits, and dashed lines unstable ones. Bifurcating families are labeled with numerals and the two branches with the letters A and B.

As we can see in Fig. 1 the S principal family remains stable for the whole energy range studied, up to 30000 cm^{-1}. Contrary to that, the bend family has an early transition to instability, the first found at 733.2 cm^{-1}, after which it turns stable again. Other instability regions were located at 1034.6 and 1543.8 cm^{-1}, but it permanently becomes unstable at the energy of 1958.6 cm^{-1}.

We found some interesting bifurcations of the B family at 201.7, 870.7, 1176.4, and 1326.5 cm^{-1}, which give rise to the families B1, B2, B3, and B4 respectively. As we can see in Fig. 1, at these bifurcation points the principal B family shows characteristic *gaps* in its continuation diagram. A gap appears since the principal family is smoothly split and is connected to the two bifurcating families, branches A and B.

Contopoulos[29] has studied this phenomenon on a 2-D model rotating galactic type potential. He used classical perturbation theory and showed, that gaps in the continuation diagram appear in the cases of n/1 (n even) resonance conditions between the two characteristic frequencies of the hamiltonian; in our case n/1 is the ratio of the frequencies that correspond to the angle, θ, and distance, R, coordinates. Using action-angle variables $(J_1, \theta_1, J_2, \theta_2)$, and the fact that under a resonance condition the hamiltonian is dominated by the term $\cos(m\theta_1 - 2n\theta_2)$, Contopoulos showed that gaps appear when $m = 1$, and ordinary bifurcations when $m = 2$ and n is odd. In the latter case the principal family turns to unstable after the bifurcation point. The fact that an infinite number of bifurcations may appear with an equivalent number of bifurcating families, may lead to large stochasticity.

In our case, we can see from the morphologies of the bifurcating periodic orbits (Fig. 2) that the resonances which are responsible for the gaps are the 6/1 (B1A, B1B), 8/1 (B2A, B2B), 10/1 (B3A, B3B), and 10/1 (B4A, B4B).

A systematic study of the morphologies of the B type periodic obits reveals that their shapes change significantly at energies above the last gap. It is worth mentioning that this energy is above the plateau (about 1207 cm^{-1}). Also, all the bifurcating periodic orbits from the B principal family appear with the same period as the parent one, and that means, that one pair of eigenvalues of the monodromy matrix is equal to one. The only exception is the B8A family (Fig. 1) that has a double period (one pair of eigenvalues of the monodromy matrix of the parent family is equal to -1).

We may conclude, that in contrast to the stretch family of periodic orbits, S, which remains stable for an extended energy interval, the bend family, B, shows a large number of bifurcations from low energies. That means, that excitation of the bend motion will lead the molecule to early chaotic behavior. This was one of the main conclusions in the early classical mechanical studies of the floppy molecules.[13,14] Now, we can see that the continuation/bifurcation diagrams of periodic orbits support this conclusion and provide a systematic way to explore the structure of phase space.

We have argued in previous papers, that saddle-node bifurcations are important for molecular systems,[20,30] since they create islands of stability in chaotic seas of the phase space. Saddle-node bifurcations appear saddenly, and for 2-D systems they generate one stable and one unstable family of periodic orbits. We have shown by studying several molecular systems that saddle-node bifurcations appear constantly above the barriers of isomerization, and usually, they connect the regions of the two minima of the potential function. In the case of LiNC/LiCN this type of periodic orbits describe full rotations of Li^+ ion around the CN^- fragment, and thus, we have named them in the past rotating periodic orbits.

Figure 3 shows the continuation diagrams of the rotating type periodic orbits for the LiNC/LiCN system. Figure 4 presents the morphologies of representative periodic orbits, one for each saddle-node family, and Table II tabulates initial conditions, period, and the stability for one periodic orbit of each family. As before the solid lines mean stable orbits and the dashed lines unstable orbits. From Fig. 4, we can see that all saddle-node periodic orbits (SN) correspond to n/1 resonances. The resonance ratio decreases for the SN bifurcations at higher energies. Also, another characteristic of the saddle-node bifurcations is that, in one branch the period of periodic orbits increases and in the other branch decreases with the energy.

Although, there is always a stable branch at the origin of the saddle-node bifurcation, this branch may turn to unstable as the energy increases. A characteristic example is that of the SN6 bifurcation where both branches A and B appear as unstable in Fig. 3. For a small energy interval around the critical point the SN6B family is stable, then it becomes unstable, and at higher energies it turns to stable again. From the continuation diagram of Fig. 3 we can see that most SN families are unstable, but some of them like the SN3B has a stable part that extends for an energy interval of 8778 cm^{-1}. The SN6B, SN7B, and the SN8B families that appear at high excitation energies of the molecule, also show intervals of stability. Thus, we conclude that above the energy of 10000 cm^{-1} the phase space may have stability islands because of the genesis of the saddle-node periodic orbits.

To have an estimate of the regions of phase space that these families affect, we plot in Fig. 5 the Poincaré surface of sections at the energy of 14867 cm^{-1} and with $\theta = 0.91799$. The three islands of stability seeing in this figure, correspond to the SN3B, SN6B, and SN7B. We shall see in the following section that the extended stability properties of the SN3B family has a profound effect in the quantum mechanical behavior of the molecule.

It is interesting to note the white zones in the upper part of the Poincaré surface of sections. This region is magnified in other Poincaré surfaces of section that we have plotted. Obviously, the white area means that chaotic trajectories escape quickly from that particular region of phase space. To explore the dynamics of the system in this area, we seek the periodic orbit that influences that particular region of phase space. This is the unstable principal family that is generated from the saddle point of the potential.

From Moser's theorem[26] we know that one single unstable family of periodic orbits emanates from the saddle point (not to be confused with the saddle-node bifurcations that appear at energies above the saddle point). We label it as TSA (Transition State) and its evolution with the energy is shown in Fig. 6a. It remains singly unstable for the whole studied energy interval (25000 cm^{-1}).

In Fig. 5 we mark the intersection of the TSA periodic orbit with the Poincaré surface of section with (x), where we also show the stable and unstable manifolds of this periodic orbit, W_s^+ (W_s^-), and W_u^+ (W_u^-), respectively. The signs $\pm$ denote the two opposite directions of the eigenvectors. The unstable manifold is propagated forwards in time and the stable manifold backwards in time. The stable and unstable manifolds, W_s^+, W_u^- of the TSA periodic orbit are extended along the white zones in the Poincaré surface of section. Since neighboring trajectories escape in the (θ, P_θ) plane, that region appears white in the plane of projection.

Borondo et al.[31] have found a saddle-node periodic orbit that originates above the plateau but below the saddle point of the potential at the energy of 3441.3 cm^{-1}, thus, the periodic orbit remains in the LiNC well. It describes mainly stretch of the Li^+ ion relative to the center of mass of CN^-, and it corresponds to a 1/1 resonance. Figure 6b shows the continuation diagram of this saddle-node bifurcation, (SNP2A, SNP2B), and Fig. 7 shows the morphologies of representative periodic orbits.

These periodic orbits have been used to explain some characteristic enhancements in the distribution of the probability densities of the eigenfunctions of LiNC in configuration space. The generation of these saddle-node periodic orbits was justified by invoking adiabatic potentials, the origin of which may be attributed to the plateau of the potential. This is an interesting result, but it is worth mentioning that the new potential function of Makarewitz and Ha[21] predicts a genuine T-shaped minimum instead, from where we expect the generation of two principal families, one for stretch and one for bend.

Nevertheless, in spite of a non genuine minimum in Essers et al. potential function the simple type periodic orbits SNP2 exist, and it is reasonable to assume that similar periodic orbits with bend excitation should also exist. Indeed, we have located another saddle-node bifurcation at energy of 2928.7 cm^{-1}, (SNP1A, SNP1B), and the periodic orbits describe mainly bend motion. Its continuation diagram is shown in Fig. 1, where its position in the LiNC minimum can be traced. Morphologies of representative periodic orbits can be found in Fig. 7, whereas, initial conditions for the periodic orbits of both, SNP1 and SNP2, bifurcations are given in Table I.

A continuation diagram was constructed for LiCN minimum, and it is shown in Fig. 8. Table III tabulates initial conditions for representative periodic orbits. The stretch family (S) remains stable up to 13026.5 cm^{-1}, and above it it becomes unstable. The B family of LiCN develops gaps that correspond to the resonances 4/1 and 6/1. The morphologies of the periodic orbits of LiCN are similar to those of LiNC and we do not show them.

4 Periodic orbits, semiclassical quantization, and quantum correspondence

The nodal patterns of the eigenfunctions of LiNC/LiCN revealed regular states highly localized in the configuration space as well as irregular states that tend to occupy extended regions of the configuration space. From the periodic orbit analysis we could predict that the localization is related with states that correspond to stretch excitations, and the irregular diffused states with bend excitations, which, of course, are strongly coupled with the stretch mode. Indeed, this was found in the first quantum calculations,[13,14] and the more recent ones[11,12] showed that stretch quantum levels of (v_s,0) type can be found at very high energies. v_s is the quantum number for the stretch mode and 0 for the bend mode.

Another interesting type of localized quantum states are those of rotating type mainly assigned as $(0,v_m)$, and found even at energies up to 12500 cm^{-1} in the quantum calculations.[11,12] These eigenstates appear above the barrier of isomerization and describe full rotation of Li^+ around the CN^- fragment. Interesting enough, the distribution of the energy differences of the adjacent energy levels tends to follow a Wigner distribution rather than a Poissonian distribution, and that means, that the system may be characterized as chaotic. This conclusion refers to the average behavior of the system, and it tends to hide the regularity of a number of eigenstates.

An approximate scheme to obtain the semiclassical spectrum from the periodic orbits, even for unstable trajectories, is through partial summations of Gutzwiller trace formula.[3] Although, the criticism about its convergence is well documented in the literature, previous applications[9,10,32] encourages one to use it, especially if low resolution spectra are asked.

According to Gutzwiller a semiclassical approximation of the density of states can be obtained by writing:

$$N(E) = \sum_n \delta(E - E_n) = \overline{N}(E) + N^{osc}(E), \tag{5}$$

where $\overline{N}(E)$ is the smoothed part of the density given by the Thomas-Fermi approximation, and $N^{osc}(E)$ is the fluctuating part that can be expressed according to the trace formula as the sum over all classical periodic orbits at a given energy

$$N^{osc}(E) = Re \sum_{po} \frac{T_{po}}{\pi\hbar} \sum_{j=1}^{\infty} \frac{\exp[ij(S_{po}/\hbar - \mu_{po}\pi/2)]}{[det(M_{po}^j - 1)]^{1/2}}. \tag{6}$$

The first summation runs over all primitive periodic orbits with period T_{po} and action S_{po}, and the second summation with respect to j is over multiple traversals of the same periodic orbit. μ_{po} is the Maslov index (number of caustics), and M_{po}^j is the stability matrix describing the time evolution of the displacements of periodic orbit after j loops.

The determinant can be computed from the eigenvalues of monodromy matrix

$$det(M_{po}^j - 1) = \prod_{i=1}^{2(N-1)} (\lambda_{po}^j(i) - 1), \tag{7}$$

where $\lambda_{po}^j(i)$ is the jth power of ith eigenvalue (a real or complex number) which defines the stability of periodic orbit. All these quantities are computed as functions of the total energy during the periodic orbit analysis.

A regularization scheme is introduced[3,33] to insure the convergence of the trace formula with respect to j. The usual method of regularization is to multiply the terms of the formula with the smoothing quantity:[33,34]

$$f(E) = \exp(-\frac{\gamma j T_{po}(E)}{\hbar}), \tag{8}$$

where $\gamma > 0$ is a decay parameter.

Gutzwiller trace formula applied to specific stable families results in the semiclassical quantization of particular periodic orbits, as has been discussed by Miller.[35]

Partial summation of Gutzwiller trace formula is justified by assuming localization of the eigenfunctions in configuration space, and thus, influence of them by a limited number of periodic orbits. Since, the quantum results show that the most localized eigenfunctions are for the $(v_s, 0)$ and $(0, v_b)$ energy levels, we have applied Eq. (5) by separately summing up over specific families of periodic orbits. These are: the stretch family of periodic orbits, the bend principal family and all bifurcating families from it, and finally, we apply trace formula for the saddle-node family of SN3B type that shows an extended energy region of stability.

In Tables IV and V we compare the energy differences of the adjacent stretch quantum levels, (v_s,0), v_s=0-21, and for the rotating levels (0,v_m), v_m=51-79. The agreement is quite good. The assignment of the quantum levels was given by Tennyson and Henderson.[12] Also, good agreement is found for the stretch overtones (v_s=0-17) of the LiCN isomer. For the bend levels it was not possible to achieve such quantitative agreement as can be seen in Table VI. The energies were obtained by assigning the quantum bend levels to the peaks in the fluctuating semiclassical density of states (Fig. 9). The bars at the top of Fig. 9 mark the quantum levels. The long bars correspond to the bend overtons (0, v_b), (v_b = 0-36), and the short ones to the bend-stretch combinations, (v_s, v_b), (v_s = 1-3, v_b = 2-12). Notice, that in the semiclassical spectrum peaks for even and odd progressions appear, whereas in the stick spectrum quantum levels with even quantum numbers are only assigned.

We can see in Table VI an erratic variation of the quantum mechanical energy differences ΔE, and this is reproduced by the semiclassical calculations. We attribute this behavior to the multiple bifurcations of the bend family of periodic orbits.

¿From the above, we conclude that in the cases where there is a one to one correspondence between periodic orbits and eigenfunctions the semiclassical estimates of the energy levels are satisfactory. On the other hand, in the strong chaotic mixing regions the convergence of the trace formula is slow (requires more families of periodic orbits), and thus, a less accurate spectrum is obtained.

As we saw from the previous sections, at high energies above the saddle-point of the potential barrier, the principal family of bend mode have become unstable and chaos dominates in the region connecting both minima of the potential. This would be the correct scenario to apply RRKM theory for the isomerization rate constants. However, a look at Fig. 5 demonstrates the existence of stability islands that correspond to saddle-node periodic orbits of rotating type. These stability islands remain even at very high energies, and the semiclassical calculations of the preceding section also show, that in a wide range of energies, rotating type quantum states exist, which seem to be related to one specific family of rotating type periodic orbits, that of the family SN3B.

Although, only a few of the eigenstates that cover this range of energies (7500 up to 13000 cm^{-1}) have clearly been assigned as rotating type states, there are more eigenfunctions of rotating type which cannot be assigned, since, they have not a regular nodal pattern. In Fig. 10 the eigenfunctions, that correspond to the Nos 333 and 810 levels, (7539.8 and 12337.4 cm^{-1} respectively), are shown, having the two periodic orbits of the SN3B family superimposed. These periodic orbits are those which have semiclassically been quantized, (0,51) and (0,73) in Table V.

Figure 10 provides a nice example of the scarring of the eigenfunctions by saddle-node periodic orbits. It is really impressive to see how close the nodes of the eigenfunctions follows the path of the periodic orbits, and that in spite of the large energy gap between the two states. These results support our previous conclusion, that saddle-node bifurcations are important for molecular dynamics by bringing stability in the chaotic regions of phase space.

In order to further validate the above conclusion, we have solved the time dependent Schrödinger equation with an initial wave packet centered on the rotating type periodic orbit that matches with the quantum state (0,51). The quantum equations of motion were solved numerically using a method which combines Close-Coupling and pseudospectral techniques.[6] The wave packet was expanded in a basis of Legendre polynomials for the angular part and it was discretized in the radial part on a grid. To propagate the wave packet in time we used a second order differentiation (SOD) scheme

$$\Psi_{k+1} = \Psi_{k-1} - \frac{2}{\hbar} i \Delta t \hat{H} \Psi_k. \tag{9}$$

k denotes the time step and the action of the Hamiltonian $\hat{H}$ on the wave packet Ψ_k is calculated by Fast Fourier transform techniques.[36] The basis of Legendre polynomials was increased until no significant change was observed. Also the SOD propagation method satisfied the conservation of norm and the expectation value of the energy.

The initial wave packet was centered on the rotating type periodic orbit shown in Fig. 10, and has a period of 171.7 fs. The wave packet was propagated for 1300 fs, and that corresponds to a resolution for the energy of 25 cm^{-1}. The spectrum is reproduced in Fig. 11. The eigenlevels obtained from the DVR calculations[12] and assigned to the rotating type states are depicted as stick lines. The highest intensity peak is that which corresponds to the eigenstate No. 333. Even if we can expect a priori some regular progressions corresponding to rotating type states, the wave packet is run for enough long time to bounce between the two minima several times and overlap with other periodic orbits. However, as seen in this figure, the regular rotating type states dominate completely the dynamics, and they cause this simulated SEP spectrum to appear very regular. No other progressions are observed in the range of energy for which the family SN3B is stable, although at higher energies than the one shown, some additional peaks with smaller intensities can be seen.

5 Discussion and conclusions

The large number of converged eigenfunctions available for the LiNC/LiCN system has allowed for a thorough test of the Period Orbit Method in analyzing molecular dynamics and assigning vibrational spectra with periodic orbits. The phase space structure portrayed by the continuation/bifurcation diagrams is consistent with the quantum mechanical picture as is deduced from the nodal patterns of the 900 eigenfunctions of this prototype system. At high energies regular highly localized quantum states are interwoven among irregular states in the same fashion as islands of stability in phase space are spread in chaotic seas. The association of the regular localized eigenfunctions with periodic orbits, and thus, with particular regions of phase space, elucidates this behavior.

The early bifurcations encountered in the evolution of the bend principal family is the mechanism which leads to chaotic dynamics in LiNC. The phenomenon of bifurcations with gaps is observed for this molecular system. At the same time an erratic variation of the energy differencies among the vibrational levels is found, but it is difficult to say that this is due to the gaps. A better study of this phenomenon is definitely required.

Furthermore, LiNC/LiCN enabled us to demonstrate in a clear way the importance of saddle-node bifurcations, especially those of rotating type. Semiclassical quantization, but also time dependent quantum calculations, show the correspondence of this type of periodic orbits with the rotating eigenfunctions.

The interest in studying the quantum manifestations of saddle-node rotating type periodic orbits stems not only in assigning highly excited spectra, but also, in the theory of isomerization reactions. These periodic orbits are the bound analogues of the resonant periodic orbits (RPOs) found in collinear reactive scattering systems.[37] The RPOs connect both minima of the potential energy surface and are the classical objects responsible for the resonances observed in the quantum reaction probabilities. In the isomerization process, LiNC $\Longleftrightarrow$ LiCN, it is seen that the classical trajectories allowing for the exchange of probability between both minima are the stable rotating type periodic orbits. The central quantity that provides the reaction rates is the cumulative reaction probability,[38] which can be calculated through the flux-flux autocorrelation function. If we perform a dynamical calculation of this function using wave packets one would expect in principle this periodic orbits to guide the evolution of the wave packet through the isomerization barrier.

It is well known in mathematics[39] that the dynamics of a system significantly changes above stationary points of the potential function. It is, therefore important to note that the plateau of the potential inside the LiNC well, which is not a stationary point, causes significant changes in the topology of the eigenfunctions, through the saddle-node bifurcations SNP1 and SNP2.

If the Newhouse theorem[40,41] applies here, we expect the SN bifurcations to emerge from tangencies of stable and unstable manifolds of unstable periodic orbits. How the SNP1 and SNP2 are emanated when no families of periodic orbits are expected from the plateau? We shall address such questions in future publications.

Semiclassical approximations are more successful in integrable cases, but for classical chaotic systems (mixed dynamics) are still regarded with some caution. Gutzwiller trace formula provides an approximate answer, but it allows us to make contact with the energy spectrum. Other approaches have also been suggested. Heller used a cellular method[42] and tried to organize the dynamics of the system using classical trajectories in a hierarchical structure avoiding the root search. Also for a chaotic regime, an extension of the Fourier method has been proposed,[43] which uses the most dominant terms of the Fourier expansion to give a numerically truncated approximate torus, the semiclassical analog of the wavefunction.

Summarizing, the results of the present study validate the conclusion that a periodic orbit analysis provides important dynamical information about the vibrationally highly excited molecules. The recent application of MOP in acetylene, a 6-D system, has shown the extentability of the method to polyatomic molecules.

Acknowledgment

We are grateful to Dr. Tennyson for supplying us the eigenenergies of LiNC/LiCN. This work was supported by a grant in the frame of a bilateral agreement between Greece and Spain. This work has also been supported in part by DGICYT (Spain) under grant PB92-181. RG gratefully acknowledges a doctoral grant from the MEC (Spain).

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TYPE	E	R	θ	P_R	P_θ	T	STAB.
B	.0025041	4.3641913	3.1415927	0.	14.7166468	12555.892	S
B1A	.0025041	4.5254251	3.1415927	0.	8.4769923	10894.878	U
B1B	.0025041	4.2017013	3.1415927	0.	9.4149024	10893.962	S
B8A	.0034041	4.3953127	3.1415927	.7137277	16.8418960	27662.052	U
B2A	.0050041	4.5277901	3.1415927	0.	17.0043498	14947.810	U
B2B	.050040	4.2311766	3.1415927	0.	18.7183491	14928.124	S
B7A	.050040	4.3004833	3.1415927	0.	20.4862174	17181.487	S
B3A	.0060041	4.5158060	3.1415927	0.	19.8960038	19548.073	U
B3B	.0060041	4.2555146	3.1415927	0.	21.6212443	19500.905	S
B4A	.0064741	4.4792370	3.1415927	0.	22.0445001	20200.164	S
B4B	.0065041	4.3045271	3.1415927	0.	23.4864756	20265.599	S
B6A	.0104841	4.2381856	3.1415927	6.7026889	25.2715696	18576.131	U
B6B	.0104841	4.2381856	3.1415927	-6.7026889	25.2715696	18576.131	U
B5A	.0130041	4.7370476	3.1415927	0.	23.1075409	16527.070	S
B5B	.0130041	4.4887775	3.1415927	0.	32.3970183	16527.070	S
S	.0025041	4.3487021	3.1415927	7.0956298	0.	1818.858	S
SNP1A	.0150741	4.4156593	3.1415927	0.	35.9919952	15094.908	U
SNP1B	.0150741	4.2313162	3.1415927	0.	34.8441054	18864.871	S
SNP2A	.0157003	3.7500000	1.9429267	13.3982490	-9.6193867	2221.021	S
SNP2B	.0157003	3.7500000	1.9676388	13.4639292	-9.9496242	2204.236	U

TABLE I Initial conditions for periodic orbits of LiNC, and the saddle-node periodic orbits that originate in the LiNC minimum. Atomic units are used.

TYPE	E	R	θ	P_R	P_θ	T	STAB.
SN1A	.0180041	4.2095966	3.1415927	0.	37.7938726	15009.520	U
SN1B	.0180041	4.1047007	3.1415927	0.	33.9850383	13987.152	U
SN2A	.0200041	4.1608813	3.1415927	0.	38.6241492	12729.261	U
SN2B	.0200041	4.0746767	3.1415927	0.	34.8364172	11877.531	U
SN3A	.0405041	5.3457859	3.1415927	0.	29.1471124	8199.718	U
SN3B	.0405041	5.0941213	3.1415927	0.	42.8992023	6548.515	U
SN4A	.0230041	4.7959435	3.1415927	0.	35.5748362	11486.788	S
SN4B	.0230041	4.6406821	3.1415927	0.	40.9131321	10813.230	S
SN5A	.0280041	4.9933818	3.1415927	0.	32.5650651	9666.328	U
SN5B	.0280041	4.7523858	3.1415927	0.	42.9345263	8282.726	U
SN6A	.0701833	3.8661075	3.1415927	0.	63.9261112	6787.717	U
SN6B	.0700041	4.3009503	3.1415927	0.	77.6974282	5787.819	S
SN6B1A	.0700041	3.9246520	3.1415927	8.2768547	65.2869510	6578.983	U
SN7A	.0700041	6.1343468	3.1415927	0.	24.8880564	6571.404	U
SN7B	.0700041	6.0540247	3.1415927	0.	30.1371542	5960.262	S
SN8A	.0961777	3.6507596	3.1415927	0.	60.1375883	4881.158	U
SN8B	.0961728	3.8311477	3.1415927	0.	76.7013272	3689.564	S
TSA	.0166903	4.3186548	.9330950	2.7594448	2.7996240	2026.410	U

TABLE II Initial conditions for saddle-node and transition-state periodic orbits. Atomic units are used.

TYPE	E	R	θ	P_R	P_θ	T	STAB.
B	.012420	4.817650	0.	0.	13.483930	8917.56	S
B1A	.011660	4.939559	0.	0.	5.2673680	7939.98	U
B1B	.011490	4.6821700	0.	0.	6.032060	7929.65	S
B2A	.014934	5.002160	0.	0.	15.594340	9828.70	S
B2B	.014487	4.693810	0.	0.	17.830610	9810.39	S
B3A	.015960	4.999300	0.	0.	18.492340	11854.06	U
B3B	.015149	4.748299	0.	0.	20.461420	11591.17	S
B4A	.016408	4.991872	0.	0.	19.617630	13747.81	U
B4B	.016408	4.702970	0.	0.	22.350510	13747.81	U
B5B	.015766	4.781019	0.	0.	22.022460	15453.94	S
S	.057590	4.794730	0.	30.803820	0.	2586.87	S

TABLE III Initial conditions for periodic orbits of LiCN isomer. Atomic units are used.

Level	E	ΔE	Semiclassical
(0,0)	0.0		
(1,0)	754.4	754.4	754.99
(2,0)	1498.4	744.0	744.02
(3,0)	2231.8	733.4	735.24
(4,0)	2954.8	723.0	724.27
(5,0)	3667.1	712.3	711.10
(6,0)	4368.9	701.8	702.32
(7,0)	5060.1	691.2	691.35
(8,0)	5740.6	680.5	680.37
(9,0)	6410.6	670.0	671.59
(10,0)	7070.0	659.4	660.62
(11,0)	7718.6	648.6	647.45
(12,0)	8356.6	638.0	638.67
(13,0)	8984.2	627.6	627.70
(14,0)	9601.4	617.2	616.72
(15,0)	10208.0	606.6	607.94
(16,0)	10804.4	596.4	594.78
(17,0)	11390.0	585.6	588.19
(18,0)	11965.0	575.0	575.02
(19,0)	12531.0	566.0	566.24
(20,0)	13086.0	555.0	555.27
(21,0)	-	-	544.30

TABLE IV Comparison of the quantum and semiclassical calculations for the stretch mode states of LiNC. Energies in cm^{-1}.

Level	E	ΔE	Semiclassical
(0,51)	7539.80	-	190.94
(0,52)	7737.10	197.30	197.52
(0,53)	7938.30	201.20	199.72
(0,54)	8141.90	203.60	201.72
(0,55)	8349.50	207.60	204.31
(0,56)	-	-	206.30
(0,57)	-	-	208.30
(0,58)	8989.70	-	210.70
(0,59)	-	-	212.89
(0,60)	9418.60	-	215.08
(0,61)	9634.00	215.40	215.09
(0,62)	-	-	217.28
(0,63)	10075.70	-	219.47
(0,64)	10299.50	223.80	221.67
(0,65)	10520.50	221.00	221.67
(0,66)	-	-	223.87
(0,67)	-	-	223.86
(0,68)	11197.50	-	223.86
(0,69)	-	-	228.26
(0,70)	11652.00	-	226.06
(0,71)	11879.76	227.76	228.25
(0,72)	12108.25	228.49	228.25
(0,73)	12337.40	229.15	230.45
(0,74)	12566.89	229.49	228.26
(0,75)	12796.65	229.76	230.44
(0,76)	-	-	232.65
(0,77)	-	-	230.45
(0,78)	-	-	232.64
(0,79)	-	-	230.45

TABLE V Comparison of the quantum and semiclassical calculations for the rotating type states. Energies in cm^{-1}.

Level	E	ΔE	Semiclassical
(0,0)	0.0		
(0,2)	247.2	247.2	254.58
(0.4)	469.0	221.8	232.65
(0,6)	665.6	196.6	193.13
(0,8)	836.8	171.2	122.91
(0,10)	982.3	145.5	162.4
(0,12)	1111.7	129.4	151.4
(0,14)	1245.3	133.6	136.12
(0,16)	1390.3	145.0	140.47
(0,18)	1545.4	155.1	138.27
(0,20)	1708.4	163.0	147.04
(0,22)	1874.8	166.4	162.4
(0,24)	2036.8	162.0	199.7
(0,26)	2244.9	208.1	221.7
(0,28)	2418.2	173.3	144.86
(0,30)	2531.3	113.1	127.3
(0,32)	2761.8	230.5	208.44
(0,34)	2918.4	156.6	169.05
(0,36)	3025.0	106.6	107.54

TABLE VI As Table IV but for the bend mode states of LiNC. Energies in cm^{-1}.

Figure Legends

1. Projection of the bifurcation diagram of LiNC in (E, R) plane showing the principal families of periodic orbits, bifurcations of them, and saddle-node periodic orbits that originate inside the LiNC minimum. The symbols denote the stretch (S), and bend (B) principal families of LiNC, and SNP1A and SNP1B the saddle-node periodic orbits with bend mainly excitation (see text). Solid lines mark stable periodic orbits and dashed lines unstable periodic orbits.

2. Morphology of representative periodic orbits in (R, θ) plane for LiNC. All these figures are symmetric with respect to the line $\theta = \pi$ and they are restricted inside to the LiNC minimum.

3. Projection of continuation/bifurcation diagram for the saddle-node (SN) families of periodic orbits of LiNC/LiCN.

4. Morphology of representative saddle-node periodic orbits in (R, θ) plane. These orbits are symmetric with respect to the $\theta = \pi$ line, and describe full rotations of the Li^+ ion around the CN^- fragment.

5. Poincaré surfaces of sections obtained by integrating trajectories at the energy of 14867 cm^{-1}, and for $\theta = 0.91799$ and $P_\theta > 0$. The islands enclose the stable saddle-node periodic orbits SN3B, SN6B, and SN7B. The X sign denotes the position of the unstable transition state periodic orbit (TSA), and W_s^+ (W_s^-), and W_u^+ (W_u^-) are the stable and unstable manifolds that are associated with it.

6. (a) Projection of the continuation diagram of the principal family of periodic orbits originated from the transition state of LiNC/LiCN. (b) Projection of the continuation diagram of the saddle-node family of periodic orbits emerged inside the LiNC minimum and having mainly stretch excitation.

7. Morphologies of representative periodic orbits for the transition state and saddle-node periodic orbits found inside the LiNC well.

8. Projection of the continuation diagram of periodic orbits of LiCN isomer.

9. The fluctuating part of the density of energy levels given by Gutzwiller semiclassical trace formula for LiNC molecule. The principal B family and all located bifurcations are used. The vertical lines at the top of the plot show the energies obtained with the quantum mechanical calculations and assigned by the quantum numbers (v_s, v_b), where (v_s=1-3, v_b=2-12) (short lines) and (0,v_b), (v_b=0-36) (long lines).

10. Contour plots for the rotating type eigenstates, level No. 333 (0,51), and level No. 810 (0,73), at energies 7539.8 and 12337.4 cm^{-1}, respectively. Superimposed are the SN3B periodic orbits at the same energies.

11. The quantum mechanical spectrum obtained by solving the time dependent Schrödinger equation and with an initial Gaussian wave packet centered on the saddle-node periodic orbit that corresponds to the quantum eigenstate No. 333 (see Fig. 10). The stick spectrum at the top of the figure is obtained from the time independent calculations.