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Homoclinic motions in the vibrational spectra of floppy systems: The LiCN molecule

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Recent experimental and theoretical methods allowed the efficient investigation of highly excited rovibrational states of molecular systems. At these levels of excitation the correspondence principle holds, and then classical mechanics can provide intuitive views of the involved processes. In this respect, we have recently shown that for completely hyperbolic systems, homoclinic motions, which are known to organize the classical chaotic region in Hamiltonian systems, imprint a clear signature in the corresponding highly excited quantum spectra. In this Communication we show that this result also holds in mixed systems, by considering an application to the floppy LiNC/LiCN molecular system. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1876212]

The development of modern experimental techniques,[1] such as stimulated emission pumping,[2] or femtochemistry,[3] greatly broadened the horizons of classical molecular spectroscopy. In addition to their experimental performance, these methods have the great advantage, from a theoretical point of view, of providing a direct link between spectroscopy and the underlying nuclear dynamics.[4,5].

At very low excitation, molecular dynamics take place in the vicinity of Born–Oppenheimer potential energy surface (PES) minima, where the motion corresponds to normal modes. The associated spectra are simple, consisting of band progressions easily assignable. As energy increases, anharmonicities and coupling terms grow in importance.[6] Spectra become distorted due to the influence of resonances,[7] and the different peaks can be hierarchically organized in terms of polyads.[8,9] This reflects the importance of the intramolecular energy transfer processes taking place inside the molecule.[10] At very high excitation energies, the interactions become too large and the picture based on normal mode states is no longer valid. Classically, the motion becomes chaotic, as invariant tori are destroyed following the fate dictated by the Kolmogorov–Arnold–Moser theorem.[11] However, the complexity of the emerging chaotic sea is organized by periodic orbits (PO) and their associated manifolds.[11] The corresponding spectra can become very complex, but usually show simple low resolution features related to the above mentioned classical structures.[5,12] The associated nonlinear dynamical effects control chemically interesting processes, such as intramolecular vibrational relaxation[13] or chemical reactivity.[14,15]

The importance of POs also extends to quantum mechanics. Gutzwiller was able to build his celebrated semiclassical theory[16] for the quantization of chaotic systems solely in terms of POs information. Other striking manifestations of POs have been described in the literature; for example, recurrences in the Fourier transform of the quantum density of states[17] or the "scarring" of high lying eigenfunctions.[18] The term scar was coined by Heller to indicate a strong localization of quantum density taking place along unstable POs, and he constructed a systematic theory for this phenomenon based on wave packet propagation.[4,18] Other important contributions have been made to scar theory; for a comprehensive review see, for example, Ref. 19. More recently, the effect of bifurcations in mixed systems on scarring has been considered.[20] They cause "superscars" with enhanced localization in wider regions of configuration space.

The importance of POs and their associated properties in quantum spectra is well known. Each PO introduces a frequency in the energy spectrum associated to its period.[16] Then, the dynamics along POs induce recurrences in the autocorrelation function that, when Fourier transformed, define an envelope in the spectrum, giving rise to peaks,[4] centered at energies given by a Bohr–Sommerfeld (BS) quantization condition and with widths proportional to $\hbar\lambda$ (being λ the Lyapunov exponent of the PO). These results are obtained when considering the short time dynamics associated to the PO, and do not take into account, for example, developments

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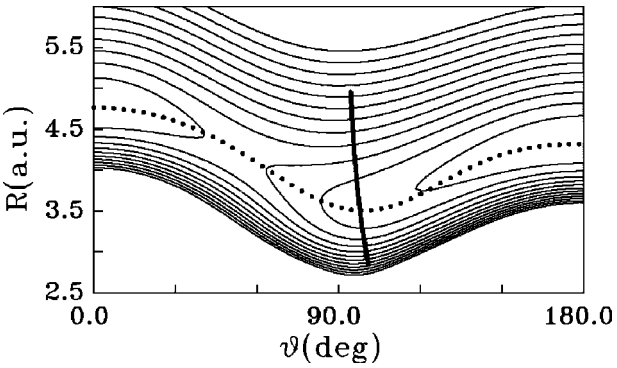

FIG. 1. Contours plot of the potential energy surface for the LiNC/LiCN isomerizing system. $\theta=0$ corresponds to the LiCN minimum and $\theta=180°$ to LiNC. The minimum energy path, $R_e(\theta)$, connecting the two isomers is shown as a dotted line. We have also plotted superimposed the unstable PO relevant to our work.

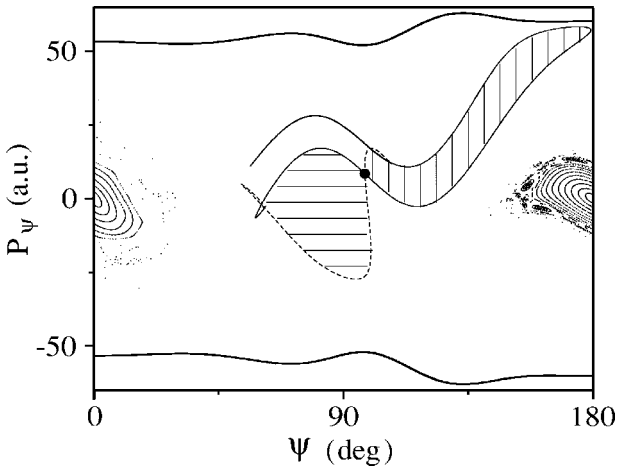

FIG. 2. Classical composite Poincaré surface of section for the LiNC/LiCN system at an energy of $E=9197.3$ cm^{-1}. Regular motion takes place at the invariant tori around LiCN (left) an LiNC (right). The rest of the available phase space (left blank in the figure) up to the boundaries corresponds to chaotic isomerizing motion. Embedded in it, the fixed point (full circle) and unstable (full line) and stable (dashed line) manifolds corresponding to the PO in Fig. 1 are represented.

taking place past the point at which the emanating manifolds first cross. For these longer times a homoclinic tangle[11] develops, and complicated quantum interference effects take place. Tomsovic and Heller[21] considered this long time limit, showing that accurate semiclassical wave functions can be constructed after the Ehrenfest time ($\sim|\ln\hbar|$) when the underlying chaos has had time to developed finer structures than a quantum cell.

In a recent work,[22] we have shown how this homoclinic motion imprints a clear signature in the quantum spectrum of the stadium billiard, a completely hyperbolic system. This motion induces fluctuations in the spectral widths corresponding to wave functions localized along unstable POs, that have a surprisingly simple oscillatory behavior in terms of the homoclinic area. This result can be understood in terms of the coherence of the associated classical motion, which constitute the natural extension of the local hyperbolic structure around the PO. In this Communication we show that this result also holds for the case of systems with mixed regular and chaotic phase space, and illustrate this effect with an application to the floppy LiNC/LiCN molecular system.

In this work, we use a two degrees of freedom model for the molecular vibrations of LiNC/LiCN, that has been extensively studied in the literature.[12] In it, the C-N distance is held constant at its equilibrium value, r_e, and the two remaining vibrational coordinates, R and θ, are defined, respectively, as the distance from the Li atom to the center of mass of the C-N fragment, and the Li-N-C angle. The classical vibrational ($J=0$) Hamiltonian is given by

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

where μ_1 and μ_2 are the Li-CN and C-N reduced masses, respectively. A contours plot of the PES, $V(R,\theta)$, is plotted in Fig. 1. It shows two minima at $\theta=0$ and 180° which correspond to the two stable linear isomers LiCN and LiNC, respectively. Motion in the bending angle is very floppy, thus sampling extensive regions in configuration space. This is the origin of chaos in the problem.

The classical dynamics of this model can be best monitored by constructing Poincaré surfaces of sections (PSOS), using the minimum energy path connecting the two isomers, $R=R_e(\theta)$, as sectioning plane. This SOS is made an area preserving map by using the following canonical transformation[23]

$$\rho=R-R_e(\theta),\quad P_\rho=P_R,$$

$$\psi=\theta,\quad P_\psi=P_\theta-\left(\frac{dR_e}{d\theta}\right)_{\theta=\psi}P_\rho. \tag{2}$$

In Fig. 2 a composite PSOS, computed at an energy of $E=9197.3$ cm^{-1} (corresponding to the energy of the 429th quantum state of LiNC/LiCN), is shown. The two isomer wells appear as islands of regularity centered at $\theta=0$ and 180°, respectively. The rest of the available phase space (intentionally left blank to avoid visually complicating the figure) is ergodically filled with irregular isomerizing trajectories. We also present the structures (fixed point and manifolds) associated to the PO shown in Fig. 1. This trajectory is a 1:1 resonant inversion hyperbolic orbit, originating at a saddle–node bifurcation, and corresponds to a motion mainly excited along the R coordinate, running at $\theta\sim98°$. Saddle-node POs are known to play an important role in the quantum mechanics of the LiNC/LiCN[24] and HCP.[25]

To carry out our investigation we use wave functions, $|\gamma_n\rangle$, highly localized on POs, as the most suitable quantum analog to PO motion. Here, index n indicates increasing excitation along the direction of the motion. Such states can be defined in a number of ways;[26–28] in our case, we have used the dynamical method[26] consisting in Fourier transforming for BS quantized values of the energy, E_n, a wave packet, $|\phi(t)\rangle$, initially launched in the vicinity of the PO under study, after having being propagated for a short time,

$$|\gamma_n\rangle = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt\, e^{-t^2/T^2}\, e^{iE_n t/\hbar}|\phi(t)\rangle. \tag{3}$$

Here T represents a cutoff time eliminating the unwanted long time part of the dynamics; in our case it is taken equal to the period of the PO. This procedure includes information not only on the PO, but also about the neighboring hyperbolic structure, formed by the corresponding unstable and stable manifolds.[29] Actually, the nonstationary wave functions defined in this way constitute a natural tool to study scarring.[18]

The corresponding analysis in the energy domain renders a spectrum,

$$I(E) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt\, e^{-t^2/T^2}\, e^{iEt/\hbar}\langle\phi(0)|\phi(t)\rangle, \tag{4}$$

consisting of a progression of bands centered at the BS quantized values of the energy, E_{BS}, associated to consecutive scar states, as defined in (3). Notice that only those bands with E_{BS} close to the energy of the center of the initial wave packet will be clearly observed, since the overall shape of the spectrum corresponds to a Gaussian centered at this energy point.[4] Furthermore, these bands spread across a certain width, σ_n, in the eigenvalues spectrum, E_μ, of the system, with intensity weights given by the squared modulus of the overlap with the associated eigenfunctions, $|\mu\rangle$. Accordingly,

$$\sigma_n = \sqrt{\sum_\mu |\langle\mu|\gamma_n\rangle|^2 (E_\mu - E_n)^2}, \tag{5}$$

expression which provides information on how the scarred structures are embedded in the quantum mechanics of the system. Actually, a Fourier analysis of their fluctuations can be used to extract information about the relevant classical invariants, as will be shown in the next section.

Before that, an important technical point should be addressed. Floppy molecular systems are typical examples in which the underlying classical mechanics changes significantly with energy, as opposed to what happens with mechanically scaling systems, such as billiards. This is a serious problem when trying to extract dynamical information from quantum molecular vibrational spectra.[30] For example, the value of the homoclinic area associated to the PO under consideration, which, as stated in the Introduction, plays a key role in our study, changes significantly along the range of energies considered in our calculations. A suitable strategy to solve this problem consists in considering the value of $\hbar$ as a varying parameter of the calculation, and perform the Fourier analysis using bands widths all computed at the same value of the excitation energy. In this way, a family of Hamiltonians with the same classical behavior is considered.

In Fig. 3 we show, as an example, the spectrum corresponding to scar states with even $n=6-14$ computed for $\hbar=1.285$, using as initial wave function:

$$\phi(R,\theta) = 2^{-1/2}[\chi_>(R,\theta) + \chi_<(R,\theta)], \tag{6}$$

being $\chi_{\gtrless}(R,\theta)$ harmonic oscillator coherent states of the form

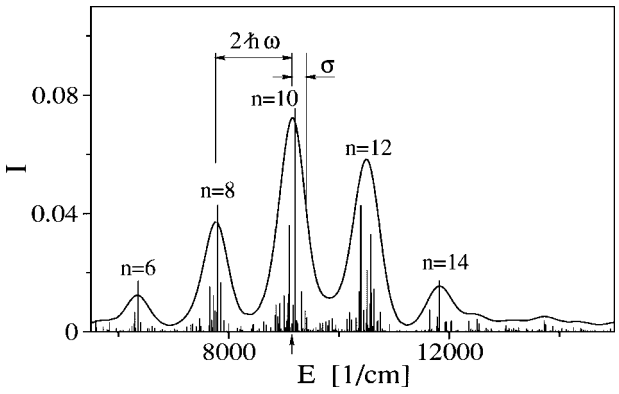

FIG. 3. Spectrum corresponding to scar states localized along the periodic orbit of Fig. 1 with even $n=6-14$ calculated for a value of $\hbar=1.285$ (see text for details). The distribution of the scar states among the different eigenstates of the system is given by the stick spectrum.

$$\chi_{\gtrless}(R,\theta) = (2/\pi)^{1/2}(\alpha_R\alpha_\theta)^{1/4}\exp[-\alpha_R(R-R_{\gtrless})^2] \times\exp[-\alpha_\theta(\theta-\theta_{\gtrless})^2] \tag{7}$$

centered, respectively, on the outer and inner turning points, $(R_{\gtrless},\theta_{\gtrless})$, of the PO represented in Fig. 1, and with values of the parameters $\alpha_R=16.114$ and $\alpha_\theta=14.123$. In it, the magnitudes of some quantities relevant to our study, namely, band width, σ, and band spacing, $2\hbar\omega$, have been indicated. The corresponding spectra for the odd quantum numbers are obtained in a similar way, substituting the plus sign in Eq. (6) by a minus. By computing separately even and odd spectra, the obtained distributions of bands are more sparse, and then the widths can be calculated more accurately.

As can be observed, the center of band $n=10$ coincides, for this value of $\hbar$, with the value of the working energy, $E=9197.3\ \mathrm{cm}^{-1}$ (whose position is marked with an arrow in the horizontal axis). This position is defined (approximately) by the BS quantization condition on the PO:

$$\tilde{S} = \frac{S}{2\pi} = \hbar(n)\left(n+\frac{3}{4}\right), \tag{8}$$

where $\tilde{S}=13.814$ is the value of the reduced action of the PO at the working energy. Notice the Maslov index equal to 3 in the previous equation, unusual for a one-dimensional vibration. This is due to the presence of a self-conjugate point in the middle of the trajectory,[31] in addition to two turning points at the ends. The corresponding width for the Fourier analysis is computed using Eq. (5). Finally, the value of $\hbar$ is changed until a new band moves to the position of the working energy, and then the procedure is repeated until a large number (which could be infinity, in principle) of widths has been calculated. These values can be obtained by means of Eq. (8).

The corresponding results, once made dimensionless dividing by a characteristic energy at each value of $\hbar(n)$,

$$\tilde{\sigma}_n = \frac{\sigma_n}{\hbar(n)\omega}, \tag{9}$$

are shown, as a function of n, in the left inset to Fig. 4. (In our case $\omega=530.8\ \mathrm{cm}^{-1}$.) As can be seen, they show a slightly oscillatory behavior superimposed to a clear increas-

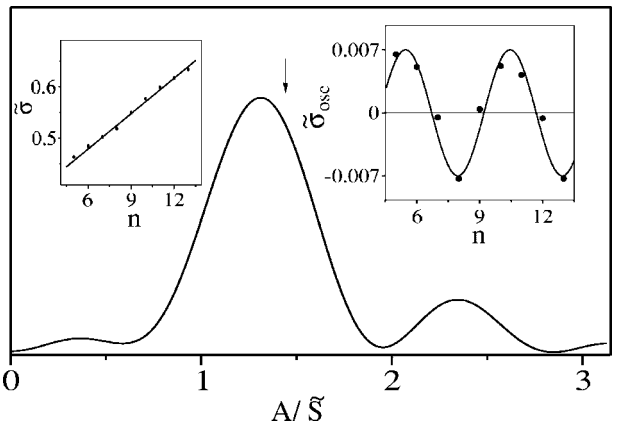

FIG. 4. Fourier spectrum of the oscillatory part (right inset) of the dimensionless widths, as defined in Eq. (5), (left inset) corresponding to the scar functions peaks in Fig. 3.

ing linear tendency. The oscillatory part, $\tilde{\sigma}_{\mathrm{osc}}$, is shown in the right inset of the figure, and the corresponding Fourier spectrum is presented in the main body. As can be seen, only one important peak exists, that actually appear very broad due to poor resolution associated to the small number of available data points. The position of the center was obtained by fitting the band to a Gaussian function, and the obtained value of $S=17.4$ is seen to agree very well with the magnitude of the homoclinic phase space area of $A_h=20.1$ (marked with an arrow in the figure) computed by integration of any of the two shaded regions in Fig. 2.

The interpretation of this result is clear, and has been thoroughly discussed in Ref. 22, by applying some ideas contained in Ref. 32 and alternative views of the same problem.[33] The analysis of the spectral characteristics of the scar states calculated by means of Eq. (3) requires, in addition, to the BS quantization condition on the action of the PO (controlling the position of the corresponding peaks) another one consisting on the quantization of the phase space area of the "homoclinic torus" defined by the associated manifolds. When these two conditions are fulfilled simultaneously, scar states are best defined, and accordingly, its width in the eigenvalues spectrum is narrower. On the contrary, when only the first condition is fulfilled, scar states are more poorly described, and they appear more spread in the spectrum of eigenvalues.

Summarizing, we have showed that homoclinic areas imprint a clear signature in the low resolution features of the spectra of dynamical systems with mixed regular and chaotic phase space. In particular, we have discussed how the fluctuations of the relative spectral widths corresponding to wave functions highly localized along POs (scars) oscillate in a very simple way, controlled by the quantization of the associated primary homoclinic motions.

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