Resonance-induced spectral tuning

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A diabatic correlation diagram technique is extended to assign effective quantum numbers and classify sequences for extremely high excitations in a coupled two-mode model of an isomerizing system, with multiple wells separated by a potential barrier. At low values of the stretch quantum number n_s, level spacings for sequences of bend excitations $n_b = 0, \ldots$ show a pattern of a smooth dip at the barrier, characteristic of the zero-order uncoupled system. In higher sequences $n_s = 3 - 5$, the spectral pattern is modified with the onset of a prominent nonlinear resonance. The level spacing "tunes" to a flattened pattern similar to a harmonic oscillator, and the smooth dip at the barrier becomes almost vertical. This behavior is explained by the influence of periodic orbits of the resonance on the quantum spectrum and wave functions. In the $n_s = 6$ sequence the tuning reverts to a pattern more similar to zero order.

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I. INTRODUCTION

In an earlier paper [1] we developed a method to assign sequences of levels in a model for an isomerizing system, based on diabatic correlation diagram assignments of approximate quantum numbers. The problem of making quantum number assignments in systems where these are only approximately or even fuzzily defined has occupied many workers. The use of the diabatic correlation assignments here and in Ref. [1] follows use of similar or related techniques [2–12] to assign a variety of spectral systems other than the isomerization model. Here, we put the method to a more stringent test than in Ref. [1], attempting to assign levels with an extreme degree of combined stretch and bend excitation, coupled by a strong anharmonic resonance overlain by widespread classical chaos. Expecting to confront the limits of the assignment method, we meet instead with surprising success, while encountering a striking phenomenon that we call "resonance-induced spectral tuning."

In Ref. [1] we considered spectra of a model system of coupled stretch and bend, with an isomerization barrier in the bend coordinate. We used the diabatic correlation technique to assign effective approximate stretch and bend quantum numbers n_s,n_b. We found that it is possible to assign sequences, each with fixed stretch quantum number $n_s = 0$–3 and bend quantum number $n_b = 0, \ldots$ all the way up to the barrier at $n_b = 23$; it was even possible to assign further sequences of above-barrier states. We found patterns in the sequences of the coupled system very similar to the pattern of the zero-order system, in particular, the pattern of a dip in the level spacings as the barrier is approached, the quantum correspondent of a dip to zero in the frequency.

In this paper we test prospects for spectral assignment in a regime of extreme excitation, qualitatively different from that handled so far in experimental spectroscopic analysis. We investigate whether meaningful sequences persist, especially near the barrier, when we push the previous analysis to higher $n_s = 4$–6, where the classical chaos greatly increases. The system is devised so as to have the common complication of a prominent nonlinear resonance. This was already present in the lower sequences in Ref. [1], but it becomes a far more significant factor at higher values of n_s.

We find that we are able to assign meaningful sequences in this regime where we frankly expected to see the method break down. Moreover, we find unanticipated, yet regular alterations in the energy level patterns of the sequences. These will turn out to be related to the strong anharmonic resonance. One feature is a "tuning" of the sequence to a harmonic-like pattern. (There was already a slight hint of this for $n_s = 3$, as briefly noted in Ref. [1].) A second notable feature is that the smooth dropoff to a dip in the energy spacings approaching the barrier becomes a much more abrupt plunge in the tuned spectrum. The resonance island chain appears to "protect" the quantum states from the influence of the approaching barrier and, remarkably, or at least unexpectedly to us, this is reflected in the spectrum. As noted in the final section, experimental and computational systems are starting to become available where one might begin to look for these phenomena.

II. ISOMERIZATION MODEL AND SPECTRAL SEQUENCES

The system, consisting of two coupled nonidentical anharmonic oscillators, was devised as a model for isomerization [1]. One degree of freedom is a bend b in an asymmetric double-well potential, similar to the bending motion in a system with two isomeric forms, with coordinate ϕ. Figure 1 shows the double-well potential. The second degree of freedom is a Morse oscillator, similar to a stretching vibration s, with coordinate r. The Hamiltonian is

$$H = \frac{p_r^2}{2m} + D(1 - e^{-\beta r})^2 + \frac{p_\phi^2}{2Mr_0^2} + V(\cos(\phi)) + \kappa r \sin^2\phi = H_{0s} + H_{0b} + \kappa r \sin^2\phi, \quad (1)$$

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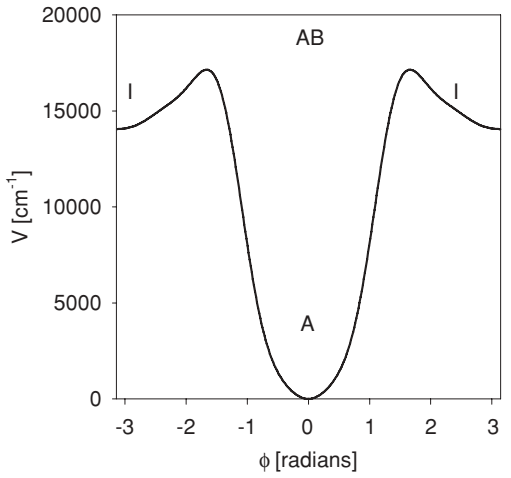

FIG. 1. Double-well potential $V(\cos(\phi))$ in the Hamiltonian (1). This potential is described more fully in Ref. [1]. The regions are denoted A (acetylene), I (isomer), and AB (above barrier).

with parts for the zero-order stretch, zero-order bend, and coupling.

Classical and quantum calculations on this system are described in detail in Ref. [1] with values of the parameters in (1) adjusted to model the acetylene molecule C_2H_2, whose isomerization is important in combustion processes. The coupling induces a mixed classical phase space with regular and chaotic regions. Several examples of the surface of section plots are given in Ref. [1].

We will be concerned with excitations in the stretch mode s and in the bend mode b in the large well A below the barrier. (Levels in the isomer well I and the above-barrier region AB in Fig. 1 were considered in Ref. [1], but are not relevant here.) The zero-order system with coupling $\kappa = 0$ has levels assigned with well-defined quantum numbers (n_s,n_b). The spectrum can be organized into sequences with a given quantum number n_s in the high-frequency mode, and excitations in the low-frequency mode $n_b = 0,1,\ldots,23$, with $n_b = 23$ the maximum value of n_b in the A well below the barrier.

Figure 2(a) shows the spectral pattern of the sequences of the uncoupled system. At the potential barrier, Fig. 2(a) shows a smooth dropoff to a dip in the spacings of adjacent levels. Such a dip or minimum is well known to be characteristic of a potential barrier [13] or of a separatrix [14] in the classical phase space. In fact, this spectral dip at a separatrix has been observed in analysis of experimental spectra [15,16].

The patterns of the uncoupled system in Fig. 2(a) are based on the good zero-order quantum numbers n_s,n_b. When the coupling κ is nonzero, these quantum numbers cease to be exactly valid. Nonetheless, it is often useful to assign effective quantum numbers. In Ref. [1], we showed how a diabatic correlation diagram technique can be used to assign approximate quantum numbers to spectra of the coupled system (1), even though it is nonintegrable, with a mixture of regular and chaotic regions. We were able to assign levels of the coupled system in terms of effective stretch and bend quantum numbers, formally analogous to the rigorous quantum numbers n_s,n_b of the zero-order system. Using these assignments, we classified the levels into bend sequences

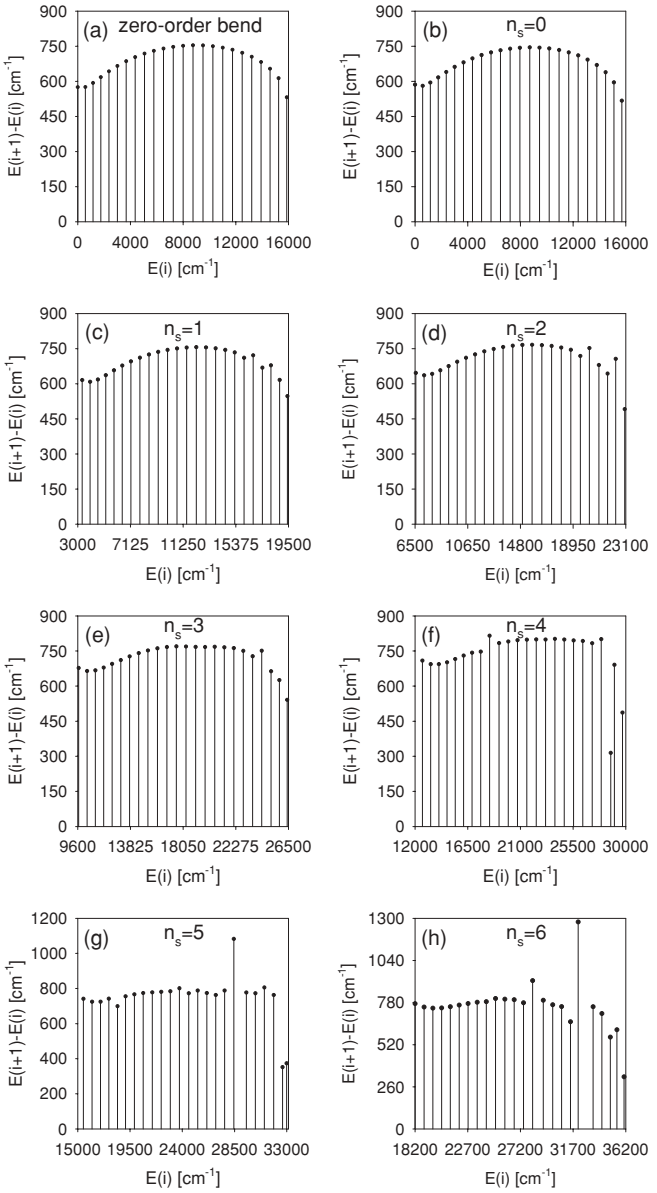

FIG. 2. Patterns of energy level spacings between eigenstates. (a) Uncoupled stretch-bend system; (b–h) coupled system sequences with $n_s = 0$–6.

$(n_s,0),(n_s,1),\ldots$. We classified sequences for $n_s = 0$–3 in Ref. [1]; in this paper, we extend the assignments up to $n_s = 6$, a very high degree of stretch excitation with energy well above the isomerization barrier. The assignments naturally become increasingly difficult as the stretch quantum number increases. In Ref. [1], we were able to assign above-barrier states for $n_s =$ 0–3. Here, we only attempt to assign below-barrier acetylene states for higher n_s.

Figures 2(b)–2(g) shows the level spacing patterns for the sequences $n_s = 0,\ldots,6$ of the coupled system. The $n_s = 0$ sequence is very similar to Fig. 2(a) for the uncoupled system, with a smooth dropoff to a dip at the barrier. This is readily understood since nearly all of the states in the $n_s = 0$ sequence are associated with Einstein-Brillouin-Keller (EBK) tori having the character of the zero-order system. The sequence patterns are very similar for $n_s = 1,2$. There are some

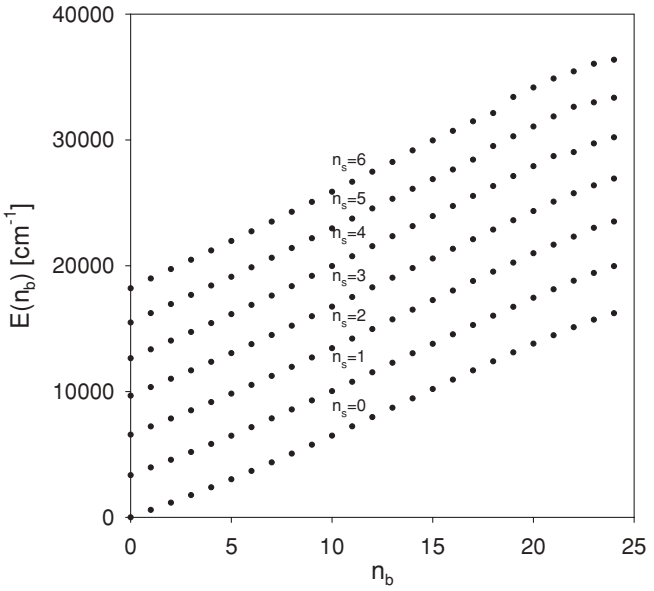

FIG. 3. Energy levels of the sequences.

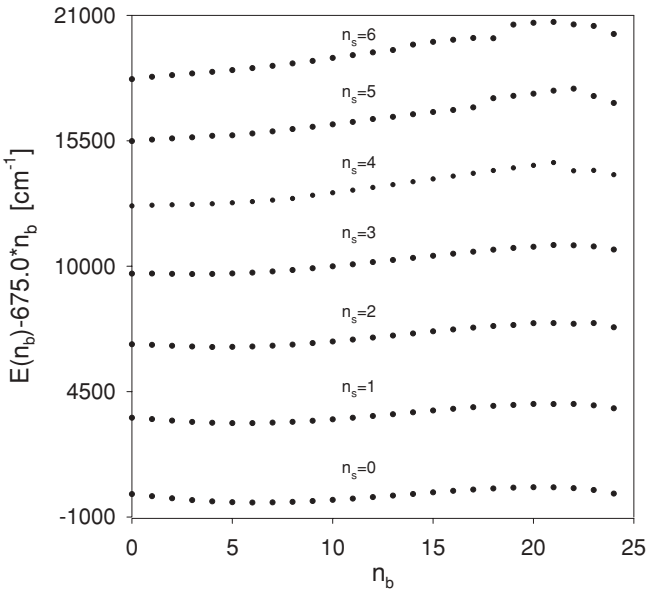

FIG. 4. "Leveled" sequences with an amount $n_b \times 675$ cm^{-1} subtracted from each level.

"bumps" in a few of the spacings. These are attributable to a 4 : 1 nonlinear resonance coupling, as discussed in Ref. [1]. The system has a pronounced 4 : 1 resonance due to the frequency ratio of the anharmonic stretch and bend.

Starting with $n_s = 3$, there begins a noticeable flattening in the level spacings in the middle of the sequence. The flattened region grows in extent in the $n_s = 4$ sequence. Furthermore, the smooth dropoff to the barrier becomes more abrupt. For $n_s = 5$, the flattening is almost complete, except for resonance "bumps," and continues almost up to the barrier. The sequence now ends in a very abrupt plunge to the barrier. For $n_s = 6$, the pattern reverts to one more like the uncoupled system, though individual levels are strongly perturbed.

Another way to present the sequences is shown in Fig. 3, where instead of the level spacings of Fig. 2, we plot the energy levels themselves as a function of the effective bend quantum number n_b. The grouping into regular sequences is evident. However, some slight irregularities are visible for high n_b values of the $n_s = 4,5,6$ sequences.

The similarities and differences among the sequences are brought out more vividly in Fig. 4, in which a quantity $n_b \times 675\ \text{cm}^{-1}$ is subtracted from each level. The resulting "leveled" sequences are very similar for $n_s = 0$–3, but for $n_s = 4$–6, they display marked irregularities, in particular, some "fractured" regions at high n_b.

We will explain these features of the spectrum in relation to the 4 : 1 nonlinear resonance between the coupled stretch and bend. In our account, the resonance tunes the spectrum, producing both the flattening and the alteration of the dip pattern near the barrier.

III. 4 : 1 NONLINEAR RESONANCE

The system has an approximate frequency ratio $\omega_1 : \omega_2 \approx 4 : 1$. As the coupling κ increases from zero, the system acquires a strong 4 : 1 nonlinear resonance with an island chain, a ring of alternating stable and unstable periodic orbits in the surface of section. The eruption of the island chain is seen in Fig. 5, just after its occurrence at a little under 14000 cm^{-1}. The chain persists for higher energies, migrating through the surface of section. We will relate the migration of the chain to the phenomenology of the changing spectral patterns, focusing on $n_s = 0,3,5$, and 6.

The island chain does not visibly affect the overall spectral pattern of the $n_s = 0,1,2$ sequences. Consider the $n_s = 0$ sequence in Fig. 2(b). Even though the higher levels of this sequence are at energies above the emergence of the islands, and the island chain is very prominent, the sequence is very much like the zero-order sequence of Fig. 2(a). The reason is

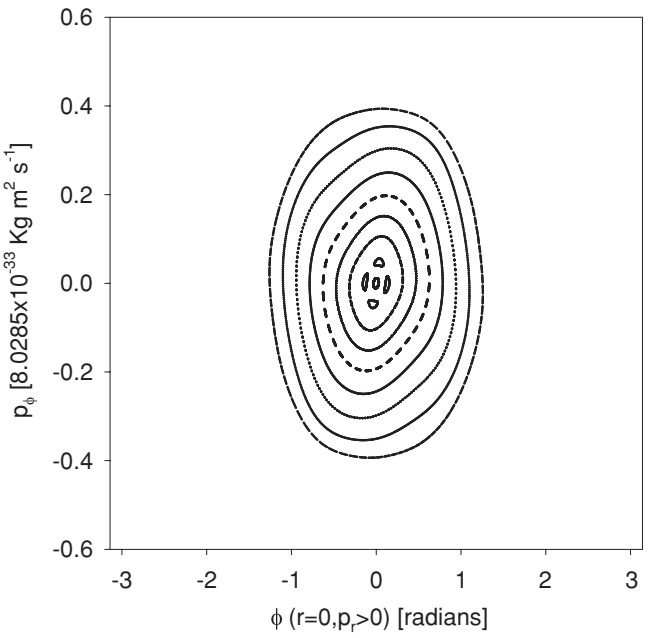

FIG. 5. Eruption of the island 4 : 1 resonance island chain in the surface of section at total energy (including zero-point energy) of $E = 14367$ cm^{-1}.

that the levels with $n_s = 0$ and high values of n_b correspond to the region of phase space near the barrier. This is far from the island chain, which is close to the middle of the surface of section.

The first indication that the resonance chain can shape the overall spectral pattern is seen in Fig. 2(e) for the level spacings of the $n_s = 3$ sequence, where the sequence acquires the pronounced flattened region in the middle. In terms of classical phase space structure, the pattern is associated with the following events. The $n_s = 3$ sequence starts out with a surface of section with no resonance zone, and has zero-order type tori. Eventually the resonance erupts in the middle of the surface of section. As energy increases, the island chain migrates outward from the center toward the barrier. Several surfaces of section showing the migration of the resonance islands can be found in Ref. [1]. The effect on the sequence pattern begins to be manifest when the migrating island chain starts to "catch" and destroy EBK-quantizing tori of a sequence. In the $n_s = 3$ sequence, the first 13 levels correspond to invariant EBK tori, but the torus for level 14 is destroyed and supplanted by the migrating island chain. Higher levels of the sequence are similarly trapped or "hung up" on the island chain as it migrates with increasing energy toward the barrier. Correspondingly, these levels are found to have the flattened pattern in the level spacing pattern in Fig. 2(e). Finally, for the highest values of n_b in the $n_s = 3$ sequence, the levels "break out" of the island chain. The spectrum once again resembles the zero-order system, with a dip in the level spacing as the sequence approaches the barrier.

Similar behavior occurs in the higher n_s sequences, with the portion of the sequence in which the resonance dominates the states peaking for $n_s = 5$, with almost a complete flattening of the level spacing pattern and a very abrupt plunge at the barrier. The island chain begins to lose its hold on the $n_s = 6$ sequence, with a reversion to a pattern more like zero order.

Finally, the resonance is connected to the fractures in sequences $n_s = 4$–6 seen especially in Fig. 4. The fractures are associated with the very large bumps seen in the level spacings at high n_b for $n_s = 4$–6 in Fig. 2; in turn, the bumps are associated with the resonance, as discussed at length in Ref. [1]. We will have no more to say in this paper about the fractures except to note that none of the other observations and conclusions of this paper are at all inconsistent with the presence of the fractures.

IV. SPECTRAL TUNING BY RESONANT PERIODIC ORBITS

We have seen that the spectral flattening and the steepening of the dip in higher n_s sequences is associated with states getting trapped or hung up on the resonance island chain. What physical effects of the resonance on the quantum states cause these changes in the spectral pattern? It is not possible to answer this with exactitude. The states in question are often very disordered due to chaos, so they do not correspond to classical structures for which a well-established quantization procedure is known (e.g., EBK quantization of invariant tori). Nonetheless, it is possible to give qualitative explanations for the observed patterns. (There is some evidence [17–19] that in chaotic systems there can be an analog of EBK quantization of a pseudoaction for the chaotic remnants of tori known as cantori. This has even been extended recently to computation of a semiclassical wave function for a chaotic system [19]. However, despite these and other advances [20–26] in semiclassical treatment of chaotic systems, there is as yet no generally used semiclassical theory specifically for eigenstates in the chaotic regime.)

Many of the states in question have quantum wave functions that resemble either the stable or unstable 4 : 1 periodic orbit, as seen in Ref. [1] for several states from the $n_s = 3$–5 sequences. Although we would not claim that "scarring" [21] is responsible for the detailed patterns we see, a look at the 4 : 1 periodic orbits in coordinate space is revealing. We will view these in two ways that shed light on the flattening of the sequences, and the abrupt steepening of the dip at the barrier.

First, we seek a quantum condition on the 4 : 1 periodic orbits (POs) that will give insight into the energy level spacing pattern of the quantum states of the actual system. For this purpose, we use the Bohr-Sommerfeld condition, as explicated in a study of the relation between Bohr-Sommerfeld and Einstein-Brillouin-Keller quantization [27]:

$$I = \frac{1}{2\pi}\int_0^T (p_1\dot{x}_1 + p_2\dot{x}_2)d\tau = \hbar\gamma(N + 1/2). \qquad (2)$$

The POs that we seek are orbits of the 4 : 1 resonance that satisfy (2) with quantizing Bohr-Sommerfeld action $I = (N + 1/2)$. Figure 6 shows a series of these POs. As is to be expected, the POs are far different in character from stretch or bend POs. They are also much different than orbits on zero-order type tori of the stretch-bend system.

When the energy level spacings of these orbits are plotted the result is Fig. 7. It is seen that there is a curved "step" leading into a long flattened region. This is similar, at the corresponding energies, to the onset and continuation of the flattened regions in Figs. 2(e)–2(g) of the quantum state

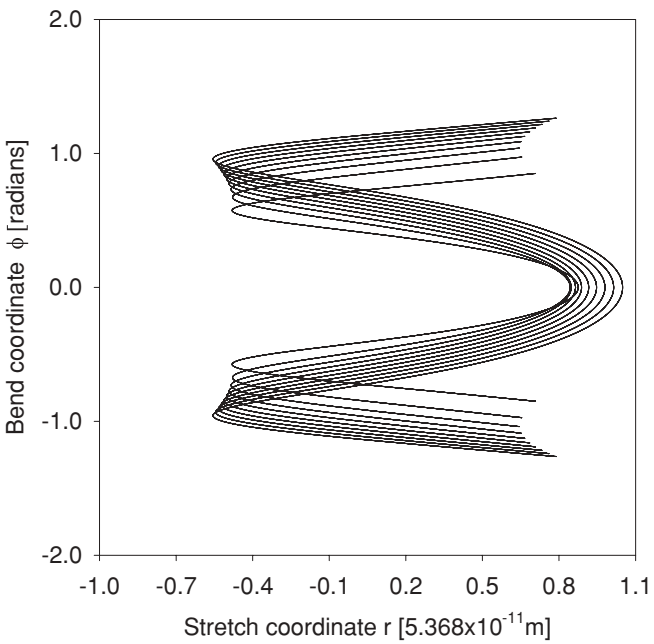

FIG. 6. Trajectories of unstable 4 : 1 orbits satisfying Bohr-Sommerfeld quantization conditions.

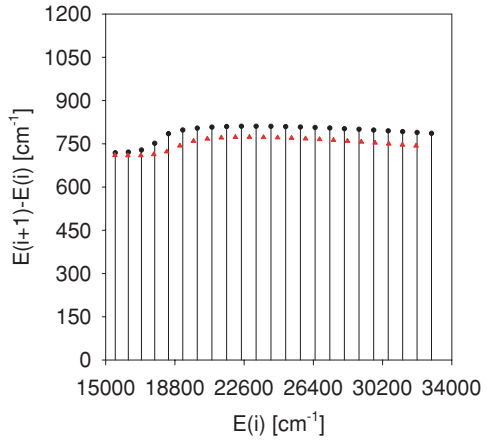

FIG. 7. (Color online) Energy level spacing pattern for the Bohr-Sommerfeld 4 : 1 POs. Circles are stable orbits; triangles are unstable orbits.

sequences for $n_s = 3$–6. This suggests that states that are hung up on the island chain have a flattened spectral pattern characteristic of the excitations of the quantizing 4 : 1 POs.

A look at some wave functions is revealing. In Figs. 8(a)–8(d) four examples show how the PO structure of the resonance overtakes the wave functions with increasing stretch excitation. Figure 8(a) shows the wave function of the coupled system assigned as $(n_s,n_b) = (0,19)$. This looks like a pure bend excitation, though even here there is some effect of the coupling, as seen in the curvilinear character of the probability distribution. Much different is the state (4,10), which looks like the stable resonant PO. This state was shown in Fig. 11 of Ref. [1], along with a state resembling the unstable PO. The interesting point now is that this kind of behavior continues

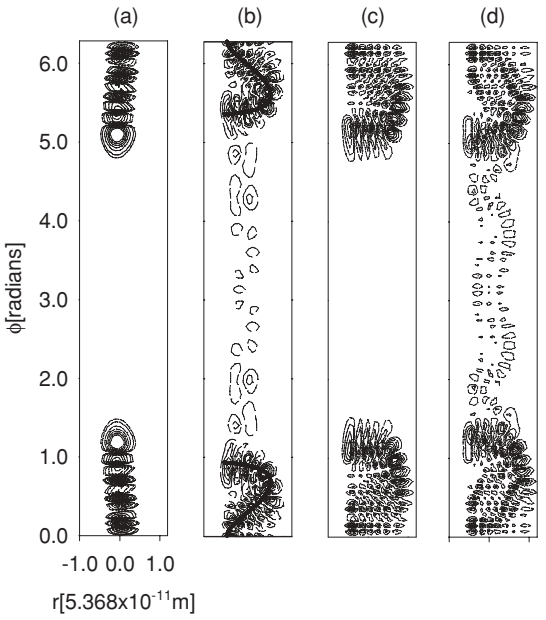

FIG. 8. (a)–(d) Wave functions of the coupled system assigned, respectively, by the diabatic correlation diagram technique as $(n_s,n_b) = (0,19),(4,10)$ (with an overlay of the stable periodic orbit), (5,19), and (6,19).

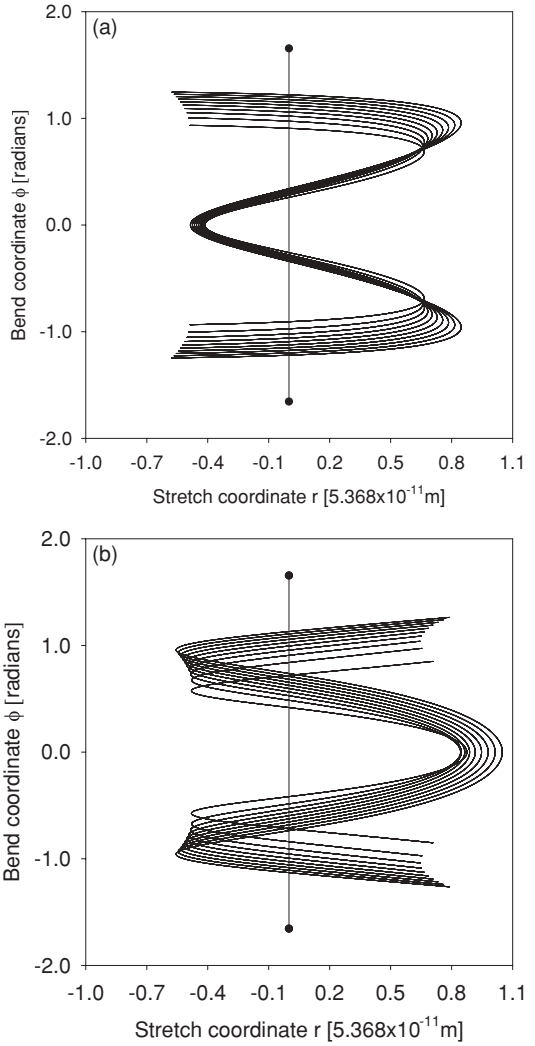

FIG. 9. (a) Stable POs and (b) unstable POs with energies corresponding to energies of the $n_s = 5$ levels with $n_b = 5,7\ldots,23$. Vertical line in each figure is pure bend trajectory with maximal range (i.e., to barrier) of zero-order uncoupled system.

for higher quantum numbers, as seen in Figs. 8(c) and 8(d) for the states assigned (5, 19) and (6, 19).

A second view of POs is also revealing. Instead of the plot of Fig. 6 of POs of orbits satisfying Bohr-Sommerfeld quantization conditions, in Fig. 9 we plot 4 : 1 resonant POs at the energies of a series of actual states of the $n_s = 5$ sequence. A notable characteristic of the POs in Fig. 9 is that the orbits at the energy levels approaching $(n_s,n_b) = (5,23)$ avoid the barrier region.

These are the levels whose assignments would seem to indicate that there would be a smooth dip as the barrier energy is approached. The barrier avoidance accounts in a qualitative way for the abrupt steepening of the dip that is seen instead. Since states associated with the resonance and its POs do not "feel" the presence of the approaching barrier, their level spacing does not drop off smoothly to a dip. Instead, the level spacing remains flat until it plunges abruptly when the levels reach the energy of the barrier. This is seen most clearly for $n_s = 5$ in Fig. 2. On the other hand, for the adjacent sequences $n_s = 4$ and 6, the levels at high n_b are not hung

up on the resonance, so they have an energy spacing pattern more characteristic of the barrier.

Close scrutiny of Fig. 9 then raises the following question. The zero-order system has states up to $n_b = 23$ quanta in the bend, as seen in Fig. 2(a). This is repeated in the low-lying sequences of the coupled system [e.g., $n_s = 0$, Fig. 2(b)]. In higher sequences, we have claimed that the nominal bend excitations are actually more like the 4 : 1 resonant POs. Figure 9 shows that the PO at the energy of the ($n_s = 5$,$n_s = 23$) quantum state is far removed in space from the barrier. There is clearly room for higher energy POs before the barrier is reached. However, the $n_s = 5$ sequence indeed ends at $n_b = 23$. The explanation is that higher energy states have strong admixtures of above-barrier character, which is to be expected on energetic grounds. Hence, what might be expected to be higher states in the sequence are instead classified more properly as above-barrier; some cases are already seen in Ref. [1].

V. CONCLUSIONS

This paper has extended the sequence assignments of the isomerization model of Ref. [1], based on diabatic correlation diagrams, to a degree of stretch-bend excitation (n_s,n_b) $\sim$ (6,23) that would represent an extreme if realized in experimental spectroscopy of a relevant physical system. The assignment scheme remains useful at the highest levels of excitation, all the way up to the isomerization barrier. Interesting patterns of flattening of the level spacings and a marked steepening of the dip at the barrier are revealed by the assignment scheme. These patterns are accounted for in terms of a strong 4 : 1 nonlinear resonance which "tunes" the spectral sequences. A qualitative explanation comes from the observation that resonant periodic orbits that obey Bohr-Sommerfeld quantization conditions exhibit behavior similar to the quantum states of the sequences.

Without a suitable classification scheme, it is very unlikely that these patterns would be detected. It is noteworthy that the patterns were found through use of the diabatic correlation assignment of sequences. No use was made of the more standard method of analysis of resonant systems, with an effective resonance Hamiltonian, assigning "polyads" of fixed total quantum number [28]. It seems unlikely that the standard assignments would be useful all the way up to the barrier; in fact, this was a principal motivation for developing the sequence approach. The relationship of the sequence assignments to the standard analysis is nonetheless an interesting question. A generalization that merges these approaches could be very illuminating.

In this connection it is worth noting that something like the "protection" of the wave function from the barrier has been seen in systems described by a simple resonance Hamiltonian (e.g., in studies [16,34] of molecules such as HCP). See the remarks in the review article Ref. [34] concerning their Fig. 7 on how the HCP bend mode "B" is displaced away from a 2 : 1 resonance, and mode "SN" associated with a saddle node bifurcation becomes more bendlike along the reaction coordinate. This was seen in further detail in Ref. [16]. This "protection" may be a common feature of systems with a nonlinear resonance where a putative "reaction mode" like the bend is approaching a barrier. However, we did not anticipate from experience with Ref. [16] that we would see the flattened spectra for stretch-bend combination states with high n_s and n_b that we see here in the present rather chaotic system, which is only somewhat "scarred" by the 4 : 1 resonance. We can speculate that such states correspond to something like the highly marbled interior states such as 4 . . . 6 on the polyad phase sphere in Fig. 7 of Ref. [16]. Again, the relationship of the correlation diagram assignments to phase space analyses of integrable single resonance Hamiltonians is an interesting topic which merits exploration.

The findings here for a model system are presented in the hope they will motivate the measurement of extreme excitation states and the search for resonance tuning phenomena. Especially interesting is the behavior of sequences as they approach the potential barrier, with the steepening of the dip at the barrier, apparently due to avoidance of the barrier by resonant periodic trajectories. In the model investigated here, the bend degree of freedom corresponds closely to the reaction coordinate in the isomerization, with the potential barrier as transition state naively conceived. If observed in real systems, resonant tuning of the dynamics near the barrier could be an interesting phenomenon in relation to new phase space concepts of the transition state [29–32].

Of perhaps greater immediate interest, it may be profitable to look for the tuning phenomenon in experimental and computational systems where an isomerization barrier is being approached, in particular, the phenomenon of the resonance "protecting" the quantum states from the barrier, as seen in the present model system. Experimental and computational systems with sufficient data are becoming available (e.g., spectra [33] of the complex HO_2 formed in the important combustion reaction of $H + O_2$).

It is well established that a smooth dropoff to a dip in the level spacings is characteristic of the approach to a phase space separatrix [14–16]. The search for the resonance-induced change in the spectral pattern at a barrier is therefore not limited to a potential energy barrier, but rather is likely to be a general feature of a "dynamical barrier" constituted by a separatrix.

ACKNOWLEDGMENTS

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