Extraction of Information on Molecular Motion from Chaotic Spectra

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I. Introduction

A reader performing a quick perusal of lists of titles appearing in the chemical, physical, mathematical, biological, and engineering scientific literature cannot fail to note that in recent years there has been a virtual explosion in the use of the word "chaos". Such diverse phenomena and fields as heartbeats, brain waves, weather patterns, turbulent flows, periodic chemical reaction, and particle accelerator design have all felt the impact of this relatively new concept. In this Account we try to explain what chaos means to spectroscopy and how chaotic motion impacts on atomic and molecular spectroscopy. As always in spectroscopy, the problem will be to go from spectral observations in the form of spectral lines and bands to a model of the molecule and its motions. The model of the molecule and the types of molecular motions are what we aim to learn. The reason we believe in our model is that when the equations of quantum and/or classical mechanics are applied to the model, the experimentally measured spectrum or features thereof are reproduced. The common feature that a spectroscopic problem has with the other fields that use the "chaos" label is that the equations describing the motion (in our case, the equation of classical mechanics) are nonlinear and have at least one class of solutions that are exquisitely sensitive to initial conditions. In what follows we shall attempt to describe

what a chaotic spectrum is and how we use the ideas of chaos to extract from it a model of the molecular motion.

A chaotic spectrum is congested and complex. The lines are transitions between states, one or both of which cannot be assigned quantum numbers other than that for the energy and total angular momentum. As such the spectral lines are intrinsically unassignable. It is also fair to say that the inability of spectroscopists to make an assignment only hints, but does not demonstrate, that a spectrum is chaotic. The final word comes when interpretative methods that assume that the spectrum is chaotic succeed in explaining features of the spectrum. Chaotic spectra have been seen in many systems, the most famous of which are the rovibrational spectrum of the ground state of acetylene around 27 000 cm^{-1},[1] the photodissociation spectrum of excited predissociating H_3^+[2] and the rovibrational spectrum above 250 cm^{-1} of the sodium trimer, Na_3.[3] In atomic physics the best known chaotic spectra are those involving transitions ending near the ionization threshold of the hydrogen atom in a 6-T magnetic field.[4] Generally chaotic spectra appear when highly excited electronic and/or rovibrational states are probed. In floppy molecules like Na_3 and in nonrigid clusters, chaos and chaotic spectra appear at surprisingly low energies. In spectroscopically identifying reactants, products, and transition states of chemical reactions, chaotic spectra appear.[2] The chemical dynamics then involves chaotic

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(1) Abramson, E.; Field, R. W.; Imre, D.; Innes, K. K. *J. Chem. Phys.* 1985, *83*, 453–465.
(2) Carrington, A.; Kennedy, R. A. *J. Chem. Phys.* 1984, *81*, 91–112.
(3) Boyer, M.; Delacretaz, G.; Ni, G.-Q.; Whetten, R. L.; Wolf, J.-P.; Woste, L. *Phys. Rev. Lett.* 1989, *62*, 2100.
(4) Holle, A.; Wiebush, G.; Main, J.; Hager, B.; Rottke, H.; Welge, K. H. *Phys. Rev. Lett.* 1986, *56*, 2594.

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dynamics and hence our added interest.

The question addressed here is how information about the motions of the system's constituent particles can be extracted from a chaotic spectrum. Due to space limitations in this Account, only one system, the sodium trimer, will be used as an example. It has been chosen because it is the simplest to understand and therefore requires less background to analyze and describe.

II. Regular and Chaotic Spectra

A. Regular Spectroscopy, Regular States, and Regular Motions.

Spectroscopy as most chemists know it is regular spectroscopy and refers to that type of atomic and molecular spectroscopy typically covered in the books of G. Herzberg.[5] Regular spectroscopy assumes that the initial and final states of a transition can be assigned N (equal to the number of degrees of freedom) quantum numbers. More fundamentally, it assumes that there exists a coordinate system, albeit convoluted or even nonanalytically related to the usual textbook coordinates, in which the major part, H_0, of the Hamiltonian, H, of the system is essentially separable. For vibrational motions,[6] such coordinate systems are normal modes, local modes, mixed modes, etc. Since the system is essentially separable, quantum mechanics tells us that each degree of freedom (ith mode) has its own associated quantum levels n_i and its own one degree of freedom wave functions $\psi°_{n_i}$ with $n_i - 1$ nodes. The states of H_0 have a wave function, $\psi°_{\bar{n}}$, which is the product of the N one-mode wave functions $\psi°_{n_i}$. If n_i is the quantum number associated with the state of the ith degree of freedom, then $\bar{n} = (n_1, n_2, ..., n_N)$ is the assignment of the state of H_0. Regular spectroscopy assumes that $\bar{n}$ can be used to label (regular) states of the full system controlled by H in the sense that a perturbation theory starting with H_0 and $\psi°_{\bar{n}}$ will converge to an exact unique eigenstate, $\psi_{\bar{n}}$ of H. If two or more different H_0's and $\psi°_{\bar{n}}$'s give convergent results, the one with the biggest integral overlap of $\psi°_{\bar{n}}$ and $\psi_{\bar{n}}$ converges faster and is the better assignment. The pattern of states of the system and therefore the pattern of lines in the spectrum can then be related to changes in the various n_i quantum numbers.

As said, chaotic spectroscopy involves high densities of lines and therefore a high density of states. This latter means that we are working in the correspondence region and that quantum guided classical (and vice versa) ideas will be used to interpret chaotic spectra. For this reason, and because particle motions are thought of classically, it behooves us, before discussing chaos, to review first the semiclassical view of a regular quantum state $\bar{n}$ and to consider the associated classical motions. Semiclassical mechanics associates the state $\bar{n}$ with a very particular "quantizable" trajectory that moves in the $2N$-dimensional phase space of positions (q) and momenta (p) of the vibrating atoms. This trajectory like most trajectories in the regular state region can be shown to move on the surface of an N-dimensional torus which itself lies on the surface defined by the trajectory's constant energy, $E = H(p,q)$.

(5) Herzberg, G. *Molecular Spectra and Molecular Structure, Volume I, II, III*; Nostrand: New York, 1966; *Atomic Spectra and Atomic Structure*; Dover Publications: 1944.

(6) For simplicity and without loss of generality, our discussion will be restricted to vibrational motions.
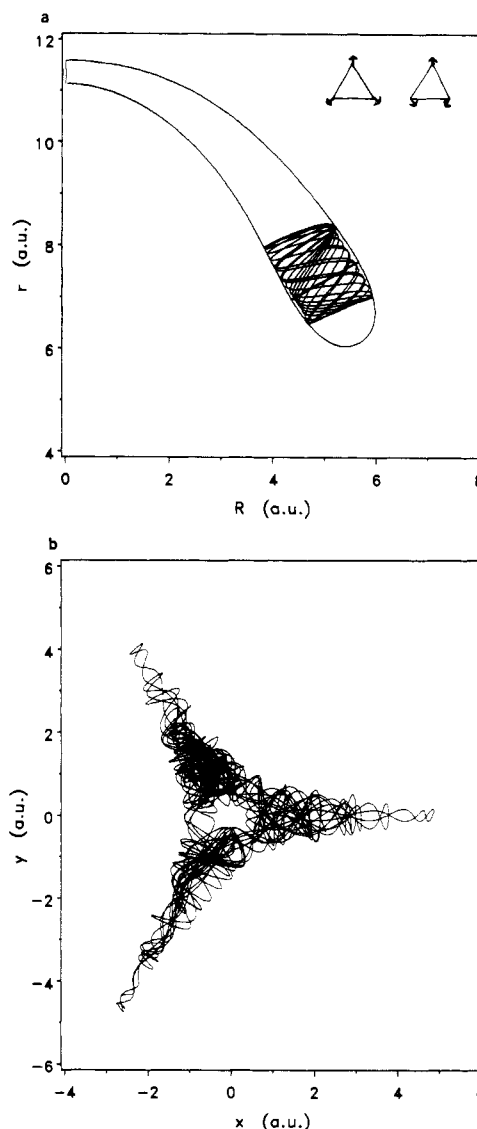
Figure 1. (a) A quasiperiodic trajectory computed at $E = 575$ cm^{-1} and $J = 0$ for Na$_3$ represented by the potential surface of ref 12. R and r are mass scaled Jacobi coordinates, and the solid outer line is an equipotential for Na$_3$ held in C_{2v} position. The dark line through the quasiperiodic trajectory is a symmetric stretch periodic orbit typical of many periodic orbits (tori in 1D) which have been tested and found not to contribute significantly to the spectra. In the upper-right corner are, in the more recognizable displacement coordinates, pictures of the coupled motions represented by the trajectory. (b) A chaotic trajectory for Na$_3$ run at $E = 575$ cm^{-1}. It is generic to the region of the experiment. Figures 1a and 1b differ in initial conditions. Figure 1b reprinted with permission from ref 7. Copyright 1989 American Institute of Physics.

Phase space is essentially filled with such trajectories on tori, but the $\bar{n}$ quantum state is associated with that particular torus (trajectory) that has N independent constants of the motion called actions $\bar{J}$ (which all tori in the regular region have) that satisfy $J_i = (n_i + {}^1/_2)$ when computed from the trajectories' motion. All tori, including our quantizable ones, when projected into the coordinate plane, reveal a quasiperiodic (almost but never quite periodic) motion.

Figure 1a shows a projection of such a quasiperiodic trajectory for the Na$_3$ trimer where a time-stepped reading of the trajectory's coordinates would enable visualization of a simultaneous bending and symmetric stretch of the obtuse triangular molecule. In the figure,

the usual "arrow" diagrams are given for the two modes in the usual displacement coordinates.[5] Our figure looks different because Figure 1a is in internal Jacobi coordinates. In molecules, regular quantum states generally roughly occur in the same energy and mode coupling ranges in which classical tori (quasiperiodic trajectories) exist. Moreover, regular wave functions have their regions of big amplitude in the same region of coordinate space as the quantizable quasiperiodic trajectories; off the torus, the wave functions damp exponentially.

B. Chaotic Spectra, Chaotic States, and Chaotic Motions. As the energy increases, the nonlinear mode coupling between once nearly separable modes or coordinates usually becomes larger and/or the potential changes its nature and scale, again usually becoming larger. When this happens, our regular tori and states begin to disappear. If no new separable H_0 can be found (e.g., normal to local mode transition), many things now happen. First, because of the big couplings, a splitting occurs, which, along with the increase in potential dimensions of degenerate levels, causes a high density of states. The states themselves no longer are dominated by a $\psi^{\circ}{}_n$, and as such the wave functions can only be labeled by a few ($<N$) such quantum numbers as energy (E) and total angular momentum. The wave functions also become erratic in nodal pattern, highly oscillatory in amplitude, and generally delocalized, being confined only by the potential itself. Trajectories also become in the same sense delocalized by filling the energy shell and by becoming erratic in motion, sensitive to initial conditions, and, in short, chaotic.

Figure 1b shows such a trajectory in the case of Na_3. The propellor shape is due to the trigonal nature of the bounding potential and reflects the possibility of Na interchange. The one-to-one correspondence between trajectories and states is lost as is "assignability". Transitions into such a region yield congested, unassignable chaotic spectra. The trajectories and particle motions, the wave function's nodal patterns and amplitude gyrations, and the spectral lines become so complex that they defy systematic cataloging or categorizing. Statistical patterns and distributions of lines[7,8] which are detached from dynamic interpretations are used for a minimal and relatively uninformative categorization of the spectra.

It would seem that nothing dynamically worth knowing can be learned from chaotic spectra. This would remain true were it not for a saving grace. In our description of the onset of chaos, we assumed that as the potential (coupling) grew larger in strength and size, it affected all coordinates at once. Fortunately this does not happen for the cases studied so far until such high energies that dissociation and ionization has occurred. What does happen?[9-11] Simply put, the potential coupling and changes cause only some degrees of freedom to go chaotic. The mechanical results of this can be anticipated from our above discussion. Depending on the system, tori can still exist in $n = 1$ or $n = 2$ or

... $n = N - 1$ reduced dimensions; we call these reduced-dimension tori. Most N-dimensional trajectories act chaotically in all degrees of freedom except when they approach the region of phase space where the reduced-dimension tori exist. At this point, they move nearly quasiperiodically in the reduced-dimension space, i.e., they mimic the motion on the reduced-dimension tori for several picoseconds before they leave the region and again act chaotically. As such, a subset of almost regular motions exists for this short time. Correspondingly, the wave function looks chaotic (low amplitude, highly oscillatory, no simple model patterns) and is unassignable except in those regions of coordinate space and energy where the quantizable reduced-dimension tori exist; there it looks regular and has much bigger amplitude (square root of the probability) than in other regions of space and energy. Since most of the trajectory and ψ is chaotic, the state density is still high due to the coupling among the chaotic coordinates and the ranges of the regular coordinates not near the reduced-dimension tori. The high-resolution spectrum is however still uninterpretable. This is unfortunate as there exists a simply understood motion, namely, that almost-quasiperiodic motion that mimics the reduced-dimension tori. This regular motion inserted into the chaotic trajectory is itself a short-lived (here picoseconds) species.

Like motion in all short-lived species, e.g., transition states, resonant scattering states, etc., knowledge of it is worth having. What can one do to go from the experimental spectrum to the knowledge of the motion of the reduced-dimension tori? The answer comes from the essence of chaos. Chaotic trajectories (or more precisely the parts of a trajectory that are chaotic) are greatly different if the initial conditions change and in particular if the energy changes. Likewise chaotic wave functions change greatly with energy in regions not located over configuration-space projections of the reduced-dimension tori. Low-resolution experiments that average over energy should, because they average the different erratic motions or wave function oscillations, deemphasize the chaotic motions, and emphasize the regular spectra of the regular inserted motions that mimic the reduced-dimension tori. We now turn to the question of how one calculates these low-resolution spectra which are seen to reveal the dynamics of reduced-dimension tori. The Na_3 system will be our example;[3,7] comparison of experiment and theory will be the "proof" of our ideas.

III. Low-Resolution Spectra of the Sodium Trimer

In the experiment of interest, sodium trimer is produced in an optimally cooled beam assuring that it is in its ground vibronic state and low ($J < 20$) rotation state.[3] It is then excited with a single photon to the lowest regular vibrational state of the electronically excited C $^2E''(0)$ state. From parallel regular type spectroscopic experiments, the geometry of the C state and its frequencies are known, and from this a simple normal mode ground vibrational wave function $\psi_{initial}$ can be constructed.[11,10] A second laser is used to stimulate emission (stimulated emission pumping[1]) down to the rovibration levels of the ground state. Since those molecules that do not emit are ionized by absorbing a second photon of the first laser, the ionization signal

(7) Gomez Llorente, J. M.; Taylor, H. S. *J. Chem. Phys.*, in press.

(8) Pechukas, P. *Phys. Rev. Lett.* **1986**, *51*, 943 and references therein.

(9) Taylor, H. S.; Zakrzewski, J. *Phys. Rev. A* **1988**, *38*, 3732.

(10) (a) Gomez Llorente, J. M.; Zakrzewski, J.; Taylor, H. S.; Kulander, K. C. *J. Chem. Phys.* **1988**, *89*, 5859–5960; (b) *J. Chem. Phys.* **1989**, *90*, 1505.

(11) (a) Gomez Llorente, J. M.; Pollack, E. *Chem. Phys. Lett.* **1987**, *138*, 125–130; (b) *J. Chem. Phys* **1988**, *89*, 1195; (c) *J. Chem. Phys.* **1989**, *90*, 5406.
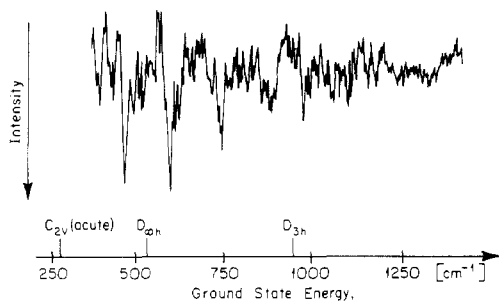
Figure 2. The stimulated emission pumping spectrum of Na_3 referred to in the text from ref 3. Reprinted with permission from ref 7. Copyright 1989 American Institute of Physics.
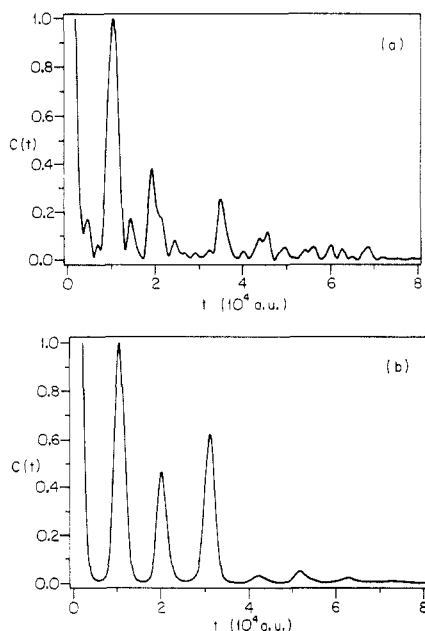
Figure 3. The survival probability $C(t)$ of (a) the stimulated emission pumping experiment and of (b) theory. The peak at $t = 2$ is an overtone of the one at $t = 0.5$. The first and third peaks are fundamentals. Reprinted with permission from ref 7. Copyright 1989 American Institute of Physics.

dips at the emission frequencies. The spectrum below 250 cm^{-1} is regular, assignable, and explainable[3] as due to four observed out of five theoretically possible levels. In terms of three normal modes, these are a symmetric stretch mode, a bend mode, and an asymmetric stretch mode at frequencies 139, 49, and 87 cm^{-1}, respectively. Figure 1a (upper-right corner) shows pictures of two of these motions.

Figure 2 shows a low-resolution (5 cm^{-1}) spectrum in which the reproducible fine structure hints at a very congested, erratic, chaotic high-resolution spectrum, and the gross outlines show the low-resolution spectra and are suggestive of a double oscillation.[3] The frequencies of the latter double oscillation, which we anticipated in a general sense in the previous section, show up better in the magnitude square of the Fourier transform of the spectrum. This quantity, symbolized as $C(t)$, is plotted in Figure 3a, and two frequencies are seen at 130 and 40 cm^{-1}.[7] A theory exists for computing $C(t)$ by using only classical mechanics.[7] The expression for $C(t)$ assumes that the motion is classically chaotic and inputs at each point on a grid of energies in the spectral region, a classical trajectory (which is expected to be and is chaotic) that is computed by using a well-tested (in the regular region) "ab initio" potential for Na_3.[12]
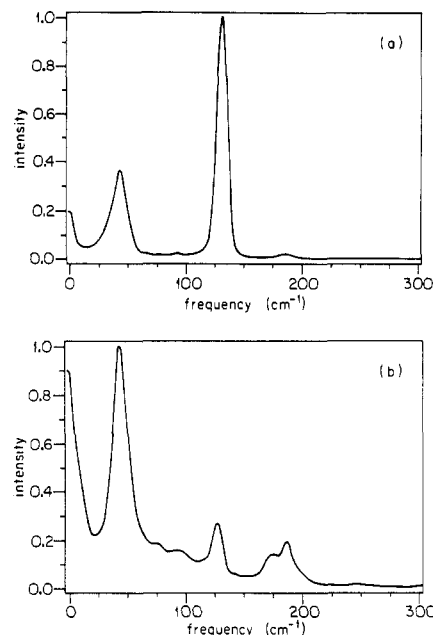
Figure 4. The averaged power spectrum of (a) the symmetric stretch coordinate and of (b) the bend coordinate. Reprinted with permission from ref 7. Copyright 1989 American Institute of Physics.

Also input is a dipole transition operator function and $\psi_{initial}$ which defines the Franck–Condon transition region. If we are correct, our reduced-dimension torus, if it exists, must lie in this region if it is to contribute to the spectrum. $C(t)$ can also be shown formally to be a survival probability function for the initially prepared local excitation. This is a function that has peaks at periods T ($=2\pi/\omega$) of repetitious motions (as could be expected if reduced-dimension tori exist). Since the experiment measures relative intensity, the computed $C(t)$ is matched at one value of t to the experiment as shown in Figure 3b.[13] The agreement of theory and experiment is excellent. Figure 3a yields $\omega_1 = 130$ cm^{-1} and $\omega_2 = 40$ cm^{-1}, and Figure 3b yields $\omega_1 = 128$ cm^{-1} and $\omega_2 = 44$ cm^{-1}. Since we used an ergodic (complete chaos phase space) assumption in deriving the expression for $C(t)$ and chaotic trajectories in computing the result, we can now safely deem the spectrum "chaotic".

Having demonstrated the chaotic nature of the motion and the spectrum, we turn to the heart of our research, namely, the problem of extracting and interpreting the regular motion that is argued to come from a reduced-dimension torus inserted in the chaotic motion.[7] The inserted regular motion is in this case two dimensional, since two fundamental frequencies for $C(t)$ are seen in Figure 3b. This motion can be analyzed by computing averaged power spectra[14] of various coordinates evaluated along the three-dimensional chaotic trajectory. Power spectra are basically Fourier transforms of the time evolution of a coordinate. The chaotic regions of the trajectories over which we average contribute small, almost never repeated, peaks at the myriad of frequencies necessary to describe chaos. The regular region's insert, when visited and revisited, always adds to the intensity at the regular insert fre-

(12) Thompson, T. C.; Izmirlian, G., Jr.; Lemon S. J.; Truhlar, D. G.; Mead, C. A. *J. Chem. Phys.* **1985**, *82*, 5597–5603.

(13) The figures here are all from ref 7, where more details about their construction are available.

(14) Dumont, R. S.; Brumer, P. *J. Chem. Phys.* **1988**, *88*, 1481.

quencies. At all energies in the spectral region, a result similar to Figure 4 occurs; namely, if the symmetric stretch or the bend coordinate is used, one obtains two narrow peaks at frequencies 131 and 44 cm^{-1} near those of Figure 3. Clearly one can safely assume that in Figure 4a (4b), which is for the symmetric stretch (bend) coordinate, the big peak is the frequency of this symmetric stretch (bend), and the small peak is that of the bend (symmetric stretch). Note no asymmetric stretch appears, and a power spectrum of the asymmetric stretch gives no sharp peaks. Conclusion: our torus is reduced to two dimensions and must be a two degree of freedom symmetric stretch and bend family of tori that exist in the transition region and hence in the same region of position space, but at higher energy than the three-degree (symmetric stretch, bend, and asymmetric) tori that give the regular levels (by emission from the same regular states). Our three-dimensional torus has lost a degree of freedom, the asymmetric stretch, and has become a chaotic trajectory with a two dimensional reduced dimension tori insert.

Now having decided what one expects to see and where to see it, it is a simple matter to search the transition region for such an insert. We also need to check that other long-lived inserts do not exist. This latter is here the case except for a 1D torus (stable periodic orbit, see Figure 1a) which does not contribute significantly to $C(t)$. Such an insert was found and can be demonstrated to be very similar to a two degree of freedom torus (symmetric stretch and bend) by the following procedure. First, near the insert, the asymmetric displacement coordinate and its conjugate momentum are set to 0, predestining the trajectory to lie in two dimensions. The resulting motion is the two-dimensional (symmetric stretch and bend) torus and actually was used as our example in Figure 1a. The frequencies of this torus are 135 and 46 cm^{-1} and are extremely close to those of Figure 4 (obtained with the chaotic trajectory). Now the momentum and/or the position displacement of the asymmetric stretch is set near but not equal to 0. Motion similar to that of the torus is observed for picoseconds after which the trajectory moves ever farther away in the asymmetric stretch direction until it becomes chaotic in all variables; time reversal demonstrates the approach to the torus. The long-time power spectrum again becomes that of Figure 4.

Recalling that the ground-state potential has a three blade propellor shape with symmetrically equivalent wells (that hold the five regular states), one in each blade, and three cols and saddle points at small radii between the blades, a pleasing physical picture arises from our results. At low energies, the four observable levels can be viewed as the result of a semiclassical quantization of tori with fundamental normal-mode frequencies ω_{01} = 139 cm^{-1} (symmetric stretch or breathing), ω_{02} = 49 cm^{-1} (obtuse bend), and ω_{03} = 87 cm^{-1} (asymmetric stretch). Such tori lie in each one of the three symmetrically equivalent wells of the potential surface. The normal-mode frequencies calculated

quantum mechanically in ref 2 (142, 58, and 94 cm^{-1}, respectively) support this conclusion. (For completeness, we note that the fifth bound state (011) at roughly 136 cm^{-1} due to selection rules has not been observed experimentally.) Past the fourth level, the vibrational amplitudes are quite large and floppy, and the trajectory feels the confining walls of the potential. At about 250 cm^{-1} and along the asymmetric stretch coordinate (acute bend saddle point) direction, the walls fall away and open to the col between two of the three equivalent regions. Initially, only motion in this direction becomes unstable, leaving a C_{2v} two degree of freedom family of tori describable as the combination of a symmetric stretch mode (now because of anharmonicity $\omega_1 \approx 135$ cm^{-1}) and an obtuse bend mode (now $\omega_2 \approx 40$ cm^{-1}). Later, as we move far along the asymmetric stretch direction and far from the two-dimensional torus, complete chaos takes over until a reduced-dimension torus is again approached.

IV. Summary and Conclusion

At this point our mission has been accomplished. We have a quantitative reproduction of the experimental spectral correlation function and a physical model of the motions consistent with it.[7,9] The low-resolution spectrum is the key to the dynamics of chaotic spectra.[7,15] Other examples of the success of our ideas in interpreting chaotic spectra and extracting essential motions are seen in ref 10, which extracts motions in the chaotic region that accompany the photodissociation of H$_3^+$[10,11] and in ref 9, 10, and 14, where the motions of the highly excited electron in a hydrogen atom in a 6-T (very strong) magnetic field are explained by using the quantum version of our theory to reproduce the low resolution of a chaotic two photon absorption spectrum.

For completeness we note the existence of a fully quantum mechanical theory[10b] of low-resolution spectra in the chaotic region which treats the regions near the reduced-dimension tori as a transition state, or equivalently as a resonance state, and then using resonance scattering methods reproduces with relatively simple calculations the low-resolution spectra. The simple theory and example emphasized here were chosen for discussion because they require less background to comprehend while still exhibiting the important chemical features of the problem.

Lastly we note that many of the ideas we used here for the classical mechanical description are similar to concept and ideas used in analyzing chaos in heartbeats and all the other phenomena and fields mentioned in the first paragraphs of this Account.

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(15) This does not mean high-resolution spectra should not be measured. Low-resolution spectra can be simulated from high-resolution spectra but not vice versa. Detailed measurement never fails to eventually reveal unexpected phenomena.