Chaotic attractor with hysteresis in laser-driven molecules

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Period-doubling bifurcations into a chaotic state are found in a quantum statistical model of multiphoton excitation of a molecule when the laser field is modulated sinusoidally. This chaotic state characterizes a strange attractor coexisting with a periodic one. Interesting dynamical behavior associated with these attractors is described and practical implications of this molecular property discussed.

Chaotic behavior associated with a strange attractor of dynamical systems[1–6] has been the subject of great recent interest, not only as an unsolved problem in mathematics, but also because of its numerous applications to many fields.

Since molecular vibrational motion is known to be highly nonlinear, we would expect to find dynamical instability at the molecular level if some dissipative mechanisms, such as collisions, interaction with external field, energy flow to a reservoir, can effectively couple with the molecular motion. The evidence of the existence of such instability has been found[7] in a model of ir multiphoton vibrational excitation of a molecule derived from the quantum Liouville equation by Narducci, Mitra, Shatas, and Coulter.[8] It was shown that the steady-state surface formed by plotting the average vibrational excitation (z_0) as a function of frequency detuning (Δ) (between the laser frequency and the fundamental frequency of the pumped vibrational mode) and the Rabi rate (Ω_R) takes the shape of a cusp catastrophe as shown schematically in Fig. 1(a). Linear stability analysis of the steady states reveals that the upper and lower branches are stable and the middle branch unstable. Thus this model predicts that laser-driven molecules exhibit bistable and hysteretic properties. However, classical solutions of a driven damped anharmonic oscillator,[9] such as the Duffing oscillator, show not only bistable and hysteretic properties, but also instability which leads to an infinite sequence of period-doubling bifurcations into a chaotic state. Careful search over the control-parameter space has not resulted in any clue to such an instability region association with either the upper or lower branch.[10] We report in this paper that, if the amplitude of the driven field is harmonically modulated, cascading bifurcations into a chaotic state do appear in the Narducci model. The chaotic state coexists with a periodic solution, and results in some interesting dynamical behavior.

The model consists of a set of three first-order differential equations given by

$$\begin{aligned} \dot{x} &= -x + \Delta y - \alpha y z \ , \\ \dot{y} &= -\Delta x - y + \alpha x z - \Omega_R(t) \ , \\ \dot{z} &= -2\Omega_R(t) y - \lambda z \ , \end{aligned} \tag{1}$$

where x and y are the real and imaginary parts of the expectation value of the annihilation operator for the pumped mode, that is, quantities proportional to the average coordinate and momentum. z is the averaged vibrational excitation, α is the scaled anharmonicity, and λ is the ratio of the longitudinal relaxation time to the transverse one. Modula-

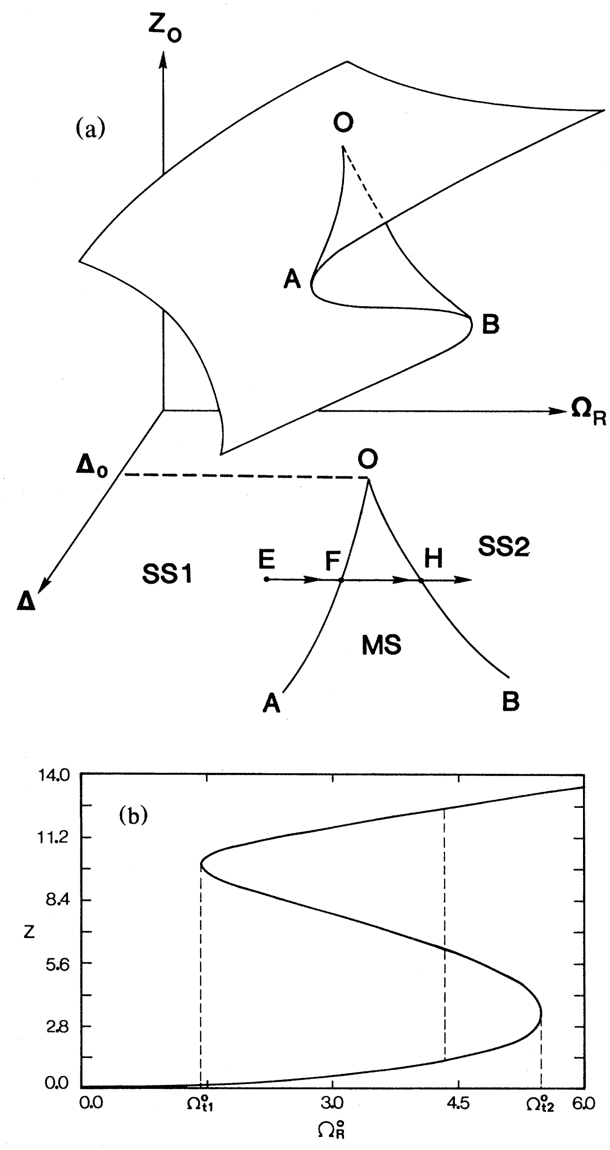

FIG. 1. (a) A schematic plot of the steady-state value of average vibrational excitation (z) vs Rabi frequency (Ω_R) and detuning (Δ). SS1 and SS2 denote regions of steady states 1 and 2, respectively, MS denotes the multistable region. EFH marks a path in the control plane which exhibits hysteresis when reversed. (b) Steady-state z value plotted vs Ω_R^0 for $\alpha=1$, $\lambda=0.1$, and $\Delta=10$. $\Omega^0_{t1,2}$ denotes turning points. For $\Omega_R^0 \gtrsim 4.34$ every trajectory converges to a 1P orbit around the upper branch.

TABLE I. Birfurcation thresholds and the geometrical factors.

	ω_k	δ_{calc}[a]
1P–2P	0.414 85	
2P–4P	0.393 14	
4P–8P	0.389 756	6.4161
8P–16P	0.388 993 5	4.4359
16P–32P	0.388 828 3	4.6345
Chaos with periodic windows	0.388 783–0.364 776 1	
32P–16P	0.364 685 2	
16P–8P	0.364 613 8	
8P–4P	0.364 282	4.6471
4P–2P	0.362 96	3.9843
2P–1P	0.3590	2.9955

[a]δ_{calc} is obtained according to the formula $\delta_{calc}=(\omega_k-\omega_{k+1})/(\omega_{k+1}-\omega_{k+2})$.

tion of the laser field is modeled by $\Omega_R(t)=\Omega_R^0\cos^2(\omega t)$ with a period of $T_0=\pi/\omega$. One way to convert the nonautonomous Eqs. (1) into autonomous ones is to set $u=\cos^2\omega t$ and $v=\sin 2\omega t$. The corresponding steady states, which are equivalent to those obtained by taking the time average of Eqs. (1), form again a surface of the shape of a cusp catastrophe, but with the scale of the Ω_R axis compressed by a factor of 2. We find it convenient to refer to this set of steady states when we describe the dynamical behavior. For clarity we shall focus on cases with parameters set at $\alpha=1$, $\lambda=0.1$, and $\Delta=10$. The steady-state values of z plotted versus Ω_R^0 form an S-shaped curve as shown in Fig. 1(b) with the two turning points located at $\Omega_{t1}^0=1.41$ and $\Omega_{t2}^0=5.50$. Numerical studies show no points on the steady-state curve are stable and close to the lower branch we find a set of 1P limit cycles (a periodic solution with n loops in the phase portrait will be denoted by nP) with the period equal to that of the modulation field. This set of limit cycles does not really circle around the lower branch of the S curve but around some larger-z values, and their lower edges almost touch the lower branch of the S curve. The corresponding basin of attraction exists only up to $\Omega_R^0\simeq 4.34$. Beyond $\Omega_R^0\simeq 4.34$ all phase-space trajectories which originated from points around the lower branch move up and eventually converge to limit cycles around the upper branch.

From here on we start to lower the value Ω_R^0 and integrate Eqs. (1) by using an initial point close to the attractor of the previous Ω_R^0 value (here a value close to the upper branch), corresponding to the experimental situation of varying the control parameter of a system adiabatically. For Ω_R^0 between 1.4 and about 2.5 we have found a domain in the $\omega\Omega_R^0$-control parameter space where trajectories exhibit chaotic behavior characterized by a strange attractor. The transition from periodic to chaotic behavior takes place via a sequence of period-doubling bifurcations with a geometrical factor in agreement with the universal constant predicted by Feigenbaum's renormalization theory.[11] We list, in Table I, the bifurcation thresholds and the calculated geometrical factors obtained by lowering ω with Ω_R^0 fixed at 1.7. These thresholds are computed by measuring the distances D between the bifurcating pairs on the Poincaré surface of section, and then by using the critical power law,[12] $D_i=C_i|\omega-\omega_k|^{1/2}$, where C_i is a constant for the ith pair and ω_k is the threshold modulated frequency at which a limit cycle of a period of $2^{k-1}T_0$ bifurcates to one of period 2^kT_0.

The geometrical factors approach the Feigenbaum's universal constant $\delta=4.669\,210\,2$ as the order of bifurcation, k, increases. Chaotic trajectories characterizing a strange attractor appear at and below $\omega_\infty=0.388\,783$, calculated from the formula $\omega_\infty-\omega_k\propto\delta^{-k}$. An example of a strange attractor at $\omega=0.378$ ($\Omega_R^0=1.7$) is shown in Fig. 2 projected onto the y-z plane. In addition to the fact that chaotic trajectories occur in a domain following an infinite sequence of period-doubling bifurcations, one other evidence we have for the fact that Fig. 2 represents a strange attractor comes from taking its power spectrum. The spectrum obtained from a fast Fourier-transform program shows noisy broad-band peaks at the first subharmonics of the entrainment frequency and sharp peaks at the entrainment frequency and its overtones. This is to be compared with the sharply peaked spectra obtained for periodic orbits.

In order to reveal the detailed structures of a strange at-

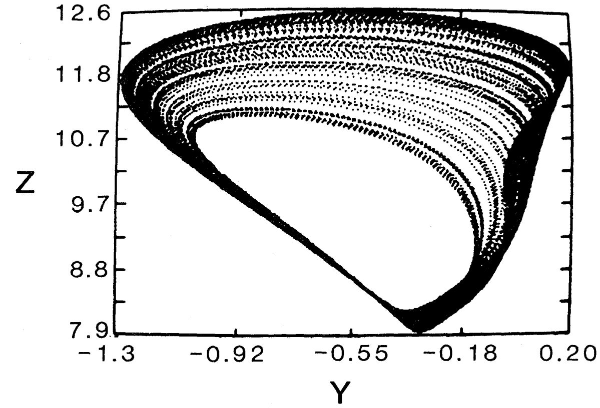

FIG. 2. Projection of a strange attractor at $\Omega_R^0=1.7$ and $\omega=0.379$ onto the y-z plane.

tractor, we have taken a sequence of Poincaré surfaces of section around the strange attractor. The clear bending structure on the right-hand side of Fig. 2 is shown on the Poincaré surfaces of section to be inward in a right-handed coordinate system. If we move clockwise from here around the strange attractor, the ribbonlike structure folds and "cuts" into itself such that a curve intersecting itself appears on the Poincaré section. The crossing loop shrinks and the ribbon folds in some new direction (up) as we move across the most constricted region of the attractor as seen in Fig. 2. A part of the "ribbon" shows finer-layer structure when we expand the scale of the plot. Thus the strange attractor obtained here looks like a loosely knitted ribbon which stretches, twists, bends onto itself, and even intersects itself. The first three features characterize the exponential divergence and irreversible mixing of trajectories on a strange attractor as described by Shaw.[13] Periodic windows of 6P, 7P, 14P, and 21P have been found inside the chaotic domain. Further reduction of the ω value leads to inverse period-doubling bifurcations, listed also in Table I.

If Ω_R^0 is further lowered to a value below 1.4, we can no longer find the proper initial conditions for any ω which would lead to an attractor around the upper branch. Instead 1P limit cycles around some small-z value close to the lower branch have always been found. This is consistent with Fig. 1(b), where $\Omega_{I1}^0 = 1.41$.

For $\Omega_R^0 > 2.8$ and small ω some trajectories we obtained reveal that two basins of attraction are fused into one. An example is shown in Fig. 3 for $\Omega_R^0 = 4.0$ and $\omega = 0.01$, where the trajectory originated from the point $x = 1$, $y = 0$, and $z = 15$ converges to a periodic orbit which goes between the lower and the upper branch. Slight increase of Ω_R^0 may then produce a trajectory which, when initiated at the lower branch, moves up in z value ever so slowly and eventually settles down into a limit cycle around the upper branch.

The above description of dynamical behavior implies that there is a domain in the $\omega\Omega_R^0$-parameter space where two attractors coexist. Thus similar to the case of constant-amplitude laser field hysteresis is expected in some molecules driven by a sinusoidally modulated laser field, red-shifted from the fundamental frequency of the vibrational mode. However, much richer dynamical behavior is seen here around the upper branch. The bistable and hysteretic property of molecules, if verified experimentally, is an important, fundamental property of molecules. From a practical point of view it is potentially useful in fabricating memory and amplifying devices at molecular level, with the switching time of the order of molecular vibration. The range of laser intensity at which we expect to observe molecular bistability of SF_6 is estimated to be about 20 to 400 MW/cm^2, if the laser frequency is detuned by about 35 cm^{-1} to the red. SF_6, however, may not be the best molecule to study experimentally because this range of intensity overlaps that required for ir multiphoton dissociation. To avoid competition with dissociation processes smaller molecules like triatomic or tetratomic molecules may be more appropriate for this purpose. Collisions may serve as a dissipative mechanism, but so far it is not clear whether its existence is necessary for the observation of the bistable property. Finally we should mention that processes involving electronic and vibrational transition may also exhibit bistable properties.[14] These are interesting processes to study for the transition time involved can be of the order of 10 fsec and the range of frequency is such that tunable sources are readily available.

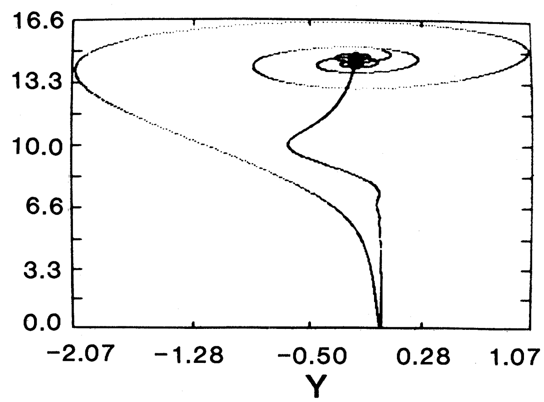

FIG. 3. Phase portrait of $\Omega_R^0 = 4.0$ and $\omega = 0.01$ which converges to a periodic orbit going around both the upper and lower branches.

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