Onset and Synchronization of Complex Dynamic Behavior in the Light-Sensitive Belousov−Zhabotinsky Reaction with Periodic and Nearly Periodic Switching

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In this paper we studied the behavior of a model of a periodically driven photosensitive Belousov−Zhabotinsky reaction. The computations were carried out with a two-variable Oregonator model modified to account for photosensitivity. The external light intensity was periodically switched between two levels. By keeping the total cycle length fixed while varying the duration of the positive and negative perturbations, a variety of dynamical behaviors can be observed, including phase locking, torus oscillations, periodic transitions, and chaos. The results suggest that not only are the forcing frequency and amplitude important, as was already known, but the detailed waveform of the external forcing is also essential in determining the behavior of a driven dynamical system. Two scenarios have been investigated in this study: (a) the system was driven between two limit cycles; (b) the system was driven between excitable and oscillatory states. Random modulation of the durations of the positive and negative perturbations (low and high illumination states) leads to synchronization of complex behavior. Calculating the leading Lyapunov exponent confirms that this form of random driving may be used to suppress chaotic behavior.

1. Introduction

Chemical reactions driven with a periodic perturbation have been the subject of many experimental and computational studies in the past 30 years.[1−22] In particular, the potential for increasing yields of chemical reactions by periodic perturbations has drawn significant attention from chemical engineers.[1−3] Substantial improvement in overall yield has been predicted in modeling studies,[23,24] and the possibility of increased selectivity among a range of reaction products has also been examined.[16,18,22,25−27] A number of studies on periodically driven chemical reactions have reported the observation of entrainment and consecutive bifurcations leading to chaos.[9−15] Entrainment occurs when a periodic perturbation of sufficiently large amplitude is applied to a self-oscillating system and the frequency of the oscillating system is synchronized by the frequency of the driving signal. Outside the entrainment regions one may find quasiperiodic oscillations that show a countable number of periodic oscillations.[12,16]

Dolnik and co-workers investigated experimentally and theoretically the dynamics of forced excitable and oscillatory Belousov−Zhabotinsky (BZ) reactions.[15] They observed periodic and aperiodic regimes in a phase plane. The experimentally determined firing numbers and computed rotation numbers were used to characterize the dynamics. Aris and co-workers studied several reactor models and found some common features of the responses of a dynamical system to periodic forcing.[9−12] They observed that for small and intermediate forcing amplitudes these responses are organized around several common qualitative patterns such as the interplay between entrainment and quasiperiodicity.

While the influence of the amplitude and the frequency of the periodic forcing has been investigated thoroughly in several experiments and many theoretical investigations,[9−17] the impact of the durations of the on and off perturbations (i.e., the waveform) has not received much attention. In this study our focus has primarily been directed to the duration of the on and off perturbations at a fixed driving frequency. Square-wave switching is adopted in our study. Theoretical studies of forced dynamical systems have tended to focus on sinusoidal forcing so that the effect of square-wave forcing has been explored in relatively few studies[21,22] despite its easy experimental realizability. Our study was carried out with a two-variable Oregonator model[28] modified to account for the influence of light, thus describing a photosensitive BZ reaction.[29,30] The study of photosensitive chemical oscillators has attracted intense interest in recent years, due to the ease with which the kinetics can be externally influenced.[29−37] Petrov et al. observed resonant pattern formation in a periodically driven reaction−diffusion photosensitive BZ reaction.[31] Spatiotemporal stochastic resonance has also been reported in a spatially extended photosensitive BZ system.[32] In a recent study Amemiya and co-workers studied the photoinduced behavior in the $Ru(bpy)_3^{2+}$-catalyzed BZ reaction by adopting an Oregonator-class model.[33]

The influence of noise on nonlinear dynamic systems has attracted increasing interest over the past several years. One of the constructive influences of noise, known as stochastic resonance (SR), has been reported in homogeneous and reaction−diffusion chemical systems by several groups.[32,38−41] A recent study on a periodically forced two-variable biological model system shows that the noisy switching between two states may tame chaotic phenomena and favor synchronization.[20] The constructive influence of random fluctuations will also be characterized in this study. In contrast to existing studies[32,37] in which the noise is added to the actual value of the parameter being perturbed, here the random fluctuations are added to the *duration* of the perturbation. This study is thus complementary to this earlier work.

Two scenarios are investigated here. One is the forcing between two limit cycles. The other is the switching between a

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limit cycle and a stable fixed point. For both situations, we consider both periodic and irregular switching. These switching protocols are easily realizable experimentally in a photosensitive reaction. With periodic switching, we find the expected variety of dynamic regimes, including quasiperiodicity, phase locking, and chaos. When we introduce variability to the switching times, chaos is no longer observed and the resulting systems display excellent synchronization properties.

2. Model

The model adopted here is a two-variable Oregonator,[28,42] modified to describe the photosensitive BZ reaction[29,30] (the oxidation and bromination of malonic acid by acidic bromate in the presence of metal catalyst $Ru(bpy)_3^{2+}$). The dimensionless form of the model using Tyson−Fife[43] scaling is

$$\epsilon \frac{du}{dt} = \frac{(fv + \phi)(q - u)}{(q + u)} + u(1 - u) \tag{1}$$

$$\frac{dv}{dt} = u - v \tag{2}$$

Here u and v are the dimensionless concentrations of $HBrO_2$ and $Ru(bpy)_3^{3+}$, respectively, f is an adjustable stoichiometric parameter, ϵ and q are scaling parameters, and ϕ represents the rate of bromide production from the irradiation. This rate is proportional to the applied light intensity.[35,44−48] This modified Oregonator model has been used extensively to qualitatively characterize the dynamic behavior of photosensitive BZ reactions, in particular the spatially extended BZ system.[49] We decompose the photochemically induced bromide production into $\phi = \phi_0 + \phi_p$, where ϕ_0 represents production at a background light intensity, and ϕ_p represents an applied perturbation. We consider a square-wave perturbation, i.e., $\phi_p = \pm c$, where c is an adjustable constant. In this study the following parameter values are used: $\epsilon = 0.02$, $q = 0.02$, $f = 1.0$, $\phi_0 = 0.03$ for the oscillatory condition and $\phi_0 = 0.07$ for the excitable system.

The periodic forcing is implemented by switching the light intensity between two levels. Since the excitability of the BZ system decreases with an increase in light intensity, we call it a negative perturbation when ϕ_p takes a positive value ($\phi_p = c$), corresponding to the enhancement of the illumination. Accordingly, it is called a positive perturbation when the forcing ϕ_p takes a negative value ($\phi_p = -c$). The durations of the positive and negative perturbations are, respectively, T_{-c} and T_{+c}, and the overall period of the periodic forcing is $T_{total} = T_{-c} + T_{+c}$. In addition, we will study the effect of random fluctuations in T_{-c} and T_{+c}. This study is thus complementary to earlier work in which noise was added to the value of light intensity.[31,32,34,37] Random fluctuations in T_{-c} and T_{+c} are Gaussian distributed with zero mean value.

3. Results

3.1. Noise-Free System. We first consider switching between two limit cycles. With the parameter values listed above and in the absence of perturbations, a supercritical Hopf bifurcation occurs when the background light intensity (ϕ_0) decreases below a threshold value 0.0599. Here we choose $\phi_0 = 0.03$ and $c = 0.02$. Therefore ϕ varies between the two levels $\phi = 0.05$ and $\phi = 0.01$, both below the bifurcation threshold. When $\phi = 0.05$, the oscillation period is 3.167 (in dimensionless units), whereas the period becomes 2.215 when $\phi = 0.01$. The relative positions of the two limit cycles in the concentration space are shown in

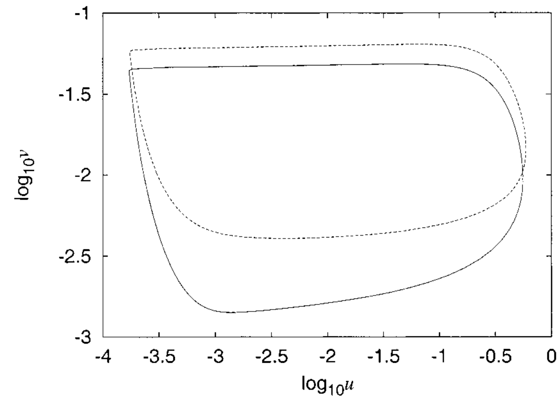

Figure 1. Limit cycles for the unperturbed system. The solid line represents the oscillation when $\phi = 0.05$, whereas $\phi = 0.01$ for the dashed cycle. (Other parameter values are given in the text.)

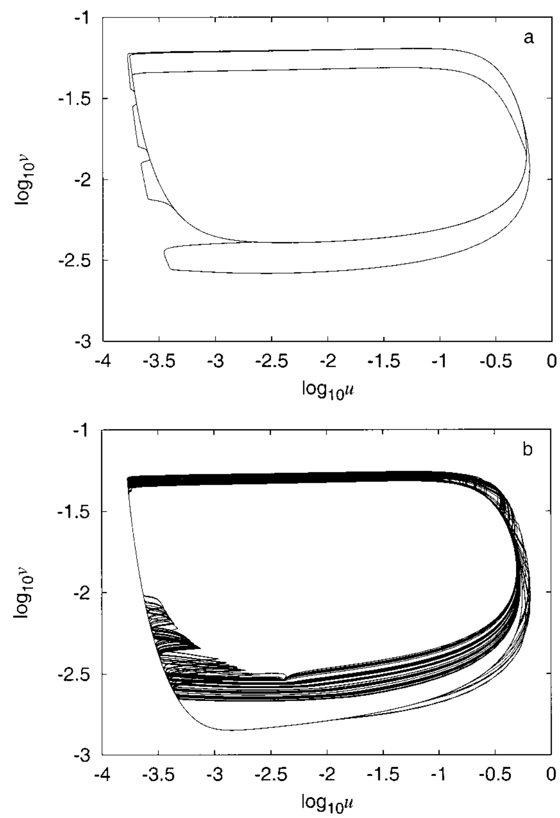

Figure 2. Phase plot for the periodically perturbed system. Calculations were carried out at constant $T_{total} = 1.8$, but different durations of the positive and negative perturbations: (a) $T_{+c} = 0.07$, $T_{-c} = 1.73$ and (b) $T_{+c} = 0.9$, $T_{-c} = 0.9$. Here, $\phi_0 = 0.03$, $c = 0.02$. Other parameter values are listed in the text. In panel (a), we see an example of 1:5 phase locking; panel (b) shows a chaotic trajectory with a leading Lyapunov exponent of 0.065.

Figure 1. As can be seen in the figure, the limit cycle is shifted to lower values of v with the increase in illumination while the oscillation amplitude of u barely changes.

Figure 2 presents two phase plots in the $u-v$ concentration space calculated at the same cycle length (T_{total}) but different durations of the positive and negative perturbations. Figure 2a shows clearly that when the perturbation switches from one level to the other, the system is forced to jump from one limit cycle to the other. Since the duration of the positive (T_{-c}) and negative perturbations (T_{+c}) are much shorter than the period of the oscillation, several switches occur within one oscillation cycle. However, the overall behavior is still simple (periodic). In contrast, the trajectory in Figure 2b is much more complex. A

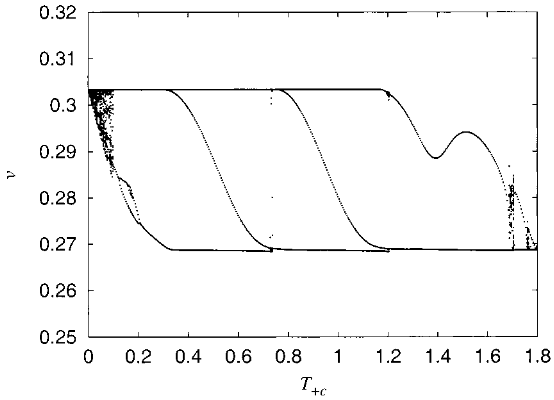

Figure 3. Bifurcation diagram calculated at a fixed perturbation period $T_{\text{total}} = 1.8$. We show the maxima in v. The duration of the negative perturbation is varied gradually and the duration of the positive perturbation is adjusted accordingly to fit the fixed total cycle. Here, $\phi_0 = 0.03$, $c = 0.02$.

calculation of the leading Lyapunov exponent[50] shows a positive value, indicating that the behavior in Figure 2b is chaotic. When other combinations of the durations of the positive and negative perturbation are used, qualitatively different attractors such as period-4 and period-8 have been found.

The bifurcation diagram with respect to the duration of the negative perturbation (T_{+c}) at a fixed perturbation frequency ($T_{\text{total}} = 1.8$) is shown in Figure 3. Points plotted in this figure are the maximum values of v during its time evolution. These maxima vary between the maximal values of v reached on the two limit cycles at $\phi = 0.01$ and $\phi = 0.05$. When $T_{+c} = 0$, the behavior of the driven system is that of the unperturbed system with $\phi = 0.01$, i.e., a simple limit cycle. As the duration of the negative perturbation is increased, quasiperiodic oscillations arise and develop into chaotic behavior. Stroboscopic plots (not shown) indicate that the chaos arises via the quasiperiodic route.[51] When T_{+c} becomes larger than 0.15, a narrow parameter window exhibiting forward and reverse period-doubling transitions can be seen. When T_{+c} is small ($T_{+c} < 0.3$), the system cannot reach the maximum of the $\phi = 0.05$ limit cycle before switching back to the $\phi = 0.01$ limit cycle. Similarly the maximum of the $\phi = 0.01$ limit cycle is not achievable when T_{+c} takes a large value (>1.2).

When values of T_{total} different from that in Figure 3 are used, qualitatively different bifurcation diagrams are obtained, confirming the well-known importance of the frequency of the external forcing.[9−13] We would like to emphasize that the dynamic behavior of the system depends on the actual values of the durations of the positive and negative perturbations, not just on their ratio.

Figure 4 presents a bifurcation diagram using the duration of the negative perturbation (T_{+c}) as a control parameter while the duration of the positive perturbation remains constant at $T_{-c} = 0.35$. Calculations using the period of positive perturbation (T_{-c}) as a variable with a constant T_{+c} exhibit a pattern similar to that shown in Figure 4, where a variety of exotic dynamical behaviors such as period doubled oscillations, quasiperiodicity, and chaos are observed. This result illustrates that those complex behaviors obtained by adjusting the frequency of external forcing at fixed T_{-c}/T_{+c} ratio can also be obtained by merely varying the duration of one or the other of the positive or negative perturbations. It is interesting to note that the bifurcation diagram has an approximate periodicity with the period corresponding to the oscillatory period of the $\phi = 0.05$ limit cycle (3.167 dimensionless units). This phenomenon is not difficult to understand as the behavior of this forced dynamical system at any given time corresponds to motion near a limit cycle. The nature of the dynamics is determined by the set of points on each limit cycle at which switching occurs. When the time spent on one of the limit cycles is extended by an integer multiple of the period, the set of switching points will be roughly the same as before. As a result, qualitatively similar bifurcation structures arise. However, additional transits around the limit cycle are inserted in each oscillatory period of the time series.

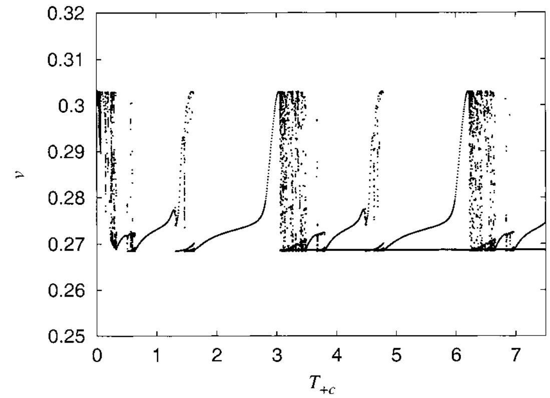

Figure 4. Bifurcation diagram varying T_{+c} for fixed $T_{-c} = 0.35$.

The second scenario being investigated is the switching between excitable and oscillatory conditions. Here the background photochemical bromide production ϕ_0 is set to 0.07, and $c = 0.03$. Therefore, the light intensity ϕ varies between two levels, $\phi = 0.04$ (oscillatory) and $\phi = 0.10$ (excitable, where the system will respond to an above-threshold perturbation with a large excursion). Figure 5 presents three stroboscopic plots which were calculated with different combinations of T_{-c} and T_{+c} while the overall duration of the perturbation (T_{total}) is fixed. For periodic oscillations there are a finite number of points in the stroboscopic plot, the number of points corresponding to the period of the oscillation (Figure 5a), whereas quasiperiodic oscillations show up as a closed curve in the stroboscopic map (Figure 5b). The chaotic behavior shown in Figure 5c indicates that the chaos arises from quasiperiodic (torus) bifurcation.[51]

When other combinations of T_{-c} and T_{+c} are used, qualitatively different attractors such as period-3, period-6, etc., have been observed. The complete bifurcation diagram with respect to the continuous variation of T_{+c} is shown in Figure 6, where the period of the perturbations (T_{total}) is fixed. When the duration of the negative perturbation (T_{+c}) tends to zero, the system exhibits a simple limit cycle which develops into quasiperiodic oscillations with an increase in T_{+c}. At the other end of the bifurcation diagram, where T_{-c} tends to zero, the system only fluctuates around lower values of v and no excitation can occur as the duration of the positive perturbation T_{-c} is too short to generate an above-threshold perturbation. Transitions between periodic oscillations and complex oscillations take place when T_{-c} and T_{+c} both take intermediate values.

The phase diagram of the duration of the positive perturbation T_{-c} versus the duration of the negative perturbation T_{+c} is plotted in Figure 7, where each curve represents a bifurcation diagram calculated at fixed T_{-c} while T_{+c} is increased gradually. The points in each bifurcation diagram are the maximum values of v in the time series. When the system only fluctuates around low values of v no point is collected. This "no-excitation" behavior always occurs when T_{-c} is small and T_{+c} is sufficiently large. A single positive perturbation is then not strong enough to induce an excursion, while the long negative perturbations eliminate the possibility that an accumulation of positive

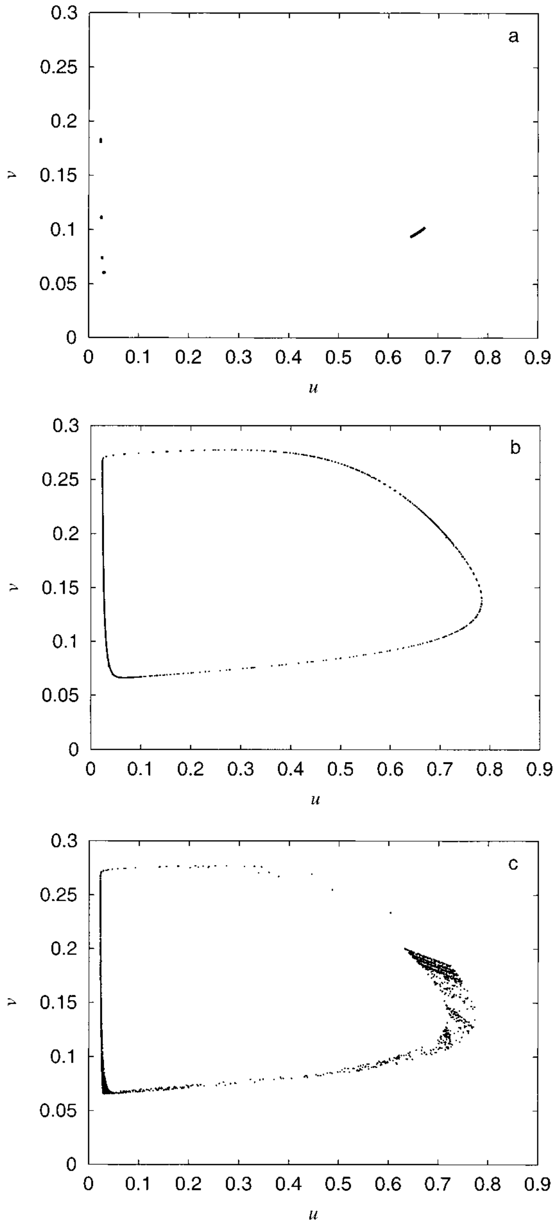

Figure 5. Stroboscopic plots calculated at a constant cycle length but different durations of the positive and negative perturbations with $\phi_0 = 0.07$, $c = 0.03$ and (a) $T_{+c} = 0.42$, $T_{-c} = 0.18$; (b) $T_{+c} = 0.01$, $T_{-c} = 0.59$; and (c) $T_{+c} = 0.15$, $T_{-c} = 0.45$. In these stroboscopic plots, points are collected at every half period of the positive perturbation (i.e., when $T_{-c}/2$ time units have elapsed since the illumination was reduced).

perturbations will trigger an excitable response. For example, the bottom curve of Figure 7 (at $T_{-c} = 0.05$) "runs out" after a few points. It is however interesting to see that the no-excitation phenomenon can also be observed when T_{+c} takes intermediate rather than large values (next two curves of Figure 7, $T_{-c} = 0.1$ and 0.15). This is due to the balance between the relaxation and excitation time scales: In that region of the phase diagram, excursions toward the limit cycle during the positive perturbation are, after a short transient, exactly offset by motion back toward the equilibrium point during the negative perturbation. As a result, the system oscillates between two points near the equilibrium point.

It can also be seen in Figure 7 that the dynamic regions exhibiting complicated oscillations are separated by regions showing simple periodic oscillations, shifting to a lower value of T_{+c} when T_{-c} is increased and eventually disappearing. Meanwhile a new dynamic window exhibiting complex oscillations arises at large values of T_{+c}. The period of the perturbing illumination ($T_{total} = T_{+c} + T_{-c}$) clearly plays an important role, as evidenced by the roughly diagonal motion of the regions of complex oscillations across this diagram, but it is equally clear that each line of the diagram is not a simple translation of the previous, reinforcing our contention that the waveform can be significant as well.

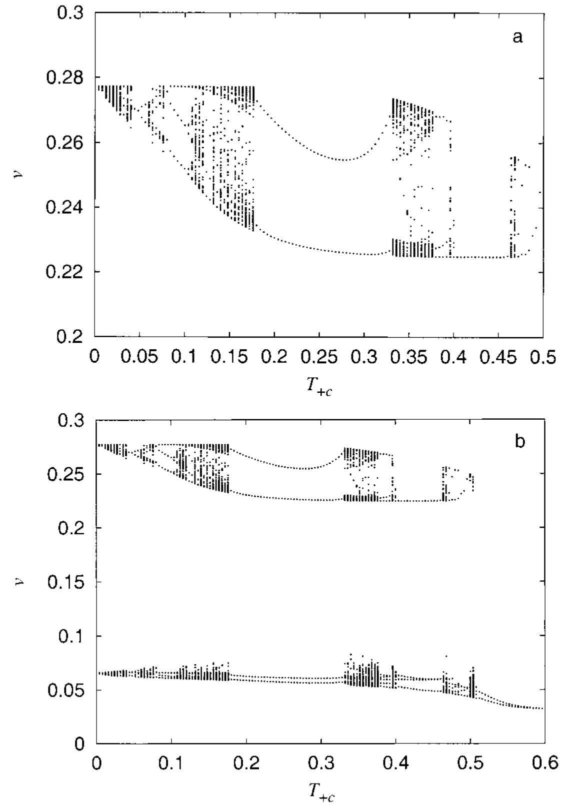

Figure 6. Bifurcation diagram calculated at a fixed perturbation frequency $T_{total} = 0.6$. The duration of the negative perturbation is varied gradually and the duration of the positive perturbation is adjusted accordingly to keep the total cycle constant. $\phi_0 = 0.07$, $c = 0.03$. Panel (a) shows maxima in v only while panel (b) shows both maxima and minima.

3.2. Influence of Irregularity in the Duration of the Perturbation. As stated earlier, stochasticity is introduced by perturbing T_{-c} and T_{+c}, rather than adding noise to the light intensity (ϕ). This is an essential difference from earlier studies on the perturbed photosensitive BZ reaction.[31,32,34,37] Two systems with the same parameters but different initial conditions are investigated. We imagine that both systems are being illuminated by the same source so that they are subject to a common $\phi(t)$. Figure 8 plots the time evolution of the difference between the two systems. For the parameters used here, we are switching between two limit cycles, and chaos is observed in the absence of irregularity in the duration of light perturbation. Stochastic variation of T_{-c} and T_{+c} was turned on at $t = 300$. After a transient period, the difference between the two systems becomes zero, indicating the achievement of synchronization. Calculations of the leading Lyapunov exponent show that it changes from a positive to a negative value after the fluctuations are switched on, suggesting that a stochastic process of this type can be used to tame the chaotic behavior of driven dynamical systems. The length of the transient period decreases with increasing variance of the switching times. When the variance is too small, $\phi(t)$ is nearly periodic, the two systems are chaotic and synchronization is impossible. Successful synchronization

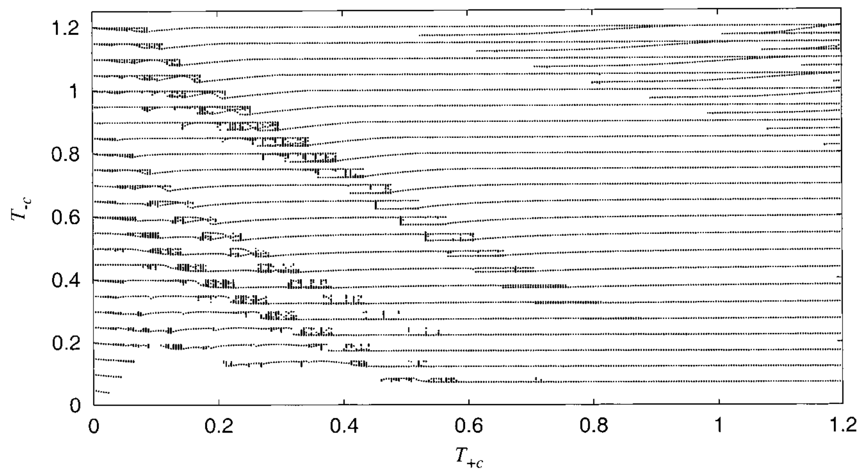

Figure 7. Phase diagram of the duration of the positive perturbation (T_{-c}) versus the duration of the negative perturbation (T_{+c}). Each dotted curve represents maxima in v collected at a fixed T_{-c} while T_{+c} is varied. From bottom to top, the value of T_{-c} equals 0.05 to 1.20 in steps of 0.05.

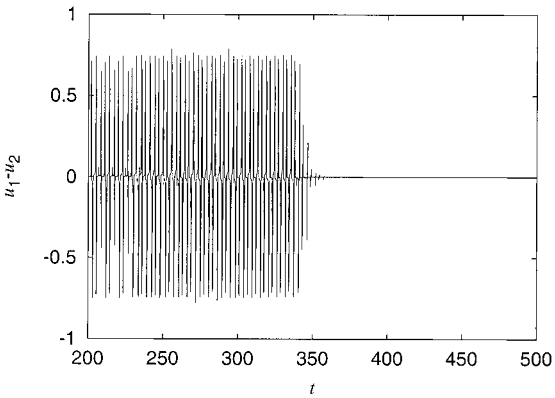

Figure 8. Time evolution of the difference between two identical uncoupled photosensitive BZ systems which are subjected to the same time-varying light intensity but start from different initial conditions: (1) $u_0 = 0.6$, $v_0 = 0.4$; (2) $u_0 = 0.01$, $v_0 = 0.01$. Other parameters $T_{+c} = 1.704$, $T_{-c} = 0.096$, $\phi_0 = 0.03$, $c = 0.02$. For these parameters we are switching between two limit cycles and the resulting dynamics is chaotic. Fluctuations in the durations of the perturbations begin at $t = 300$. Gaussian distributed white noise with zero mean value is used here. The variance of the noise (σ) is 0.02. To avoid the noise value becoming larger than T_{-c} or T_{+c}, it is truncated at 2σ.

has also been obtained when only T_{-c} or T_{+c} fluctuates. There is no difference in the minimum variance value needed to achieve synchronization when noise is added either to T_{-c} or to T_{+c}, or to both.

For the case in which the system was driven between excitable and oscillatory states (studied from a different perspective by L'Heureux, Kapral, and Bar-Eli),[52] the same effect of fluctuations in the positive and negative perturbation durations was observed (not shown). In this situation however, if the noise is added to both the negative and positive perturbations, the minimum noise variance required to achieve synchronization turns out to be smaller than if noise is added only to the positive or negative perturbation. If only one of the perturbation durations fluctuates, there is no difference in the minimum variance required to obtain synchronization whether it is the positive or the negative perturbation duration that is noisy.

4. Discussion

Periodically driven dynamical systems are common in nature, such as forced chemical and biological systems. Earlier studies[9−15] have characterized the effect of the amplitude and the relative frequency of the driving force. In this study, we explored the importance of the duration of the positive and negative perturbations at a fixed forcing frequency. The results have shown that for a periodically driven dynamical system, the durations of the positive and negative perturbations are both essential in determining the overall dynamic behavior and can each be used as a control parameter to manipulate this behavior. A variety of dynamic phenomena such as torus oscillations, periodic transitions, phase locking, and chaos have been achieved by merely adjusting the duration of the positive or negative perturbations while the length of the cycle remains constant.

Calculations of the leading Lyapunov exponent and simulations such as that shown in Figure 8 indicate that the observed chaotic behavior may be suppressed by allowing the durations of the perturbations to fluctuate. The constructive influence of noise therefore may be used as an alternative to gross changes in the parameters or to chaotic control techniques[53−57] to regularize the behavior of a forced dynamical system. Control methods provide a simple means for stabilizing unstable periodic states by supplying tiny but precise perturbations to the system. A sufficient amount of data from the system is required to determine an unstable orbit and the required perturbation size. Our method for suppressing chaos by allowing variation in the switching times is much simpler to implement. This constructive influence of noise may be advantageous for industrial production, where time-varying control parameters may enhance both the production rate and the selectivity of the reaction.[23−26]

In this study, synchronization was obtained by adding Gaussian distributed white noise to the durations of the positive and/or negative perturbations. For both cases studied here (switching between two limit cycles or between a limit cycle and an excitable fixed point), synchronization was achieved equally easily whether we added noise to T_{+c} or to T_{-c}. This is different from an earlier study on a mitosis model, where the system was found to be more sensitive to the variation of the "on" perturbation.[20] Chaos in these systems is due to oversampling by trajectories of a region in phase space where expansion occurs. In the mitotic model, the parametric driving completely changes the flow in phase space, introducing a strong asymmetry between up- and down-regulation. For the BZ reaction with the parameters used in this study, the two flows are structurally similar so that the two transitions, from high to low values of ϕ_p and vice versa, are equivalent, at least to a first approximation.

We have also briefly studied other types of random variation such as random selection between two values of T_{+c} and two values of T_{-c},[52] and qualitatively the same results were observed. This and earlier studies[20,58] suggest that external signals that incorporate randomness in some way may often turn out to be superior synchronizers.

A variety of studies have shown that various kinds of noise can regularize the behavior of a system.[58−62] The noisy switching times used in our study are a variation on the dichotomous (or telegraphic) noise processes studied by others.[52,59,63−66] These studies have shown a variety of effects ranging from stochastic resonance[52] to stochastic coherence.[59,65,66] Our observation of synchronization in these systems is no doubt closely related to stochastic coherence. The latter phenomenon is the appearance of nontrivial structure in the coarse-grained probability density.[59,67,68] Since we can obtain similar synchronization properties with a variety of dichotomous noise processes, it seems likely that the systems we have studied will show similarly structured probability densities. It seems equally likely that the peaks in the probability density act as organizing centers for synchronization. This hypothesis awaits investigation.

The Oregonator model has been very successful in qualitatively describing experimental observations in the BZ reaction. Accordingly we expect that the phenomena observed in this study may be observed in a real photosensitive BZ experiment.

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References and Notes

(1) Bailey, J. E. *Chem. Eng. Commun.* **1973**, *1*, 111.
(2) Sincic, D.; Bailey, J. E. *Chem. Eng. Sci.* **1977**, *32*, 281.
(3) Cordonier, G. A.; Schmidt, L. D.; Aris, R. *Chem. Eng. Sci.* **1990**, *45*, 1659.
(4) Boiteux, A.; Goldbeter, A.; Hess, B. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 3829.
(5) Daido, H.; Tomita, K. *Prog. Theor. Phys.* **1979**, *61*, 825.
(6) Daido, H.; Tomita, K. *Prog. Theor. Phys.* **1979**, *62*, 1519.
(7) Kai, T.; Tomita, K. *Prog. Theor. Phys.* **1979**, *61*, 54.
(8) Mankin, J. C.; Hudson, J. L. *Chem. Eng. Sci.* **1984**, *39*, 1807.
(9) Kevrekidis, I. G.; Schmidt, L. D.; Aris, R. *Chem. Eng. Commun.* **1984**, *30*, 323.
(10) Kevrekidis, I. G.; Schmidt, L. D.; Aris, R. *Chem. Eng. Sci.* **1986**, *41*, 1263.
(11) Kevrekidis, I. G.; Aris, R.; Schmidt, L. D. *Chem. Eng. Sci.* **1986**, *41*, 905.
(12) McKarnin, M. A.; Schmidt, L. D.; Aris, R. *Chem. Eng. Sci.* **1988**, *43*, 2833.
(13) Vance, W.; Ross, J. *J. Chem. Phys.* **1989**, *91*, 7654.
(14) Schreiber, I.; Dolník, M.; Choc, P.; Marek, M. *Phys. Lett. A* **1988**, *128*, 66.
(15) Dolník, M.; Finkeová, J.; Schreiber, I.; Marek, M. *J. Phys. Chem.* **1989**, *93*, 2764.
(16) Scott, S. K. *Chemical Chaos*; Oxford: U.K., 1991.
(17) Förster, A.; Hauck, T.; Schneider, F. W. *J. Phys. Chem.* **1994**, *98*, 184.
(18) Schneider, F. W. *Annu. Rev. Phys. Chem.* **1985**, *36*, 347.
(19) Aronson, D. G.; McGehee, R. P.; Kevrekidis, I. G.; Aris, R. *Phys. Rev. A* **1986**, *33*, 2190.
(20) Closson, T. L. L.; Roussel, M. R. *Phys. Rev. Lett.* **2000**, *85*, 3974.
(21) Sato, S.; Doi, S. *Math. Biosci.* **1992**, *112*, 243.
(22) Hohmann, W.; Lebender, D.; Müller, J.; Schinor, N.; Schneider, F. W. *J. Phys. Chem. A* **1997**, *101*, 9132.
(23) Alarcón, T.; Pérez-Madrid, A.; Rubí, J. M. *J. Chem. Phys.* **1998**, *108*, 7367.
(24) Lazar, J. G.; Ross, J. *Science* **1990**, *247*, 189.
(25) Otawara, K.; Fan, L. T. *J. Phys. Chem. A* **1997**, *101*, 9678.
(26) Schinor, N.; Hohmann, W.; Kraus, M.; Müller, J.; Schneider, F. W. *Phys. Chem. Chem. Phys.* **1999**, *1*, 827.
(27) Lee, J.; Parulekar, S. J. *Chem. Eng. Sci.* **1996**, *51*, 217.
(28) Field, R. J.; Noyes, R. M. *J. Chem. Phys.* **1974**, *60*, 1877.
(29) Kuhnert, L.; Agladze, K. I.; Krinsky, V. I. *Nature* **1989**, *337*, 244.
(30) Krug, H.-J.; Pohlmann, L.; Kuhnert, L. *J. Phys. Chem.* **1990**, *94*, 4862.
(31) Petrov. V.; Ouyang, Q.; Swinney, H. L. *Nature* **1997**, *388*, 655.
(32) Kádár, S.; Wang, J.; Showalter, K. *Nature* **1998**, *391*, 770.
(33) Amemiya, T.; Ohmori, T.; Yamaguchi, T. *J. Phys. Chem. A* **2000**, *104*, 336.
(34) Steinbock, O.; Zykov, V.; Müller, S. C. *Nature* **1993**, *366*, 322.
(35) Sørensen, P. G.; Lorenzen, T.; Hynne, F. *J. Phys. Chem.* **1996**, *100*, 19 192.
(36) Muñuzuri, A. P.; Dolnik, M.; Zhabotinsky, A. M.; Epstein, I. R. *J. Am. Chem. Soc.* **1999**, *121*, 8065.
(37) Wang, J.; Kádár, S.; Jung, P.; Showalter, K. *Phys. Rev. Lett.* **1999**, *82*, 855.
(38) Förster, A.; Merget, A.; Schneider, F. W. *J. Phys. Chem.* **1996**, *100*, 4442.
(39) Guderian, A.; Dechert, G.; Zeyer, K.-P.; Schneider, F. W. *J. Phys. Chem.* **1996**, *100*, 4437.
(40) Hohmann, W.; Müller, J.; Schneider, F. W. *J. Phys. Chem.* **1996**, *100*, 5388.
(41) Amemiya, T.; Ohmori, T.; Yamamoto, T.; Yamaguchi, T. *J. Phys. Chem. A* **1999**, *103*, 3451.
(42) Field, R. J. In *Oscillations and Traveling Waves in Chemical Systems*; Field, R. J., Burger, M., Eds.; Wiley-Interscience: New York, 1985; p 65.
(43) Tyson, J. J.; Fife, P. C. *J. Chem. Phys.* **1980**, *73*, 2224.
(44) Kádár, S.; Amemiya, T.; Showalter, K. *J. Phys. Chem.* **1997**, *101*, 8200.
(45) Hanazaki, I.; Mori, Y.; Sekiguchi, T.; Rabai, G. *Physica D* **1995**, *84*, 228.
(46) Ram Reddy, M. K.; Szlávik, Z.; Nagy-Ungvarai, Zs.; Müller, S. C. *J. Phys. Chem.* **1995**, *99*, 15 081.
(47) Agladze, K.; Obata, S.; Yoshikawa, K. *Physica D* **1995**, *84*, 238.
(48) Yamaguchi, T.; Shimamoto, Y.; Amemiya, T.; Yoshimoto, M.; Ohmori, T.; Nakaiwa, M.; Akiya, T.; Sato, M.; Matsumura-Inoue, T. *Chem. Phys. Lett.* **1996**, *259*, 219.
(49) Epstein, I. R.; Showalter, K. *J. Phys. Chem.* **1996**, *100*, 13 132.
(50) Rangarajan, G.; Habib, S.; Ryne, R. D. *Phys. Rev. Lett.* **1998**, *80*, 3747.
(51) Steinmetz, C. G.; Larter, R. *J. Chem. Phys.* **1991**, *94*, 1388.
(52) L'Heureux, I.; Kapral, R.; Bar-Eli, K. *J. Chem. Phys.* **1989**, *91*, 4285.
(53) Ott, E.; Grebogi, C.; Yorke, J. A. *Phys. Rev. Lett.* **1990**, *64*, 1196.
(54) Peng, B.; Petrov, V.; Showalter K. *J. Phys. Chem.* **1991**, *95*, 4957.
(55) Petrov, V.; Gaspar, V.; Masere, J.; Showalter, K. *Nature* **1993**, *361*, 240.
(56) Schneider, F. W.; Blittersdorf, R.; Förster, A.; Hauck, T.; Lebender, D.; Müller, J. *J. Phys. Chem.* **1993**, *97*, 12 244.
(57) Hjelmfelt, A.; Ross, J. *J. Phys. Chem.* **1994**, *98*, 1176.
(58) Parmananda, P.; Jiang, Y. *J. Phys. Chem. A* **1998**, *102*, 4532.
(59) Irwin, A. J.; Fraser, S. J.; Kapral, R. *Phys. Rev. Lett.* **1990**, *64*, 2343.
(60) Pradines, J. R.; Osipov, G. V.; Collins, J. J. *Phys. Rev. E* **1999**, *60*, 6407.
(61) Lythe, G. D.; Proctor, M. R. E. *Physica D* **1999**, *133*, 362.
(62) Milstein, G. N.; Tretyakov, M. V. *Physica D* **2000**, *140*, 244.
(63) Hänggi, P.; Riseborough, P. *Phys. Rev. A* **1983**, *27*, 3379.
(64) Van den Broeck, C.; Hänggi, P. *Phys. Rev. A* **1984**, *30*, 2730.
(65) Fraser, S. J.; Kapral, R. *Phys. Rev. A* **1992**, *45*, 3412.
(66) Fraser, S. J.; Kapral, R. *Phys. Rev. E* **1997**, *56*, 2582.
(67) Stark, J. *Phys. Rev. Lett.* **1990**, *65*, 3357.
(68) Irwin, A. J.; Fraser, S. J.; Kapral, R. *Phys. Rev. Lett.* **1990**, *65*, 3358.