

Two-Parameter Stochastic Resonance in a Model of the Photosensitive Belousov–Zhabotinsky Reaction in a Flow System

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Stochastic resonance (SR) is shown in a two-parameter system, a model of the photosensitive Belousov–Zhabotinsky reaction in a flow system. Light flux and a flow rate are control parameters in a newly developed Oregonator-type model, and the oscillatory behavior of the system is the dynamical observable. Modulation of an excitable focal steady-state close to a Hopf bifurcation by a periodic signal in one parameter and noise in the other parameter is found to give rise to SR. The scenario and novel aspects of SR in this system are discussed.

I. Introduction

Stochastic resonance (SR) has been observed in a wide range of physical,¹ chemical,^{2–6} and biological^{7–9} systems. The mechanism of SR was originally proposed for a bistable system^{10,11} to account for periodicity in the Earth's ice ages.¹² Recent theoretical studies have proved that SR occurs in a wider class of situations, including excitable,¹³ threshold-crossing,^{14,15} and threshold-free^{16,17} systems. Stochastic resonance in spatio-temporal systems^{18–21} has also become of much interest, particularly in studies of pattern formation and parallel detection²² of signals in biological media. Now SR has pervaded diverse areas of science, and its technical application has also been carried out.²³

A combination of an input signal and optimized additive noise may give rise to SR in all of the systems mentioned above. Despite many examples of SR in different scientific areas, it is worth noting that all the experimental studies and their modeling studies have been performed under the same conditions in which both a signal and noise are added to a system from identical physical sources. For instance, they are electrical voltage,¹⁸ flow rates,^{4–6} water motion,^{7,13} air-current,⁸ electrical potential,⁹ and magnetic flux.²³ In such cases, a signal is buried in noise from the identical physical source, and both the signal and the noise can be assigned to *one parameter* in the models.^{4–6,13,23} Under some circumstances, however, the sources of a signal and noise may be different,^{2,3,17,24} and SR under such a condition will be more general in nature than that we already know.

In this paper, we take into account two different physical phenomena (light flux and a flow rate) for a signal and noise in a real chemical reaction system. We have used the Oregonator²⁵ model, modified in this study to describe the photosensitive²⁶ Belousov–Zhabotinsky (BZ) reaction^{27,28} that includes the photoinduced generation of both inhibitor Br^- ^{26,29–35} and activator HBrO_2 ^{35–38} in a flow system.³⁹ The two experimentally controllable parameters, light flux and a flow rate, are independent bifurcation parameters in the model. A signal and noise are added to the constant component of each parameter. An excitable focal steady state close to a Hopf bifurcation is modulated by a periodic signal in one parameter and noise in

the other parameter. Noise in the light flux affects the dynamics of the system significantly depending on the concentrations of bromomalonic acid (BrMA)^{34,35} and bromate (BrO_3^-) that are the sources of photoinduced generation of Br^- and HBrO_2 , respectively. Thus we have investigated two different cases by changing the concentration of BrMA . The computational results show that SR occurs in this system under the condition where a signal and noise are added to the different physical inputs. Our system also covers usual framework of SR in a chemical reaction system wherein noise in a flow rate or light flux is added to a periodic signal in the flow rate^{4–6} or in the light flux, respectively.

II. Model

Photosensitive Flow-Oregonator. A modified Oregonator model accounting for the photosensitivity³⁵ of the BZ reaction in a flow system is presented here for the first time. The model involves the following reaction steps, which has recently been proposed by Kádár and co-workers³⁵



where $\text{A} = \text{BrO}_3^-$, $\text{P} = \text{HOBr}$, $\text{X} = \text{HBrO}_2$, $\text{Y} = \text{Br}^-$, $\text{Z} = \text{Ru}(\text{bpy})_3^{3+}$, $\text{M} = \text{MA}$ (malonic acid), $\text{G} = \text{Ru}(\text{bpy})_3^{2+}$, $\text{E} = \text{Ru}(\text{bpy})_3^{2+*}$ (excited state of $\text{Ru}(\text{bpy})_3^{2+}$), $\text{V} = \text{BrMA}$, and h is the stoichiometric factor. Processes (O1)–(O5) represent the Oregonator while processes (P0)–(P3) represent the photochemical reaction of the catalyst; (P0) is the photoactivation of $\text{Ru}(\text{bpy})_3^{2+}$ with the forward reaction rate proportional to the

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TABLE 1: Differential Equations for Modified Oregonator Model

	ref
Kinetic Terms	
$F_X = k_{O1}AY - k_{O2}XY + k_{O3}AX - 2k_{O4}X^2 + k_{P2}EA$	
$G_Y = -k_{O1}AY - k_{O2}XY + hk_{O5}MZ + k_{P1}EV$	
$H_Z = 2k_{O3}AX - k_{O5}MZ + k_{P1}EV + 2k_{P2}EA$	
Reaction Rates for Process (P1) and (P2)	
$k_{P1}EV = \frac{V}{0.089 + V + 15 H^2 A} \Phi$	35, 42
$k_{P2}EA = \frac{15 H^2 A}{0.089 + V + 15 H^2 A} \Phi$	35, 42
Steady-State Approximation for E	
$dE/dt = \Phi - k_{-p0}E - k_{P1}EV - k_{P2}EA - k_f E \approx 0$	35, 42

light flux (Φ), and the reverse reaction a first-order quenching process with a rate constant of k_{-p0} , and (P1) and (P2) represent the photoinduced generation of Br^- , $HBrO_2$, and $Ru(bpy)_3^{3+}$ from the reaction of $Ru(bpy)_3^{2+}$ *⁴⁰ with $BrMA$ and BrO_3^- . The flow terms are added to the differential rate equations as³⁹

$$\begin{aligned} \frac{dX}{dt} &= F_X - k_f X \\ \frac{dY}{dt} &= G_Y - k_f(Y - Y_0) \\ \frac{dZ}{dt} &= H_Z - k_f Z \end{aligned} \quad (1)$$

where F_x , G_y , and H_z are the kinetic terms for the chemical reaction (O1)–(P2) as listed in Table 1, k_f is the flow rate, and Y_0 is the concentration of Y in the feed flow solution. It is noted that A , M , and V are constants in this flow system, whereas they were variables in a batch system.³⁵

The reaction rate eq 1 can be nondimensionalized using the Tyson's scaling⁴¹

$$x = \frac{2k_{O4}}{k_{O3}A}X, \quad y = \frac{k_{O2}}{k_{O3}A}Y, \quad z = \frac{k_{O4}k_{O5}M}{(k_{O3}A)^2}Z, \quad \tau = k_{O5}Mt \quad (2)$$

The dimensionless rate equations then become

$$\begin{aligned} \epsilon \dot{x} &= x(1 - x) + y(q - x) - \epsilon \kappa_f x + p_2 \phi \\ \epsilon' \dot{y} &= 2hz - y(q + x) + \epsilon' \kappa_f (y_0 - y) + p_1 \phi \\ \dot{z} &= x - z - \kappa_f z + \left(\frac{p_1}{2} + p_2\right) \phi \end{aligned} \quad (3)$$

These equations involve the following dimensionless parameters

$$\epsilon = \frac{k_{O5}M}{k_{O3}A}, \quad \epsilon' = \frac{2k_{O4}k_{O5}M}{k_{O2}k_{O3}A}, \quad q = \frac{2k_{O1}k_{O4}}{k_{O2}k_{O3}} \quad (4)$$

and

$$y_0 = \frac{k_{O2}}{k_{O3}A}Y_0, \quad \kappa_f = \frac{1}{k_{O5}M}k_f, \quad \phi = \frac{2k_{O4}}{(k_{O3}A)^2}\Phi \quad (5)$$

with

TABLE 2: Parameters Used in the Model

	ref
rate constants	
$k_{O1} = (2 M^{-3} s^{-1}) H^2$	43
$k_{O2} = (3 \times 10^6 M^{-2} s^{-1}) H$	43
$k_{O3} = (42 M^{-2} s^{-1}) H$	43
$k_{O4} = 3 \times 10^3 M^{-1} s^{-1}$	43
$k_{O5} = 5 M^{-1} s^{-1}$	a
stoichiometric factor and concentrations	
$h = 0.5$	a
$H = 0.37 M$	b
$A = 0.15 M$	b
$M = 0.2 M$	b
$V = 0.05 M$ or $0.005 M$	b
$Y_0 = 1 \times 10^{-4} M$	c
initial conditions	
$X_0 = 0 M$	c
$Y_0 = 1 \times 10^{-4} M$	c
$Z_0 = 0 M$	c

^a Parameters in the Oregonator, arbitrarily assigned in this work. ^b Assigned in this work with a reference to the literature.³⁵ ^c Arbitrarily assigned in this work.

$$p_1 = \frac{V}{0.089 + V + 15 H^2 A}, \quad p_2 = \frac{15 H^2 A}{0.089 + V + 15 H^2 A} \quad (6)$$

Equation 4 is consistent with the Tyson's scaling, and eq 5 involves two scaled control parameters, Φ and k_f . The dimensionless form for ϕ is consistent with the scaling by Krug et al.²⁶ The newly introduced coefficients, p_1 and p_2 , can be derived from a series of photochemical reactions of the catalyst, $Ru(bpy)_3^{2+}$, in the BZ reaction.^{35,42} The rate constants⁴³ and the other parameters used in the model are listed in Table 2. Two values of $BrMA$ concentration were used to investigate the dynamics of the system with the same values of the other parameters.

Periodic and Stochastic Modulation of Light Flux and Flow Rate. The light flux and the flow rate that are composed of a constant, a periodic, and a stochastic component can respectively be expressed as follows:

$$\Phi = \Phi^0 \left(1 + \alpha_1 \sin\left(\frac{2\pi}{T_1}t\right) + \beta_1 \xi(\delta) \right) \quad (7)$$

$$k_f = k_f^0 \left(1 + \alpha_2 \sin\left(\frac{2\pi}{T_2}t\right) + \beta_2 \xi(\delta) \right) \quad (8)$$

where Φ^0 and k_f^0 are the constant components; α_1 and α_2 are the amplitudes of the sinusoidal signals with periods T_1 and T_2 , respectively; β_1 and β_2 are the noise amplitudes of equally distributed random numbers, $\xi(\delta)$, between -1 and 1 ; and δ is the duration of the pulse of a single noise event.⁴⁻⁶ The system was modulated under the following two conditions to show *two-parameter SR*: (i) a periodic signal in the flow rate ($\beta_2 = 0$) with random noise in the light flux ($\alpha_1 = 0$), and (ii) a periodic signal in the light flux ($\beta_1 = 0$) with random noise in the flow rate ($\alpha_2 = 0$). The constant components and the amplitudes of the periodic signals were chosen in such a way that the system remained in the steady state without the random noise. The noise pulse occurred every 10 s, and its duration was set to 5 s.

Equations 2–8 with the values of the parameters listed in Table 2 were solved numerically using the Gear method.⁴⁴ To quantify the SR effect, the time series of the data (60 000 s) were analyzed by examining an interspike distribution at the period of a signal,⁴⁻⁶ which is an alternative of examining the signal-to-noise ratio from the power spectra of the corresponding time series.⁷ An interspike histogram was made as follows:

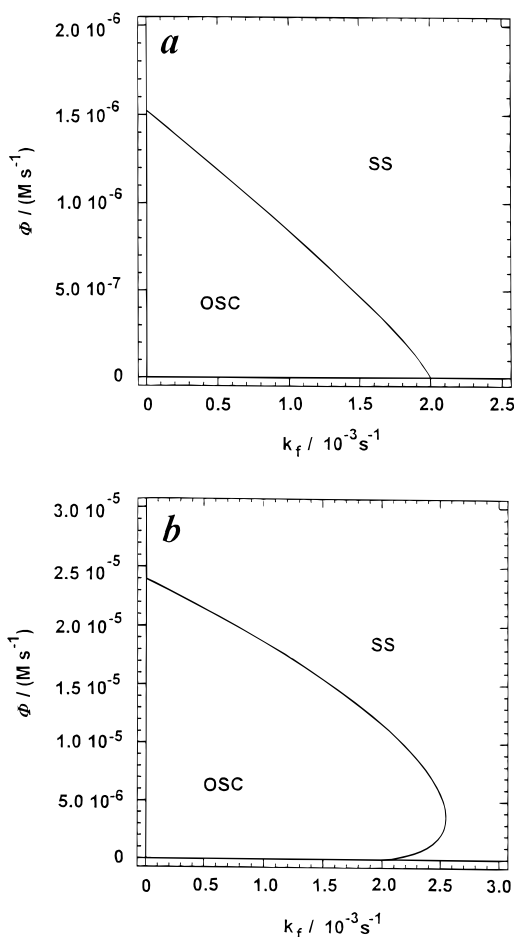


Figure 1. Bifurcation diagram of a modified Oregonator model (eqs 2–8 with $\alpha_1 = \alpha_2 = \beta_1 = \beta_2 = 0$) spanned by the flow rate (k_f) and the light flux (Φ). (a) $V = 0.05$ M, (b) $V = 0.005$ M ($V = \text{BrMA}$). The other parameters used are listed in Table 2. The lines divide the region into the steady state (SS) and the oscillatory state (OSC), where a Hopf bifurcation occurs.

the number of adjacent spikes (NAS), whose time interval was in the range between 270 and 330 s (i.e., $(1 \pm 0.1)T_1$ or $(1 \pm 0.1)T_2$), was plotted as a function of the noise amplitudes. A different random number was used in each calculation, and the NAS obtained from six calculations was averaged at each value of the noise amplitudes. The standard deviations of the NAS were found to be reasonable magnitudes to quantify the SR effect, if the time series of more than 30,000 s were analyzed. We analyzed the time series of 60 000 s in this study, and the analysis shows the NAS divided by this value in the histogram.

III. Results

Linear Stability Analysis. A linear stability analysis for the three-variable system (eqs 2–8 with $\alpha_1 = \alpha_2 = \beta_1 = \beta_2 = 0$) has been carried out according to the procedure described in the literature.⁴⁵ The condition for a Hopf bifurcation, which is characteristic of the Oregonator²⁵ and a modified Oregonator,²⁶ was investigated with the values of parameters listed in Table 2. The bifurcation lines spanned by the flow rate and light flux are shown in Figure 1: (a) for a high concentration (0.05 M) of BrMA and (b) for a low concentration (0.005 M) of BrMA. The shapes of the two boundary lines, which divide the region into excitable steady state (SS) and oscillatory state (OSC), differ greatly from one another in view of the effect of light on this flow system. When light flux is increased under a certain flow rate condition, only photoinhibition^{31–33,38} of oscillations occurs

in Figure 1a, while photoinduction^{36,38} of oscillations also takes place over a limited range of the flow rate where the boundary line has a positive slope in Figure 1b. Numerical integration of eqs 2–8 indicates that the photoinhibition and the photoinduction occur through a subcritical Hopf bifurcation under the investigated conditions; undamped large-amplitude oscillations stopped or started abruptly when the value of the light flux was increased gradually. The period of oscillations increased from 60 s, under the dark and zero-flow rate conditions, to 100 s by increasing the light flux and the flow rate. The bifurcation diagrams were used to determine an excitable focal steady-state close to the Hopf bifurcation for the SR study.

Periodic Signal in Flow Rate and Noise in Light Flux. The response of the system modulated by a periodic signal in the flow rate and noise in the light flux was first investigated. Figure 2 shows the results as a function of the noise amplitude in the case of the high concentration of BrMA. When a sinusoidal signal ($\alpha_2 = 0.05$, $T_2 = 300$ s) was imposed on a constant component in the flow rate without noise in the light flux ($\beta_1 = 0$), the system exhibited no response (Figure 2a). Irregular spikes of oscillations began to appear at the noise amplitude of $\beta_1 = 0.15$ when the bifurcation line was crossed by the noise (Figure 2b). More spikes appeared with increasing the noise amplitude, and the time interval between the adjacent spikes approached the period of the sinusoidal signal in the flow rate at the noise amplitude of $\beta_1 = 0.2$ (Figure 2c). When the noise amplitude was further increased, the system generated more spikes with the period of the autonomous oscillations, which resulted in the decrease in the NAS whose time interval was between 270 and 330 s, $(1 \pm 0.1)T_2$, as shown in Figure 2d ($\beta_1 = 0.3$). Figure 3 summarizes the NAS as a function of the noise amplitude. A maximum of the NAS, which is the fingerprint of SR, was obtained at the noise amplitude of $\beta_1 = 0.2$.

Periodic Signal in Light Flux and Noise in Flow Rate. The above system was second studied by imposing a periodic signal ($\alpha_1 = 0.05$, $T_1 = 300$ s) in the light flux and noise in the flow rate. The NAS as a function of the noise amplitude is also shown in Figure 3. Once again we can see a maximum of the NAS at the noise amplitude of $\beta_2 = 0.4–0.45$. These results show that SR occurs in this system when a periodic signal and noise are applied to different control parameters.

SR in the Case of the Low Concentration of BrMA. An excitable focal steady-state close to the Hopf bifurcation in the case of the low concentration of BrMA was also modulated in a similar manner as mentioned above: (i) a periodic signal in the flow rate with noise in the light flux and (ii) a periodic signal in the light flux with noise in the flow rate. The NAS as a function of the noise amplitude is shown in Figure 4. A maximum of the NAS was obtained in each case, however, the characteristic peak of SR in the case of (i) appeared in a range of the noise amplitude that was 10-fold smaller than the noise amplitude in the flow rate in the case of (ii).

IV. Discussion

The results of SR in this system can be interpreted by the threshold scenario of SR.^{14,15} In general, a threshold is considered to be unperturbed and constant in time, and SR may occur when the sum of a periodic signal and additive noise crosses the threshold as shown in Figure 5a. For instance, a Hopf bifurcation point in a flow rate is used as a constant threshold for SR in chemistry.^{4–6} In the case of SR presented in this study, a periodic signal in one parameter (e.g., the flow rate) changes the threshold of the other parameter (e.g., the light

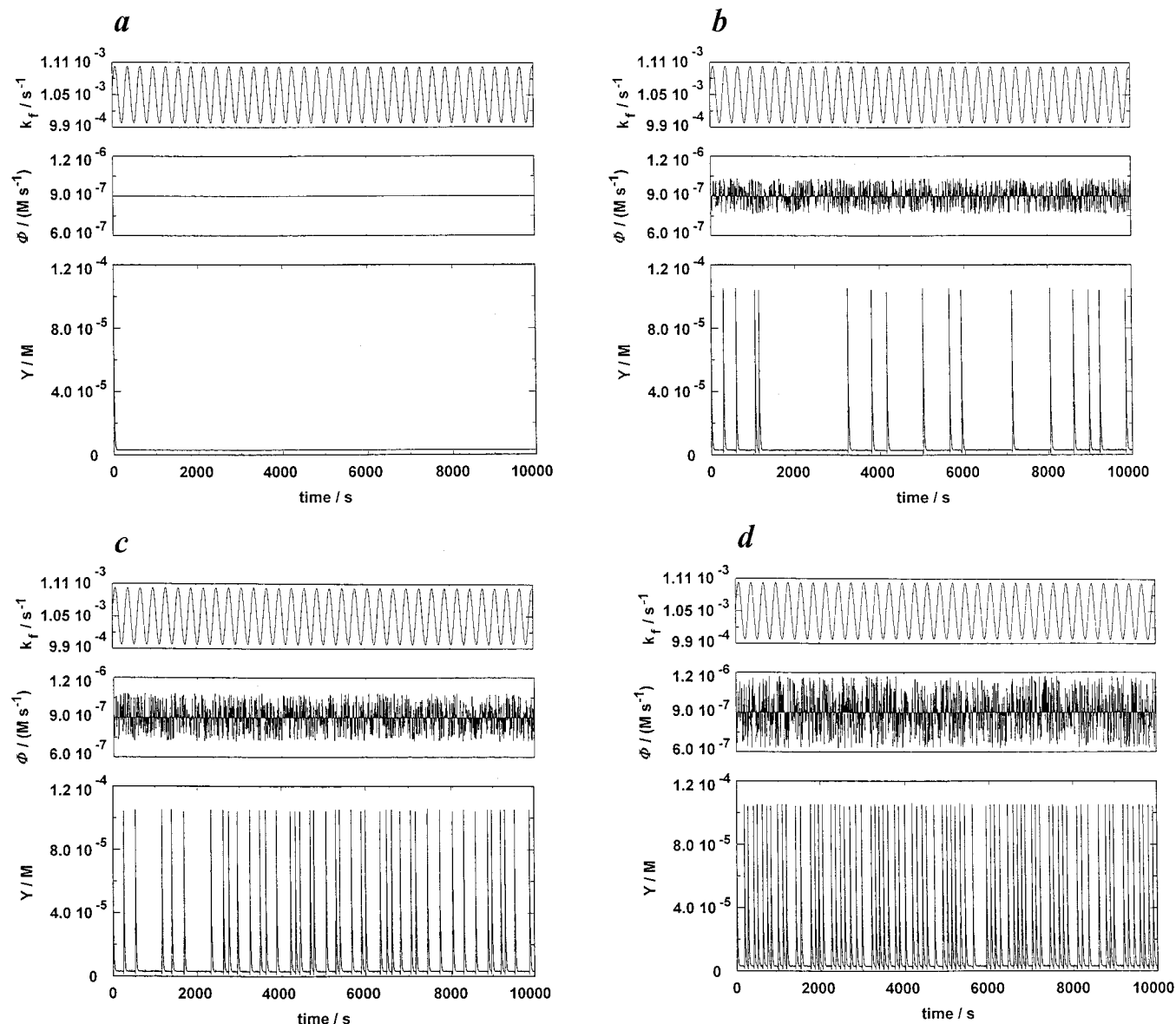


Figure 2. Oscillations in Y (bromide concentration) as a function of the noise amplitude (β_1) in the light flux ($\Phi^0 = 9 \times 10^{-7} \text{ M s}^{-1}$, $\alpha_1 = 0$) under periodic modulations in the flow rate ($k_f^0 = 1.05 \times 10^{-3} \text{ s}^{-1}$, $\alpha_2 = 0.05$, $T_2 = 300 \text{ s}$, $\beta_2 = 0$). (a) $\beta_1 = 0$, (b) $\beta_1 = 0.15$, (c) $\beta_1 = 0.2$, and (d) $\beta_1 = 0.3$. The numerical integration of eqs 2–8 was carried out up to $6 \times 10^4 \text{ s}$, and the result up to $1 \times 10^4 \text{ s}$ is shown. The parameters used are the same as those in Figure 1a ($V = 0.05 \text{ M}$).

flux) as shown in Figure 5b. Addition of noise to the latter parameter (the light flux) can give rise to SR when the noise crosses the periodically modulated threshold. When the fluctuations in the two parameters are exchanged one another (i.e., a periodic signal in the light flux and noise in the flow rate), the system also gives rise to SR by the same scenario.

Two-parameter system has characteristic aspects that can never be observed in one-parameter system. Selective enhancement in a signal in one of the two parameters might take place under simultaneous periodic modulations of the two parameters with noise in one parameter, depending on the periods, amplitudes, and phases of the two modulations. Further, stochastic unresonance may also occur, if there is no relative change in the threshold as a result of an in-phase movement of the two periodic signals.⁴⁶

A different role of the two parameters, the light flux and the flow rate, in the dynamics of the present system accounts for the 10-fold difference in the noise amplitude for the SR peak obtained in the case of the low concentration of BrMA (Figure 4). An excitable focal steady-state close to the Hopf bifurcation

is very sensitive to noise in the light flux that generates activator HBrO_2 . Addition of noise with a small amplitude in the light flux to the focal steady state was found to induce oscillations, even if the amplitude was too small to cross the bifurcation line. The oscillation is of excitable nature, thus a pulse in noise that has an amplitude above a critical value induces one oscillation. The excitability of a focal steady state decreases with increasing the distance between the focal point and the bifurcation line. Thus the periodically modulated threshold induces a periodic change in the excitability of a focal steady state. The system shows no excitable response to the flow rate, and noise in the flow rate cannot induce any oscillations unless it crosses the bifurcation lines. This excitable character of the system may explain the aforementioned 10-fold difference in the range of the noise amplitudes over which SR occurs. The difference in the peak height (Figure 4) is probably related to the excitable nature as well; however, the difference remains unexplained yet. In the case of the high concentration of BrMA, the same excitable nature of the system may explain the difference in the noise amplitude for the SR peak. In this case,

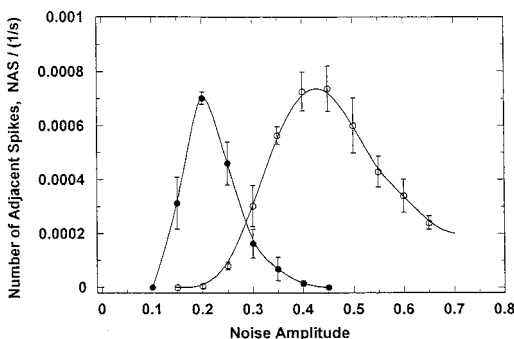


Figure 3. Interspike histogram in the case of the high BrMA concentration ($V = 0.05$ M). The number of adjacent spikes (NAS) in Y , whose time interval was between 270 and 330 s (i.e., $(1 \pm 0.1)T_1$ and $(1 \pm 0.1)T_2$), was plotted as a function of the noise amplitude under the two conditions: (●) a periodic signal in the flow rate ($k_f^0 = 1.05 \times 10^{-3} \text{ s}^{-1}$, $\alpha_2 = 0.05$, $T_2 = 300$ s, $\beta_2 = 0$) with noise in the light flux ($\Phi^0 = 9 \times 10^{-7} \text{ M s}^{-1}$, $\alpha_1 = 0$); (○) a periodic signal in the light flux ($\Phi^0 = 9 \times 10^{-7} \text{ M s}^{-1}$, $\alpha_1 = 0.05$, $T_1 = 300$ s, $\beta_1 = 0$) with noise in the flow rate ($k_f^0 = 1.05 \times 10^{-3} \text{ s}^{-1}$, $\alpha_2 = 0$). The NAS is divided by the integration time, 6×10^4 s. Error bars are the standard deviations of the NAS with a set of six random numbers at each noise amplitude. The solid line is to guide the reader's eye. The parameters used are the same as those in Figure 1a.

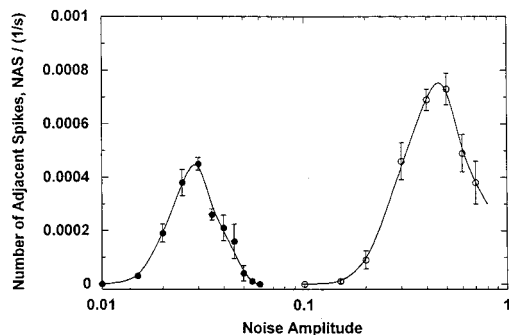


Figure 4. Interspike histogram in the case of the low BrMA concentration ($V = 0.005$ M) under the two conditions: (●) a periodic signal in the flow rate ($k_f^0 = 1.7 \times 10^{-3} \text{ s}^{-1}$, $\alpha_2 = 0.05$, $T_2 = 300$ s, $\beta_2 = 0$) with noise in the light flux ($\Phi^0 = 1.5 \times 10^{-5} \text{ M s}^{-1}$, $\alpha_1 = 0$); (○) a periodic signal in the light flux ($\Phi^0 = 1.5 \times 10^{-5} \text{ M s}^{-1}$, $\alpha_1 = 0.05$, $T_1 = 300$ s, $\beta_1 = 0$) with noise in the flow rate ($k_f^0 = 1.7 \times 10^{-3} \text{ s}^{-1}$, $\alpha_2 = 0$). The NAS is divided by 6×10^4 s. Error bars are the standard deviations of the NAS with a set of six random numbers at each noise amplitude. The solid line is to guide the reader's eye. The parameters used are the same as those in Figure 1b.

less effect of noise in the light intensity was observed, because the value of the light flux at the Hopf bifurcation is about 10-fold smaller than that in the case of the low concentration of BrMA.

From the experimental point of view, a modified Oregonator model used in this study is realistic enough to reproduce the experimentally observed behavior of the photosensitive BZ reaction in a batch system.³⁵ The photochemical production of activator HBrO_2 ^{36–38} through the process (P2) is crucial to the quantitative agreement between the experiments and the model, in addition to the photochemical production of inhibitor Br^- ^{29–34} through the process (P1). The good agreement between the experimental and modeling results³⁵ in the batch system suggests that the model can readily be applied to the flow system as well. In practice, the bifurcation diagram as shown in Figure 1b can explain the experimental behavior such as the photoinhibition^{31,38,47} and the photoinduction^{36,38,47} of oscillations in the flow system.

A photosensitive flow–Oregonator model (eq 3) can be reduced to a simple form by replacing the three photochemical

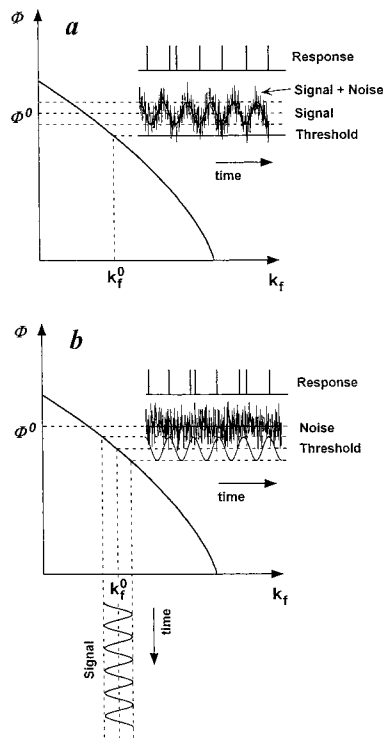


Figure 5. Threshold paradigm of SR. (a) One-parameter system: a threshold is constant in time and the system responds when the sum of a signal and additive noise crosses the threshold. (b) Two-parameter system: a periodic modulation in one parameter changes a threshold of the other parameter, and the system responds when noise in the latter parameter crosses the modulated threshold.

processes with only one process that represents zero-order kinetics for the production of Br^- proposed by Krug, et al.²⁶ The reduction can be made as follows: $p_2 = 0$, p_1 in the $dz/d\tau$ equation is equal to zero, and p_1 in the $dy/d\tau$ equation is equal to 1. This reduced form of a modified Oregonator model in a batch system has been found to be very useful, particularly in studies of the effect of light on spatio-temporal behavior in the BZ system.^{48,49} However, if we use the simple scheme for the photochemical reaction, the resulting flow–Oregonator model is considered to be *quasi two-parameter* system, because both the light flux term (ϕ) and the flow term ($\epsilon'k_f y_0$) control the system in the same way under the conditions where the other flow terms are negligibly small: $\epsilon k_f = 8.6 \times 10^{-4} \ll 1$, $k_f = 2 \times 10^{-3} \ll 1$, and $\epsilon'k_f = 4.6 \times 10^{-6} \ll q = 9.5 \times 10^{-5}$, with $k_f = 2 \times 10^{-3}$. Contrarily, the model presented in this study involves two independent bifurcation parameters that will represent the different physical roles in the real photosensitive BZ reaction in a flow system.

V. Conclusion

Computational study of a model of the photosensitive BZ reaction in a flow system showed that SR occurs in the situation where a periodic signal and noise are added to the different physical inputs (a flow rate and light flux). The two bifurcation parameters control the investigated system differently, which resulted in the difference in the noise amplitudes for the SR peak. The model is based on the experimental behavior of the photosensitive BZ reaction and is readily applied to the SR experiments. *Two-parameter SR* or, in general, *multiparameter SR* may widely be seen in biological^{7–9} and natural^{10–12} systems, which are always suffered from many kinds of periodic and noisy fluctuations.

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- (42) The concentration of Ru(bpy)₃^{2+*}, *E*, is obtained by assuming the steady-state approximation ($dE/dt \approx 0$). The effect of the flow term on decrease in *E* is negligible if at least one of the rate constants k_{-p_0} , k_{p_1} , or k_{p_2} for the quenching reactions of *E* are much larger than the flow rate ($k_f \approx 10^{-3}$). The values of these constants are unknown in this system; however, it is quite reasonable to assume k_{-p_0} , k_{p_1} , $k_{p_2} \gg k_f$ on the basis of rate constants for quenching reactions of *E* in other reactions.⁴⁰ We set $k_f/k_{p_1} = 0$, and $k_{-p_0}/k_{p_1} = 0.089$ M and $k_{p_2}/k_{p_1} = 2.05$ according to the literature.³⁵ The steady-state approximation for *E* also holds under the periodic and the stochastic modulations of the light flux and the flow rate, if at least one of the values of k_{-p_0} , k_{p_1} , or k_{p_2} is as large as the value of a rate constant for a well-known quenching reaction of *E*.⁴⁰
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