# Stirring-Induced Oscillations in an Excitable Chemical System with Inhomogeneous Reaction Dynamics

**Jichang Wang***

*Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario ON N9B 3P4, Canada*

*Received: February 28, 2003; In Final Form: June 26, 2003*

This study illustrates a new role played by stirring in a reaction system subjected to a constant inhomogeneous external forcing. The studied model system is an excitable photosensitive Belousov−Zhabotinsky (BZ) reaction, where the inhomogeneous forcing is implemented via a spatially inhomogeneous global illumination or a homogeneous local light illumination. Because illumination reduces the excitability of the BZ system via producing an additional amount of bromide, the above stirred system is expected to stay at a stationary state regardless of the mixing rate. In contrast, our numerical calculations show that under moderate stirring rates global oscillations of simple and complex modes are obtained in this otherwise nonoscillatory chemical system. The onset of oscillatory behavior is due to stirring-induced fluctuations in the bromide concentration, which is known to be capable of inducing excitations at the vicinity of a Hopf-bifurcation point. Counterintuitively, our calculations further illustrate that having a large inhomogeneity in the external forcing does not necessarily favor the occurrence of stirring-induced oscillatory behavior.

## I. Introduction

In the last two decades, stirring effects have been observed in a variety of oscillating chemical systems including the chlorite and iodide reaction and the 1,4-cyclohexanedione-bromate-acid oscillatory system.[1−29] As a prototypical model in the study of nonlinear chemical kinetics, the Belousov−Zhabotinsky (BZ) reaction has been extensively investigated to understand the effects of stirring on chemical oscillations.[9−18] For example, Menzinger and his group studied stirring effects on the bistability of the BZ reaction in a continuous flow stirred tank reactor (CSTR) and reported that inhomogeneous perturbations generated by imperfect mixing of reactants were responsible for stirring and mixing effects.[11] Experiments performed by Farage and co-workers illustrated that stirring sensitivity resulted in modifications of their oscillation periods and amplitudes, and the period was particularly sensitive to the stirring rate.[15] In addition, results from cerium- and ferroin-catalyzed BZ reactions suggest that stirring sensitivity is to be reaction dependent.[17]

Computational investigations on stirring effects have also been pursued independently by several groups.[17,24−27] Noszticzius and co-workers showed that different stirring effects in the BZ reaction can be modeled semiquantitatively by a diffusion-controlled radical−radical reaction step of a radicalator.[17] Investigations with cellular mixing models and probabilistic cellular automaton models have been carried out, respectively, by Ali and Menziner and by Vanag in an effort to understand the role of inhomogeneity in observed stirring effects.[25−27] Their studies show that stirring effects in a CSTR could arise from an incomplete mixing of the reagent feed streams and be interpreted in the framework of different micromixing theories.[30,31] Although existing computational studies have thoroughly characterized local fluctuations of chemical concentrations as the potential source of stirring effects, impacts of stirring in the presence of a constant inhomogeneous external forcing have not been examined.

In complementing existing computational studies, this report investigates the role of stirring in a photosensitive BZ system subjected to an inhomogeneous light illumination. It is motivated by the fact that illumination from a halogen light bulb and other light sources is often inhomogeneous in the absence of any carefully designed control. Yet, there is no concrete result on the importance of having a homogeneous light forcing in the study of stirred photosensitive BZ reaction system. In addition, the inhomogeneity can also be caused by such as that light illumination is only applied to part of the stirred reactor. As shown in the following, our results illustrate that in the presence of an inhomogeneous light illumination stirring can behave as a bifurcation control parameter to induce oscillatory phenomena in an otherwise non self-oscillatory system. These observed stirring-induced oscillations also exhibit subtle dependence on the degree of inhomogeneity of the external forcing. In general, the inhomogeneous external forcing may also come from other sources as well. For example, a reaction system in a large three-dimensional reactor may experience different local temperatures, which consequently impose inhomogeneous effects on the local reaction rate constants.

## II. Model

The photosensitive BZ reaction, which is the oxidation and bromination of malonic acid by acidic bromate in the presence of metal catalyst, $Ru(bpy)_3^{2+}$,[32] is employed here as our model system because its photosensitivity provides us an easy approach to implement external forcing. The understanding of the BZ reaction has been developed primarily in terms of the Field−Körös−Noyes (FKN) mechanism.[33] Based on the FKN scheme,

---

* To whom correspondence should be addressed. E-mail: jwang@uwindsor.ca. Fax: + 1 519 973 7098.

10.1021/jp034522n CCC: $25.00

Field and Noyes derived the following three-variable Oregonator model:[34]

$$A + Y \rightarrow X + P \tag{1}$$

$$X + Y \rightarrow 2P \tag{2}$$

$$A + X \rightarrow 2X + 2Z \tag{3}$$

$$2X \rightarrow A + P \tag{4}$$

$$B + Z \rightarrow fY \tag{5}$$

$$\rightarrow Y \tag{6}$$

The concentration variables are $A = \mathrm{BrO_3}^-$, $X = \mathrm{HBrO_2}$, $Y = \mathrm{Br}^-$, $Z = \mathrm{Ru(bpy)_3}^{3+}$, $B =$ organic substrates, and $P$ represents inert products. $f$ is a stoichiometric coefficient and is adjusted in this study to manipulate the reaction dynamics. To account for the photosensitivity, an additional schematic reaction producing $\mathrm{Br}^-$ is included here as reaction step (6), where its rate constant $k_6$ is proportional to the applied illumination intensity and is varied to reflect the strength of the external forcing.[35-38] Here we use rate constants suggested by Field and Försterling:[34] $k_1 = 1.3\ \mathrm{M^{-1}\ s^{-1}}$, $k_2 = 2 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$, $k_3 = 34\ \mathrm{M^{-1}\ s^{-1}}$, $k_4 = 3 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$, and $k_5 = 0.02\ \mathrm{M^{-1}\ s^{-1}}$. Using Tyson-Fife scaling,[40] the reaction rate equations of the above Oregonator model have the following dimensionless form:[41]

$$\frac{du}{d\tau} = \left(\frac{1}{\epsilon}\right)(qw - uw + u - u^2)$$

$$\frac{dv}{d\tau} = u - v$$

$$\frac{dw}{d\tau} = \left(\frac{1}{\epsilon'}\right)(\phi - qw - uw + fv)$$

in which reactants $A$ and $B$ are treated as constants, implying that the studied BZ reaction is an open system. Variables $u$, $v$, and $w$ are dimensionless concentrations of $\mathrm{HBrO_2}$, $\mathrm{Ru(bpy)_3}^{3+}$, and $\mathrm{Br}^-$, respectively. $\varphi$ represents the rate of bromide production from irradiation.[41] Using the above Field-Försterling rate constants, we derived $\epsilon = 0.06$, $\epsilon' = 1.8 \times 10^{-4}$, and $q = 1.14 \times 10^{-4}$. $f$ equals 2.3 through out this study. Under the above conditions, the unperturbed BZ system is nonoscillatory.

To simulate the effect of stirring, we use the approach which has been employed earlier by Ruoff to simulate excitations induced by fluctuations in closed anaerobic classical BZ systems:[14] The stirred BZ reaction solution is partitioned into a large number of short-lived fluid packages as shown in Figure 1, where $i$ is the cell index and $N$ is the total number of cells. Fluid cells are allowed to evolve freely according to their local reaction dynamics for a certain lifetime $\tau$. Mixing occurs only at the end of their lifetime $\tau$, in which the average concentration values over all cells are calculated and are then assigned to the corresponding chemical species in each individual cell. Therefore, the effect of stirring rates can be characterized by simply varying the value of $\tau$. Because our emphasis is on the effect of stirring in the presence of an inhomogeneous external forcing, statistical fluctuations in chemical concentrations are not incorporated into our current study, though these processes are inevitable in stirred reacting chemical media.[24-31]

Two types of inhomogeneous external forces are characterized here. The first one is that a homogeneous light is applied only to part of the stirred reactor. This protocol can be achieved easily in practical experiments. The second is that illumination is applied to the whole reactor; however, the light source itself has spatially inhomogeneous intensity. Indeed, without any controlled compensation, the intensity of a light beam emitted by a halogen lamp or other light sources is often inhomogeneous in space with a higher intensity at the center of the beam. To account for such type of inhomogeneity, we use $\Delta I$ to denote the difference between the highest and the lowest intensity of the light beam. Although the light intensity may vary smoothly in practice, $\Delta I$ is discretized when implementing the cellular model in the following calculations. The light intensity in each cell is calculated according to $\varphi_{i+1} = \varphi_i + \Delta I/N$, where $i$ is the cell index and $N$ is the total number of cells. We introduce $\xi = \Delta I/N$ to represent the inhomogeneity of the illumination.

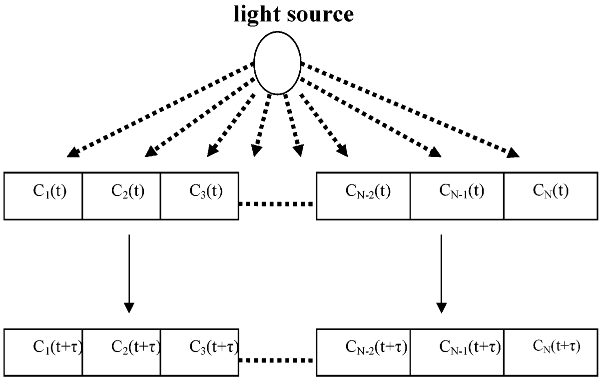

**Figure 1.** Schematic of the mixing cell model, which describes an open photosensitive Belousov−Zhabotinsky system exposed to inhomogeneous light illumination. $C_i(t)$ represents the concentrations of reactants in the cell "$i$". The light intensity is assumed to increase from cell "**1**" to cell "**N**". During the cell lifetime $\tau$ chemicals in each cell evolve freely accordingly to its local BZ reaction dynamics. An average concentration value over all cells is calculated at the end of the cell lifetime and is assigned to each individual cell.

## III. Results and Discussion

We first consider the case where the BZ system is partitioned into a small number of cells. Such a configuration requires less computational power, yet is capable of producing illustrative results. Figure 2 characterizes the influence of stirring in the presence of an inhomogeneous global light forcing. The light intensity applied to each individual cell is calculated according to $\varphi_{i+1} = \varphi_i + \xi$, where $\varphi_1 = 0$ and $\xi = 5 \times 10^{-4}$. Values of other parameters are given in the above section. Note that the unperturbed BZ system is nonoscillatory, staying at a stationary reduction state. The three time series are calculated under different cell lifetime $\tau$: (a) 1.00, (b) 3.70, and (c) 4.42 (dimensionless time units). A short cell lifetime corresponds to a fast stirring process, and vice verse. Because light illumination induces the additional production of bromide, which is an inhibitor in the BZ reaction, the illuminated BZ system is expected to remain at the reduced stable stationary states. A stationary state is indeed obtained in Figure 2a, even though the inhomogeneous light forcing drives the system to different local stationary states. It is because differences in local stable steady states resulted from the different light forcing are quickly averaged out by the fast mixing process. In this light, the BZ system shall exhibit small amplitude fluctuations under a slow mixing. Calculations at low stirring rates ($\tau > 10$) do show that the BZ system fluctuates with a small amplitude ($\Delta v < 0.0002$).

Large amplitude oscillations are obtained (see Figure 2b), however, when the stirring rate is decreased from Figure 2a. The onset of these peculiar behaviors in the absence of self-oscillating dynamics could be due to the following effects:

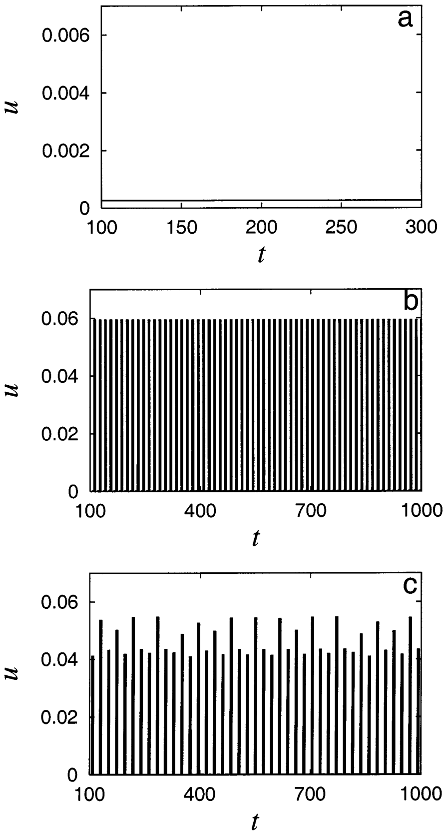

**Figure 2.** Time series of the BZ reaction obtained at different cell lifetimes $\tau$: (a) 1.0, (b) 3.7, and (c) 4.42 (dimensionless time units). Values plotted in this figure are the average concentration of variable $v$ over all individual cells. A longer cell lifetime $\tau$ corresponds to a slower mixing process. Both periodic and irregular oscillations are obtained when the stirring rate is decreased. $\xi = 5 \times 10^{-4}$ and values of other parameters are given in the context.

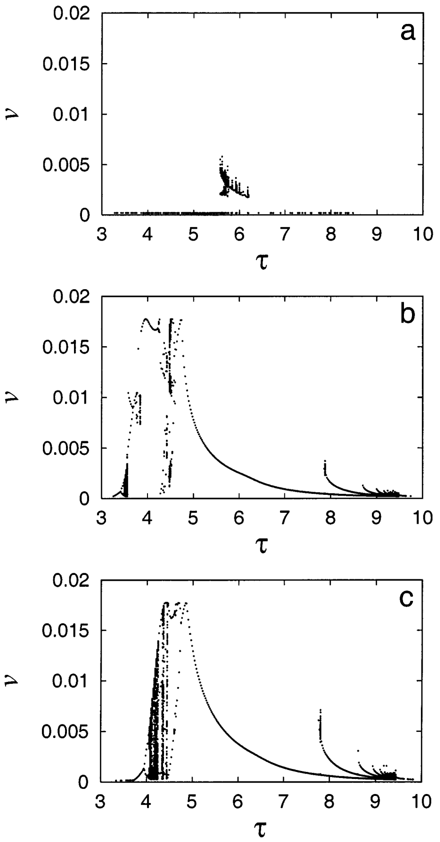

**Figure 3.** Bifurcation diagrams of the BZ reaction with respect to the variation of cell lifetime $\tau$. Points shown here are the maxima of the average concentration of $v$ per oscillation cycle shown in Figure 2. These results are achieved under three different degrees of inhomogeneity in the reaction dynamics: (a) $\xi = 1 \times 10^{-4}$, (b) $\xi = 5 \times 10^{-4}$, and (c) $\xi = 1 \times 10^{-3}$.

Inhomogeneous light forcing leads to different stationary states in each cell, and an average value which is different from their stationary states is obtained when these cells are mixed. Therefore, perturbations are introduced upon the mixing. Under low stirring rates the perturbation occurred in each cell has longer time to evolve freely according to the local reaction kinetics. Although all these perturbed cells are expected to eventually decay back to their stationary states, the relaxation process may nevertheless be quite different. It has been reported recently that a pulse-light perturbation at the vicinity of a Hopf-bifurcation point can induce a large amplitude excitation in excitable BZ media.[42] Such a mechanism also plays an essential role here in inducing excitations in those cells which receive an above threshold perturbation upon mixing. If there are a large number of cells recovering through large amplitude excursions, the system will then exhibit large amplitude bulk oscillations as shown in Figure 2b. Because each cell has different relaxation times because of the different light intensities, the average concentration value over all cells may exhibit an irregular oscillatory pattern. An example of complex oscillations is shown in Figure 2c. The above result thus presents a new role played by stirring in nonlinear chemical reactions.

Oscillations revived by decreasing the stirring rate have been reported earlier in the methylmalonic acid and oxalic malonic acid BZ reactions.[43,44] These results have been understood based on the fluctuations of $Br^-$ concentration in the reactor: The decrease of stirring rate corresponds to an increase of random fluctuations in the BZ reaction, which consequently increase the total number of short-lived local domains having concentrations of $Br^-$ above or below the average $Br^-$ concentration. As discussed by Ruoff,[14] when $Br^-$ concentration in a cell is below the critical $Br^-$ concentration, an excitation will occur, which forms a nucleus in the BZ system. Results shown in Figure 2 can be explained in a similar way, except here fluctuations result from the inhomogeneous external forcing. Another essential difference is that here excitation cells are actually created by the increase of bromide concentration.[42] Whether this excitation mechanism has also played an important role in the methylmalonic acid and oxalic malonic acid BZ reactions will be investigated in our future work.

Figure 3 presents three bifurcation diagrams calculated as a function of the mixing rate, where the value of $\xi$ is increased from Figure 3a–c. Points plotted here are the maximum values of the average concentrations of $Ru(bpy)_3^{3+}$ per oscillatory cycle. All three bifurcation diagrams show the developments of oscillatory phenomena as well as transitions between simple and complex oscillations. No oscillatory behavior could be obtained when the cell lifetime $\tau$ is too short ($<3$). When $\xi$ is increased from $1 \times 10^{-4}$ to $5 \times 10^{-4}$, the threshold stirring rate, beyond which large amplitude oscillations arise, shifts to a smaller $\tau$ value. Meanwhile, the oscillation amplitude also increases. This is consistent with earlier reports which show that large concentration fluctuations require faster mixing to be homogenized.[8,14] Here, the inhomogeneous light illumination posts constant fluctuations. It is interesting to note that if the mixing rate is too slow, large amplitude oscillations vanish again. We believe that it is because at low stirring rates excitations ignited by these intrinsic perturbations decay to low

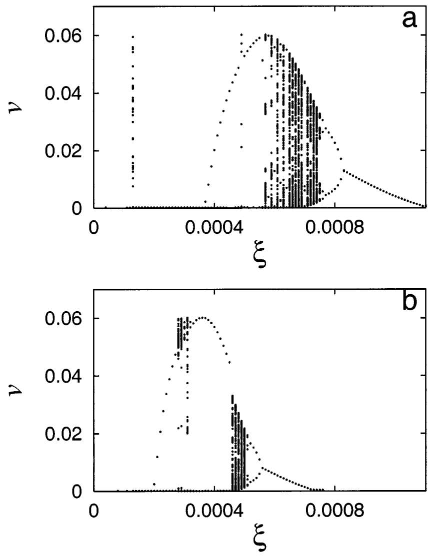

**Figure 4.** Bifurcation diagrams of the BZ system with respect to $\xi$, where the stirring rate is kept constant at (a) $\tau = 3.8$ and (b) $\tau = 3.5$. Points shown here are the maxima of the average concentration of $v$ per oscillation cycle. Notably, no large amplitude oscillation can be obtained if the inhomogeneity in the reaction dynamics is too big.

amplitudes before they can excite other cells via the following mixing. Consequently, large amplitude bulk oscillations become less favorable. Further increase of $\xi$ does not have any significant influence on the maximum amplitude of these oscillations (see Figure 3c); however, the threshold stirring rate is decreased. This is in contrast to our experience that a system with large inhomogeneities requires faster mixing to become homogeneous. Such a counter-intuitive change could result from that when $\xi$ changes the average dynamics of the system also changes. To shed light on this question, calculations at a fixed stirring rate but different $\xi$ values are carried out in the following.

Figure 4 presents two bifurcation diagrams calculated as a function of $\xi$, while the stirring rate is kept constant. Points shown in Figure 4 are the maximum values of the average concentrations of $\mathrm{Ru(bpy)_3^{3+}}$ per oscillatory cycle. As shown in this figure, there is no large amplitude bulk oscillation when $\xi$ is smaller than $2 \times 10^{-4}$, implying that a sufficient inhomogeneity in the external forcing is necessary for the observed stirring-induced oscilllations. On the other hand, reversal bifurcations occur when $\xi$ is above $5 \times 10^{-4}$, which lead the system back to a stationary state. The reverse bifurcation at a large inhomogeneity could be understood based on the effect of $\xi$ on the excitation threshold of the studied system: An increase of $\xi$ means that increasing numbers of cells are being exposed to light perturbations of high intensities. As a result, more fluid cells become less capable of being excited by fluctuations of the same magnitude. Collectively, when the total number of excited cells is below a certain level, no bulk oscillation can be obtained.

As discussed earlier, the inhomogeneity of a beam light may in practice be a smooth variation in space. To make our simulation close to real experiments, the studied BZ system is divided into a large number of cells. Figure 5 presents a bifurcation diagram calculated at the condition where the system is divided into 100 cells. Other parameters including $\Delta I$ are the same as that in Figure 3b. Because the total number of cells is 10 times larger than that in Figure 3b, $\xi$ becomes 10 times smaller. Points plotted in this figure are the maximum values of the average concentration of $u$ per oscillation cycle. The overall structure of this bifurcation diagram becomes simpler comparing with that shown in Figure 3b. However, the onset of oscillatory phenomena as well as transitions between simple and complex oscillations can still be seen.

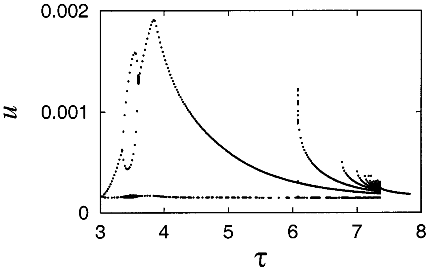

**Figure 5.** Bifurcation diagram of the BZ reaction as a function of cell lifetime $\tau$. Here the system is divided into 100 fluid cells. Other parameter values are the same as used in Figure 3b. Points shown here are the maxima of the concentration of $u$ per oscillatory cycle. Similar to results shown in Figure 3, transitions from a stationary state to large amplitude oscillations can be seen, although the inhomogeneity $\xi$ is 10 times smaller here.

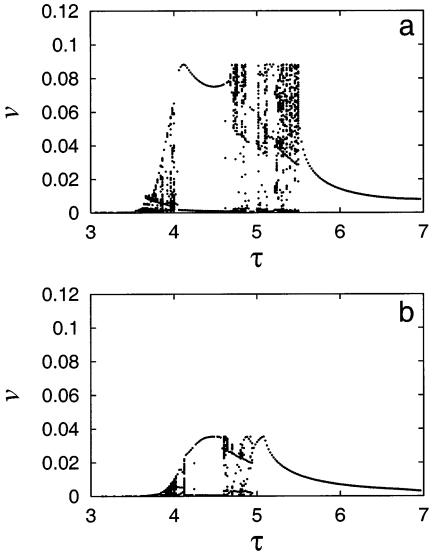

**Figure 6.** Bifurcation diagrams of the BZ reaction with respect to the variation of cell lifetime $\tau$. Illumination is applied only to part of the reactor: (a) 50% and (b) 80%. Points shown here are the maxima of the average concentration of $v$ per oscillation cycle. Light intensity $\varphi$ equals 0 and 0.005 in the illuminated and the unilluminated regions, respectively. Other parameters are the same as used in the above calculations: $\epsilon = 0.06$, $\epsilon' = 1.8 \times 10^{-4}$, $q = 1.14 \times 10^{-4}$, and $f = 2.3$.

Another probable scenario in real experiments is that illumination is only applied to part of a reactor, which occurs due to various reasons such as limited by the size and the shape of a light source. Figure 6 presents two bifurcation diagrams, in which (a) 50% and (b) 80% of the reactor are illuminated by light. Light intensity $\varphi$ equals 0.005 and 0, respectively, at those illuminated and unilluminated cells. Other parameters are the same as that provided in the model section. The system is divided into 100 cells in this calculation; when the total number of cells is increased or decreased by a factor of 10, the above bifurcation diagrams do not change. Oscillatory phenomena as well as transitions between simple and complex oscillations are achieved in both a and b. Similar to the situations under inhomogeneous global light illumination, only simple dynamical behavior can be achieved at low and high stirring rates. This result therefore further illustrates the significance of having homogeneous global forcing in the study of temporal reaction dynamics.

## IV. Conclusion

Complementing earlier investigations of stirring effects in nonlinear chemical systems, this study investigated the role of mixing in systems having an inhomogeneous external forcing. Our results illustrate that the stirring rate can become a bifurcation control parameter to induce a variety of oscillatory phenomena in an excitable system. As shown in Figure 3, the stirring-induced oscillatory behavior depends on the degree of inhomogeneity of the external forcing. However, a large inhomogeneity in the external forcing does not always favor the occurrence of stirring-induced oscillations. This is because a large $\xi$ in this study means that the average reaction dynamics of the studied system becomes less excitable. As a result, fewer nucleus sites can be developed, and consequently, bulk oscillations become less favorable.

Stirring effects in reacting chemical systems have been characterized in earlier studies on the basis of concentration fluctuations. These fluctuations include the imperfect mixing of fresh chemicals with the bulk solution in a CSTR, local variations in the transport rates, and stirring-dependent loss of chemicals in a batch reactor. In this study, we considered concentration fluctuations imposed by an inhomogeneous external forcing while ignoring fluctuations which have been characterized earlier. Our results illustrate that having a spatially homogeneous forcing in a stirred system is as important as that in reaction−diffusion media.[45] Otherwise, the coupling between mixing and inhomogeneous forcing may induce a variety of oscillatory phenomena even in the absence of self-oscillatory dynamics. Gaspar and co-workers have expressed their concerns on the importance of having a homogeneous light forcing in the study of photosensitive BZ oscillations. They described in their experiments that the length of the filament of the halogen lamp was similar to the height of the reaction vessel in order to get equal amount of illumination in every part of the system.[46]

Parameters used in this study are directly derived from a set of rate constants which have been successful in qualitatively simulating BZ oscillations. We therefore believe that the above observed phenomena can also be achieved in real photosensitive BZ experiments. In particular, the protocol of illuminating part of a reactor can be easily implemented. However, our calculations show that it is important to have the dynamics of the excitable BZ system stay at the vicinity of a Hopf-bifurcation point, where the excitation threshold is small. In addition, our cellular model can also be understood as a system consisting of a large number of excitable reactors which are mixed periodically at a time interval $\tau$. Therefore, our results further suggest that a system consisting of different excitable elements may exhibit spontaneous simple and complex global oscillations. Such a scenario has been recently reported in the excitable pancreatic $\beta$ cells, in which studies show that every single $\beta$ cell is excitable; however, global oscillations are obtained when these cells are coupled together.[47]

**Acknowledgment.** This research is supported by Natural Sciences and Engineering Research Council of Canada and by a startup grant from the University of Windsor.

## References and Notes

(1) Roux, J. C.; DeKepper, P.; Boissonate, J. *Phys. Lett. A* **1983**, *97*, 168.

(2) Farage, V. J.; Janjic, D. *Chem. Phys. Lett.* **1982**, *93*, 621.

(3) Menzinger, K.; Boukalouch, M.; DeKepper, P.; Boissonade, J.; Rous, J. C.; Saadaoui, H. *J. Phys. Chem.* **1986**, *90*, 313.

(4) Menzinger, M.; Giraudi, A. *J. Phys. Chem.* **1987**, *91*, 4391.

(5) Luo, Y.; Epstein, I. R. *J. Chem. Phys.* **1986**, *85*, 5733.

(6) Nagypal, I.; Epstein, I. R. *J. Phys. Chem.* **1986**, *90*, 1217.

(7) Sevcik, P.; Adamcikova, L. *Chem. Phys. Lett.* **1988**, *146*, 419.

(8) Ali, F.; Menzinger, M. *J. Phys. Chem.* **1991**, *95*, 6408.

(9) Menzinger, M.; Jankowski, P. *J. Phys. Chem.* **1986**, *90*, 6865.

(10) Dutt, A. K.; Menzinger, M. *J. Phys. Chem.* **1990**, *94*, 4867.

(11) Strizhak, P.; Menzinger, M. *J. Phys. Chem.* **1996**, *100*, 19182.

(12) Vanag, V. K.; Melikhov, D. P. *J. Phys. Chem.* **1995**, *99*, 17372.

(13) Pojman, J. A.; Dedeaux, H.; Fortenbery, D. *J. Phys. Chem.* **1992**, *96*, 7331.

(14) Ruoff, P. *J. Phys. Chem.* **1993**, *97*, 6405.

(15) Farage, V. J.; Janjic, D. *Chimia* **1980**, *34*, 342.

(16) Lopez-Tomas, L.; Sagues, F. *J. Phys. Chem.* **1991**, *95*, 701.

(17) Noszticzius, Z.; Bodnar, Z.; Garamszegi, L.; Wittmann, M. *J. Phys. Chem.* **1991**, *9*, 6575.

(18) Ruoff, P. *Chem. Phys. Lett.* **1982**, *90*, 76.

(19) Zhang, Y.-X.; Foerster, P.; Ross, J. *J. Phys. Chem.* **1992**, *96*, 8898.

(20) Epstein, I. R. *Nature* **1995**, *374*, 321.

(21) Resch, P.; Munster, A. F.; Schneider, F. W. *J. Phys. Chem.* **1991**, *95*, 6270.

(22) Dutt, A. K.; Muller, S. C. *J. Phys. Chem.* **1993**, *97*, 10059.

(23) Ali, F.; Menzinger, M. *J. Phys. Chem.* **1992**, *96*, 1511.

(24) Hlavacova, J.; Sevcik, P. *Comput. Chem.* **1994**, *18*, 21.

(25) Ali, F.; Menzinger, M. *J. Phys. Chem. A* **1997**, *101*, 2304.

(26) Vanag, V. K. *J. Phys. Chem.* A **1997**, *101*, 8964.

(27) Menzinger, M.; Ali, F. *J. Phys. Chem. A* **1997**, *101*, 8966.

(28) Villermaux, J. *Rev. Chem. Eng.* **1991**, *7*, 51.

(29) Bourne, J. R.; Rys, P.; Suter, K. *Chem. Eng. Sci.* **1977**, *32*, 711.

(30) Puhl, A.; Nicolis, G. *J. Chem. Phys.* **1987**, *87*, 1070.

(31) Nicolis, G.; Frisch, H. *Phys. Rev. A* **1985**, *31*, 439.

(32) Zhabotinsky, A. M. Introduction: The Early Period of Systematic Studies of Oscillations and Waves in Chemical Systems. In *Oscillations and Travelling Waves in Chemical Systems*; Field, R. J., Burger, M., Eds.; Wiley: New York, 1985.

(33) Field, R. J.; Koros, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649.

(34) Field, R. J.; Noyes, R. M. *J. Chem. Phys.* **1973**, *60*, 1877.

(35) Field, R. J.; Forsterling, H.-D. *J. Phys. Chem.* **1986**, *90*, 5400.

(36) Kádár, S.; Amemiya, T.; Showalter, K. *J. Phys. Chem. A* **1997**, *101*, 8200.

(37) 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.

(38) Srivastava, P. K.; Mori, Y.; Hanazaki, I. *Chem. Phys. Lett.* **1992**, *190*, 279.

(39) Peddy, M. K. R.; Szlavik, Z.; Nagyungvarai, Z.; Müller, S. C. *J. Phys. Chem.* **1995**, *99*, 15081.

(40) Tyson, J. J.; Fife, P. C. *J. Chem. Phys.* **1980**, *73*, 2224.

(41) Krug, H.-J.; Pohlmann, L.; Kuhnert, L. *J. Phys. Chem.* **1990**, *94*, 4862.

(42) Wang, J. *Chem. Phys. Lett.* **2001**, *335*, 123.

(43) Ruoff, P.; Schwitters, B. *Z. Phys. Chem.* **1983**, *135*, 171.

(44) Sevcik, P.; Adamcikova, I. *J. Chem. Phys.* **1989**, *91*, 1012.

(45) Showalter, K.; Kapral, R. Eds. *Chemical Waves and Patterns*; Kluwer Academic: Dordrecht, 1993.

(46) Gáspár, V.; Bazsa, G.; Beck, M. T. *Z. Phys. Chemie (Leipzig)* **1983**, *264*, 43.

(47) Cartwright, J. H. E. *Phys. Rev. E* **2000**, *62*, 1149.