Effects of Noise and Coupling on the Spatiotemporal Dynamics in a Linear Array of Coupled Chemical Reactors

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The noisy dynamics of a nonlinear chemical reaction in a linear array of three identical continuous-flow stirred tank reactors (CSTRs) coupled via diffusion-like mass transfer is investigated numerically. All three subsystems are initially run in stable stationary states near a Hopf bifurcation point. Noise, coupling, and nonlinearity of the chemical reaction cooperate to organize spatiotemporal order of the coupled system when the first subsystem is subjected to external parametric noise. The signal-to-noise ratio of the response of each subsystem to the external noise goes through a maximum, indicating the occurrence of resonance. Synchronization phenomena are also observed when the coupling strength reaches a critical value. The applications of coupling strength in controlling resonance effect in the coupled system are discussed.

I. Introduction

Motivation for the investigation of the dynamics of coupled chemical system stems from its importance to the understanding of spatiotemporal phenomena observed in complex chemical and biological systems.[1−3] Many complex systems in nature can be modeled by chemical or biochemical reaction systems which are carried out in continuous-flow stirred tank reactors (CSTRs) coupled by means of mass exchange. The coupling can be implemented by passive diffusion-like mass transfer,[4−18] active pumping,[19−24] or electric coupling.[25−30] In the past decades, dynamics of coupled chemical and biological systems has been investigated extensively. There are many papers dealing with coupled system of which we only cite a few. For details of experimental and theoretical works on coupled chemical and biochemical systems, cf. refs 1−30 and references therein. However, most scientists investigated the deterministic dynamics of coupled system without taking into account the effects of random perturbation. Although Marek's group[16,17] has studied the effects of noisy coupling that had a distribution on mass-coupled Belousov−Zhabotinsky (BZ) reactions, very limited attention is paid to the effects of external fluctuations on coupled CSTRs.

It is well-known that the interaction between nonlinear dynamics and noise can lead to nontrivial phenomena such as noise-induced phase transitions[31] and stochastic resonance[32−34] (SR). SR is a phenomenon wherein the response of a nonlinear system to a weak periodic signal can be optimized by the assistance of a particular nonzero level of noise. Since it was originally proposed by Benzi and co-workers[32] to account for the periodic recurrence of Earth's ice ages, many scientists whose majors vary from biology to physics to chemistry have paid considerable attention to this counterintuitive phenomenon in which noise plays a constructive role rather than a negative one.[33,34] Recently it was shown that nonlinear systems in the presence of noise could also display SR-like behavior even without an external signal.[35−40] This kind of phenomenon can be called autonomous SR,[35,36] coherence resonance[37−40] or internal SR. Experimental evidences of this kind of phenomenon in an electronic monovibrator circuit[39] and an optical system[40] have been reported recently. SR and autonomous SR in coupled physical and biological systems have also attracted many scientists' attention.[41−52] Array enhanced stochastic resonance[43−45] (AESR) was first proposed by Lindner et al.[43] in linearly coupled bistable units. They showed how noise, coupling, and bistable potential cooperated to enhance the response of a single "stochastic resonator" and to organize spatiotemporal order of the coupled system. The first experimental evidence of AESR was reported by Löcher et al.[45] in a system of coupled diode resonators. On the basis of the idea of AESR, noise enhanced propagation[46−49] in a linearly coupled system was investigated experimentally and theoretically when an external periodic signal was only injected into the first unit. Recently, noise-induced coherence in neural networks,[50] coherence resonance in globally coupled Hodgkin−Huxley (HH) neurons,[51] and array-enhanced coherence resonance in coupled nonidentical FitzHugh−Nagumo (FHN) systems[52] also indicated the positive role of noise in coupled nonlinear systems. These phenomena can also be called a kind of spatiotemporal SR.[53,54] However, these phenomena were observed when each elementary unit was subjected to random noise, and most of the elementary unit is of bistable characteristics.

In the present work, we study the spatiotemporal dynamics of a nonlinear chemical reaction in a linear array of three identical CSTRs coupled via diffusion-like mass transfer when the first subsystem is subjected to external parametric noise. All three subsystems are initially run in stable stationary states near a Hopf bifurcation point. We show that noise, coupling, and nonlinearity of the chemical reaction can cooperate to organize spatiotemporal order of the coupled system and to induce synchronization phenomena under appropriate conditions. The applications of coupling strength in controlling resonance

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effect in this coupled system are also discussed. Our numerical investigation may provide some instructions for future experimental work.

II. Model

The model used in the present work describes an exothermic, irreversible reaction[55] A → B carried out in a continuous-flow stirred tank reactor (CSTR). The total mass flow (with rate *j*) carries heat and components A and B continuously in to and out of the reactor; heat is removed through a cooling coil with temperature *T*; component A reacts to form component B and heat is released. The mass balance and the energy balance for component A can be described by the following differential equations:[55]

$$\frac{\mathrm{d}x}{\mathrm{d}t} = f(x,y) = 1 - x - xDE(y) \qquad (1)$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} = g(x,y) = (1+\epsilon)^{-1}[-\beta y + xBDE(y)] \qquad (2)$$

where $E(y) = \exp[y/(1+\eta y)]$, $\epsilon = 0.65$, and x, y, and t are dimensionless concentration, temperature, and time, respectively. The parameters β, η, B, and D are related to the control parameters j and T through the following equations:[55]

$$\beta = 1 + \frac{4.08}{j}, \qquad \eta = \frac{T^*}{8827}, \qquad B = \frac{271.46}{\eta T^*},$$
$$D = \frac{8.2365 \times 10^{11} \mathrm{e}^{-1/\eta}}{j}, \qquad T^* = \frac{885.8j + 11.02T}{2.7j + 11.02}$$

A detailed linear stability analysis for this two-variable system has been carried out by Vance and Ross.[55] There is a supercritical Hopf bifurcation point at $T \approx 301.71$ K, keeping mass flow rate j at a constant value of 0.662 g s^{-1}. Limit circles occur when the value of the control parameter T is below 301.71 K. For details of the bifurcation diagram of the autonomous system, cf. Figure 1 in ref 55. Internal stochastic resonance in this reaction system has been studied by us when the mass flow rate j was subjected to external random noise.[56]

For a linear array of three identical CSTRs coupled by means of mass exchange, the mass balance and the energy balance for reaction component A in the coupled system are described by the following differential equations:

$$\frac{\mathrm{d}x_1}{\mathrm{d}t} = f(x_1,y_1) + k_\mathrm{d}(x_2 - x_1), \qquad \frac{\mathrm{d}y_1}{\mathrm{d}t} = g(x_1,y_1) \qquad (3)$$

$$\frac{\mathrm{d}x_2}{\mathrm{d}t} = f(x_2,y_2) + k_\mathrm{d}(x_1 + x_3 - 2x_2), \qquad \frac{\mathrm{d}y_2}{\mathrm{d}t} = g(x_2,y_2) \qquad (4)$$

$$\frac{\mathrm{d}x_3}{\mathrm{d}t} = f(x_3, y_3) + k_d(x_2 - x_3), \qquad \frac{\mathrm{d}y_3}{\mathrm{d}t} = g(x_3,y_3) \qquad (5)$$

where $f(x,y)$ and $g(x,y)$ denote the kinetic terms for the identical chemical reaction in each reactor. The subscripts 1, 2, and 3 denote the first, the second, and the third reactors, respectively. The second terms in the left-hand of eqs 3−5 denote mass exchange between adjacent reactors, i.e., the three reactors are coupled by diffusion-like processes, material is transferred from one reactor to its nearest neighbors at a rate proportional to the difference in the concentrations of adjacent reactors. The coupling strength k_d (mass transfer coefficient) is set to the same value for adjacent reactors. In the numerical study, we assume that the time scale of the mass exchange between adjacent reactors is very small compared with the time scale of the reaction, and the effect of time delay[57] is neglected. But in experiment this effect must be taken into consideration carefully, since such delays play a significant role in the dynamics of a system.[3,10] To study the noisy dynamics of the coupled system, the control parameter T of each subsystem is initially set to be slightly larger than the value of the supercritical Hopf bifurcation point, so that each subsystem is at a stable stationary state (for simplicity, the three subsystems are set at an identical stable stationary state), then the first subsystem is subjected to external parametric noise:

$$T_1 = T^0[1 + \xi(t)], \qquad T_2 = T_3 = T^0 \qquad (6)$$

where T^0 ($T^0 = 301.8$ K) is the constant value of control parameter T at stable stationary state and $\xi(t)$ is Gaussian noise with zero mean $\langle \xi(t) \rangle = 0$ and autocorrelation function $\langle \xi(t_1)\xi(t_2) \rangle = \sigma^2 \delta(t_1 - t_2)$ (σ denotes the noise intensity). Since the temperatures in the three reactors may be different, there also will be heat exchange associated with the mass transfer, but we have neglected this detail in the coupled system. From now on, the first, second, and third reactors are denoted as CSTR1, CSTR2, and CSTR3, respectively. In the past decade, the responses of the coupled system to external periodic stimulation injected into the first unit of two and three mass-coupled CSTRs containing the BZ reagent, were studied by Marek's group.[12,16] Here, we investigate the coupled system in the following two ways: (i) varying noise intensity with a constant coupling strength; (ii) varying coupling strength with a constant noise intensity. Equations 3−6 are integrated using a simple forward Eular algorithm[35] with a fixed time step of 0.001 time units (dimensionless). In each calculation, the time evolution of the coupled system lasts 800 time units; the first 200 time units are discarded due to transient behavior. To quantify the phenomena occurring in the coupled system, the time series of x of each subsystem are analyzed by the Fourier power spectrum.

III. Results and Discussion

Although only CSTR1 is subjected to external parametric noise, all three subsystems exhibit oscillations. A typical part of the time series of the oscillation in each reactor and the corresponding Fourier power spectra are shown in Figure 1. The contour of the oscillation in either CSTR2 (Figure 1b) or CSTR3 (Figure 1c) is smoother than that in CSTR1 (Figure 1a), but the amplitudes of the oscillations in both CSTR2 and CSTR3 are smaller than that in CSTR1. To quantify the spatiotemporal behavior in this coupled system, the signal-to-noise ratio (SNR) of the Fourier power specrum is calculated as in refs 35, 36, 38, and 39. SNR $= H/(\Delta f/f_\mathrm{p})$, where H is the peak height normalized to the noise background and $(\Delta f/f_\mathrm{p})$ denotes the relative width of the peak with central frequency f_p, and full width at half-maximum Δf. The quality of the peaks of both CSTR2 and CSTR3 is better than that of CSTR1 (Figure 1d). Above phenomena may suggest that the negative effects of external noise are suppressed by the intrinsic properties of the coupled system, i.e., nonlinearity and coupling, while the constructive role of noise is displayed.

The SNR as a function of noise intensity for three different coupling strengths of each subsystem is shown in Figure 2. At a weak coupling strength of $k_\mathrm{d} = 0.01$ (Figure 2a), the three subsystems behave like independent systems as if they were not connected. However, this weak coupling results in a decrease of the resonance effect (as SR, the SNR going through a

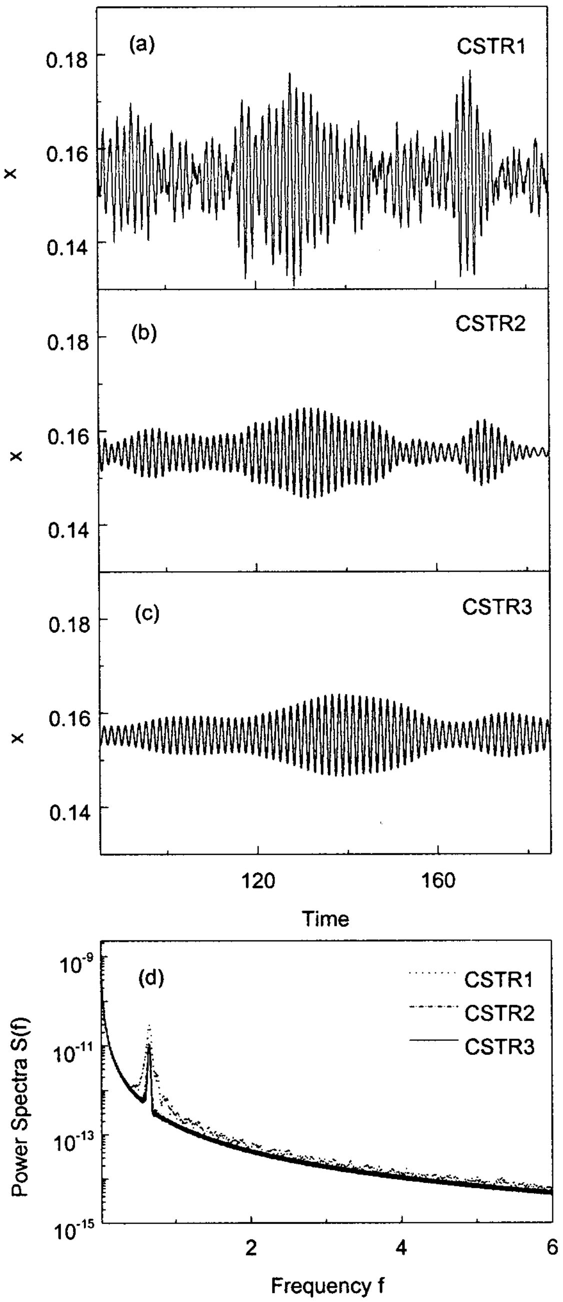

Figure 1. Oscillations and corresponding power spectra in the coupled system with a moderate coupling strength of $k_d = 0.1$, and noise intensity of $\sigma = 0.006$: (a) oscillations in CSTR1; (b) oscillations in CSTR2; (c) oscillations in CSTR3; (d) power spectra of the oscillations in three reactors.

maximum is the fingerprint of resonance) in CSTR1 compared with the internal stochastic resonance in a single system, weak resonance in CSTR2, and no resonance in CSTR3. When the coupling strength is set at a moderate value of $k_d = 0.1$ (Figure 2b), the resonance effect in CSTR3 is stronger than that in either CSTR1 or CSTR2, which may indicate that the resonance effect is transferred from CSTR1 to CSTR2 and CSTR3 and is amplified by the assistance of noise, coupling, and nonlinearity of the chemical reaction. Although this phenomenon is just like noise-enhanced propagation,[46−49] a cooperative phenomenon involving signal, noise, coupling, and nonlinearity, the external signal is absent in the present study. At a stronger coupling strength of $k_d = 0.8$ (Figure 2c), there is enough mass exchange between adjacent reactors to equalize the concentrations of all reaction components in the three reactors, which results in a single, three-parted reactor. Similar effects of coupling have been illustrated by Bar-Eli et al.[6−8] and Crowley et al.[10] in their experimental and theoretical studies on coupled chemical oscillators (each subsystem was initially run in oscillatory state). Under these stronger coupling conditions, the SNRs of the three subsystems vary approximately synchronously and go through maxima at an equal noise intensity of $\sigma \approx 0.005$.

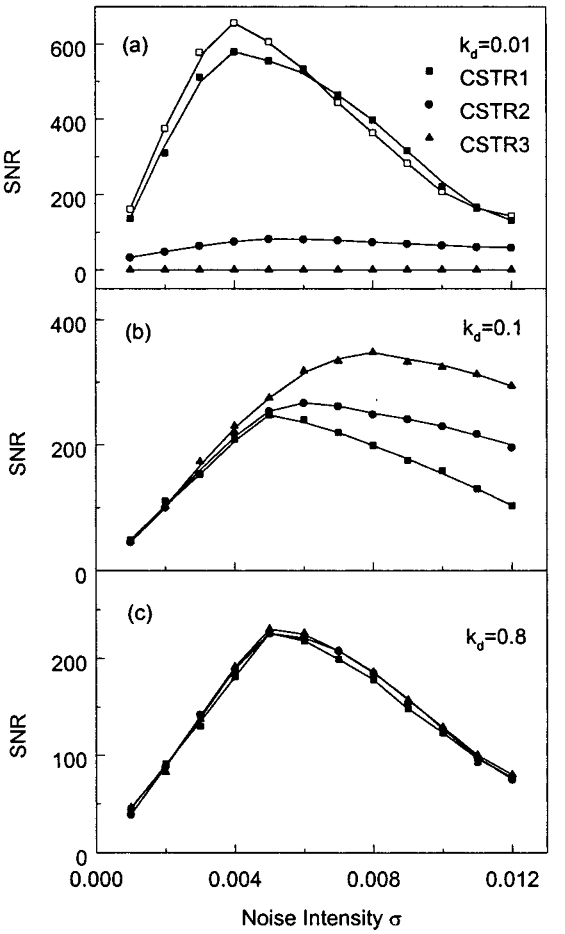

Figure 2. SNR as a function of noise intensity with a constant coupling strength: (a) $k_d = 0.01$; (b) $k_d = 0.1$; (c) $k_d = 0.8$. CSTR1 (square), CSTR2 (circle), CSTR3 (up triangle), internal SR in a single system (open square). Solid lines are drawn to guide the eye.

Generally speaking, CSTR1 responds more or less periodically to the stochastic perturbation and thus perturbs CSTR2 in a more or less periodic fashion, leading to a more periodic response in CSTR2, which then perturbs CSTR3 in a quite periodic fashion, leading finally to a nearly periodic response in CSTR3. At the same time, the strongly periodic CSTR3 feeds back into CSTR2 and CSTR1, which presumably reinforces the resonance effect in them. Therefore, coupling can enrich the noisy dynamics of a nonlinear system, and the resonance behavior in a coupled system is more robust than that in a single system.

The SNR as a function of coupling strength for three different noise intensities is shown in Figure 3. In each of the three cases ($\sigma = 0.003$, 0.006, and 0.009, respectively), the SNR of CSTR1 first decreases and then increases with the increment of coupling strength. It goes through a minimum and a maximum at $k_d \approx 0.5$ and $k_d \approx 0.6$, respectively, while the SNRs of both CSTR2 and CSTR3 go through maxima at an equal coupling strength of $k_d \approx 0.2$. The occurrence of the minimum and maximum SNRs of CSTR1 may be due to the combined effects of external parametric noise and the mass exchange between CSTR1 and

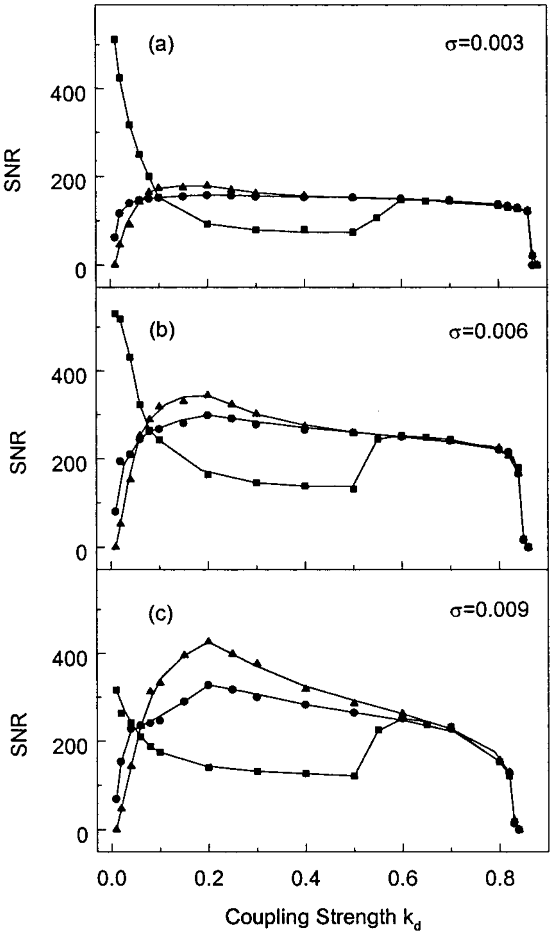

Figure 3. SNR as a function of coupling strength with a constant noise intensity: (a) $\sigma = 0.003$; (b) $\sigma = 0.006$; (c) $\sigma = 0.009$. The symbols are the same as those in Figure 2.

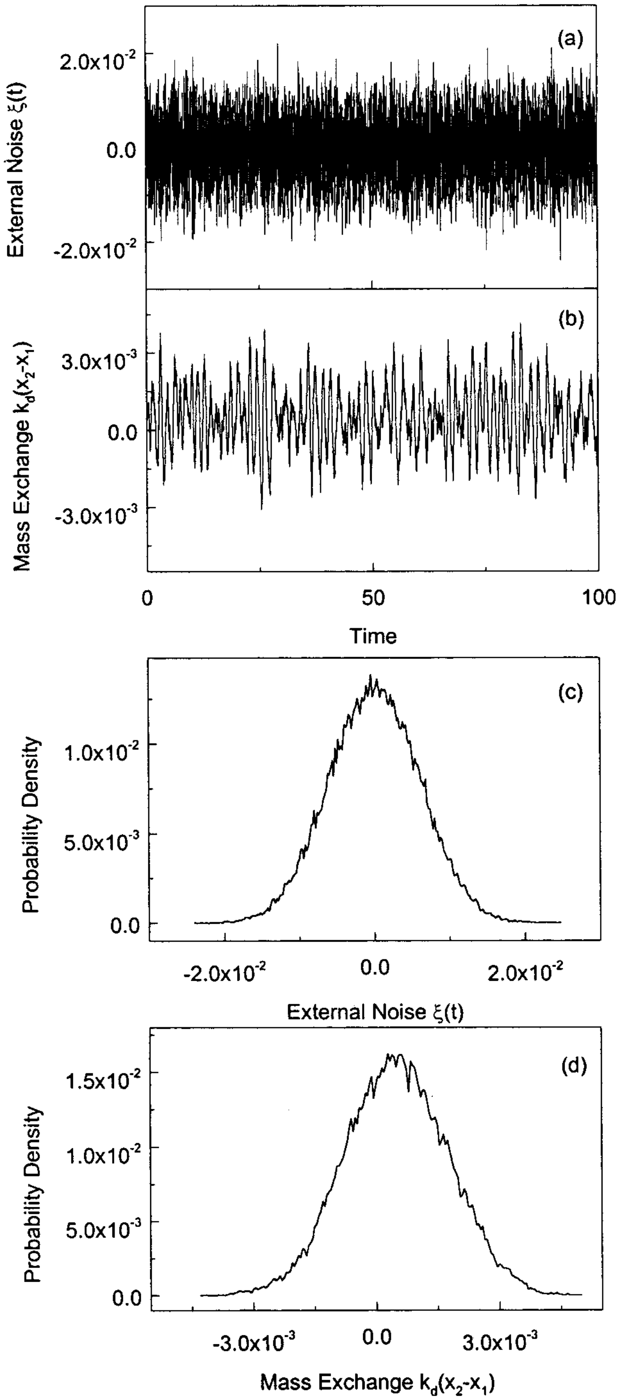

Figure 4. Time series and probability distributions of external noise $\xi(t)$ and mass exchange in CSTR1, i.e., $k_d(x_2 - x_1)$ with $\sigma = 0.006$, and $k_d = 0.3$, respectively: (a) time series of $\xi(t)$; (b) time series of $k_d(x_2 - x_1)$; (c) probability distribution of $\xi(t)$; (d) probability distribution of $k_d(x_2 - x_1)$.

CSTR2, i.e., $k_d(x_2 - x_1)$, cf. eqs 3 and 6. The external parametric noise $\xi(t)$ (Figure 4a,c) injected into the first reactor is spatially incoherent, while the diffusion-like mass exchange (Figure 4b) is spatially coherent, and like $\xi(t)$, it has a Gauss-type distribution (Figure 4d) relating to the intrinsic property of the nonlinear chemical reaction, the linear diffusion-like coupling, and the external noise. In addition, the mass exchange terms, cf. eqs 4 and 5, in CSTR2 and CSTR3 are of the same distribution as that in CSTR1, which give rise to the oscillation and resonance behaviors in both CSTR2 and CSTR3 when external noise is injected into CSTR1. The variation of the SNR of CSTR1 showed in Figure 3 reveals both constructive and destructive influences of the combined action of spatially incoherent external noise and spatially coherent coupling on the spatiotemporal order of the coupled system. When Hauptmann et al.[49] investigated signal transfer in coupled nonlinear systems, similar variation of the SNR was found as spatially incoherent and spatially coherent external noise were added to the coupled system. Hence, with the variation of coupling strength, resonance phenomena also occur in the coupled system.

A part of the time series of the oscillation in each reactor as a function of the coupling strength with a constant noise intensity is shown in Figure 5. With the increment of coupling strength, the phase and amplitude differences of the oscillations in three subsystems decrease. When the coupling strength reaches a critical value of $k_d \approx 0.6$, synchronization (phase locking) of the oscillations in three subsystems is observed (Figure 5c), and the SNRs of the three subsystems vary synchronously (Figure 6) and go through maxima at an equal noise intensity of $\sigma \approx 0.007$, which indicates the occurrence of spatiotemporal synchronization in the coupled system. In addition, in the synchronization region ($k_d \geq 0.6$), the optimal noise intensity for the maximum SNR shifts to a lower value with the increment of coupling strength (Figures 2c and 6). If the coupling strength is strong enough, the three subsystems are synchronized into stable stationary states, and CSTR1 and CSTR3 are at the almost same stable state (Figure 5d). In addition, the minimum coupling strength that can synchronize the three subsystems into stable stationary states monotonically shifts to a lower value with the increment of the noise intensity (Figure 7). Phase death[10,24] is the term given to the steady state produced by coupling two

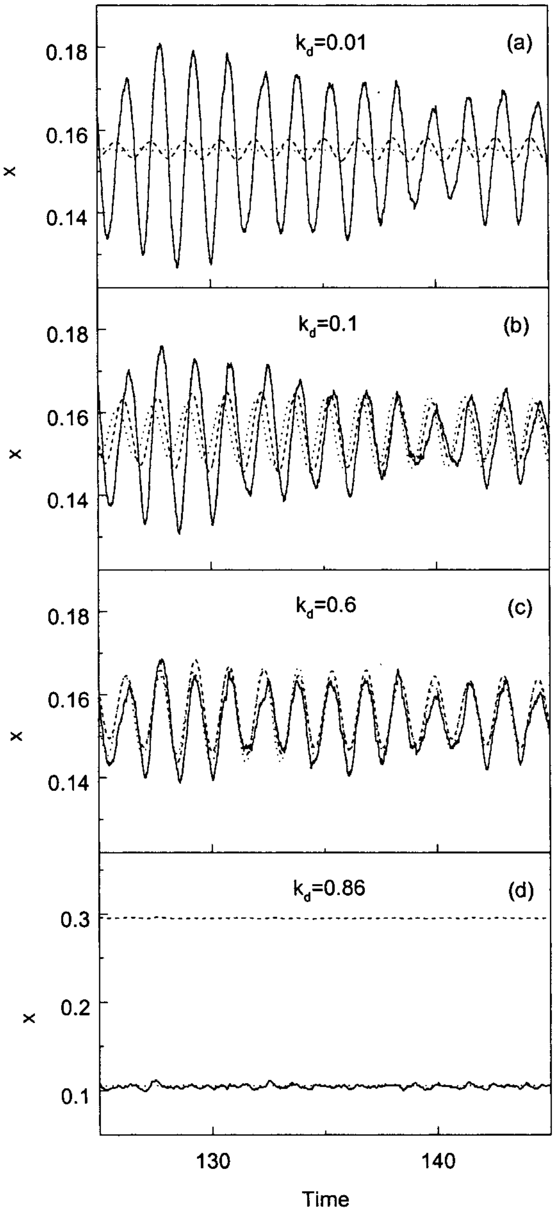

Figure 5. Part of the time series of the oscillation in each reactor as a function of coupling strength with a constant noise intensity of $\sigma = 0.006$: (a) $k_d = 0.01$; (b) $k_d = 0.1$; (c) $k_d = 0.6$; (d) $k_d = 0.86$. CSTR1 (solid line), CSTR2 (dashed line), CSTR3 (dotted line).

and more oscillators. This effect of coupling has been studied by Bar-Eli et al.[6−8] numerically and experimentally in coupled chemical oscillators. Synchronization in nonlinear systems is of considerable interest due to its important role in living systems.[16,24,30,58,59] It has been investigated extensively in coupled chemical oscillators. As early as 1975, Marek and Stuchl[4] studied synchronization of oscillations in two interacting CSTRs with the BZ reaction. Synchronization observed in this coupled system is also a cooperative phenomenon. Synchronization as the attendant of array-enhanced stochastic resonance and coherence resonance in coupled systems has been reported.[43−45,51,52] Recent observations of synchronization by interacting coherence resonance oscillators,[60] and noise-enhanced phase synchronization in excitable media[61] modeled by locally coupled FHN systems indicated similar underlying dynamics.

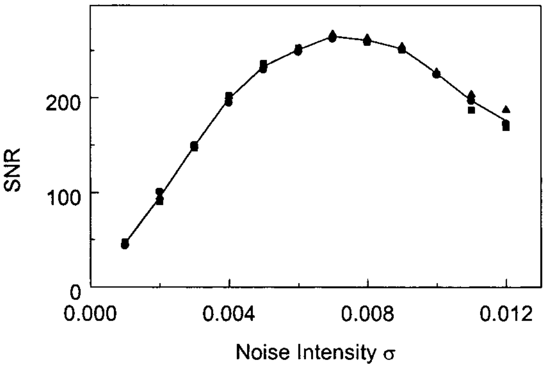

Figure 6. Spatiotemporal synchronization in the coupled system: SNR as a function of noise intensity with a constant coupling strength of $k_d = 0.6$. The symbols are the same as those in Figure 2.

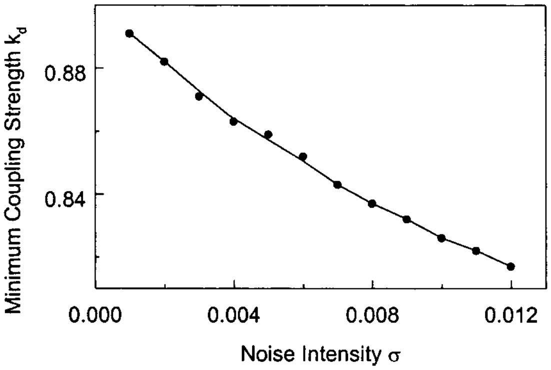

Figure 7. Minimum coupling strength that can synchronize the three subsystems into stable stationary states as a function of noise intensity.

The numerical results showed above indicate that noise, coupling, and intrinsic properties of the nonlinear chemical reaction can cooperate to organize the spatiotemporal order of the coupled system and to induce synchronization phenomena. For a single system, autonomous SR[35,36] or coherence resonance[37−40] is now a pronounced phenomenon in nonlinear systems. The spatiotemporal order occurring in this coupled system depends not only on the external noise but also on the coupling. Like array-enhanced stochastic resonance,[43−45] we view the phenomenon occurring in this coupled system as a nontrivial extension of autonomous SR. It was also a cooperative phenomenon involving noise, coupling, and nonlinearity of the chemical reaction. But it is not identical with AESR because no deterministic external signal is injected into the system, and only the first unit is subjected to random noise.

Recently, the idea of controlling SR has been illustrated by Gammaitoni et al.[62] using a modified Schmitt trigger. Similar results have been reported by Amemiya et al.[63] in the photosensitive BZ reaction. They realized controlling SR by injecting into the system another periodic modulation and considering the difference of the initial phases of the two periodic signals as a tunable parameter, which can give rise to enhancement or suppression of the SR effect. In the present work, we give another possible way of controlling resonance effect in the coupled system by changing coupling strength between adjacent reactors. The enhancement or suppression of resonance effect in each subsystem can also be realized when the coupling strength is considered as another tunable parameter except for the noise intensity (Figure 2 and 3).

In the previous studies on diffusively coupled chemical oscillators, many experimental setups have been constructed. However, one of the difficulties that must be taken into account in such an experiment is that the flows in to and out of each reactor must be carefully balanced to avoid net transfer between adjacent reactors. To eliminate experimental problems caused by unequal mass transfer and time delay, as early as 1989, Crowley and Epstein[3,10] have designed a new type of coupled chemical reactors which provided a tunable coupling strength.

IV. Conclusions

In the present work, we investigate the dynamics of a nonlinear chemical reaction in a linear array of three identical CSTRs coupled by means of mass exchange when the first subsystem is subjected to external parametric noise. We show how noise cooperates with coupling and nonlinearity of the chemical reaction to organize spatiotemporal order of the coupled system and to induce synchronization phenomenon. The numerical results imply that external fluctuations can induce internal order in a complex system under appropriate conditions. One of the major motivations of the investigation on SR, SR-like phenomenon, and these phenomena in coupled systems is their applications in biology.[33] Recent observation of noise-induced spiral waves in cultured networks of rat brain cells,[64] noise-supported traveling waves in the photosensitive BZ reaction,[65] and noise-induced transition from pulsating spots to global oscillations in excitable media,[66] also indicated the constructive role of random noise in complex systems and similar underlying dynamics. Because of the simplicity of the model used in the present work, we expect the phenomenon reported here is general in many complex systems that can be modeled by chemical or biochemical reaction systems in CSTRs coupled by means of mass exchange. Since no fundamental theory of this kind of phenomenon exists as yet, further experimental and theoretical work will be helpful to future research.

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