Noise-enhanced phase locking in a chemical oscillator system

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Dynamical responses of a chemical oscillator to an external electric field were investigated in the Belousov-Zabotinsky reaction system with the catalyst $Ru(bpy)_3^{2+}$ [tris-(2,2′-bipyridine) ruthenium (II)] immobilized in cation exchange beads. Periodic forcing above the threshold induced phase locking, whose synchronization region has a shape similar to the Arnold tongue. When a certain amount of noise together with a subthreshold periodic signal was imposed on the chemical oscillator, 1:1 phase locking to the periodic signal occurred. Its degree passed through a maximum with increase in the noise intensity, a manifestation of stochastic resonance in the form of noise-enhanced phase locking. The experimentally observed features were reproduced in a numerical simulation with a forced Oregonator reaction-diffusion model.

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I. INTRODUCTION

The dynamic response of nonlinear systems to external perturbations has been extensively investigated. In particular, phase locking of oscillators is a typical phenomenon of self-organization in physical, chemical, and biological systems [1]. External periodic forcing above a threshold induces an $n:m$ phase locking pattern with m firings for n forcing periods, depending on the forcing amplitude [2–4]. Then the forcing frequency-amplitude plane shows a resonance region, called an Arnold tongue. Naturally, forcing these systems with a subthreshold periodic signal yields no phase locking. It has recently been found that in excitable systems the addition of a certain amount of noise can trigger firings even for control parameters below the threshold. This phenomenon, called stochastic resonance (SR), has been observed in many nonlinear systems, such as electronic trigger circuits [5,6], bistable ring lasers [7], neuronal networks [8,9], and chemical reaction systems [10–12]. Such SR effects are characterized as the enhancement of the response to a weak input signal in nonlinear systems with a threshold, i.e., a kind of noise-induced oscillation. Alternative effects of SR have been examined in overdamped bistable oscillators driven by a subthreshold periodic signal and noise, in terms of phase locking [13–15]. The phenomenon of SR in excitable systems is now familiar, but stochastic phase locking in limit cycle systems, which results from forcing with both subthreshold periodic signals and additive noise, has not been experimentally examined.

In this paper, we investigate the effects of additive noise on phase locking of a single chemical oscillator to a subthreshold electric sinusoidal field. In the experiment we use a discrete type of Belousov-Zabotinsky (BZ) reaction system: the redox reaction is confined to the surface of beads by immobilizing the tris-(2,2′-bipyridine) ruthenium (II) complex $Ru(bpy)_3^{2+}$, in cation exchange beads of submillimeter size [16,17]. Thus we regard the $Ru(bpy)_3^{2+}$-loaded beads as chemical oscillators. Electric fields are known to have pronounced effects on dynamic behaviors of chemical waves [18–20]. The sensitive responses to electric fields are related to the fact that most chemical species relevant to wave propagation are ionic. We find the phenomenon of noise-enhanced phase locking as a manifestation of the SR effect. Some experimental findings are numerically simulated using a modified Oregonator reaction-diffusion model.

II. EXPERIMENTS

Experimental procedures are similar to that reported in an earlier paper [21]. The initial composition of the BZ reaction solution was $[NaBrO_3]=0.36M$, $[NaBr]=0.044M$, $[CH_2(COOH)_2]=0.21M$, $[H_2SO_4]=0.65M$. Reagent grade chemicals were used without further purification. The cation exchange beads (DOWEX, 50W-4X) of about 0.5 mm in diameter were loaded with a solution of $[Ru(bpy)_3^{2+}]=2.5\times10^{-5}$ mol/g beads. When the $Ru(bpy)_3^{2+}$-loaded beads were suspended in the BZ solution, the chemical waves were periodically initiated and propagated on the bead surface. The chemical waves localized on the bead surface were monitored through a charge-coupled device camera attached to a microscope. The change in color was transformed into a change in light intensity by averaging the gray level of the intensity from the fixed small area on the bead surface corresponding to a grid of 3×3 pixels. The period of the oscillation strongly depended on the temperature and the composition of the BZ solution. In order to obtain a stable natural period, the temperature of the BZ solution was maintained at $23\pm0.5\,^{\circ}C$. The catalyst $Ru(bpy)_3^{2+}$ is photosensitive, and generally the natural frequency of the oscillation decreases with an increase in the intensity of illuminated light. The natural frequency employed in this experiment ranged from 0.01 to 0.02 Hz. The temporal resolution for successive images was limited by the time required for data storage. The present system allowed examination of successive images at time intervals of 0.1 s.

An electric field was applied across the bead with the aid of platinum wire electrodes of 0.6 mm in diameter. Electrodes were placed 2 mm apart and parallel in the liquid layer. The bead was placed in contact with one of two electrodes. All measurements were made after the electric current

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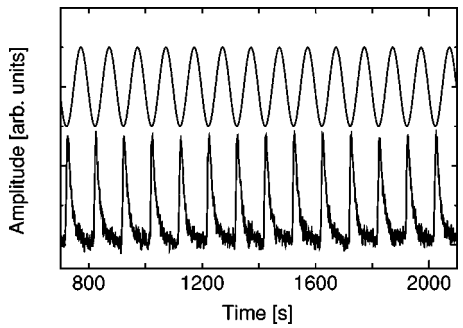

FIG. 1. 1:1 phase locking at $T_e/T_o=0.9$ and $V_e=0.4$ V. The upper trace is the time series of the voltage of the electrode in contact with the bead, and the lower one is the time series of the intensity from the oscillator.

reached an equilibrium value. For the perturbation experiment a weak sinusoidal signal and equally distributed noise were superimposed on the electric field according to $V_e \sin 2\pi t/T_e+\beta\xi(t)$, where V_e is the amplitude, T_e the period, β the noise amplitude, and $\xi(t)$ random numbers equally distributed between 1 and -1 whose average is zero. The periodic signal amplitude was taken small enough not to induce phase locking without noise.

III. RESULTS AND DISCUSSION

The applied sinusoidal voltage $V_e \sin 2\pi t/T_e$ was in the range of $0.2 \leqslant V_e \leqslant 0.8$ V and $0.6 \leqslant T_e/T_o \leqslant 1.5$, where T_o is the natural period of the chemical oscillator. Figure 1 shows phase locking of the oscillator to the electric field with the period ratio of $T_e/T_o=0.9$ and $V_e=0.4$ V. We can see that the firing of the oscillator occurs without time delay when the voltage of the electrode that the bead contacts reaches a negative maximum. This can be explained by acceleration of the oxidizing reaction, which is due to a decrease of the concentration of Br^- in the vicinity of the bead. This frequency locking was very stable, and was observed in a wide range of control parameters above threshold values. Figure 2 shows the region of 1:1 entrainment as a function of the forcing period and the forcing voltage. We can see that its shape is similar to the Arnold tongue. The tongue shape is somewhat asymmetric, which may be characteristic of the present system.

On the basis of these results, we investigated whether or not 1:1 phase locking results from forcing with both subthreshold periodic signals and additive noise. In the traditional description of SR in excitable systems, the response of the system is measured by the signal-to-noise ratio (SNR) in the power density spectra of output time series [5–9]. Then the SNR exhibits a resonance curve as a function of noise intensity. However, such an analysis does not seem to be always suitable for a forced synchronization system such as the present one, since the instantaneous phase difference, which provides important information about phase locking of a self-sustained oscillator to an external force, cannot be estimated. Hence, we attempted a different analysis to characterize the noise-induced enhancement of external periodic forcing. When t_k labels the times of successive firing events

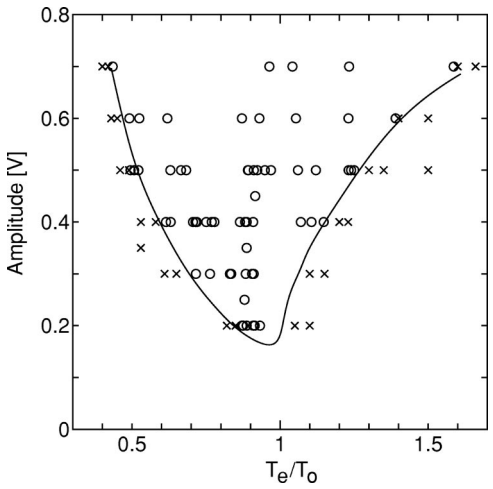

FIG. 2. 1:1 entrainment region in the frequency-voltage plane. Symbols represent the states of a 1:1 entrainment (○) and entrainment other than 1:1 (×).

$\{t_k\}$, the instantaneous period is $T_k=t_{k+1}-t_k$ for $t_k<t<t_{k+1}$. A definition of the instantaneous phase is then given by [14]

$$\varphi(t)=2\pi\frac{t-t_k}{T_k}+2\pi k \quad t_k<t<t_{k+1}. \tag{1}$$

When the oscillator is fully synchronized with the forcing period T_e, $\varphi(t)$ exactly gives $2\pi t/T_e$. Hence, the instantaneous phase difference $\Phi(t)$ is given by $\Phi(t)=\varphi(t)-2\pi t/T_e$. The time series of $\Phi(t)$ is shown in Fig. 3 for different values of the noise amplitude under a periodic stimulus with amplitude $V_e=0.1$ V and frequency $T_e/T_o=0.9$, where the pulse duration of noise was set to 0.225 s. For weak noise intensity the phase difference decreases almost linearly with time. This indicates that the oscillator oscillates with a constant frequency independent of external perturbation. Since the natural frequency is smaller than the forcing frequency, $\Phi(t)$ decreases with time. At an optimal noise amplitude $\Phi(t)$ is held almost constant. This indicates

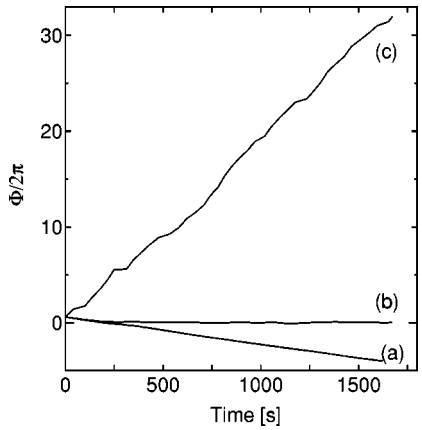

FIG. 3. Time series of the instantaneous phase difference for various values of the noise amplitude at $T_e/T_o=0.9$. (a) $\beta=0.1$ V, (b) $\beta=0.3$ V, and (c) $\beta=0.6$ V.

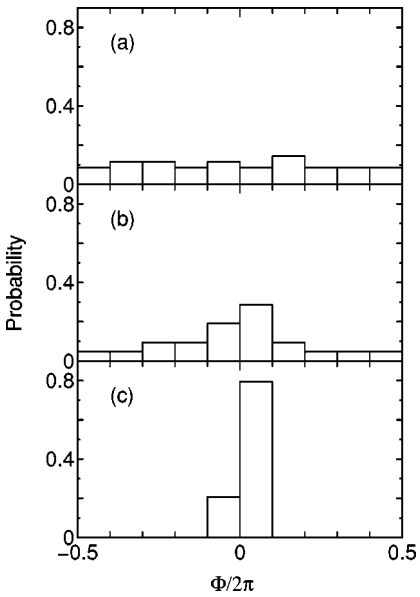

FIG. 4. Distribution of the phase difference at $T_e/T_o=0.9$ (a) outside the synchronization region ($\beta=0.1$ V), (b) near the boundary ($\beta=0.15$ V), and (c) inside the synchronization region ($\beta=0.3$ V).

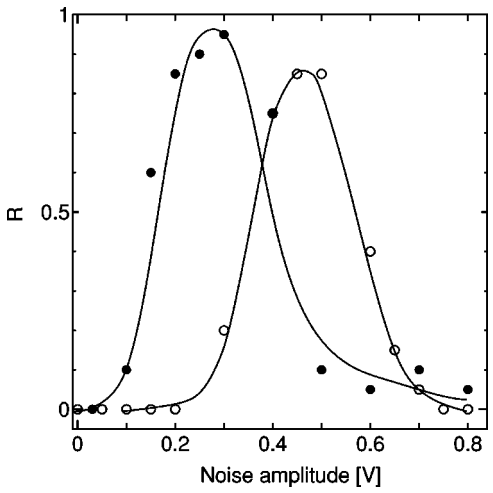

FIG. 5. Degree of the occurrence of 1:1 entrainment under forcing with both subthreshold periodic signals and additive noise.

that the oscillator is synchronized by the periodic external force. With further increase in the noise amplitude, the phase becomes unlocked again. It is remarkable that the phase difference fluctuates in a random manner depending on the noise level. Figure 4 illustrates the distribution of the phase observed stroboscopically with the period of the periodic external force, for three regimes of noise intensity. In the nonsynchronized state, the phase difference attains almost the same value over 2π. Increase of the noise intensity makes a zero phase difference more probable. In the synchronized state, the distribution becomes sharp around zero phase difference. This will provide us with an alternative diagnosis of synchronization.

We developed an *ad hoc* definition of SR to provide a direct measure of the degree of phase locking. In the synchronized state induced by the external periodic force alone, as seen from Fig. 1, a firing occurs just as the applied periodic voltage attains the negative maximum. We employed this state as the reference state with the zero phase difference $\Phi(t)=0$. As seen from Figs. 3 and 4, in contrast, in the synchronized state that is induced by forcing with both a subthreshold periodic signal and an additive noise, firings did not always occur at zero phase difference. Hence it is necessary to permit a definite width around $\Phi(t)=0$ as a criterion for the occurrence of noise-induced phase locking. In this study we set this width as $-\pi/5\leqslant\Phi(t)\leqslant\pi/5$. To investigate the SR effect, we calculated the degree of entrainment R defined as

$$R=\frac{N_0}{N_{\text{total}}}, \tag{2}$$

where N_0 is the number of occurrence of one firing in the above-defined width for successive firing events N_{total}. Figure 5 shows R as a function of the noise amplitude for different values of T_e/T_o when the amplitude of the periodic stimulus is fixed at 0.1 V. It is seen that in every case R passes through a maximum with an increase of the noise amplitude. This shows clearly that there exists an optimal noise amplitude for phase locking. This can be considered as a manifestation of a different kind of SR, namely, noise-enhanced phase locking. The optimal noise amplitude becomes smaller and the peak height becomes higher as the value of T_e/T_o approaches 1. This behavior is understandable from the tonguelike shape of the synchronization region shown in Fig. 2. In the case of $T_e>T_o$, no entrainment is observed even if noise is superimposed on the periodic forcing of 0.1 V. After a firing, generally the reaction medium comes into the refractory period during which a second firing cannot spontaneously occur. When the sum of the periodic signal and additive noise exceeds the threshold sufficiently, however, it can change the state of the reaction medium, and can consequently induce a second firing even if $T_e<T_o$. For $T_e>T_o$, in contrast, the refractory state of the oscillator is randomly perturbed by the strong additive noise, and consequently a second firing can easily occur within T_e after a firing, which results in a disturbance of the 1:1 entrainment. This may account for the asymmetric phase locking observed.

We conducted numerical simulation of phase locking to complement the experiments. We modified the three-variable Oregonator model to take into account the effects of an external electric field. In the present reaction medium the catalyst $Ru(bpy)_3^{2+}$ is immobilized, so that its self-diffusion is negligible and its drift driven by the electric field is also negligible. Since the autocatalytic species $HBrO_2$ is not charged, it is not influenced by the electric field. Including additional drift terms for the charged species [22,23], a modified Oregonator model in a one-dimensional system is then given by

$$\frac{\partial u}{\partial t}=\frac{1}{\epsilon}(qw-uw+u-u^2)+D_u\frac{\partial^2 u}{\partial x^2}, \tag{3}$$

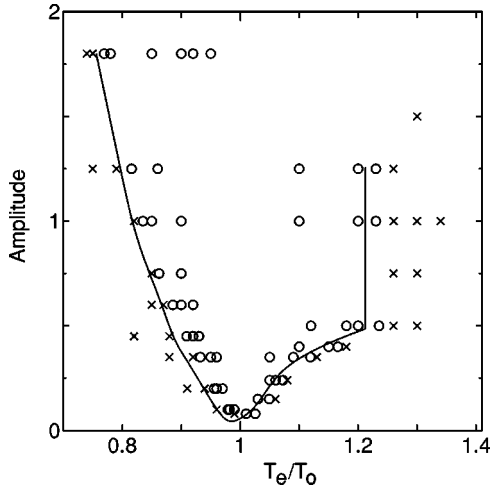

FIG. 6. 1:1 entrainment region for the three-variable Oregonator model in the frequency-amplitude plane. Symbols represent the states of a 1:1 entrainment (○) and entrainment other than 1:1 (×).

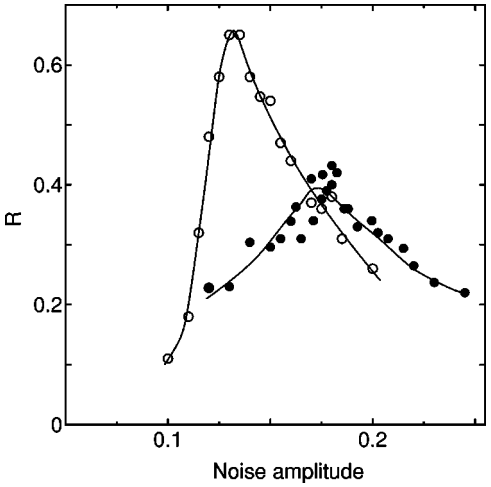

FIG. 7. Degree of occurrence of 1:1 entrainment under forcing with both subthreshold periodic signals and additive noise in the three-variable Oregonator model, where the open and solid circles indicate the cases of $T_e/T_o=0.98$ and $T_e/T_o=0.91$, respectively.

$$\frac{\partial v}{\partial t}=u-v, \tag{4}$$

$$\frac{\partial w}{\partial t}=\frac{1}{\epsilon'}(-qw-uw+fv)+D_w\frac{\partial^2 w}{\partial x^2}+K_wE\frac{\partial w}{\partial x}, \tag{5}$$

where the variables u, v, and w describe the concentrations of $HBrO_2$, the $Ru(bpy)_3{}^{2+}$ catalyst, and Br^-, respectively. D_u and D_w denote the diffusion coefficients of $HBrO_2$ and Br^-, respectively. The term $K_wE\partial w/\partial x$ describes the additional flux of Br^- driven by the electric field. The ionic mobility K_w depends on the charge and D_w. The numerical values of the parameters $q=0.002, f=1.4, \epsilon=0.01$, and $\epsilon'=0.0001$ as well as the values of the diffusion coefficients $D_u=1.0$ and $D_w=1.12$ were chosen according to Schmidt and Müller [24]. Then the natural period T_0 was 4.29. The electric field E composed of a periodic signal and random noise is expressed as

$$E=A\sin\frac{2\pi}{T_e}t+B\xi_\tau(t), \tag{6}$$

where A and T_e are the amplitude and the period of the sinusoidal signal, respectively, B is the noise amplitude, and $\xi_\tau(t)$ is a random number equally distributed between -1 and 1 with duration time τ. The computation was performed by the Crank-Nicholson method with a grid spacing $\Delta x=0.011$ and time steps $\Delta t=5.9\times10^{-5}$. Figure 6 shows the 1:1 entrainment region as a function of the frequency and the amplitude of the sinusoidal signal without noise. Its shape is similar to the Arnold tongue, and is somewhat symmetric compared with that obtained in the experiment.

When a subthreshold sinusoidal signal and noise were superimposed on the electric field, phase locking occurred in a finite region of the noise amplitude. In this model, however, the phase slips occurred even at optimal noise amplitude, so that the system was only partially synchronized. To evaluate the degree of phase locking, we calculated R using Eq. (2) for successive firing events $N_{\text{total}}=150$. In this case N_0 was taken as the number of firings with the phase difference of $-\pi/5\leqslant\Phi(t)\leqslant\pi/5$. We chose the amplitude of the sinusoidal signal such that it is close to the threshold value for phase locking: phase synchronization did not occur for small amplitudes far from the boundary. The results for $T_e=4.2$ and 3.9 are shown in Fig. 7, with a noise pulse duration $\tau=40\Delta t$. In every case R passes through a maximum with increasing noise amplitude, showing the characteristics of SR. The optimal noise intensity becomes smaller and its peak becomes sharper as the value of T_e/T_o approaches 1. Such a SR effect occurred only for relevant τ: when extremely large or small τ was chosen, the time series of $\Phi(t)$ became irregular with increasing noise amplitude. In addition, an increase of τ within the relevant range tended to shift the position of the peak to smaller values of the noise amplitude. These computational results are consistent with the experimental results, but there are some differences in some details. In the experiment R took a value of almost 1 at the optimal noise amplitude, corresponding to the fully synchronized state, whereas in the calculation R is always less than 1. In addition, in the calculation the occurrence of SR is limited to the region of T_e/T_o slightly smaller than a unity, where in the experiment SR was observed in a wide range of $T_e/T_o\leqslant1$. In the calculation, in particular, the additive noise must be weak for the occurrence of SR.

IV. CONCLUSION

We have investigated synchronization of a chemical oscillator to an external electric field. When a periodic signal alone was applied in the electric field, a synchronization region similar to the Arnold tongue was observed in the forcing frequency-amplitude plane. When a subthreshold periodic signal and noise were simultaneously imposed on the oscillator, stochastic resonance manifested itself in the form of noise-enhanced phase locking. The optimal noise ampli-

tude depended on various control parameters, such as the period and the amplitude of the periodic signal, and the noise pulse length. These experimental findings were qualitatively reproduced in a numerical simulation with a forced Oregonator model. Thus we can say that a weak noise has a positive effect on the phase locking of a self-sustained chemical oscillator to external fields.

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