Dynamics of a stochastic oscillator in an excitable chemical reaction system

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Dynamics of an excitable Belousov-Zabotinsky reaction system subject to a subthreshold periodic signal and additive noise is investigated using cation exchange beads loaded with the cationic catalyst. We find two kinds of resonance phenomena with respect to the noise amplitude. At the first resonance, the regular oscillation appears with the period equal to the signal period, which is identified as a conventional stochastic resonance. The second resonance is a great contrast to conventional stochastic resonance, in which the regular oscillation appears in a characteristic fashion like phase locking of deterministic oscillators, depending on the signal period and a noise amplitude. Results are explained in terms of the interplay of periodic forcing and the noise-induced oscillator with the period determined by an intrinsic time scale of the system.

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Effects of noise on nonlinear systems have attracted considerable attention. There are many examples showing that noise can have a constructive effect on the formation of order, such as noise-induced transitions [1,2], noise-enhanced phase locking [3–5], and noise-sustained spatiotemporal patterns in spatially extended systems [6–9]. Phenomena of noise-induced enhancement of temporal regularity are roughly classified into two groups according to the presence of an external signal, coherence resonance (CR) [10–13], and stochastic resonance (SR) [14–18]. The phenomenon of CR, also called autonomous stochastic resonance [19–22], has been observed in excitable systems driven by noise alone. The most striking characteristic of CR is that the period of regular oscillation induced for a moderate amount of noise is determined by a time-scale characteristic of the system. This has been experimentally confirmed in excitable optical [23] and chemical reaction systems [24]. A noise-driven excitable oscillator can be thus regarded as a ''CR oscillator,'' i.e., a stochastic oscillator with an intrinsic period which characterizes the time-dependent properties of the system.

On the other hand, the phenomenon of SR occurs in the presence of both a subthreshold periodic signal and additive noise. The SR effect is characterized as noise-enhanced detection of a weak input signal, so that the period of induced oscillation is naturally determined by that of a periodic input signal. In the case of a bistable system, SR is understood as a phenomenon that takes place when the mean rate of noise-induced hopping between the potential wells coincides with the frequency of the signal [16–18]. This phenomenon is called a time-scale matching, which has also been found in the numerical simulation with an excitable FitzHugh-Nagumo model [25,26] and the leaky integrate-and-fire model for neural excitations [27,28]. In the case of an excitable system, the degree of resonance is magnified by tuning the period of the external signal to the intrinsic period of the system, in contrast to conventional SR.

In this paper, we study experimentally the effects of external noise on an excitable medium of Belousov-Zabotinsky (BZ) reaction. In particular, our attention is focused on the phenomenon of time-scale matching between the forcing period and the intrinsic period of the system. The excitability of the reaction medium is adjusted by controlling the intensity of illuminated light. An electric field is employed as an external forcing to stimulate the excitable medium, since the electric field has pronounced effects on dynamic behaviors of chemical waves. Such a combined use of two independent external fields has several advantages in the studies of resonance. First, the intrinsic time scale is clearly determinable and second, the degree of excitability is freely controllable [24]. We find that a variety of resonance patterns appear depending on two time scales, i.e., the intrinsic period of the system and the forcing period, with increase in the noise amplitude.

Experiments were carried out with a localized reaction system in which the tris-(2,2′-bipyridine) ruthenium (II) complex $[\mathrm{Ru(bpy)}_3^{2+}]$ was immobilized in the cation exchange beads of a submillimeter size [29,30]. The experimental setup is almost the same as those described in an earlier paper [24]. 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 to the surface of the reaction medium. The bead was placed in contact with one of the two electrodes. A periodic signal and noise were superimposed on the electric field according to

$$V_e \sin\frac{2\pi t}{T_e} + D\xi_\delta(t), \tag{1}$$

where V_e is the amplitude, T_e is the period, D is the noise amplitude, and $\xi_\delta(t)$ are random numbers equally distributed between 1 and -1 whose average is zero, with the duration time δ.

The initial composition of the BZ reaction solution was as follows: $[\mathrm{NaBrO_3}]=0.36$ M, $[\mathrm{NaBr}]=0.044$ M, $[\mathrm{CH_2(COOH)_2}]=0.21$ M, $[\mathrm{H_2SO_4}]=0.65$ M. The cation exchange beads of about 0.5 mm in diameter were loaded with a $\mathrm{Ru(bpy)}_3^{2+}$ solution of $[\mathrm{Ru(bpy)}_3^{2+}]=2.5\times10^{-5}$ mol/g beads. At this composition, the system was initially in oscillatory regime. The excitable steady state was realized by taking advantage of a high photosensitivity of $\mathrm{Ru(bpy)}_3^{2+}$ [31]. The period of oscillation increased monotonically with increasing illuminated light intensity I, and finally the excitable steady state appeared for the light inten-

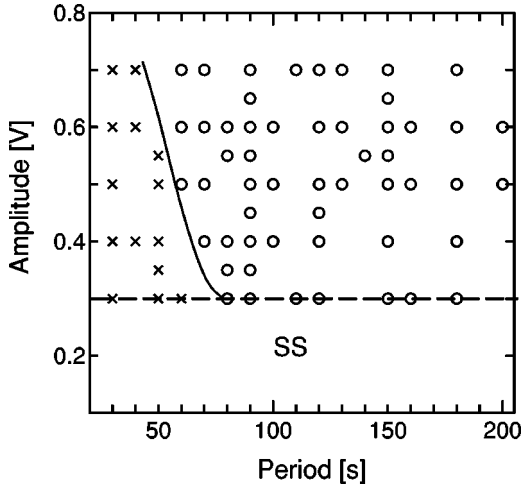

FIG. 1. Period-voltage subspace for the periodically forced excitable medium without noise. The dash line divides the region into the oscillatory state and the excitable steady state (SS). Symbols represent the state with the period equal to the forcing period, i.e., 1:1(○) and states other than 1:1(×).

sity of more than about $I_c=9$ mW. Then the period under the dark was estimated by extrapolation to be approximately 60 s, which agrees closely with the value found in Ref. [24]. This value is considered as the intrinsic period of the present system, T_{CR}, taking into account that the oscillatory period varies with the intensity of illumination light. All measurements were performed at the excitable steady state near the Hopf bifurcation point and at the temperature of 24 $\pm 0.5\,^{\circ}$C.

We checked the effect of a periodic electric field on the excitable medium induced under light illumination of $I=10.0$ mW, in the absence of noise. Figure 1 shows the phase diagram in the plane of T_e and V_e. One can see that the system becomes oscillatory above about $V_e=0.3$ V. In the measurements, the value of V_e was always fixed to a subthreshold value of 0.1 V. First, we examined the case where T_e is close to T_{CR}. Figure 2 shows the time series of light intensity (gray level) from the BZ oscillator for various noise levels, where $T_e=70$ s and $\delta=0.225$ s. For small D below about 350 mV, the system exhibits no response [Fig. 2(a)]. When D is increased, irregular firings appear abruptly. For suitable values of D, the oscillation becomes almost regular with the period of 70 s [Fig. 2(b)]. For further increase in D, the regularity of firing remains almost unchanged up to 650 mV [Figs. 2(c) and (d)], above which the firing becomes irregular again, accompanied by the decrease of the firing rate [Fig. 2(e)].

Let the time of the kth firing event be t_k. From successive firing events $\{t_k\}$, the interspike intervals are defined as $T_k=t_k-t_{k-1}$ for $t_{k-1}<t<t_k$ $(k=1,2,\ldots,N)$. To characterize the coherence of the spike train, we use the coherence measure R, the reciprocal of the standard deviation of T_k, defined by

$$R=\frac{\langle T\rangle}{\sqrt{\langle T^2\rangle-\langle T\rangle^2}}, \tag{2}$$

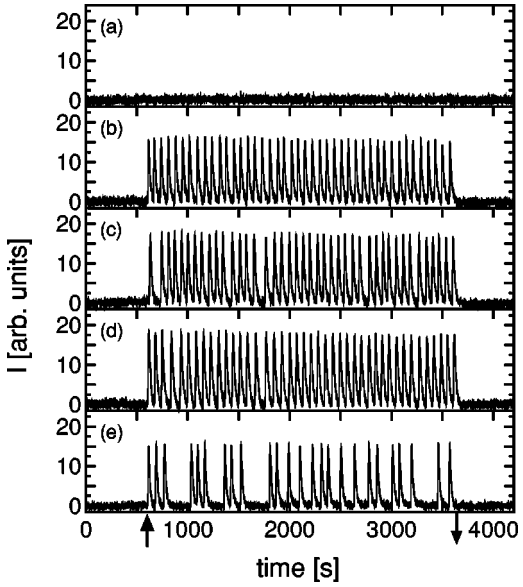

FIG. 2. Time series of the light intensity from the chemical oscillator as a function of the noise amplitude D for $T_e=70$ s and $I=10$ mW: (a) $D=350$ mV, (b) $D=450$ mV, (c) $D=600$ mV, (d) $D=650$ mV, and (e) $D=700$ mV. Upward and downward arrows indicate the time at which the electric field was turned on and off, respectively.

where $\langle T^n\rangle=1/N\Sigma_{k=1}^{N}T_k^n$. Figure 3 shows R as a function of the noise amplitude D. The curve is convex, which clearly suggests the occurrence of stochastic resonance. It should be noted that R passes through two maxima, although its separation is not so clear, with increasing D. To confirm the existence of two maxima, we examined the effect of SR at different values of T_e. Figure 4 shows the temporal behaviors of the light intensity from the BZ oscillator for various noise levels at $T_e=120$ s. Here the value of T_e is approximately twice T_{CR}. For small D, the system exhibits no response. Irregular firings appear for D above a certain value [Fig. 4(a)] and around $D=450$ mV, the oscillation becomes

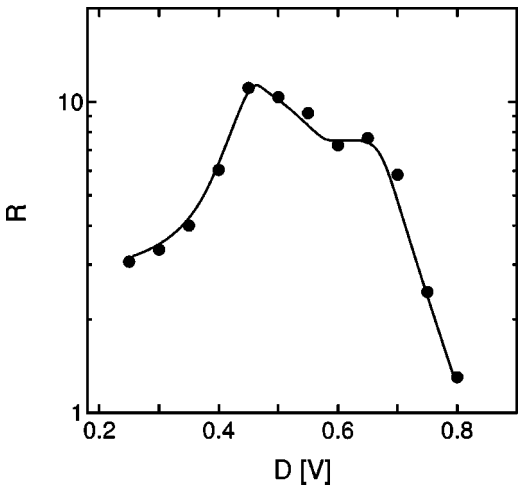

FIG. 3. Coherence measure as a function of the noise amplitude for $T_e=70$ s and $I=10$ mW. The solid line is drawn to guide the eye.

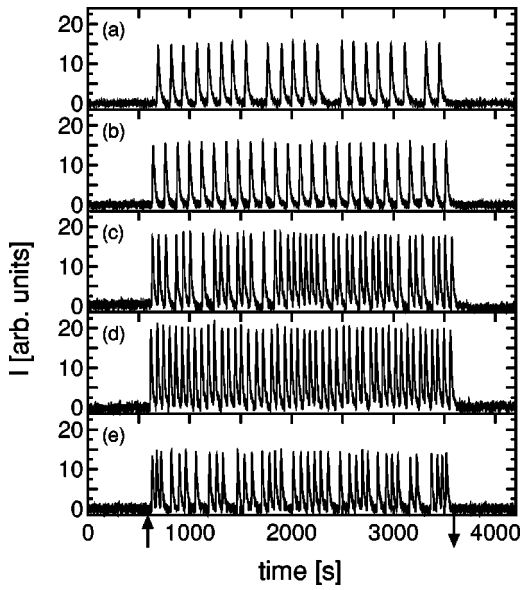

FIG. 4. Time series of the light intensity from the chemical oscillator as a function of the noise amplitude D for $T_e=120$ s and $I=10$ mW: (a) $D=300$ mV, (b) $D=450$ mV, (c) $D=600$ mV, (d) $D=700$ mV, and (e) $D=800$ mV. Upward and downward arrows indicate the time at which the electric field was turned on and off, respectively.

almost regular [Fig. 4(b)]. Its period coincides with the forcing period. For further increase in D, the oscillation becomes irregular once [Fig. 4(c)], but near $D=700$ mV, the regular oscillation appears again with the period of 60 s [Fig. 4(d)]. This value is just half the forcing period. With further increasing D, firing becomes irregular again, accompanied by the decrease of the firing rate [Fig. 4(e)]. Figure 5 shows the coherence measure R as a function of D. In this case, we find two distinct maxima with respect to the noise amplitude. One results from the regular oscillation with the period of 120 s and the other one from the regular oscillation with the period of 60 s. Thus in either case, there are always two optimal

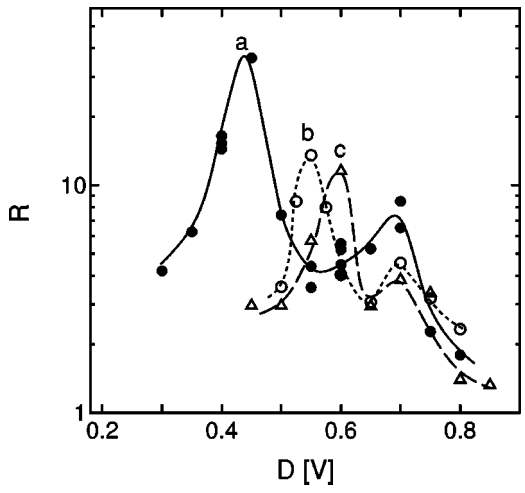

FIG. 5. Coherence measure as a function of the noise amplitude for $T_e=120$ s under the illuminated light intensity of 10 mW (a), 20 mW (b), and 30 mW (c). Lines are drawn to guide the eye.

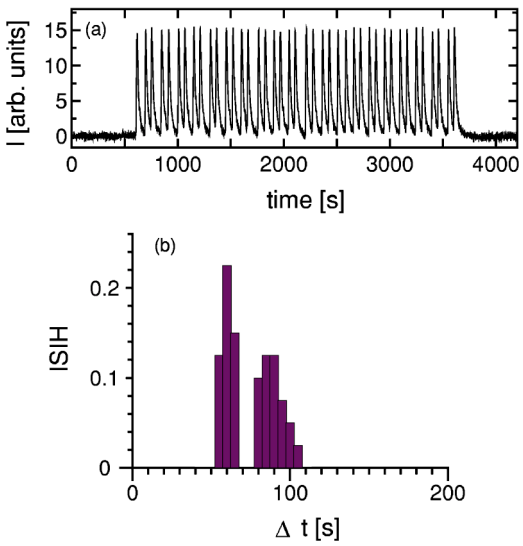

FIG. 6. Time series of the light intensity from the chemical oscillator (a) and the ISI histogram (b) at the optimal noise level for $T_e=150$ s and $I=10$ mW.

noise amplitudes, D_{opt1} and D_{opt2} ($D_{\mathrm{opt1}}<D_{\mathrm{opt2}}$) which maximize R. It is worth mentioning that the addition of a large amount of noise can induce the regular oscillation with the period different from T_e, while in the noise-free case the period of induced regular oscillation is always equal to T_e even if V_e is increased, as seen in Fig. 1.

Let us discuss the origin of two maxima in the R-D curve. The coherent oscillation induced at D_{opt1} has always the same period as the forcing period. This resonance is just characterized as an enhancement of a subthreshold periodic signal, so that it is considered to be conventional SR. In contrast, the coherent oscillation induced at D_{opt2} has the period close to T_{CR}. In addition, the value of D_{opt2} is approximately close to the optimal noise amplitude for coherence resonance in the signal-free case reported in Ref. [24]. From these results, it is reasonable to suppose that a noise-induced oscillator, i.e., a CR oscillator, is excited near D_{opt2}. Such a CR oscillator should interact with either the periodic forcing or the SR oscillator already induced near D_{opt1}. In the case of a deterministic self-sustained oscillator, periodic forcing with a sufficiently large amplitude induces $n{:}m$ phase locking pattern with m firings for n forcing periods. From the viewpoint of phase locking, the response patterns observed at D_{opt2} can be interpreted as stochastic versions of phase locking, such as 1:1 for $T_e=70$ s and 1:2 for $T_e=120$ s. Then, the CR oscillator adjusts its own period T_{CR} to attain some kind of phase locking, such as a deterministic oscillator. In order to justify this interpretation, the case of $T_e=150$ s was checked. Figure 6 shows the time series of the most regular oscillation corresponding to the second resonance. One can see that the two kinds of time intervals, 60 s and 90 s, appear alternately, corresponding to T_{CR} and T_e-T_{CR}, respectively. It is evident from the interspike interval histogram (ISIH) that two firings for one forcing period, namely, 1:2 entrainment occurs. It is interesting to notice that a noise-induced oscillator shows resonance behaviors similar to those observed in deterministic oscillatory systems.

We used a light-induced excitable medium and an electric stimulation in this experiment. We checked how resonance patterns vary with increasing the illuminated light intensity I beyond the bifurcation point I_c. As shown in Fig. 5, there still exist two maxima in the R-D curve for the illuminated light intensity up to about three times I_c. With increasing I, D_{opt1} proportionally increases, while D_{opt2} hardly varies. This result is consistent with our proposal that the CR oscillator takes part in the occurrence of the second resonance. The resonance peak became lower with increasing I and no resonance was observed under extremely intense illumination.

In conclusion, we have experimentally investigated the response of the excitable BZ chemical reaction system to a periodic electric field in the presence of noise. The results have been analyzed by using R, the reciprocal of the standard deviation of time intervals between successive firing events. We have found that R reveals two maxima with respect to the noise amplitude. One corresponds to conventional stochastic resonance, in which the regular oscillation appears with the period equal to the forcing period. The other results from the interaction between the noise-induced oscillator and the external periodic forcing, in which the regular oscillation appears in a characteristic fashion, such as 1:1 and 1:2 phase locking observed in deterministic oscillators, depending on the forcing period. It follows from this that the coherence resonance oscillator behaves like a deterministic oscillator, and its period is robust for variations in the forcing period and excitability.

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