Experimental observation of coherence resonance in an excitable chemical reaction system

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Dynamics of an excitable Belousov-Zabotinsky reaction system under an external noise are investigated using cation exchange beads loaded with the cationic catalyst. When a noise amplitude is increased above a certain value, an oscillatory state appears. It is shown that the coherence of these noise-excited oscillations is maximal for a suitable value of the noise amplitude. This phenomenon is characterized by using various statistical measures, such as the signal-to-noise ratio in the power spectrum, the correlation time of the noise-excited oscillation, and the standard deviation of time intervals between successive firing events. We find the experimental evidence that the period of coherent oscillation is determined by a characteristic time scale of the system.

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The dynamic response of nonlinear systems to external noise has been extensively investigated. Of particular interest is the phenomenon of stochastic resonance (SR), arising when a certain amount of noise is superimposed on a subthreshold signal [1–5]. This phenomenon, which is characterized as the enhancement of the response to a weak input signal, has been observed in many nonlinear systems such as an excitable or a bistable system. Recently, it has been shown that, even in the system which no external periodic forcing was assumed in contrast to the usual setup of SR, noise can be helpful in inducing a coherent behavior [6–8]. Pikovsky and Kurths showed that the correlation time of the noise-induced oscillation is maximal for a certain noise amplitude, using the excitable FitzHugh-Nagumo system [8]. This SR-like behavior was named coherence resonance (CR), which was also called autonomous SR [6,9] or internal signal SR [10]. The similar phenomenon was recently found also in a bistable system [11]. The most striking characteristic of CR is that a time scale of induced oscillations is determined not by an external modulation as in stochastic resonance but by an intrinsic dynamics of the system. Experimental observation of CR was reported on the excitable system using a monovibrator circuit [12] and an optical system using a laser diode [13]. To our knowledge, however, an experimental evidence of the involvement of intrinsic dynamics in the induction of CR has never been shown explicitly.

In this paper, we experimentally investigate the response of an excitable chemical oscillator to noise in the electric field. We use a discrete type of the Belousov-Zabotinsky (BZ) reaction system [14,15], in which the tris-(2,2'-bipyridine) ruthenium (II) complex, $Ru(bpy)_3^{2+}$, is immobilized in the cation exchange beads of a submillimeter size. Then the excitable steady state is realized by utilizing the photosensitivity of $Ru(bpy)_3^{2+}$. We find the phenomenon of CR and show the evidence that the CR is deeply related to intrinsic dynamics of the system.

Electric fields are known to exhibit pronounced effects on dynamic behaviors of chemical waves [16–19]. Sensitive responses to electric fields are related to the fact that most chemical species relevant to wave propagation are ionic. 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. The initial composition of the BZ reaction solution was $[NaBrO_3]=0.36$ M, $[NaBr]=0.044$ M, $[CH_2(COOH)_2]=0.21$ M, $[H_2SO_4]=0.65$ M. Reagent grade chemicals were used without further purification. The cation exchange beads of about 0.5 mm in diameter were loaded with a $Ru(bpy)_3^{2+}$ solution of $[Ru(bpy)_3^{2+}]=2.0\times10^{-5}$ mol/g beads. When the $Ru(bpy)_3^{2+}$-loaded beads were suspended in the BZ solution, the redox reaction with a limit cycle appeared on the surface of the beads after the elapse of a certain time. The color change due to the redox reaction was transformed into the change in light intensity by the imaging system. The temperature of the BZ solution was maintained at $24\pm0.5\,^{\circ}$C. The photoinhibition or photoinduction of the oscillation is known to occur depending on the initial composition of the BZ solution, because the catalyst $Ru(bpy)_3^{2+}$ is photosensitive [20]. In the present system, the effect of the photoinhibition was observed, as shown in Fig. 1. One can see that the period of oscillation increases monotonously with increasing the intensity of illuminated light, and finally the excitable steady state appears above about 9 mW. The period under the dark was obtained as $T_0=63$ s by a best curve fitting to the data. This value is considered to be the period of the intrinsic oscillation in the present system. The Hopf bifurcation is generally subcritical for the light flux. We selected the excitable steady state near the Hopf bifurcation point for the study of the CR effect. The added noise is represented by $D\xi_\delta(t)$, where D is the amplitude, and $\xi_\delta(t)$ are random numbers equally distributed between -1 and 1 with the duration time δ.

Figure 2 shows the dependence of the temporal behaviors of the light intensity from the BZ oscillator on the level of input noise, where we chose the duration time of $\delta=0.225$ s and the illuminated light intensity of 10.0 mW. For a small noise amplitude, the system exhibits no response [Fig. 2(a)]. When the noise amplitude is increased above

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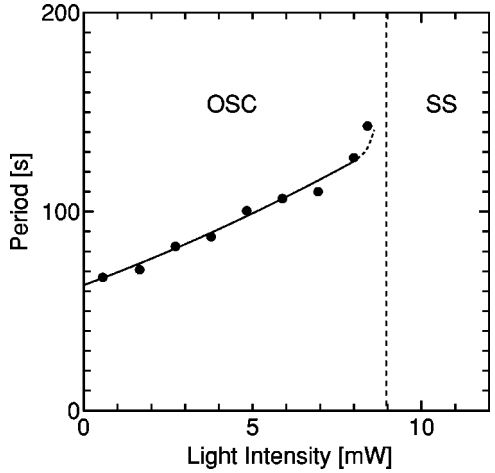

FIG. 1. Period of chemical oscillation as a function of intensity of illuminated light. The dash line divides the region into the oscillatory state (OSC) and the excitable steady state (SS).

about 400 mV, the oscillation, though irregular, appears abruptly [Fig. 2(b)]. When the electric field is turned off, the system is entirely restored to the excitable steady state. For suitable values of the noise amplitude, the oscillation becomes almost periodic [Fig. 2(c)]. When the noise amplitude is further increased, the oscillation becomes irregular again, accompanied by the decrease of the firing rate [Fig. 2(d)]. These behaviors are characterized by the power spectra of time series shown in Fig. 3. The spectrum corresponding to

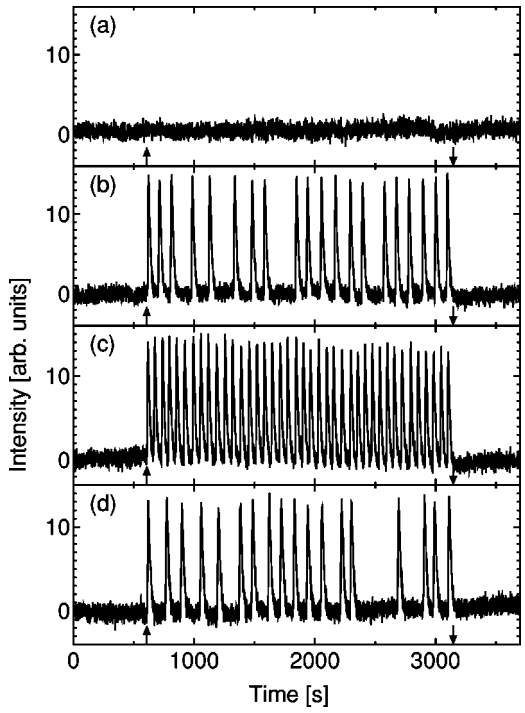

FIG. 2. Time series of the light intensity from the chemical oscillator as a function of the noise amplitude D: (a) $D=350$ mV, (b) $D=600$ mV, (c) $D=750$ mV, and (d) $D=900$ mV. Upward and downward arrows indicate the time at which the electric field was turned on and off, respectively.

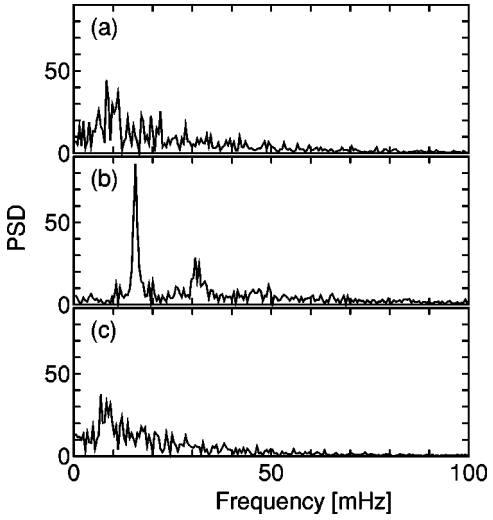

FIG. 3. Power spectral densities (PSD) of the time series in Fig. 2. Here (a), (b), and (c) correspond to (b), (c), and (d) in Fig. 2, respectively.

Fig. 2(c) exhibits a higher and narrower peak at a higher frequency than those of Figs. 2(b) and 2(d). It should be noted that the peak frequency of the most regular oscillation completely coincides with the natural frequency under the dark, namely, $f_0=1/T_0=15.9$ mHz. This suggests that a coherent oscillation occurs around the moderate noise level, and its period is determined by a time scale of the intrinsic dynamics of the system. With an increase in the noise amplitude, the principal peak frequency ω_p of the power spectra increases until a maximum is reached, and then decreases. This behavior is inconsistent with the results reported earlier [8,12,13], in which ω_p increases monotonously with increasing the noise amplitude. To characterize the noise-induced coherent behavior observed in the power spectra, we calculate the factor $\beta=h/(\Delta\omega/\omega_p)^{-1}$ as defined in Ref. [6], where h is the peak height normalized to the noise background at ω_p, $\Delta\omega$ is the width of the peak at half-maximum height, and thus $\Delta\omega/\omega_p$ is the relative width of the peak and its reciprocal corresponds to the quality factor Q of a signal. Therefore, β represents the degree of the coherence. Figure 4 shows the dependence of β on the noise amplitude. One can see that β passes through a maximum at $D_{opt}=770$ mV with an increase in D. To further characterize the coherent behavior, we introduce other quantities. One is the normalized autocorrelation function $C(\tau)$ defined by

$$C(\tau)=\frac{\langle\tilde{I}(t)\tilde{I}(t+\tau)\rangle}{\langle\tilde{I}^2\rangle}, \tag{1}$$

where $I(t)$ is the light intensity from the BZ oscillator, τ is the delay time, and $\tilde{I}(t)=I(t)-\langle I\rangle$. All the calculated correlation functions show underdamped oscillations, but their damping constants are much smaller for the moderate noise level. The characteristic correlation time is then evaluated as $\tau_c=\int_0^\infty C^2(\tau)d\tau$, following Pikovsky *et al.* [8]. In limited and discrete sampling as in the present case, τ_c is evaluated by

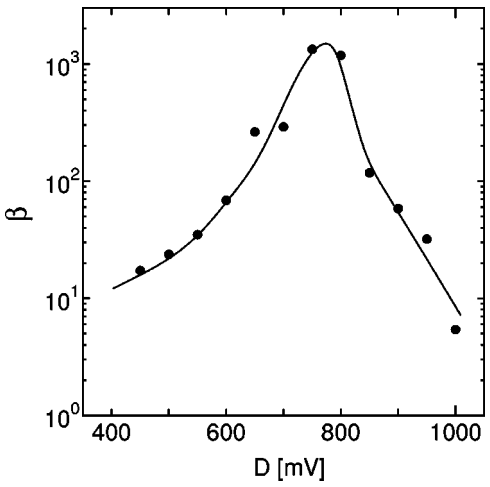

FIG. 4. Degree of the coherence $\beta = h(\Delta\omega/\omega_p)^{-1}$ as a function of the noise amplitude. The solid line is drawn to guide the eye.

$$\tau_c = \sum_{k=1}^{N} C^2(\tau_k)\Delta t, \tag{2}$$

where $\tau_k = k\Delta t$ with Δt being the sampling time, and N is the longest delay-time number with delay-time increment Δt. Figure 5 shows the dependence of τ_c on the noise amplitude D. The τ_c-D curve clearly shows the coherence resonance maximum at D_{opt}.

A time interval between successive firing events T, namely, the instantaneous period, fluctuates depending on the noise level, as seen from Fig. 2. Further confirmation of CR is achieved by evaluating these fluctuations. Then we calculate R_θ, the standard deviation of the normalized time interval $\theta = T/\langle T\rangle$, $\langle T\rangle$ being an average value of T. In Fig. 6(a), R_θ is plotted as a function of the noise amplitude. The minimum is clearly observable at D_{opt}, thus evidencing that there always exists the optimal noise amplitude that induces the most regular oscillation. When a noise with a longer duration time $\delta = 0.625$ s was chosen, the optimal noise amplitude

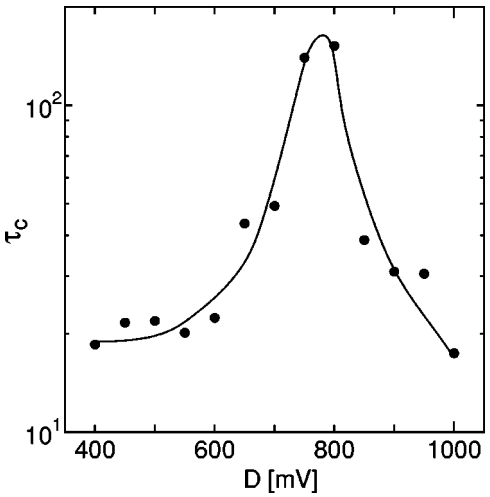

FIG. 5. Correlation time of noise-induced oscillations as a function of the noise amplitude. The solid line is drawn to guide the eye.

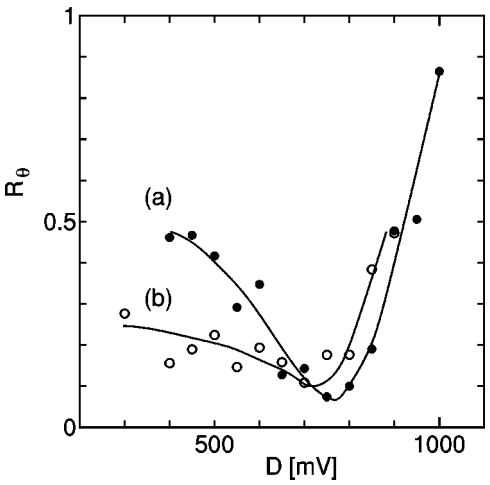

FIG. 6. Standard deviation of the normalized time interval as a function of the noise amplitude: (a) noise pulse length $\tau = 0.225$ s and (b) $\tau = 0.625$ s. Solid lines are drawn to guide the eye.

was shifted to the lower value, $D = 720$ mV, as shown in Fig. 6(b). Nevertheless, the period of the most regular oscillation was equal to that in the case of $\delta = 0.225$ s, i.e., 63 s. This confirms the participation of the intrinsic dynamics in the occurrence of CR. The δ dependence of the optimal noise amplitude has been also observed in the stochastic resonance in the photosensitive BZ reaction system [21]. The phenomenon of CR was not observed for extremely large or small δ.

We checked how the excitability and coherence resonance properties vary with increasing illuminated light intensity beyond the bifurcation point. The phenomenon of CR was still observed for an increase in illuminated light intensity up to about five times; the optimal noise amplitude hardly varied, but the resonance peak became lower with increasing the light intensity. In addition, the average period of induced regular oscillation remained almost equal to the period T_0 under the dark. For extremely intense illumination, however, no resonance was observed. Further detail work is in progress.

The time interval is described by the sum of two characteristic times: an activation time t_a and an excursion time t_e. Those times have the different sensitivity to noise, which is considered to be responsible for the occurrence of CR. The excursion time is almost independent of the noise amplitude and has the role of a refractory time during which next firing cannot spontaneously occur. In contrast, t_a generally decreases with the noise amplitude according to the Kramers formula [22]. Hence, the average value of the time interval $\langle T\rangle$ is expected to decrease with increasing the noise amplitude. Such an expected behavior has been observed in both the numerical simulation and experiments [8,12,13]. However, this is not the case for the present experiment; $\langle T\rangle$ increases for increasing the noise amplitude beyond the optimal value, as shown in Fig. 3. Thus, it seems that the appearance of CR is deeply related to the nature of the excitable system. According to the Field, Körös, and Noyes mechanism, sensitive responses to electric fields are mainly related to a field-induced transport of the inhibitor Br^-. Such an additional flux of Br^- is proportional to the ionic mobility

of Br^- that depends on the diffusion coefficient. Strong noise electric field with $D > D_{opt}$ forces the rapid change in the transport direction of Br^-. However, Br^- cannot diffuse in response to such a rapid change because of the finite diffusion coefficient of Br^-. As a result, a field-induced redistribution of Br^- would likely be incomplete. This may account for the unexpected behaviors of ω_p in Fig. 3, namely, the decrease in ω_p for increasing D above D_{opt}.

In conclusion, we have experimentally investigated effects of an external noise electric field on the excitable BZ chemical reaction system. We have shown the existence of coherence resonance by using various statistical quantities: the signal-to-noise ratio β in the power spectrum, the correlation time of the noise-excited oscillation, and the standard deviation of time intervals between successive firing events. We have demonstrated that, at an optimal noise level, the period of coherent oscillation is determined by the time scale of the intrinsic dynamics of the system and not by an external periodic signal as in stochastic resonance. The present system, which is controlled by two independent bifurcation parameters, seems useful for the study of different types of noise-induced enhancement of the temporal regularity. Recently, the phenomenon of noise-enhanced synchronization has been observed in the BZ system similar to the present one [23].

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