Experimental Observation of Internal Signal Stochastic Resonance in the Belousov−Zhabotinsky Reaction

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We show experimentally the phenomenon of internal signal stochastic resonance in the Belousov−Zhabotinsky reaction without external signal. The chemical reaction is placed in an excitable state near a Hopf bifurcation in a CSTR. When the flow rate is perturbed by stochastic noise, noise-induced oscillations are observed, and two closely spaced, large-amplitude spikes appear nearly periodically at the proper noise level. More importantly, analysis from the power spectra and interspike interval histogram of the time series output, the coherence of these noise-induced oscillations, is maximal at an optimal noise intensity, indicating the occurrence of internal signal stochastic resonance.

1. Introduction

The phenomenon of stochastic resonance (SR) has continuously attracted considerable attention in different fields of science.[1−11] Typical SR is the result of the cooperative effect of noise and an external periodic signal acting upon a nonlinear system such as a bistable or an excitable system in such a way that the response of the system to the weak external signal is greatly enhanced for a certain value of the noise strength.

In studying SR, the signal is adopted generally as an external input modulation of a nonlinear system. However, very recently, it has been shown that SR-like behavior can occur in the absence of an external signal as a consequence of the intrinsic dynamic of the nonlinear system driven by noise,[12−18] in which the external signal is repalced by an "internal signal": the deterministic oscillations of the system. The dynamical system is placed in a steady state near a saddle-node bifurcation[12,13] or Hopf bifurcation,[14−16] where the deterministic oscillation is absent. When the control parameter is randomly modulated driven by noise, noise-induced coherent oscillations (NICO) appear. Due to the nonuniformity of the noise-induced oscillations, the signal-to-noise ratio (SNR) and other quality factors go through a maximum with the increment of noise intensity, showing the characteristic of SR. We call this phenomenon internal signal stochastic resonance (ISSR). Contrary to the usual SR, ISSR appears as a response of a nonlinear system to purely noisy excitation and no external periodic force is assumed.

Although numerous numerical simulations on this phenomenon exist,[12−17] there are few experimental observations except that very recently D. E. Postnov et al. reported their experiment using a monovibrator circuit.[18] In the present work, we confirm the phenomenon of ISSR in the Belousov−Zhabotinsky (BZ) reaction without external signal experimentally. When an excitable state of the system close to a Hopf bifurcation at a flow rate is imposed on the flow rate of reactants into the reactor with stochastic noise and a threshold is crossed, noise-induced large-amplitude oscillations are observed. The coherence of the these noise-induced oscillations, estimated from the power spectra and interspike histogram of the time series output, is maximal at an optimal noise intensity, and internal signal stochastic resonance occurs in the BZ reaction.

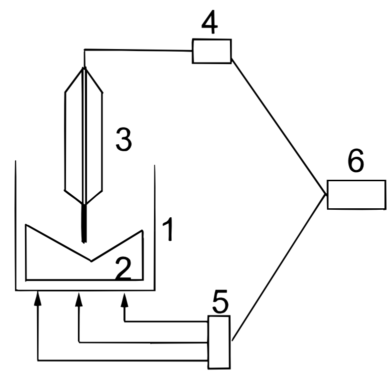

Figure 1. CSTR (3.4 mL volume): 1, reactor; 2, unsymmetric Teflon stirrer; 3, Pt/Ag/AgCl redox electrode; 4, ion analyer; 5, syringe pump; 6, computer. The flow rate of the three feed lines is varied by stochastic noise.

2. Experimental Section

Materials. All the reagents were of analytical grade and used without further purification.

The chemical system was composed of malonic acid, sulfuric acid, cerous sulfate, and potassium bromate. The water was purified by ion exchange (water purification system Milli-Q, Millipore.). All solutions were equilibrated with air.

Reactor. The experimental setup is shown in Figure 1. A CSTR of 3.4 mL volume is used. The real reaction volume is about 1.98 mL. The volume of an unsymmetric magnetic stirrer is about 1 mL. The state of the system was monitored by a MA235 ion analyer (Mettler Toledo) with a Pt/Ag/AgCl

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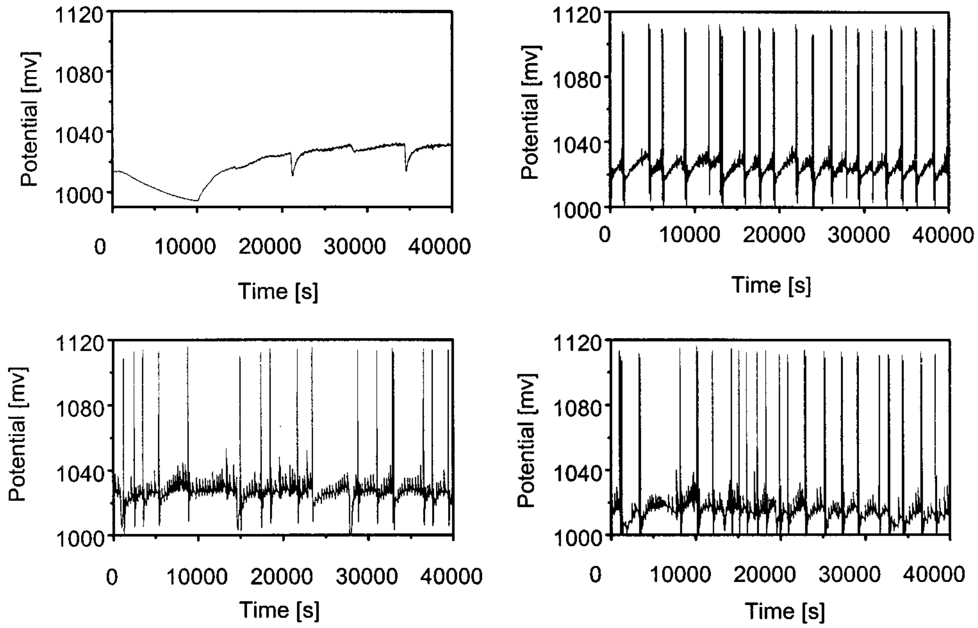

Figure 2. Experimental time series of 40 000 s. (a, top left) Time series with noise intensity $\beta = 0$. (b, bottom left) Time series with $\beta = 0.012$ showing some noise-induced bursts. (c, top right) Time series with $\beta = 0.09$ at the optimal signal-to-noise ratio. (d, bottom right) Time series with $\beta = 0.18$ above the optimal noise intensity.

reference electrode. The data of the electrode signal was collected via the Software Wedge (Mettler Toledo) at a rate of 0.5 Hz. The reactor is fed with a multichannel syringe pump (Cole. Parmer), which is driven by a computer via a DA converter. We used three gastight syringes (Hamilton) containing the reactant solutions with the following concentrations:

syringe 1: 0.14 M $KBrO_3$

syringe 2: 0.002 M Ce^{3+} from $Ce_2(SO_4)_3$, 0.3 M malonic acid

syringe 3: 1.0 M H_2SO_4

The experiments are carried out at a temperature of 25.0 °C and a stirring rate of 1360 rpm. The real reaction volume and stirring rate affect the experiments.

Modulation of the Flow Rate. We choose a constant flow rate of $k_f{}^\circ = 1.20 \times 10^{-2}$ mL/m ($t = 55$ min) near the Hopf bifurcation (about $k_f = 1.21 \times 10^{-2}$ mL/m), producing an excitable state. A stochastic noise with a constant delay τ is imposed on the flow rate by a computer. Equation 1 shows the total variation imposed in the flow rate. β is the noise amplitude.

$$k_f = k_f{}^\circ(1 + \beta\xi(t)) \quad (1)$$

$\xi(t) = \sum_{j=0}^{\infty}\xi_j\Gamma(t - j\tau)$, where j is an integer and $\Gamma(x) = 1$ for $0 \le x < \tau$ and 0 otherwise; ξ_j are equally distributed random numbers between 0 and 1.[19] In our study, the delay time $\tau = 2$ s; i.e., k_f is changed once every 2 s for all experiments.

3. Results

The BZ reaction was run in an excitable state near the Hopf bifurcation at a constant flow rate of $k_f{}^\circ = 1.20 \times 10^{-2}$ mL/m (Figure 2a). After at least two residence times have elapsed, a stochastic modulation was imposed. When a slight level of external noise ($\beta = 0.012$) was added, noise helped the control parameter crossing the threshold point into the oscillation region, so noise-induced large-amplitude oscillations started (Figure 2b), When the noise amplitude increased, the number of single spikes decreased and the number of two closely spaced cycles increased. Figure 2c shows a time series obtained at the maximum of the stochastic resonance at the noise amplitude ($\beta = 0.09$),

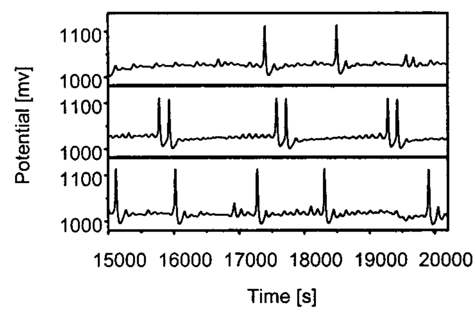

Figure 3. A section of the experimental time series (for better viewing). (top) Noise-induced single spike at $\beta = 0.012$. (middle) Noise induced the two closely spaced spikes at $\beta = 0.09$. (bottom) Noise-induced bursts at $\beta = 0.18$.

and the bursts mainly consist of two spaced spikes per oscillation. The intervals between the two spikes are about from 120 to 160 s. Figure 2d shows a time series at $\beta = 0.18$ above the optimal value of the noise, where the oscillations of two spikes have decreased. Figure 3 gives the section of these time series for better viewing. These results show that both small and large noise-induced oscillations appear to be rather irregular, while for moderate noise relatively regular coherent oscillations are observed (the excursion time to activation time ratio is about 1/10 at the optimal noise level $\beta = 0.09$).

It is interesting to see the influence of noise intensity on the features of averaged power spectra. An example of the Fourier spectra of three individual time series output is given (Figure 4). For small noise, the broad peak at high frequency in the power spectrum can be observed (Figure 4, curve 1). For a higher noise amplitude $\beta = 0.09$, the highest peak shifts to lower frequency become relatively high, and higher harmonics appear in the power spectrum (Figure 4, curve 2). Notice that the features of power spectra in ISSR are different from those in SR. First, the fundamental frequency in each spectrum corresponding to the highest peak is closed to the inherent frequency of the deterministic oscillations in ISSR, but the fundamental frequency in SR is equal to the frequency of the external periodic signal. Second, the peaks in each spectrum are noise-expanded

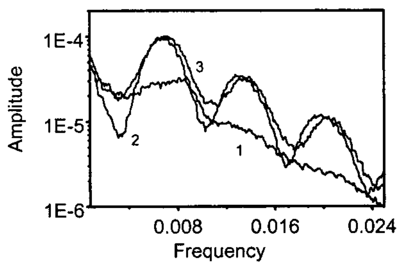

Figure 4. Average power spectra (curves 1, 2, and 3 correspond to $\beta = 0.012$, 0.09, and 0.18, respectively).

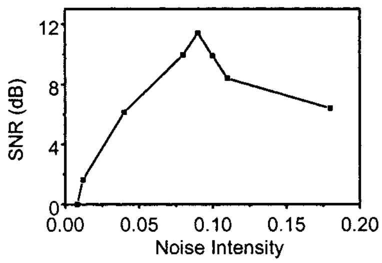

Figure 5. SNR as the function of noise level. The signal-to-noise ratio passes through a maximum at approximately $\beta = 0.09$.

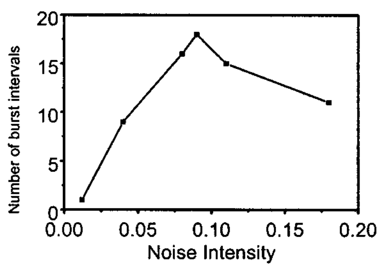

Figure 6. Interspike histogram curve: number of burst intervals occurring from 120 to 160 s versus the noise intensity (maximum at approximately $\beta = 0.09$).

peaks in ISSR, but the peaks in SR are δ-peaks. At a too high noise level, we can see that the highest peak is absorbed by the increasing level of noise background (Figure 4, curve 3). To analyze the function of the noise-induced coherent oscillations with noise intensity, we can calculate the signal-to-noise ratio (SNR) as proposed in ref 17. The SNR curve clearly shows a SR maximum in Figure 5.

The number of burst intervals occurring between 120 and 160 s as a function of the noise is shown in Figure 6. A maximum value is found at the same noise amplitude $\beta = 0.09$ as the curve of SNR.

4. Discussion

In our experiment, noise-induced oscillations have been found, and two closely spaced, large-amplitude spikes appear nearly periodically at the proper noise level. More importantly, we reported a new stochastic resonance-like behavior, i.e., internal signal stochastic resonance purely driven by noise in the absence of external signal in the BZ reaction.

The reason for the NICO and ISSR is physically clear. In our system, noise plays a 2-fold role. On the one hand, it stimulates coherent oscillations of the system. For a weak noise, the control parameter does not reach the oscillation region and rarely bursts. With increasing noise intensity, noise draws the control parameter crossing the threshold point and noise-induced oscillations appear. At a much larger noise, the system speeds more time in the oscillation region which makes the noise-induced oscillations more coherent. On the other hand, with increasing noise level, noise also naturally spoils the coherent motion activated by itself, leading to the well-known effect of amplitude and phase fluctuations. With the competition of these two tendencies, a resonance-like behavior occurs at an optimal noise, i.e., manifestation of the ISSR. From the Figures 2 and 3, ISSR is the result of an optimal balance between the two characteristic times of the excitable system: the activation time and excursion time as shown in the literature.[15,18]

Since external stochastic noise is unavoidable, we believe the ISSR behavior is a constructive effect of noise, which may be important in both nature and technology.

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