Noise-induced oscillation and stochastic resonance in an autonomous chemical reaction system

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An autonomous three-variable chemical reaction model, which has been developed to describe kinetic oscillations in the NO+CO reaction, subjected to external parametric noise, is investigated. Noise-induced coherent oscillations (NICO's) in the absence of deterministic oscillations are observed near supercritical Hopf bifurcation points, and the NICO strength goes through a maximum with increments of noise intensity, characteristic of the occurrence of stochastic resonance. On the other hand, these phenomena do not appear if the limit cycle is created by a saddle-loop bifurcation. [S1063-651X(99)07511-X]

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I. INTRODUCTION

The phenomenon of stochastic resonance (SR) has been extensively studied in the past decades [1]. Since it was originally proposed to account for the periodic oscillation of the Earth's ice ages [2], more and more scientists, the majority from biology, physics, and chemistry [3], have paid considerable attention to the rather ''counterintuitive'' phenomenon that noise with suitable intensity can increase the detectability of a weak input signal to a nonlinear system: the signal-to-noise ratio goes through a maximum with the variation of the noise intensity. The original model of SR included a symmetry bistable system, a weak input periodic signal, and additive external Gaussian white noise [4]. With the development of its application, however, the concept of SR has been widely extended. For example, the nonlinear system can be monostable [5], excitable [6], threshold free [7], spatially extended [8], etc; the input signal can be aperiodic or even chaotic [9]; and the noise can be colored, multiplicative or even be the intrinsic randomness of a deterministic chaotic system [10].

Very recently, Gang *et al.* [11] proposed that the external signal can also be replaced by an ''internal signal,'' such as periodic oscillation in a deterministic system. When the control parameter is located near the bifurcation point between a stable node and a limit cycle, where the deterministic steady state is the stable node, noise induced coherent oscillation (NICO) is found, and the strength of the NICO reaches a maximum with increments of the noise intensity, showing the characteristic of SR, a phenomenon which here we call *internal signal stochastic resonance* (ISSR). Soon later, Rappel and Stroget [12] presented a simple numerical analysis which suggested that these effects were simple consequences of the nonuniformity of the motion along the limit cycle. They finally proposed that the mechanism of the creation of a limit cycle in this system is an infinite-period bifurcation, and stated that ''one would not expect to find this type of stochastic resonance in systems whose oscillations are created by Hopf bifurcations.'' Now a straightforward question arises: is this assertation a universal criterion, or just applicable to the specific model?

In the present work, we have adopted a chemical catalytic reaction system, the NO+CO catalytic reduction system, to study the NICO and henceforth ISSR behavior. We prefer a chemical reaction system rather than the mathematical dynamic model proposed in textbooks because of its realistic application and abundant bifurcation character. For the system under consideration here, for example, kinetic oscillations are observed which can be created via supercritical Hopf bifurcation or saddle-loop (SL) bifurcation. So it has provided an appropriate model for us to determine what on Earth plays the key role in generating NICO and ISSR behaviors. According to the present work, we found that NICO and ISSR also exist near Hopf bifurcation, but they do not appear near the SL bifurcation, which is counterexample to Rappel and Stroget's assertation. Our work implies that bifurcation character may play an important role in the observed dynamics in the presence of external noise.

II. MODEL AND RESULTS

The catalytic reduction of NO with CO on Pt(100) has been extensively studied both experimentally and theoretically. Many interesting dynamical phenomena have been observed, including kinetic oscillation, chaos, and pattern formation [13–17]. The reaction is assumed to process via the molecular dissociation of NO on the surface as the rate-limiting step, which is followed by the reaction of an oxygen atom with adsorbed CO to form CO_2 and the recombination of nitrogen atoms to form N_2 as follows:

$$\mathrm{CO}+{*}\rightleftharpoons \mathrm{CO}_a, \tag{1a}$$

$$\mathrm{NO}+{*}\rightleftharpoons \mathrm{NO}_a, \tag{1b}$$

$$\mathrm{NO}_a+{*}\rightarrow \mathrm{N}_a+\mathrm{O}_a, \tag{1c}$$

$$2\mathrm{N}_a\rightarrow \mathrm{N}_2+2{*}, \tag{1d}$$

$$\mathrm{CO}_a+\mathrm{O}_a\rightarrow \mathrm{CO}_2+2{*}. \tag{1e}$$

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where the asterisk and a denote a free adsorption site and an adsorbed species, respectively. Following Ref. [17], the rate equations for the three adsorbate coverages: θ_{CO}, θ_{NO} and θ_{O} read

$$\frac{d\theta_{\mathrm{CO}}}{dt}=k_1 p_{\mathrm{CO}}(1-\theta_{\mathrm{CO}}-\theta_{\mathrm{NO}})-k_2\theta_{\mathrm{CO}}-k_3\theta_{\mathrm{CO}}\theta_{\mathrm{O}}, \tag{2a}$$

$$\frac{d\theta_{\mathrm{NO}}}{dt}=k_1 p_{\mathrm{NO}}(1-\theta_{\mathrm{CO}}-\theta_{\mathrm{NO}})-k_4\theta_{\mathrm{NO}}-k_5\theta_{\mathrm{NO}}\theta_{\mathrm{empty}}, \tag{2b}$$

$$\frac{d\theta_{\mathrm{O}}}{dt}=k_5\theta_{\mathrm{NO}}\theta_{\mathrm{empty}}-k_3\theta_{\mathrm{CO}}\theta_{\mathrm{O}}, \tag{2c}$$

with

$$\theta_{\mathrm{empty}}=\max\left[\left(1-\frac{\theta_{\mathrm{CO}}+\theta_{\mathrm{NO}}}{\theta_{\mathrm{CO,NO}}^{\mathrm{inh}}}-\frac{\theta_{\mathrm{O}}}{\theta_{\mathrm{O}}^{\mathrm{inh}}},0\right)\right].$$

These equations describe the adsorption and desorption of NO and CO (k_1, k_2, and k_4), the dessociation of NO (k_5), and the surface reaction between O_a and $\mathrm{CO}_a(k_3)$. The number of empty sites, θ_{empty}, depends on the NO, CO, and oxygen coverages. If they exceed certain values, $\theta_{\mathrm{NO,CO}}^{\mathrm{inh}}$ and $\theta_{\mathrm{O}}^{\mathrm{inh}}$, no free sites are available and NO dissociation is inhibited. The various constants, which depend on temperature via Arrhenius law $k_i=\nu_i\exp(-E_i/RT)$, are all taken from experiments. Notice that the activation energy for NO and CO desorption, $E_{\mathrm{act}}^{\mathrm{NO,\,CO}}$, decrease with increasing coverage due to repulsive interactions:

$$E_{\mathrm{act}}^{\mathrm{NO,\,CO}}(\theta)=E_{\mathrm{act}}^{\mathrm{NO,CO}}(0)-k_6(\theta_{\mathrm{NO}}+\theta_{\mathrm{CO}})^2,$$

which proves to be necessary for the occurrence of kinetic oscillation.

Figure 1 displays two typical local bifurcation diagrams concerning the creation of limit cycle of the model (see Ref. [17]). In Fig. 1(a), where the control parameter is p_{NO}, one observes two supercritical Hopf bifurcation points at $p_{\mathrm{NO}}\simeq 3.2255\times 10^{-7}$ mbar and 4.05×10^{-7} mbar, between which is the oscillation region. In Fig. 1(b), the control parameter is the temperature T and the oscillation begins with a Hopf bifurcation at $T\simeq 420.5$ K and ends with a SL bifurcation at $T=413$ K when T decreases. To study the noise-induced oscillation behavior, we choose the control parameter p_{NO}^0 or T_0 properly, such that it is quite close to the bifurcation point but the deterministic steady state is the stable node, and perturb it by noise: $p_{\mathrm{NO}}=p_{\mathrm{NO}}^0[1+2D\Gamma(t)]$ or $T=T_0[1+2D\Gamma(t)]$ [here D is the noise intensity, and $\Gamma(t)$ denotes the Gaussian white noise with zero mean value $\langle\Gamma(t)\rangle=0$ and unit variance $\Gamma(t)\Gamma(t')=\delta(t-t')$]. Now the rate equations change to stochastic differential euqations, and they can be simulated by a simple Eular forward procedure.

Now we will study the influence of noise on the observed dynamics near the Hopf bifurcation point $h1$ in Fig. 1(a), choosing $p_{\mathrm{NO}}^0=3.22\times 10^{-7}$ mbar. For $D\neq 0$, an obvious peak appears in the power spectrum of the times series $\theta_{\mathrm{NO}}(t)$, which indicates the occurrence of NICO. With increments of D the peak becomes higher and wider, and, if D is too large, the peak is annihilated into the noise background. This behavior is depicted in Fig. 2(a), where the power spectrum curves are obtained from averaging over 100 independent runs for each D. Interestingly, it seems that the variation tendency of the NICO strength with D shows the characteristic of SR. The relative NICO strength can be measured by h or $\beta=h/\Delta\omega$; here h is the peak height and $\Delta\omega$ the width of the peak at the height $h/2$. The variation of h and β with D are shown in Fig. 2(b), where both values go through a maximum, demonstrating the occurrence of ISSR. Notice that the maximum of $h-D$ curve lies at $D=3e-3$, and that of $\beta-D$ at $D=4e-4$, which is due to the faster increment of $\Delta\omega$ than that of h. We have also investigated the effect of parametric noise near the Hopf bifurcation points $h2$ and $h3$, and similar results were obtained. However when we perturbed the control parameter T near the SL bifurcation points shown in Fig. 1(b), we did not observe NICO behavior.

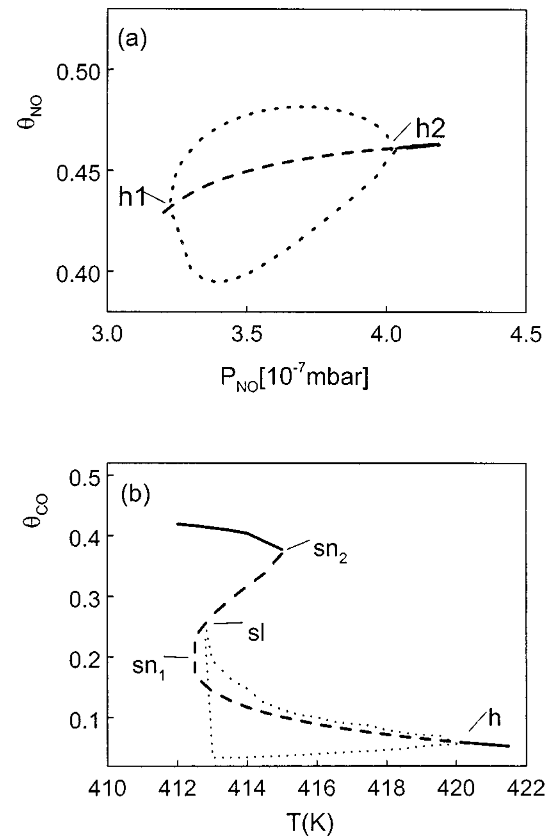

FIG. 1. Typical bifurcation diagrams for the NO+CO reduction system. Solid line: stable node; dashed line: unstable node or foci; dotted line: the amplitude of the oscillation. (a) $h1$ and $h2$: supercritical Hopf bifurcation. (b) sn1 and sn2: saddle-node bifurcation; sl: saddle-loop bifurcation; h; Hopf bifurcation.

III. DISCUSSION

In fact, the occurrence of NICO near the Hopf bifurcation points is not so surprising. Due to the perturbation of the control parameter, the system enters the oscillation region now and then, and therefore the deterministic limit cycle is

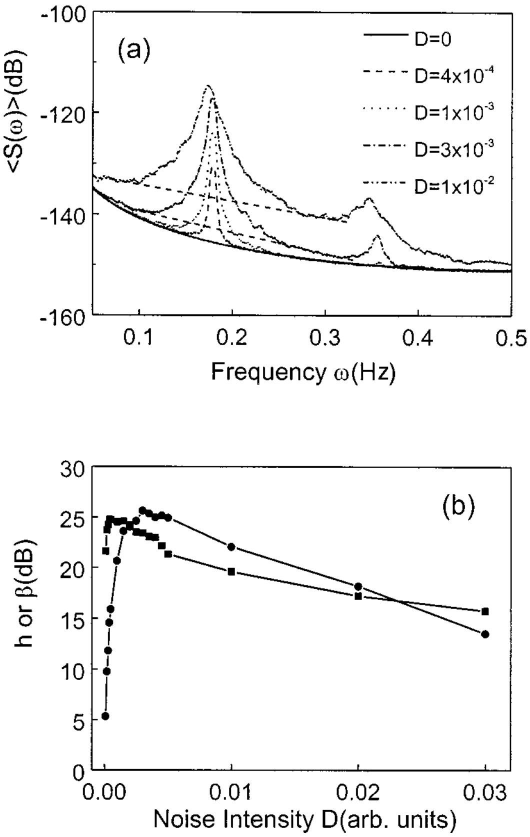

FIG. 2. The average power spectrum of the noise induced oscillation for different noise intensity. The dashed lines denote the baseline for large noise. (b) Dependence of the peak height h (circles) and β (squares) on the noise intensity near the Hopf bifurcation point $h1$. Stochastic resonance behavior is observed.

occasionally random modulated, resulting a Gaussian-expanded peak in the power spectrum. This disccusion can also help in understanding why the SL bifurcation point cannot lead to NICO. The key difference is that on the right side of the SL bifurcation point T_{sl}, two stable attractors, the upper stable node and the stable limit cycle, coexist. Which state the system finally reaches depends on the initial conditions. So, when the control parameter T is perturbed into the right side of T_{sl}, oscillation *surely does not* occur such that one cannot observe NICO. According to this discussion, one expects that the structure of the bifurcation diagram plays an important role in the observed noisy dynamic behavior near the bifurcation points.

However, the occurrence of ISSR is rather counterintuitive, and it cannot be explained by previously reported theoretical models. First, a potential model applicable to bistable or excitable systems is not suitable here, for there is no potential barrier to hinder the hopping between the stable node and the limit cycle. On the other hand, the threshold-free model proposed by Bezrukov and Vodyanoy [7] does not work either, because an exponential relationship between input and output rates was needed there. In addition, the Hopf bifurcation here is supercritical and the motion on the deterministic limit cycle is quite uniform such that the ''nonuniform motion'' condition proposed by Rappel and Stroget [12] is not yet satisfied. So a new mechanism must be responsible for the ISSR observed in the present work. In fact, one only needs to account for the increment of the NICO

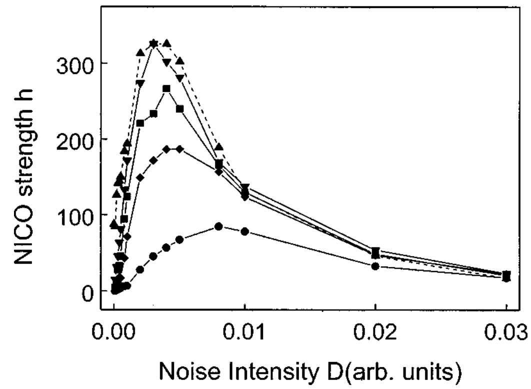

FIG. 3. The ISSR curves for different choices of p_{NO}^{0}. From the bottom to the top, $p_{\mathrm{NO}}^{0}\times 10^{7}$ in turn reads 3.20, 3.22, 3.223, 3.325, and 3.226 mbar. Notice that, according to the dashed line, a deterministic oscillation appears $(D=0)$, and a stochastic resonance behavior is also observed.

strength in the small D range. In the present work, we think that two facts might be responsible for this. First, there exists a distance between p_{NO}^{0} and the correct Hopf bifurcation point p^{*}. Second, with the increment of the control parameter p_{NO}^{0}, the strength of the deterministic oscillation also increases remarkably. So with the increment of D from zero, the chance for the system to pass across the distance $p^{*}-p_{\mathrm{NO}}^{0}$ to enter the stronger oscillation region would increase such that the NICO strength could be enhanced. Of course, if D is too large, the coherent oscillation would be annihilated by the noise. In the present work, we have also performed numerical simulation work to investigate the influence of p_{NO}^{0} on the ISSR. We find that with the approach of p_{NO}^{0} to p^{*}, the ISSR peak becomes left shifted and higher, which implies that a smaller D can lead to the maximum NICO strength. Even when p_{NO}^{0} is slightly larger than p^{*}, e.g., $p_{\mathrm{NO}}^{0}=3.226$, one still can observe the ISSR. These results are presented in Fig. 3. Notice that they are inconsistent with the above discussions. However, one expects that a more complete and convincing explanation is necessary, and a proper theoretical model would be greatly helpful in future work.

In the present work, we have studied the noisy dynamic behavior near the Hopf and saddle-loop bifurcation points in a chemical catalytic reaction system. For Hopf bifurcation, noise-induced coherent oscillation (NICO) is found, and its strength goes through a maximum with the variation of the noise intensity, indicating the occurrence of internal signal stochastic resonance (ISSR). However, this behavior is not observed near the saddle-loop bifurcation, which implies that the structure of the bifurcation diagram could play an important role in the observed noisy dynamics. In addition, a possible explanation for the observed NICO and ISSR is given, which is partly demonstrated by numerical simulations. Of course, a proper theoretical model would be greatly helpful in the future work.

ACKNOWLEDGMENTS

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