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Cite as: J. Chem. Phys. **110**, 3591 (1999); https://doi.org/10.1063/1.478227
Submitted: 27 August 1998 . Accepted: 04 November 1998 . Published Online: 04 February 1999

Lingfa Yang, Zhonghuai Hou, and Houwen Xin

Stochastic resonance in the absence and presence of external signals for a chemical reaction

Lingfa Yang, Zhonghuai Hou, and Houwen Xin[a)]
Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui, 230026, People's Republic of China

(Received 27 August 1998; accepted 4 November 1998)

A catalytic reduction of NO with CO on Pt(100) surface is adopted to study its response under random perturbation. Noise-induced oscillations and noise-induced frequency shifts have been observed when the system works in the vicinity of the oscillatory region and meanwhile is subjected to random modulation of its feeding speed. Stochastic resonance behavior can be recognized from the noise-induced peak in the power spectrum even though in the absence of external signals. The numerical results have been obtained near supercritical Hopf bifurcation points, but are not confined to the classification of bifurcation. When the system falls into bistable regions, noise can help an external weak signal to induce state-to-state transitions and also shows a stochastic resonance behavior except for the case that the system has an isolated bifurcation scheme. © *1999 American Institute of Physics.* [S0021-9606(99)70706-3]

I. INTRODUCTION

Random noise can be beneficial to the formation of ''order,'' rather than destroy it. This paradoxical point of view has been increasingly reported in many nonlinear systems recently, and gradually accepted by many scientists. Stochastic resonance (SR) is one of the most prominent phenomena in which noise represents a useful tool to improve the detection of a weak signal, to transport its random energy to enhance the signal oscillation.

The concept of SR was originally proposed by Benzi *et al.*[1] to account for the periodicity in Earth's ice ages, but has since been shown to occur in many systems such as in physical sensitive devices and sensory neuron systems.[2] The notion of SR has been widened to include many different mechanisms. The unifying feature of all these systems is the increased sensitivity to small perturbations at an optimal noise level and the existence of a resonance peak on the plot of signal-to-noise (SNR) versus noise intensity. The effect of SR requires three basic ingredients:[3] a suitable nonlinear system, a weak signal and a source of noise.

In studying SR, the signal is adopted generally as an ''external'' input modulation of a nonlinear system, then, one looks at the periodic contribution of the output at the same frequency as input. Recently, Hu *et al.*[4] took the initiative to present a kind of SR in an autonomous system without external periodic force, which we here call autonomous stochastic resonance (ASR). Near the oscillatory region they find a noise-induced oscillation and a noise-induced shift in frequency. Their results were reexamined later by Rappel *et al.*[5] and ascribed to the nonuniformity of the limit cycle. We particularly notice that in their studies the oscillation is terminated by a saddle-node bifurcation and Rappel *et al.*[5] draw the conclusion that one would not expect to find this type of stochastic resonance in systems whose oscillations are created by a Hopf bifurcation. We are afraid that we can not accept this viewpoint. In this paper, we present an ASR behavior which can occur in a chemical reaction whose oscillations are both created and ended by supercritical Hopf bifurcation. In addition, the frequency shifts are found, but the shift direction tends to the opposite direction as that indicated in Refs. 4 and 5.

SR phenomena have been studied mainly in bistable systems in the past years. It therefore gives a wrong impression: All bistable systems can show SR if the input is modulated properly by an external periodic signal and a suitable level of noise. Our present study shows that this conclusion is not universal, because some bistable systems can definitely not show SR. It is the bifurcation scheme that accounts for the occurrence of SR. In this paper, we present a bifurcation scheme, which can change from an isolated circle to a mushroomlike shape through a transcritical bifurcation. The result shows that the response of the reaction is much different before and after the bifurcation when the system is subjected to external modulations.

Up to now, almost all the studies on SR, both theoretically and experimentally, have concentrated on physical or biophysical systems, but few of them involve chemical reactions except experimental studies by Schneider's group in homogeneous reactions[6–8] and our recent numerical results[9] in a surface catalytic reaction Pt(110)/CO+O_2. In this paper, we adopt a reaction of catalytic reduction of NO with CO on a Pt single crystal surface that has been thoroughly investigated in the past decades.[10] The reaction exhibits an abundance of kinetic behaviors including sustained rate oscillations and pattern formations, and its reaction model[11–13] has been well organized and shows a series of interesting bifurcation schemes.

a)Author to whom correspondence should be addressed; electronic mail: lfyang@ustc.edu.cn

II. THE MODEL AND ITS BIFURCATION SCHEME

The reaction of Pt(100)/NO+CO proceeding in an ultrahigh vacuum chamber is well understood (see Ref. 10 and references cited therein). The mechanism can be described by the following steps:[10,13]

$$\mathrm{CO(gas)}+*\rightleftharpoons \mathrm{CO_{ad}}, \tag{I}$$

$$\mathrm{NO(gas)}+*\rightleftharpoons \mathrm{NO_{ad}}, \tag{II}$$

$$\mathrm{NO_{ad}}+*\rightarrow \mathrm{N_{ad}}+\mathrm{O_{ad}}, \tag{III}$$

$$2\mathrm{N_{ad}}\rightarrow \mathrm{N_2(gas)}\uparrow+2*, \tag{IV}$$

$$\mathrm{CO_{ad}}+\mathrm{O_{ad}}\rightarrow \mathrm{CO_2(gas)}\uparrow+2*. \tag{V}$$

The adsorption of CO(gas) or NO(gas) requires a vacant site; in the opposite direction, the desorption of CO(ad) or NO(ad) releases an adsorption site (I, II). Following the adsorption of NO(gas), the dissociation of adsorbed NO requires another free adsorption site. Therefore, this step is regarded as a rate-limiting one (III). The following two reactions IV and V produce gas species which are removed from the surface immediately and release two adsorption sites each. The competition between the vacant sites' consumption in I, II, and III and their supply in IV and V shows an autocatalytic behavior. Certainly, this scheme neglects N_2O formation because it is unstable in low pressure or room temperature.

Imbihl *et al.*[11] have built a three-variable model from reactions I to V to describe adsorbate coverages θ_{CO} for adsorbed CO, θ_{NO} for adsorbed NO, θ_{O} for adsorbed oxygen. That is,

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

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

$$\frac{d\theta_{\mathrm{O}}}{dt}=k_5\theta_{\mathrm{NO}}\theta_{\mathrm{empty}}-k_3\theta_{\mathrm{CO}}\theta_{\mathrm{O}}, \tag{3}$$

with

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

All the coefficients of adsorption (k_1), desorption (k_2 and k_4), dissociation (k_5) and combination (k_3 and k_7), have been listed in Refs. 11 and 12, which were originally taken from experimental data. Because of the repulsive interaction between adsorbed CO and NO, their desorptions become easy. Their temperature dependence is expressed via the Arrhenius law, $k_{2,4}=\nu_{2,4}\exp(-E^{\mathrm{NO,CO}}/RT)$, and their active energy barriers,

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

decrease with the increase of the surface coverage. When $\theta_{\mathrm{NO,CO}}$ exceeds $\Theta_{\mathrm{NO,CO}}\simeq 0.61$, and adsorbed oxygen exceeds $\Theta_{\mathrm{O}}\simeq 0.4$, no free sites provide for $\mathrm{NO_{ad}}$ dissociation, and the reaction is inhibited.

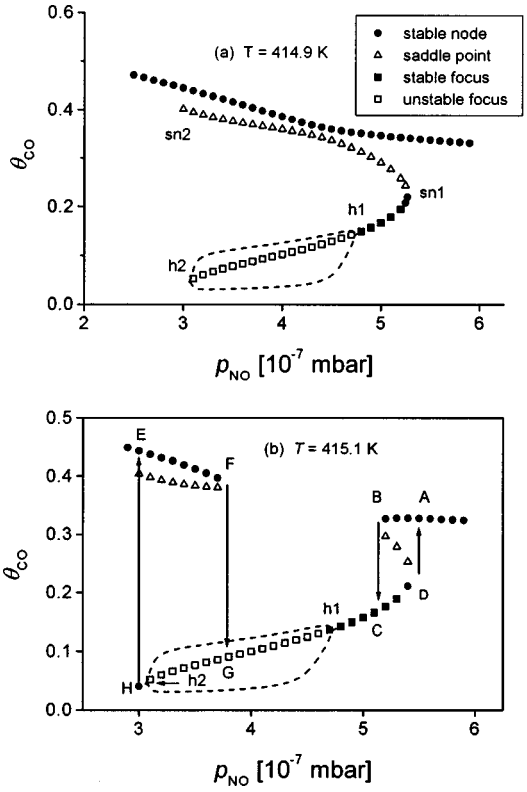

FIG. 1. Bifurcation diagrams show the existence of an isolated branch of the steady-state solution as p_{NO} is varied as bifurcation parameter before a transcritical bifurcation occurs (a) and the existence of a mushroomlike multiple steady-state solution after the transcritical bifurcation occurs (b). When p_{NO} is modulated, the reaction shows kinetic hysteresis marked by loop *ABCD* and loop *EFGH* in (b). In contrast, there is not any hysteresis in the isola (a). The existence range for kinetic oscillations is terminated by two supercritical Hopf bifurcation points h1 and h2. The amplitude of the oscillations (the upper and lower turning points) is represented by the dash lines. The legends for (a) are also suitable for (b).

The kinetic behavior of this model can be understood by its bifurcation scheme. First, one can get a steady state (fixed point) by solving the equations $d\theta_{\mathrm{CO}}/dt=0$, $d\theta_{\mathrm{NO}}/dt=0$ and $d\theta_{\mathrm{O}}/dt=0$. Then, one can get its stability using a linear stability analysis method. A fixed point should fall into one of the kinds: a stable or unstable node, a stable or unstable focus, or a saddle point. Here we show the system's multistability in one-dimensional bifurcation diagrams (see Fig. 1), which agrees well with Imbihl's results.[11] The low branch has an oscillatory region that both starts and terminates both by supercritical Hopf bifurcation. The amplitude of the oscillations (the upper and lower turning points) represented in Fig. 1 is obtained from the numerical integration of Eqs. (1)–(3).

Keeping $p_{\mathrm{CO}}=3\times 10^{-7}$ mbar, we notice there exists a transcritical bifurcation at about $T=415$ K. At low temperature, the low isolated region separates with the upper branch [Fig. 1(a)]. With the increase of temperature, the upper branch approaches the isolated region and finally touches it to cause a transcritical bifurcation. The diagram seems mushroom-like [see Fig. 1(b)]. We pay special attention to these two cases: before and after the transcritical bifurcation, to study their different responses under external perturbations.

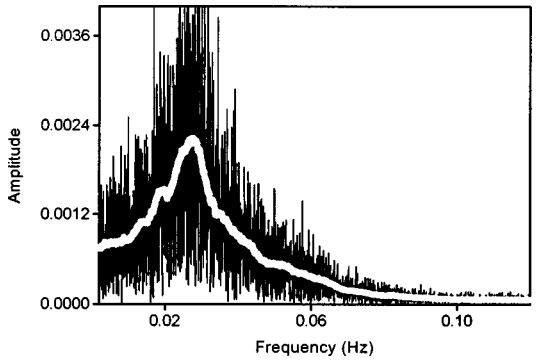

FIG. 2. Noise-induced oscillation on power spectrum. The background line is obtained directly from FFT. The white overlay curve is a smoothing curve from adjacent averaging of 100 points.

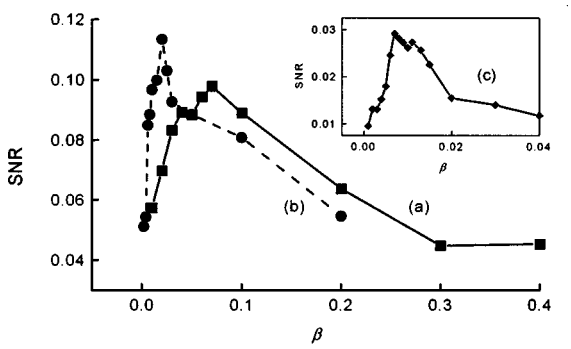

FIG. 3. The signal-to-noise ratio: SNR evaluated from the power spectrum versus noise level. The constant partial pressure $p_0=4.80$(a), 4.75(b) and 3.05(c) in units of 10^{-7} mbar for different locations in Fig. 1(a). Each curve displays a peak for stochastic resonance.

III. COHERENT MOTION AND STOCHASTIC RESONANCE RESPONSE

The time evolution of many nonlinear systems shows nonuniformity. In some parts of the trajectory the system evolves quickly, but in other parts it goes slowly. This reveals an interior asymmetry of a nonlinear system. When the asymmetric system is subjected to a zero-mean symmetric perturbation, its response may show a coherent motion to some extent. A Gaussian-type white noise has a zero mean value $\langle \xi(t) \rangle = 0$, and its correlation $\langle \xi(t)\xi(t') \rangle = 2D\delta(t-t')$ is a white spectrum. It is often adopted to simulate internal fluctuation or external uncertainty.

As usual, the response of a nonlinear system to a white noise input is no longer a white spectrum. If we modify the reaction conditions carefully so that the system works ''near'' the oscillatory region but not ''in'' the region, presenting noise to the control parameters may induce an oscillatory motion. By power spectrum analysis of the output, a noise-induced peak can be found. With an increase of noise level, the peak becomes broad but higher first and then collapses at high noise level. We give another definition of the SNR as the height of the peak over its half-width, because a sharp and high peak is much more recognized. A resonance-like behavior can be obtained from the curve of the SNR to the noise level. Because this performance appears in the absence of an external signal, one calls it autonomous stochastic resonance (ASR). In contrast with SR in a general sense, ASR can be understood as the noise resonating with the intrinsic signal instead of the external signal.

Figure 2 shows a noise-induced oscillation peak in the power spectrum at the frequency corresponding to the intrinsic oscillation. It is a response of the system to external noise input

$$p_{\mathrm{NO}}=[1+\beta\xi(t)]p_0,$$

where β is noise intensity. The nonperturbation pressure of NO is $p_0=4.80\times10^{-7}$ mbar. It is apparently out of the oscillatory region marked by h1, $p_{\mathrm{NO}}=4.71\times10^{-7}$ mbar, and h2, $p_{\mathrm{NO}}=3.06\times10^{-7}$ mbar. For a small noise, the noise-induced peak is sharp but low. At increasing noise level, it becomes high but broad. By power spectrum analysis of the output, we plot the SNR as a function of noise level in Fig. 3(a). The curve shows clearly a SR peak at $\beta=0.07$. If the constant pressure becomes closer to the oscillatory region, for example, $p_0=4.75\times10^{-7}$ mbar, the SR peak becomes higher and shifts to low level of noise [see Fig. 3(b)]. At the other end of the oscillatory region, $p_0=3.05\times10^{-7}$ mbar, the noise-induced oscillation can also be found, and the response also has a SR peak shown in Fig. 3(c). However, the SR peak is very small and appears at very small noise because too much noise can result in a jump from the isola to the opposite stable state, but the reverse process never happens.

Figure 4 displays the frequency shift of the noise-induced oscillation peak. With the increase of noise level, the peak shifts to lower frequency, not to higher frequency as indicated in Refs. 4 and 5

IV. STOCHASTIC RESONANCE WITH EXTERNAL SIGNAL

A general feature of a system exhibiting stochastic resonance is its increased sensitivity to small perturbations when an appropriate dose of noise is added. In its simplest form, SR occurs in a bistable system driven by a periodic external force. The periodic force raises two potential wells alternately; when the noise is sufficiently strong, the overdamped particle can jump over the potential barrier. The key point is that the external signal, itself, is not strong enough to cause any transitions or excitations; the increasing noise helps the transitions or excitations gradually, makes them true, and can make the transition synchronized with weak perturbation.

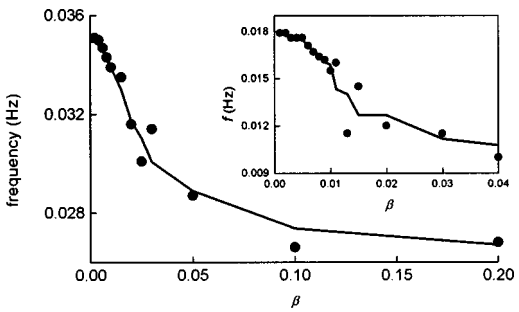

FIG. 4. Frequency shift of the noise-induced oscillation peak as a function of the noise level. The plot and the insert plot corresponds to Figs. 3(b) and 3(c), respectively. The lines are only drawn to guide the eyes.

However, a too strong noise counteracts the aforementioned correlation, thereby reducing the response. So there exists a SR peak with the increase of noise level. Now the question is whether all bistable systems can show a SR behavior.

Bifurcation schemes for low-dimension systems generally fall into four basic classes: ''S'' type, ''Z'' type, isolated, and mushroomlike. The two stable states, corresponding to a stable node, a focus or a stable limit cycle surrounding an unstable focus, are usually separated by a saddle point. Hysteresis behavior can occur as modulation of the control parameter for the other three cases except for the isolated bifurcation scheme. Figure 1(a) displays an isolated bifurcation where the bistable region is clearly shown within two saddle-node bifurcation sn1 and sn2, and the low branch is isolated. Under a strong modulation, the low branch may lose its stability to jump up to the high branch. However, the inverse process never occurs. In these circumstances, one never expects to have a general SR response.

After a transcritical bifurcation, the isola develops into a mushroomlike scheme shown in Fig. 1(b). This bifurcation diagram exhibits two hysteresis regions when the system is subjected to external modulation. At $p_0=5.3\times10^{-7}$ mbar, we applied a small periodic signal (amplitude α, frequency f_s) together with a Gaussian noise component (intensity β). That is,

$$p_{\mathrm{NO}}=[1+\alpha\sin(2\pi f_s t)+\beta\xi(t)]p_0.$$

For $\alpha=0.03$, $f_s=1/400s^{-1}$, and let the noise be added 100 times per signal period. The integration of the ODEs lasts not less than 100 signal periods. We adopt a fast Fourier transform (FFT) power spectrum analysis method to analyze one of the state variables, for example, θ_{CO}. Then, the SNR can be obtained from the spectrum. Figure 5(a) shows the results. As the noise level is increased, a SR peak can be recognized at about $\beta=0.055$.

In parallel to the above, we choose another site $p_0=3.3\times10^{-7}$ mbar to study SR. Let $\alpha=0.12$, $f_s=1/1500s^{-1}$, and the other conditions remain unchanged. We obtain a similar SNR curve shown in Fig. 5(b). As shown in Fig. 1(b), the kinetic behaviors for the two bistable regions are much different. In the loop $ABCD$, both the upper branch AB and the low branch CD are stable steady states. In contrast, in another loop $EFGH$, EF still keeps a stable steady state, but most of the branch GH falls into the oscillatory region. In the absence of noise, one can find mixed-mode oscillations and rich phase-locking phenomena in power spectrum under external periodic modulation. However, the local dynamical difference, regardless of the difference between a steady state and an oscillatory state, has no influence on the occurrence of SR.

V. CONCLUSION

A typical surface chemical reaction Pt(100)/CO+NO is adopted to study its dynamical response under random perturbation in the ''absence'' and ''presence'' of external periodic weak modulation. Resonance behavior can be found for both of them.

First, the reaction exhibits an oscillatory region that is both created and ended by continuous Hopf bifurcation. As the NO pressure approaches the oscillatory region, we apply a Gaussian type noise to modify the feeding system of partial pressure of NO. Noise-induced oscillations and noise-induced frequency have been found, and the response may display an autonomous stochastic resonance behavior that shows the positive effect of the noise. Our numerical results have revealed these nonlinear phenomena are constant regardless of a Hopf bifurcation or a saddle-node bifurcation coming into or out of the intrinsic oscillations.

Second, stochastic resonance in bistable regions has been found. Each stable state may relate to a stable node, or a stable focus, even an unstable focus but existing a stable limit cycle. This difference does not present an obstacle to the occurrence of stochastic resonance. However, if the bifurcation scheme has an isolated branch causing the transition between the two stable states to be inreversible, one never expects to observe the stochastic resonance behavior in general sense.

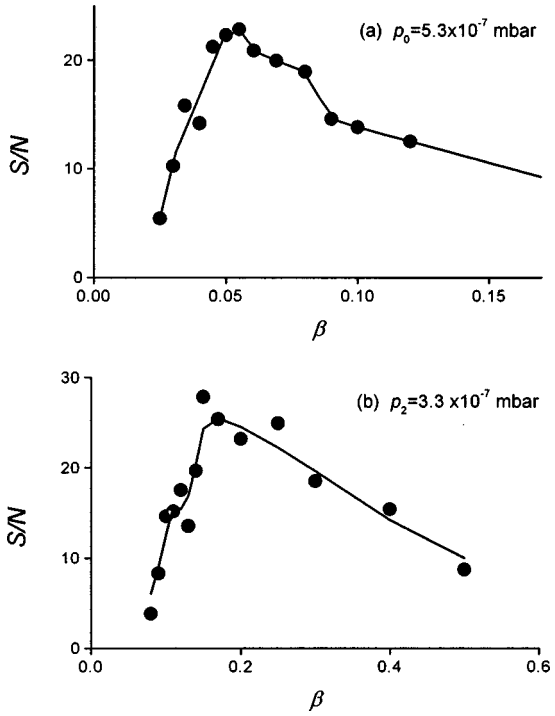

FIG. 5. SNR output as the function of noise level. Locating $p_0=5.3$(a) and 3.3(b) in units 10^{-7} mbar, the system works corresponding to the loop $ABCD$ and the loop $EFGH$ in Fig. 1, respectively. Both show a stochastic resonance peak.

ACKNOWLEDGMENTS

This research was supported by the National Natural Science Foundation of China and the National Laboratory of Theoretical and Computational Chemistry of China.

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