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# Stochastic resonance in catalytic reduction of NO with CO on Pt(100)

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This paper presents a stochastic resonance occurring in a chemical reaction Pt(100)/NO+CO. The results were from numerical simulation of the nonlinear kinetic behavior of a three-variable reaction model obtained from the law of mass actions. The model exhibits a special region in the bifurcation scheme, where a stable node coexists with a stable limit cycle. When one of the control parameters is perturbed by a weak, low frequency periodic signal riding on a suitable external noisy background, transitions between the steady state and oscillatory state may become regular unexpectedly, and signal to noise ratio is thus enhanced at the signal frequency in the Fourier transform power spectrum of the time series output. That refers to stochastic resonance, in which the noise may play a constructive role in the detection of weak signals. The findings may suggest a new method to develop chemical sensitive devices in the field of applications. The paper also discusses the conditions of occurrence of stochastic resonance, and studies the laws it follows. © *1998 American Institute of Physics.* [S0021-9606(98)70339-3]

## I. INTRODUCTION

In the past, catalytic reduction of NO with CO has been thoroughly investigated on Pt single crystal.[1–6] These studies revealed a variety of interesting dynamic phenomena, such as oscillations, deterministic chaos and complex spatial-temporal patterns.

The oscillations, first reported by King *et al.*, occur at extremely low pressure on Pt(100),[5] and no oscillation was found on the other low-index surfaces (110) or (111). The oscillations were recognized in two separate temperature windows:[6] one is local damped oscillations in the lower-lying T window, the other is sustained oscillations in the upper-lying T window which couples with surface phase transition between $1\times1$ and hex. This paper focuses on the sustained rate oscillations, especially on the oscillations co-existing in a steady state in a special multistable region.

When the autonomous kinetic oscillation is subjected to a periodic modulation of its external control parameters, various phenomena may appear through its responses, such as super-, sub-, or simple harmonic entrainments with phase locking, and resonance behaviors. In past years, periodic forcing has been applied to kinetic oscillations that occur in the catalytic oxidation of CO on Pt surface experimentally[7,8] and theoretically.[9] In the Pt(100)/NO+CO system, the responses under periodic and random perturbation have been studied experimentally when the system exhibiting damped kinetic oscillation in the lower T window.[10] To our regret there has been no similar work for the upper T window exhibiting sustained rate oscillations to study the cooperative effect in the system with external periodic signal accompanied by noise.

The sustained rate oscillations are characterized as they may develop an interesting transition from one single state to multiple steady states where oscillations coexist in a steady state. In these circumstances studying the responses of the system under both periodic signal and noise perturbation has a special motivation for the study of the cooperative effect between the signal and noise through the nonlinear system.

When a weak signal is applied to one of steady/stationary states in multistability, the system is expected to have a small amplitude response. When only noise is applied, and its intensity is strong enough, transitions between/among the different states are triggered affirmatively, and certainly the transitions seem random. The question is that if the noise is modulated by a weak signal, what is the response? One may guess it is also exhibiting randomness. However recent studies[11,12] have shown that the response may become more regular sometimes, and the signal to noise ratio thus is enhanced at the signal frequency in the power spectrum. That is the so-called stochastic resonance (SR), in which the noise plays a constructive role in the detection of the weak signal.

The concept of SR was originally put forward in the seminal papers by Benzi and collaborators wherein they addressed the problem of the periodically recurrent ice ages.[13] A first experimental verification was obtained by Fauve and Heslot in a noise-driven electronic circuit known as a Schmitt trigger.[14] The studies in this field are excited by several experimental results, including ring lasers,[15] superconducting quantum interface devices,[16] and sensory neurons in biology.[17] In the past, SR was studied mainly in bistable systems. The first nonbistable systems discussed were excitable systems[18] in 1993. Later, the notion of SR has been widened to integrate-and-fire dynamics,[12] even nondynamical systems without thresholds,[19,20] and its applications or potential uses cover physical devices, communications, sensory neuron, etc.

It is well known that many chemical reactions exhibit

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multistability, such as reactions in the continuously stirred tank reactor (CSTR), or heterogeneous reactions. One would expect that rich SR behavior exists. It may therefore appear as a surprise that, so far, few chemical systems have been touched upon except the studies of SR by Schneider's group in homogenous reactions including the BZ reaction,[21] peroxidase-oxidase reaction,[22] and minimal-bromate reaction.[23] In this research, we concentrated on studies of SR in a typical heterogeneous reaction model: catalytic reduction of NO with CO on Pt(100), and expected the simulation results might help experimental studies.

The Pt(100)/NO+CO has been thoroughly investigated. The mechanism is well understood, and its reaction model has been provided.[24–26] This paper begins with analyzing the bifurcation scheme of a three-variable model to show the multistability, then, investigates the response of the system to external periodic perturbation or/and noise, and searches for proper conditions for the occurrence of stochastic resonance. Finally, the law of SR submitted to is also discussed.

## II. THE MODEL

The use of the single crystal surface in UHV systems to study oscillations has led to detailed insights into the mechanism of these oscillations. It allowed the formation of mathematical models based on experimental facts. The reaction of Pt(100)/NO+CO is assumed to proceed via the molecular dissociation of NO as the rate-limiting step, followed by reaction of the combination of nitrogen and carbon dioxide. They are

$$\mathrm{CO}+{*}\rightarrow \mathrm{CO}_{\mathrm{ad}}, \tag{R1}$$

$$\mathrm{NO}+{*}\rightarrow \mathrm{NO}_{\mathrm{ad}}, \tag{R2}$$

$$\mathrm{NO}_{\mathrm{ad}}+{*}\rightarrow \mathrm{N}_{\mathrm{ad}}+\mathrm{O}_{\mathrm{ad}}, \tag{R3}$$

$$2\mathrm{N}_{\mathrm{ad}}\rightarrow \mathrm{N}_2+2{*}, \tag{R4}$$

$$\mathrm{CO}_{\mathrm{ad}}+\mathrm{O}_{\mathrm{ad}}\rightarrow \mathrm{CO}_2+2{*} \tag{R5}$$

(ad = adsorbed state; * = vacant site).

From the reaction scheme above, a three-variable model can be easily derived via the law of mass actions,

$$\frac{d\theta_{\mathrm{CO}}}{dt}=k_1p_{\mathrm{CO}}(1-\theta_{\mathrm{CO}}-\theta_{\mathrm{NO}})-k_2\theta_{\mathrm{CO}}-k_3\theta_{\mathrm{CO}}\theta_{\mathrm{O}}, \tag{D1}$$

$$\frac{d\theta_{\mathrm{NO}}}{dt}=k_1p_{\mathrm{NO}}(1-\theta_{\mathrm{CO}}-\theta_{\mathrm{NO}})-k_4\theta_{\mathrm{NO}}-k_5\theta_{\mathrm{NO}}\theta_{\mathrm{empty}}, \tag{D2}$$

$$\frac{d\theta_{\mathrm{O}}}{dt}=k_5\theta_{\mathrm{NO}}\theta_{\mathrm{empty}}-k_3\theta_{\mathrm{CO}}\theta_{\mathrm{O}}, \tag{D3}$$

with

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

where the state variables $\theta_{\mathrm{CO}},\theta_{\mathrm{NO}},\theta_{\mathrm{O}},\theta_{\mathrm{empty}}$, stand for coverage of CO, NO, O and vacant sites, respectively. The control parameters $(p_{\mathrm{CO}},p_{\mathrm{NO}},T)$ are recognized as partial pressures of CO and NO, and temperature of the catalysis.

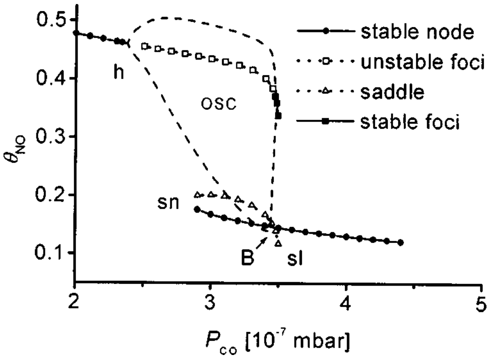

FIG. 1. Bifurcation diagram showing the coexistence of steady state and kinetic oscillations ($T=414.4$ K, $p_{\mathrm{NO}}=3.5\times10^{-7}$ mbar). Starting from low partial pressure of CO, the upper branch loses its stability in Hopf bifurcation (*h*) and develops kinetic oscillation, and suddenly gains stability when the loop touches the low stable node, and finally disappears in the saddle-loop (sl) bifurcation. The dashed lines mark the oscillation amplitude. The low branch is for steady state, and up-triangle line for saddle ranging from saddle node (sn) bifurcation to sl bifurcation. The saddle and node cross superficially at point B, corresponding to the upper branch ending oscillation and gaining stability. Within the multiple states region from sn to sl, there includes a narrow bistable state from point B to sl bifurcation.

Considering the activation energies for desorptions of CO and NO decreasing with increasing coverage due to repulsive interactions, the energy barriers for both are expressed as

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

This reaction model was first proposed by Imbihl *et al.*[24,25] All the coefficients of adsorption, desorption, dissociation and reaction obtained from experiments were published there, and a detailed bifurcation analysis has been conducted.

By incorporating the adsorbate-driven $1\times1\rightleftharpoons$ hex phase transition, the three-variable model has been extended to six variables.[26] Despite the better qualitative agreement with experimental results, the modified model seems no extra significance to the sustained oscillation mechanism, because the hex phase is inefficient with respect to NO dissociation. Therefore, we adopt the three-variable model here.

We paid special attention to the existence of a region which exhibits multistability. We plotted the bifurcation diagram in Fig. 1 through a linear stability analysis method to the fixed points.

The multistability region can be recognized within saddle-node(sn) bifurcation and saddle- loop(sl) bifurcation. Determined by the initial conditions, the system may reach either the steady state or the stationary state of oscillation after a long time of evaluation. It is possible to reach one of the two bistable states if it is in the narrow bistability region. With increasing $p_{\mathrm{CO}}$, the oscillations raise their amplitude and lower their frequencies. Near the end of the oscillation region, the reaction shows an extremely narrow product peak, the so-called ''surface explosion'' due to an autocatalytic behavior.

## III. STOCHASTIC RESONANCE

To understand the properties of a nonlinear system, such as its stability, responses to external perturbation, or the cooperative effects between/among inputs through nonlinear systems, an important method is to present the system under different kinds of perturbation. Among them, periodic modulation of one of the control parameters is often used.

Another kind of perturbation is ''noise.'' It may come from intrinsic fluctuation, or instability of the feed control system, even being added deliberately for some special purpose. Generally, noise may not account for macrodynamics because its effects are much weakened by long-time averaging. However, noise might sometimes show its significance near bifurcation, and cause new instability, or extra dynamical behavior.

Stochastic resonance is a typical nonlinear phenomenon. It is a cooperative effect between noise and signal. It requires three basic ingredients:[11] (i) nonlinear system with an energetic activation barrier, or more generally, a form of threshold, (ii) a weak coherent input signal, (iii) a noise that is inherent in the system, or that is added to the input externally.

In this part, we will investigate the responses of a Pt(100)/NO+CO system when it is subjected to periodic perturbation and/or noise to study the cooperation effect and the constructive role of noise. The partial pressure of CO, $p_{\mathrm{CO}}$, was chosen as the control parameter, and the response behavior was recognized by one of the state parameters $\theta_{\mathrm{NO}}$.

In experiments, the control parameters are $p_{\mathrm{CO}}$, $p_{\mathrm{CO}}$ and $T$. The measurable outputs are partial pressures of $\mathrm{CO}_2$ and $\mathrm{N}_2$ corresponding to their production rates. The rate of $\mathrm{CO}_2$, for instance, can be regarded as direct proportional to the product of the coverage of CO and O, and in rough approximation, proportional to the coverage of CO because $\theta_{\mathrm{O}}$ is very small all the time, i.e., $r_{\mathrm{CO}_2} \propto \theta_{\mathrm{CO}}\theta_{\mathrm{O}} \sim \theta_{\mathrm{CO}}$. Therefore state variable $\theta_{\mathrm{CO}}$ or $\theta_{\mathrm{NO}}$ was found to give sufficient information for the present study as $r_{\mathrm{CO}_2}$ or $r_{\mathrm{N}_2}$ does.

First, the control parameter $p_{\mathrm{CO}}$ was located at $p'_{\mathrm{CO}} = 3.3\times10^{-7}$ mbar, subjected to periodic perturbation ($\alpha = 0.05$, $f_s = 1/800$ Hz), i.e., $p_{\mathrm{CO}} = p'_{\mathrm{CO}}[1+\alpha\sin(2\pi f_s t)]$. It was found that the oscillatory state responds with an amplitude-modulation and frequency-modulation (AF-FM) output [Fig. 2(a)]; the steady state answers with also a weak periodic output [Fig. 2(b)]. No transitions burst.

Secondly, when the system was under only random perturbation, a Gaussian-type white noise $\xi(t)$ here, i.e., $p_{\mathrm{CO}} = p'_{\mathrm{CO}}[1+\beta\xi(t)]$, with $\beta = 0.3$, it responds with random transitions occurring between the steady state and the kinetic oscillations [Fig. 2(c)].

Finally, both signal and noise were applied to the control parameter at the same time, i.e., $p_{\mathrm{CO}} = p'_{\mathrm{CO}}[1+\alpha\sin(2\pi f_s t) + \beta\xi(t)]$, and stochastic resonance appears [Fig. 2(d)] under suitable conditions ($\alpha = 0.15$, $f_s = 1/800$ Hz, $\beta = 0.1$). The transitions seem regular.

Next we discuss suitable conditions for occurring SR.

(i) A proper amplitude signal. The transitions between the oscillation and the steady state seem to have a threshold related to the energy barrier in the bistable system. If $\alpha < \alpha_c = 0.18$, no transition occurs, and the weak input signal is difficult to detect directly.

(ii) A proper frequency. There are several orders of magnitude difference among frequencies of signal $f_s$, natural oscillation $f_0$, and noise $f_n$, i.e., $f_s < f_0 < f_n$, with $f_s = 1/800\ \mathrm{s}^{-1}$, $f_0 = 14 f_s$ (locating $p_{\mathrm{CO}} = 3.3\times10^{-7}$ mbar), and $f_n = 100 f_s$.

(iii) A proper location of the control parameter. The partial pressure of CO was located at $p'_{\mathrm{CO}} = 3.3\times10^{-7}$ mbar, where the system stays in one of the two states with almost equal probabilities in the process of transitions resulting from noise [Fig. 2(c)]. For lower $p'_{\mathrm{CO}}$, the system tends to remain at the oscillation more often, and the excitation to the opposite state becomes more difficult. For higher $p'_{\mathrm{CO}}$, the situation reverses.

(iv) A proper intensity of noise. The signal to noise ratio (SNR), evaluated from the power spectrum as noise intensity increases, was plotted in Fig. 3. There exists a peak apparently at about $\beta = 0.1$, where the transitions become more regular [Fig. 2(d)]. That indicates the occurrence of stochastic resonance. Weak noise

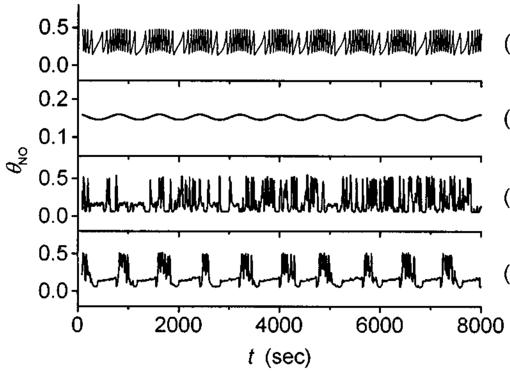

FIG. 2. Responses to external perturbation of the nonlinear system in multistable region at $p_{rmCO}$ mbar. The oscillatory state responds to a low frequency sinusoid periodic weak signal ($\alpha = 0.05$, $f_s = 1/800$ Hz) with an amplitude-modulation and frequency-modulation (AF-FM) output (a); the steady state answers the signal with another weak periodic output (b). A strong enough noise input ($\beta = 0.3$) causes transitions to occur between the steady state and the kinetic oscillations (c). A relatively regular resonance occurs when a broadband noise is modulated by a weak signal under the proper conditions ($\beta = 0.1$ for signal $\alpha = 0.15$, $f_s = 1/800$ Hz). This is called stochastic resonance (d).

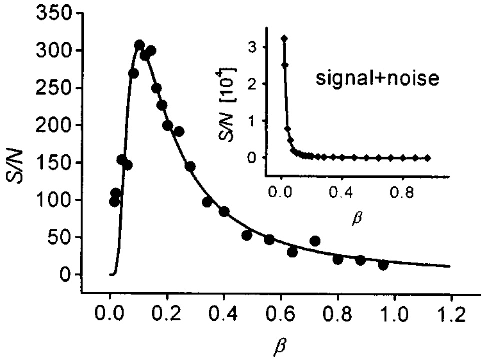

FIG. 3. The signal to noise ratio (SNR) evaluated from the power spectrum vs noise amplitude in numerical simulation of the reaction model (filled circles). The solid line is for the best fit using formula (F). The maximum is reached at about $\beta = 0.1$ and $\lambda = 1044$. The insert plot is for the sharp decrease of the SNR as noise intensity increases if the output is assumed as simply mixing the signal with noise directly.

was found to excite little transition. In contrast, big noise increases the randomness of the transitions. At the left side of the peak, SNR rises steeply with increasing intensity of noise. It seems contradictory to the general concept that the noise plays a positive effect in the signal detection. When the noise is supposed simply as an addition to the signal (see the insert plot of Fig. 3), SNR decreases sharply with the increasing of noise, and the signal is easily annihilated in the noisy background.

In Fig. 3, the solid line is a fitting curve from formula

$$R=\frac{S}{N}\simeq\lambda\left(\frac{A}{\beta}\right)^2\exp\left(-\frac{2\Delta U}{\beta}\right), \tag{F}$$

where, $\Delta U\simeq\beta_{\max}$ stands for the height of the potential barrier. This formula was originally given to a one-dimension bistable model. It is obtained from the Fockker-Planck equation under adiabatic approximation, and $\beta\ll1$, $A\ll1$.[27,28] We found under $\Delta U=0.1$, and $\lambda=1044$, the simulation dots show a good agreement with the fitting curve although the formula is for a bistable system. This also reveals that there might exist two symmetrical potential wells in this system, separated by $p_{\mathrm{CO}}=3.3\times10^{-7}$ mbar.

## IV. DISCUSSION AND CONCLUSION

Bifurcation analysis was used to analyze a typical surface catalytic reduction model, Pt(100)/NO+CO, and a special region was found to have multiple states. Within the special region, numerical simulation results show that there exists a stochastic resonance behavior when one of the control parameters $p_{\mathrm{CO}}$ is periodically modulated and includes a noisy component. The results reveal: first, noise makes the detection of a weak signal possible. Without noise, the direct detection may be difficult, even impossible. With the help of noise, even a weak signal can cause excitations or transitions through a special nonlinear system in multistability. By analysis of these excitations or transitions, the input signal can be reconstructed.

Secondly, the noise may play a constructive role to increase signal to noise ratio by making the weak periodic signal more clear through the mechanism of stochastic resonance. In contrast, with traditional methods in linear systems, when the signal is magnified, the noise is also magnified simultaneously, and even worse, an extra noise is introduced unavoidably in the process. With the increase of noise intensity, the signal is easily annihilated in the noisy background.

Finally, when stochastic resonance occurred was in action, the system was found to show more sensitivity to external input than usual. Therefore, these findings might suggest a new method to develop chemical sensitive devices in fields of application.

In addition, the reason for choosing a Pt(100)/NO+CO system is that the mechanism of the reaction has been well understood. Other systems such as NO+$H_2$ and NO+$NH_3$ were found to have similar oscillation mechanisms, and show multistability.[1] Therefore, stochastic resonance is also expected there. By the way, stochastic resonance was found in the Pt(110)/CO+$O_2$ model in the bistable region and near discontinuous bifurcation.[29] The studies may suggest that stochastic resonance is a common phenomenon in catalytic surface reactions.

## ACKNOWLEDGMENTS

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