Stochastic resonance in surface catalytic oxidation of carbon monoxide

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Stochastic resonance is a nonlinear cooperative effect between external signal and noise, in which the noise can play a constructive role to increase the signal-to-noise ratio in the detection of a weak signal. A surface catalytic reaction model, to describe oxidization of carbon monoxide carrying out far from equilibrium, was adopted to study the stochastic resonance. By computer simulation, we found noise can induce state-to-state transitions, and stochastic resonance behavior may appear at narrow bistable states or near discontinuous Hopf bifurcations, while a weak periodic signal riding on noise is input controlling. © *1998 American Institute of Physics.* [S0021-9606(98)51629-7]

I. INTRODUCTION

Noise gives a deep impression of its negative effects. It smears clear signals or patterns, and makes detection of weak signals impossible. Therefore, one always tries to minimize its effects. That is true in linear systems. However, recent research has established that noise can play a constructive role in the detection of weak signals by a mechanism known as stochastic resonance (SR).

The concept of SR was originally put forward in the seminal papers by Benzi and his collaborators wherein they addressed the problem of the periodically recurrent ice ages.[1] A first experimental verification was obtained by Fauve and Heslot in a noise-driven electronic circuit known as a Schmitt trigger.[2] The most notably in the study of the phenomenon of SR, is observed in experiments including ring lasers,[3] superconducting quantum interface devices,[4] and sensory neurons in biology.[5] Up to now, many SR phenomena have been studied in bistable systems. However, the notion has been widened to excitable systems,[6] integrate-and-fire dynamics,[7] and even nondynamical systems without thresholds,[8,9] and its applications, or to put its potential uses, cover physical devices, communications, and sensory neuron.

It is known that most of the chemical reactions carry out far from equilibrium. They may exhibit various complex nonlinear behavior. One, therefore, expects that rich SR behavior may exist in chemical systems. But so far as we know, very little about chemical systems has been touched upon except the studies of SR by Schneider's group in homogeneous reactions including the BZ reaction,[10] peroxidase–oxidase reaction,[11] and minimal-bromate reaction.[12] In this paper, we concentrate on SR in a typical heterogeneous reaction: catalytic oxidation on a single surface, by analysis of the behavior of a set of ordinary differential equations under periodical modulation and noisy component adding to control parameters. This study might help researchers to find SR in this system experimentally.

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II. REACTION MODEL

The catalytic oxidation of carbon monoxide has attracted a lot of attention for more than two decades, due not only to its application, but also to its theoretical significance. The system may exhibit complex spatial-temporal self-organization, even under extreme conditions, i.e., in ultrahigh vacuum (UHV) chambers, keeping strictly isothermal, and over a single crystal surface. Therefore, the complexity is not from the reaction steps themselves as in the homogeneous reaction, but from the rearrangement of surface atoms in reactions. The nonlinear behavior in this system such as bistability, oscillation, chemical waves, and entrainment under external periodically driven, have been studied in detail both experimentally and theoretically, mainly by Ertl's group.[13–19]

The catalytic oxidation of CO follows the Langmur–Hinshelwood (LH) mechanism.

$$\mathrm{CO(gas)} + * \underset{k_2}{\overset{k_u}{\Leftrightarrow}} \mathrm{CO(ad)},$$

$$\mathrm{O_2(gas)} + 2* \overset{k_v}{\longrightarrow} 2\mathrm{O(ad)},$$

$$\mathrm{CO(ad)} + \mathrm{O(ad)} \overset{k_3}{\longrightarrow} \mathrm{CO_2}\uparrow + 2*.$$

A three-variable reaction model has been proposed by Krisher, Eiswirth and Ertl,[15,16] to describe the adsorption, desorption, reaction and diffusion processes

$$\dot{u} = k_u P_u S_u \left[1 - \left(\frac{u}{u_s} \right)^3 \right] - k_2 u - k_3 uv - D_{\mathrm{eff}}, \tag{1}$$

$$\dot{v} = k_v P_v S_v \left[1 - \frac{u}{u_s} - \frac{v}{v_s} \right]^2 - k_3 uv - D_{\mathrm{eff}}, \tag{2}$$

$$\dot{w} = \begin{cases} -k_5 w; & u \leqslant u_1 \\ k_5 \left(\sum_{i=0}^{3} r_i u^i - w \right); & u_1 < u < u_2. \\ k_5 (1-w); & u \geqslant u_2 \end{cases} \tag{3}$$

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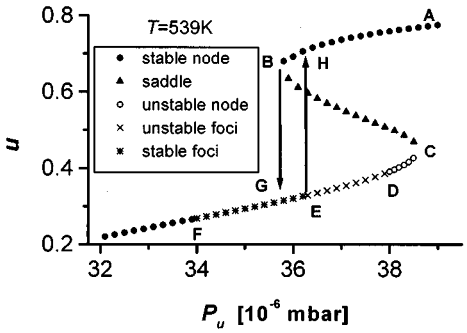

FIG. 1. Bistability of the reaction model $CO+O_2$. The saddle and node annex at point B, and below it, only low-covered state of CO exists. The low branch loses its stability, and turns to the opposite state at point E, needs not develop till the other node-saddle annexation at point C. Therefore, the bistability exists in a narrow region.

Here, three variables u, v, and w stand for coverages of adsorbed CO and O, and fraction of 1×1 phase on surface; u_s and v_s stand for saturation of CO and O; k_u and k_v are their adsorption coefficient; k_2, k_3, and k_5 for desorption coefficient, reaction rate, and transition coefficient separately, determined by temperature through Arrhenius law; S_u and S_v for sticking coefficients, assuming $S_u=1$, $S_v=0.6w+0.4(1-w)$. P_u and P_v stand for the partial pressure of CO and O_2 gases. These parameters, except the effective diffusion $D_{\rm eff}$, were given elsewhere.[13,15,16,19] The term $D_{\rm eff}$, determined mainly by temperature and surface structure, has been studied over fractal surface recently by us,[20] and is not included here.

By analysis of linear stability of Eqs. (1)–(3), we obtained the properties of the nonlinear dynamical behavior: bistability and oscillatory states, plotted in Figs. 1 and 2, respectively.

III. STOCHASTIC RESONANCE

To understand the properties of a nonlinear system, such as its stability, response to external input, or the cooperative effect between two inputs through nonlinear systems, one can present the system under periodic perturbation, or under noise influence, or under both. There, the periodic perturbation method is often adopted, however, noise must be considered if influence of the noise may lead to new instability, or extra dynamical behavior.

The behavior of oscillators under the influence of external periodic perturbations has attracted considerable interest both in experiment and theory. The systems studied include Jesephson junctions, nonlinear electronic conductors, hydrodynamic systems, biological oscillations, as well as homogeneous and heterogeneous chemical reactions. The oscillatory chemical reaction $CO+O_2$ under periodic perturbation has been studied by Eiswirth *et al.* experimentally,[17,18] and by Krischer *et al.* theoretically.[19] All control parameters, namely the temperature of the catalyst and the partial pressures P_v and P_u, could, in principle, be modulated. However, variations of temperature affect all activated steps of the oscillations, and the results would therefore be difficult to interpret. In most cases, P_v or P_u was modulated. Certainly, in experiments, the partial pressures are controlled by pumping, reaction, and evacuation rates, and have residence time. However, because the reactions take place in UHV, the reaction rate is slow. Therefore, the gas diffusion rate can be regarded as infinity, the time delay in gas can be neglected, and the modulation of the partial pressure becomes realizable.

SR, a typical nonlinear phenomenon, is a cooperative effect between noise and signal. It requires three basic ingredients: (i) nonlinear systems with an energetic activation barrier, or more generally, a form of threshold, (ii) a weak coherent input signal, (iii) some noise that is inherent in the system, or that adds to the input externally. Here, we focused on its occurrence condition and appearance. We adopt the catalytic oxidation of CO as the nonlinear system, sinusoid modulation as the weak signal, and together with a Gaussian-type noise. They are

$$P_u=P_{u0}[1+A\ \sin(2\pi f_s t)+D\xi(t)]. \tag{4}$$

There, the constant pressure P_{u0} is modulated by a sinusoid wave, a kind of simple signal (amplitude A, and frequency f_s). The Gaussian-typed noise, $\xi(t)$, is often employed to simulate instantaneous, multivariate, random force subjected by Brownia particles, or random thermal fluctuation. The statistical properties of white noise are

$$\langle\xi(t)\rangle=0;\quad \langle\xi(t)\xi(t')\rangle=2D\delta(t-t');$$

$$S(\omega)=\int e^{-i\omega\tau}2D\delta(\tau)d\tau=2D. \tag{5}$$

We analyzed time-serial output by power spectral. Signal-to-noise ratio (SNR) is defined as the ratio of signal strength over noise strength at frequency f_s, and SR behavior refers to appearance a peek on SNR curve while increasing noise intensity D.

We simulated Eqs. (1)–(3), and (4), with time step $\tau_0=1$ ms, lasting $2^{22}=4\,194\,304$ steps. The simple data collected are not less than 25 000 points, once. We found the system showing different behavior under different parameters. The system suppresses input modulation while far from bifurcation. However, it becomes very sensitive while

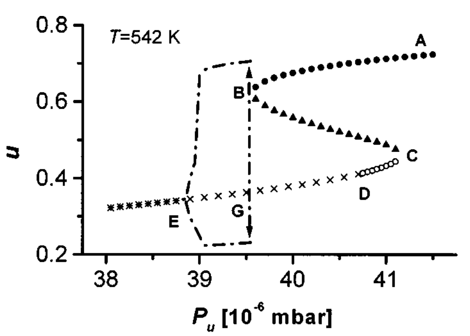

FIG. 2. Chemical oscillation of the reaction model $CO+O_2$. The system starts oscillation at super-Hopf bifurcation (E), and gains its amplitude marked by dash–dot lines. The oscillation disappears abruptly at discontinuous Hopf bifurcation (G), and then turns on the upper branch. (Here, the legends are same as that in Fig. 1.)

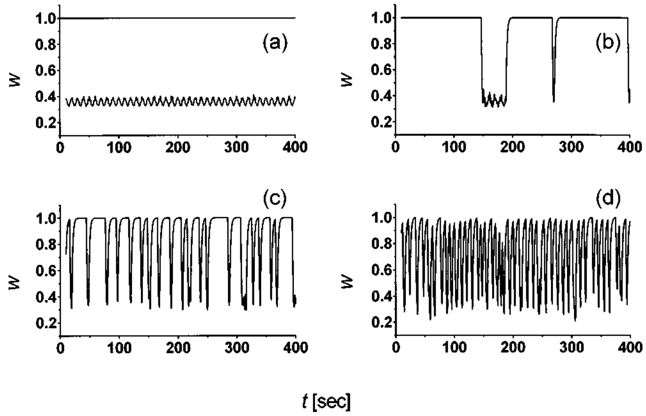

FIG. 3. The time serial response of external signal and noise while the system is in bistability region (keeping signal amplitude $A=0.2$ and frequency $f_s=0.1\ \mathrm{s}^{-1}$ unchanged). (a) No burst occurs under a weak noise $D/A=0.2$. The low state shows weak response to input modulation, but the high state does not show any response due to strong suppression. (b) While $D/A=0.4$, some noise-induced transitions burst. (c) Optimal value of $D/A=1.5$, stochastic resonance behavior appears, where a 1:1 quasiperiod of bursts are exhibited due to the cooperation of signal and noise. (d) Strong noise overwhelms the input signal, and the transition becomes irregular.

within a bistable state, or near discontinuous Hopf bifurcation, where the influence of the noise may lead to transitions frequently between the two states, or between one stable state and an oscillatory state, respectively, resulting in SR.

A. Within a narrow bistable state

While $T=539$ K, $P_v=1.3\times10^{-4}$ mbar, there exists a narrow bistability within range $P_u=36.00\times(1\pm0.25)\times10^{-6}$ mbar (see Fig. 1). Determined by initial conditions, the system may tend toward $(u,v,w)\approx(0.32,\ 0.14,\ 0.35)$—low state, or $(u,v,w)\approx(0.69,\ 0.03,\ 1.00)$—high state. Both of them remain unchanged if the modulation of P_u is within 0.25. On decreasing P_u, the high state drops to the low state at point B, while on the other hand, rises the low state up at point E.

At $P_u=36.00\times10^{-6}$ mbar, we added a signal with an amplitude $A_1=0.2$, and frequency $f_s=0.1$ Hz. The system remains in one of the two states; no transition occurs between them [Fig. 3(a)]. Then, let the signal plus Gaussian noise as input, and increase its intensity gradually, transitions start in Fig. 3(b), and become more regular in Fig. 3(c). But for too strong a noise, the transitions become irregular [Fig. 3(d)]. So there exists a suitable strength, where the output just shows original signal, and results in SR. A power spectrum of Fig. 3(c) is shown in Fig. 4, from which we can

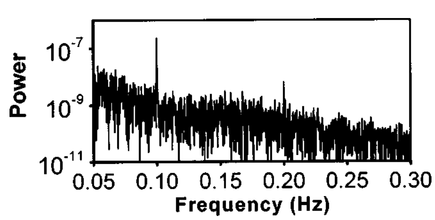

FIG. 4. Power spectra analysis of time serial while the noise is optimal, where two signal peeks show at frequency 0.1 Hz and frequency doubling 0.2 Hz.

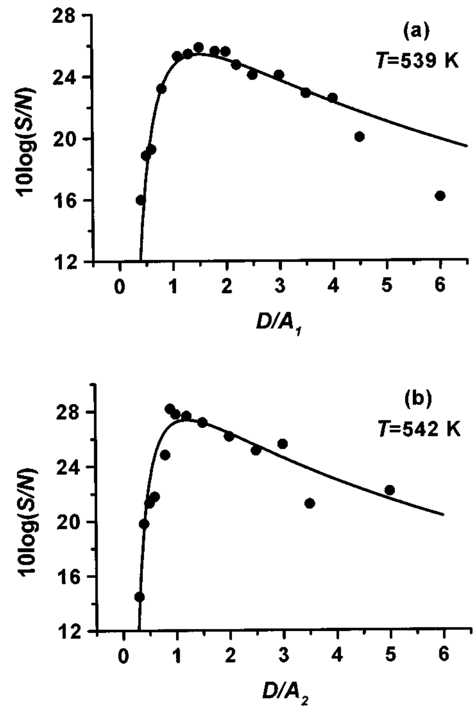

FIG. 5. The signal-to-noise ratio (filled circles) together with the best fit (solid line) obtained using formula (6). The parameter of the best fit are $\lambda=5800$, $\Delta U/A_1=1.5$ (a); $\lambda=5800$, $\Delta U/A_2=1.2$ (b), where A_1 and A_2 are signal amplitudes.

obtain values of SNR, then plotted in Fig. 5(a) as increasing noise intensity.

In Fig. 5, the dots are simulation results, and the solid line is a fitting curve from formula

$$R=\frac{S}{N}\approx\lambda\left(\frac{A}{D}\right)^2\exp\left(-\frac{2\Delta U}{D}\right), \tag{6}$$

where, $\Delta U\approx D_{\max}$ stands for height of the potential barrier. This formula is given to one-dimension bistable model. It is obtained from the Fokker–Planck equation under adiabatic approximation, and conditions $D\ll1$, $A\ll1$.[21,22] There exists a SR peek, evidently.

In addition, we emphasize a ''narrow'' bistable state. Under lower temperature, the bistable regime is much wider. To cause state-to-state transitions needs much stronger modulation, and the SR behavior in the original sense disappears.

B. Near Hopf bifurcation

At $P_u=39.8\times10^{-6}$ mbar in Fig. 2, with $A_2=0.25$ this modulation is not strong enough to cause transitions between the stable state and oscillatory state, but with the help of noise, the transitions may occur. Another SNR curve was obtained, and is plotted in Fig. 5(b).

By fitting with Eq. (6), we were surprised that the parameter λ and potential height $(\Delta U=1.5A_1=1.2A_2)$ are both the same as that above. It suggests that both of the two cases share a same potential barrier determined mainly by temperature, and the large difference between their dynamics behavior has little influence on the curve fitting. In addition, our results agree that SR is determined by the nonlinear system itself, and is little related with external conditions, such as amplitude and frequency of signal.

IV. CONCLUSION

Through analysis of a typical surface catalytic reaction model, Pt/CO+O_2, stochastic resonance behavior was found while one of the control parameters, P_u, is periodically modulated and includes a noisy component, where the noise plays a constructive role to make the weak periodic signal more clear by increasing the signal-to-noise ratio. In contrast with traditional methods, while the signal is magnified, the noise is also magnified simultaneously. These two results have distinct differences. In addition, while stochastic resonance acting, the system becomes much more sensitive to external input signals than usual. Therefore, these two findings might suggest a new method to develop chemical sensitive devices in field of applications. By the way, stochastic resonance is one aspect in which the noise shows a positive effect. Noise may also play a constructive role, or create new orders, or support wave traveling in many reaction-diffusion systems, and these studies seem in the ascendant.

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