

Stochastic bi-resonance without external signal in the CO+O₂ catalytic oxidation reaction system

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The noisy dynamic behavior of a surface catalytic reaction model to describe the oxidation of carbon monoxide is investigated when the control parameter is perturbed by external noise near a supercritical Hopf bifurcation point. Noise induced coherent oscillation (NICO) is observed and the NICO strength goes through two maxima with the increment of the noise intensity D from zero, characteristic of the occurrence of stochastic multiresonance without external signal. The frequency of the NICO also increases with the increment of D . © 1999 American Institute of Physics.
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I. INTRODUCTION

The study of stochastic resonance (SR) has gained ever growing attention in recent years.¹ This phenomenon shows the rather counterintuitive effect of noise, i.e., it can enhance the detectability of a weak input signal into a nonlinear system. Since it was originally proposed to account for the periodic oscillation of the Earth's ice ages,² SR has found its application in many scientific fields and its concept has been widely extended. The original SR model included a symmetry bistable system, a weak periodic input signal, and additive external noise.³ But now, the nonlinear system can be monostable,⁴ excitable,⁵ threshold-free,⁶ or spatial-extended,⁷ etc.; the input signal can be aperiodic and even chaotic;⁸ and the noise can be colored, multiplicative, or even substituted by the intrinsic randomness of a deterministic chaotic system.⁹ Very recently, Hu Gang *et al.*¹⁰ reported the first example of SR in which the external signal is replaced by an internal signal of the system: the deterministic oscillation. When the control parameter is located near the bifurcation point between a stable node and a stable limit cycle, where the deterministic oscillation is absent, noise induced coherent oscillation (NICO) is observed and the NICO strength goes through a maximum with the increment of noise intensity from zero, showing the characteristic of stochastic resonance, which might here be named by internal signal stochastic resonance (ISSR).

It's known that most of the chemical reaction processes carry out far from equilibrium and they often exhibit abundant nonlinear behavior such as multistability, chemical oscillation, chemical chaos, etc.¹¹ One, therefore, expects that SR should be common in chemical systems. However, the first report considering SR in chemical reaction systems only came out very recently, where Schneider's group¹² studied SR experimentally in homogeneous reaction systems including the BZ reaction, peroxidase-oxidase reaction, and

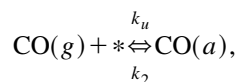
minimal-bromate reaction. After that, our group has performed numerical studies on SR behavior in surface catalytic reaction systems¹³ including the catalytic oxidation of carbon monoxide (CO+O₂) and the catalytic reduction of nitrogen monoxide with carbon monoxide (NO+CO). We found that SR could appear near narrow bistable states or near discontinuous Hopf bifurcations. Furthermore, if the control parameter is located near the supercritical Hopf bifurcation point in the absence of the deterministic oscillation, NICO and henceforth ISSR behavior were also observed in the NO+CO reduction system.¹⁴

In various nonlinear chemical reaction systems, chemical oscillation is very general, which can result from various types of bifurcation. So one may ask how does the bifurcation character influence ISSR behavior? One expects that a deep study into this subject may open further perspective in the study of SR and it can also help in understanding the noisy dynamics of a complex chemical reaction system. In the present work, we have numerically studied NICO and ISSR behavior in the CO+O₂ system near a supercritical Hopf bifurcation point. What interests us most is that two maxima appear in the ISSR curve.

II. THE REACTION MODEL

The catalytic oxidation of carbon monoxide has attracted considerable attention for more than two decades, due not only to its great application, but also to its theoretical significance. Much interesting spatio-temporal self-organization behavior has been observed including bistability, oscillation, chaos, spiral waves, soliton waves, turbulence, etc. For more details in these studies, one should turn to the excellent work by Ertl's group.¹⁵⁻²⁰

The catalytic oxidation of CO on the single crystal surface of platinum follows the Langmuir-Hinshelwood (LH) mechanism:



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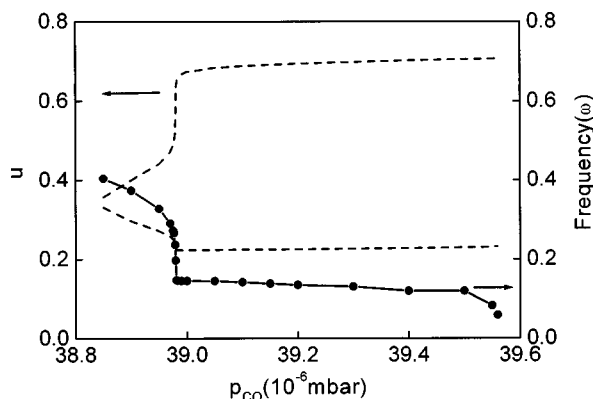
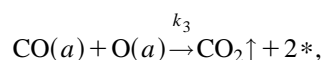
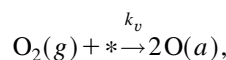


FIG. 1. The amplitude (dash lines) and frequency (solid line) of the deterministic oscillation in the CO+O₂ system for $T=539$ K and $p_v=1.3 \times 10^{-4}$ mbar.



where $*$ and (a) denote a free adsorption site and an adsorbed species, respectively. Following the work of Krischer, Eiswirth, and Ertl,^{15,16} the rate equations for the adsorbate coverages read:

$$\frac{\partial u}{\partial t} = k_u p_u s_u \left[1 - \left(\frac{u}{u_s} \right)^3 \right] - k_2 u - k_3 u v,$$

$$\frac{\partial v}{\partial t} = k_v p_v s_v \left[1 - \frac{u}{u_s} - \frac{v}{v_s} \right]^2 - k_3 u v,$$

$$\frac{\partial w}{\partial t} = \begin{cases} -k_5 w; & u \leq u_1 \\ k_5 (\sum_{i=0}^3 r_i u^i - w); & u_1 < u < u_2 \\ k_5 (1 - w); & u \geq u_2 \end{cases}$$

Here, the variables u , v , and w stand for the coverages of CO(a), O(a), and the fraction of 1×1 phase on the surface, respectively; k_u and k_v denote their adsorption coefficients, and k_2 the desorption coefficient of CO(a), k_3 the reaction rate, k_5 the transition coefficient. If the coverage of CO(a) or O(a) exceeds the saturation values u_s or v_s , further adsorption would be hindered. s_u and s_v are the sticking coefficients with $s_u = 1$ and $s_v = 0.6w + 0.4(1 - w)$. p_u and p_v are the partial pressures in the gas phase. The exact values of the parameters are not provided here; one can turn to Refs. 15, 16.

By linear stability analysis of the above rate equations, one can easily obtain the nonlinear behavior of the model. Choosing $T=542$ K and $p_v=1.3 \times 10^{-4}$ mbar and taking p_u as the control parameter, there exists a supercritical Hopf bifurcation point at $p_u \approx 38.845 (\pm 0.005) \times 10^{-6}$ mbar, and the oscillation region ends by a discontinuous Hopf bifurcation at $p_u \approx 39.56 \times 10^{-6}$ mbar. In Fig. 1, we plotted the bifurcation diagram in these parameter region, where the dash lines denote the amplitude of the deterministic oscillation. From Fig. 1, one can see that with the increment of p_u , the amplitude of the oscillation increases very rapidly in the beginning and suddenly saturates to a nearly constant value.

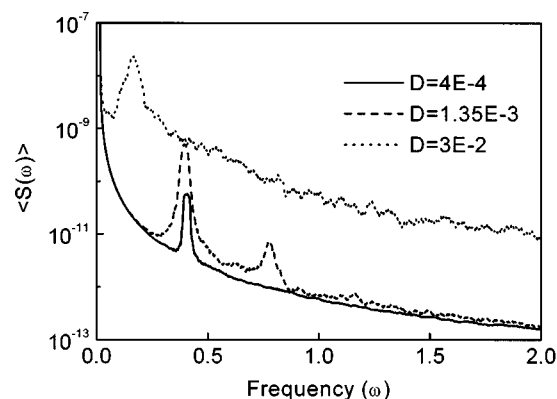


FIG. 2. The power spectrum of the noise induced coherent oscillation for $D=4 \times 10^{-4}$, 1.35×10^{-3} and 0.03, respectively. Notice each curve is obtained by averaging over 50 independent runs.

Accordingly the variation of the oscillation frequency ω is also shown in Fig. 1: ω first decreases very rapidly and suddenly ends at a constant value. Notice that this interesting transition character considerably influences the observed noisy dynamic behavior as described in detail in the next section.

III. RESULTS

To study the NICO and ISSR behavior, we properly choose the control parameter p_u such that it's quite close to the supercritical Hopf bifurcation point, while the deterministic oscillation is absent, and perturbed it by noise as: $p_u = p_u^0 (1 + 2D\Gamma(t))$, here D is the noise intensity, and $\Gamma(t)$ Gaussian white noise with zero mean and unit variance, i.e., $\langle \Gamma(t) \rangle = 0$ and $\langle \Gamma(t)\Gamma(t') \rangle = \delta(t-t')$.

In the present work, we choose $p_u^0 = 38.83 \times 10^{-6}$ mbar. For $D=0$, the power spectrum of the output time series $u(t)$ shows no peak but an even background. However, even when D is as small as 1×10^{-4} , an obvious sharp peak appears, indicating the occurrence of NICO. The frequency of NICO (0.4065) nearly equals to that of the deterministic oscillation at $p_u = 38.85 \times 10^{-6}$ mbar (0.4041). When D increases, this peak becomes higher and wider, and it's obviously shifted to lower frequency. This peak is annihilated into the noise background when $D \approx 0.005$. However, for further increasing D , one observes that the amplitude of the noise induced oscillation sharply increases and another obvious peak emerges in the power spectrum with a even lower frequency. This peak also becomes higher and wider if D further increases, but now the frequency remains nearly unchanging ($\omega \approx 0.15 \pm 0.02$), which approximately equals to that of the large-amplitude deterministic oscillation ($\omega \approx 0.145 \pm 0.01$). Of course, a very large noise level would also annihilate this NICO.

In Fig. 2, we have plotted three typical power spectrum for noise intensity $D=10^{-4}$, 1.3×10^{-3} and 0.03, respectively. In Fig. 3, the NICO strength is plotted against the noise intensity, where the NICO strength is measured by the height of the peak h (notice that a more appropriate measure of the signal-to-noise ratio of the NICO might be $h/\Delta\omega$; here $\Delta\omega$ is the width of the peak at the height $h/2$, but in the

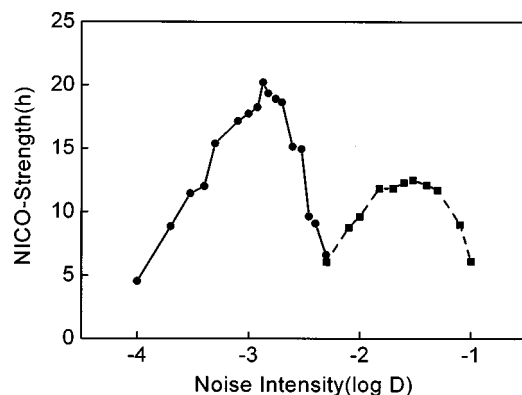


FIG. 3. Stochastic bi-resonance observed in the CO+O₂ system.

present work we only consider the quantitative behavior and h is also acceptable). One sees that stochastic bi-resonance occurs. Another interesting phenomena can be seen from Fig. 2 for $D=1.3\times 10^{-3}$: a double-frequency component (DFC) is also present. A detail study shows that DFC only exhibits in a narrow range of D from $\sim 1.0\times 10^{-3}$ to $\sim 1.5\times 10^{-3}$, and its strength attains the maximum at nearly the same D level as the first resonance. In the second resonance range, however, the DFC behavior is not observed.

The occurrence of NICO is not so surprising. Noise draws the control parameter into the oscillation region now and then, such that the deterministic oscillation is occasionally random modulated, resulting in a Gaussian-expanded peak in the output power spectrum. However, the occurrence of ISSR is not so straightforward. It might be due to that an increment of noise intensity (in the small range) could enhance the chance for the system to enter the oscillation region and that the strength of the deterministic oscillation also increases with the increment of p_u . One expects that a proper theoretical model would help understanding this behavior.

The stochastic bi-resonance behavior observed in the present work is rather interesting. Intuitively, one may draw the conclusion that it's due to the specific transition character of the deterministic oscillation as depicted in Fig. 1, for the frequency of the NICO clearly reflects that transition character. This bi-resonance behavior implies some frequency-selection effect: Different noise intensity prefers to support signal with different frequency. A deep investigation into this behavior may open further perspectives in the future work.

ACKNOWLEDGMENTS

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