

Standing Waves in Catalysis at Single-Crystal Surfaces

Herbert Levine and Xiaoqin Zou

Department of Physics and Institute for Nonlinear Science, University of California, San Diego, La Jolla, California 92093

(Received 16 April 1992)

Recent experiments have demonstrated the existence of standing waves for the catalytic reaction $\text{CO} + \text{O} \rightarrow \text{CO}_2$ on a Pt(110) surface. We study this reaction by adding spatial coupling terms to a kinetic reaction scheme originally proposed by Eiswirth, Krischer, and Ertl. We argue that the standing waves arise from a novel mechanism involving the parametric driving of finite-wave-vector waves via a globally oscillating reaction rate. This interaction is possible because of the (near) resonance of these two modes.

PACS numbers: 82.20.Mj, 82.65.-i

Some of the most interesting examples of spatial patterns in nonequilibrium systems occur in chemical reaction dynamics [1]. The best known of these reactions is that of Belusov-Zhabotinskii (BZ) [2] but there are a wide variety of other cases [3,4]. Structures that are seen typically include targets, rotating spirals (or their three-dimensional analogs), and most recently Turing cells [5].

One experimental system that has recently received attention is the catalysis of CO to CO_2 on a single-crystal substrate [6]. The advantages of this system are that the reaction dynamics is relatively simple and the system is inherently two dimensional. Ertl and co-workers have pioneered the use of photoemission microscopy to provide high-resolution images of the spatial structures that arise in the oscillatory regime of this reaction. Aside from spirals and targets, the system also supports standing waves when the Pt(110) surface is used [6].

These standing waves are the subject of this investigation. We will propose an explanation of this behavior that relies on the resonant driving of standing waves by a global oscillation of the reaction. To model this nonlinear interaction, we will expand the evolution equations about a codimension two point where both waves and the global oscillation become unstable; the resulting amplitude equations predict modulated standing waves whose existence is then verified by direct simulation. At the end, we will compare our results with the experimental findings.

We start with the reaction scheme of Eiswirth, Krischer, and Ertl (EKE) [7,8]. There are two "fast" reactions corresponding to changes in the CO (c) and O (o) coverages,

$$\dot{c} = k_c s_c P_{\text{CO}} \left[1 - \left(\frac{c}{c_s} \right)^3 \right] - k_4 c - k_3 c o, \quad (1)$$

$$\dot{o} = k_o s_o P_{\text{O}_2} \left[1 - \frac{c}{c_s} - \frac{o}{o_s} \right]^2 - k_3 c o. \quad (2)$$

Here k_c and k_o are the rates (actually rates per unit partial pressure) at which CO and O molecules hit the surface, s_c , s_o are the sticking probabilities, and P_{CO} , P_{O_2} are the respective partial pressures. The actual formation of CO_2 (which immediately desorbs) occurs with rate k_3 .

The form of the oxygen adsorption is due to the requirement that O_2 dissociates upon binding and that O requires a clean binding site.

As discussed in EKE, this system is bistable. To actually obtain the observed oscillation, one must couple this reaction to a slow surface reconstruction. Specifically, at low CO coverage the surface reconstructs to a 1×2 structure; this reconstruction couples to Eqs. (1) and (2) via the assumption that the oxygen sticking probability depends on the fraction of unreconstructed surface a via

$$s_o = a s_{o1} + (1 - a) s_{o2}. \quad (3)$$

For the reconstruction dynamics, \dot{a}/k_5 is taken to equal

$$\begin{aligned} & -a \text{ for } c \leq c_1, \\ & \left(\sum_{i=0}^3 r_i c^i - a \right) \text{ for } c_1 < c < c_2, \\ & 1 - a \text{ for } c \geq c_2. \end{aligned}$$

The values of all of the parameters in the standing wave regime ($T \sim 540^\circ\text{C}$) are given in Table I.

In this paper, we will focus on one-dimensional structures and ignore the presence of dislocations [6] which make the actual pattern rather complex. To study spatial patterns, we must modify the reaction equations to allow for the coupling of different spatial locations. One coupling is provided by CO diffusion; we will assume [3] $D \sim 10^{-4}$ mm²/sec (in the wave propagation direction, since the diffusion is anisotropic). In addition, there is a coupling due to pressure fluctuations which, on the time scale on the reaction, equilibrate instantaneously. Observationally [9], the CO partial pressure is in phase with the CO coverage and out of phase with the O coverage. The variation in P_{O_2} has not been measured but simple arguments suggest that it behaves similarly. Thus we postulate

$$P_{\text{CO}} = \bar{P}_{\text{CO}} (1 + \alpha \bar{c} - \alpha' \bar{o}), \quad (4)$$

$$P_{\text{O}_2} = \bar{P}_{\text{O}_2} (1 - \beta \bar{o} + \beta' \bar{c}),$$

where \bar{c}, \bar{o} means the spatially averaged coverages. These global couplings are presumably not independent, but the

TABLE I. Parameters for the EKE reaction; here $k_i = k_i^0 e^{-E_i/kT}$ for $i=3,4,5$.

CO	k_1	Flux	$4.18 \times 10^5 \text{ s}^{-1} \text{ Torr}^{-1}$	
	s_c	Sticking coefficient	1	
	c_s	Saturation coverage	1	
O ₂	k_2	Flux	$7.81 \times 10^5 \text{ s}^{-1} \text{ Torr}^{-1}$	
	s_{o_1}	Sticking coefficient on 1×1	0.6	
	s_{o_2}	Sticking coefficient on 1×2	0.4	
	o_s	Saturation coverage	0.8	
Rates	k_3	Reaction	$k_3^0 = 3 \times 10^6 \text{ s}^{-1}$	$E_3 = 10 \text{ kcal/mol}$
	k_4	CO desorption	$k_4^0 = 2 \times 10^{16} \text{ s}^{-1}$	$E_4 = 38 \text{ kcal/mol}$
	k_5	Phase transition	$k_5^0 = 10^2 \text{ s}^{-1}$	$E_4 = 7 \text{ kcal/mol}$
	r_i	Coefficients for phase transition	$r_3 = -1/0.0135$	$r_2 = -1.05r_3$
			$r_1 = 0.3r_3$	$r_0 = -0.026r_3$
	c_i	Critical coverages for phase transition	$c_1 = 0.2$	$c_2 = 0.5$

actual relationships among them are not yet clear. It will turn out that these global coupling terms are helpful (but not essential) in analyzing why this system can support standing waves.

As discussed in EKE, the reaction dynamics without coupling exhibits a Hopf bifurcation to an oscillatory state. Upon addition of spatial coupling, one can ask about the relative stability of a global oscillation versus a wave with wave vector q . The answer, of course, depends on the assumed coupling parameters. In the absence of global coupling, diffusion adds a term $-Dq^2$ to the (1,1) element of the stability matrix $\partial F_i / \partial \psi_j(\psi^{(0)})$, where we have introduced the notation

$$\psi = (c, o, a), \quad \frac{\partial \psi}{\partial t} = F, \quad F(\psi^{(0)}) = 0$$

and $\psi^{(0)}$ is the fixed point. This clearly suppresses the bifurcation. On the other hand, some of the global coupling terms (α' and β') can enhance the instability of the system to finite- q perturbations as compared to $q=0$ ones. Another way of saying this is to point out that there exists the possibility of a codimension two bifurcation where at some \bar{P}_{O_2} , \bar{P}_{CO} values, both $q=0$ and $q=q^*$ simultaneously become unstable. Analyzing the possible structure then requires a derivation of coupled amplitude equations for the waves and the global oscillation.

Before proceeding, it is essential to understand what we are proposing. In the "real" system with some set of α , α' , β , β' , there may or may not be a codimension two bifurcation. Nevertheless, our system is always close to such a point since the growth rates of the q^* mode and the global mode are partially identical. Because of this, expanding about the pure global mode bifurcation point is not useful for finite excursions into the unstable regime and instead we must keep open the possibility that the amplitude of the q^* mode is equally important. Therefore, we analyze the system by locating a nearby codimension two point and thereby keep both the global am-

plitude and the wave amplitude as slowly varying dynamical objects. This approach will be checked for consistency by determining (numerically) that (modulated) standing waves can exist even for parameter values without a codimension two point.

To be precise, let us first focus on $\alpha'=0.1$, $\beta'=0.1$, $\alpha=\beta=0$, and $q^*=46 \text{ mm}^{-1}$. A simple stability calculation shows that there is a codimension two point at $\bar{P}_{CO} = 2.48 \times 10^{-5} \text{ Torr}$, $\bar{P}_{O_2} = 4.7 \times 10^{-5} \text{ Torr}$; the locus of Hopf bifurcation points is plotted in Fig. 1. Furthermore, if we compare the two Hopf frequencies,

$$\omega_0 = 0.409, \quad \omega_q = 0.407,$$

we find that these are sufficiently close that we must allow for the possibility of resonance between the two oscillators. So, we proceed by applying standard bifurcation analysis to the evolution equation near the point where the $q=0$ and $q=46 \text{ mm}^{-1}$ modes jointly bifurcate. We assume

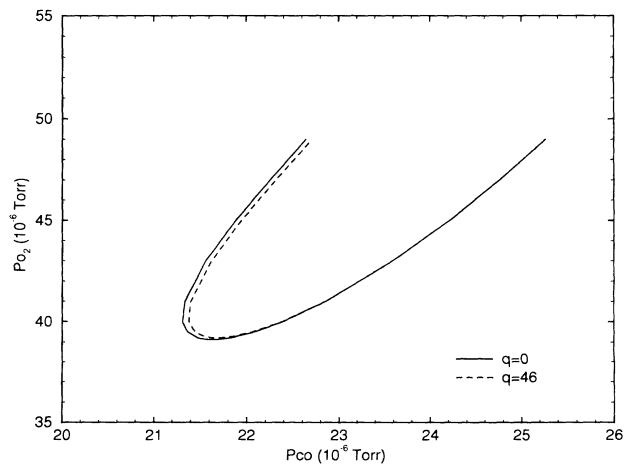


FIG. 1. Contours of the Hopf bifurcation with $\alpha=0$, $\beta=0$, $\alpha'=0.1$, and $\beta'=0.1$.

$$\Psi = \Psi^{(0)} + A_0 \Psi_0 e^{-i\omega_0 t} + A_R \Psi_q e^{iqx - i\omega_0 t} + A_L \Psi_q e^{-iqx - i\omega_0 t} + \text{c.c.}, \quad (5)$$

where Ψ_0, Ψ_q are the eigenvectors of the bifurcating modes. Expanding to third order and using the fact that the right- and left-going waves will have zero spatial average, we find the Landau equations,

$$\begin{aligned} \dot{A}_0 &= \epsilon \lambda_0 A_0 - g_0 |A_0|^2 A_0 - g_1 (|A_R|^2 + |A_L|^2) A_0 - g_3 A_L A_R A_0^*, \\ \dot{A}_R &= \epsilon \lambda_q A_R - i \Delta \omega A_R - g_q |A_R|^2 A_R - g'_1 |A_0|^2 A_R - g_2 |A_L|^2 A_R - g'_3 A_0^2 A_L^*, \\ \dot{A}_L &= \epsilon \lambda_q A_L - i \Delta \omega A_L - g_q |A_L|^2 A_L - g'_1 |A_0|^2 A_L - g_2 |A_R|^2 A_L - g'_3 A_0^2 A_R^*. \end{aligned} \quad (6)$$

Here, $\Delta \omega$ is the resonance detuning $\omega_q - \omega_0$, λ_0, λ_q are the two unfolding parameters of the bifurcation, and ϵ the distance from the codimension two point. The g coefficients in the expansion are given in Table II for this specific case; details of this calculation as well as the variation of these coefficients with the system parameters will be given elsewhere [10]. In what follows, we will drop the resonance detuning as being negligibly small as long as we are a finite distance ϵ from the bifurcation point.

The most important feature of the above equations is the presence of the self-induced parametric driving term with coefficient g_3 . These terms allow for the existence of modulated waves where the global average coverages and the coverages at wave vector q synchronously oscillate. To investigate this possibility, we assume a global oscillation $A_0 = \sqrt{\epsilon} d e^{i\Omega \tau}$, $A_R = A_L = 0$ (where $\tau = \epsilon t$) and study its stability. Since the Hopf bifurcation to the global oscillation is supercritical ($\text{Reg}_0 > 0$), we immediately obtain $d = (\text{Re} \lambda_0 / \text{Reg}_0)^{1/2}$ and $\Omega = \text{Im} \lambda_0 - \text{Im} g_0 d^2$. Assuming a perturbation $\delta A_L = \delta A_R = b(\tau) e^{i(\Omega \tau + \gamma)}$, we find the stability condition

$$\text{Re} \lambda_q - d^2 (\text{Reg}'_1 + \cos 2\gamma \text{Reg}'_3 + \sin 2\gamma \text{Im} g'_3) < 0, \quad (7)$$

where the phase γ is determined by

$$\begin{aligned} d^2 (\text{Reg}'_3 \sin 2\gamma - \text{Im} g'_3 \cos 2\gamma + \text{Im} g_0 - \text{Im} g'_1) \\ = \text{Im} (\lambda_0 - \lambda_q). \end{aligned} \quad (8)$$

Evaluating this expression along the direction $\text{Re} \lambda_q \approx \text{Re} \lambda_0$, we find [10] that $\text{Im} (\lambda_0 - \lambda_q)$ is very small and that the global mode is in fact unstable. This occurs because the phase γ is adjusted to make $\text{Reg}'_3 e^{-2i\gamma} < 0$ and hence the global oscillation pumps energy into the standing wave. The system instead exhibits a modulated wave with $A_0 = \sqrt{\epsilon} d e^{i\Omega \tau}$, $A_R = A_L = \sqrt{\epsilon} b e^{i(\Omega \tau + \gamma)}$; the respective amplitudes are obtained by solving the coupled (complex) equations

$$\lambda_q - (g_q + g_2) \tilde{b}^2 - \tilde{d}^2 (g'_1 + g'_3 e^{-2i\gamma}) = i \tilde{\Omega}, \quad (9)$$

$$\lambda_0 - g_0 \tilde{d}^2 - \tilde{b}^2 (2g_1 + g_3 e^{2i\gamma}) = i \tilde{\Omega}$$

for the four unknowns \tilde{d} , \tilde{b} , γ , and $\tilde{\Omega}$, the frequency shift of the modulated wave.

So, we have seen that for this specific set of global coupling parameters, the catalysis system has a codimension two bifurcation with a 1:1 resonance. This gives rise to an instability of the globally oscillating mode to a standing wave (standing since the parametric coupling disallows traveling wave states). We now imagine perturbing the parameters, perhaps even to a set for which there is no such bifurcation. We argue that the resonance behavior encompassed by the amplitude equations given above will still dominate the nonlinear dynamics of the system. That is, the change $\Delta \alpha$, $\Delta \beta$, $\Delta \alpha'$, $\Delta \beta'$ away from the codimension two point will modify the unfolding parameters λ_0 , λ_q , and $\Delta \omega$ by a small amount but the system will still be accurately described by Eqs. (6) above. Physically, the nonlinear wave resonance is strong enough to overcome small detuning and small differences in the relative growth rates.

To verify this picture, we have performed direct numerical simulations of the equations of motion with and without global coupling terms. To do this we choose \bar{P}_{CO} and \bar{P}_{O_2} to lie inside the Hopf bifurcation curves for both $q=0$ and $q=q^*$. For example, in one run we set $\bar{P}_{\text{CO}} = 2.41 \times 10^{-5}$ Torr, $\bar{P}_{\text{O}_2} = 4.70 \times 10^{-5}$ Torr, and simulated the system without global couplings in a box which sets $q^* = 32.22 \text{ mm}^{-1}$. We start the system with a random set of a , c , and o values close to the (unstable) steady-state values. The CO concentration profile which emerges at late times is plotted in Fig. 2. Notice that there is a modulated wave having both $q=0$ and $q \neq 0$ components. This nonlinear state of the system exists for some small but finite range of parameter space around this point [10]. In fact, even if we set $\alpha' = \beta' = 0$ and have $\alpha, \beta > 0$ (but not too large) we can still find stable modulated wave (MW) states—here the global coupling is attempting to completely synchronize the surface oscillations but is “overcome” by the parametric forcing.

We have already pointed out that these standing waves exist in a fairly narrow parameter range. In fact, we were unable to locate any standing waves until we performed the bifurcation analysis and learned which was the relevant regime. This seems to be consistent with

TABLE II. Amplitude equation parameters in sec^{-1} for $\bar{P}_{\text{CO}} = 2.48 \times 10^{-5}$ Torr, $\bar{P}_{\text{O}_2} = 4.70 \times 10^{-5}$ Torr.

g_0	(1454.05, -7523.35)	g_q	(2723.57, -7116.96)
g_1	(3005.38, -14957.24)	g'_1	(2898.22, -14955.70)
g_3	(3057.19, -14928.53)	g'_3	(1469.11, -7461.73)
		g_2	(2013.51, -11959.55)

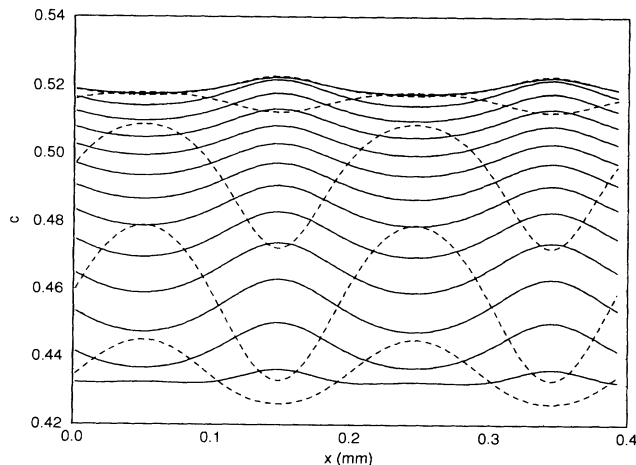


FIG. 2. CO concentration profiles at 1-s intervals, no global coupling; here $\bar{P}_{\text{CO}}=2.41 \times 10^{-5}$ Torr, $\bar{P}_{\text{O}_2}=4.70 \times 10^{-5}$ Torr, $q=32.22 \text{ mm}^{-1}$. Solid lines (from top to bottom) are followed in time by dashed lines (from bottom to top).

similar findings in the experimental studies to date; one finds the standing waves only in a rather definite part of the $P_{\text{CO}}-P_{\text{O}_2}$ plane [11].

One question as yet unresolved is the question of wavelength selection. In our simulations, say without global coupling, stable MW states exist for (approximately) $30 \leq q \leq 50 \text{ mm}^{-1}$. Our approach has been to find a nearby codimension two point for this range of q and show that the nonlinear dynamics results in the MW state. In principle, this approach might reveal why there is a finite band of allowed states since the Landau equation parameters vary with q ; this has not yet been attempted. Experimentally, the system does seem to have a fairly well selected wave vector, in the neighborhood of $q \approx 100 \text{ mm}^{-1}$. Given the large uncertainties in the parameters entering into the reaction dynamics, this should be viewed as reasonably good agreement.

In summary, we have shown that adding spatial coupling terms to the reaction kinetic scheme of EKE results

in stable (modulated) standing waves. The existence of this nonlinear state has been analyzed by arguing that the most important nonlinear interaction is the pumping of standing wave modes by the almost resonant global oscillation. Our findings agree qualitatively with experimental findings with regard to pattern wave vector and narrowness of parameter range.

We acknowledge useful conversations with C. Surko, S. Yamamoto, and especially R. M. Eiswirth and G. Ertl. This work is supported by the U.S. NSF under Grant No. DMR91-15413.

-
- [1] For a general introduction, see *Oscillations and Traveling Waves in Chemical Systems*, edited by J. E. Field and M. Burger (Wiley, New York, 1985), and also the special issue of *Physica (Amsterdam)* **49D**, *Waves and Patterns in Chemical and Biological Media*, edited by H. Swinney and V. Krinsky. For a more recent review, see E. Meron (to be published).
 - [2] S. C. Muller, T. Pless, and B. Hess, *Physica (Amsterdam)* **27D**, 87 (1987).
 - [3] R. Imbihl, M. P. Cox, G. Ertl, H. Müller, and W. Brenig, *J. Chem. Phys.* **83**, 1578-1587 (1985).
 - [4] J. M. Davidenko *et al.*, *Nature (London)* **355**, 349 (1992); H. Levine and W. Reynolds, *Phys. Rev. Lett.* **66**, 2400 (1991), and references therein.
 - [5] V. Castets, E. Dulos, J. Biossonade, and P. de Kepper, *Phys. Rev. Lett.* **64**, 2953 (1990).
 - [6] S. Jakubith, H. H. Rotermund, W. Engel, A. von Oertzen, and G. Ertl, *Phys. Rev. Lett.* **65**, 3103-3106 (1990).
 - [7] R. M. Eiswirth, K. Krischer, and G. Ertl, *Appl. Phys. A* **51**, 79-90 (1990).
 - [8] K. Krischer, R. M. Eiswirth, and G. Ertl, *Surf. Sci.* **251**, 900-904 (1990).
 - [9] R. M. Eiswirth, P. Möller, K. Wetzl, R. Imbihl, and G. Ertl, *J. Chem. Phys.* **90**, 510-521 (1989).
 - [10] H. Levine and X. Zou (to be published).
 - [11] R. M. Eiswirth (private communication).