

Traveling-wave fragments in anisotropic excitable media

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Experiments with an anisotropic chemical excitable medium—a catalytic chemical reaction on a single crystal surface—reveal a kind of stable wave pattern representing single traveling-wave fragments. Their existence is attributed to the presence of a strong state-dependent diffusion anisotropy in the medium. A simple theory of traveling fragments setting general conditions for their observation is proposed. Its conclusions are confirmed by numerical simulations of a reaction-diffusion model. Our analysis suggests that traveling-wave fragments are a general property of excitable media with strong state-dependent anisotropy.

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Phenomena of spatiotemporal self-organization in excitable media have attracted considerable interest in various fields from physics to biology. In chemical systems, wave formation has been extensively studied with various reaction systems of the Belousov-Zhabotinskii (BZ) type and the properties of target patterns, spiral waves, and stationary spots have been investigated [1–3]. These reactions occur in the fluid phase where diffusion is isotropic, and hence a question arises whether different kinds of patterns can be expected if the medium is anisotropic. When the diffusion constants of all species are made anisotropic by the same factor, the result would be an elliptical distortion of the patterns. The situation is different when the anisotropy varies depending on the state of the system. This is the situation realized in catalytic surface reactions. Such an anisotropy cannot in general be removed by rescaling the coordinates and the effects which are not found in isotropic media may therefore be observed [4–7]. In this paper we present experimental examples of different types of structures along with a theoretical analysis.

The standard method for initiating spiral waves in the BZ reaction consists of breaking a propagating excitation wave [8]. The appearing wave fragment grows, curls at its open ends, and eventually forms a pair of spiral waves. This evolution of a wave fragment is observed when the excitability of the medium is not too small. If the excitability is low, the wave fragment contracts and finally disappears [9]. Hence wave fragments in usual excitable media, such as the BZ reaction, are unstable: they either transform into a rotating spiral wave or vanish.

Here we report on the observation of single wave fragments in a surface reaction that are steadily traveling along a certain crystallographic direction. The reaction studied is the catalytic reduction of NO with hydrogen on a Rh(110) surface. The Rh(110) surface easily dissociates NO into atomic oxygen, O(ad), and atomic nitrogen, N(ad), and the dissocia-

tion products then recombine and react with dissociatively adsorbed hydrogen, H(ad), to the product molecules N₂ and H₂O. At low pressure in the 10⁻⁶ mbar range the process is truly isothermal. Under these conditions the reaction system represents an excitable medium, i.e., we observe target patterns and spiral waves. For imaging these patterns we employ photoemission electron microscopy (PEEM) [10]. This method, which yields a resolution of 0.1–1 μm, is sensitive to local work function variations. A strongly electronegative adsorbate such as oxygen is therefore imaged as a dark area while the nitrogen-covered and bare surface appear bright in PEEM.

In previous investigations, we have demonstrated that rectangularly shaped chemical wave patterns whose sides are oriented along two main crystallographic directions of Rh(110), i.e., along [1 $\bar{1}$ 0] and [001], can be observed in this system [4]. If we first generate such target patterns and then decrease the partial pressure p_{H_2} of hydrogen, we observe that those parts of the pattern which are oriented along the [001] direction dissolve and only the parts oriented along the [1 $\bar{1}$ 0] direction remain. A further decrease of p_{H_2} leads to shrinking of fragments. If we wait until the fragments reach the size of a small nucleus and then increase back the hydrogen partial pressure, steadily traveling wave fragments are produced which are shown in Fig. 1.

Motion and evolution of individual wave fragments for different reaction conditions are demonstrated in Fig. 2. When the partial pressure p_{H_2} is high, the fragment evolves into a pair of counterrotating spirals [Fig. 2(a)]. For slightly lower partial pressure, steadily traveling and expanding wave fragments are observed [Fig. 2(b)]. When the pressure is further decreased, the fragments shrink [Fig. 2(c)].

The fragments shown in Fig. 2(b) travel at a constant velocity of 1.28 μm/s in the [001] direction while simultaneously expanding in the orthogonal direction, i.e., along [1 $\bar{1}$ 0]. The bright area (low work function) forming the head of a traveling-wave fragment can be attributed to adsorbed nitrogen, while the black areas (high work function) are indicative of adsorbed oxygen. The triangular-shaped gray

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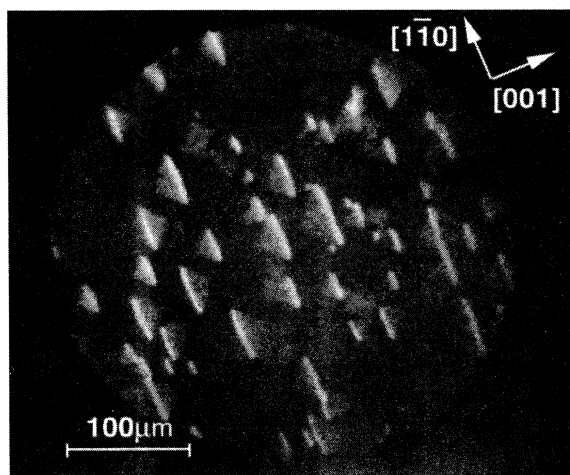


FIG. 1. Traveling-wave fragments in the catalytic NO-H₂ reaction on Rh(110) ($p_{\text{H}_2} = 4.6 \times 10^{-6}$ mbar, $p_{\text{NO}} = 1.8 \times 10^{-6}$ mbar, $T = 620$ K). The fragments are moving in the [001] direction. The excited bright zone in the front is followed by the light gray refractory tail.

zones (intermediate work function) following the bright white stripes correspond to refractory tails of the wave fragments. The leading edges of the fragments exhibit a slight curvature. The trajectories of the fragment ends represent straight lines forming a cone symmetric to the [001] direction. For given parameters, the angular width of the cone is the same for any wave fragment in a medium; it is somewhat less than that of the cone formed by the refractory tail of a fragment. If two wave fragments traveling in the opposite direction collide, they annihilate each other. Note that traveling-wave fragments have previously been seen in experiments with a different catalytic surface reaction [11,12]; however, they were present in large numbers and interacted in a complicated way so that a study of the properties of an individual fragment was not possible.

In the following we construct a phenomenological model explaining the appearance of traveling-wave fragments and demonstrate by numerical simulations that these phenomena are reproduced when the state-dependent anisotropy is included in a typical reaction-diffusion model to reflect the microscopic picture of surface diffusion.

The observed wave patterns can be explained qualitatively, if the excitability of the medium is effectively angle dependent [6]. Suppose that along a certain direction the excitability is sufficient to induce growth and curling of the wave fragment while in the orthogonal direction it is so low that a fragment with this direction of motion should shrink. A flat wave fragment propagating in the high excitability direction would then first grow and curl. But, as curling proceeds and the propagation direction of the wave near its tip is changed, the speed of the growth would diminish because the medium's excitability experienced by the moving tip is decreased. Since at larger angles the growth is replaced by contraction, the tip would not complete in this case a full rotation and produce a spiral wave. Instead, a curved wave fragment traveling through the medium would be produced.

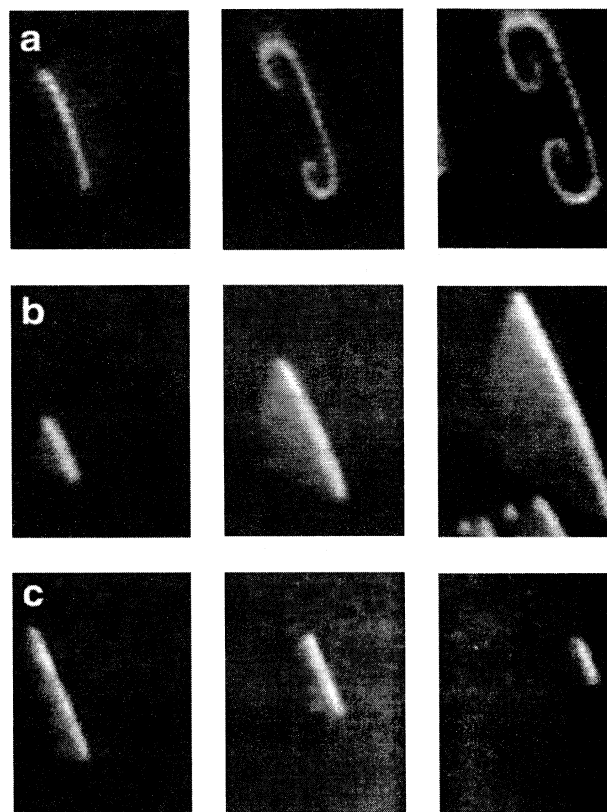


FIG. 2. Evolution of a single wave fragment for different experimental conditions in the catalytic surface reaction: (a) $p_{\text{H}_2} = 5.5 \times 10^{-6}$ mbar, $p_{\text{NO}} = 1.8 \times 10^{-6}$ mbar, $T = 580$ K, the time interval Δt between the frames is 3 s; (b) $p_{\text{H}_2} = 4.6 \times 10^{-6}$ mbar, $p_{\text{NO}} = 1.8 \times 10^{-6}$ mbar, $T = 620$ K, $\Delta t = 30$ s; (c) $p_{\text{H}_2} = 4.4 \times 10^{-6}$ mbar, $p_{\text{NO}} = 1.8 \times 10^{-6}$ mbar, $T = 620$ K, $\Delta t = 30$ s. Subsequent frames are shifted to accommodate the entire traveling object. The size of the frames is $75 \times 100 \mu\text{m}$.

In the kinematic theory of wave propagation in excitable media [13,14] the narrow excitation zone is modeled by a single curve. If a wave is broken, its tip corresponds to an open end of this curve. Any element of the curve moves in its normal direction with velocity $V = V_0 - Dk$ depending on the local curvature k of this element. Moreover, the curve can grow or shrink at its open end with velocity $G = G_0 - \gamma k_0$ that depends on the curvature k_0 at the end point; note that G_0 reflects the effective excitability of the medium [6]. If a medium is anisotropic, both V and G also depend on the angle α between the local propagation direction and the anisotropy axis. Suppose that the velocity G changes its sign at a certain angle α_0 . Then, for higher angles, sprouting of the tip is replaced by its contraction. When this occurs, sprouting and curling of the wave fragment continues only until this angle is reached and steadily traveling wave fragments with a constant angular width of $2\alpha_0$ are thus produced. Figure 3 shows the evolution of wave fragments obtained by the numerical integration of the kinematic equations for anisotropic excitable media [5,6].

Since simple anisotropy could be scaled out by stretching the coordinates—a transformation which does not change the

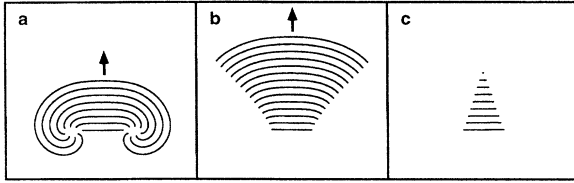


FIG. 3. Kinematics of wave fragments. Time evolution of an initially flat fragment with small perturbations near its open ends is shown. The angular dependence of the tangential tip velocity is $G_0 = A - B(\sin\alpha)^2$, the normal propagation velocity is constant. The vertical direction represents $\alpha = 0$. The kinematical parameters are $V_0 = 1.5$, $D = 1.0$, $\gamma = 1.5$, $B = 1.0$, and (a) $A = 1.5$, (b) $A = 0.5$, (c) $A = -0.5$.

sign of the tip velocity—such behavior of the wave fragments is possible only in reaction-diffusion systems with the state-dependent anisotropy. In the catalytic surface reaction considered here a state-dependent anisotropy is realized by two different types of surfaces reconstructions induced by atomic oxygen and nitrogen, respectively. While atomic oxygen generates so-called missing-row type reconstructions consisting of atomic troughs along the $[1\bar{1}0]$ direction, atomic nitrogen gives rise to the Rh-N chains which are oriented perpendicular to the direction of oxygen-induced troughs [15–17]. Assuming that diffusional anisotropy is merely determined by the substrate geometry, the change from oxygen to nitrogen which occurs in the reaction front causes a rotation of the anisotropy axis by 90° .

Pattern formation on catalytic surfaces can be described by a two-component model with a fast activator variable (u) representing an adsorbate coverage (changing rapidly due to adsorption and reaction processes) and a slow inhibitor variable (v) representing the degree of surface reconstruction and acting as a negative feedback on the coverage [18]. In order to demonstrate that a state-dependent diffusion anisotropy explains the appearance of steadily traveling wave fragments, we have numerically integrated a modification of the well-known FitzHugh-Nagumo model for an excitable medium given by equations

$$\begin{aligned} \partial_t u &= (u - u^3/3 - v)/\varepsilon + \partial_x[D_x(v)\partial_x u] + \partial_y[D_y(v)\partial_y u], \\ \partial_t v &= u + b - av. \end{aligned} \quad (1)$$

Because surface reconstructions are nondiffusive, we assume that spatial coupling is only due to diffusion of the adsorbate represented here by the activator species u . As noted above, under our experimental conditions the diffusional anisotropy of the adsorbate (activator) species is controlled by the surface structure. This state-dependent anisotropy of diffusion due to adsorbate-induced reconstructions is modeled in (1) by introducing a steplike dependence of diffusion coefficients on the surface reconstruction variable v ,

$$D_x = D_0, \quad D_y(v) = \begin{cases} D_1, & v \leq v_{\text{crit}} \\ D_2, & v > v_{\text{crit}}. \end{cases} \quad (2)$$

Diffusion in the x direction is kept constant, but in the y

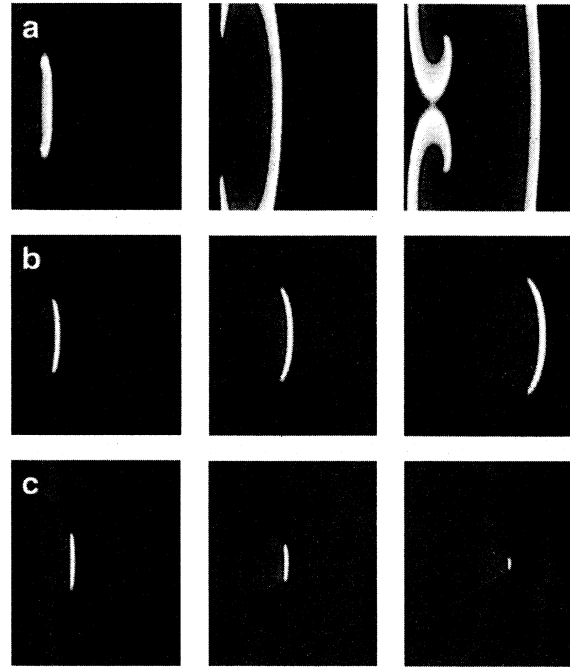


FIG. 4. Evolution of fragments in a numerical simulation of the surface reaction. The model parameters are $a = 0.5$, $\varepsilon = 0.25$, $D_0 = 0.25$, $D_1 = 1.0$, $D_2 = 3.0$, $v_{\text{crit}} = -0.4415$ and (a) $b = 0.97$, (b) $b = 1.12$, (c) $b = 1.18$. The y direction (which exhibits state-dependent diffusion) is parallel to the vertical axis. The time step is 0.000 18, the coordinate step is 0.04, and the grid length is 345×512 . Subsequent frames are separated by time intervals $\Delta t = 2.0$.

direction we switch the diffusion constant between two values, depending on the degree of reconstruction (v).

The results of numerical simulations are shown in Fig. 4. When the excitability of the medium (controlled by parameter b in this model) is sufficiently high, a pair of counterrotating spiral waves develops from the initial flat wave segment [Fig. 4(a)]. Upon decreasing excitability, traveling-wave fragments are found [Fig. 4(b)] which transform, at still lower excitabilities, into the shrinking fragments [Fig. 4(c)]. The angular width of the traveling fragments shown in Fig. 4(b) depends on the parameter b , and the parameter window within which these patterns exist increases with the degree of the state-dependent anisotropy in the system characterized by the difference between D_1 and D_2 .

As shown above, traveling-wave fragments represent another type of persistent pattern in excitable media with state-dependent anisotropy. Though the reported experiments have been performed for a particular system with a catalytic surface reaction, the theory is general and applies for excitable systems with state-dependent diffusion anisotropy of various origins.

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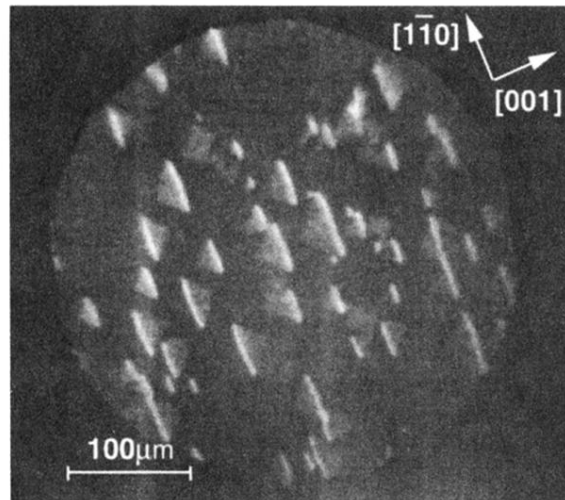


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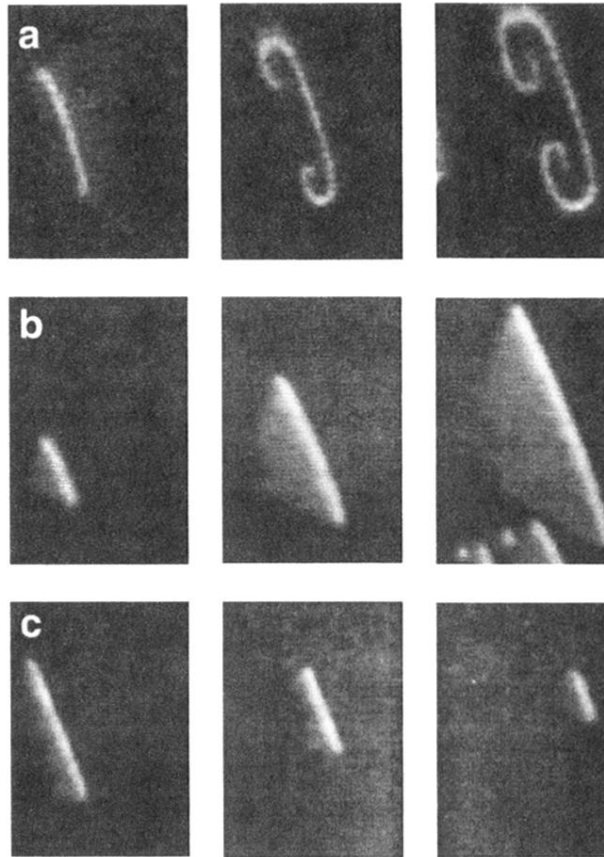


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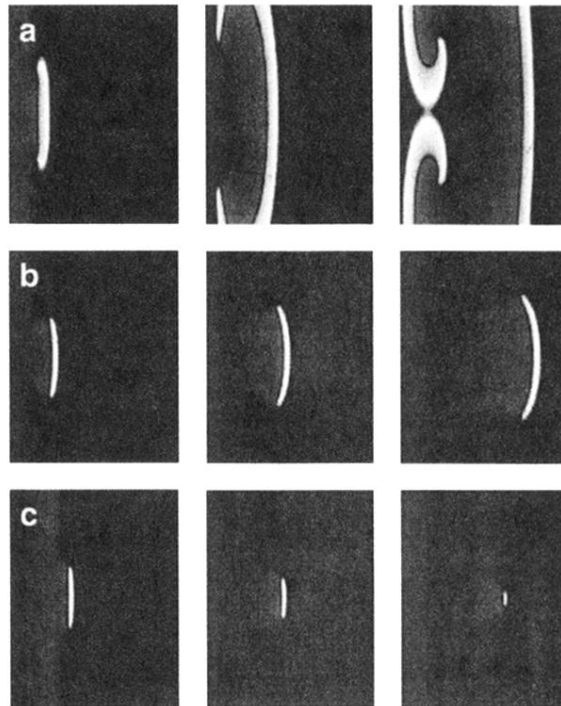


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