Successive splitting of autowaves in a nonlinear chemical reaction medium

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The phenomenon of wave splitting is investigated in a two-dimensional excitable light-sensitive Belousov-Zhabotinsky reaction medium after extremely changing the intensity of illuminated light for a short time. It is found that successive wave splitting and nonannihilation collision between two waves of different amplitudes occur spontaneously under narrow experimental conditions. Experimental observations are approximately reproduced in the specific parameter range by a numerical simulation with a Bär-Eiswirth model.

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I. INTRODUCTION

Spatiotemporal dissipative structures formed in nonequilibrium systems have been extensively investigated. The Belousov-Zabotinsky (BZ) reaction is one of the most studied experimental systems in which various chemical waves, for example, concentric (target) and spiral-shaped waves, have been observed [1,2]. Generally, waves consist of an activator forming a wave front and an inhibitor forming a waveback; an activator triggers the medium to an excited state, and a following inhibitor restores the excited medium to the resting state [3,4]. For this reason, a wave propagates outward from a target center or a spiral center, and cannot reverse spontaneously the direction of the propagation. In addition, if counterpropagating waves collide, they annihilate each other.

Backfiring and nonannihilation collision, apparently conflicting general properties of autowaves described above, have recently attracted interests [5–8]. The phenomenon of backfiring has been studied in reaction media with particular compositions. In the BZ system dispersed in water-in-oil microemulsion and a highly oxidized BZ system, it has been observed as inwardly propagation of concentric waves [9] and splitting of reduction waves [7,10], respectively. In the classical BZ system, in contrast, it has been studied by changing the system dynamics with external forcing. Applications of high decelerating electric field [11,12] and irradiation of a high-intensity light pulse [13] cause splitting of traveling wave, resulting in the backward propagation of the newly formed wave. Since such splitting is induced with the aid of external forcing, in general, it is not repeated spontaneously if the external forcing is turned off. Spontaneous multiple splitting was nevertheless observed by controlling the intensity and the duration of applied light pulse [14]. However, in Ref. [14], it was neither explained nor modeled. It is now of interest to examine whether or not spontaneous repetition of backfiring and nonannihilation collision after an application of external forcing is peculiar in the classical BZ system.

In this paper, we address the phenomenon of wave splitting induced in a two-dimensional excitable light-sensitive BZ reaction medium after extremely changing illuminated light intensity for a short time. We find that multiple splitting of autowaves can take place spontaneously in the narrow experimental condition. We explain multiple splitting and numerically reproduce the observed behaviors, using a Bär-Eiswirth model which takes into account the effects of light stimulation.

II. EXPERIMENT

Experiments were carried out in a two-dimensional Belousov-Zhabotinsky reaction medium in which the light sensitive catalyst ruthenium bipyridine complex $[Ru(bpy)_3^{2+}]$ was immobilized in a silica-gel matrix of 0.5 mm thick [using a solution of 1.25 ml of 20% Na_2SiO_3, 0.60 ml of 20 mM $Ru(bpy)_3SO_4$, 2.0 ml of 10 M H_2SO_4, and 0.75 ml of H_2O]. The gel was placed into an open reactor that was continuously fed with fresh, catalyst-free BZ reaction solution at a pumping rate of 1 ml/h to maintain constant, nonequilibrium conditions. The initial composition of the catalyst-free BZ solution was $[NaBrO_3]=0.385$ M, $[NaBr]=0.135$ M, $[CH_2(COOH)_2]=0.318$ M, and $[H_2SO_4]=0.356$ M. At this composition, the system was initially in an oscillatory regime. Reagent grade chemicals were used without further purification. The temperature of the BZ solution was maintained at 24 ± 0.5 °C. A computer-controlled video projector was used to illuminate the gel from below through a 460 nm bandpass filter. The images of the wave patterns were detected in transmitted light by a charge-coupled device camera (CCD) and recorded on a video recorder. The excitability of the system was controlled, utilizing the photosensitivity of $[Ru(bpy)_3^{2+}]$, by varying the light intensity on an eight-bit gray scale between 0 and 255, which was calibrated to illumination intensity at the gel surface.

Increasing the light intensity ϕ drove the medium from an oscillatory through an excitable to an inhibitory regime where the wave propagation was not possible [15]. Figure 1 shows the phase diagram of wave patterns. We see that there are three regimes separated by two thresholds, ϕ_{c1} and ϕ_{c2}. Among these regimes, the phenomenon of hysteresis was observed. On increasing ϕ, the reaction medium can sustain both target and spiral waves for $\phi<\phi_{c1}$ (regime I), only the spiral wave for $\phi_{c1}\leqslant\phi\leqslant\phi_{c2}$ (regime II), and no waves for $\phi>\phi_{c2}$ (regime III). On decreasing ϕ from above ϕ_{c2}, on the other hand, no wave patterns appeared until ϕ reached ϕ_{c1}. Thus the Hopf bifurcation is subcritical for the light

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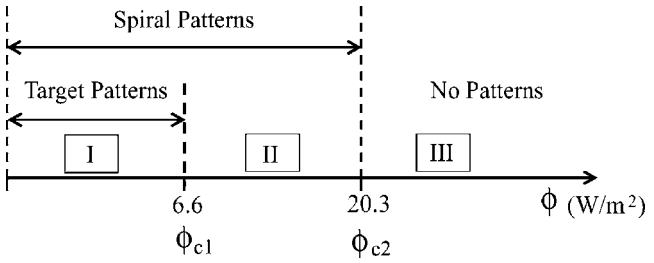

FIG. 1. Phase diagram of wave patterns as a function of the intensity of illuminated light.

flux. In the experiments we imposed an abrupt change in light intensity for a short time, as an external stimulation to trigger wave splitting. Furthermore, we paid attention to the intensity of illumination before and after the stimulation, as well as that of the stimulation. The phenomenon of wave splitting was studied on a single spiral wave prepared in the following manner. Based on a traveling wave emerged spontaneously at the low illumination intensity, a pair of counterrotating spiral wave was first formed by breaking its wave front with a spot of intense light. One of spiral waves was then suppressed with the light spot in order to leave a single spiral wave in the medium [16].

After the stimulation of the intensity above ϕ_{c2} was applied to the system in the regime II for 8 s, a single splitting of an autowave was observed as in Ref. [13]. Here an intense illumination lasting longer than 8 s completely annihilated such an autowave. When the state of the medium before and after the stimulation was in the regime II just below ϕ_{c2}, no splitting occurred. Thus, the stimulation intensity and its duration time, the state of the system before and after the stimulation, and the composition of BZ solution, can be significant control parameters for the occurrence of the wave splitting. Then we tried to induce splitting of autowaves by controlling these parameters.

Figure 2 shows the spatiotemporal pattern revealed when the system was driven from the regime II through the regime III to the regime I. First two wave fronts, traveling from left to right, emerge on the left-hand side of the picture before t_1. Then, a homogeneous light of the high intensity of $\phi > \phi_{c2}$ is delivered between t_1 and t_2. Here the duration time of the stimulation was controlled in such a way that the autowave was not annihilated completely. Once ϕ is lowered below ϕ_{c1}, the attenuated wave recovers, broadens, and then splits into two waves propagating in opposite directions. The newly created wave independently propagates backward, while the original wave keeps propagating in its own direction. Hereafter the created wave behaves like a attenuated wave just after the stimulation; it immediately recovers the same amplitude and shape as those of the ordinary wave, further grows up, and finally splits again into two wave fronts. One disappears upon collision with a third front that appears on the left-hand side of the picture after t_2, and the other splits again. This sequence of events is repeated. Note that the position at which the wave splits into two waves gradually shifts rightward, its direction being in agreement with that of the propagation of the original wave.

In the light-sensitive BZ system, an illumination of light over a certain level suppresses both activator and inhibitory

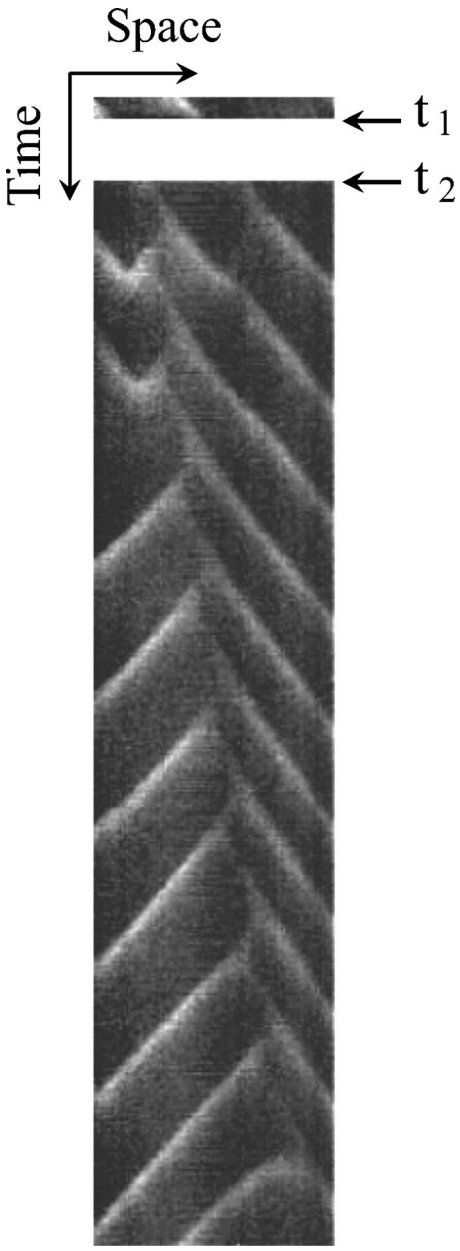

FIG. 2. Spatiotemporal pattern of the autowave after an external stimulation, i.e., an intense illumination between t_1 and t_2 (intensity 23 W/m^2, lasting 8 s), where the wave propagation is unobservable for that period because of halation of the CCD camera. Under a stationary illumination of 3.2 W/m^2, the wave successively splits into two waves propagating in opposite directions.

waves. Once the light intensity is abruptly lowered below that level, both waves begin to recover their own ordinary states. However, there generally exits a large difference between their recovery times; the activator wave recovers much earlier than the inhibitory wave. Consequently, the activator wave has enough time to jump over the inhibitory wave, and can trigger a wave propagating backward [13]. Thus, the difference in recovery time can be an important factor for the occurrence of wave splitting. In that case, it must be possible to induce wave splitting as well through another process of illumination on condition that such a difference can be im-

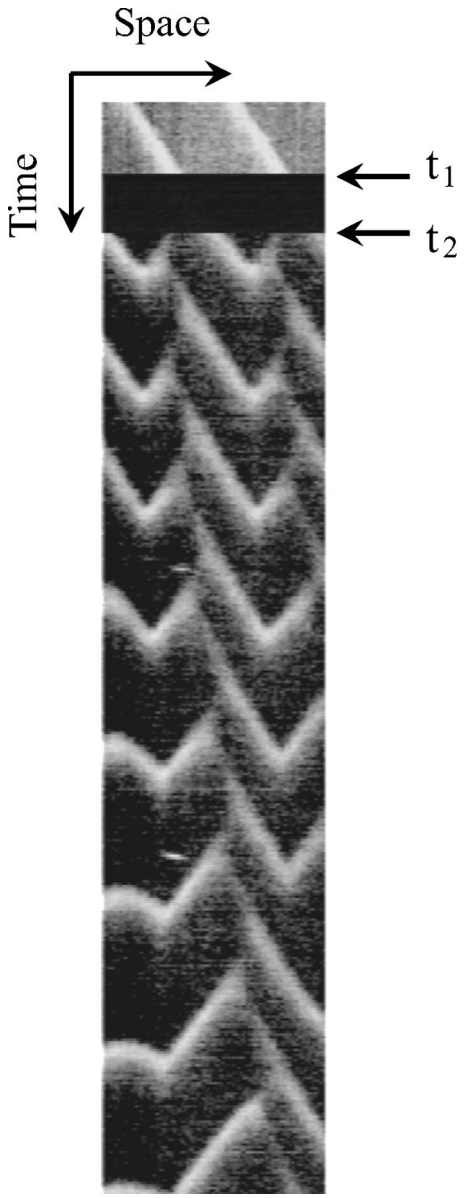

FIG. 3. Spatiotemporal pattern of the autowave after an external stimulation, i.e., a nonillumination between t_1 and t_2 (lasting 8 s), where the wave propagation is unobservable for that period. Under a stationary illumination of 3.2 W/m^2, the wave successively splits into two waves propagating in opposite directions, similar to the case of an intense illumination.

posed in the system. Figure 3 shows the spatiotemporal pattern revealed after the medium is nonilluminated instead of intense illumination. First two wave fronts, traveling from left to right, emerge on the left side of the picture before t_1. Then, the pulse of darkness is delivered between t_1 and t_2. We focus on the time evolution of the left wave front after t_2. It splits into two wave fronts in such a way that the created front propagates leftward, while the original front disappears after colliding with a wave front originated from the right wave front. The created front splits into two fronts. One disappears upon collision with a third front that appears on the left-hand side of the picture after t_2, and the other splits again. Successive splitting occurs with the repetition of these events. Interestingly the first splitting already occurs in the course of the stimulation. This is because the growth of the activator is more accelerated in the dark compared with that of the inhibitor, and consequently the activator wave can jump over the inhibitory wave in the course of the stimulation. The process leading to splitting after the stimulation are similar to those seen in Fig. 2. In addition, the position of wave splitting also gradually shifts in the direction of the propagation of the original wave. Here we would like to emphasize that splitting is repeated spontaneously, as illustrated in Figs. 2 and 3, in contrast to splitting induced every application of an external stimulation [17]. Such a phenomenon apparently conflicts the general properties of autowaves.

Counterpropagating waves of the same size generally annihilate each other upon head-on collision, as seen in Fig. 3. However, this is presumed not to be the case if the sizes of two waves are not the same. On this presumption, the wave created through wave splitting, its amplitude being initially small, was allowed to collide with the ordinary wave by controlling the frequency of the spiral wave. As expected, the ordinary wave keeps its own propagation although attenuates, whereas the small wave disappears, as shown in Fig. 4. This is not an apparent phenomenon as observed in two-dimensional records of the three-dimensional system [18,19]. The collision-stable wave recovers its initial state, broadens, and then splits again into two waves, just like a wave after the stimulation. Thus nonannihilation collision can serve as a stimulation inducing wave splitting. Therefore, it is possible to sustain splitting through nonannihilation collision if the spiral wave with the appropriate frequency is prepared. Such a successive splitting is regarded as spontaneous, because no external forcing is involved in it.

III. REACTION-DIFFUSION MODEL

In order to reproduce numerically the experimental results, we employ the model introduced by Bär and Eiswirth [20], which is a modified version of a piecewise linearized FitzHugh-Nagumo model. This model readily renders wave splitting and more complex wave dynamics in the excitable media [17], given by

$$\frac{\partial u}{\partial t} = \frac{1}{\varepsilon} u(1-u)\left(u - \frac{v+b}{a}\right) + D_u \nabla^2 u, \tag{1}$$

$$\frac{\partial v}{\partial t} = f(u) - v, \tag{2}$$

where $f(u)=0$ for $u<1/3$, $f(u)=1-6.75u(u-1)^2$ for $1/3 \leqq u \leqq 1$, and $f(u)=1$ for $u>1$. The variables u and v correspond to the concentrations of activator and inhibitor, respectively, D_u is the diffusion coefficient of the activator. In the case of BZ system, the role of the inhibitor in a two-variable model is played by the catalyst $Ru(bpy)_3^{2+}$. Since $Ru(bpy)_3^{2+}$ is immobilized in a silica-gel matrix, there is no corresponding diffusion term for v. The decisive parameters in this model are ε and b. The parameter ε determines the relationship between the time scales of u and v. The parameter b

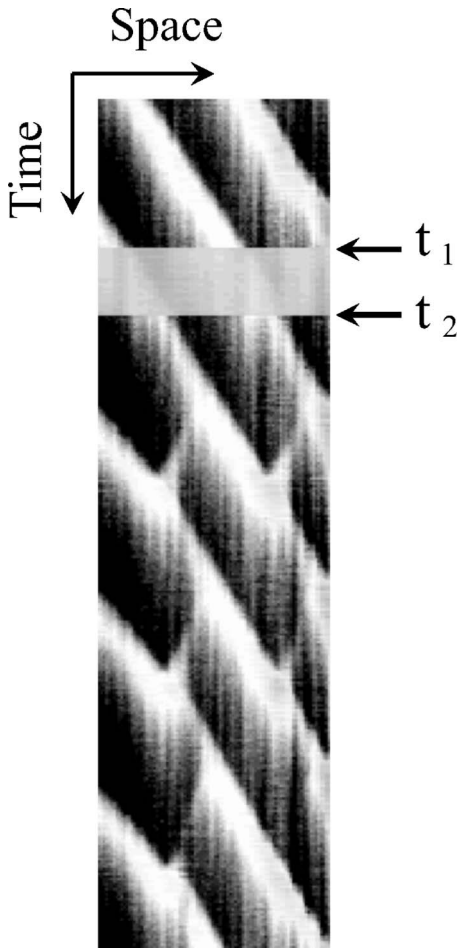

FIG. 4. Nonannihilation collision between two waves of different amplitudes after an intense illumination between t_1 and t_2 (intensity 23 W/m^2, lasting 8 s). Under a stationary illumination of 11.5 W/m^2, wave splitting mediated by collision occurs.

controls the excitability of the medium such that increasing b increases the threshold of excitation, i.e., b would correspond to the intensity of illuminated light in the experiments. The values of parameters are chosen such that the time scale of u is much faster than that of v, $\varepsilon=0.065$, $a=0.84$, $D_u=1$, $b=0.18$ if the stimulation is on, and $b<0.14$ if it is off. The computation was performed in a one-dimensional medium by the improved Euler method with a grid spacing $\Delta x=0.1$, and time steps $\Delta t=0.0025$. The boundary condition at both ends of the interval was taken to be zero flux.

Figure 5 shows the spatiotemporal pattern induced after abruptly changing the value of b from 0.18 to 0.131 370 35. One can see that the wave propagating rightward splits into two waves propagating in opposite directions just after the change in b. The newly created wave which propagates backward recovers immediately the state of the ordinary wave, broadens, and splits again into two waves. This sequence of events is repeated with shifting the position of splitting in the direction in which the original wave propagates. These behaviors are consistent with the experimental results. Here we can see that there are two types of splitting courses which alternate every splitting, paying attention to the change in thickness of the spatiotemporal pattern. The

FIG. 5. Spatiotemporal pattern of successive wave splitting after abruptly changing the value of b from 0.18 to 0.131 370 35 at the time denoted by the dashed line.

difference in splitting course may be responsible for the shift of the splitting position.

The number of splittings n changes stepwise depending on the value of b, as shown in Fig. 6. Note that a lot of splitting are constrained within a very narrow range, i.e., $0.131\,370<b<0.131\,372$. Interestingly n takes only even numbers for $b>b_{\mathrm{opt}}$ and odd numbers for $b<b_{\mathrm{opt}}$, where b_{opt} is the optimal value that maximizes n. In this narrow range of b, nonannihilation collision between two wave of different sizes occurs, as shown in Fig. 7. The collision-stable wave splits into two waves spontaneously, as observed in the experiment (see Fig. 4). Thus the model requires specific control parameters to reproduce the phenomena of successive wave splitting and nonannihilation collision, which corresponds to the narrow experimental condition under which those take place.

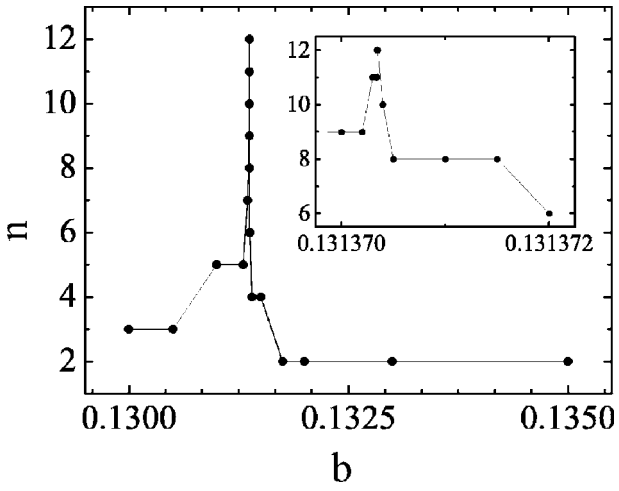

FIG. 6. Number of wave splittings n as a function of b. Inset, expanded view for n versus b.

The successive occurrence of wave splitting can be interpreted according to the idea of Muñuzuri *et al.* [13]. A chemical wave is composed of activator and inhibitory waves. The activator wave changes the medium from a resting state to an excited state, followed closely by the refractory tail (inhibitory wave). The back of a chemical wave propagating outward cannot be excited immediately after its passing, so that a chemical wave cannot propagate backward. When the stimulation is now imposed, both activator and inhibitory waves are photochemically suppressed. Once the stimulation is turned off, the activator wave being a fast variable recovers its initial state much faster than the inhibitory wave being a slow variable [Fig. 8(a)]. Consequently the activator wave can jump over the inhibitory wave, and the wave front of the activator propagating backward appears, in addition to the forward-propagating wave front [Fig. 8(b)]. Then the wave splits into two waves propagating in opposite directions [Fig. 8(c)]. At this time, both activator and inhibitor in the newly created wave are still small. Whether subsequent splitting occurs or not strongly depends on the state of the medium after the stimulation, i.e., the value of b. For small b, the inhibitory wave can recover at the ordinary rate, and consequently prevents the activator propagating backward. In other words, the wave does not split subsequently. For large b (<0.18), on the other hand, both activator and inhibitory waves remain almost suppressed. Therefore, the activator wave cannot recover early enough to jump over the inhibitory wave. In such a parameter range, wave splitting itself does not occur at all. For the optimal value b_{opt}, the activator wave recovers much earlier compared to the inhibitory wave, and consequently can jump over the inhibitory wave that does not yet recover [Fig. 8(d)]. Then the activator wave triggers a wave propagating forward [Fig. 8(f)]. Hereafter, this sequence of events is repeated.

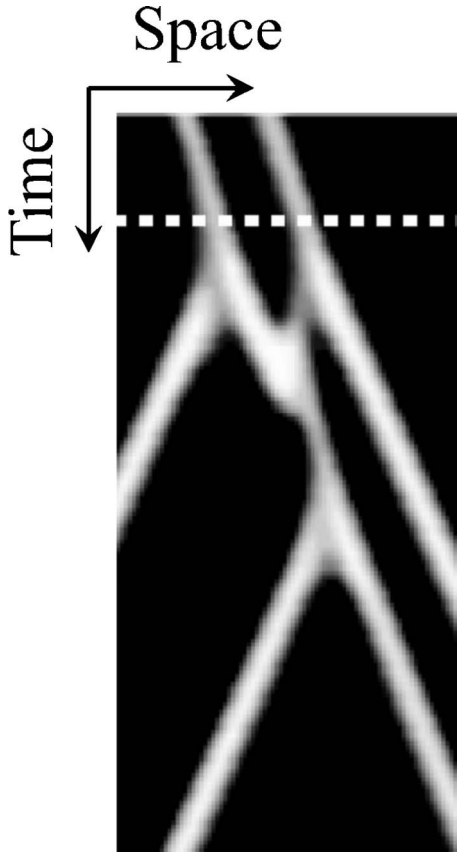

FIG. 7. Nonannihilation collision between two waves of different amplitudes, where such waves originate from two waves generated with the time interval of $2000\Delta t$. The dashed line denotes the time when the value of b is changed abruptly from 0.18 to 0.131 370 35.

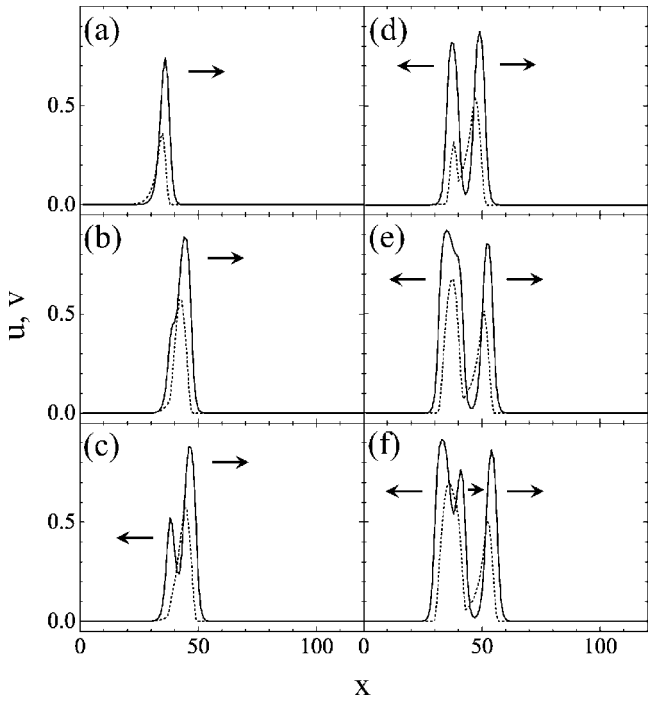

FIG. 8. Mechanism of successive splitting. Each figure shows the shape of the activator (solid line) and inhibitory (dotted line) waves with a time lapse; (a) before the stimulation and (b)–(f) after the stimulation. Arrows show the propagation direction of the activator wave.

IV. CONCLUSION

We have investigated both experimentally and numerically behaviors of the autowave revealed in a two-dimensional excitable medium after the stimulation for a short time. We have observed that spontaneously repeated wave splitting and nonannihilation collision between two waves of different amplitudes under the narrow experimental condition. In addition, we have found that such nonannihilation collision can serve as a trigger that causes wave splitting. The numerical simulation has been able to reproduce experimentally observed behaviors in the very narrow parameter range, corresponding to the narrow experimental condition. These phenomena apparently conflict the general properties of autowaves. In inducing these phenomena, it is essential to impose a large difference in reaction rate between the activator and the inhibitor and to adjust the intensity of illumination to an appropriate level after a stimulation. If these conditions are satisfied, splitting always occurs after the autowave is suppressed, regardless of whether a trigger is external (light illumination) or internal (collision). In practice, however, its repetition is limited within several 10 times. For this reason, successive splitting can be regarded as a sort of relaxation phenomenon. It may be associated with a chemical memory effect that the areas impressed by a light pulse shows a phase shift in the oscillating reaction until finally the medium is homogenized again [21]. Thus successive splitting does not conflict general properties of autowaves.

Recently, it has been reported that a finite number of light pulses, each of which causes a single splitting of waves, completely annihilate erratic spiral breakups leading to turbulence associated with heart fibrillation [17]. In contrast, multiple splitting as observed in this experiment may be counter-productive to such a control of turbulence.

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[1] A. T. Winfree, Science **175**, 634 (1972).
[2] *Chemical Waves and Patterns*, edited by R. Kapral and K. Showalter (Kluwer, Dordrecht, Netherlands, 1995).
[3] V. I. Krinsky, *Self-Organization: Autowaves and Structures Far from Equilibrium* (Springer-Verlag, Berlin, 1984).
[4] A. T. Winfree, in *Lecture in Complex Systems*, edited by L. Nadel and D. Stein (Addison-Wesley, Reading, MA, 1993), p. 207.
[5] H. R. Brand and R. J. Deissler, Phys. Rev. Lett. **63**, 2801 (1989).
[6] S. Fauve and O. Thual, Phys. Rev. Lett. **64**, 282 (1990).
[7] P. Kaštánek, K. Kosek, D. Šnita, I. Schreiber, and M. Marek, Physica D **84**, 79 (1995).
[8] J. Wang and I. Mann, J. Chem. Phys. **119**, 7924 (2003).
[9] V. K. Vanag and I. R. Epstein, Science **294**, 835 (2001).
[10] F. Sakamoto and K. Miyakawa, J. Phys. Soc. Jpn. **69**, 2775 (2000); **70**, 2263 (2001).
[11] H. Ševčíková and M. Marek, Physica D **9**, 140 (1983).
[12] H. Ševčíková, M. Marek, and S. C. Müller, Science **257**, 951 (1992).
[13] A. P. Muñuzuri, V. Pérez-Villar, and M. Markus, Phys. Rev. Lett. **79**, 1941 (1997).
[14] A. P. Muñuzuri, Ph. D. thesis, Universidad de Santiago de Compostela, Spain, 1996.
[15] V. Gáspár, G. Bazsa, and M. T. Beck, J. Phys. Chem. **264**, 43 (1983).
[16] O. U. Kheowan, V. S. Zykov, O. Rangsiman, and S. C. Müller, Phys. Rev. Lett. **86**, 2170 (2001).
[17] M. Woltering and M. Markus, Phys. Lett. A **297**, 363 (2002); Physica D **168-169**, 23 (2002).
[18] K. I. Agladze, V. I. Krinsky, A. V. Panfilov, H. Linde, and L. Kuhnert, Physica D **39**, 38 (1989).
[19] H. Linde and E. Engel, Physica D **45**, 13 (1991).
[20] M. Bär and M. Eiswirth, Phys. Rev. E **48**, R1635 (1993).
[21] L. Kuhnert, Nature (London) **319**, 393 (1986).