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Breakup of propagating waves through the development of a transient unexcitable regime

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Spontaneous breakup of propagating waves was investigated in this paper with a ferroin-catalyzed Belousov-Zhabotinsky reaction modified with the inclusion of a second substrate, 1,4-cyclohexanedione (CHD). The presence of CHD, which forms a separate chemical oscillator with acidic bromate, led to the development of a scattered unexcitable regime in the studied medium, where as waves passed through these unexcitable media, the propagation was disrupted, causing the creation of free ends. It thus presents a new avenue through which a chemical wave breaks up to form spirals. By manipulating the concentrations of CHD, sulfuric acid, and bromate, unexcitable regimes of different sizes with different survival times were obtained. Kinetic data on wave speed prior to and after the unexcitable window illustrates that the occurrence of an unexcitable regime is not due to depletion of components needed for wave propagation.

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I. INTRODUCTION

In spatially extended media, the coupling of nonlinear reaction kinetics and chemical transportations can lead to the formation of concentration profiles (i.e., chemical waves) propagating at a constant speed without attenuation [1–5]. In a two-dimensional medium, those chemical waves may appear as a propagating front, target pattern, or spirals [6]. In nature, spirals are found ubiquitously. For instance, spiral waves are seen in a number of different media including carbon monoxide oxidation on platinum crystals [7], aggregation of slime moulds [8,9], and the myocardium of the heart [10]. Depending on the local reaction dynamics, an above-threshold perturbation or the presence of a heterogeneous particle is sometimes required for initiating waves [11]. However, these initial waves normally have a closed geometry such as a circular pattern [10]. How propagating waves break up to form free ends has attracted increasing attention in the past three decades due to its close connection to the formation of spiral turbulence [12–17].

It is generally thought that the presence of an external disturbance or internal thermal fluctuations is necessary for causing symmetry breaking [11]. In earlier research, Müller and co-workers demonstrated that collisions of high-frequency target waves with a physical object in a reaction-diffusion medium may lead to the creation of free ends, which will bend inward forming two oppositely rotating spirals [18]. Further perturbation can result in multi-armed spirals [19]. More recent investigations, especially those on the spontaneous occurrence of spiral turbulence, have shown that when the initial wave activity is a spiral, the breakup of the spiral arms (i.e., the spontaneous creation of more free ends) could take place through three different mechanisms [20–32]. The meandering of spiral tips, caused by the variation of a bifurcation control parameter [33], is one of the routes where due to the Doppler effect within the regime of short wavelength the wave number may become larger than permitted by the system [20]. As a result, spiral breakups take place in such a region. Such a Doppler instability has been seen both in excitable and in oscillatory media. The second approach involves the formation of a superstructure due to long-wavelength modulations in an oscillatory medium [22,23,28]. The third scenario of spiral turbulence formation is via the transverse instability of the line defects of the period-2^n spiral waves [24,25].

This study explores a new avenue of inducing the breakup of propagating waves, where these free ends may subsequently develop into stable spirals or spiral turbulence. The paper is organized as follows. In Sec. II, we describe the theoretical background of the proposed research. Section III presents the experimental procedure employed in this research. Experimental observations on the breakup of propagating fronts through the occurrence of transient unexcitable regime are presented in Sec. IV, in which the occurrence of scattered multiple unexcitable regions and kinetic data regarding wave speeds are characterized as a function of the initial compositions of the reaction-diffusion medium. Section V summarizes our finding.

II. THEORETICAL BACKGROUND

In the past two decades, there has been increasing interest in the behavior of coupled dynamical systems, in which amplitude death could take place when the coupled oscillators drive each other to a fixed point and stop oscillating [34–36]. In the absence of coupling, the individual subsystems were on limit cycles of different periods or chaotic oscillations. The new fixed point is created by the coupling. Notably, the fixed point (the nonoscillatory state arising from the coupling of two oscillators) could be excitable or unexcitable. When the nonoscillatory state is excitable, the coupled system will be able to support propagating waves, behaving like other regular excitable media reported in the literature [1–5]. However, if the fixed point is unexcitable, it would then eliminate any wave activity passing through it from the surrounding region, creating free ends at the boundary of this unexcitable regime. As discussed in the literature [34–36], the occurrence of the amplitude death phenomenon depends on the

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coupling strength and the dynamics of the two suboscillators.

The chemical system to be investigated here is constructed via adding a second substrate, 1,4-cyclohexanedione, into the classic Belousov-Zhabotinsky (BZ) oscillator, in which one suboscillator is the classic BZ reaction while the other arises from 1,4-cyclohexanedione-bromate reactions. Coupling of the two chemical oscillators is established through the following steps:

$$\mathrm{BrO_3{}^- + HBrO_2 + H^+ \rightarrow BrO_2{}^{\cdot} + H_2O}, \tag{1}$$

$$\mathrm{Fe(phen)_3{}^{2+} + BrO_2{}^{\cdot} + H^+ \rightarrow Fe(phen)_3{}^{3+} + HBrO_2}, \tag{2}$$

$$\mathrm{H_2Q + 2BrO_2{}^{\cdot} + 2H^+ \rightarrow Q + 2HBrO_2}, \tag{3}$$

$$\mathrm{Fe(phen)_3{}^{3+} + MA \rightarrow Fe(phen)_3{}^{2+}} + \text{other products}, \tag{4}$$

$$\mathrm{Fe(phen)_3{}^{3+} + CHD \rightarrow Fe(phen)_3{}^{2+}} + \text{other products}, \tag{5}$$

where H_2Q is an intermediate produced from CHD and MA denotes malonic acid [3,37–39]. Reactions (1), (2), and (4) represent some of the keys steps from the classic BZ oscillator [3], while steps (1), (3), and (5) represent important steps in the catalyzed CHD-bromate oscillator [37–39]. Coupling takes place through steps (2) and (3) competing for the bromine dioxide radicals as well as through reactions (4) and (5) with the oxidized metal catalyst ferriin. Earlier study has illustrated that the initial concentration of reactant in a closed chemical system can act as a bifurcation control parameter, in which its slow decrease led the system to evolve through different dynamic regimes [40]. In this coupled chemical system, the continuous consumption of reactants causes changes in the dynamics of the two suboscillators and may lead the system to evolve to the point where the two suboscillators produce the behavior of coupling-induced amplitude death, i.e., forming a fixed point that could be excitable or unexcitable.

Our earlier kinetics study of the BZ reaction in the presence of CHD illustrates the occurrence of the amplitude death phenomenon as the reaction system evolves in time [37]. Since reactants are consumed continuously in time, the behavior of amplitude death (i.e., nonoscillatory evolution) eventually disappears after a transient time between 150 and 800 min. As a result, the stirred system exhibits sequential oscillations, where two groups of spontaneous oscillations are separated by a period of nonoscillatory evolution [37]. More importantly, the nonoscillatory state could be unexcitable and thus eliminate all existing wave activities. Upon the disappearance of amplitude death behavior as a result of continuous consumption of reactant, a batch of new wave activity occurred spontaneously in the medium, leading to the observation of sequential waves [41]. Different from the study of sequential waves, a key condition in this envisioned new avenue of spiral formation is whether the nonoscillatory state (i.e., amplitude death behavior) can be controlled to take place locally, being surrounded by an oscillatory medium. As a result, when waves propagate through the unexcitable region, free ends are created at the boundary of this unexcitable regime.

In a reaction-diffusion system, the consumption of local reactants is determined by the number of waves propagating through the region. In other words, the dynamics of the reaction in the region experiencing more wave activities varies faster than the other part of the medium. Consequently, those areas may evolve into the parameter range suitable for the amplitude death behavior earlier than the rest of the medium. Once these scattered unexcitable regimes emerge, waves from the surrounding areas are broken up upon propagating into it. Later, the unexcitable region regains its property to support wave propagation, and free ends formed at the interface are able to develop into spirals. Depending on the number and size of the unexcitable regimes occurring in the reaction-diffusion medium, they may develop into spiral turbulence. The following experiments illustrate that wave activity near the core of a spiral is denser than that in other parts of the medium, and the nonoscillatory dynamics (i.e., unexcitable dynamics) commences from those regions.

III. EXPERIMENTAL METHODS

To minimize the hydrodynamic influence on the breakup of propagating waves, pattern formation was investigated with a thin layer of cation-exchange beads, where the metal catalyst ferroin was immobilized onto the surface of these beads while all other reactants were kept in the aqueous solution phase. This configuration ensures that wave activity is only formed on the surface of these beads. The gravity warrants that these beads do not move when being subjected to a small magnitude disturbance (e.g., any impact on the lab desk). The reaction solution was prepared through the stock solutions of $NaBrO_3$ (Aldrich, 99%), 0.6 M, dissolved in distilled water; malonic acid, 0.8 M, dissolved in distilled water; and sulfuric acid (Aldrich, 98%), 3.0 M, diluted with distilled water. 1,4-cyclohexanedione (Fluka, 98%) was dissolved directly in the reaction mixture. All chemicals were used in their commercial grade without further purification.

The analytical grade 100–200 mesh cation-exchange resin (Dowex 50W-X4) was purchased from the Fisher Scientific company. The cation resin was first washed five times with distilled water to modify its acidity. To load the catalyst ferroin, which was prepared with $FeSO_4 \cdot 7H_2O$ (Aldrich) and 1,10-phenanthroline (Aldrich) according to a 1:3 stoichiometric relationship, onto the resin, 20.0 g of resin was mixed with 50.0 mL of 1.25×10^{-3} M ferroin solution and the mixture was stirred vigorously for 1 h. The ferroin solution became transparent at the end of the process, presumably due to the complete absorption of ferroin by the cation beads. The mixture was left unstirred for 24 h. To begin our experiments, 30.0 mL of the BZ reaction solution (without ferroin) was prepared according to desired concentrations and was mixed with 3.0 g of the beads loaded with ferroin. The mixture was poured into a Petri dish (9.0 cm in diameter), in which the beads formed a thin film of 0.4 ± 0.1 mm on the bottom of the Petri dish. The Petri dish was maintained at room temperature of 26.0 ± 1.0 °C. Pattern formation was

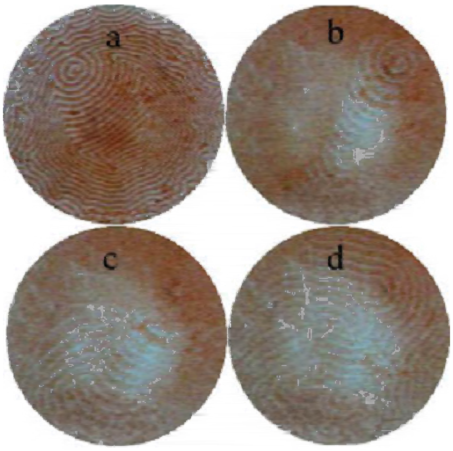

FIG. 1. (Color online) Snapshots of waves in the CHD-modified ferroin-catalyzed BZ reaction: (a) 127 min, (b) 470 min, (c) 528 min, and (d) 614 min after mixing all reagents together. The initial concentrations are [CHD]=0.0097 M, $[BrO_3^-]$=0.080 M, [MA]=0.085 M, and $[H_2SO_4]$=0.42 M. White represents a high concentration of ferriin, whereas dark represents a high concentration of ferroin. Unexcitable dynamics occurred from outside of the medium.

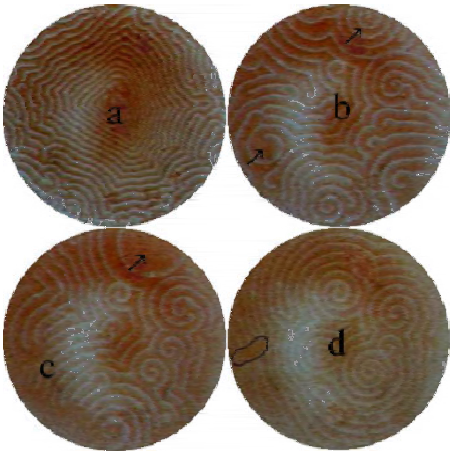

FIG. 2. (Color online) Snapshots of waves in the CHD-modified ferroin-catalyzed BZ reaction: (a) 192 min, (b) 378 min, (c) 437 min, and (d) 540 min, after mixing all reagents together. The initial concentrations are [CHD]=0.0096 M, $[BrO_3^-]$=0.080 M, [MA]=0.085 M, and $[H_2SO_4]$=0.4 M. White represents a high concentration of ferriin, whereas dark represents a high concentration of ferroin. Scattered unexcitable regimes are developed under this condition.

monitored with a CCD camera equipped with a zoom lens. The CCD camera was connected to a personal computer running a frame grabber program (Matrox Imaging Library).

IV. RESULTS AND DISCUSSION

A. Scattered unexcitable regimes

Our earlier study illustrates that a high concentration of CHD facilitates the occurrence of sequential oscillations in the CHD-ferroin-BZ reaction system [37]. More importantly, the nonoscillatory state, created through the coupling of two suboscillators, could become unexcitable and thus did not support wave propagation in the spatially extended medium [41]. Figure 1 presents a series of snapshots of the wave activity under the conditions $[BrO_3^-]$=0.080 M, [MA] =0.085 M, $[H_2SO_4]$=0.42 M, and [CHD]=0.0097 M. Wave activities presented in Fig. 1(a) last for more than 6 h and then begin to disappear near the edge of the Petri dish. This disappearance then spreads toward the center of the medium, which causes the formation of many wave segments. As shown in the snapshot of Fig. 1(b), these wave segments could not immediately rotate to form a nice spiral due to being surrounded by unexcitable regime. This is illustrated in Fig. 1(c), where these surviving wave segments gradually intruded into the area that did not support wave activity a moment earlier. Later, the whole medium regains its excitability as evidenced by the presence of waves across the whole medium. In a distinct difference from the case of sequential waves, here the unexcitable regime does not develop into the whole medium. Figures 1(b) and 1(c) clearly demonstrate the creation of free ends through the occurrence of locally unexcitable regime. In principle, every new free end created above has the potential of forming a new spiral wave. As a result, numerous spirals could be developed here, in the absence of external perturbation or spiral instabilities.

The breakup of propagating waves in the absence of external disturbance is therefore proven to be possible. The idea of wave disruption in the absence of external disturbance refers to physical interference with the medium. Here, the internal disturbance is a result of the natural evolution of the nonlinear dynamical system. More specifically, the unexcitable regime (which occurs as the consequence of amplitude death behavior) acts as the disturbance that causes the breakup of propagating waves. This point is better reflected in Figs. 2(c) and 2(d), in which the development of multiple free ends is achieved. Reaction conditions used in Fig. 2 are $[BrO_3^-]$=0.080 M, [MA]=0.085 M, $[H_2SO_4]$=0.40 M, and [CHD]=0.0096 M. The concentration of CHD is reduced slightly in this experiment while the acid concentration is decreased in comparison to the conditions used in Fig. 1. Arrows in Fig. 2(b) highlight the region that starts to evolve into the unexcitable dynamics. Notably, for both unexcitable regimes, it began near the core of a spiral. This is consistent with the fact that wave activity is denser near the spiral tip and thus consumes chemicals faster there. As a result, the bifurcation parameter in the area near the spiral tips will first enter into the window where the coupling causes amplitude death phenomenon (nonoscillatory state) [34–36]. The decrease in the total number of wave activity may consequently prevent the rest of the medium from exhibiting amplitude death behavior. Figure 2(d) shows that there is a narrow unexcitable region, in which waves are broken up when propagating through it.

B. Dependence on the reaction compositions

When attempting to find an ideal condition to produce the breakup of propagating waves and the subsequent formation

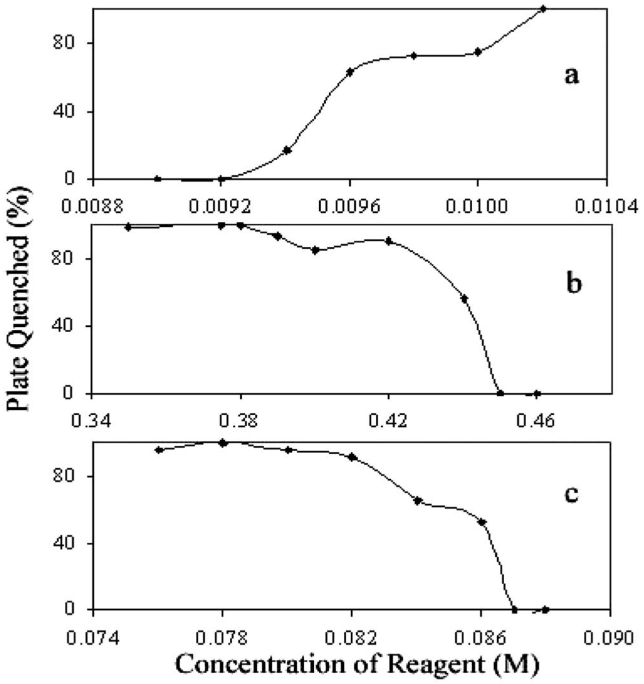

FIG. 3. Plot of the percentage of the unexcitable regime as a function of the concentration of (a) CHD, (b) H_2SO_4, and (c) BrO_3^-. Other reaction conditions are (a) $[H_2SO_4]=0.4$ M, $[MA]=0.085$ M, and $[BrO_3^-]=0.080$ M; (b) $[CHD]=0.0097$ M, $[MA]=0.085$ M, and $[BrO_3^-]=0.080$ M; and (c) $[H_2SO_4]=0.38$ M, $[MA]=0.085$ M, and $[CHD]=0.0097$ M

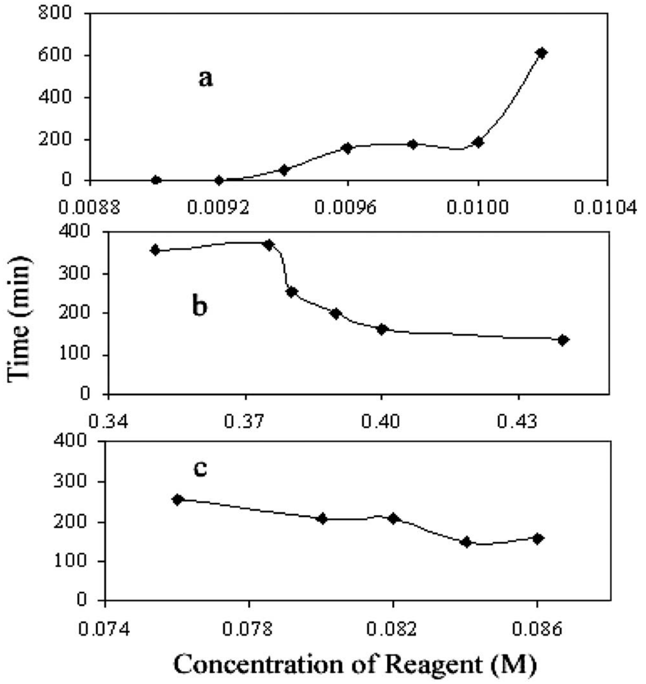

FIG. 4. Plot of the lifetime of the unexcitable regime as a function of the concentration of (a) CHD, (b) H_2SO_4, and (c) BrO_3^-. Other reaction conditions are the same as those used in Figs. 3(a)–3(c), respectively.

of spiral turbulence, trials were conducted over a broad range of CHD, bromate, and sulfuric acid concentrations. The total percentage of the Petri dish that became unexcitable was measured with respect to changing concentrations of the previously mentioned three species. The area data were collected by superimposing a grid onto an image of the reaction. The percentage of the quenched plate was plotted against the concentration of the three variables, where the measurements taken represent the maximum amount of plate quenching that occurred. The plots for CHD, acid, and bromate are shown, respectively, in Figs. 3(a)–3(c). Figure 3(a) shows a sigmoidal pattern as the concentration of CHD increases, further confirming the strong influence of CHD concentration to the characteristics of the unexcitable dynamics. Conversely, graphs in Figs. 3(b) and 3(c) indicate that for the acid and bromate, an increase in concentration actually causes a decrease in the percentage of plate quenched over the ranges measured.

The lifetime of the unexcitable regime is plotted in Fig. 4 as a function of the initial concentrations of (a) CHD, (b) sulfuric acid, and (c) bromate. Similar to its influence on the spatial size of the unexcitable regime, a sigmoidal pattern is seen in Fig. 4(a) as the concentration of CHD is increased gradually. Notably, there is a rapid increase in the lifetime as CHD concentration approaches the top threshold level. A similar rapid change in the lifetime is also seen in Fig. 4(b), where the concentration of acid is adjusted as the sole parameter. The above results show that, for the acid and CHD, there is a small concentration range over which the unexcitable dynamics changes rapidly. On the other hand, an increase in the concentration of bromate causes a more gradual decrease in the lifetime of the unexcitable medium over the range measured.

A unique feature of this approach of spiral formation is that the unexcitable region (i.e., internal disturbance) is a result of the coupling of two suboscillators rather than due to the depletion of chemicals required to support wave propagation in those areas. If the above hypothesis is valid, the propagation rate of these initial waves and the waves reappearing in those transient unexcitable regimes should not exhibit a great difference. In Fig. 5, wave speeds at different times around the unexcitable window were measured as a function of CHD, sulfuric, acid and bromate. The waves that were measured to represent pre-unexcitable data were those that were the last in a set of waves and followed by an inactive medium [see the wave segment labeled A in Fig. 5(a)]. The arrow also indicates the propagation direction of the waves. Waves selected to represent post-unexcitable data were collected from waves first entering into the previously unexcitable area as indicated by the label B. Notice that these waves are propagating into an inactive medium.

In all the cases investigated here, the speed of waves just entering previously unexcitable media is consistently higher than that of the waves that arise just before an area loses wave activity (pre-unexcitable waves). This provides solid support that there is no significant change in the concentration of reactants. In the classic BZ reaction, the velocity of wave propagation is proportional to $(k[H^+][BrO_3^-]D)^{1/2}$, where k is the rate constant of the autocatalytic reaction process and D is the diffusion coefficient of the autocatalyst $HBrO_2$. H^+ and BrO_3^- are the reagents involved in the auto-

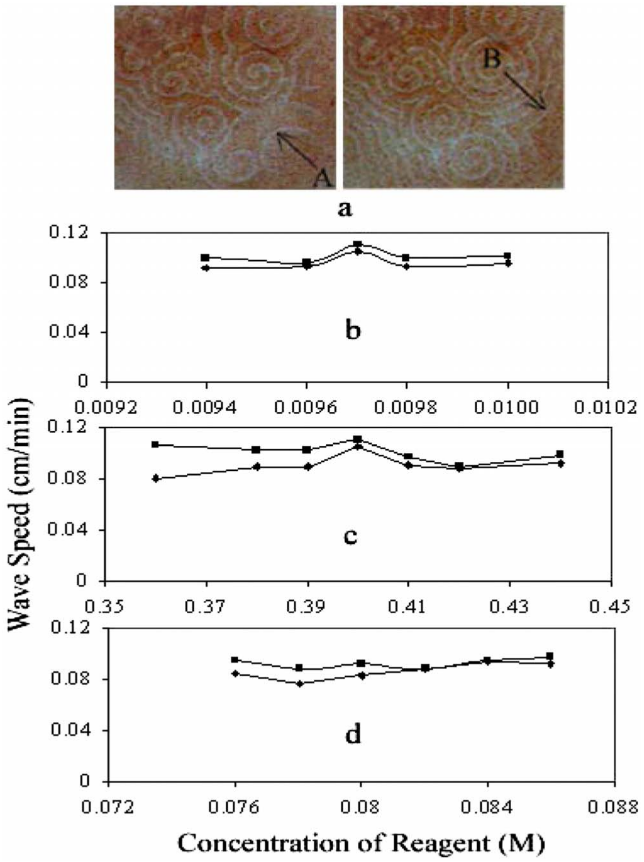

FIG. 5. (Color online) Plot of the propagation speed of the initial (▲) and revival (■) waves as a function of the concentration of (a) CHD, (b) H_2SO_4 and (c) BrO_3^-. The initial concentrations of other reagents are (a) $[BrO_3^-]=0.080$ M, [MA]=0.085 M, and $[H_2SO_4]=0.4$ M; (b) [CHD]=0.0097 M, [MA]=0.085 M, and $[BrO_3^-]=0.080$ M; and (c) $[H_2SO_4]=0.4$ M, [MA]=0.085 M, and [CHD]=0.0097 M.

catalytic reactions. In the system investigated here, there are two different autocatalytic cycles: one arising from the reaction of ferroin and bromine dioxide radicals [steps (1) and (2)] and the other being accomplished through the reaction of hydroquinone and bromine dioxide radicals [steps (1) and (3)]. An earlier study in the classic BZ reaction shows that the wave velocity depends on the nature of the catalyst used [42]. As shown in Fig. 5, the coexistence of two autocatalytic cycles, in which ferroin and hydroquinone act as the catalyst, clearly alternates the dependence of the wave velocity on the concentration of acid and bromate. Here, there is no significant change in the wave speed when the concentration of CHD or bromate is adjusted. At low acid or bromate concentration, the post-unexcitable waves propagate faster than the pre-unexcitable waves, implicating that the production of autocatalyst $HBrO_2$ is accelerated after the system evolves out of the unexcitable dynamics. The effect of acid on the different wave speeds displayed a similar pattern to the bromate measurements, but unlike the bromate trials the difference in wave speed is not consistent across all trials.

V. SUMMARY

This research presents an approach of inducing the breakup of propagating waves, namely through the temporary development of unexcitable dynamics in a local medium. In contrast to our study of sequential waves [41], in which a high concentration of CHD is required to achieve a long-lasting nonoscillatory state, here the CHD concentration needs to be at a model level so that the coupling-induced nonoscillatory state does not spread into the whole reaction-diffusion medium. Unlike the breakup arising from spiral instabilities [20–32], the approach presented here also works for initially symmetric wave activity such as circular waves. When these concentric symmetrical waves pass into nonexcitable media, free ends are formed, resulting in symmetry breaking in the absence of external perturbation or internal thermal fluctuations. A limitation of this approach is that it may only be obtained in the coupled nonlinear dynamical systems. Nevertheless, this may have played a role in the development of complex spatial structures in nature [4,5]. We would also like to point out that in most of our experiments, the unexcitable regime starts near the core of a spiral, implicating that the reactivity in those areas is stronger than that in the rest of the medium.

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