PHYSICAL REVIEW E **78**, 025101(R) (2008)

Breathing spiral waves in the chlorine dioxide–iodine–malonic acid reaction-diffusion system

Igal Berenstein,[1] Alberto P. Muñuzuri,[1] Lingfa Yang,[2] Milos Dolnik,[2] Anatol M. Zhabotinsky,[2] and Irving R. Epstein[2]
[1]*Group of Complex Systems, Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, Spain*
[2]*Department of Chemistry and Volen Center for Complex Systems, MS 015, Brandeis University, Waltham, Massachusetts 02454-9110, USA*

(Received 31 August 2007; revised manuscript received 23 February 2008; published 11 August 2008)

Breathing spiral waves are observed in the oscillatory chlorine dioxide-iodine-malonic acid reaction-diffusion system. The breathing develops within established patterns of multiple spiral waves after the concentration of polyvinyl alcohol in the feeding chamber of a continuously fed, unstirred reactor is increased. The breathing period is determined by the period of bulk oscillations in the feeding chamber. Similar behavior is obtained in the Lengyel-Epstein model of this system, where small amplitude parametric forcing of spiral waves near the spiral wave frequency leads to the formation of breathing spiral waves in which the period of breathing is equal to the period of forcing.

DOI: 10.1103/PhysRevE.78.025101 PACS number(s): 82.40.Ck, 82.20.−w

Periodic waves are usually generated by local pacemakers both in excitable and oscillatory media. If the pacemaker frequency is significantly higher than the intrinsic oscillation frequency of the medium, trigger waves are produced. If the pacemaker frequency is close to that of the basic oscillation of the medium, the resulting waves resemble phase waves [1,2]. Spiral waves have long attracted considerable attention, since they are generated by local pacemakers created by phase singularities in parametrically homogeneous media. Recently, trigger spiral waves with local wavelength modulation indicative of breathing behavior have been reported in the Belousov-Zhabotinsky reaction-diffusion (BZRD) system as intermediary patterns between regular spiral waves and spiral turbulence [3,4]. Later, breathing spiral waves (BSW) were observed in BZRD media where the local dynamics generated period-2 oscillations [5,6]. Here we report observation of BSW in the oscillatory chlorine dioxide-iodine-malonic acid (CDIMA) reaction-diffusion system.

The CDIMA reaction is carried out in a one sided CFUR, which has been described previously [7]. We use a 0.3-mm-thick layer of 2% agarose gel as the working medium. The feed concentrations are $[I_2]_0=0.37$ mM, $[MA]_0=1.8$ mM, $[ClO_2]_0=0.14$ mM, and $[PVA]_0=0.5$ or 0.7 g/l, where MA is malonic acid and PVA is polyvinyl alcohol. The temperature is kept at 4.0 ± 0.2 °C, while the residence time in the feeding CSTR chamber is 230 s.

The experiments start with 0.5 g/L of PVA, which gives bulk oscillations in the CSTR with a period of about 150 s. Bulk oscillations should also arise in an ideal gel layer, but imperfections in the gel lead to formation of spiral waves [8]. The concentration of PVA in the CSTR is then increased to 0.7 g/L, which shifts the period of oscillation in the CSTR to 180 s. After a transition period of about 10 h, stable BSW are established (Fig. 1). The measured fundamental period of these BSW is about 220 s, while the period of breathing is about 180 s, which coincides with the period of oscillation in the feeding CSTR. At higher PVA concentrations, around 0.85 g/l, dashed waves and Turing structures appear [9], an observation in agreement with the results of Rudovics *et al.* [10], despite the rather different geometries of the CFURs used by the two groups. If the final [PVA] of 0.7 g/l is set from the beginning of the experiment, only regular spiral waves without breathing are seen. Thus there is bistability between the regular spirals and the breathing spirals.

In our experiments, we use a one-sided CFUR with oscillations in the feeding CSTR chamber. As a result the interface of the gel layer with the CSTR is subjected to spatially uniform oscillations in the concentrations of active intermediates of the CDIMA reaction. These oscillations in the CSTR produce global periodic forcing of spiral waves in the CFUR. Our experimental results suggest that breathing occurs when the frequency of this forcing is relatively close to that of the spiral waves.

To test this hypothesis, we carry out simulations with the Lengyel-Epstein (LE) model [11] of the CDIMA reaction. In the experiment bulk oscillations in the CSTR are the source of the global forcing. Therefore a reaction-diffusion model of

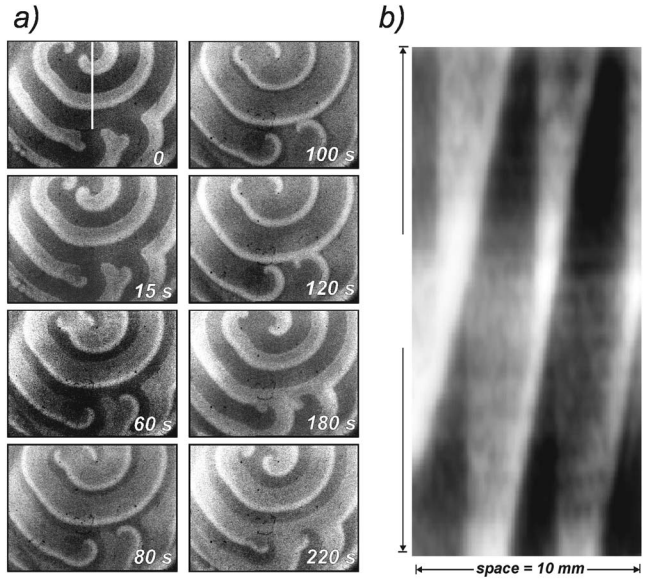

FIG. 1. (a) Snapshots of breathing spiral waves taken with visible light—experimental results. The breathing period is about 180 s; the period of the spiral wave at the top is about 220 s. Frame size 20 mm × 15 mm. (b) A space-time plot taken along the vertical line shown in the first frame. Dark areas correspond to higher concentrations of I_3^-.

the working gel layer is a 3D problem with time-periodic Dirichlet conditions at the boundary, which represent the interface between the layer and the CSTR, and zero-flux boundary conditions elsewhere. Since the thickness of the gel layer is much less than the wavelength of the spiral waves, we replace this 3D problem by a 2D approximation with zero-flux boundary conditions and the global periodic forcing term inserted into the right-hand side of the equation for the slow variable. We also neglect differences in concentrations of the initial reagents between the CSTR and the gel layer, which gives equal frequencies of bulk oscillation in the gel layer and the CSTR.

The resulting model is

$$\sigma \frac{\partial u}{\partial t} = a - u - 4\frac{uv}{1+u^2} + f(t) + \nabla^2 u, \tag{1}$$

$$\frac{\partial v}{\partial t} = b\left(u - \frac{uv}{1+u^2}\right) + d\nabla^2 v. \tag{2}$$

Here u and v are the dimensionless concentrations of $[I^-]$ and $[ClO_2^-]$, respectively; a, b, d, and σ are dimensionless parameters. We use a set of parameters that qualitatively conforms to the conditions of our experiment: $a=12$, $b=0.45$, $d=1.07$. The parameter σ, which characterizes the strength of the complexation of I_3^- by PVA, is equal to $1+K[I_2]_0[PVA]_0$, where K is the equilibrium constant for the complexation reaction. Preliminary simulations close to the Hopf bifurcation ($\sigma=11.4$) do not give breathing, so we choose lower values of σ, which simulate qualitatively the change in [PVA] from 0.5 to 0.7 g/l. Since the model is quite simplified we do not attempt to fit the experimental data in detail but rather choose integer values for σ equal to 2 and 3, respectively.

We take the global forcing term as $f(t)=A\cos(\omega t)$ with $A=0.03$ in all our simulations. The frequency of forcing, ω, is determined from simulations of the autonomous model with no forcing. The autonomous model essentially simulates experiments in a two-sided CFUR where the reactants of the chemical oscillator are divided between two feeding chambers [12].

To model spiral wave behavior we create a narrow strip of strong phase gradient perpendicular to one side of the square representing the medium and extending from the midpoint of that side to the center of the medium. The size of this region and the phase gradient can be varied in a wide range to produce the phase singularity, which generates a one-armed spiral wave whose core lies close to the center of the system. The development of the spiral wave is very slow. It takes about 179 periods of oscillations to form three full rotations of the spiral. This differs drastically from the dynamics of BZ trigger spiral waves, where each period of oscillation in the spiral adds a full rotation to the growing spiral [13]. The development of spiral waves in the autonomous model is also very slow and is almost identical to the case when global periodic forcing is present.

Figures 2(a) and 2(b) show snapshots at the extremes of the breathing motion during a full rotation of the established spiral. A space-time plot along a line drawn through the core of the spiral [Fig. 2(c)] exhibits slight oscillations in the speed and shape of the waves. The period of the spiral wave, $T_s=13.9$ t.u., is nearly the same as that of the bulk oscillations, 14.1 t.u..

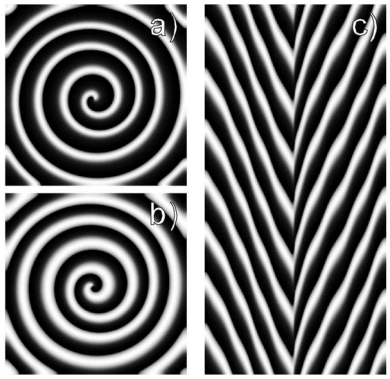

FIG. 2. Weak breathing under periodic forcing. (a) Snapshot with a minimum width of the u-rich region during one rotation of the spiral. (b) Snapshot with maximum width. (c) Space-time plot along a line drawn through the core of the spiral. Time increases vertically; 100 t.u. are shown. Parameters: $a=12$, $b=0.45$, $d=1.07$, $\sigma=2$, $A=0.03$, and $\omega=0.45$. System size: 512×512 space units. White corresponds to high concentration of u.

Changing the parameters to $\sigma=3$ and $\omega=0.41$ results in the appearance of strong oscillations of both the speed and shape of the waves (Fig. 3), which are comparable with those observed in the experiment (Fig. 1). The period of the BSW is identical to that of the global forcing, 15.3 t.u. (Fig. 4).

The visible breathing in Fig. 3 results from oscillations in the speed of the phase waves, with a considerable phase shift between acceleration of the wave front and that of the wave back. Figure 4 shows how the u profile along a line drawn through the spiral core in Fig. 3 varies in time, while Fig. 5 demonstrates that the shape of the time-dependent oscillations at different points outside the spiral core is constant in time and independent of position. Once the spiral wave has

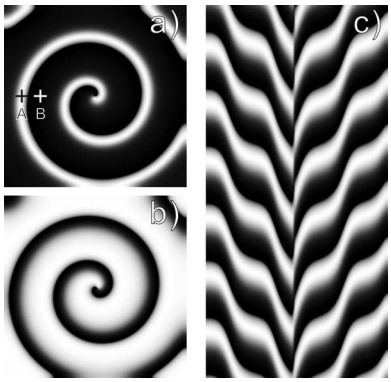

FIG. 3. Strong breathing under periodic forcing. (a) Snapshot with minimum width of the u-rich region during one rotation of the spiral. Crosses labeled A and B indicate the points where oscillations shown in Fig. 5 are calculated. (b) Snapshot with maximum width. (c) Space-time plot along a line through the core of the spiral. Time increases vertically; 100 t.u.. are shown. Parameters and system size as in Fig. 2, except $\sigma=3$ and $\omega=0.41$.

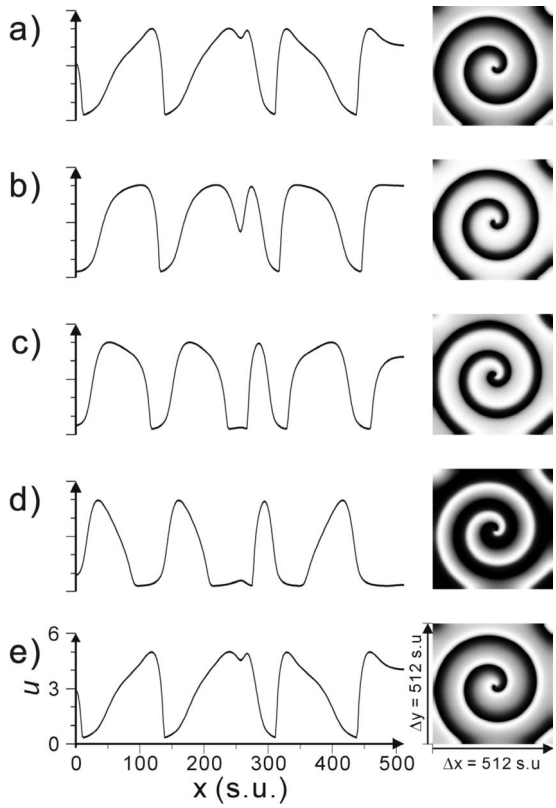

FIG. 4. Profiles of u along a horizontal line drawn through the spiral core in the snapshots shown at the right. One period (T_s=15.3 t.u.) of the spiral wave is shown; snapshots are taken at (a) 0, (b) $0.1T_s$, (c) $0.3T_s$, (d) $0.4T_s$, (e) $1.0T_s$. From the simulation shown in Fig. 3.

been established, the characteristics of the patterns shown in Figs. 2–5 are independent of the specific initial conditions chosen to generate the wave, which is typical for an attractor.

The results of our simulations shown in Figs. 2 and 3 are in good qualitative agreement with the experimental behavior in Fig. 1. We see uniform breathing in the entire medium, except in the core of the spiral. This observation differs from the breathing found in the BZRD [3–6]. The calculated dependence of the magnitude of breathing on [PVA] is also in good accord with experiment. On the other hand, there are quantitative differences between the simulations and the experiment. For instance, the periods of rotation of the spiral waves and of the bulk oscillations in the CSTR differ significantly in the experiment. We do not try to simulate the experiment more precisely, since accurate values of the rate constants involved are not available [10,14]. There may also be differences in the concentrations of the reagents between the CSTR and the gel layer, whose magnitude is difficult to estimate because of our limited knowledge about the interface between the CSTR and the gel layer [10]. An advantage of our model is that it presents a simple limiting case. Even with these simplifications, the model displays breathing patterns that are very close to those seen in the experiment.

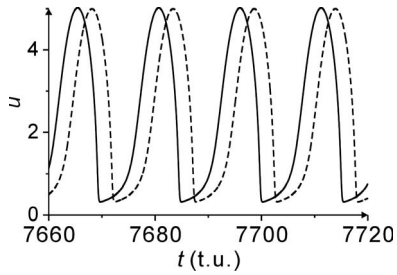

FIG. 5. Oscillations of u calculated at points labeled A and B in Fig. 4(a). The solid line corresponds to A (50, 256), the dashed one to B (100, 256).

Oscillations in the speed of chemical waves have been found in several models, sometimes accompanied by moderate breathing [15–17]. Spatially nonuniform breathing of spiral waves has been found in autonomous BZ reaction-diffusion systems [3–6]. Here we have demonstrated spatially uniform strong breathing of spiral waves both in the CDIMA reaction-diffusion system subjected to global periodic forcing and in the corresponding version of the Lengyel-Epstein model.

This work was supported by the MCyT (Spain) under Project Nos. FIS2004-03006 and FIS2007-64698 and Xunta de Galicia (Spain) under Project No. PGIDIT05PXIC20607PN and the National Science Foundation under Grant No. CHE-0615507.

[1] E. J. Reusser and R. J. Field, J. Am. Chem. Soc. **101**, 1063 (1979).
[2] G. Bordiougov and H. Engel, Physica D **215**, 25 (2006).
[3] Q. Ouyang and J. M. Flesselles, Nature (London) **379**, 143 (1996).
[4] H. Y. Guo, L. Li, Q. Ouyang, J. Liu, and Z. She, J. Chem. Phys. **118**, 5038 (2003).
[5] J. S. Park and K. J. Lee, Phys. Rev. Lett. **88**, 224501 (2002).
[6] J. S. Park and K. J. Lee, Phys. Rev. E **73**, 066219 (2006).
[7] I. Berenstein, M. Dolnik, A. M. Zhabotinsky, and I. R. Epstein, J. Phys. Chem. A **107**, 4428 (2003).
[8] J. Boissonade, E. Dulos, and P. De Kepper, in *Chemical Waves and Patterns*, edited by R. Kapral and K. Showalter (Kluwer, Dordrecht, 1995), pp. 221–268.
[9] L. Yang, I. Berenstein, and I. R. Epstein, Phys. Rev. Lett. **95**, 038303 (2005).
[10] B. Rudovics *et al.*, J. Phys. Chem. A **103**, 1790 (1999).
[11] I. Lengyel and I. R. Epstein, Science **251**, 650 (1991).
[12] Q. Ouyang and H. L. Swinney, Nature (London) **352**, 610 (1991).
[13] A. M. Zhabotinsky and A. N. Zaikin, J. Theor. Biol. **40**, 45 (1973).
[14] A. K. Horváth *et al.*, J. Phys. Chem. A **104**, 5766 (2000).
[15] K. G. Shkadinsky, B. I. Khaikin, and A. G. Merzhanov, Combust., Explos. Shock Waves **7**, 15 (1971).
[16] B. N. Vasiev, Phys. Lett. A **323**, 194 (2004).
[17] E. M. Nicola, M. Bär, and H. Engel, Phys. Rev. E **73**, 066225 (2006).