Light Effect on the Spiral Wave Period in a Ferroin-Catalyzed Belousov−Zhabotinsky Reaction

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Received: April 1, 2004

By use of a He−Ne laser beam to control the tip trajectory of a spiral, we quantitatively measure the relation between the spiral period and the intensity of the laser beam in an excitable ferroin-catalyzed Belousov−Zhabotinsky reaction. We find that the period dependence on light intensity has two different phases: a fast increase phase and a slow increase phase. Numerical simulations based on the modulated Oregonator model and the assumption that local concentration of ferriin decreases as laser power increases are conducted, which suggest two possible mechanisms leading to the increase of the spiral period with the intensity of the laser beam.

Introduction

The Belousov−Zhabotinsky (BZ) reaction as a convenient system for displaying excitable or oscillatory spirals has become the interest of many experimentalists. Recently, research in this field has been focused on the spiral-tip motion control because the potential application on certain kinds of fatal cardiac diseases, such as cardiac arrhythmia and fibrillation.[1,2] In the BZ reaction, methods of controlling the spiral-tip motion or changing the geometric character of the spiral have been extensively studied both in experiment and in theory,[3−12] and several effective methods have been developed. For example, electrodes are applied to establish an electronic field that motivates reactive ions to move in a certain direction;[3,4] light illumination is used to change local or global reaction dynamics according to the photosensitive properties of metal catalyst.[5−12] Much research work has been done on the latter method, especially in ruthenium (Ru)-catalyzed BZ reaction. The research includes modeling the light-sensitive reaction,[5] studying dynamic features of spiral rotation controlled by light-induced artificial cores,[6,7] finding the light-induced rotation frequency shift,[8] and using different forms of illumination to control chemical waves.[9−12] However, the sensitivity to visible light on the ferroin-catalyzed BZ reaction is seldom explored, except when used on conducting spiral tip in open reactors.[13] The reason may be that the BZ reaction catalyzed by ferroin is much less light sensitive compared to that catalyzed by $Ru(bpy)_3$. Recently, Tóth et al.[14] reported initiation of waves in the ferroin-catalyzed spatially extended BZ reaction with illumination of He−Ne laser, where the catalyst is loaded on a polysulfone membrane. They found that, from the deeper red area that has just been illuminated by a He−Ne laser, it can develop a circular oxidation pulse. This phenomenon is in contrast to the inhibitory effect of visible light in the Ru-catalyzed BZ system. Thus the ferroin-catalyzed BZ system might give us a different prospect of the control method based on the light sensitivity of the excitable media. In this paper, we study the attraction effect of the laser light on the spiral tip and its influence on the period of spiral waves, which may give us more understanding on the BZ reaction mechanism.

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Experimental Observation

Our experiments are conducted in a spatial open reactor. The heart of the reactor is a thin porous glass disk (Vycor glass), 0.4 mm thick and 25.4 mm in diameter, which has 25% void space and 100-Å average pore size. The porous glass is used to prevent convection in the reaction medium. Each surface of the disk is in contact with a compartment where the reactant concentrations are kept homogeneous and constant by highly precise pumps and magnetic stirrers. The chemicals are fed asymmetrically: malonic acid, potassium bromide, and SDS are in side A, sulfuric acid and ferroin are in side B, and sodium bromate is fed on both sides so that side A is kept in a reduced state and side B is kept in an oxidized state. Both sides are kept from oscillating. The chemicals diffuse into the middle of the porous glass disk, where the BZ reaction occurs and wave patterns form. The quasi-two-dimensional spatial patterns are wholly illuminated by a halogen light source with a band-pass filter at 550 nm, allowing only blue light to pass through. Images of the patterns are taken by a black/white charge coupled device camera, then digitized and stored in a computer for later processing.

A 50-mW He−Ne laser is used as a perturbing illumination. The convergent laser beam is injected to the reaction media through the transparent compartment A. The intensity of the laser beam is served as the control parameter in our experiment; it can be adjusted by using two polarizers and measured with a laser power meter. The other control parameters are kept fixed through the whole experiment: $[MA]_0^A = 0.2$ M, $[KBr]_0^A = 0.03$ M, $[SDS]_0^A = 0.1$ mM, $[NaBrO_3]_0^{A,B} = 0.15$ M, $[H_2SO_4]_0^B = 0.6$ M, and $[Ferroin]_0^B = 1.0$ mM. The reaction temperature is 25 ± 0.5 °C.

First we prepare a spiral in the media as in ref 15 and set the asymptotic behavior of the spiral in the meandering regime, where the movement of the spiral tip follows a hypocycloidal trajectory.[15] Then we illuminate the spiral tip with a convergent

10.1021/jp048577g CCC: $27.50
Published on Web 06/17/2004

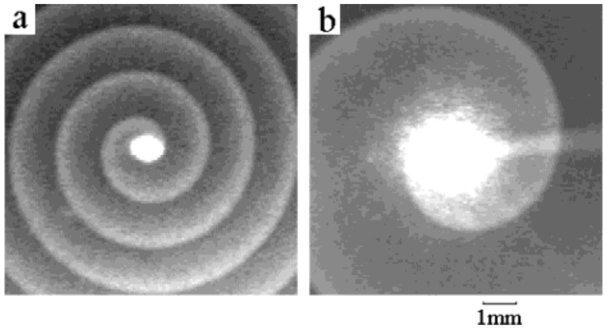

Figure 1. Spirals with the tip illuminated by a laser beam of different power: (a) 0.15 mW; (b) 9.77 mW.

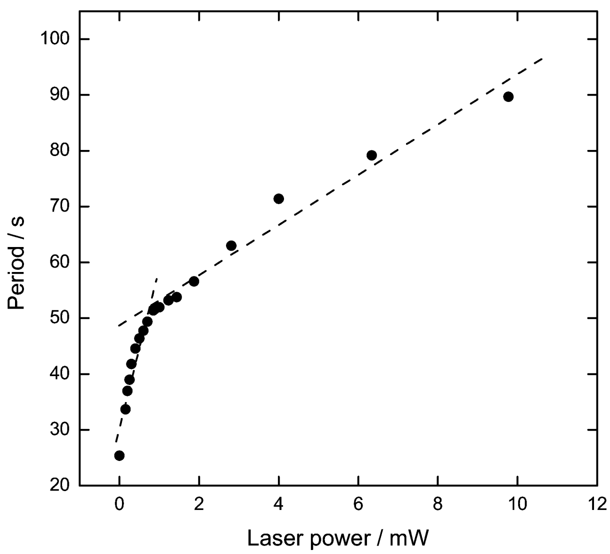

Figure 2. Spiral period as a function of laser power measured in the experiments. Dashed lines are presented to guide the eyes.

laser beam and increase the intensity of the laser beam step by step to see how the spiral changes its behavior. The range of the intensity of the laser beam is from 0.15 to 9.77 mW. Under this light-intensity range, although we cannot observe the true pattern of spiral tip movement because of the very bright scattering spot of laser beam in the local illuminated area (see Figure 1), according to the wavelength distribution outside of the center as shown in Figure 1a, we still can determine that the tip's motion follows almost a rigid circular trajectory so that a meandering spiral changes to a simple spiral under light illumination on its tip. If the spiral tip meanders from the outside of the light spot into the region of the light spot, it will be locked in this local area and can never escape. In this sense, the light beam has an attractive effect on spiral tips. When the light intensity is increased from 0.15 to 9.77 mW, the attractive effect becomes stronger and both the period and the wavelength of spiral waves become larger, as shown in Figure 1b. From these observations, we conclude that the laser beam can change the movement pattern of the spiral tip, forcing it to move along the light spot.

Next, we study the influence of the laser intensity on the period of the spiral waves. The experimental results of this study are summarized in Figure 2. One observes that the period dependence on light intensity shows two different phases, both of them can be approximated as a linear relation between the period and the light intensity. When the laser light intensity is less than about 0.9 mW, the period of spiral waves increases quickly, with the mean rate of increase about 30 s/mW; when the laser power is larger than 0.9 mW, the rate of the increase gets smaller, which is about 5 s/mW. This observation suggests that there may exist two mechanisms of light influence on spiral periods.

Simulation Model and Results

We conduct a simulation to see what underlies the experimental observations. The reaction−diffusion model we choose is based on the model proposed by Rovinsky and Zhabotinsky,[16] which simulates the ferroin-catalyzed BZ reaction. It has the following form

$$\epsilon \frac{\mathrm{d}x}{\mathrm{d}\tau} = x(1-x) - 2q\alpha \frac{z}{1-z}\frac{x-\mu}{x+\mu} + D_x\nabla^2 x \tag{1a}$$

$$\frac{\mathrm{d}z}{\mathrm{d}\tau} = x - \alpha\frac{z}{1-z} + D_z\nabla^2 z \tag{1b}$$

where x and z correspond to the concentrations of [HBrO] and [Ferriin], respectively, α, μ, and q are the system's parameters determined by reaction condition, and D_x and D_z are diffusion coefficients. This model is thought to be more suitable for simulating the ferroin-catalyzed BZ reaction as the reversibility of the reduction of ferriin is considered.

Considering that the most possible absorber of the 632.8-nm light is ferriin and according to the experimental fact that the color of the area illuminated by strong laser beam turns dark, which means that the decrease of the concentration of the oxidized catalyst, it is reasonable to assume that the direct effect of the laser is to decrease the concentration of ferriin. For simplicity, we also consider that the concentration of ferriin in that area is homogeneous. Thus the reaction dynamics in the illuminated area becomes

$$\epsilon \frac{\mathrm{d}x}{\mathrm{d}\tau} = x(1-x) - 2q\alpha \frac{z_0}{1-z_0}\frac{x-\mu}{x+\mu} + D_x\nabla^2 x \tag{2a}$$

$$z = z_0 \tag{2b}$$

where z_0 is the fixed value of z in the illuminated area. Its value decreases with the increase of the light intensity of the laser beam.

The simulation parameters we choose are $\epsilon = 0.1$, $\alpha = 0.02$, $\mu = 0.002$, $q = 1.5$, $D_x = 1.0$, and $D_z = 0.6$. The radius of the homogeneously illuminated area R and the value z_0 in the area are taken as control parameters. We integrate the system numerically using Euler's method with time step $\Delta t = 5 \times 10^{-3}$ and space step $h = 0.25$ on a 280×280 grid of spatial points. The boundaries are set to be no flux ones, and nine-point Laplacian approximation is used to simulate the diffusion. We initiate a spiral whose tip is essentially in the center of the media. Then we let the variable z in the center circular area keep a constant value according to parts a and b of eq 2, which represent the effect of the laser on the catalyst, and other areas still obey the unperturbed dynamics of parts a and b of eq 1. After 500 time units, when the system has come to an asymptotic state, we begin to count the period of the spiral by recording the time intervals when the x variable decreases across a fixed value. The ultimate period is the mean of the periods counted in 500 time units.

The simulation results also show the attractive effect of the light beam. When the spiral tip hits the center circular area where the value of z is fixed, it will travel around the circle. At the same time, a meandering spiral becomes a simple spiral. We then keep the radius of the area R fixed and study the dependence of spiral period on the value z_0 in the center area,

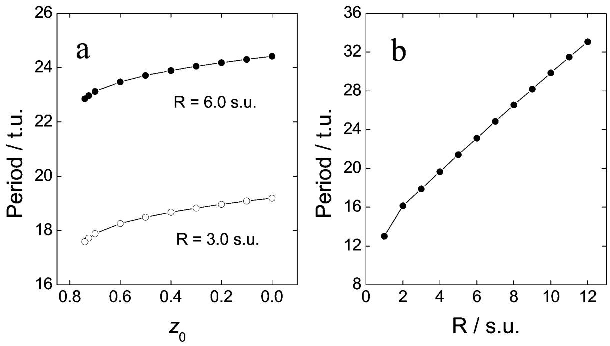

Figure 3. Simulation results: (a) spiral period as a function of the fixed value of z in a center circular area for different radius of center area, $R = 6.0$ su. (●) and $R = 3.0$ su. (○); (b) spiral period as a function of the radius of the constant z area, when $z_0 = 0.7$.

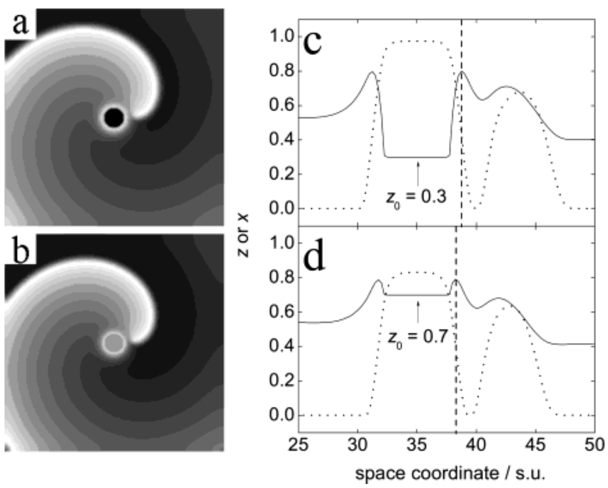

Figure 4. (a) and (b) Attracted spiral moving around a circular area of $R = 3.0$ su. with $z_0 = 0.3$ and 0.7, respectively. Gray scale represents the level of z. (c) and (d) One-dimensional distribution of z (solid line) and x (dotted line) along the horizontal midline in a and b, respectively. The vertical dashed lines indicate the location of the peak of z close to the border of the illumination core.

which corresponds to the effect of light intensity on the spiral period in the experiment. The relation between the period of the attracted spiral and the value z_0 is plotted in Figure 3a for a different radius of center area, $R = 6.0$ su. and 3.0 su. With a fixed value of R, the spiral period increases with the increase of z_0, but the increment of the period is not significant. On the other hand, when we fix the value of z_0 and increase the value of R, relatively large changes are induced. We show the latter in Figure 3b, when $z_0 = 0.7$. Moreover, we find that, when the radius is large enough, the period of the spiral seems to linearly depend on the radius.

Discussion and Conclusion

The simulation results in Figure 3 suggest two mechanisms leading to the period increase of the spiral, which can explain the two different phases of the period dependence on light intensity in our experimental observation: a slow increase phase and a fast increase phase.

To get more insight on these two different mechanisms, we plot two examples with $z_0 = 0.3$ and 0.7 in Figure 4. Because higher illumination causes lower z_0, the darker area in Figure 4a illustrates higher intensity of the external laser beam compared with Figure 4b. Parts c and d of Figure 4 show one-dimensional distributions of variables z and x along the horizontal midline in parts a and b of Figure 4, respectively. One can see that a lower value of z_0 causes a higher value of x in the illuminated area. While x recovers spatially from the high value in the illuminated area to the surrounding low value, z experiences a maximum. The ring of this maximum in the two-dimensional system determines the trajectory of the spiral tip. When the value of z_0 becomes lower, the maximum is located further from the illuminated area, as indicated by the dashed lines in parts c and d of Figure 4. Therefore, the circular trajectory of the spiral tip gets longer. On the other hand, outside of the circular area, the system is under the same condition so that the speed of the spiral tip is almost constant for different values of z_0. As a result, a longer trajectory of the spiral tip means a longer spiral period. This explains the curve in Figure 3a. The difference of z_0 causes only a small change of the circular trajectory. For example, in parts c and d of Figure 4, when z_0 decreases from 0.7 to 0.3, the diameter of the trajectory increases only from $D = 6.5$ to $D = 7.5$ so that the spiral period increases slowly with the decrease of z_0 in the simulation or with the increase of the laser light intensity in the experiment. It is easy to understand the second mechanism, which is directly related to the diameter of illustrated area. That is, a larger R causes a longer circular trajectory of the spiral tip, so that the period will increase linearly with the diameter of illuminated area, as shown in Figure 3b.

In the experiment, it is reasonable to consider that the two mechanisms together lead to the phenomenon of the increase of the spiral period with the laser intensity, as shown in Figure 2. Because the intensity distribution of the laser used in our experiment is not homogeneous but Gaussian, the intensity is strong in the center and weak on the edge. When the laser intensity is small, the size of the area effectively illuminated by the laser will get bigger as the whole intensity increases, and according to the second mechanism, the period of the spiral will get longer. When the laser intensity is high enough, the effectively illuminated area will not increase obviously, but the intensity on the edge of the area will keep on increasing. According to the first mechanism, the spiral period will continue increasing. However, as the influence on the period change of the first mechanism is much weaker than that of the second one, the spiral period increases slowly with the increase of the laser intensity.

In conclusion, we find that the laser light can change the movement pattern of the spiral tip, forcing it to move around the light spot, and the relation between the spiral rotation period and the laser power is a monotonic increasing one, which has two phases with different rates of increase. Our simulation suggests that such relation in the ferroin-catalyzed BZ reaction is related to the increase of the effectively illuminated area and the decrease of oxidized catalyst ferriin, which are both caused by the power increase of the laser. However, further understanding on how the laser influences the local dynamics of the ferroin-catalyzed BZ reaction is still needed, which ought to give a more vivid image of the real case of the pattern formation in such system.

Acknowledgment. This work is supported by the Chinese Natural Science Foundation and Department of Science and Technology in China.

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