Desensitization effects in the ruthenium-catalyzed Belousov-Zhabotinsky reaction

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The influence of visible light on the velocities of spiral waves in the $[Ru(bpy)]_3^{2+}$-catalyzed Belousov-Zhabotinsky (BZ) reaction is well documented. However, there are only few reports showing the effect of the way a change in the applied intensity is made, or on "desensitization" or "memory" type phenomena. In this paper, we present observations showing significant changes in spiral tip dynamics without varying the light intensity during the course of the experiments. We produce further evidence showing that changes in wave velocity and inhibitory effects are depending on whether the increase in intensity is applied in one large step or in a number of smaller steps. Also, the tip trajectories before and after the spiral waves have been subjected to an increase and subsequent decrease in intensity levels are different, suggesting a change in excitation of the system. The experimental results are separated into two groups depending on the light sensitivity of the system and the behavior of the spiral tip. Simulation results demonstrate that the different tip trajectories observed in the experiments can be modeled by only varying the excitation threshold. Our observations indicate that there must be at least two different competing pathways for the reaction mechanism not only in the oscillatory BZ system but also in excitable media and that intermediates may also play an important part in determining the excitation of the system and not just the initial concentrations of the reactants.

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INTRODUCTION

The Belousov-Zhabotinsky (BZ) reaction is probably the most convenient laboratory system to study the dynamics of spiral waves in excitable media, especially when the $[Ru(bpy)]_3^{2+}$ catalyst is used. This catalyst is sensitive to visible light at 453 nm, enabling the external control of the wave dynamics by varying the intensity of the applied illumination. A large variation of photoinduced behavior has been reported [1–6].

Below a certain threshold value of the light intensity no effects on the spiral wave dynamics are observed. When the intensity is increased above this threshold photoinduction has been reported but a further increase leads to photoinhibition in the oscillatory BZ system. Above a maximum value wave propagation is totally inhibited and the waves are destroyed. In between these two values a large range of spiral tip motions can be seen. The intensity values at which the spiral waves are destroyed depend on the way in which illumination is applied to the system. Agladze *et al.* [7] found three different scenarios in their open system, depending on the rate of change of light intensity. Fast light changes destroyed the waves, whereas slow changes caused the spiral core to increase and diminish its rotation rate. Intermediate increases caused the spiral wave to survive but multiple wave breaks appeared at the periphery. Using a gel reactor and low concentrations of ruthenium Markus *et al.* [8] reported that they could obtain ripple formation without breakup and breakup without ripple formation in spirals, depending on the procedure they were using.

Our experiments support the observations that the reaction of the system to increased values of intensity does depend strongly on the procedure taken. For example, the maximum intensity above which spiral waves are destroyed in the experiments can be increased by up to 2 W m^{-2}, and in some cases even more, if the luminosity is increased in small steps instead of one big step. Also, the excitability of the system can change during an experiment without intervention from the outside, implying that there exists some kind of "desensitization or adaptation" effect to high intensity levels. This effect is also evident in the changing spiral tip trajectories, i.e., the tip movement before the system has been subjected to higher intensities is different to the one after the intensity has been increased, reduced, and increased again to the previous level.

These results have profound effects on photochemical image processing [9–11] as one of the prerequisites for image processing is the ability to go back to the starting point. Zou *et al.* [12] obtained a very high image definition when projecting a picture onto a nonlinear optical membrane containing $Ru(bpy)_3Cl_2$. They claim that the medium can be returned to its original state through illumination with white light. However, the experimental evidence produced here shows that the closed system can "remember" its previous state and a complete reset to zero is not possible.

The results from the experiments have been divided into two groups, A and B, depending on the light sensitivity of the spiral wave and the trajectories the spiral tip traces with increasing intensity. Both groups exhibit desensitization effects. The shapes of the tip trajectories with increasing light intensity can be different for the two groups. These variations in the tip traces can easily be simulated by changes in the excitation threshold using Barkley's model. The effects of aging of the solution on the experimental results have been considered and it seems unlikely that they play any part in the observed phenomena. The experimental observations indicate that one needs to consider at least two different chemical pathways for the reaction mechanism, one supporting inhibition and the other one photoinduction, and that these pathways are competing under certain conditions. Moreover, the concentrations of intermediates may be more important than was previously assumed.

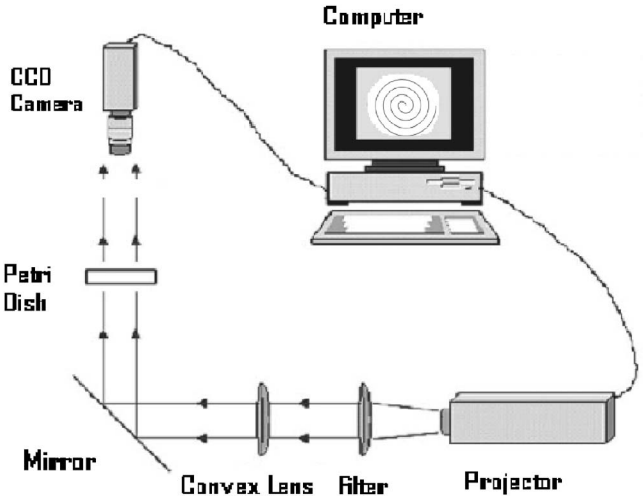

FIG. 1. Experimental setup.

EXPERIMENTAL SETUP

The experimental setup is shown in Fig. 1. In order to minimize convection effects, a thin (0.33 ± 0.02 mm) layer of silica gel (3 ml of a mixture of 2 ml of 15% sodium trisilicate, 0.09 ml 5 M H_2SO_4, 4.2 mM $Ru(bpy)_3SO_4$ and H_2O) is prepared in a Petri dish of 7 cm diameter.

In the experiments, 2 ml of standard BZ mixture [composed of 0.95 ml of 1 M $NaBrO_3$, 0.21 ml of 4 M malonic acid (MA), 0.50 ml H_2O, 0.39 ml of 5 M H_2SO_4, and 0.45 ml of 1 M NaBr] is slowly added on top of the gel. Usually, target waves appear almost immediately at the rim of the Petri dish. As soon as the target waves appear, the reservoir is enlarged by adding 8 ml of BZ mixture diluted to half the concentration values of the standard mixture. The final concentrations are 4.2 mM [ruthenium], 0.2 M [$NaBrO_3$], 0.09 M [NaBr], 0.17 M [MA], and 0.4 M [H_2SO_4]. The gel and solution are kept at an ambient temperature of 22 ± 1 °C.

A cold light source of high illumination intensity (Schott KL 1500) is applied to break the wave front. One of the open ended wave-front segment as well as other spontaneously appearing wave fronts are being destroyed by application of the light spot, so that only one spiral wave survives in the Petri dish. For the experiments we ensure that the spiral core is located far away from the rim of the Petri dish and that there are a sufficient number of spiral arms before placing the dish into the line of the projector beam. This takes about 10 min at room light.

The gel in the Petri dish is uniformly illuminated from below by a video projector (Hitachi CP-S860). A computer programme has been written in C++ to control the output of the video projector as well as the data collection via a frame grabber (Data Translation, DT3155) and storage. The images are stored as tiff files. A dual Radeon 7500 Series graphics card is used to provide the second monitor for the experiment. The intensity of the light from the video projector is measured prior to each experiment with a photometer (Tektronix J 1812). The photometer was placed in the same position as the Petri dish during the experiments. The light of the video projector is passing through a cold glass filter (KG4) and a band-pass filter (BG6, 310–530 nm). Then the beam passes through a convex lens before it is being reflected upwards by a tilted mirror towards the Petri dish holder (consisting of a ground glass plate in a frame) and a charge-coupled device (CCD) camera (Hamamatsu C3077).

EXPERIMENTAL RESULTS

In the experiments the spiral waves can be separated into two groups depending on the maximum light intensity at which they are being destroyed. In group A we have the spirals which can be destroyed by homogeneous light with intensities of less than 2.5 W m^{-2} and in group B the spirals are being destroyed by intensities in the range of 2.5–4.0 W m^{-2}. This division applies only when the intensity has been increased in one or two large steps. Using a number of smaller steps causes a "desensitization" or "adaptation" effect, resulting in a considerable increase in intensity levels to which the spiral waves in both groups can be subjected before destruction. At low luminosity no differences in spiral wave dynamics between the two groups have been observed. At higher intensities the tip dynamics differs between the two groups. Spiral waves belonging to group B exhibit either no wavelength increases or only small changes in wavelength over a range of intensities, whereas the spirals belonging to group A show a continuous increase in wavelength with light intensity. Desensitization phenomena occur in both groups.

The division of the spiral waves into two groups at an intensity level of 2.5 W m^{-2} is somewhat arbitrary. This value was chosen because the distribution of the intensity levels which destroyed the spirals seems to center around 2 W m^{-2} for group A and 3 W m^{-2} for group B. There are very few experiments where the maximum value lies in the region around 2.5 W m^{-2}.

The experiments have been carried out intermittently over nearly two years. The results are fairly robust to small volume changes (± 0.05 ml) of the reactants. Variations in the layer thickness of the gel have also been excluded [13]. Spirals in group B show some response to the purity of $NaBrO_3$, but the ones in group A do not. Increased ruthenium concentrations decrease the light sensitivity of the system but not enough to explain such large variations. We have been assured by the manufacturer that the ruthenium does not contain any impurities. We have also used reactants from different manufacturers for both the BZ solution and the gel. It can happen that for several months almost all results from experiments belong to group A and then suddenly the majority of results fall into group B. There also exist time periods when the results can fall into either group almost from one day to the next. However, as always two gels are prepared at the same time and the experiments are done consecutively, we can say that if the first experiment is very light sensitive (or not), so will be the second.

The trend in the experiments is that we may obtain spirals with a higher light sensitivity when using less pure or low concentrations of $NaBrO_3$, low [ruthenium] or high concentrations of malonic acid (MA) [14]. Less light-sensitive spi-

rals can result from using low [NaBr], high [H_2SO_4], low [NaSi], low [MA], higher [ruthenium] or a purer $NaBrO_3$. But these trends do not explain the large difference in light sensitivity between the two groups. Also, there is no evidence that changes in the environmental conditions influenced the experimental results. However, one possible explanations is the existence of at least two different competing reaction pathways at the same time, one favoring inhibition and the other one activation. We have not been able to discover why sometimes one is favored over the other in the reaction, especially when one considers that the results do not depend on small variations in the initial concentrations.

RESULTS FROM EXPERIMENTS WITH SPIRALS IN GROUP A

Desensitization effects had first been observed with spirals belonging to group A while applying a Laplacian filter. (The filters are calculated from the spiral image and then projected back onto the spiral in the Petri dish. The calculations are updated every 2000 ms. The time set aside for taking the image and calculating the filter is 350 ms. During this time the spiral is illuminated by homogeneous light [15].) The filter was used to destroy the spiral waves in the Petri dishes. Waves emerging from the rim were then allowed to form new spirals and again subjected to filtered light with the same intensity as before. Once the spiral waves had been destroyed a couple of times, the new waves survived at higher intensity levels than the ones that have been destroyed previously. This seems to indicate some kind of "memory" or "desensitization" of the system. The effect is sometimes visible even after the waves have been destroyed only once. The same results were obtained when using homogeneous white light at a slightly higher intensity instead of filters to destroy the spiral waves. Aging effects can be excluded here as the whole procedure can take less than 30 min.

A further surprising result from our experiments is shown in Fig. 2. This figure shows the tip trace (white line) of a sequence of images taken from an experiment with a mean filter. Because of the mean filter, the experiment could be carried out at an intensity of only 890 mW m^{-2}. At first the tip moves out in a fairly straight line, then the curvature is increasing until the tip traces a circle with a diameter of less than 1 mm. Subsequently, the tip is drifting back in the direction of its original position and finally it ends up rotating rigidly close to its starting point. The total time of the experiment is 1880 sec.

Experiments with various filters show that very often drifting is induced by them, sometimes accompanied by sudden and unexplained changes of direction. However, a change in excitability is not due to the filters. To exclude the possibility that this behavior of the spiral tip had anything at all to do with the applied filter, spiral waves were illuminated with homogeneous light. In Fig. 3 we show the tip trace of one such experiment at a constant intensity of 1.68 W m^{-2}. At the beginning of the experiment the tip traces out a very large loop. Subsequently, the loops become smaller and smaller until the tip rotates rigidly. The time taken for the trace shown is 1100 sec.

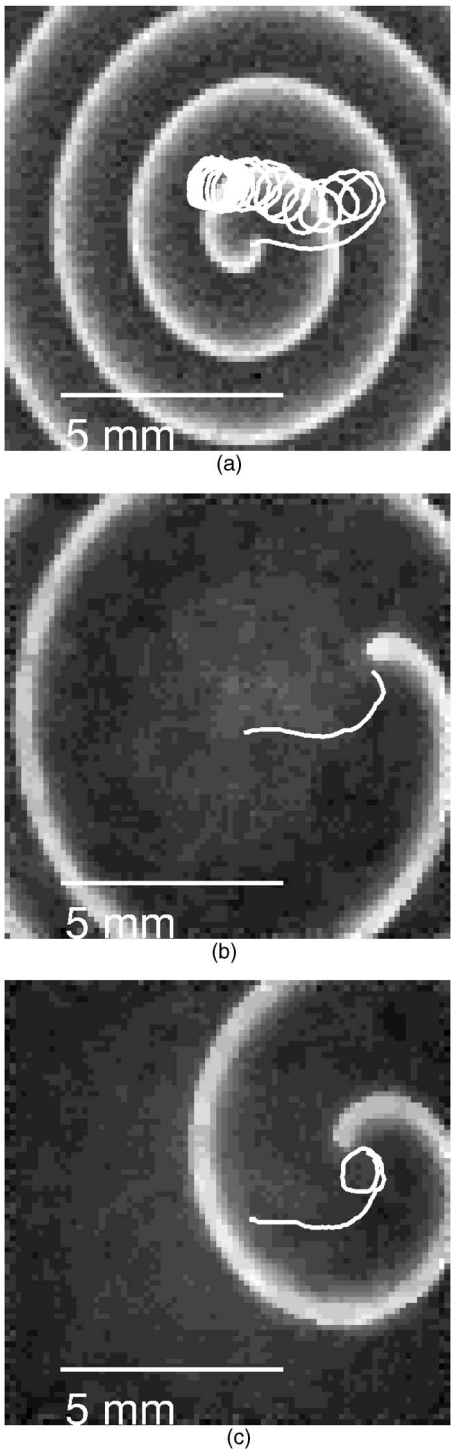

FIG. 2. Observations of desensitization with a mean filter at low luminosity. The first image (a) shows the tip trace over the total time of the experiment (1880 s) overlaid on the first spiral image of the series. The second image (b) is taken 80 sec after start of the experiment. For (b) and (c) the spiral images are the last in the series. The time difference between (b) and (c) is 23.5 sec.

That the term "desensitization" may not correctly describe the observed effect can be seen in Fig. 4 which shows the results of an experiment carried out with homogeneous illumination. At first, the tip moves out in a fairly straight line.

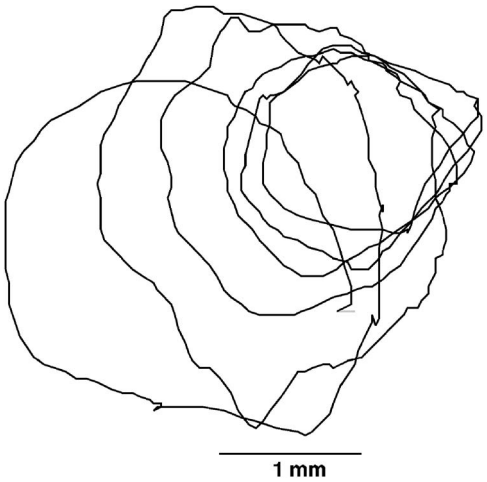

FIG. 3. Tip trajectory of a spiral at a constant intensity of 1.68 W m^{-2}. At first the tip traces out the larger circles but then the loops become smaller.

Then, it starts to curve and trace out a small circle which is followed by a larger one. After that the tip continues moving out of the observation area. The intensity is 1.16 W m^{-2} and the total time taken for the trace is 470 sec. These observations seem to indicate a kind of "competition" between two or more different reaction pathways where either one or the other prevails at any one time.

Evidence for a kind of "memory" of the system's previous state is obtained when comparing the movement of spiral tips at the same intensity but with different histories. With increasing intensity two different sequences of spiral tip behavior have been observed. In the majority of experiments the sequence of spiral tip movement with increasing intensities

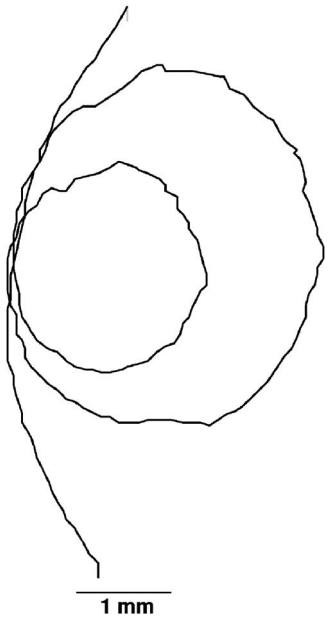

FIG. 4. At first the tip starts moving out of the observation area, then it traces the small circle followed by the larger one before it continues on its way out of the observation area. The applied intensity is 1.16 W m^2.

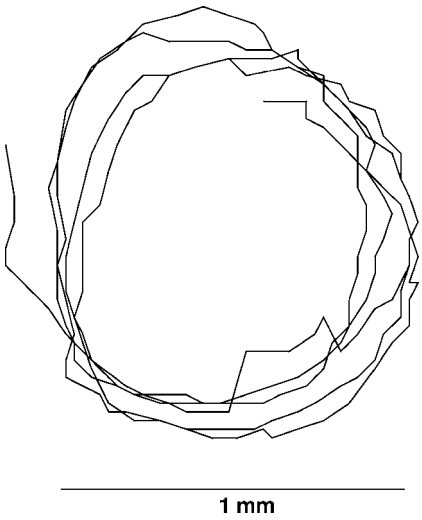

FIG. 5. Spiral tip trajectory exhibiting rigid rotation at an intensity of 2.2 W m^{-2}.

is meandering, rigid rotation, and then destruction either by fading or by the tip moving out of the recording area in a fairly straight line or tracing a circle with a very large radius (zero curvature). Breakup was only observed in connection either with fading or zero curvature but never on its own. These observations apply to both group A and group B. Group A spirals can exhibit a second sequence, where the tip is undergoing rigid rotation and the radius increases continuously with increasing intensity until the circles traced out by the tip are larger than the size of the observation area (usually 1 cm^2). Once this has happened an increase in intensity does not lead to ever larger circles but to destruction of the spiral wave by fading or zero curvature. Thus there seems to be a cutoff value for the radius beyond which rigid rotation cannot be sustained.

For a system that can be reset to zero by illumination the spiral tip movement would remain the same after decreasing and increasing the light intensity. This is not the case. In Fig. 5 the spiral tip is rotating rigidly at an intensity of 2.2 W m^{-2}. This indicates that the value of the intensity is close to the maximum intensity required for destruction of this spiral. Subsequently, the intensity was reduced to 1.0 W m^{-2} and brought back up to 2.2 W m^{-2} in four steps. This took about 20 min. The meandering tip is shown in Fig. 6. The wavelength was reduced from 3.4 to 2.5 mm between the two observations. Rigid rotation occurred again at an intensity of 3.1 W m^{-2} and zero curvature at 4.0 W m^{-2}. These results have been repeatedly obtained in many experiments and clearly indicate a change in excitation of the system before and after reducing the intensity. One possible explanation for this observation could be that the concentrations of intermediates play a greater part in the reaction than was assumed. Changes in their concentration levels due to the sudden decrease in intensity may affect the excitation of the system, i.e., the spiral wave "remembers" having been subjected to a higher intensity level. The effect of varying concentrations of intermediates during the experiments may also be responsible for the "unstable" circular traces with diameters greater than 1 cm and the distribution in the level of intensities destroying the two groups.

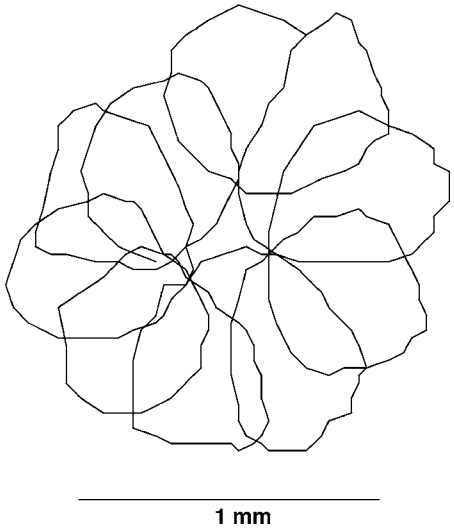

FIG. 6. Spiral tip trajectory of the same system and at the same intensity as in Fig. 5 but with a different history.

RESULTS FROM EXPERIMENTS WITH SPIRALS IN GROUP B

Similar changes in tip movement with different histories have also been observed in experiments with the less light-sensitive spirals. Spiral waves belonging to this group react even more dramatically when the intensity is slowly increased in a number of steps. It seems that this procedure causes a buildup in "tolerance" to intensity levels far above the threshold value at which the spiral waves are normally destroyed when the intensity is increased in only one step. Again always two gels are prepared at the same time for the experiments: one of the gels is illuminated at low intensities (≤ 1.0 W m^{-2}) for about 5 min and then the intensity is immediately switched to a level at which the spirals in previous experiments for this group were being destroyed (i.e., about 3–4 W m^{-2}). The other gel is brought towards the same high intensity level but in a number of steps. The results show clearly that in each case the spirals which were slowly introduced to the high intensity survive at levels that normally destroy the spirals in other gels which were not desensitized.

There is the possibility that the observed differences in spiral wave behavior in this group could have something to do with aging, as the spirals which have been brought up slowly to a certain intensity level (desensitized) are, of course, older than the ones which are subjected to this intensity level immediately. Because the closed reaction system does not provide a steady inflow of reactants, the concentrations slowly decrease over the course of time. This depletion of substrates induces slow transients in the wave dynamics that typically lead to an increase in the wavelength and the period of spiral waves. Moreover, the tip trajectory of the aging spiral is expected to expand into larger areas. However, in the experiments aging effects usually start to occur after about 4 h when the wave front is getting broader and after $4\frac{1}{2}$ h the spiral waves start to get fainter. After 5 h the gel is becoming clear in some areas and remaining that way. These clear regions do not break up or seem to interfere in any way with the wave fronts traveling across them.

Nagy-Ungvarai *et al.* [16] studied aging processes of thin solution layers in the cerium-catalyzed BZ reaction. They showed that at sulphuric acid concentrations of 0.41 M meandering starts at approximately 30 min. At about $t=160$ min hypermeandering sets in. With increasing time there follows a second, apparently quasiperiodic, domain. Subsequently, orbiting rigid rotation with a very large diameter can be observed (>2 mm). This diameter grows progressively, so that at later stages they only could trace segments of a closed circle in the accessible observation area. The boundary of spiral wave stability was reached at $t=280$ min when the diameter of orbiting rotations becomes infinite. This corresponds to a tip motion along a straight line (i.e., zero curvature). One important result of their experiments is that aging seems to depend strongly on the sulphuric acid concentration. In our experiments $[H_2SO_4]=0.468$ M. This high concentration could explain the longevity of our spiral waves. It is also interesting to note that their sequence of spiral tip movements is similar to the one we get in the ruthenium-catalyzed BZ reaction with increasing intensity. The exception is that when rigid rotation occurs again after meandering, the orbits are not increasing significantly before destruction. Also, the meander pattern in the experiments increases only slowly with increasing intensity as has been observed for aging solutions [17].

In order to exclude any aging effects from the observations, spiral waves were illuminated for one hour at 1.3 W m^{-2}. The images were then recorded at regular intervals for another hour at the same intensity. During this time no wavelength changes were observed. The tip movement can be seen in Fig. 7(a). After 2 h the intensity was increased in one step to 3.5 W m^{-2}. This caused the spiral tip to move out of the recording region in a fairly straight line.

Then we repeated the same procedure but this time the intensity was not increased to 3.5 W m^{-2} but only to 3.2 W m^{-2} and then to 3.5, 4.1, and 5.6 W m^{-2}. The time taken for each of the steps was about 5 min. During the first 2 h we recorded no changes in wavelengths. This was expected from previous experiments. We also expected from previous experiments that once a sufficiently high intensity was reached, the spiral tip would move out of the recording region in a fairly straight line. This did not happen. At an intensity of 5.6 W m^2 the spiral tip indeed moved out of the recording region but not in a straight line. Instead the spiral tip was meandering and the wavelength became larger and larger, so that at one time only one single spiral arm survived in the Petri dish [Fig. 8(a)]. Then, unexpectedly, the wavelength started to decrease again. Whereas, it varied before between 3 and 6 cm, now it varied between $2\frac{1}{2}$ and 3 cm and was still getting smaller. The increase in the number of spiral arms over time can clearly be seen in Fig. 8 as well as the superimposed tip trace. The intensity was then further increased to 6.4, 7.5, and only at 8.2 W m^{-2} did the spiral wave start to disappear slowly by fading.

The gels for these two experiments had been prepared 24 h previously, but similar results have been obtained with freshly prepared gels. Moreover, the same effects have been recorded irrespective if spirals were illuminated before the experiments or kept in the dark.

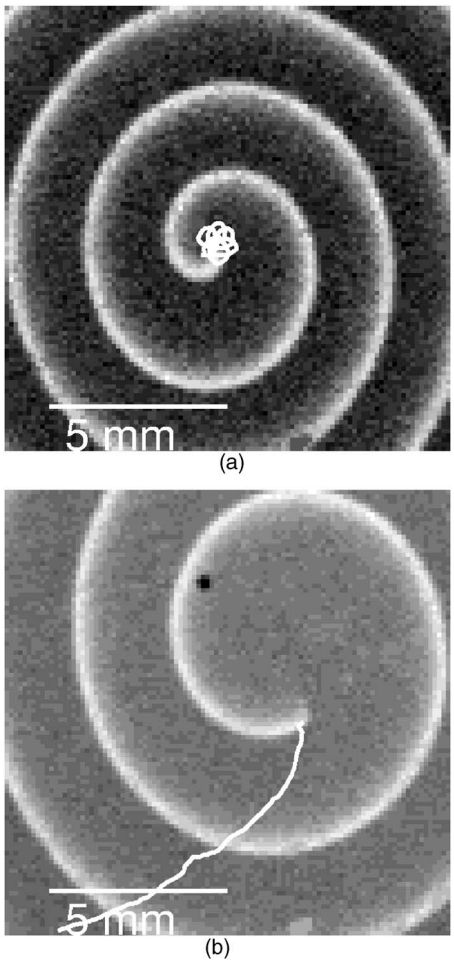

FIG. 7. Tip trajectories of aged spirals at intensities of (a) 1.3 and (b) 3.5 W m^{-2}. The intensity is increased in one step. The image shown is always the first of the series.

Comparing the results from these experiments with the ones for group A spirals clearly shows that the desensitization effect depends neither on the age of the spirals nor on the light-sensitivity of the system. These observations can be caused by changes in the excitation level of the system. As these changes occur without any variation in the experimental conditions, chemical processes within the system must be responsible for them.

SIMULATION RESULTS

For the simulations we are using Barkleys model [18–22]. In his model Barkley employs reaction-diffusion equations explicitly and allows for continuous adjustment of space-time resolution:

$$F(u,v) = \frac{1}{\epsilon}u(1-u)[u - u_{th}(v)],$$

$$G(u,v) = u - v,$$

where u^n and v^n are the values of species u (activator) and v (inhibitor), $u_{th}(v)=(v+b)/a$, the diffusion coefficient, $D_u=0$,

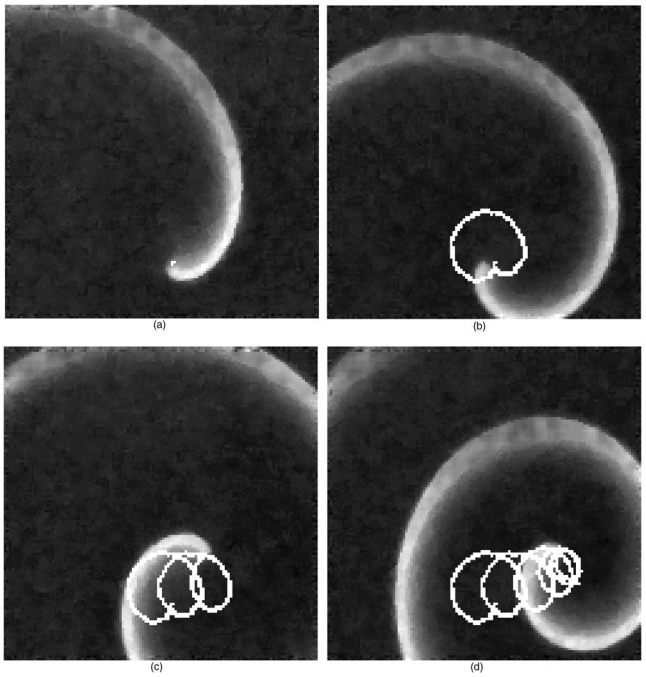

FIG. 8. Desensitization effects using old spirals. The images show clearly that the curvature increases with time. The applied intensity is 5.6 W m^{-2}. The time difference between the images is 10 min. The total time is 30 min. Here the image shown is always the last in the series from which the tip trace has been taken.

and a, b, and ϵ are constants. The parameter v_{th} denotes the excitability threshold for the fixed point. The parameter ϵ is typically small, so that the time scale of u is much faster than that of v. This system of partial differential equations is integrated on a square domain of 121×121 grid points (with a length of $L=50$ and $dt=10e^{-3}$).

Agladze *et al.* [7] have already used simulations with this model to support their observations. They showed that increasing the parameter b from 0.025 to 0.225 in one step results in the destruction of the wave, whereas increasing the parameter b slowly results in survival of the wave. Thus desensitization phenomena can be modeled by changes in the parameter b.

Our experimental observations also show that the spiral tip reacts to increases in intensity in two different ways:

(i) the tip is at first meandering and then rotating rigidly before destruction (breakup, fading, and/or zero curvature). The diameter is usually around 1 mm and does not change significantly over a range of intensities. Both groups of spirals can exhibit this sequence;

(ii) the tip traces circles of continuously increasing diameter with increasing light intensity until the orbits are greater than the observation area (1 cm^2). This behavior has mainly been observed for spirals in group A.

The simulation results in Fig. 9 show a sequence of spiral tips tracing circles with continuously increasing diameters. The parameters used for this simulation are $a=0.075$, $b=0.105$, 0.125, 0.130, and 0.131. The difference to the observations is that the radii become continuously larger, whereas the observations usually show a break in the increasing radii at around 0.5 mm. A further decrease in excitability leads to

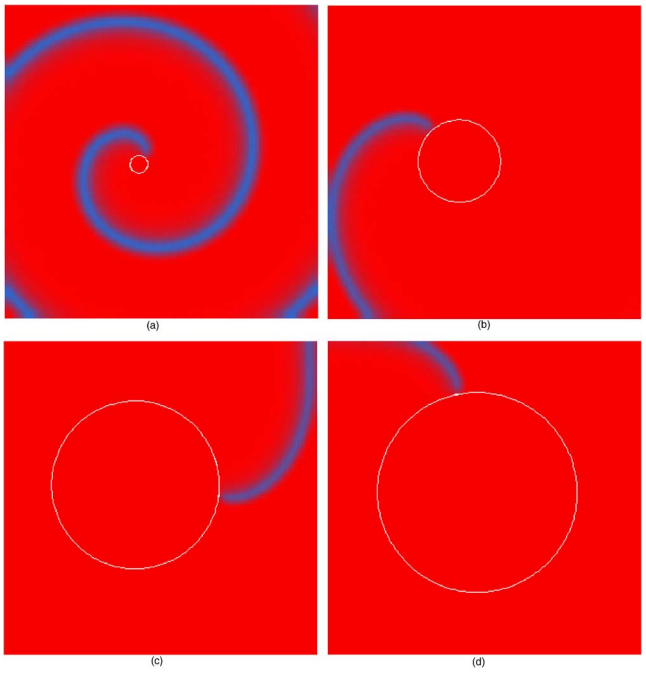

FIG. 9. (Color online) Sequence of spiral tips tracing circles of continuously increasing diameter. The values of the parameter b are 0.105, 0.125, 0.130, and 0.131, respectively.

a jump in the value of the radius that is, it becomes huge. The wave is subsequently destroyed as the spiral tip moves towards the rim of the Petri dish (zero curvature).

Figure 10 is another sequence with the same parameters as above except that $a=0.065$ and $b=0.05$, 0.06, 0.07, 0.08, 0.085, and 0.086. The tip now behaves in a complete different way to Fig. 9. It exhibits meandering followed by rigid rotation before destruction by fading combined with zero curvature. When the tip is rotating rigidly the diameter of the circle is increasing very little with increasing b.

Despite the relative simplicity of the model, the experimental results can be reproduced by changes in the parameters a and b. In the model the parameter b depicts the excitation threshold, that is an increase in b corresponds to a loss of excitability. Thus one would expect such changes to occur with variations in the initial concentrations. However, in the experiments both behaviors were observed when using exactly the same recipe. This may indicate that the concentrations of intermediates play an important part in determining the excitability of the system and not just the initial concentrations of the reactants.

REACTION MECHANISM

The main chemical processes in the nonilluminated BZ reaction are described by the Field-Körös-Noyes (FKN) mechanism [23]. The critical features of this mechanism are the competition of bromide and bromate ions for bromous acid and an autocatalytic step, which is necessary for oscillations to occur. Demas and Diemente [24] found that the BZ system becomes light sensitive if ruthenium is used as a catalyst. Under irradiation with visible light at $\lambda=452$ nm

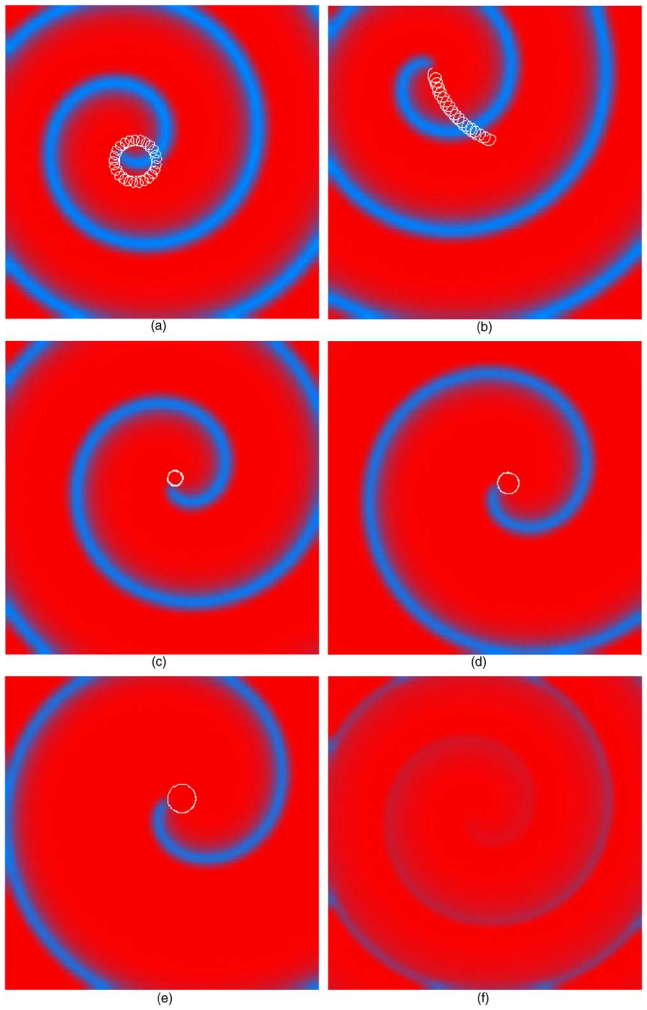

FIG. 10. (Color online) Sequence of tip traces showing first meandering and then rigid rotation before destruction of the wave. The values of the parameter b are 0.05, 0.06, 0.07, 0.08, 0.085, and 0.086, respectively.

the $Ru(bpy)_3^{2+}$ complex forms the excited state $Ru(bpy)_3^{2+*}$ due to metal to ligand charge transfer. This has a lower oxidation potential ($E_0=-0.84$ V) than the unexcited complex ($E_0=1.26$ V) and is a very strong reducing agent [1,3,25–27].

In the dark the autocatalytic process takes place with the oxidation of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$,

$$2\mathrm{Ru(II)} + \mathrm{BrO_3^-} + \mathrm{HBrO_2} + 3\mathrm{H^+} \rightarrow 2\mathrm{Ru(III)} + 2\mathrm{HBrO_2} + \mathrm{H_2O}, \quad (1)$$

where Ru(II) is $Ru(bpy)_3^{2+}$ and Ru(III) is $Ru(bpy)_3^{3+}$. If $[Br^-]$ exceeds a critical value the rapid reaction

$$\mathrm{HBrO_2} + \mathrm{Br^-} + \mathrm{H^+} \rightarrow 2\mathrm{HOBr} \quad (2)$$

prevents the autocatalytic step from occurring and the system stays in the reduced steady state, that is reaction (2) keeps $[HBrO_2]\sim 0$. If $[Br^-]$ decreases below this critical value then Eq. (1) brings the system into the oscillatory state.

A decrease of $[Br^-]$ can be observed parallel to the oxidation of Ru(II) to Ru(III) in the dark. Under illumination, however, the existing concentration of bromide ions is increasing. To explain this increase in $[Br^-]$ Kuhnert [9] proposed a mechanism in which BrO_3^- is directly reduced by the photoexcited catalyst to produce Br^-:

$$6Ru(II)^* + BrO_3^- + 6H^+ \rightarrow 6Ru(III) + 3H_2O + Br^-, \quad (3)$$

where $Ru(II)^*$ is the photoexcited $Ru(bpy)_3^{2+}$. This process can account for the observed photoinhibition [28] since it produces Br^- which then consumes $HBrO_2$ through reaction 2. It also can explain the observed reduction in wave velocity [29], amplitude, and frequency of the oscillations [3,25] under the influence of illumination.

A more effective mechanism, based on the inorganic subset of the BZ reaction, was proposed by Srivastava *et al.* [3], and Hanazaki *et al.* [30]. This process has a greater inhibitory effect than Kuhnert's as it produces Br^- and consumes $HBrO_2$ at the same time:

$$Ru(II)^* + 3Ru(II) + HBrO_2 + 3H^+ \rightarrow 4Ru(III) + Br^- + 2H_2O. \quad (4)$$

However, under certain circumstances photoinduction occurred instead of photoinhibition. To explain the observed photoinduction at low luminosity Mori *et al.* [2] proposed an additional mechanism:

$$Ru(II)^* + Ru(II) + BrO_3^- + 3H^+ \rightarrow 2Ru(III) + HBrO_2 + H_2O. \quad (5)$$

This process produces additional $HBrO_2$ and thus enhances the autocatalytic step.

Investigating the inorganic part of the Ru-catalyzed BZ reaction, Ram Reddy *et al.* [31] excluded a mechanism of direct reduction of bromate by the excited catalyst as they found a well-defined time delay between the production of $Ru(bpy)_3^{3+}$ and Br^-. They proposed an indirect path for the photochemical reduction of bromate to bromide in the presence of oxygen. Oxygen is an effective quencher of $Ru(II)^*$ and their measurements confirm that the conversion of the catalyst to its oxidized form at a normal concentration of sulfuric acid is highly sensitive to the amount of dissolved oxygen. Their results also indicate that the light sensitivity of the whole BZ reaction does not only depend on the inorganic subset of the reaction, namely the Ru(II)-bromate-sulfuric acid system, but is also strongly influenced by the organic subset.

It was assumed that on photoinhibition of oscillations in the BZ system the bromide concentration always increases upon irradiation and thus suppresses autocatalysis by the switching reaction (2). However, Sekiguchi *et al.* observed an increase of $[Br^-]$ upon photoirradiation in a minimal bromate oscillator not only with photoinhibition but even in the cases where photoinduction occurred [5]. Furthermore, Petrov *et al.* [32] showed that at low bromate concentrations the rotational frequency of spirals decreases, whereas at high concentrations an increase of the oscillation frequency can be observed even at high illumination intensities.

A further complication arises from observations made by Kaminaga and Hanazaki [33]. They found that under pulsed light perturbation the photoexcited metal complex produces additional $HBrO_2$ to enhance the autocatalytic process. They found no evidence to support the photoproduction of bromide ions in their minimal bromate oscillator.

Kádár *et al.* [6] did a mechanistic study of the photo-BZ reaction in a flow system. They concluded that irradiation gives rise to two separate processes. One pathways is the photochemical production of the inhibitor Br^- from BrMA [34] and the other generates the activator $HBrO_2$ from the reduction of BrO_3^- by the excited catalyst in the absence of BrMA. They found that at their low light intensities, the pathway producing Br^- was by far dominant with the $HBrO_2$ pathway very minor.

Using phase-response analysis Treindl *et al.* [35] also deduced the existence of these two pathways but suggested the possibility of one further reaction channel. They argued that because $HBrO_2$ may be expected to be photoproduced independently of BrMA, the *in situ* formed $HBrO_2$ may be a source of bromide ions when reacting with BrMA or other bromo-organic compounds. They also observed that after a break in illumination the bromide ions are not fully consumed again and suggest an oxidative quenching process between the excited RuII and BrMA,

$$RuII^* + BrMA \rightarrow RuIII + Br^- + CH_3O \cdot (COOH)_2 \quad (6)$$

which may only be partly reversible. If periods of light and darkness are given repeatedly, the final bromide ion steady state concentration increases during each light on or off cycle. During these illumination and darkness cycles the potential of the Pt electrode shifts to positive and negative values, correspondingly. They suggest the following substitution process:

$$RuII + MA \rightarrow Ru(bpy)_2MA^{2+} + bpy. \quad (7)$$

Most of the investigations into the reaction mechanism have been carried out with oscillatory systems and the deduced schemes do not necessarily also apply to spatial pattern formation as in this case a considerable amount of BrMA is formed [30]. Hence the predominant effect of illumination of this system is the production of the inhibitor Br^- and photoinhibition of oscillations is believed to occur through the reduction of the system by photoproduced Br^-.

Varying the initial concentration of malonic acid in the experiments changed the light sensitivity of the system slightly but could not account for the difference in behavior between groups A and B. The stepwise increase in illumination resulting in a reduced sensitivity to light was also not affected by changes in [MA] nor was the desensitization effect.

The experimental results indicate that in pattern formation as well as in the oscillatory BZ reaction there must be at least two photochemical pathways for the production of activator and inhibitor to explain the spiral tip behavior and the observed effect of desensitization of the system. Furthermore, these pathways have to compete with each other at the same intensities under certain circumstances. Another possibility could be that after some time the excited state of Ru(II) is

being quenched and starts to contribute less, or in some cases not at all, to the normal BZ reaction. However, this explanation is less likely as desensitization effects have also been observed with the short-lived spirals belonging to group A. Other explanations are that the concentrations of intermediates play an important part and affect the excitability of the system or that some reactants form irreversible combinations under certain conditions.

SUMMARY AND CONCLUSION

Using the same initial concentrations, the experimental results can be divided into two different groups, A and B, depending on their light sensitivity. Small changes in the initial concentrations have no effect on the experimental results. The sequence of spiral tip dynamics with increasing light intensity of meandering, rigid rotation, and subsequent destruction can be found in both groups. However, in group A a second sequence can be observed, where the spiral tip traces out circles of increasing diameter with increasing intensity. The spiral wave is being destroyed once a certain value of the radius has been reached.

The desensitization effect in the ruthenium-catalyzed BZ reaction seems to cause an increase in excitability at constant illumination. This effect depends on the way illumination is applied to the system and is not present when the intensity is increased to high levels in only one step. Also, our results imply that the system has a memory of its former state as increasing and decreasing the illumination several times results in changes in the tip dynamics and an increasing tolerance to higher intensities, that is the system cannot be reset to zero. It is not quite clear if memory and desensitization have the same underlying cause but both require a stepwise increase in luminosity. These differences in behavior can be reproduced in simulations by changes in the excitation threshold.

The experimental results indicate that there must be at least two different reaction pathways for the excitable medium. However, in contrast to oscillatory systems, these pathways have to operate at the same light intensity. It seems likely that changes in the concentration of intermediates play an important part in determining the excitability of the system. Further work needs to be done to clarify details of the reaction pathway and to identify the intermediates involved.

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