

Wavelength-Doubled Spiral Fragments in Photosensitive Monolayers

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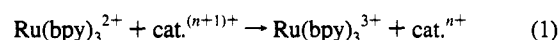
Abstract: Monolayers of a ruthenium complex derivative are formed on thin layers of Belousov–Zhabotinsky (BZ) reaction solutions to visualize specific pattern formation at the liquid–monolayer interface. A combination of luminescence and transmission detection allows simultaneous observation of wave characteristics both in the monolayer and in the BZ solution. Luminescence images of the monolayer coupled with the Mn-catalyzed BZ reaction show that the geometry of propagating spiral waves is extremely sensitive to atmospheric conditions, while spatiotemporal patterns are almost unaffected in bulk solution. A clear transition from the usual spirals to wavelength-doubled spiral fragments is found in the monolayer when the system is kept under an air atmosphere.

Introduction

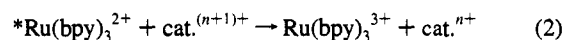
The Belousov–Zhabotinsky (BZ) reaction,¹ which is the oxidative bromination of an organic substrate in the presence of metal catalyst, provides profound, sometimes unexpected information about self-organization under nonequilibrium conditions. Two-dimensional spatial structures such as concentric waves and rotating spirals are spontaneously generated in thin layers of BZ solution. The spatiotemporal behavior of these patterns can be modified by the application of illumination^{2,3} or electric field⁴ as well as by diffusion of oxygen through the liquid–air interface.^{5–7} In addition, convective flow is induced in the solution as the oscillatory reaction proceeds,^{8–12} making wave dynamics much more complex. Here we report on a new type of spiral organization occurring in ruthenium complex monolayers spread on the surface of BZ reaction solutions. Simultaneous observation of the monolayer and the reaction solution with an air atmosphere reveals that pattern formation tends to be suppressed locally and periodically in the monolayer as the catalyst is changed from Ce to Mn, whereas spiral waves are retained in the bulk solution. The suppression effect results in a transition of perfect spirals into a wavelength-doubled state with regular fragmented shape. Undisrupted patterns can be restored in the monolayer when exposed to nitrogen. These observations and numerical studies suggest that the formation of an oxygen-controlled inhibition zone at the liquid–monolayer interface of BZ solution is the main cause for the occurrence of wavelength doubling.

Experimental Section

In previous work,¹³ a surfactant derivative of ruthenium–bipyridyl complex $\text{Ru}(\text{bpy})_3^{2+}$, $(\text{bpy})_2\text{Ru}^{\text{II}}[\text{bpy}(\text{COOC}_{18}\text{H}_{37})_2]^{2+}(\text{PF}_6^-)_2$, was spread on Ce- and Mn-catalyzed BZ reaction solutions, and luminescence images of the monolayer were visualized using fluorescence microscopy. The formation of oxidized waves was clearly observed as dark bands propagating through a bright reduced background. We attributed this behavior to the oxidation of luminescent $\text{Ru}(\text{bpy})_3^{2+}$ to nonluminescent $\text{Ru}(\text{bpy})_3^{3+}$ by the oxidized catalyst according to the reaction



However, the amount of $\text{Ru}(\text{bpy})_3^{3+}$ produced in the oxidized region was found to be quite small by visible absorption measurement. This means that oxidative quenching may play a more important role:¹⁴



At any rate, chemical reactions occur between the monolayer and the BZ solution via electron transfer, suggesting that patterns that are formed in the monolayer serve as redox indicators for what is happening in the surface layer of the BZ solution.

In the present experiments, Ce-, Mn-, and ferroin-catalyzed BZ solutions were used as monolayer substrates. The reaction mixture contained 0.44–1.28 M H_2SO_4 , 0.16 M NaBrO_3 , 0.3 M $\text{CH}_2(\text{COOH})_2$, 0.09 M HClO_4 , and 0.003 M catalyst ($\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$, MnSO_4 , or $\text{Fe}(\text{phen})_3\text{SO}_4$). In the case of the ferroin-catalyzed system, 0.03 M NaBr was added in the mixture in order to bring the system to a more reduced state, and the concentration of HClO_4 was decreased to 0.03 M because ferroin is only slightly soluble in perchlorate solutions. Immediately after the start of the oscillatory reaction, the solution was filtered through a 0.22- μm filter and placed in a petri dish (diameter 6cm), with a layer thickness of 0.7 mm, onto which $\text{Ru}(\text{bpy})_3^{2+}$ monolayers were spread. The experimental setup for direct observation is schematically illustrated in Figure 1. The whole medium was illuminated from the top by light from a 500-W Hg lamp passing through an interference filter (365 nm for the Ce system, 436 nm for the Mn and ferroin systems). The light intensity was less than 7 mW/cm². The resultant luminescence emission from the monolayer was separated with a dichroic mirror and was viewed with an ICCD camera (Hamamatsu ICCD-500). The transmitted light was simultaneously detected with a UV-sensitive Vidicon camera (Hamamatsu C2047) in order to monitor pattern formation in the BZ solution. Both images,

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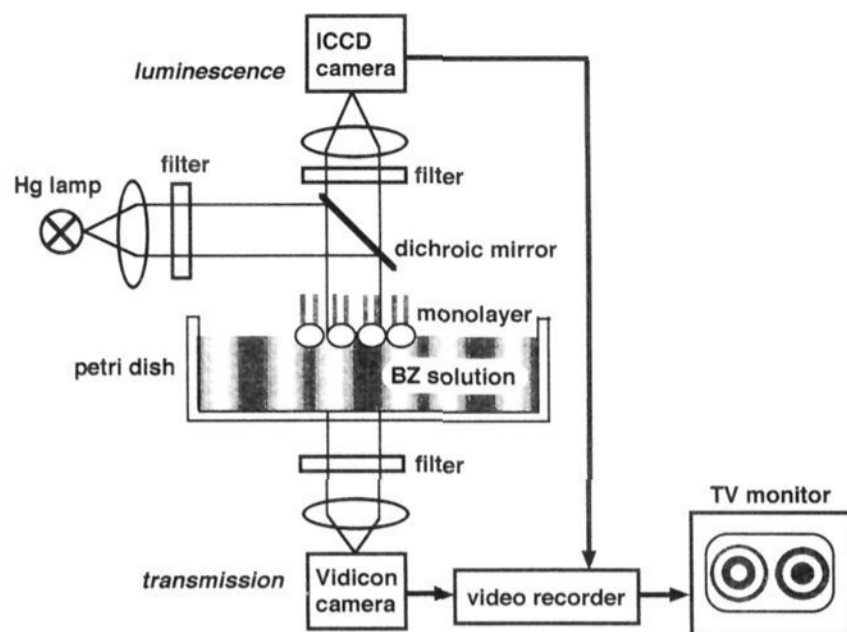


Figure 1. Schematic representation of the experimental setup.

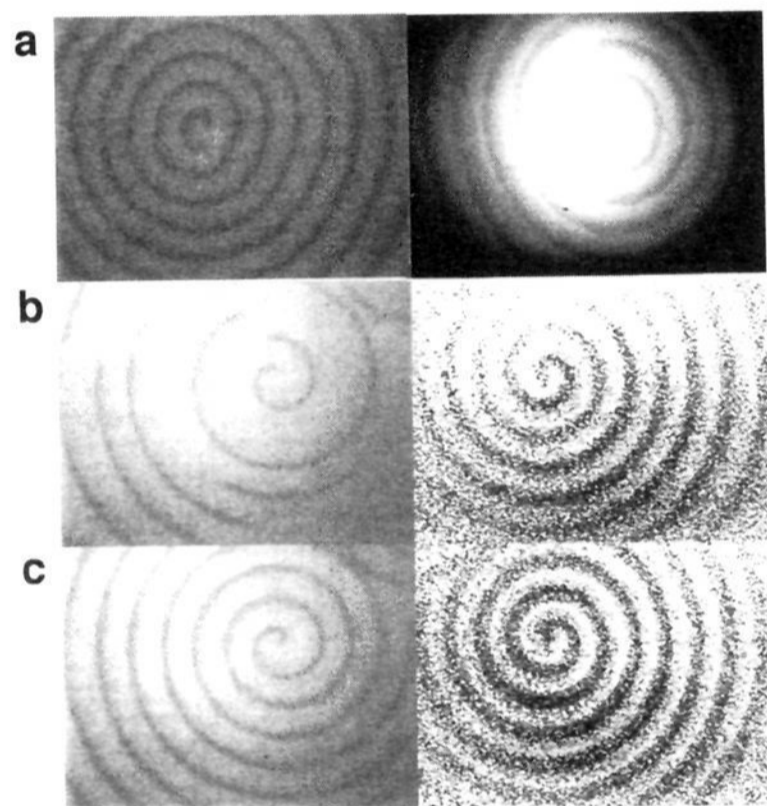


Figure 2. Simultaneous observation of chemical patterns in Ru(bpy)₃²⁺ monolayers (left-hand side) and in BZ reaction solutions with 0.72 M H₂SO₄ (right-hand side) performed 4 min after the creation of spiral waves. The catalyst of the BZ reaction is Ce (a) or Mn (b,c). For the Mn-catalyzed solution, the pattern is visualized by subtracting an image captured 8 s earlier. Fairly identical patterns observed in the Ce system in contact with air (a) remain stable for more than 30 min and are essentially unaffected by a nitrogen stream except for a slight increase in image contrast. The monolayer in the Mn system shows a disrupted pattern in contact with air (b), but the wave attains perfect shape when exposed to nitrogen (c). Image area: 1.47 × 0.92 cm.

with or without contrast enhancement, were stored on a video recorder for further analysis. The temperature was maintained at 25 ± 1 °C throughout the experiments.

Results and Discussion

Oxidized waves were spontaneously initiated at the dish boundaries. We created spiral waves by disruption of a wave front with an air blast or with a mechanical shake of the dish. Figure 2 depicts typical images obtained by simultaneous observation of the created spirals in the Ce- and Mn-catalyzed systems under constant illumination. Due to the particular arrangement of the experimental setup, the solution patterns (right-hand side in Figure 2) represent mirror images of the spirals. A similar set of images were obtained when illumination was cut off except for a short time (~5s) required to capture

each image, showing that the light intensity adopted (<7mW/cm²) had little effect on the wave dynamics. During this experiment the dish was covered with a polystyrene case having a pair of small openings, one of which was in some instances used as an inlet for a stream of nitrogen or fresh air. For the Ce catalyst, essentially the same pattern is seen to develop both in the monolayer and in the subphase irrespective of atmospheric conditions (Figure 2a). In contrast, the Mn system exhibits rather unusual luminescence patterns with an air atmosphere: near the beginning of the experiment, spirals start to undergo wave fragmentation, leading to a number of wave pieces moving in the direction determined by the initial wave (Figure 2b). Note that the spiral waves are quite robust in the bulk solution; no appreciable perturbation in wave shape was detected within the time period of observation (~20 min). Similar spatial behavior was observed over the acidity range studied (0.44–1.28 M H₂SO₄), and also when the concentration of malonic acid was decreased to 0.05 M. This type of spatial organization was found to be generic to spiral configuration: wave fragmentation did not appear for concentric target patterns under the same experimental conditions.

Perfect spirals are reproduced if nitrogen is allowed to flow through the headspace above the monolayer (Figure 2c). These waves remained highly stable in the monolayer with a nitrogen atmosphere. When the nitrogen was removed by a stream of fresh air, the wave pattern vanished completely throughout the field of view. After a period of time, however, the initial spirals suddenly became visible again. This process of global disappearance of chemical patterns repeated for several cycles with its period doubled compared to that of the initial wave, but spatial heterogeneity evolved in time to a complex spatiotemporal pattern like that in Figure 2b.

Obviously, the partial wave disappearance observed for the Mn system arises from a spatially inhomogeneous profile in wave activity in the BZ solution. The fact that the bulk pattern is undisturbed indicates that poorly excitable regions are established due to atmospheric oxygen only in the surface layer of the solution very close to the monolayer. Direct visualization of such oxygen-created inhibition zones was reported for the first time by Kuhnert et al.⁶ in the ferroin-catalyzed BZ reaction using a capillary slit method. Since then the effect of oxygen on wave characteristics has been extensively studied, and various new types of wave geometry have been found.^{7,15} We also attempted to detect luminescence patterns in Ru(bpy)₃²⁺ monolayers on ferroin-catalyzed BZ solutions, but were unable to obtain sufficient image contrast; the oxidized catalyst (ferriin) itself was slightly luminescent under visible illumination, and more essentially, luminescence from the monolayer was somewhat quenched via energy transfer to the iron complexes.

To gain further insight into the spatiotemporal character of the monolayer pattern, attention was focused on a selected pair of rotating spirals and their time course was followed over an extended period of time under open-air conditions. The six images in Figure 3 illustrate how the wave disruption typically develops. Instability appears soon after the creation of the spirals, and apparently their tips undergo wave disappearance at first (Figure 3a). The loss of wave activity prevails outward as time goes on, giving rise to wave fragmentation (Figure 3b). The fragmented pattern seems to be rather disorganized in early stages of evolution (Figure 3d), but over the course of time assumes regular behavior across the entire field with its wavelength exactly twice that of the perfect spiral (Figure 3f). This wavelength-doubling transition propagating from the spiral

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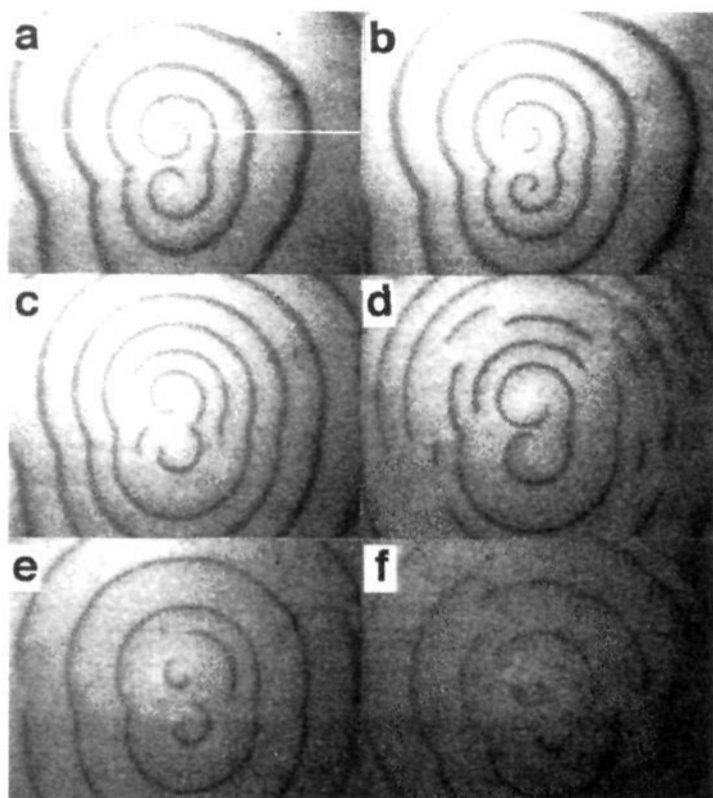


Figure 3. Transition of monolayer patterns from perfect to fragmented spirals occurring on a Mn-catalyzed BZ solution with 1 M H₂SO₄. The time elapsed between (a) and (f) is 19 min. The white line in (a) indicates the spatial cut used to extract the space–time profile in Figure 4. The loss of wave activity prevails across the monolayer with time and eventually produces a wavelenght-doubled structure in (f) where nearly straight “dislocations” are seen to extend from each spiral center to the right and to the top. Image area: 1.47 × 0.92 cm.

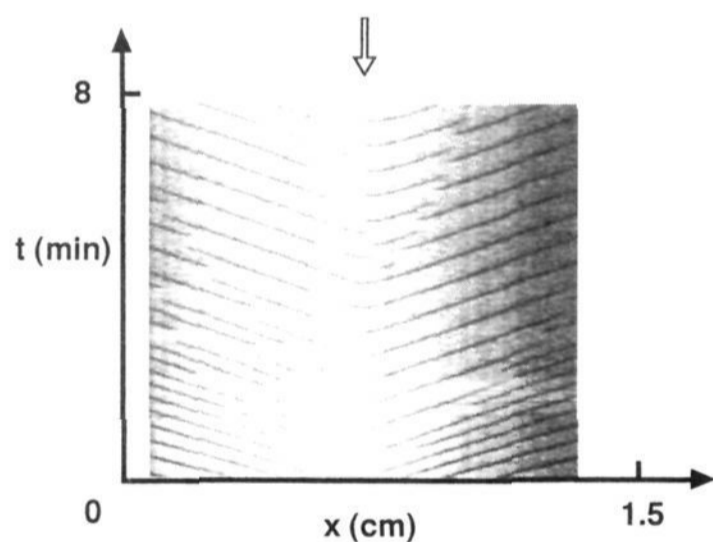


Figure 4. Space–time portrait of the spiral pattern in Figure 3 produced along the cut in Figure 3a. A transition to a wavelenght-doubled state takes place in the pattern center (open arrow) at the beginning and propagates slowly in an outward direction.

centers is more evident in the space-time portrait of Figure 4. The fragmented pattern in Figure 3f remained almost undisturbed for more than 30 min. Then the monolayer became less and less luminescent mainly because of the irreversible oxidation of Ru(bpy)₃²⁺ by BrO₃[−] present in the subphase. As a result, the image contrast became insufficient to accurately track the pattern evolution any longer.

It is remarkable that the wavelenght-doubled pattern is composed of well-defined spiral fragments. The regular spatial behavior in Figure 3f is found to be quite general in our experiments, as demonstrated by other examples in Figure 5. Interestingly, the wavelenght-doubling transition is in most cases realized for each spiral in such a simple manner that the initial spiral, with its shape given by a function $\theta(r)$, survives periodically for $\theta_0 + 4m\pi \leq \theta(r) < \theta_0 + (4m + 2)\pi$ ($m = 1, 2, \dots$) with θ_0 almost independent of m (Figure 5a). The modified spiral thus shows discontinuity at $\theta(r) = \theta_0 + 2m\pi$, which is arranged in a nearly straight line. Such “dislocations”

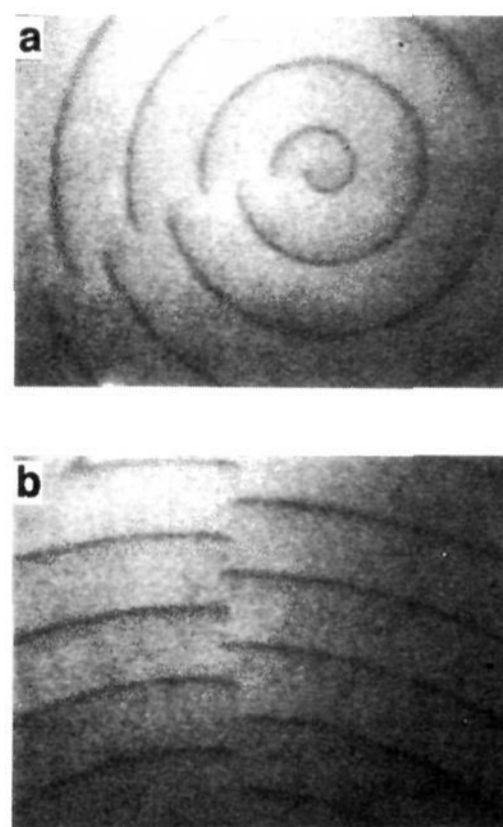


Figure 5. Examples of wavelenght-doubled patterns with clear dislocations in Ru(bpy)₃²⁺ monolayers: (a) approximately isolated spiral; (b) wave trains observed about 2 cm away from the pattern center in Figure 3f. Image area: 1.47 × 0.92 cm.

can extend over a long distance from the corresponding spiral center as far as no other spirals are created in the medium (Figure 5b).

The mechanism for the formation of wavelenght-doubled spiral fragments can be understood qualitatively as follows: the excitability of the surface layer is reduced because of the increased production of inhibiting Br[−] due to oxygen.^{7,15} The surface layer can be excited into its oxidized state by the autocatalytic species HBrO₂ diffusing in a periodic manner from perfect spirals that are sustained in the bottom layer. Once it is oxidized, however, the concentration of Br[−] cannot be completely recovered before the next trigger, i.e. HBrO₂ wave, comes. The surface layer is forced to remain in its reduced state for one more cycle of spiral rotation, and then it is ready to be oxidized again when another trigger arrives. The fact that no fragmentation occurs for concentric waves may be because the period of wave passage in the bulk solution generally exceeds the time needed for the recovery of Br[−] concentration in the surface layer. With a view to complementing this discussion, we have done preliminary calculations on our system using a modified version of the Oregonator model:¹⁶

$$\frac{\partial u}{\partial t} = \Delta u + \frac{1}{\epsilon} [u(1 - u) - fv(u - q)/(u + q) - aw^2]$$

$$\frac{\partial v}{\partial t} = \Delta v + u - v - aw^2$$

$$w = \frac{2u(1 + bv)}{c - v + [(c - v)^2 + 4au(1 + bv)]^{0.5}} \quad (3)$$

where Δ is a three-dimensional Laplacian operator ($\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$), u and v are variables denoting the HBrO₂ and catalyst concentration, respectively, and $f, q, \epsilon, a, b,$ and c are parameters. The stoichiometric factor f controls the excitability of the system. To simulate the oxygen effect, a gradient of the factor f is introduced along the solution depth (z direction) as was proposed by Zhabotinsky *et al.*¹⁵ In their work¹⁵ the

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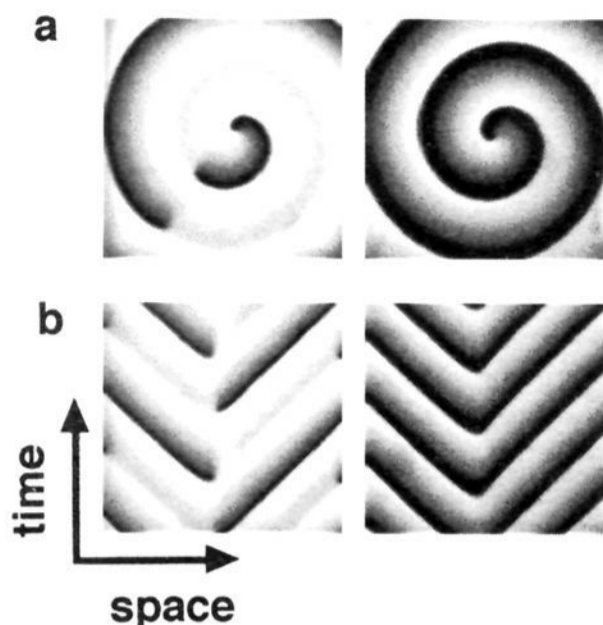


Figure 6. Gray-scale representations of the variable ν at the topmost (left-hand side) and at the bottommost (right-hand side) boundary of the system obtained from simulation: (a) spiral waves; (b) space–time plots extracted along a straight line passing through the core of the corresponding spirals in (a). The parameters for the simulation are $f = 4.0$ at the top and 2.5 at the bottom, $q = 0.0002$, $\epsilon = 0.019$, $a = 0.0056$, $b = 140$, and $c = 0.0175$. Note that the topmost wave exhibits fragmentation (a) and wavelength doubling (b).

excitability profile was approximated by an exponential function, but here f is simply assumed to vary linearly with z . The model equations were integrated by the explicit Euler method with no-flux conditions imposed on all boundaries. Figure 6 shows a typical result of our simulations performed on a $104 \times 104 \times 10$ grid. It is evident that a perfect spiral develops in the bottom part of the system, while at the top the essential features of the wavelength doubling are well reproduced. Thus the numerical calculations are in good qualitative agreement with the experimental data, indicating that the observed wavelength doubling can be explained in terms of a stationary excitability profile along the direction perpendicular to the BZ layer.

Pojman and Epstein¹² suggested that a density gradient of chemical species in the BZ reaction induces convection that travels along with each wave front. The wavelength doubling of a chemical wave should result in a rhythmic change in the density gradient and therefore in the convective flow in the

surface layer. The oscillatory surface flow observed by Miike et al.^{9,10} for ferroin-catalyzed BZ layers may be attributed to this effect. In this connection, it is necessary to comment on the role played by evaporative cooling and surface tension in the present pattern formation. We have carried out a separate set of experiments with the sample dish covered with a glass plate (air gap above the layer surface ~ 11 mm) and obtained the same wavelength-doubled spirals in the Mn-catalyzed system. This means that evaporative cooling does not contribute to the wavelength doubling. It is difficult to make measurements eliminating effects from surface tension and/or surface-tension-driven instabilities completely since a free interface between liquid and air is needed for monolayer formation. However, the surface tension of the BZ solution can be decreased by a desired amount ranging from 0 mN/m up to ~ 35 mN/m by controlling the surface pressure or surface density of the Ru-(bpy)₃²⁺ monolayer. We have observed the occurrence of wavelength-doubled spirals in the monolayer independently of its surface pressure. This implies that surface tension has no significant effect on the wavelength doubling.

In conclusion, photosensitive monolayers can be used to disclose new types of wave dynamics in the surface layer of the BZ reaction medium that might be otherwise difficult to obtain. The use of intense illumination, which is expected to contribute to not only inhibition but also induction of oscillatory reactions involving Ru(bpy)₃²⁺,¹⁷ may help to reveal even more complex, unexpected behavior at the liquid–monolayer interface. A quantitative analysis of the illumination effect on monolayer spiral waves, including multiarmed vortex, is currently underway.

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