Quantification of Turbulence in the Belousov−Zhabotinsky Reaction by Monitoring Wave Tips

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We analyze experimentally the tip's motion under conditions in which waves are disorderly distorted by "ripples". We thus reduce a complex spatiotemporal phenomenon to a purely temporal process, which we then quantify by the maximum Lyapunov exponent. In contrast to the periodic or quasiperiodic tip meanderings reported so far, we present evidence for chaotic tip motion in the case of ripples induced by oxygen in the ferroin- and the ruthenium-catalyzed reactions. For ripples induced by light in the ruthenium-catalyzed reaction, we find absence of chaos in the tip; this points to significant mechanistic differences between the action of light and that of oxygen. Our findings are corroborated by the determination of the power spectra. Chaotic meandering is relevant to spiral drift techniques owing to the essential role of the interaction of the spiral tip with external drift-inducing stimuli.

Introduction

Evidence for spatiotemporal chaos (turbulence) has been presented for the Belousov−Zhabotinsky (BZ) reaction in a gel with immobilized catalyst covered by a solution layer, the latter containing all reactants except the catalyst. These observations, as reported in refs 1 and 2, required low concentrations of the light-sensitive catalyst (the ruthenium bipyridyl complex $Ru(bpy)_3^{2+}$) and high light intensities $I \geq I_0 = 300$ mW/m^2. Above the threshold I_0, light-induced Br^- production becomes comparable to other Br^- production terms. In fact, considering our measurement that about 60% of the light is absorbed and assuming that two bromide ions are produced per photon,[3] I_0 corresponds to a flux $dBr^-/dt \approx 1.4 \times 10^{-6}$ M s^{-1}; this flux is comparable to the minimum of the Br^- production term $k_5h[Me_{ox}]$ obtained with the Oregonator,[4] which (using $h = 1$) is 2.6×10^{-6} M s^{-1}. Note that at $I \geq 2I_0$, the radiation is so strong that all waves are extinguished. Experiments reported later on[5] showed that turbulence not only occurs for $I \geq I_0$ in the ruthenium-catalyzed reaction, but that it can also occur in the dark, or with ferroin as catalyst, provided $[O_2]$ is sufficiently high.

Our observations showed that the reported disorder is related to the enhancement of fluctuation valleys, causing "ripples". In a model of this phenomenon,[6] we assumed that the enhancement is caused by Br^- produced in the refractory tail that diffusively surpasses the wave front via the upper solution layer. This is particularly significant in fluctuation valleys because the concave geometry implies converging vectors of diffusive flow of Br^-. Note that the experimental evidence for the necessity of the upper solution layer[6] makes the observed turbulence a three-dimensional phenomenon. Thus, any two-dimensional model for disorder in excitable media (as in refs 7, 8, and 9) is not appropriate to describe these observations. Note also that we had experimentally excluded convective motion in the upper layer as a cause for disorder, since we detected no motion of suspended particles;[6] for control, we doubled the layer thickness and did observe particle motion. A further indication that there is no flow is the observation of unperturbed spirals at low light intensities.[1,2]

In the present work, we describe the spatiotemporal disorder of ripples in a spiral wave by a reduction to a purely temporal phenomenon, namely the dynamics of the tip. Spiral waves are observed in a number of chemical and physical systems, their importance being either chemotechnical (CO oxidation on Pt surfaces[10]), or biochemical (intracellular Ca^{2+} waves[11] and cyclic adenosine monophosphate waves in *D. discoideum* cells[12]) or medical (heart muscle during arhythmias[13−15]). The BZ reaction,[16] which is formally analogous to these systems (see ref 17) has the advantage of easy implementation and observability.

The tip of the spiral wave is known either to rotate rigidly on a circle or to "meander" by looping around this circle.[18−20] A number of theoretical[21−24] and experimental works[25,26] have shown that the transition from rigid rotation to meandering occurs via a Hopf bifurcation leading to quasiperiodicity, i.e., to a motion that can be decomposed into periodic modes. Hitherto, no evidence has been found that this motion may become chaotic, as had been speculated in early works.[27,28] Moreover, simulations have shown that even in the case in which the well-stirred reagent is chaotic in time, there is a local supression of chaos around the spiral tip.[29]

The general interest on the motion of the spiral tip arises from the fact that this motion determines fundamental features of the whole system. One of them is tip−tip attraction leading to multiarmed spirals in aggregating *D. discoideum* cells.[12] Another one is defect turbulence driven by convective instabilities.[30] Still another one is spiral drift, which has received considerable attention, as it is related to the goal of eliminating spirals from the heart muscle using implantable devices.[15] Spiral drift in the BZ reaction can be accomplished by a number of external stimuli: an alternating current,[31] a direct current,[32−34] a gradient of excitability,[35] temporal modulation of excitability,[36] excitability edges,[37] geometrical constraints,[38] mechanical deformations,[39] interaction with other waves,[40−43] tip anchoring,[44] global feedback,[45] or feedback from single-point data.[46] In general, drifts are induced by the interaction of the external stimulus with the dynamics of the tip.

Materials and Methods

Reactions were started by pouring 3.1 mL solution (0.18 M NaBr, 0.33 M malonic acid, 0.39 M $NaBrO_3$, and 0.69 M H_2SO_4 in water) into a Petri dish on the same volume of gel (height

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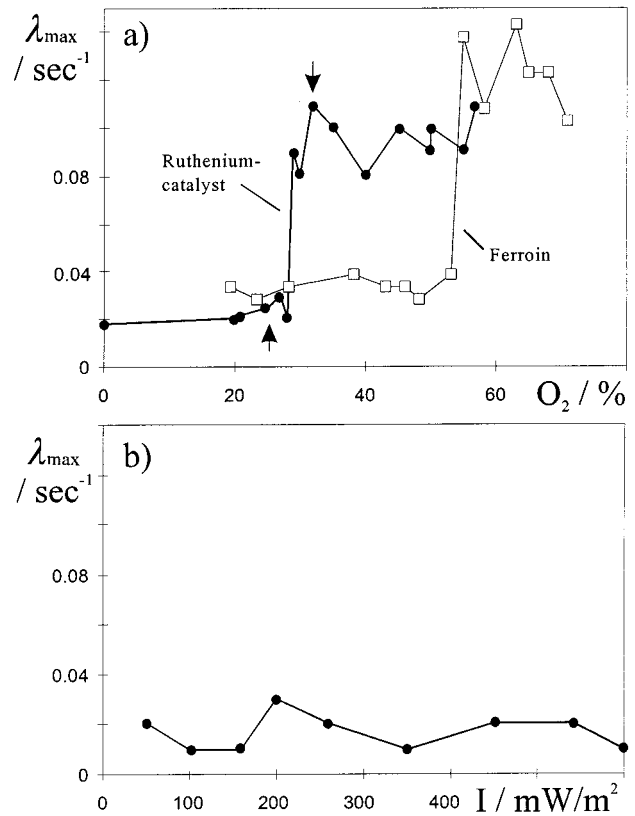

Figure 1. Maximum Lyapunov exponent λ_{max} of the spiral tip trajectory: (a) λ_{max} as function of $[O_2]$ in the dark, using the ruthenium catalyst (●) or ferroin (□); (b) λ_{max} as function of the light intensity, using the ruthenium catalyst (●) with $[O_2] = 21\%$.

0.9 mm) containing the immobilized catalyst. As the volumes of this solution and the gel were equal, the concentrations decreased to one-half of their initial value. The catalyst concentration was 0.71 mM. The temperature was held at 25 ± 1 °C. White light from a 250 W halogen lamp first passed an interference filter (450.6 nm for experiments with the Ru complex and 490 nm for the case of ferroin), then a diffusion screen, then the Petri dish, and then a video equipment. For the preparation of the gel, see ref 47. All experiments involving light and the Ru-catalyzed reagent were conducted in the same way as in ref 1. The light intensities I given in the present work were determined after light had passed the interference filter.

In order to study the influence of oxygen, we put the Petri dish into a box ($V = 1.45$ L, with a transparent bottom and top) through which we streamed an N_2-O_2 mixture coming from a gas mixing pump (Wösthoff DIGAMIX M 300/a; 0.75 L/min; 1% $[O_2]$ error; measurements were performed after a transient of 10 min). Measurements "in the dark" were done at $I = 2$ mW/m^2 which is the light intensity below which no measurements are possible.

The maximum Lyapunov exponent λ_{max} was calculated using the algorithm by Wolf et al.[48]—one time unit (T) corresponding to 10 s—with parameters SCALMIN = 0.02 mm, SCALMAX = 0.2 mm, ANGLMAX = 0.3 radians, TAU = 3T, and EVOLV = 4T. Results did not change for TAU ± T or EVOLV ± T. Because of reagent aging, evaluation was restricted to 35 min (210 data points). Successive attractor reconstructions were done sequentially using the following variables: $x(t)$, $y(t)$, $x(t + \tau)$, $y(t + \tau)$, $x(t + 2\tau)$, $y(t + 2\tau)$, ..., where x and y are the coordinates of the spiral tip. λ_{max} saturated for embedding dimensions between 4 and 8.

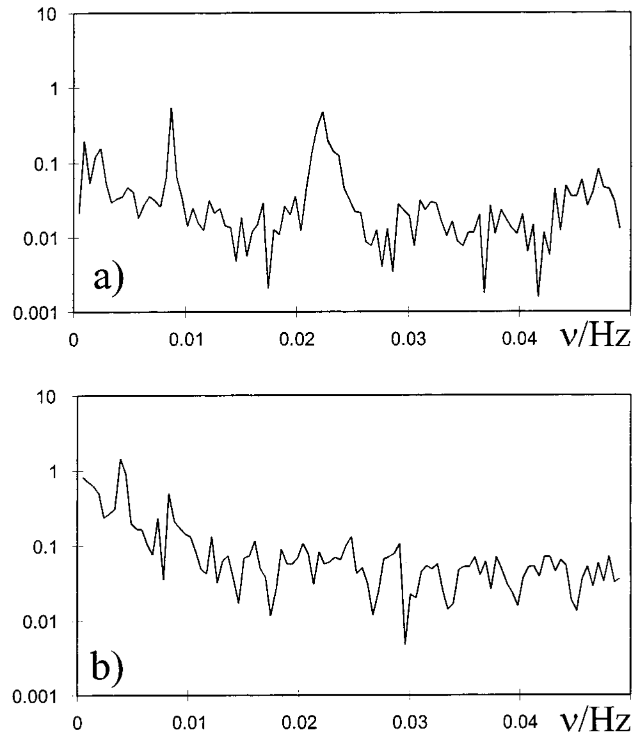

Figure 2. Power spectra of the x-coordinate of the spiral tip in the dark with the ruthenium-catalyzed reagent. Quasiperiodicity (a, $[O_2] = 25\%$) and chaos (b, $[O_2] = 33\%$) correspond to the two arrows pointing to the measured points (●) in Figure 1.

Results

We found the transition to ripples to occur at nearly the same O_2 as a sudden increase of λ_{max} from approximately zero (indicating quasiperiodicity) to positive values (indicating chaos), as shown in Figure 1a. In fact, the transition to ripples[5] occurs at $[O_2] = 30\%$ for the ruthenium catalyst and at $[O_2] = 60\%$ for ferroin. In contrast, the transition to ripples by the action of light for the Ru catalyst (occurring at $I = 300$ mW/m^2)[5] is not accompanied by a transition to chaos in the tip (see Figure 1b). The low λ_{max} values at low O_2 in Figure 1a, or for all I in Figure 1b, correspond to the quasiperiodic dynamics reported for stable spirals so far in the literature. Since quasiperiodicity actually implies $\lambda_{max} = 0$, we attribute the slightly positive values here to noise.

Particular examples illustrating different aspects of the tip dynamics are given in Figures 2−5. Figure 2 shows a drastic change of the power spectrum caused by a slight change of $[O_2]$ from quasiperiodicity ($[O_2] = 25\%$; two peaks) to chaos ($[O_2] = 33\%$; nearly continuous spectrum). The power spectra in Figure 3 show that such a change is not observed as the cause of a large increase of the light intensity at constant $[O_2]$ (from $I = 100$ mW/m^2 in Figure 3a to $I = 400$ mW/m^2 in Figure 3b). Figure 4a displays a smooth spiral with quasiperiodic tip dynamics (Figure 4b). For a better visualization, three consecutive trajectory segments of Figure 4b are shown in Figure 4c. Note that by virtue of the quasiperiodicity the fifth lobe is always a bit ahead (clockwise) of the first lobe in each segment. Figure 5 shows two snapshots of a chaotic spiral (a), the tip's trajectory (b), and four consecutive trajectory segments, illustrating the unpredictability of the chaotic dynamics (c).

Discussion

The drastic change from $\lambda_{max} \approx 0$ to $\lambda_{max} > 0$ in Figure 1a indicates that the oxygen-induced emergence of ripples is

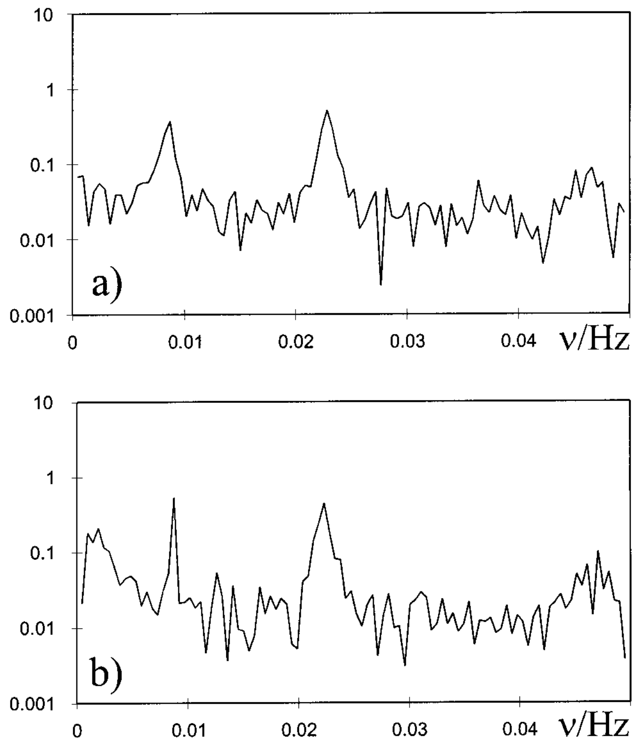

Figure 3. Power spectra of the *x*-coordinate of the spiral tip with $[O_2]$ = 21% using the ruthenium-catalyzed reagent: (a) I = 100 mW/m^2; (b) I = 400 mW/m^2.

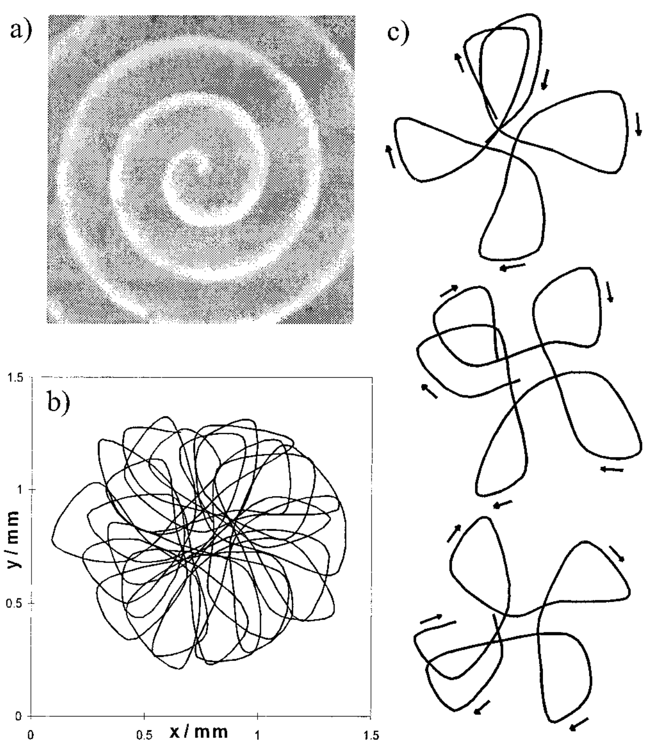

Figure 4. (a) Stable, smooth spiral (with ruthenium catalyst and $[O_2]$ = 25%; edge length 10 mm), the tip of which meanders quasiperiodically (b), as visualized by the trajectory segments in (c), which were taken consecutively every 10 s.

accompanied by a transition from quasiperiodic to chaotic motion of the tip. This is the case for both catalysts. In contrast, Figure 1b indicates that the dynamics of the tip is unaffected by the light-induced emergence of ripples. In addition to these qualitative results, λ_{max} provides a quantitative description of the system's dynamics, as it measures the sensitivity to initial

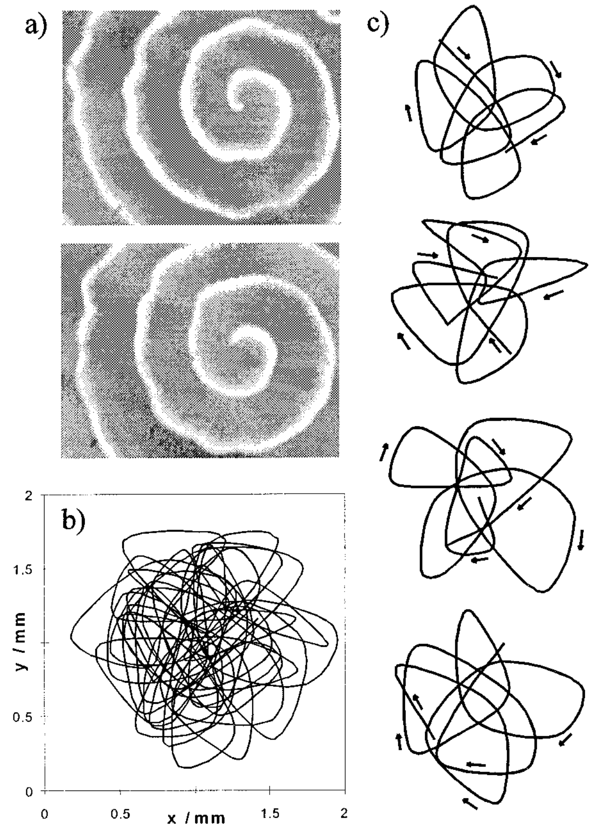

Figure 5. (a) Spiral with ripples (with ruthenium catalyst and $[O_2]$ = 55%; lower edge length 12 mm) at times 0 and 10 min, the tip of which meanders chaotically (b). (c) Consecutive trajectory segments taken every 10 s.

conditions, and thus the unpredictability. While $\lambda_{max} \approx 0$ indicates that the size of the perturbations is nearly conserved, the positive exponents λ_{max} in Figure 1a quantify the mean exponential growth of perturbations and thus the degree of chaos.

The power spectra corroborate the results obtained with λ_{max}. In fact, Figure 2 shows that the oxygen-induced transition to ripples is accompanied by a transition from a two-peak spectrum to a nearly continuous spectrum. Contrarily, light induced ripples do not affect the two-peak spectrum of the tip (Figure 3). As the logarithmic scale may be deceiving, we would like to stress that (in contrast to Figure 2b) the peaks in Figures 2a and 3a,b are more than 1 order of magnitude above the spectral background. Note also a small peak at the extreme right of these figures, corresponding to the second harmonic (twice the frequency) of the second peak. The interpretation of Figure 2b as a continuous spectrum may leave doubts since small peaks indicating quasiperiodicity with a large number of periods may be hidden within the spectral fluctuations. In the context of Figure 1, however, the spectra can be considered as supporting the evidence obtained from the determination of λ_{max}.

The drastic difference between parts a and b of Figure 1 points to a mechanistic difference between the action of oxygen and that of light. Thus, lumping both actions into one parameter, as in ref 4, would not be appropriate in an eventual modeling of the tip's dynamics. We shall now discuss known as well as open aspects involving chemical mechanisms.

For the action of light, the following reaction was proposed:[49]

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

where Ru(II)* is the photochemically excited catalyst. Later on, alternative possibilities were reported:[50]

$$\mathrm{Ru(II)^* + 3Ru(II) + HBrO_2 + 3H^+ \rightarrow 4Ru(III) + Br^- + 2H_2O}$$

and[51]

$$\mathrm{(1/}n\mathrm{)Ru(II)^* + H^+ + BrMA \rightarrow Br- + ...}$$

n being of the order of 1.5. A further, recently proposed, mechanism is accompanied by light-induced production of bromous acid (the autocatalytic species) from bromate:[3]

$$\mathrm{Ru(II)^* + BrMA \rightarrow Ru(III) + Br^- + P}$$

$$\mathrm{Ru(III) + BrMA \rightarrow Ru(II) + Br^- + P}$$

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

where P denotes organic products. The destabilization action of oxygen should be independent of light, since we found that oxygen induces ripples in the dark. However, a qualitative analogy to the action of light was given about 20 years ago by observations that oxygen enhances the production of $[Br^-]$.[52,53] Later on, Försterling et al.[54] found for the cerium-catalyzed reaction that the quotient $[Ce^{4+}]/[Br^-]$ is 2:1 in the absence and 1:1 in the presence of oxygen. This effect was roughly incorporated in a modified Oregonator model[55] by increasing two rate constants when oxygen is present. Besides this, there exists, to our knowledge, no preciser information about the chemical mechanism of the action of oxygen; nevertheless, the preceding citations allow us to retain the view that both oxygen and light destabilize the wave via Br^- production, as roughly modeled in ref 6. It remains open, however, why light does not destabilize the spiral tip.

An interesting future task is to examine to what extent ripples can be suppressed by anchoring the tip to a nonexcitable spot, which is known[44] to force the tip to a circular movement. Interesting too would be an investigation on how a spiral's drift, using any of the techniques listed above, is affected by chaotic meandering. Note that in the context of the formal analogy to heart muscle, chaotic modes are related to cardiac fibrillation (unpredictable contractions leading to rapid death), its control with implantable defibrillators being a fundamental problem of medical engineering today.

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