Change of the Shape of a Chemical Vortex Due To a Local Disturbance

Rubin R. Aliev,*,†,‡ Vasily A. Davydov,†,§ Takao Ohmori,† Masaru Nakaiwa,† and Tomohiko Yamaguchi*,†

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan, Institute of Theoretical and Experimental Biophysics, Puschino, Moscow region 142292, Russia, and Moscow State Institute of Radioengineering, Electronics and Automation, Vernadskogo 78, Moscow, Russia

Received: July 29, 1996; In Final Form: November 18, 1996[⊗]

We studied the dynamics of a chemical vortex whose core was disturbed by visible light. The observed sharp change of the shape of the vortex and the unfolding increase in the vortex wavelength proved to be tightly related to a transformation of trigger waves to phase waves. Analytical estimations and direct measurements show that the shape of the vortex is well-fitted by a logarithmic spiral. The results of experiments and of computer simulations are in a good agreement.

1. Introduction

After the discovery of the chemical vortex[1,2] it was found that such vortices can exhibit either stable or compound rotation ("meandering"),[3,4] drift in inhomogeneous media,[5] and drift due to external high-frequency stimulation[6] and in the case of parametric resonance.[7,8] The analysis of the mechanisms of the vortex dynamics shows that the phenomena mentioned above can be understood if one considers the dynamics of the tip of the vortex, i.e. a part of the vortex situated close to the core. The diameter of the core d_c is related to the wavelength so that λ/d_c is about π.[5] The ratio λ/d is nearly constant for systems of different nature.[9]

Many experimental and theoretical investigations showed that the vortex has a form of an Archimedian spiral[10,11] and the emitted waves have the wavelength close to the minimum possible in the medium (hereafter we term such waves "short waves" to distinguish from "long waves"). The dynamics of short waves differs significantly from the dynamics of long waves.[12,13] Particularly, the dynamics of long waves is described by the Burgers equation,[14] which is not valid for short waves. Recent studies of vortices in oscillatory media show that the Archimedian spiral is not the unique form of the vortex and along with a transition of short waves (trigger waves) to long waves (phase waves)[13] marked changes in the shape of the vortex occur.[15,16]

In this work we continue the study of the dynamics of a chemical vortex whose core was irradiated by visible light. In contrast to irradiation of the entire medium, which resulted in a parametric resonance and drift of the vortex without marked changes of its shape,[7,8] a local irradiation of the core induces drastic changes of the shape of vortex. Along with the changes in the shape of the vortex, we observed significant changes in the main parameters of the vortex, particularly in the wavelength of the vortex. We relate the observed effects to the transition of trigger waves to phase waves.

2. Experimental Setup and Numerical Procedure

We carried out the experiments using a typical composition of the BZ reaction:[16] $NaBrO_3$, 0.5 M; $CH_2(COOH)_2$, 0.25 M; H_2SO_4, 0.25 M; $Ru(bpy)_3Cl_2$, 2 mM. The solution was carefully stirred and poured into a 5.9 cm diameter Petri dish, which was then covered with a glass lid.

We used light from a 50 mW argon ion laser, wavelength 488 and 514.5 nm, to irradiate the medium. Light irradiation of the BZ reaction led to the production of bromide ions,[17−20] which partly suppressed wave conduction. By irradiating the core of the vortex we simply increased its diameter from 0.3 to 0.6 mm. The core of the vortex was the only part of the medium subjected to irradiation.

The dynamics was followed with a video recorder connected to an SGI Indy computer. Simple image processing was performed to measure spatio−temporal characteristics, such as frequency and wavenumber.[12]

To simulate the dynamics of vortices we used a two-variable model of the BZ reaction:

$$\frac{dx}{d\tau} = \frac{1}{\epsilon}\left[x(1-x) - \left(2q\alpha\frac{z}{1-z} + \beta\right)\frac{x-\mu}{x+\mu}\right] \quad (1)$$

$$\frac{dz}{d\tau} = x - \alpha\frac{z}{1-z}$$

It has been verified that this model adequately simulates spatio−temporal dynamics in the BZ reaction.[5,21,13] We used a set of parameters as described in ref 13. The simulations were carried out using the Euller's method of integration in rectangular coordinates.

To prevent meandering, i.e. a complicated trajectory of the vortex tip,[4] a vortex was simulated as rotating around a circular obstacle. The radius of the obstacle was assumed to be the radius of the vortex core, r_c. We carried out simulations using the two types of boundary conditions: (i) typically used for simulations of reaction−diffusion systems restriction $\partial u/\partial n = 0$, i.e. the Neumann's "no flow" condition and (ii) $\partial^2 u/(\partial n)^2 = 0$, i.e. the "constant flow" condition. The reasoning behind the use of these conditions is explained in the Results section. Identical conditions were imposed on the inner (core) and outer boundaries.

3. Results

3.1. Experimental Results. Under the chosen experimental conditions a chemical vortex is seen as an Archimedian spiral (Figure 1a,b). Irradiation of its core gives rise to an additional bromide ion production[17−20] and enlarges the core. Measure-

* To whom correspondence should be directed.
† National Institute of Materials and Chemical Research.
‡ Institute of Theoretical and Experimental Biophysics.
§ Moscow State Institute of Radioengineering, Electronics and Automation.
⊗ Abstract published in *Advance ACS Abstracts,* January 15, 1997.

S1089-5639(96)02282-7 CCC: $14.00

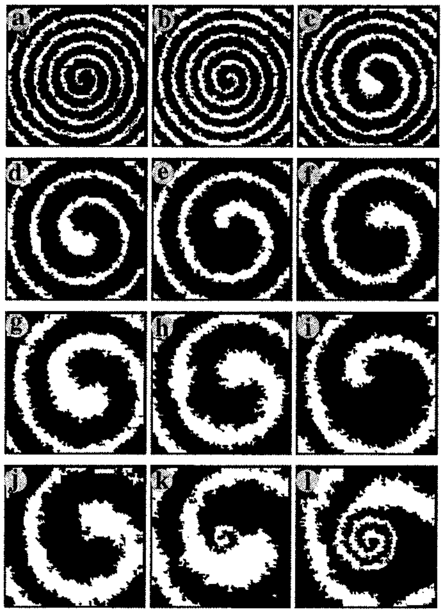

Figure 1. Change of the shape of the vortex induced by irradiation of the core: (a) Archimedian spiral, (b)−(j) irradiation turned on, unfolding increase of the wavelength is seen, (k), (l) irradiation turned off, the vortex again possesses the form of an Archimedian spiral with short wavelength. The size of each snapshot is 7.3 × 7.3 mm; the interval between snapshots is 1 min.

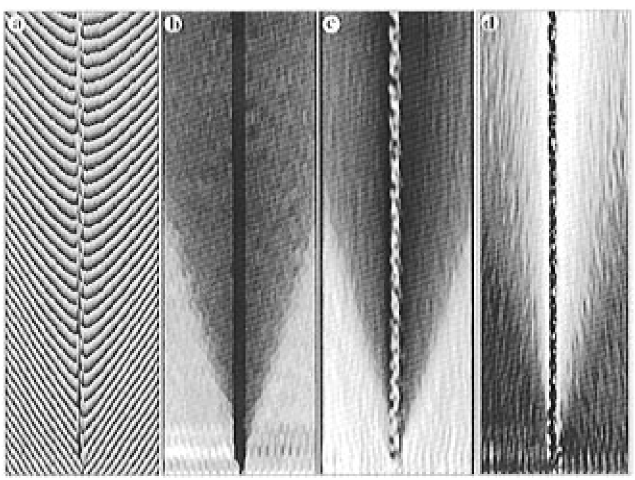

Figure 2. x-t charts of the main parameters of the vortex: (a) ferriin distribution, (b) frequency ω, (c) wave number k, (d) velocity v. For every chart space (x-axis, directed rightward) range is 1.7 cm; time (y-axis, directed upward) range is 330 s. Light shade corresponds to large value.

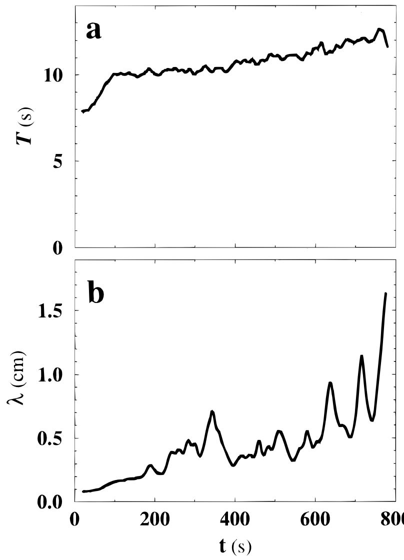

Figure 3. Time dependence of the period of rotation T (a) and wavelength λ (b). Note that T increased by less than 40%, while λ increased at least 8 times.

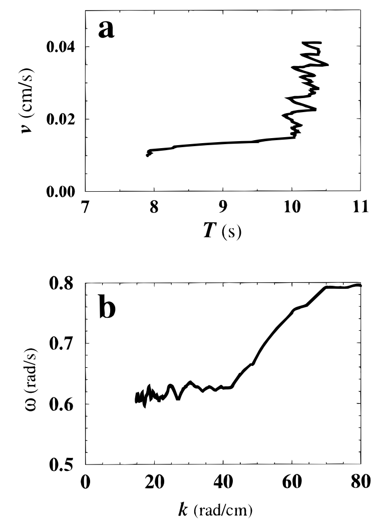

Figure 4. Experimentally measured dispersion relations (a) $v(T)$ and (b) $\omega(k)$. The branches of long waves ((a) $T > 10$, (b) $k < 45$) and short waves ((a) $T < 10$, (b) $k > 45$) are clearly distinguished.

ments made under similar conditions show that the core diameter increases from 0.3 to 0.6 mm.[16]

Following the change of the core size, the dynamics of the wave close to the core change as well.[16] In Figure 1c the thickening of the tip of the spiral is clearly seen. The thick part is seen as propagating along the vortex together with an unfolding increase of the vortex wavelength (Figure 1d−j). Switching off the irradiation returns the core size back to its initial value and the shape of the vortex to the Archimedian spiral (central part of Figure 1k,l).

To study the evolution of the main vortex parameters it is convenient to plot space−time charts. We traced the change of some of the main characteristics of the vortex along a line through the core (Figure 2). It is seen that frequency and wavenumber drop with time, while the velocity of propagation increases to infinity. Unlimited rise of the velocity is associated with a transition to phase waves. High velocity makes it impossible to have reliable measurements near the core (see Figure 2c,d).

To follow the evolution of the main characteristics of the vortex, it is instructive to trace the dynamics at a point. Figure 3 shows the time dependence of the period of rotation and wavelength measured at 1.7 mm from the center of the core. Note that there is a jump in the value of the period (from 8 to 10 s at $t = 50$ s). The further gradual changes in the period are due simply to reagent aging. Such a jump was not observed for wavelength λ (Figure 3b). The comparison of the period evolution and wavelength evolution shows that during the measured interval λ increases by a factor of at least 8, while T rises by only 40% (including reagent-aging effect). Such dynamics cannot be explained in terms of known theories.

The above data can be used to plot a dispersion curve, i.e. a dependence of velocity of propagating waves on the period in a wavetrain $v(T)$ or a dependence of frequency on the wavenumber $\omega(k)$ (Figure 4). These dependences are typical for oscillatory media. For the relation $v(T)$ two distinct parts are seen: slight dependence of v on T for $T < 10$ s and unfolding rise of v at $T > 10$ s. The first part corresponds to trigger waves,

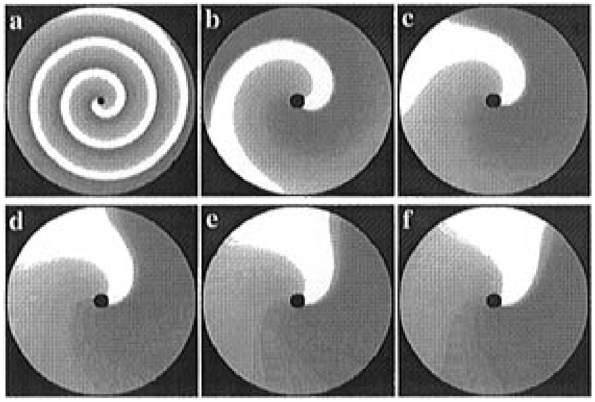

Figure 5. Computer simulations of the transition from an Archimedian spiral (a) to a phase rotor (f). Light shade corresponds to high concentration of ferriin. The black disk in the center is the core of the vortex. Snapshots are made with the interval of 50 bulk oscillations. The core size is enlarged twice just after the snapshot (a). Note that the differences between snapshots (d)−(f) are hardly seen, denoting that the transients are died out. The vortex was simulated in the medium 512 × 512 elements with Neumann's "no flow" boundary conditions.

the other corresponds to phase waves. The related parts in Figure 4b are $k > 45$ and $k < 45$ rad/cm (see ref[13] for more discussion of the correspondence between types of waves and the shape of dispersion relation).

The observed changes of the vortex shape (Figure 1) can be understood if one considers that upon increasing the core size we decrease the wavenumber $k = 1/r_c$ for waves near the tip. Thus we expect that by decreasing k below a critical[13] we have a change in the type of wave which results in a change of the shape of vortex.

3.2. Computer Simulations. We carried out computer simulations to check the hypothesis that by changing the size of the core it is possible to change the shape of the vortex.

In Figure 5a it is seen that the vortex has the form of an Archimedian spiral if the core is small. After the core enlarged (the effect of light irradiation), the shape of the vortex changes significantly (Figure 5b−f), which is seen as a thickening of the excited part (white parts in Figure 5 correspond to high concentrations of ferriin). The dynamics is very similar to those experimentally observed (compare Figure 1a−j).

For this simulation, "no flow" boundary conditions were imposed which are conventionally used for computer modeling of reaction−diffusion systems. However, better fit of the experimental situation can be achieved if constant flow conditions are imposed. This particularly assumes that there is no barrier for diffusion of chemical species near the core.

Imposing the constant flow boundary conditions, we observe similar wave patterns to occur (compare Figure 6b and Figure 5f). The difference is in the species distribution near the core, where the isophase lines are no longer perpendicular to the core boundary.

We made long-term simulations (more than 500 rotations) to study the established shape of the vortex as shown below.

3.3. Analytical Approach. In this section we estimate the shape of a stationary rotating phase rotor. To simplify the consideration we use the "kinematic" approach,[22,23] i.e. we consider motion of an isophase line as a result of interference of dispersion relation and curvature of the line.

A recent study[13] shows that the dynamics of small perturbations of the limit cycle can be described by the Burgers equation[14]

$$\frac{\partial\phi}{\partial t} = \omega_0 + A|\nabla\phi|^2 + D\Delta\phi \qquad (2)$$

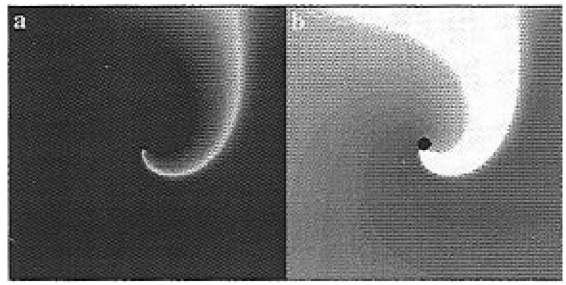

Figure 6. Phase rotor after 500 rotations: (a) bromous acid distribution and (b) ferriin distribution. Light shade corresponds to high concentration of the species. The vortex was simulated in the medium 512 × 512 elements with constant flow boundary conditions.

where ϕ is the phase of oscillations, $\nabla\phi$ and $\Delta\phi$ are the gradient and the Laplacian of the phase, ω_0 is the frequency of bulk oscillations, and A and D are constants.

To estimate the effects of dispersion $w(k)$ and of curvature K of a propagating pulse, it is convenient to consider a train of circular waves and to rewrite eq 2 in a polar coordinate system (r,ψ):

$$\frac{\partial\phi}{\partial t} = \omega_0 + A\left(\frac{\partial\phi}{\partial r}\right)^2 + DK\frac{\partial\phi}{\partial r} + D\frac{\partial^2\phi}{\partial^2 r} \qquad (3)$$

Here we assume $K = 1/r$ to be small. Introducing the frequency $\omega = \partial\phi/\partial t$ and the wavenumber $k = -\partial\phi/\partial r$, one can obtain the dispersion relation for curved pulses:

$$\omega = \omega_0 + Ak^2 - DKk \qquad (4)$$

To apply the above formula for a vortex, let us note that in the case of a stationary rotation all the isophase lines ϕ = constant have the identical shape. In this case wavenumber $k = (r\cos\theta)^{-1}$ (θ is the angle between the polar radius r and the tangent to a isophase line).

Substituting k into eq 4 we obtain an equation to describe the shape of the vortex:

$$\omega r\cos\theta = \omega_0 r\,\theta + \frac{A}{r\cos\theta} - DK \qquad (5)$$

At a distance far from the core, the curvature K must approach zero. This is satisfied provided $w = w_0$. Therefore at large r the curvature of an isophase line obeys the following equation

$$K = \frac{1}{pr\cos\theta} \qquad (6)$$

with the parameter $p = D/A$.

Now we can show that the eq 5 has a solution in the form of a logarithmic spiral: $r = r_0\exp(a\psi)$. Actually, for a logarithmic spiral the curvature K and the angle θ are

$$K = \frac{1}{r\sqrt{1+a^2}}, \quad \cos\theta = \frac{a}{\sqrt{1+a^2}}$$

It is seen that the relation between K and θ is satisfied in eq 6 if

$$p = \frac{1+a^2}{a} \qquad (7)$$

To apply the above formulas, we measured the shape of the front line for the vortex displayed in Figure 6. We introduced a polar system of coordinates (r,ψ) with the pole in the center of the core. The dependence of $\log(r)$ on ψ for the front of the

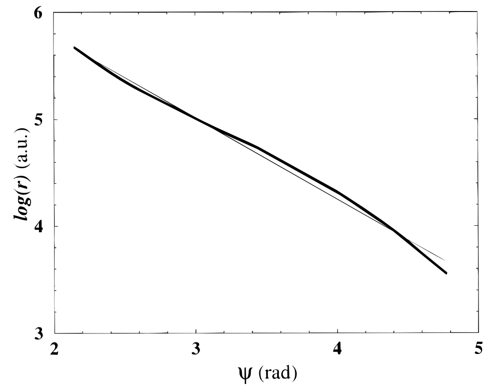

Figure 7. Front line of the phase rotor (thick line) in a polar system of coordinates. The front line is well-approximated by a straight line (thin line) with the slope $a = -0.76\ \text{rad}^{-1}$.

vortex is plotted in Figure 7. Note that this dependence is linear, and therefore the shape of the front line is actually a logarithmic spiral with the coefficient $|a| = 0.76$. Substituting this value into eq 7 we find that $p = 2.08$. It is worthwhile to emphasize that this value (the ratio of the two coefficients of the Burgers equation (2)) can be measured independently;[13] using the data from the cited paper we find $p \approx 2$ and is in a very good agreement with the above estimations.

4. Discussion

Conventionally, chemical vortices were believed to have the shape of an Archimedian spiral such that $\lambda/d_c \approx \pi$.[9] The results of recent works[15,16] show the possibility of an alternative shape. In this paper we have reported the dynamics of change of the shape of a vortex caused by a local disturbance of the vortex core. The direct measurements of changes of the wavelength λ (Figure 3) shows that the ratio λ/d_c is much larger than π. This fact is a strict evidence that the changes of the vortex shape are not just deformations of an Archimedian spiral.

An interesting question on the dynamics could be: Is there a critical size of the core across which the long-distance form of the vortex changes? Recent numerical simulations[15] show that such a critical size does exist. The asymptotic shape of the vortex is subjected to sharp changes (a bifurcation) when the core radius r_c exceeds the critical value.[15] To roughly estimate this critical value we should recall that the changes of the shape of a vortex are due to the change of the type of waves from trigger waves to phase waves near the point of inflation ($k = k_i$, $\omega = \omega_i$) of the dispersion curve $\omega(k)$.[13] Thus, it is natural to expect changes of the vortex dynamics to occur when the wavenumber $k = 1/r_c$ passes through a critical value near k_i. These speculations are well-confirmed by numerical experiments.[15]

The shape of the experimentally measured dispersion relations (Figure 4) is similar to that reported in ref 13. The dispersion relations consist of the two branches: one of trigger waves and the other of phase waves. As is mentioned above, the existence of the two clearly distinct branches and the possibility of change of the type of waves during the evolution[13] are responsible for the observed changes of the shape of vortex. Actually, a vortex with the shape of an Archimedian spiral is a source of short waves (trigger waves), while a source of long waves (phase waves), phase rotor, has a different shape.

The equation (5) used to estimate the shape of the vortex is valid for small wavenumbers only. Thus, it cannot be applied for the case of an Archimedian spiral with short wavelengths. The question if this equation admits alternative physically meaningful solutions should be a subject for a separate study.

It should be noted that the discussed phenomena were observed in a particular case of the Belousov−Zhabotinsky reaction. However the analysis of the dynamics is based on rather general descriptions. Therefore we believe that similar dynamics can be observed in oscillatory systems of a different nature.

References and Notes

(1) Zaikin, A. N.; Zhabotinsky, A. M. *Nature* **1970**, *225*, 535−537.
(2) Winfree, A. T. *Science* **1972**, *175*, 634−636.
(3) Zykov, V.; Morozova, O. L. *Biofizika* **1986**, *31*, 862−865.
(4) Winfree, A. T. *Science* **1973**, *181*, 937−939.
(5) Aliev, R. R.; Rovinsky, A. B. *J. Phys. Chem.* **1992**, *96*, 732−736.
(6) Krinsky, V. I.; Agladze, K. I. *Physica D* **1983**, *8*, 50.
(7) Agladze, K. I.; Davydov, V. A.; Mikhailov, A. S. *JETP Lett.* **1987**, *45*, 767.
(8) Braune, M.; Schrader, A.; Engel, H. *Chem. Phys. Lett.* **1994**, *222* (4), 358−362.
(9) Aliev, R. R. *Chaos, Solitons and Fractals* **1995**, *5* (3,4), 567−574.
(10) Mueller, S. C.; Plesser, T.; Hess, B. *Physica D* **1987**, *24*, 87−96.
(11) Keener, J. P. *SIAM J. Appl. Math.* **1992**, *52* (5), 1370.
(12) Aliev, R. R. *J. Phys. Chem.* **1994**, *98*, 3999−4002.
(13) Aliev, R. R.; Biktashev, V. N. *J. Phys. Chem.* **1994**, *98*, 9676−9681.
(14) Kuramoto, Y. *Chemical oscillations, waves, and turbulence*; Springer-Verlag: Berlin, 1984.
(15) Aliev, R. R. *Phys. Alive* **1996**, *4* (1), 27−31.
(16) Aliev, R. R.; Amemiya, T.; Yamaguchi, T. *Chem. Phys. Lett.* **1996**, *257* (5,6), 552−556.
(17) Kuhnert, L.; Agladze, K. I.; Krinsky, V. I. *Nature* **1989**, *337*, 244−247.
(18) Junguji, M.; Ishihara, M.; Nakazawa, T. *J. Phys. Chem.* **1992**, *96*, 4279−4281.
(19) Srivastava, P. K.; Mori, Y.; Hanazaki, I. *Chem. Phys. Lett.* **1992**, *190*, 279−284.
(20) Yamaguchi, T.; Shimamoto, Y.; Amemiya, T.; Yoshimoto, M.; Ohmori, T.; Nakaiwa, M.; Akiyjar, T.; Sato, M.; Matsumura-Inoue, T. *Chem. Phys. Lett.* **1996**, *259*, 219−224.
(21) Aliev, R. R.; Agladze, K. I. *Physica D* **1991**, *50*, 65−70.
(22) Davydov, V. A.; Zykov, V. S.; Mikhailov, A. S. *Sov. Phys. Usp.* **1991**, *34*, 665−684.
(23) Mikhailov, A. S.; Davydov, V. A.; Zykov, V. S. *Physica D* **1994**, *70*, 1−39.