Light-sensitive Belousov-Zhabotinsky reaction - a suitable tool for studies of nonlinear wave dynamics in active media

M. Braune and H. Engel
AG "Phys.-chem. Dynamik", WIP, Rudower Chaussee 5, Geb. 2.14
Berlin-Adlershof, D-1199, Germany.
e-mail: engel@pcdds.wtza-berlin.de

Abstract

A modification of the well-known Belousov-Zhabotinsky reaction, which uses the light-sensitive catalyst rutheniumbipyridil immobilized in a silicahydrogel matrix, is well suited to study wave dynamics in active media, especially under inhomogeneous or time dependent conditions of excitability. For illustration two examples are considered: the drift of spiral waves in media with spatial gradient of excitability and the compound rotation of spiral waves.

Introduction

Autowaves of chemical, physical or biological activity are striking examples of spatio-temporal selforganization in distributed active media driven far from thermodynamic equilibrium. They show characteristic properties by which they distinguish from other classes of nonlinear waves as, for example, solitons. Colliding autowaves annihilate each other due to the existence of a refractory tail behind the wave front. For the same reason, reflection on rigid boundaries is not possible (even not in a modified manner as Mach reflection in the case of solitons). Autowaves propagate in systems of quite different nature (Swinney and Krinsky, 1991). Examples include electrophysiological impulses in the cell membrane of nerve fibers and heart muscle (Winfree, 1987), (Davidenko *et al.* 1991), aggregation of slime mould cells (Gerisch, 1971) to waves in chemical systems (Field and Burger, 1985). Among chemical systems, catalytic reactions on platinum single crystals (Jakubith *et al.*, 1990) and the Belousov-Zhabotinsky reaction (Field and Burger, 1985), (Keener and Tyson, 1986) have been most intensively studied.

A common feature of autowaves propagating in all systems mentioned above is that their existence is related to the coupling between nonlinear local kinetics involving "self accelerating" steps (autocatalysis, positive feedback) and short-range transport processes as diffusion or heat conduction. Any active medium may be represented as ensemble of bistable, excitable or oscillatory elements with nearest neighbour coupling. Mathematically, autowaves are wave solutions of nonlinear evolution equations of reaction-diffusion type

$$x_t = F(x,u) + D\,\Delta x\,, \qquad (1)$$

where x denotes the vector of n state variables (concentrations, temperature etc.), F the vector of nonlinear functions describing the local dynamics and D the matrix of the diffusion coefficients. The suffix t indicates the partial derivative with respect to time and Δ is the Laplace-operator in d dimensions. To the external parameters , $\mathbf{u} = (u_1,..,u_k)$, belong kinetic coefficients, input and output flows, etc.

If we consider one-component systems (one state variable, n=1) the only possible type of wave solutions are traveling fronts. Front propagation has been most intensively studied in bistable systems (Mikhailov, 1990).

Two-component reaction-diffusion systems show a much reacher phenomenology of autowaves. In these systems the propagation of solitary pulses and of pulse trains becomes possible. The solitary pulse is characterized by a steep wave front followed by a refractory tail which corresponds to a state of the local dynamics which is not excitable. Refractoriness of the medium has the important consequence of dispersion of waves. If solitary pulses are triggered periodically or if a pulse train is propagating through the medium due to oscillatory local dynamics then the wave velocity becomes a function of the period.

A second important property of wave propagation is of geometrical nature and should be taken into account if spatial dimensions equal to two or higher are considered. Due to diffusive coupling between the active elements the wave velocity will depend on front curvature. In summarizing, dispersion and curvature govern the dynamics of autowaves in two-component active media (Mikhailov, 1990).
General, or "generic" (in the sense of being independent of the particular medium

considered), aspects of wave dynamics as, for example, compound rotation of spiral waves, drift of spiral waves in media with spatial gradients of excitability or with periodically modulated excitability should be studied in systems which among all allow to realize certain experimental demands in optimal manner. In this respect, one of the candidates for detailed experimental studies of wave dynamics is a light-sensitive modification of the BZ reaction because it allows for an elegant realization of desired space- and time dependent distributions of excitability in the medium. This possibility is important with respect to the increasing interest in studies of wave dynamics in heterogeneous and anisotrope media common to biology and chemical engineering, for example.

Light-sensitive BZ media

The BZ reaction is the oxidation of malonic acid (MA) or bromomalonic acid (BrMA) by bromate ions in acidic solution. The reaction is catalyzed by transition metal ions such as iron, ruthenium or cerium. A detailed mechanism of the BZ reaction, proposed by Field, Körös and Noyes in 1972 (FKN mechanism), involves 11 principle reactions among 12 chemical species (Field *et al.* 1972). Lateron, Field and Noyes reduced the FKN mechanism to five steps among the following three reaction species: bromous acid, $HBrO_2$ (the autocatalytic, or activator, or propagator variable), bromide ions, Br^- (the inhibitor variable), and the oxidized form of the metal ion catalyst, Me(ox) (the recovery variable) (Field and Noyes, 1974). This simplified model, the well-known Oregonator, may be further reduced to a two-variable version under the assumption, that Br^- remains always in equilibrium with the local instantaneous concentration of $HBrO_2$ (fast process). The final equations of the two-dimensional Oregonator are

$$\varepsilon x_t = x(1-x) - 2hz\frac{x-q}{x+q} + D_x \Delta x \quad , \tag{2}$$

$$z_t = x-z \; . \tag{3}$$

Here x and z denote the local concentrations of $HBrO_2$ and Me(ox), respectively, scaled by the rate constants for the five reaction steps the Oregonator takes into account and by recipe parameters to dimensionless quantities (Keener and Tyson, 1986). The parameters ε and q are determined by rate constants and chemical concentrations according to

$$\varepsilon = \frac{k_5\,[MA+BrMA]}{k_3[H^+][BrO_3^-]} \quad , \quad q = 2\,\frac{k_1 k_4}{k_2 k_3} \; . \tag{4}$$

ε represents the ratio of time scales of the fast (propagator) and the slow (recovery) variable and h is the stoichiometric coefficient in the reaction step of the Oregonator scheme which describes the Br^- release by oxidation of malonic and bromomalonic acid

$$[MA+BrMA] + Me(ox) \rightarrow h\,Br^- \tag{5}$$

and determines the excitation threshold. D denotes the diffusion coefficient of $HBrO_2$;

diffusion of the catalyst is not taken into account because in most experiments on chemical wave dynamics the catalyst is immobilized by fixing it in a gel matrix to avoid perturbations of hydrodynamical origin.

For the light-sensitive variant of the BZ reaction with Ru(bpy) as catalyst the Oregonator may be regarded as a first approximation to describe the dynamics on a qualitative level. The reason for this is that the chemical changes in the active medium during illumination are not known in detail yet. In the usual scheme of the reaction the reduced Ru(bpy) complex promotes the autocatalytic production of the activator species bromous acid. Under illumination Ru(bpy) becomes photochemically excited. The assumption is that the excited reduced complex catalyzes the production of the inhibitor bromide (Kuhnert, 1986). From this simplified view of the chemical mechanism visible light influences the ruthenium catalyzed BZ reaction Krug *et al.* (1990) proposed a simple modification of the Oregonator model. In order to take account of photochemically produced Br^-, an additional flow term was included into the equation for the bromide balance. In the two-variable version of the Oregonator this leads to substitution of the factor 2hz in equ. (2) by the term (φ+2hz), φ being the bromide flow produced photochemically.

Experimental method

Chemical wave dynamics in BZ media may be analyzed with sufficiently high spatial and temporal resolution by video- and computer-based 2D-spectrophotometry. The experimental apparatus shown schematically in Fig. 1 is quite similar to that proposed by Müller *et al.* in 1987 .

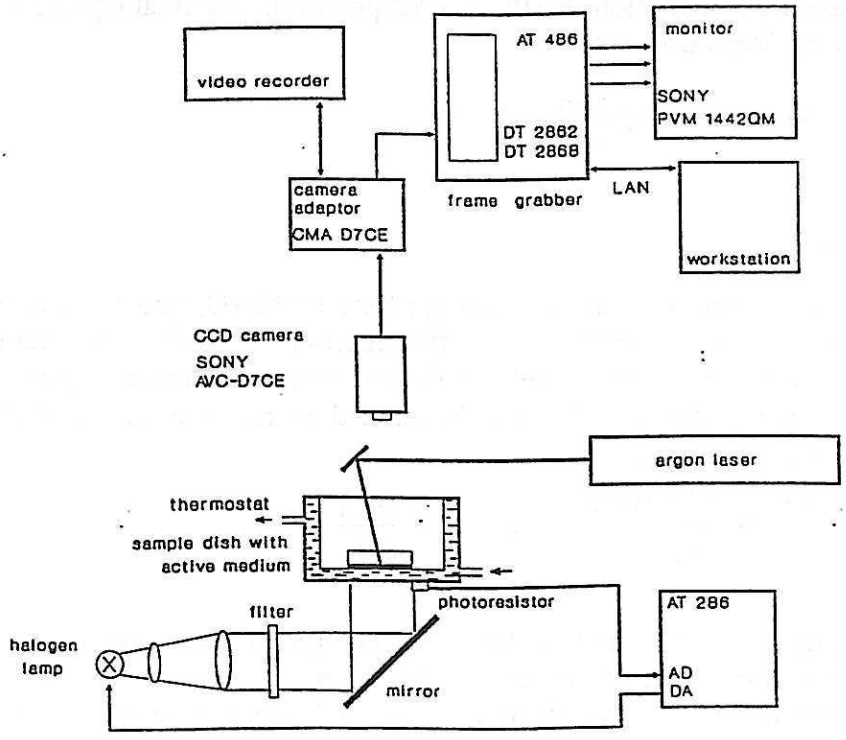

Fig.1 Experimental apparatus

Wave propagation is detected in transmission of blue light by a CCD camera (Sony AVC D7CE, image raster resolution 512x512 pixels) and stored on a time lapsed video recorder. The active medium is illuminated from below with light emitted from a halogen lamp. A special device allows variation of light intensity in accordance with a time dependent signal at the interface of the PC control unit. Passing through a cut-off filter which blocks transmission at wave lengths larger than 490 nm (to enhance the imaging contrast) the light affects the active medium with some effective intensity, P, which is determined by the photoresistor placed below the thermostate. It was tested carefully that after appropriate optical adjustment the light source provides a spatial homogeneous illumination of the active layer. The spatial homogeneity of the light beam (diameter about 10 cm) appeared to be better than 2%.

To affect the active medium locally an argon laser (488 mm line, maximal intensity 800 mW) is used. Usually, in the experiments the beam power is reduced with filters to approximately 100 mW. The diameter of the beam is variable to generate a laser spot with diameter between 0.1 and 2.0 mm. By local stimulation with the laser spiral waves may be initiated, controlled and annihilated, for example.

To image a small square section of the active layer a photolens system with close-up attachments (macro objectiv, focal length 50 mm) is used. The imaged area is between 0,5 x 0,5 and 5 x 5 cm^2 corresponding to a spatial resolution between 0.01 and 0.1 mm. Single frames of the movies stored on the time lapsed video recorder may be digitalized by an image aquisiion card (DT-2862) and analyzed on a PC using commercial software for image processing. The trajectory traced by the tip of a spiral wave is determined from the video film recorded during the experiment. At constant time intervals (e.g. 5 seconds) the playback of the movie was stopped and the chosen single frame was digitized. Tip position was localized visually moving the cursor to the point of maximal curvature of the front at the end of the spiral. The corresponding coordinates were stored in the computer.

To avoid hydrodynamical perturbations the catalyst is fixed in a thin layer of silicahydrogel (thickness about 0.5 mm). The reaction solution (composition see figure captions) is poured onto the gel layer. After the reactive species have diffused into the gel a convectionfree light-sensitive active layer covered by a feeding solution is obtained. The petri dish with the active medium is thermostated to keep fixed the temperature (with accuracy of 0.5 °C). It was found that aging processes affect the BZ medium with rutheniumbipyridil as catalyst less than the ferroin catalyzed BZ reaction. During a typical cycle of measurements with an overall duration of about 40 minutes decisive parameters of spiral wave dynamics as rotation period, wave length and wave velocity changed less than 10 %.

Let us summarize some aspects of external control and manipulation of chemical wave dynamics applying visible light to the ruthenium catalyzed BZ medium. (For a detailed discussion in the context of pattern recognition and image processing we adress the reader to the original papers of Kuhnert (1986) and Kuhnert *et al.* (1989)). Concerning wave dynamics, first of all we emphasize, that in principle using appropriate masks any desired space and time dependent distribution of excitability may be realized in the light-sensitive active medium. This opens new possibilities for the investigation of wave dynamics in heterogeneous and anisotropic active media as well as of the effect of time dependent external modulation on wave propagation. In this connection, we mention the paper by Agladze *et al.* (1987) about periodic

modulation of spiral waves which was the first attempt to exploite the light-sensitive BZ-medium to study a "generic" aspect of wave dynamics: the resonance of spiral waves.

Besides global illumination to create a certain distribution of excitability which may vary in time, local stimulation with a laser beam provides additional methodological advantages. On the one hand due to temperature increase in the region of the laser spot waves may be accelerated in the illuminated area. On the other hand, with properly adjusted intensity the inhibitory effect of visible light on the reaction may be used to stop wave propagation in the illuminated area. In this way the laser spot may be used to produce breaks in wave fronts or to prepare isolated wave segments of definite size by optical shearing. Furthermore, switching off the laser, the area illuminated previously by the laser spot after some refractory period becomes excitable again. At the point of front rupture a pair of counterrotating spiral waves will appear (compare Fig.2).

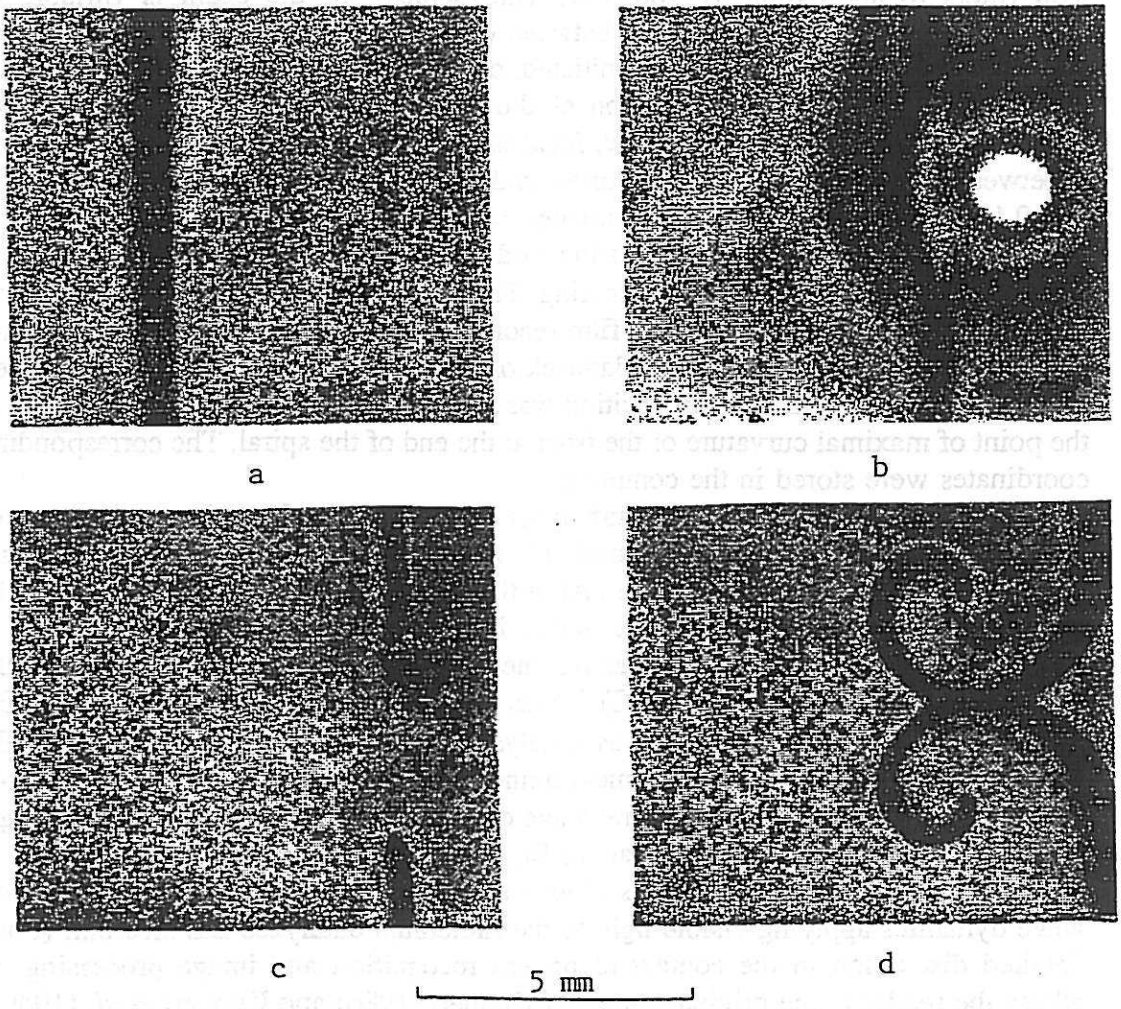

Fig.2 Optical initiation of spiral waves by cutting a wave front with a laser beam. For the duration of 10 s the laser was switched on (c) with a beam power of 200 mW.

Steinbock and Müller (1992) demonstrated the generation of pinned spiral waves using optically induced artificial cores stabilizing the motion of the spirals. A related effect is the elimination of unwanted wave sources spontaneously arisig during an experiment simply by illuminating the area covering the source.

Examples: Drift and compound rotation of spiral waves

Figure 3 shows an active gel layer with two counterrotating spiral waves. The layer was illuminated homogeneously with constant intensity P= 0,1 mW/cm². About 30 min after initiation of the spirals according to the method described in the previous chapter (Fig. 2), the active layer was partially obscured blocking the light with an opaque mask. As illustrated in Fig. 3d the mask was located in order to devide the core of the right hand spiral by the illumination edge into two parts of equal size. Obviously, this imposes a strong light gradient on the core region of the right hand spiral. The photographs on Fig. 3a-c demonstrate that under the influence of the spatial light gradient the right hand spiral exhibits a drift motion. At the same time the core center of the left hand spiral, which was not exposed to the gradient of excitability created by the light border, remains fixed.

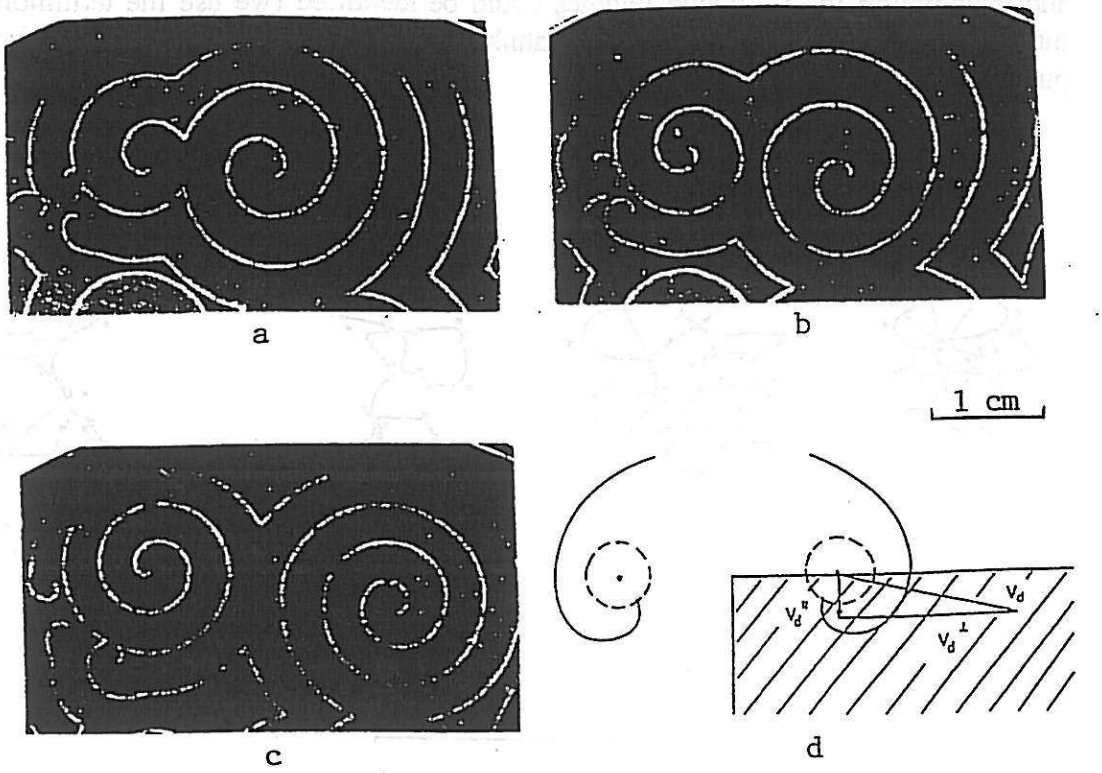

Fig.3 Two spiral waves in the light-sensitive BZ medium, the core of the right hand spiral is affected by a sharp light gradient as explained in the text (hatching corresponds to the obscured area). This spiral exhibits a drift whereas the unaffected spiral remains fixed. Time interval between photographs: a) an b) - 22:02 min, b) and c) - 32:18 min. Recipe parameters: Malonic acid - 0.15 M, $NaBrO_3$ - 0.15 M, H_2SO_4 - 0.18 M.

In this experiment, the component of the drift velocity transversal to the gradient appeared to be approximately four times larger than the longitudinal component. The direction of the perpendicular drift depends on whether the spiral is rotating clockwise or counterclockwise. The longitudinal component was directed into the shaded region on Fig. 3d, i. e., into the region characterized by higher excitability and lower period of rotation. The absolute value of the drift velocity was about 1 cm per hour (at recipe parameters and temperature indicated in the caption of Fig. 3). This value should be compared to a rotation period of about 150 s, a wave velocity of about 1 mm/min and a wavelength of about 3 mm.

Thus, in summarizing we found that in media with spatial gradient of excitability spirals drift into regions of higher rotation frequency whereby the drift is directed nearly perpendicular to the gradient. Similar results were reported by Skinner and Swinney (1991) for the ferroin catalyzed reaction. In the system under consideration the same effect was observed also using a grey wedge to generate the light gradient (Braune and Engel, 1992).

The second example to demonstrate the ability of the light-sensitive BZ medium for studies of autowave dynamics deals with the compound rotation of spiral waves (Skinner and Swinney, 1991; Jahnke *et al.* 1989; Plesser *et al.* 1990; Nagy-Ungvarai *et al.* 1993). A variety of spiral tip behavior has been observed while changing the intensity of applied illumination (Braune and Engel, 1993). At fixed recipe parameters and temperature the following regimes could be identified (we use the terminology introduced by Winfree (1991) and Jahnke and Winfree (1991) for descriptive purposes):

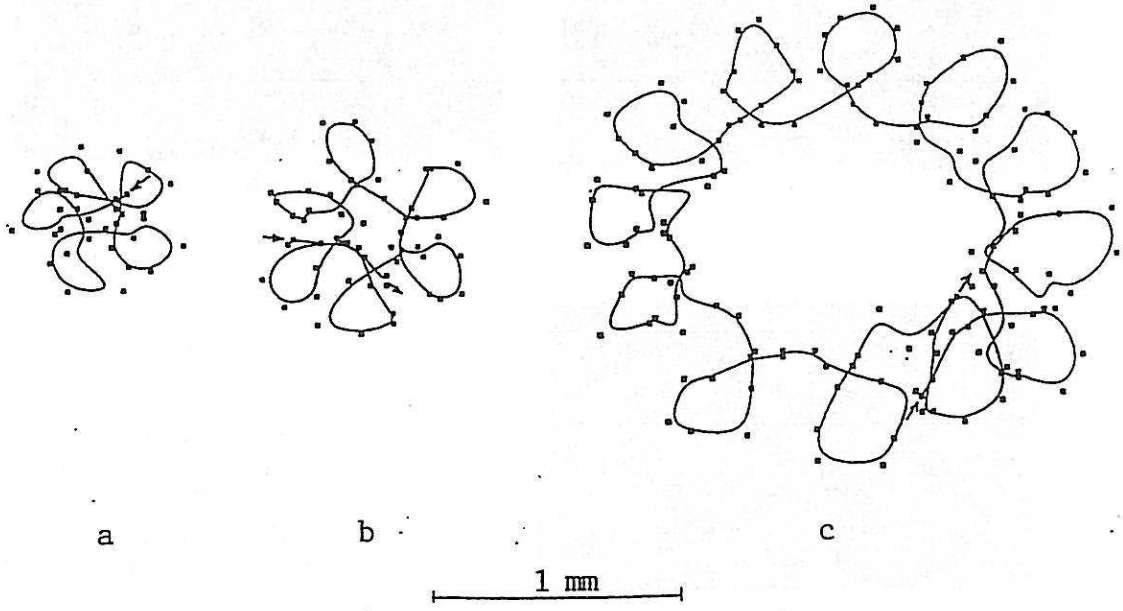

Fig.4 Spiral tip trajectories obtained for compound rotation as intensity of incident light is increased. Initial concentrations: Malonic acid - 0.33 M, KBr - 0.08 M, $NaBrO_3$ - 0.39 M and H_2SO_4 - 0.77 M; temperature T=25°C. Light intensity: (a) 0.04 mW/cm², (b) 0.12 mW/cm² and (c) 0.16 mW/cm². The arrow denotes the direction of tip motion, spiral rotation is clockwise and meander rotation is anticlockwise. Time interval between successive determination of tip position is 2s.

Rigid rotation: While it was relatively simple to observe rigid rotaion of spiral waves near the orbiting branch of the meander boundary (relative large core diameter), it was difficult to realize this regime near the pivoting branch. The reason is that the light intensity was too small in order to provide sufficiently sharp imaging contrast. Thus, at smallest possible intensity spiral tip motion was already compound and not rigid rotation.

Meander regime: We observed quasiperiodic compound rotation of spiral waves characterized by spiral tip pathes which resemble epicycloids. A typical sequence of pattern obtained in our experiments with increasing light intensity, P, is presented on Fig. 4. The number of lobes per meander pattern and the size of the area covered by the pattern increase with increasing P. If we compare this result with numerical simulation data (Jahnke and Winfree, 1991) it comes out that P and the h parameter of the Oregonator model should be closely connected. Unfortunately, neither the chemical changes during illumination nor their connection to the parameters of the model have yet been characterized.

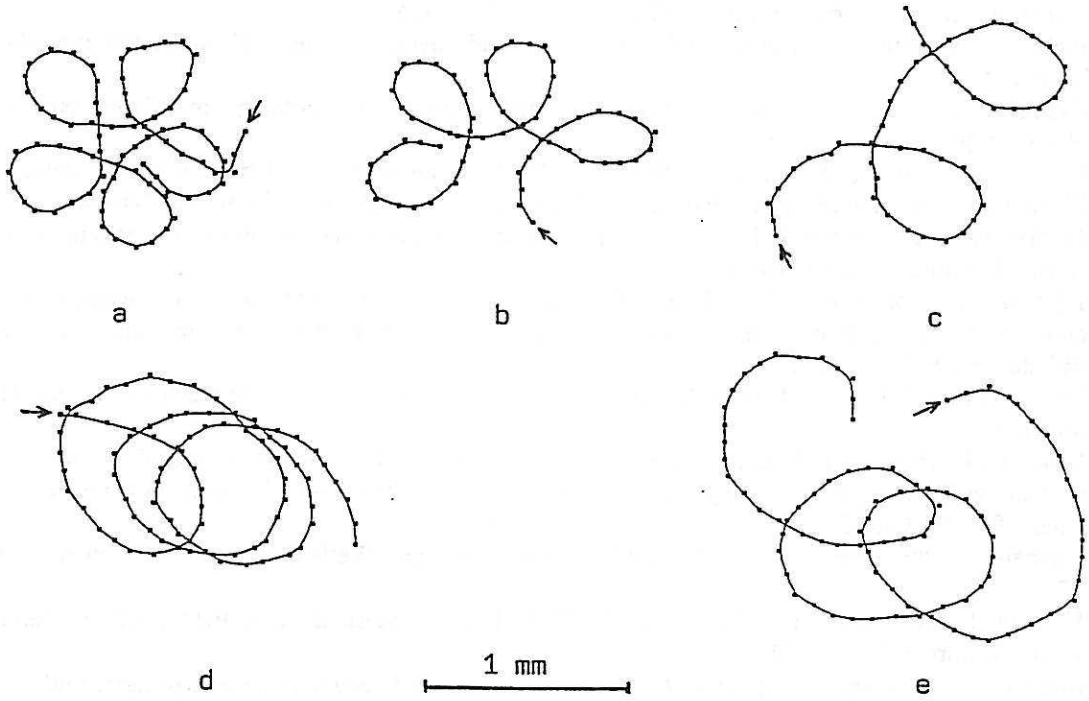

Fig.5 Transition from 'petal tip outside' to 'petal tip inside meandering'. Recipe parameters: malonic acid - 0.33 M, KBr - 0.18 M, $NaBrO_3$ - 0.3 M, H_2SO_4 - 0.5 M; T = 25°C. Time interval between successive determination of tip position 5s. Light intensity: (a) 0.12 mW/cm², (b) 0.20 mW/cm², (c) 0.28 mW/cm², (d) 0.30 mW/cm² and (e) 0.32 mW/cm².

We found (see Fig. 5) that pattern with lobes directed outwards ('petal tip outside meandering') at sufficiently high values of light intensity may transform into pattern where the lobes are directed inwards ('petal tip inside meandering'). From numerical experiments it was predicted that this transition occurs via an intermediate state characterized by the movement of the spiral's core center with constant velocity along a straight line ('straight loopy line meandering'). Fig. 5d shows the regime of straight loopy line meandering. Beyond this regime, i. e., in the parameter domain of petal tip inside meandering, meander rotation and spiral rotation have the same direction and are not opposite as in the case of spiral tip outside meandering.

Acknowledgement: This work was supported in part by a grant to H. E. of the VCI and by grant from the Deutsche Forschungsgemeinschaft.

Agladze, K.I., Davydov, V.A. and Mikhailov, A.S. 1987. Observation of a spiral wave resonance in an excitable distributed medium. JETP Lett. **45**, 767-770.

Braune, M. and Engel, H. 1992. Spiral drift in a light-sensitive active medium with spatial gradient of excitability. In: Spatio-Temporal Organization in Nonequilibrium Systems. Müller, S.C. and Plesser, Th. (eds.). projekt-verlag, Dortmund, 34-36.

Braune, M. and Engel, H. 1993. Compound rotation of spiral waves in a light-sensitive Belousov-Zhabotinsky medium. Chem. Phys. Lett. **204**, 257-264.

Davidenko, J.M., Kent, P. and Jalife, J. 1991. Spiral waves in normal isolated ventricular muscle. Physica **49D**, 182-197.

Field, R.J., Körös, E. and Noyes, R.M. 1972. Oscillations in chemical systems, part 2. Thorough analysis of temporal oscillations in the Ce-BrO_3^--malonic acid system. J. Am. Chem. Soc. **94**, 8649-8664.

Field, R.J. and Noyes, R.M. 1974. Oscillations in chemical systems, part 4. Limit cycle behavior in a model of a real chemical reaction. J. Chem. Phys. **60**,1877-1884.

Field, R.J. and Burger, M., (eds.). 1985. Oscillations and traveling waves in chemical systems. Wiley, New York.

Gerisch, G. 1971. Periodische Signale steuern die Musterbildung in Zellenverbänden. Naturwissenschaften **58**, 430.

Jahnke, W., Skaggs, W.E. and Winfree, A.T. 1989. Complex vortex dynamics in the Belousov-Zhabotinsky reaction and in the two-variable Oregonator model. J. Phys. Chem. **93**, 740-749.

Jahnke, W. and Winfree, A.T. 1991. A survey of spiral wave behaviors in the Oregonator model, Intern. J. Bifurc. Chaos **1**, 455-466.

Jakubith, S., Rotermund, H.H., Engel, W., von Oertzen A. and Ertl, G. 1990. Spatio-temporal concentration patterns in a surface reaction: Propagating and standing waves, rotating spirals, and turbulence. Phys. Rev. Lett. **65**, 3013.

Keener, J.P. and Tyson, J.J. 1986. Spiral waves in the Belousov-Zhabotinsky reaction, Physica **21D**, 307-324.

Krug, H.-J., Pohlmann, L. and Kuhnert, L. 1990. Analysis of the modified complete Oregonator accounting for oxygen sensitivity and photosensitivity of Belousov-Zhabotinsky systems. J. Phys. Chem. **94**, 4862-4866.

Kuhnert, L. 1986. Photochemische Manipulation von chemischen Wellen. Naturwissenschaften, **73**, 96-97.

Kuhnert, L., Agladze, K.I. and Krinsky, V.I. 1989. Image processing using light-sensitive chemical waves. Nature **337**, 244-247.

Mikhailov, A.S. 1990. Foundations of Synergetics.I. Distributed active systems. Springer, Berlin.

Müller, S.C., Plesser, Th. and Hess, B. 1987. Two-dimensional spectrophotometry of spiral wave propagation in the Belousov-Zhabotinsky reaction.Physica **24D**, 71-86.

Nagy-Ungvarai, Zs., Ungvarai, J., Müller, S.C. 1993. Complexity in spiral wave dynamics. CHAOS **3**, N° 1.

Plesser, Th., Müller, S.C. and Hess, B. 1990. Spiral wave dynamics as a function of proton concentration in the ferroin-catalyzed Belousov-Zhabotinsky reaction. J. Phys. Chem. **94**, 7501-7507.

Skinner, G.S. and Swinney, H.L. 1991. Periodic to quasiperiodic transition of chemical spiral rotation. Physica **48D**, 1-16.

Steinbock, O. and Müller, S.C. (1992). Chemical spiral rotation is controlled by light-induced artificial cores. Physica **188A**, 61-67.

Swinney, H.L. and Krinsky, V.I., (eds.). 1991. Waves and patterns in chemical and biological media. North-Holland, Amsterdam.

Winfree, A.T. 1987. When Time Breaks Down. Princeton Univ. Press, Princeton.

Winfree, A.T. 1991. Varieties of spiral wave behavior: An experimentalist's approach to the theory of excitable media. CHAOS **1**, 303-334.