Distinctive Sites in Chemical Waves: The Spiral Core and the Collision Area of Two Annuli

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Dynamical and structural details of traveling chemical waves in an excitable solution layer of the Belousov–Zhabotinskii reaction are sensitively detected by measurements with a two-dimensional spectrophotometer and application of perspective display techniques for data analysis. Concentration gradients of the redox couple ferroin/ferriin catalyzing the reaction are determined to a resolution of about $10 \, \mu m$. In solutions of identical chemical composition the gradients reach peak values of 8 mM/mm in a front of a spiral and 15 mM/mm in a front of a circular wave. Variation of ferroin concentration in the center of spiral rotation is less than 6% of that outside the core region. The degree of oxidation of ferroin at which the steepest concentration gradients occur is higher inside the core than at the outward-moving fronts. The core structure and the collision area between two circular fronts are represented by three-dimensional orthographic projections.

KEY WORDS: Belousov–Zhabotinskii reaction; reaction-diffusion coupling; spiral wave; wave collision; two-dimensional spectrophotometry; perspective graphics.

1. INTRODUCTION

Propagating waves of chemical activity in excitable or oscillatory solutions belong to the most frequently studied examples of chemical pattern formation due to the coupling of reaction with diffusion. A substantial part of the investigations concerned with this phenomenon of nonlinear dynamics in systems evolving far from thermodynamic equilibrium have been performed in the Belousov–Zhabotinskii (BZ) reaction,[1,2] which is a

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reaction catalyzing the overall bromination and decarboxylation of malonic acid and can be resolved into at least 20 elementary steps.[3] No other system has been discovered that exhibits a similar variety of patterns, and ever since the first observations of chemical waves were reported more than 15 years ago, the BZ reaction has remained in the focus of interest. The experimental material accumulated for this reaction supports more and more the theoretical concepts of nonequilibrium chemistry developed by I. Prigogine and his co-workers.[4,5]

Many phenomenological observations and measurements on the kinematic properties, such as wave velocities and their concentration dependence, have been collected, but only recently has a more comprehensive quantitative characterization of such spatial patterns, that is, the measurement of the distribution of chemical compounds in space, become feasible by the application of nonintrusive, space-resolved observation techniques of sufficiently high resolution. Examples are the determination of the concentration profiles of the catalyst and indicator ferroin in one dimension by measurement of transmitted light with a photodiode array,[6] the quantitative description of the spiral wave by means of a two-dimensional spectrophotometer based on computerized video equipment,[7] and a study of target patterns by similar digital methods.[8] The recording of such two-dimensional spectrophotometric data leads to a large amount of information. A particularly important aspect of the treatment of the data is their appropriate presentation. Techniques using pseudocolors and three-dimensional perspective representations have been proposed.[9,10] Equally important is the extraction of parameters that are characteristic for the specific patterns under investigation and which can be easily compared to model calculations, such as concentration gradients, wave velocities, amplitudes, and geometric shapes.[6,11]

Since most experiments on chemical waves are performed in thin liquid layers, two-dimensional techniques are well suited for their analysis. No corresponding methodology is available for quantitative measurements of three-dimensional waves, such as the experimentally found scroll waves.[12] These have been discussed theoretically in some detail,[13] but efficient observation and measurement methods still have to be developed.

This paper deals with two topics of particular interest for chemical wave propagation in an excitable solution layer of the BZ reaction: the core of the spiral wave and the area of collision of two expanding circular waves. In the following section the chemical preparation procedure, the apparatus for two-dimensional spectrophotometry, and the applied evaluation techniques are briefly described. The section of results is subdivided into the two topics under consideration. Spectrophotometric observations with the highest spatial resolution available in our laboratory are

reported, images of the recorded patterns and their three-dimensional perspective representation are given, and concentration gradients of the catalyst are determined from concentration profiles.

2. MATERIALS AND METHODS

2.1. Sample Preparation

A quiescent excitable BZ system was obtained by preparing a reactive mixture of 48 mM sodium bromide, 340 mM sodium bromate, 95 mM malonic acid, and 380 mM sulfuric acid in a final volume of 5 ml. A few minutes later, ferroin was added to the solution with a final concentration of 3.5 mM. Distilled water and reagent-grade chemicals were used. After filtering through a 0.44-μm filter, a volume of the final mixture resulting in a layer thickness of 0.65 mm was placed in a siliconized, dust-free petri dish. The layer thickness was calibrated with a ferroin solution of known concentration. The ambient temperature was $24 \pm 1\,^\circ$C.

A pair of circular waves of chemical activity was initiated by immersing a pair of silver electrodes (diameter 100 μm) with a given distance into the layer by means of a micromanipulator. Spiral-shaped waves were produced by disrupting a small section of a circular wavefront with a gentle blast of air ejected from a micropipette. Right after producing the pattern under investigation, the dish was covered with a glass plate, leaving an air gap of about 10 mm above the layer. Thus, distortion of wave fronts caused by convective flow due to evaporative cooling was prevented.[14]

2.2. Image Recording

The patterns of chemical waves evolving under the covered dish were investigated with an apparatus for space-resolved digital and computerized spectrophotometric measurements. The sample layer is illuminated with a parallel, spatially homogeneous light beam filtered with an interference filter of 490-nm peak transmittance, which corresponds to maximum absorption of the catalyst ferroin. A video camera with a raster resolution of 512×512 pixels records the light intensity transmitted through a square section as small as 2×2 mm^2 of the sample layer. The gray level of each pixel is stored as one byte in the digital memory array of a video frame buffer. This equipment is linked to a fast, large memory computer. Acquisition and storage of the two-dimensional data is feasible at a frequency up to 30 frames/min. A detailed technical description and applications to chemical patterns are reported in.[9]

2.3. Data Presentation

A comprehensive software package for the presentation of two-dimensional data arrays recorded with this spectrophotometer was developed. Applications of this package include extraction of profiles of transmitted light intensity, logarithmic conversion of intensities into concentrations using a two-dimensional version of the Lambert–Beer's law,[9] pseudocolor presentations, and fitting procedures for specific isointensity lines. Techniques for two- to three-dimensional transformations of chemical gradients as described in Ref. 15 show that quantitative information can be visualized in an effective way by perspective three-dimensional presentation, thus revealing noteworthy features that may not be detectable in the original two-dimensional images.

3. RESULTS

3.1. The Spiral Core

A typical wave pattern recorded by light absorption of ferroin at the wavelength of 490 nm is shown in Fig. 1. It consists of several spiral waves
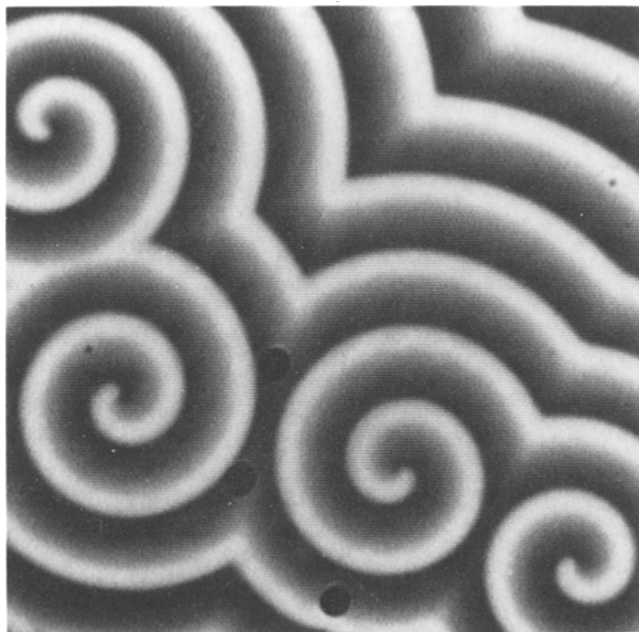

Fig. 1. Several pairs of spiral waves in the Belousov–Zhabotinskii reaction, presented as a digital image consisting of 450×450 pixels. In each pair the spirals turn around a center with opposite sense of rotation. Image section: 10×10 mm^2.

of highly regular geometry, which are arranged in pairs. Each of the spirals rotates around a center, the properties of which are characterized below. The sense of rotation is pairwise opposite, that is, the tips turn inward with a revolution period of about 17 sec, while the fronts propagate outward. Annihilation of two fronts upon collision can be seen between the two spirals to the left, as discussed in more detail in Section 3.2.

For further analysis of the innermost area of the spiral, a small section $(2.1 \times 2.1 \text{ mm}^2)$ containing only the tip and one whorl of one spiral was selected and a time series of 450×450 pixel images covering three rotations was recorded at intervals of 2.8 sec. One image from this time series is shown in Fig. 2A. Two isointensity lines around a gray level of 175 are enhanced in black. These lines are separated by a gray level interval of 10, while the difference between minimum and maximum intensity of transmitted light amounts to 65 gray levels (compare Fig. 3 below). The purpose of enhancing these selected levels is visualized in Fig. 2B, in which the inner section of image A is digitally expanded. Generally, the distance between the two black isointensity curves is small along the steep excited fronts of the wave and larger along the smooth inner slopes of the relaxing back of the wave, as expected. The feature to be emphasized is the remarkable closeness of the lines at a distinctive site near the spiral tip (arrow in Fig. 2B). This area of very steep gradients is located 54 μm away from, and thus in the immediate vicinity of, the rotation center of the spiral (white circle), which is determined further below.

The intensity profile shown in Fig. 3A was extracted from the full image of Fig. 2 and passes in the horizontal direction through this distinctive site. The data points were fitted by splines and their derivative in terms of concentration gradients of the oxidized form of the catalyst, ferriin, is plotted in Fig. 3B. Comparison of the two curves of Fig. 3 shows that the steep gradients are localized in narrow intervals of the x coordinate. An important observation is that, although the maximum values of about 8 mM/mm are the same for the outward-propagating front (left peak at $x = 0.13$ mm) and the site close to the tip (center peak $x = 1.05$ mm), they occur at different gray levels: 160 for the left peak, which is very close to the intensity minimum between waves, and 175 for the peak in the core region.

Inspection of profiles and their derivatives passing through other points close to the center of rotation reveals that the concentration gradients at the outward-propagating front reach maximum values always at 160 gray levels, whereas the peak values at the inner side of the very spiral tip (i.e., around the site marked by the arrow in Fig. 2B) occur for higher gray levels, which means for higher oxidation. These higher levels follow a systematic trend within a small gray level interval.
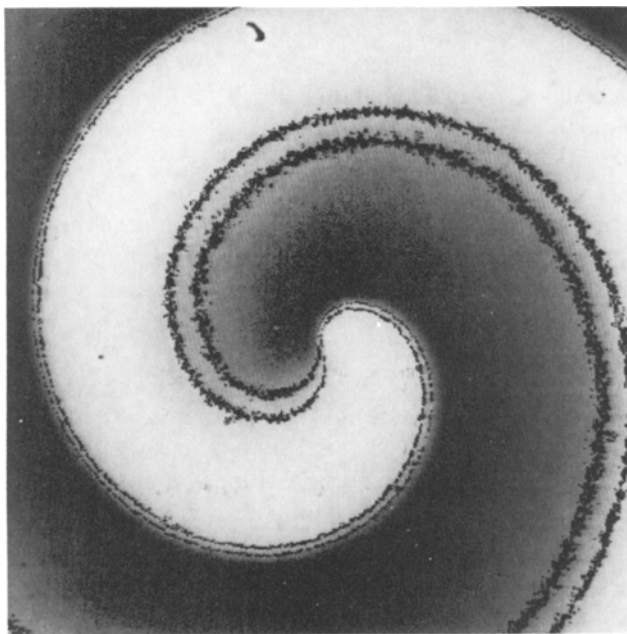
(A)
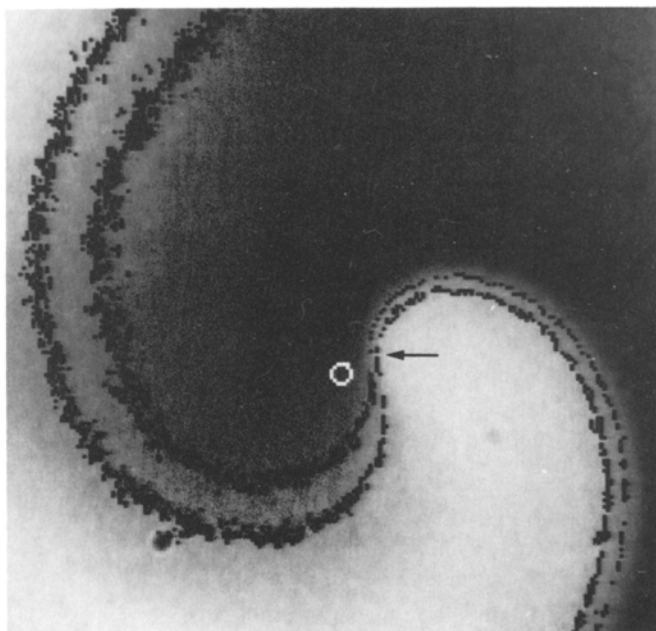
(B)

Fig. 2. (A) High-resolution image of a spiral wave. Pixel noise was reduced by a 3×3 pixel average. Two intensity levels are enhanced in black. Image section: 2.1×2.1 mm². (B) Digital expansion of the center section of image A by a factor of 2.5. The white circle indicates the center of spiral revolution. The arrow is referred to in the text.
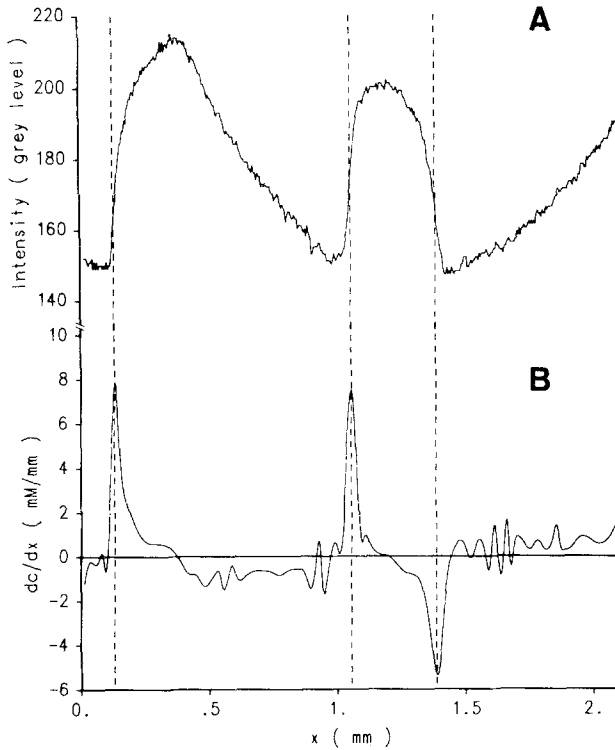
Fig. 3. (A) Profile of transmitted light intensity extracted from Fig. 2A and passing horizontally (in x direction) through the site indicated by the arrow in Fig. 2B. (B) Gradients of concentration of ferriin, the oxidized form of ferrin, derived from profile A by a spline fit and logarithmic conversion to concentration data.

Furthermore, we note the at least biphasic structure of the wavefront in the region between the zeros at $x = 0.12$ mm and $x = 0.37$ mm. The gradient of the wave back is comparatively low, with an average value of approximately 1 mM/mm (see also data given in Ref. 11).

In order to determine the rotation center of the spiral and further properties of its core, an overlay technique was applied, which has proven to be an efficient method of analysis.[7,11] If six images taken during one spiral revolution are overlaid in one image, a composite structure as shown in Fig. 4 is obtained. The wave crests of the contributing individual images can be recognized as spiral-shaped bright bands. The banded structure is gradually smeared out when additional turns of the spiral are included in the overlay.

The dark spot in Fig. 4 is the core of the spiral wave in which the variations of ferroin concentration remain significantly below those
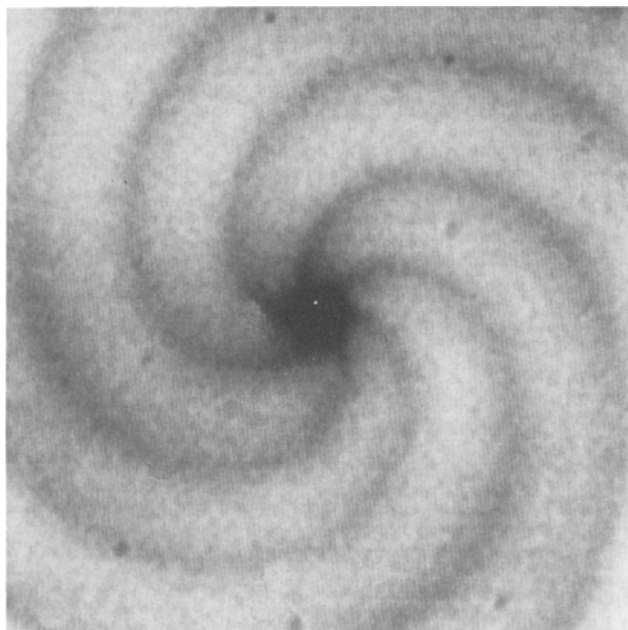
Fig. 4.   Overlay of six spiral images such as in Fig. 2A, taken during one revolution. Image section after twofold expansion: 1.05×1.05 mm². The core of the wave appears as a dark spot inside which the concentration of the catalyst varies much less than in the surrounding area.

measured in the outer region, where wavefronts travel outward. The three-dimensional perspective presentation of the core region in Fig. 5 gives a vivid qualitative impression of its "tornado"-like structure. This surface plot depicts the "high-level" envelope of transmitted light intensities and shows that the core center—the tip of the funnel—is a well-defined small site of the pattern, the spatial extent of which is not yet clearly resolved.

The intensity modulation, given as twice the standard deviation of the gray levels of a 2×2 pixel area during $2\frac{1}{2}$ spiral rotations (15 images), is 4 at the very center, 6 at a distance of 10 μm, and 20 at a distance of 37 μm. Thus, the spiral center is a singular site in the sense that locally the concentration varies less than 6% as compared to the full wave amplitude outside the core (i.e., farther than 0.35 mm away from the center[7]). These values were obtained at twofold higher optical resolution than previously reported numbers.[7,11]

During spiral rotation, the trajectory of the site of steepest gradients specified in Fig. 2 is completely contained in the inner part of the core. In Fig. 5 it is located at a level above the tip corresponding to roughly one-quarter of the total height of the funnel.
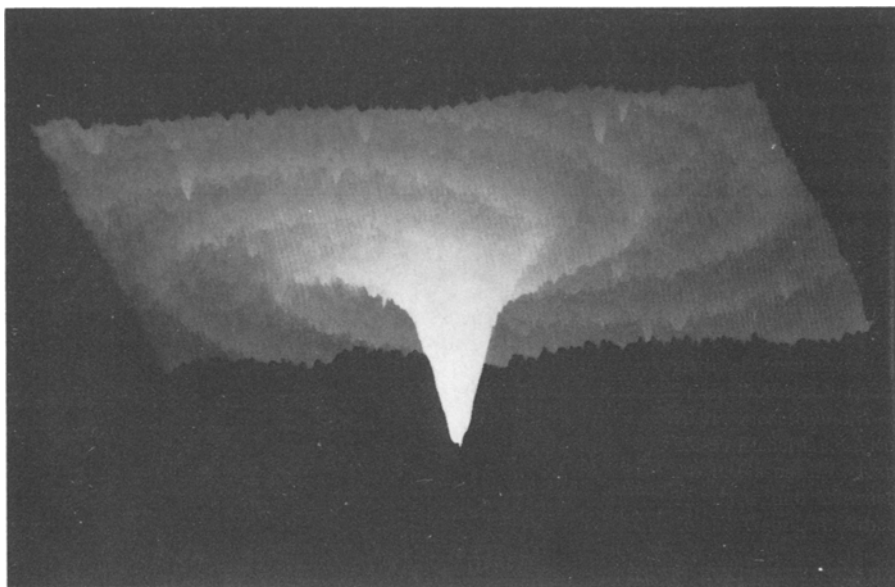
Fig. 5. Three-dimensional perspective representation by orthograhic projection of a 1.05×1.05 mm² section of an overlay image including that of Fig. 4, but constructed from 15 spiral images taken during 2.5 revolutions. The structure is looked at from below (tilt angle 110°). The pixel brightness is inverted compared to Fig. 4.

3.2. Wave Collision

One of the characteristic features of wave propagation in a chemical system is the specific type of wave interaction upon collision. As shown in Fig. 6, using the same initial chemical composition as for the spiral pattern described above, two annular fronts of excitation travel through a reduced, quiescent medium toward each other and, as one can immediately recognize, annihilate when they collide. It is important to note that no interference phenomenon is exhibited, as expected for many other types of waves in physical systems. This implies the formation of typical cusplike structures, as best seen in Fig. 6B. The images of this figure show in rapid sequence (2.5-sec intervals) three snapshots of the process of collision.

Extraction of intensity profiles and their fits by splines lead to the determination of gradients of ferriin concentration. Briefly before the collision starts (a few seconds prior to the shown image sequence) the gradients at the steep fronts are 15 mM/mm. It turns out that the two annuli are not only very similar in geometry and propagation velocity, but also in terms of concentration gradients, which, in this example, agree within 4% along the horizontal centerline of the investigated image section.
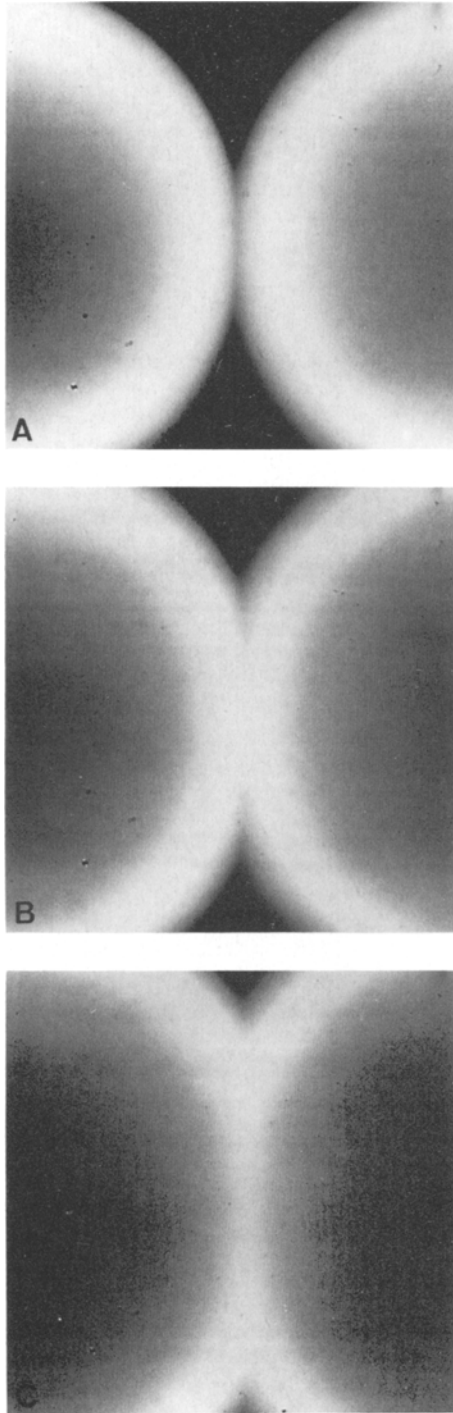
Fig. 6. Collision of two concentric waves initiated in a reduced, quiescent solution at a distance of 5 mm and observed in a 4.5×4.5 mm^2 area. The images were taken at 2.5-sec intervals.
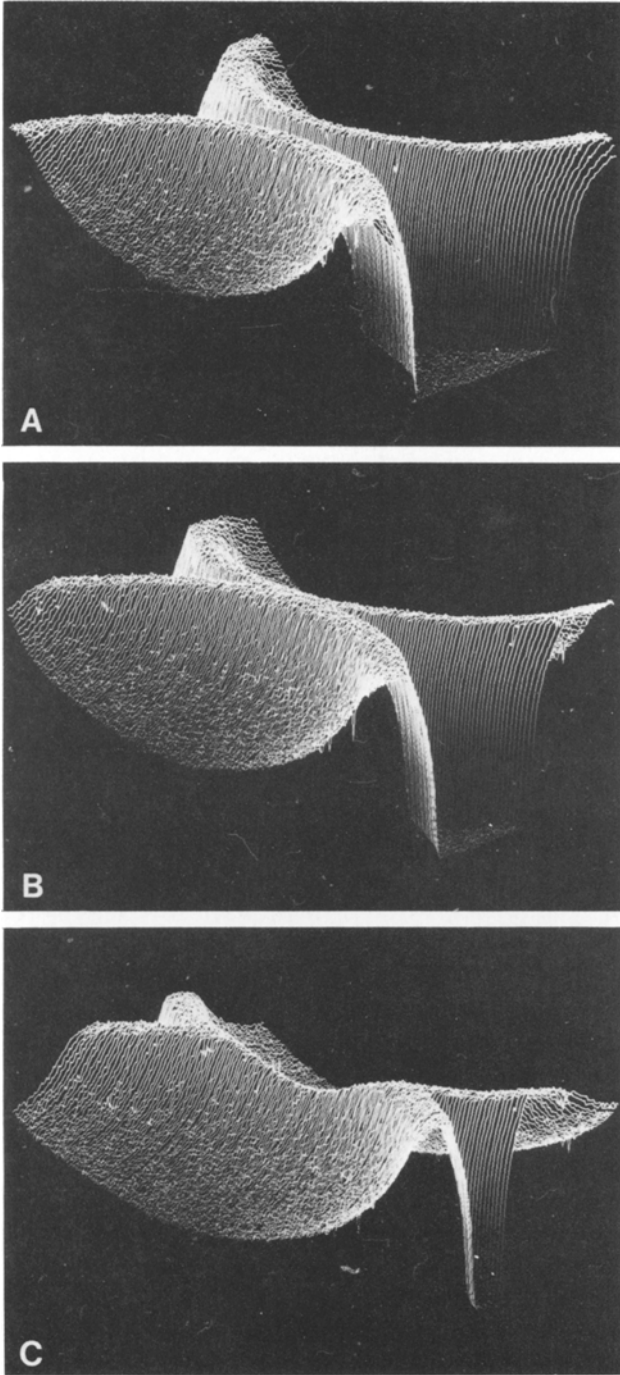
Fig. 7. Three-dimensional perspective profile images of the patterns of transmitted light of Figs. 6A–6C, rotated clockwise by an angle of 125° and tilted by 65° in an orthographic projection.

A different way to look at this wave motion is demonstrated in Fig. 7. The three profile images represent the intensity measurements of Fig. 6 in three-dimensional perspective from a particularly chosen viewpoint. They emphasize the remarkable regularity of the reaction-diffusion pattern. It can be seen in the first images (Figs. 6A, 7A) that, although collision of the lower parts of the profiles (i.e., the reduced "valleys") has definitely started, the upper parts (i.e., the excited, oxidized wave crests) are still a finite distance apart. In the second profile image (Fig. 7B), derived from the image in Fig. 6B, in which the sharp cusps have formed, the two approaching wave crests just have merged into one. Then, at a stage when the distance between the two cusps has grown substantially (Fig. 6C), one observes a dip in the area of interaction (Fig. 7C), indicating that due to the collision the crest turns to a more reduced state. The details of the concentration profiles in this particular area are not yet known experimentally or theoretically.

4. DISCUSSION

Measurements of traveling waves in an excitable layer of the BZ reaction have been presented with emphasis on several structural and dynamical details that occur in the core of a spiral wave and in the area of collision of two annuli. The detection of such details requires sufficient spatial resolution and quantification of local concentrations. This is achieved by two-dimensional spectrophotometry, which combines high optical magnification with computerized video techniques.

The analysis of profiles of a spiral wave in terms of concentration gradients of the catalyst reveals that there is a small site, located at the inner side of the tip inside the core region, where the shape of the wavefront differs from that usually observed in outward-propagating wave fronts. In particular, we find that in the vicinity of this site the concentration levels with maximum gradients are different from the corresponding levels outside the core region. In other words, the steepest part of the front inside the core is slightly shifted toward higher oxidation as compared to the outer region. In this context we mention an earlier investigation showing that the quasistationary concentration level at the center of rotation is a small interval above the level of minimum oxidation (the "valleys" between waves).[7,11] Comparison of this interval with the shift of the steepest gradient when following the fronts toward the center yields quantitative agreement. This observation may be of relevance for understanding the core properties.

The distinctive site at the tip may perhaps be considered as the point of balance between the advancing front and the receding back and is

probably related to the point of zero curvature of the isoconcentration levels (see Fig. 2). Although further analysis is necessary, for instance, by applying two-dimensional spline fits, the observations collected up to this stage clearly add to the specific properties of this particularly interesting region of the wave patterns.

The core of the spiral wave and its structure were investigated in some detail and the singular properties of the center of rotation in terms of concentration variations shown at the highest available resolution. In fact, the findings suggest that one may expect the detection of a stationary level of finite size if the resolution of the apparatus is still further improved. To this end the application of microscopy is under way. In addition, modifications of the chemistry are possible that increase the size of the core, e.g., in cerium-catalyzed systems as recently investigated in the ultraviolet range.[16] Detection of such a concentration plateau in a spiral center would be of great interest for the elucidation of the mechanism of organizing centers.

The results presented for the mutual interaction of two approaching circular wavefronts are qualitative at this preliminary stage of our investigations. The collision process is initiated by the interaction of the two annuli at their reduced parts and then moves upward to the oxidized crests. These crests mark the transition between oxidation and reduction of the catalyst. In a pattern such as shown in Fig. 7C they reveal local chemical features of the complex reaction kinetics to be analyzed further.

In terms of geometrical shape, the annihilation of the two fronts upon collision appears to occur in a perfectly symmetric manner. Seemingly, each circular wave disappears behind an imaginary "wall" along the symmetry axis between both annuli, which is in contrast to the behavior of solitons. It remains an open question whether the immediate vicinity of the two fronts results in a distortion of the wave profiles at least very close to the collision point. Ultimately, this type of interaction should be expected on the length scale of diffusion. Still higher magnification is necessary to resolve the true length scale of such effects.

It should be emphasized that all experiments were performed in a covered dish, which prevents evaporative cooling of the layer surface and thus the onset of hydrodynamic flow by natural convection. However, because of the exothermicity of the reaction and the dependence of surface tension both on temperature and chemical composition, there is no guarantee for perfect hydrodynamic stability of the thin sample layer. Any analysis of structural details of the kind presented in this paper has to take into account the possibility of interference with hydrodynamics as another source of pattern generation.

ACKNOWLEDGMENTS

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