Ordered Convective Motion in the Chaotic Phase of an Unstirred Ferroin-catalyzed Belousov Zhabotinsky Reaction

Florian Wodlei*, Mihnea R. Hristea and Giuseppe Alberti

LIVING SYSTEMS RESEARCH

SELF-ORGANIZING SYSTEMS

ALPEN-ADRIA UNIVERSITÄT KLAGENFURT I WIEN GRAZ

Conference on Complex Systems
Palma de Mallorca, October 17-21, 2022

Living Systems RESEARCH, Roseggerstr. 27/2, 9020 Klagenfurt, AUSTRIA, www.ilsr.at, *florian.wodlei@ilsr.at
Interdisciplinary research cluster on ***Self-Organizing Systems***, University Klagenfurt, https://selforganizing.wordpress.com/

Introduction

The **Belousov Zhabotinsky (BZ) reaction** is a typical example of a chemical oscillator that shows self-organizing behaviour at different levels. It is the most thoroughly studied oscillatory reaction system in homogeneous phase in chemistry. At the same time, due to its complexity, not all aspects of its dynamics are yet understood.

The BZ reaction is a periodic bromination of an organic species in acidic environment and in the presence of a catalytic color indicator in liquid phase (see Fig. 1).

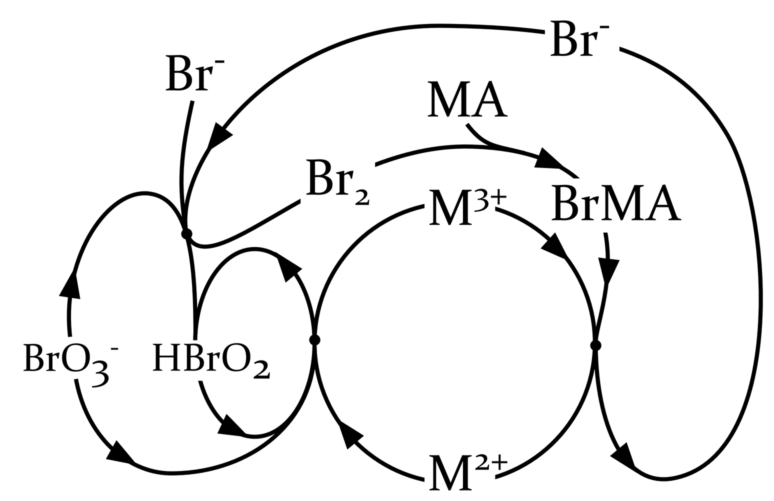

Figure 1: Schematics of the reaction cycle of the BZ reaction. malonic acid (MA), sodium bromate ($Na^+BrO_3^-$), sodium bromide (Na^+Br^-), catalyst $M^{2+/3+}$ (ferroin/ferriin).

In this study we investigated the dynamics of the BZ reaction when left unstirred in a batch reactor. Due to the fact that the system is liquid and unstirred, its dynamics will be not only governed by the *reaction kinetics*, but also by *diffusion* and *convection*. That is why the reaction dynamics becomes more complex than in a fully stirred one, where only the reaction kinetics plays a role.

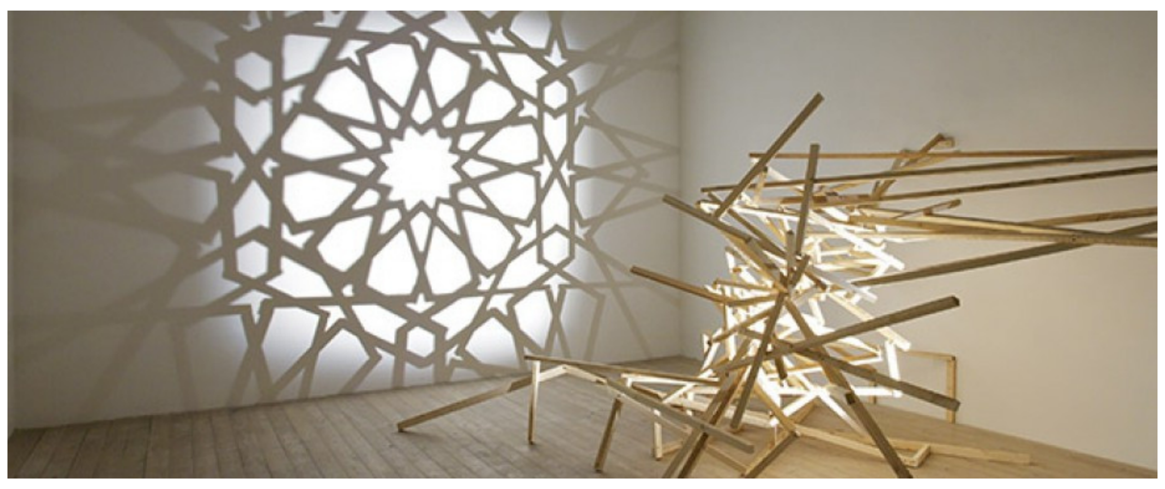

Figure 2: Artistic installation by Azerbaijan artist Rashad Alakbarov on Chaos.

In addition to the periodic color change, that takes place also when the system is stirred, a phase of aperiodic color change appears for a limited time that transits back to periodicity (see Fig. 6). The appearance of this chaotic transient was unexpected. This behavior was first discovered by Rustici et al. in a Cerium-catalyzed (Rustici et al., 1996) and later also in a Ferroin-catalyzed version (Rossi et al., 2009) of the BZ reaction. Rustici et al. (Rustici et al., 1998) also demonstrated that the transition to chaos follows a **Ruelle-Takens-Newhouse (RTN)** scenario (Newhouse et al., 1978).

We have recently discovered that, as the so-called chaotic transient takes place, periodic bulk motions in form of convective cells are created in the reaction solution (see Fig. 4). In other words, there is *hydrodynamic order* while at the same time there is *chemical chaos*. It seems to depend from which 'side' one looks at a systems as artist Alakbarov has shown (see Fig. 2).

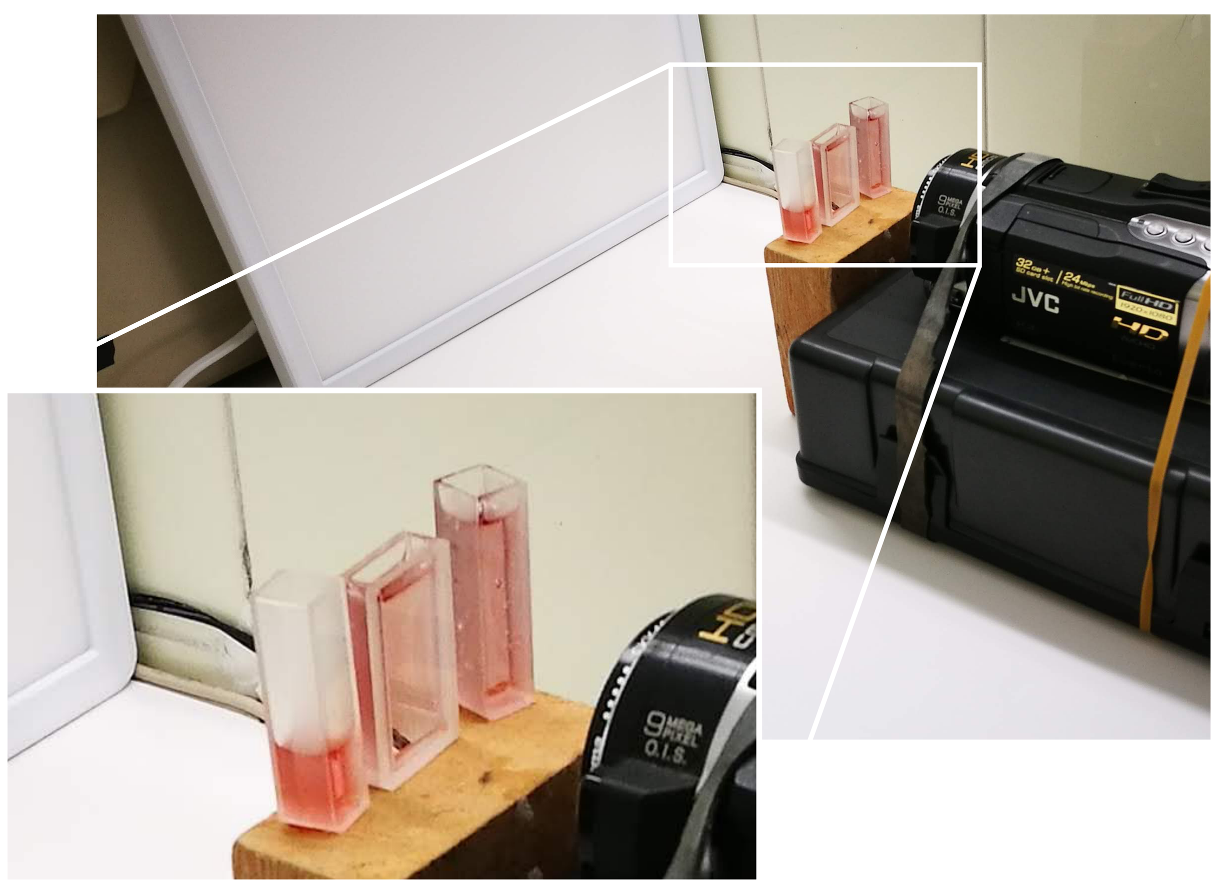

Figure 3: Optical setup. The arrangement of the LED backlight, photo spectroscopic quartz cuvettes and the video camera is shown; inset shows a zoom on the cuvettes.

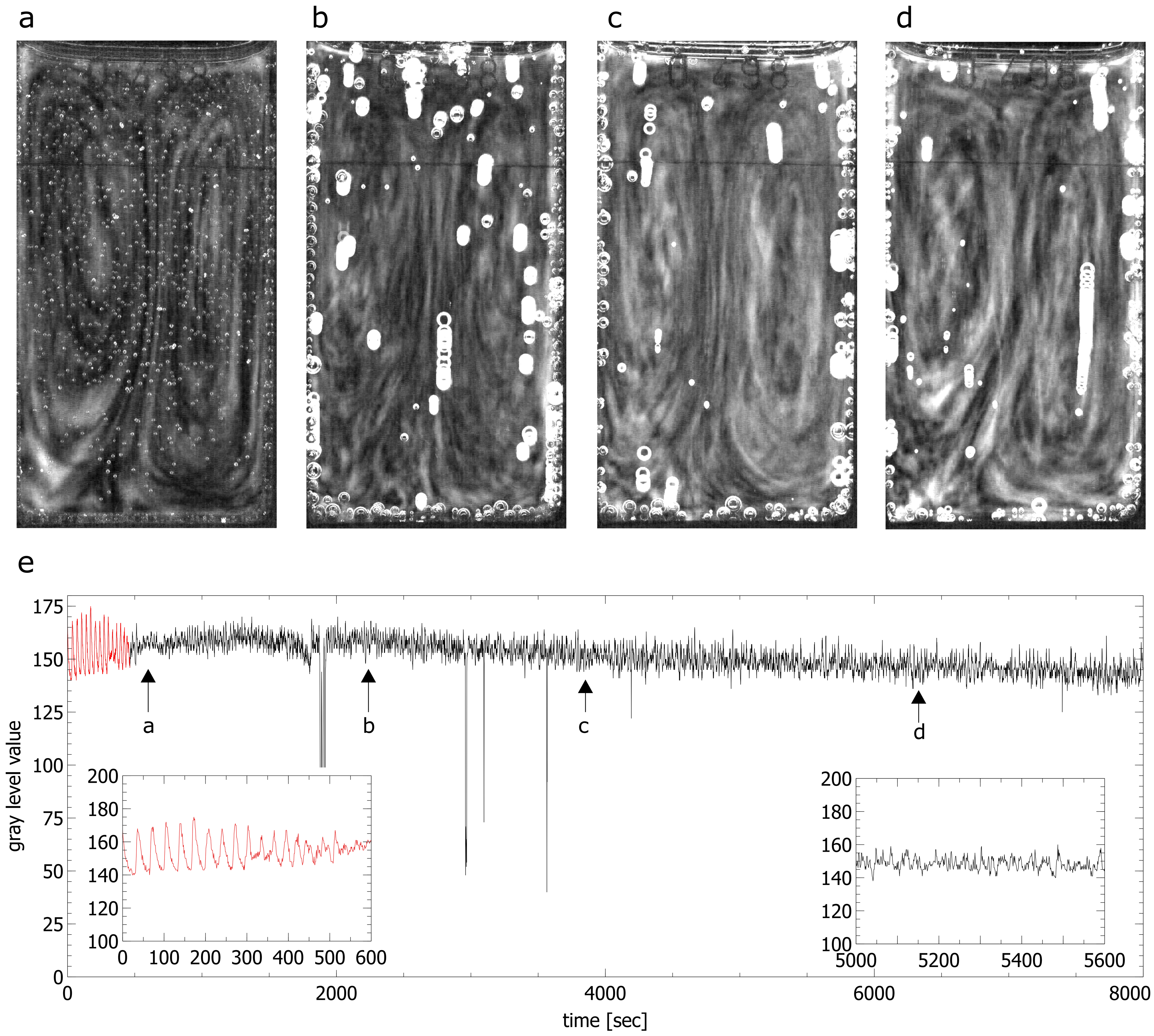

Figure 4: Convection cells in the special cuvette during the chaotic phase. (a–d) show the presence of two convection cells (liquid moves up in the middle and down on the left and right side). Images were obtained by averaging over 60 s, (e) shows the time series extracted from the video data (red part corresponds to the periodic phase). Arrows indicate the times where the images (a–d) were created.

Experimental Methods

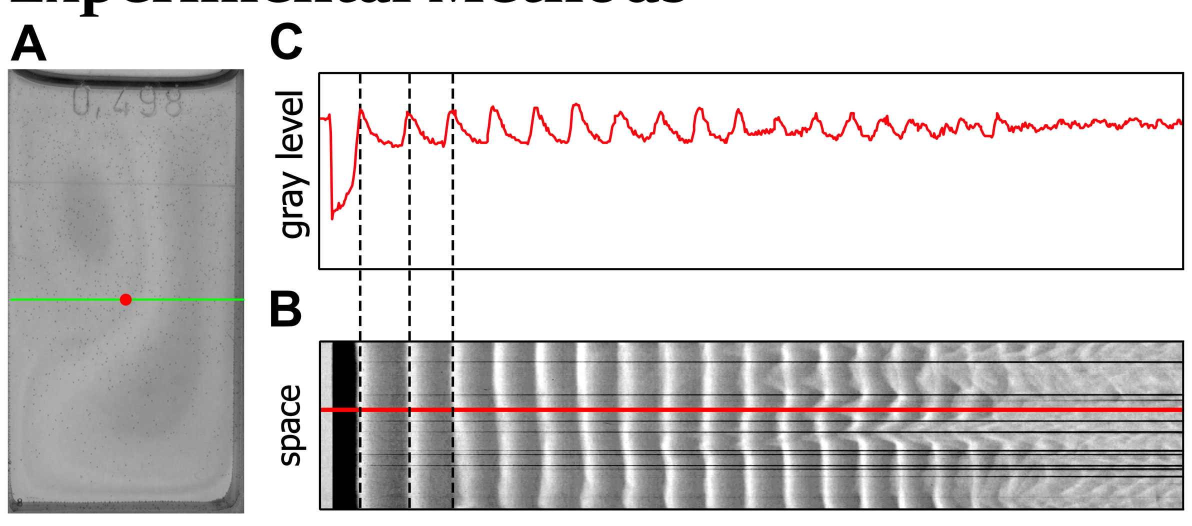

Figure 5: Extraction of time series from video data corresponding to a wavelength of around 450nm, (A) shows a video image in a special cuvette, (B) shows a space–time plot for the green cross-section line in (A), (C) shows the gray level value profile along the red line in (B) corresponding to the change in gray level at the red point shown in (A).

We recorded the entire cuvette by using a video camera instead of a spectrophotometer, which allowed us to record the whole spatial dynamics of an unstirred BZ reaction (see Fig. 3). We could extract time series from the video data (see Fig. 5).

Results and Discussion

We discovered that ordered hydrodynamical structures are correlated to the chaotic nature of the local chemical kinetics. As a first explanation of this correlation, we assume that the formed convection cells lead to a "de-synchronization" of the previously homogeneous color oscillations moving the system into a chaotic phase. With a mathematical model (not presented here) we were able to confirm the same qualitative results.

Literature

Newhouse et al. Commun. Math. Phys. 64, 35–40, 1978
Rustici et al. Chem. Phys. Lett. 263, 429–434, 1996
Rustici et al. Chem. Phys. Lett. 293, 145–15, 1998
Rossi et al.. Chem. Phys. Lett. 480, 322–326, 2009
Wodlei F, Hristea MR and Alberti G, Front. Chem. 10:88169, 2022

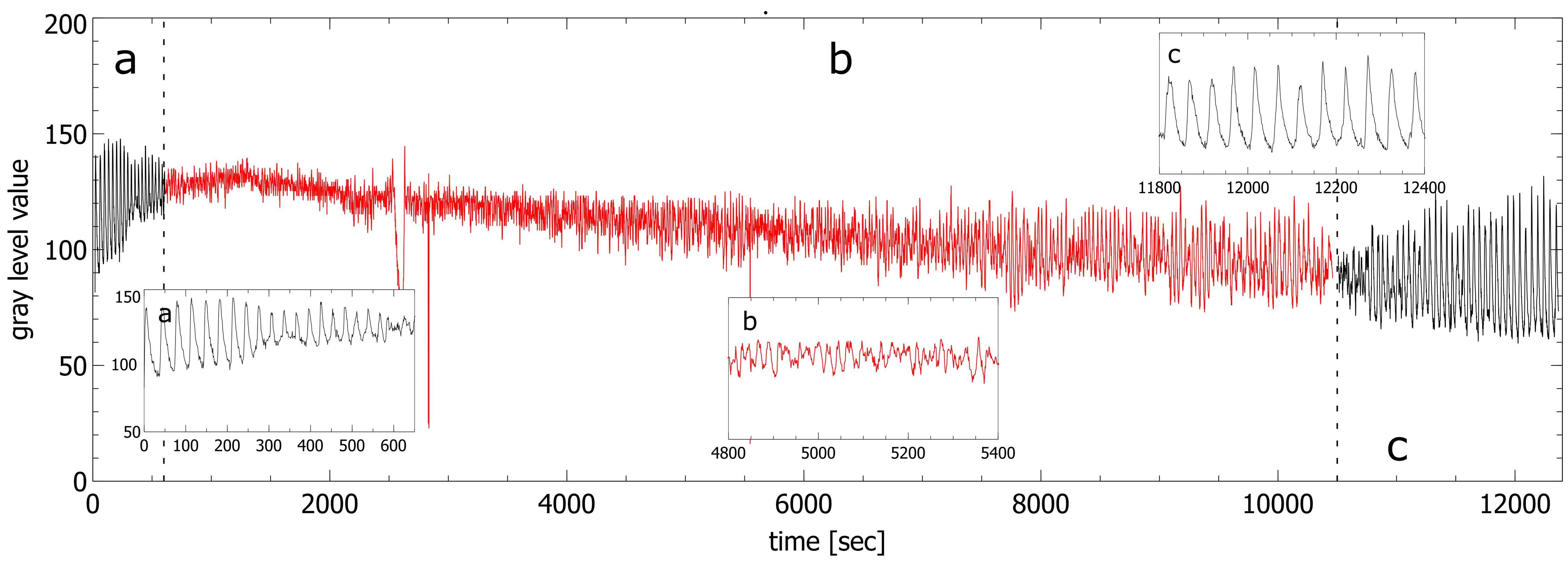

Figure 6: Oscillations of the concentration of the ferriin concentration extracted from video data of an unstirred BZ reaction carried out in a fully filled standard cuvette (spikes in the time series correspond to the passage of bubbles).