Supplement to ‘Stirring effect on the Belousov Zhabotinsky reaction’

Florian Wodlei[*,a], Mihnea R. Hristea[b]

Experimental Setup

Before filling the beaker, it was prepared with a LED/LDR combination which worked as a photometric unit (see fig. 1). Then the beaker was filled with the following components (for details see the Experiemtal facts section on the backside of this page): water, sodium bromate, sodium bromide, malonic acid, sulfuric acid, ferroin. The reaction of all this components lead to an periodic color change (from red to blue) which is known as the *Belousov Zhabotinsky reaction (BZR* or *BZ reaction)*.
After the beaker is filled, it is placed in a dark box, the *‘photometer’* which is on the top of a stir bar and connected to the computer (for details see Experimental section at the backside of this page) . Since the color of the solution is given by the redox indicator (ferroin; Fe^{2+} for the red color and Fe^{3+} for the blue color) the photometer measures the concentration of Fe^{3+}. After some few color changes the soution remains red. Then the stirring is started with constant rate (~3 Hz) and the periodic color change comes back. After approx. 30 min the stirring is stopped. The periodic color change continues for some more time and then it disappears again. The oscillations reappear after a time (~1 hour) without any external influence (for details see fig. 1 on the backside of this page).

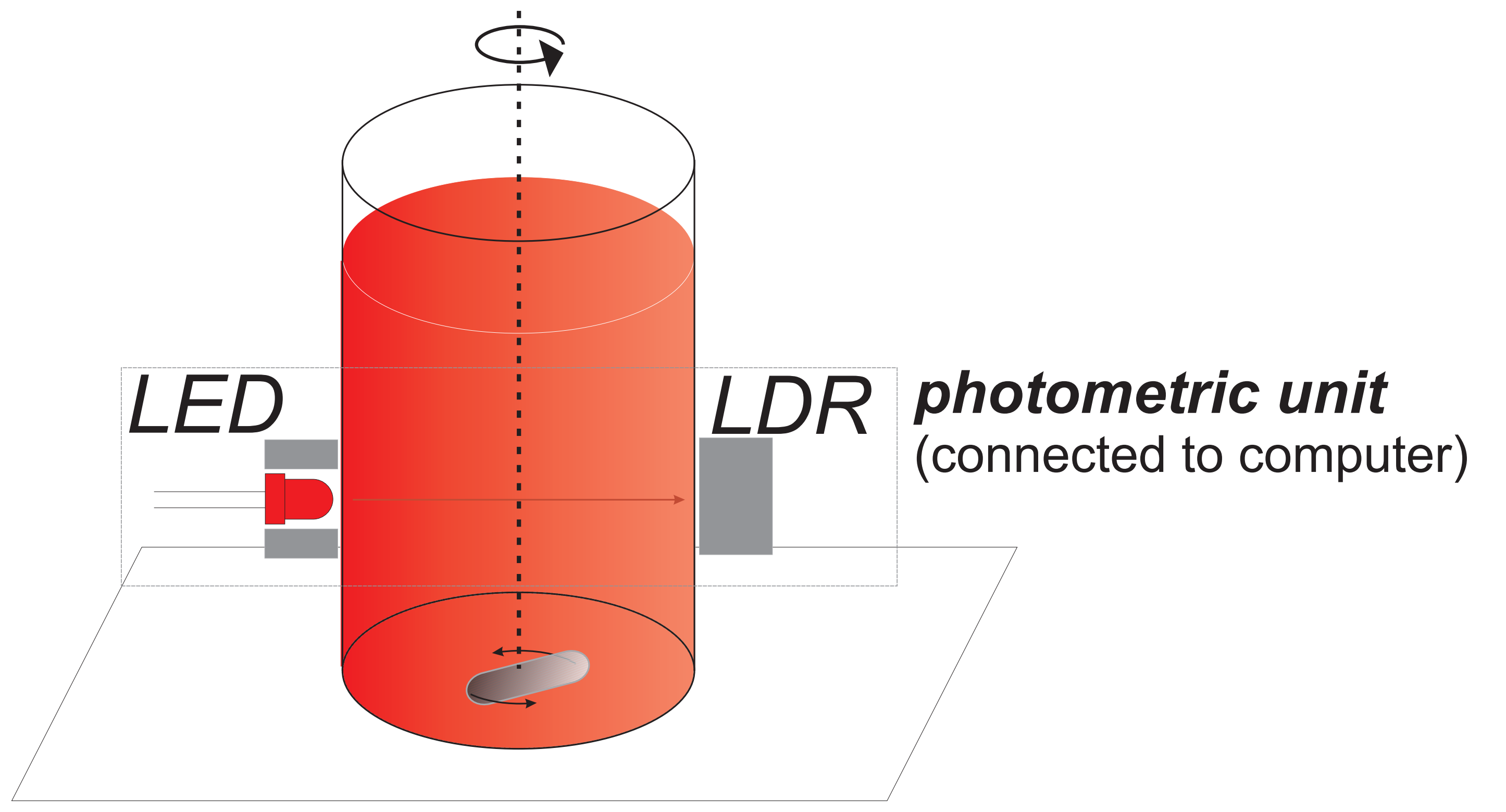

Figure 1: *Experimental setup. On the bottom of the beaker is a magnetic stir bar that rotates (rotating axis is shown as dotted line) with constant stirring rate.*

Qualitative model

As mentioned on the backside of this page our model is based on the FKN model (see reference [4,5] on backside of this page). The model describes the system by 3 coupled differential equations that are the result of the kinetics of the following overall chemical reactions

$$
\begin{aligned}
BrO_3^- + Br^- + 2H^+ &\rightarrow HBrO_2 + HBrO \\
BrO_3^- + HBrO_2 + 3H^+ + 2Fe^{2+} &\rightarrow 2HBrO_2 + 2Fe^{3+} \\
HBrO_2 + Br^- + H^+ &\rightarrow 2HBrO \\
2HBrO_2 &\rightarrow BrO_3^- + HOBr \\
Fe^{3+} + \text{organic species} &\rightarrow \frac{f}{2}Br^- + Fe^{2+} + \text{products.}
\end{aligned}
$$

The resulting differential equations can be simplified to (already in reduced variabels) (details see [4,5] on backside of this page)

$$
\begin{aligned}
\varepsilon_1 \frac{dx}{d\tau} &= \frac{q-x}{q+x} zf + x(1-x) \\
\frac{dz}{d\tau} &= x - z.
\end{aligned}
$$

where z is proportional to the concentration of Fe^{3+}. The model has three parameters i.e. $(f,q,\varepsilon_1) = \sigma$ that are constant for a given system. This model can be linearized and analyzed using standard techniques to get the qualitative behavior of the solutions (see fig. 4 on the back side of this page) which is given by different parameter sets σ.
To be able to model our experimental results (see fig. 1 on the back side of this page) it seems necessary to move within the parameter space. Such a movement is possible when the parameter set becomes *time dependent* (see *physico-chemical justification* on the backside of this page). The simplest case is the following

$$\sigma \rightarrow \sigma(t) = (f(t), q_o, \varepsilon_{1,o})$$

$$f(t) = f_o + \kappa t$$

where $f_o = 0.503$, $q_o = 10^{-3}$, $\varepsilon_{1,o} = 4 \cdot 10^{-5}$, $\kappa = 10^{-6}$. The oscillatory behaviour of this *dynamical* FKN model is shown in figure 5 on the backside of this page.

Extended model

In parallel we already started to work on an extended model that includes a flow term (aswell as an diffusion term). In general one has to solve the following set of equations (where the velocity, $\vec{v}$, obeys the Navier-Stokes equation; D is a diffusion constant)

$$\frac{\partial c_\gamma}{\partial t} = \sum_\rho \nu_{\rho\gamma} w_\rho(c_\gamma) + D\Delta c_\gamma - \vec{v} \cdot \vec{\nabla} c_\gamma$$

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Stirring effect on the Belousov Zhabotinsky reaction

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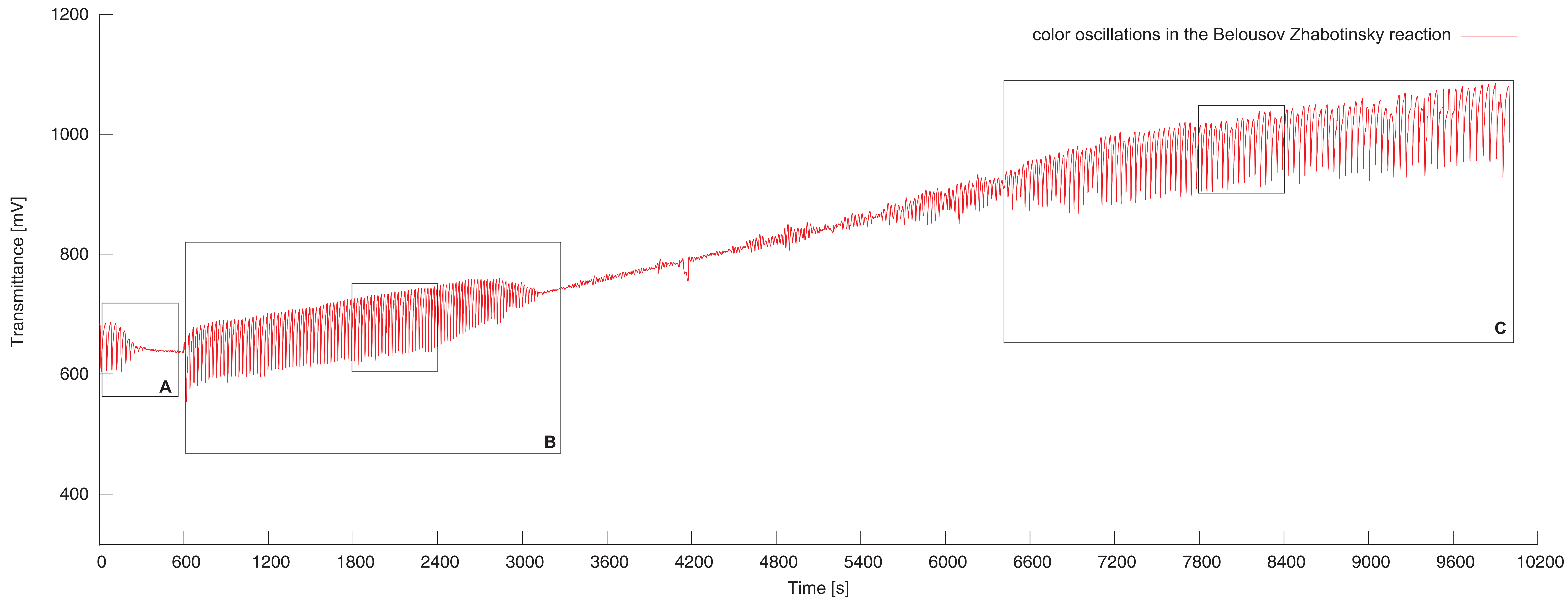

Figure 1: Overview of the periodic color change of the Belousov Zhabotinsky reaction. The different phases of the experiment are framed. **A**: Induction phase (first few oscillations right after mixing together the compounds). **B**: After disappearance of the oscillations the stirring phase is started at time 600 s and stopped at time 2270 s. **C**: Approx. 1 hour after stirring was stopped the system starts again to perform sustained periodic oscilaltion with the same amplitude as in induction phase. This illustration of the general behaviour of the Belousov Zhabotinsky reaction is taken from experimental data recorded on 10. August 2011 (for details see methods and materials section).

Abstract. ***We have studied the effect of stirring on the oscillatory behaviour of the Belousov Zhabotinsky reaction (BZR). Recently we found that the lifetime of the periodic color change in the Belousov Zhabotinsky reaction can be prolonged by a limited stirring phase (with a certain stirring rate) right after the first disappearance of the color change. In our setup this stirring effect increased the initial lifetime up to 60-fold. As a first theoretical approach to explain this effect we propose a qualitative model which is based on the autocatalytic nature of the system completed by an implicit term which incorporates the rotational flow induced by the stirring of the system.***

Keywords: Belousov Zhabotinsky reaction, stirring effect, rotational flow.

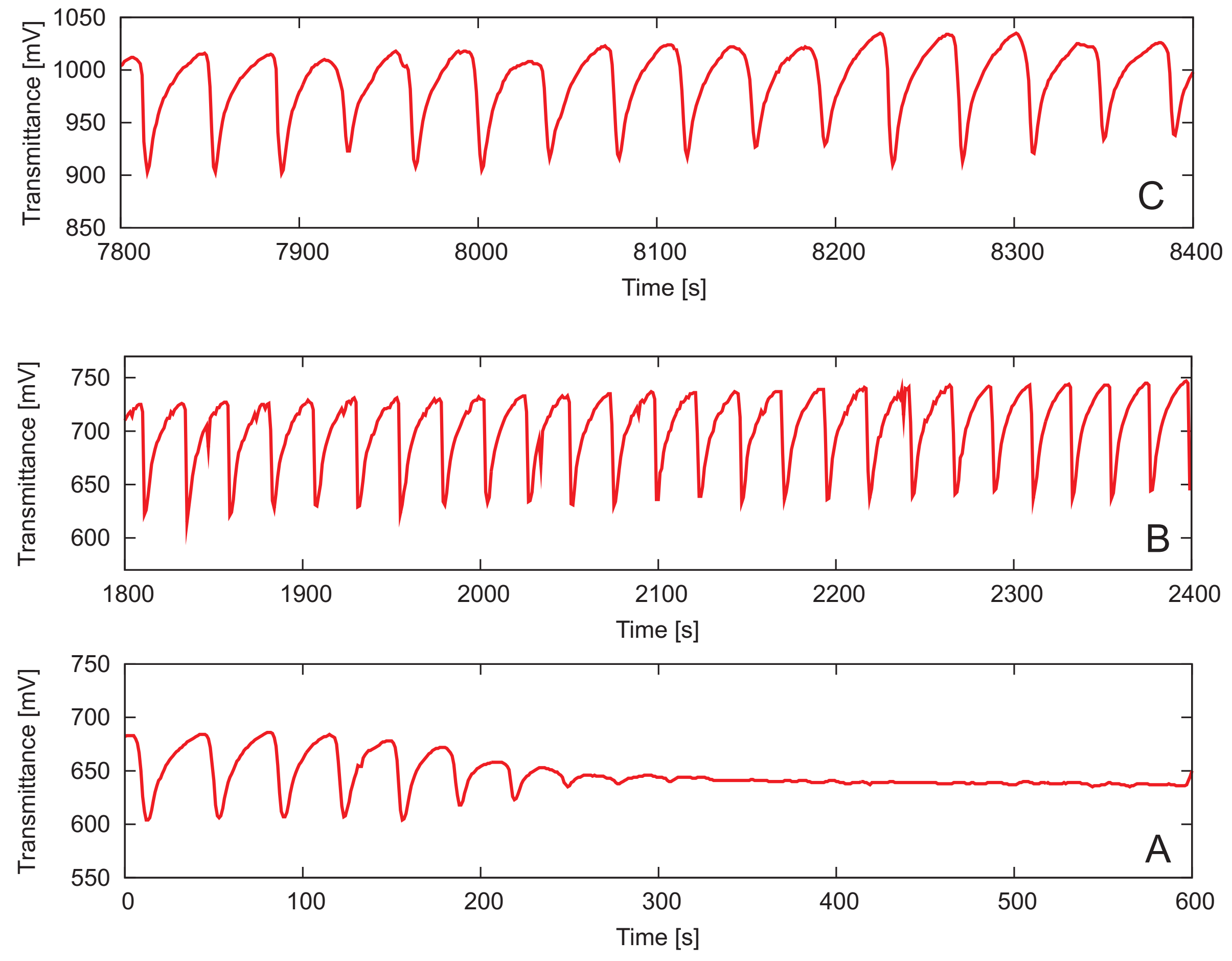

Figure 2: *Color oscillations in different phases of the reaction: A. Oscillations in the initial unstirred phase (from time 0s to 600s), B. Oscillations whitin the stirring phase (from time 1800s to 2400s) and C. oscillations in the unstirred phase C (from time 7800s to 8400s)*

Introduction

The Belousov Zhabotinsky reaction serves a number of researchers as an example of a complex system that exhibits various types of behaviours ranging from chaotic to periodic (for more details see [1,2,3]). It is a liquid phase chemical reaction system that can perform a periodic color change from red to blue. The reaction is normaly studied in a constantly stirred tank reactor (CSTR). According to our knowledge, thus far the effect of a limited stirring phase has never been investigated. In this work we report our investigation on the effect of a limited stirring phase on the behaviour of the Belousov Zhabotinsky reaction.

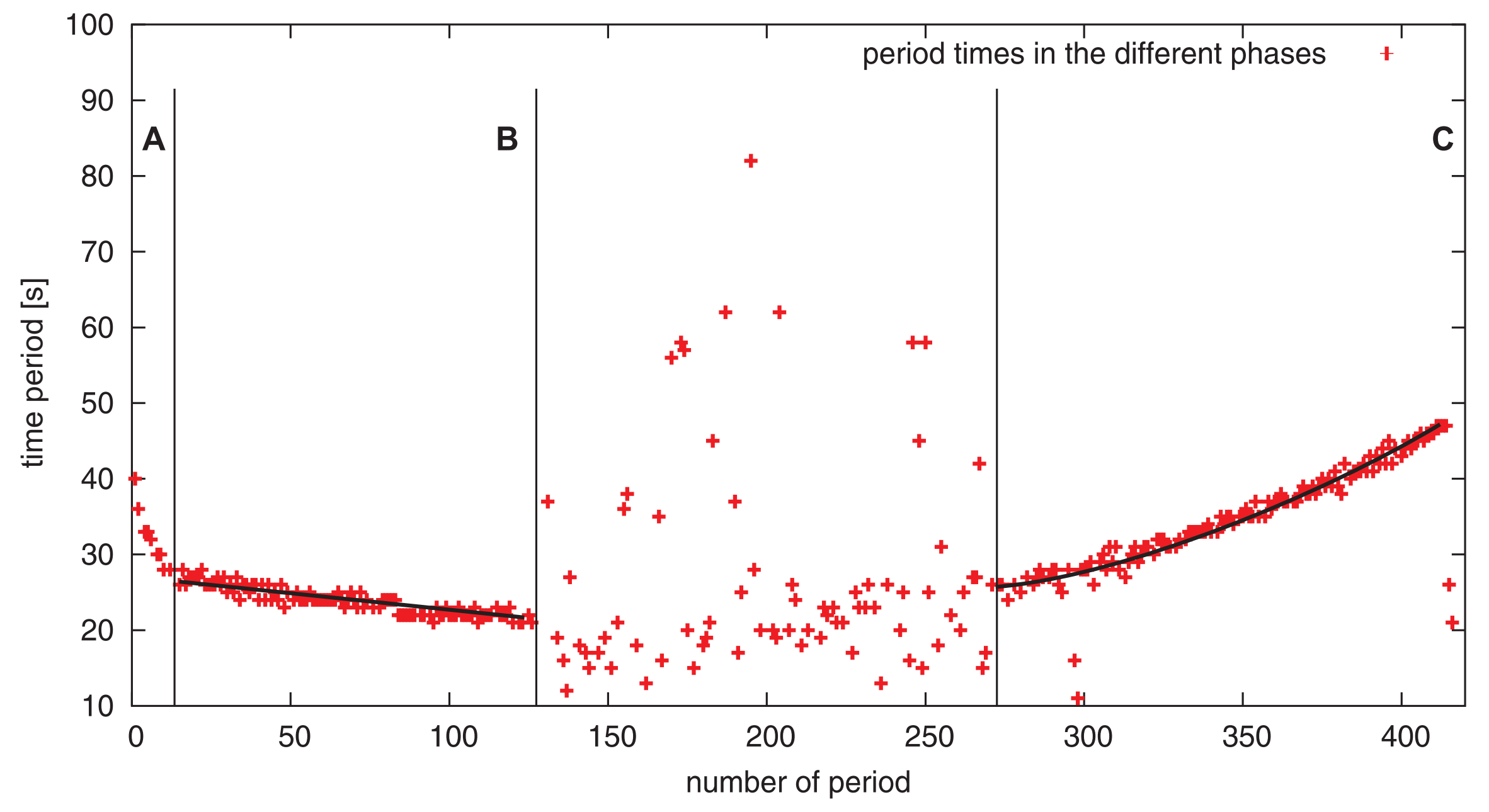

Figure 3: *Analysis of the time periods of oscillations in the different phases of the reaction. Phase A: The time period decreases relatively fast from around 40 seconds to 28 seconds. Phase B: During the stirring phase the peroid time seems to decrease in a linear manner (solid line is a guide to the eye). Between phase B and phase C there is a phase of 'small oscillations'- here the algorithm was not able to get this small oscillation and thats why this region looks chaotic. Phase C: When the sustained ocsillations occur the time periods increase in a nonlinear manner (solid line is a guide to the eye).*

Experimental facts

It seems that the effects of stirring on the BZR might have other effects too apart from the pure homogenization of the system:

- If the BZR is stirred with a 'high' rate, the color oscillations stops immediatly, but when the stirring is stopped, the oscillations restart again.
- If the BZR is stirred with a 'low' rate, the color oscillations sustain and moreover the time period of the oscillations becomes regular (see fig. 3B)

Effect of a limited stirring phase

The effect of a limited stirring phase was investigated under different conditions (changing dimension and volume of the beaker, different stirring rates and times). The general behaviour is as follows:

- The color change disappears after some few oscillations (see figure 1A, 2A)
- Stirring is started with a certain stirring rate (~ 3 Hz) and the color oscillations come back (see figure 1B, 2B) and become stable (see linear behaviour of period times in fig. 3B).
- After a time (~ 30 min) the stirring is stopped (periodic behavior continues for some more time but the oscillations become irregular and smaller) (see figure 1 B).
- A phase of 'small' oscillations (not always regular and distinguishable from the noise of the measuring apparatus) starts (can last up to 1 hour) (see figure 1 in between B and C)
- A phase of large, regular and ordered oscillations starts (can last up to 10 hours) (see figure 1C, 2C) .

Methods and materials

For the preparation of the BZR we used sodium bromate (8 ml of a 0.098 M solution), malonic acid (10 ml of a 0.024 M solution), sulfiric acid (10 ml of a 6.34 M solution), sodium bromide (4 ml of a 0.181 M solution) and ferroin (12 drops from the redox indicator, Reag. Ph. Eur., E0 in sulfuric acid 1 mol/l = +1,06 volt (Fluka) from Sigma Aldrich). For measuring the color change we used a LED/LDR combination as photometric unit, which was connected to the multimeter VC820 with USB that enabled us to record the color oscillations with the computer.

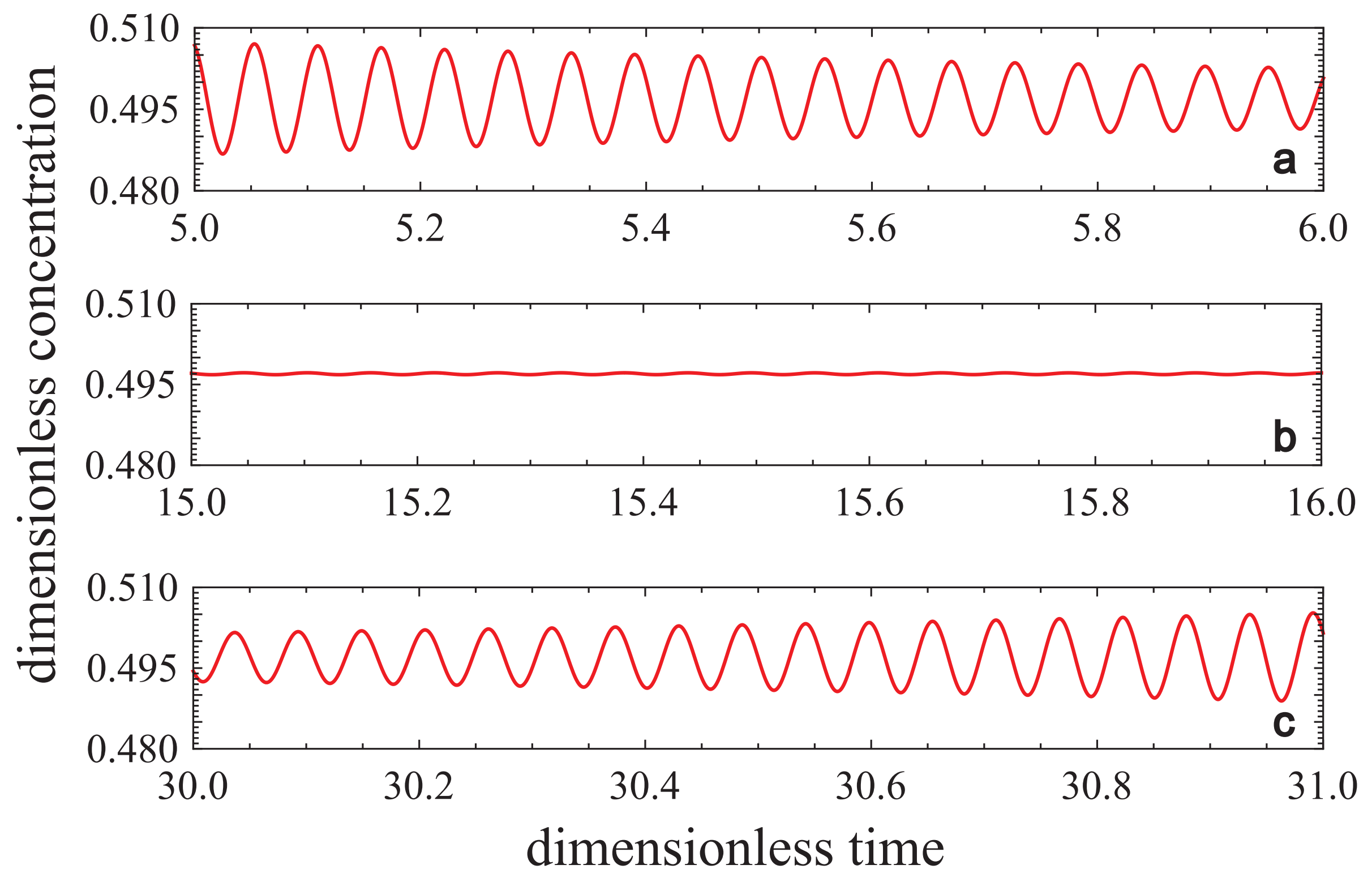

Figure 6: *Dimensionless concentration of the redox indicator for dynamic parameter f ($f(t)=f_0+10^{-6}t$, $q=10^{-3}$, $\varepsilon_1=4\cdot10^{-5}$) - detailed view.* ***a****: Shows the oscillations in the framed box a from figure 5.* ***b****: Shows the oscillations in the framed box b from figure 5.* ***c****: Shows the oscillations in the framed box c from figure 5.*

Qualitative model

Our qualitative model is based on the so called 'Oregonator' that is also know as FKN model after Field, Körös and Noyes who developed it [4,5].

The two variable FKN model has three parameters, i.e. $(f,q,\varepsilon_1)=\sigma$, that are constant for a given system. This system can exhibit different types of behaviours such as non-periodic, quasi-periodic and periodic. All this different behaviours are differentiated by different parameter sets σ_i (see figure 4). This simple model is based on the complete homogenization of the system and *does not* take into account any spatial distribution of compounds.

For our case, where the system is only stirred for a limited time we *have* to take into account an explicit flow term (as well as a diffusion term). This would lead to a set of coupled nonlinear partial differential equations. For a first qualitative model we neglect this flow term explicitly but *implicitly* incorporate it into the parameters. That means that the parameter set (i.e. σ) will be now a function of time, $\sigma=\sigma(t)$. In this '*dynamical*' FKN model it is possible that one moves within the parameter space as time pass by. The effect on the oscillatory *behaviour* of such a movement is shown in figure 5.

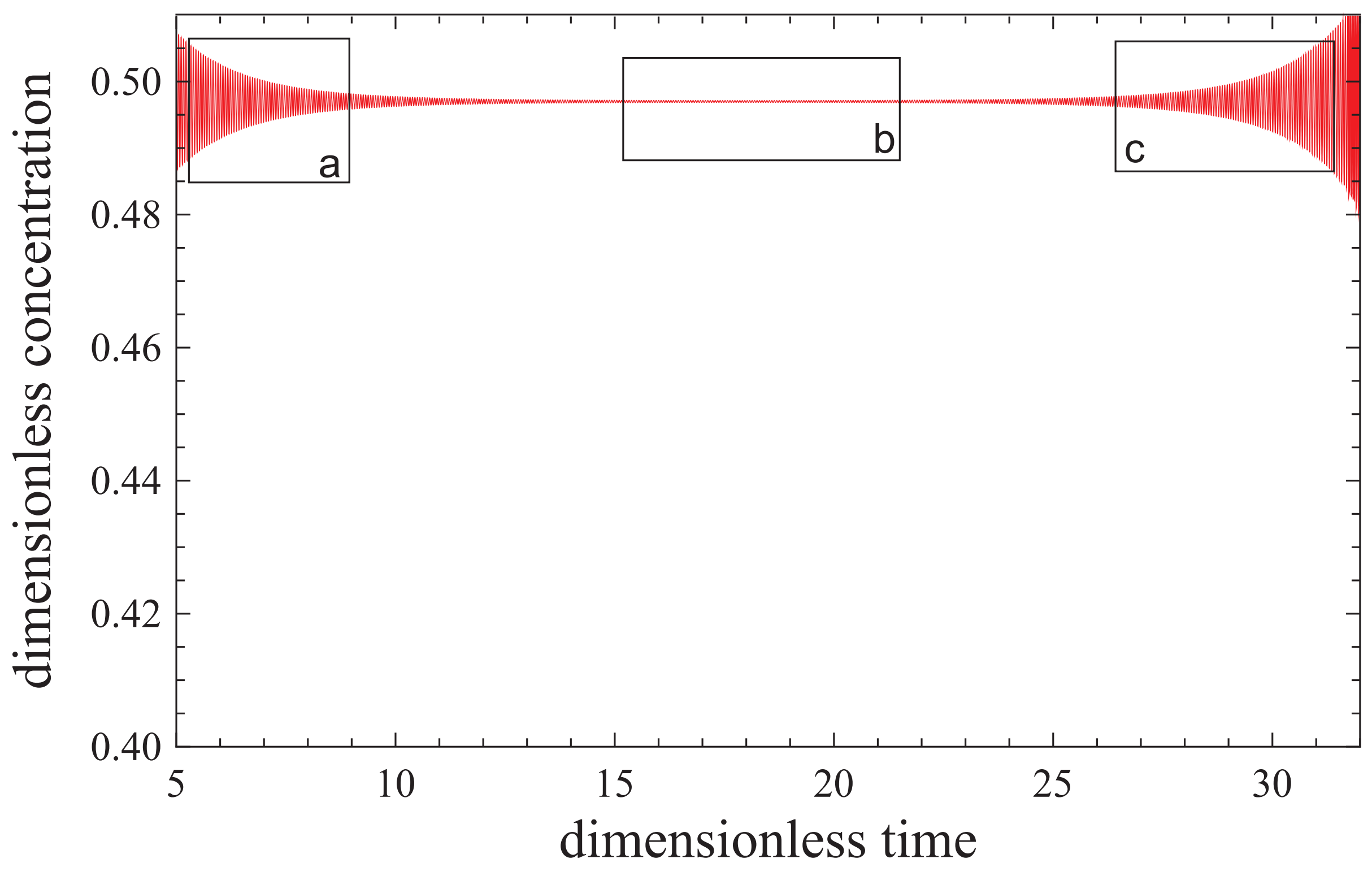

Figure 5: *Dimensionless concentration of the redox indicator for dynamic parameter f ($f(t)=f_0+10^{-6}t$, $q=10^{-3}$, $\varepsilon_1=4\cdot10^{-5}$) . For this case the oscillatory behaviour becomes also dynamic. Framed regions are in detail shown in figure 6.*

Physico-chemical justification

The time dependency of the parameters has not only a mathematical meaning it can also be understood in a physico-chemical way. Since q and ε_1 are composed of kinetic constants and *f* is a stoichiometric constant of an overall reaction, those parameters are strikingly connected to the chemical reactions taken place in the solution. It might be that the stirring of the system has some effect on the reactions in the sense that some reactions are more favourable in the stirring phase anf other are not and thus leading to a *change* in the parameters.

Outlook

What we present here is a first model which is able to describe the qualitative *behaviour* of the real system. In parallel we have already started to model the system by the complete set of coupled nonlinear partial differential equations which already includes an *explicit* flow term. The detailed solution is still one of our investigation matter and will be reported in a future article.

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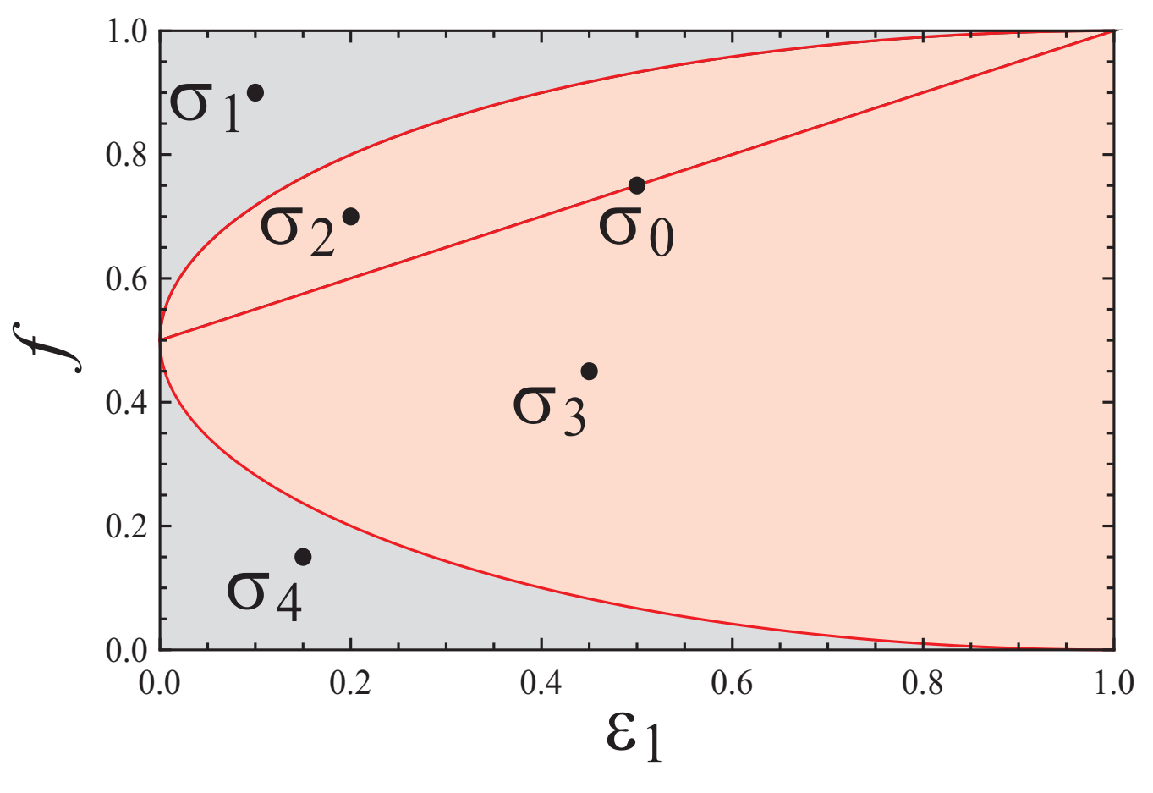

Figure 4: *Parameter space of the linear system (for q=0). The different points (σ_i) denote the different possible behaviors of the system. σ_1: Non-oscillatory behaviour with increasing amplitude. σ_2: quasi-oscillatory behaviour with increasing amplitude. σ_0: oscillatory behaviour with constant amplitude (limit cycle). σ_3: quasi-oscillatory behaviour with decreasing amplitude. σ_4: Non-oscillatory behaviour with decreasing amplitude.*

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