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Effect of temperature in a closed unstirred Belousov–Zhabotinsky system

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Abstract

Complex periodic and aperiodic behaviours are reported in an unstirred Belousov–Zhabotinsky oscillatory reaction performed at temperatures varying between 0°C and 8°C. A route to chaos following a Ruelle–Takens–Newhouse (RTN) scenario is identified. Thus, temperature effects on the coupling between chemical kinetics, diffusion and convection, seem to be responsible for the observed RTN scenario. In this Letter we demonstrate that the temperature is a bifurcation parameter for the sequence period-1 → quasiperiodicity → chaos. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Many theoretical and experimental works have been accumulated in oscillatory reactions [1]. Changes in the dynamic behaviour of an oscillating chemical system and its evolution after varying the controlling parameters have been observed and studied. The most widely studied chemical system is the Belousov–Zhabotinsky (BZ) reaction [2]. In open systems perfectly stirred a great variety of dynamical behaviours are observed. These experiments allow one to observe systems in asymptotic regimes, which means in a long time limit. As the parameters (i.e. reagent concentration and/or residence times) are varied, the qualitative structure of dynamics can change. These qualitative changes are called bifurcations [3]. In batch reactors oscillations are still observed but they exist only for a finite time interval. Sequences of complex transient oscillations have been observed both in cerium and in ferroin catalysed [4,5] closed stirred systems. Johnson et al. [6] explained theoretically this complex behaviour with a model based on the Gyorgyi–Field mechanism [7–9]. In a closed unstirred batch reactor, the BZ reaction can support a constant-velocity wave front resulting from the coupling between diffusion and kinetics [10]. These waves have been extensively studied by many investigators [11–13]. As a wave front propagates, concentration and thermal gradients are formed that alter the density of the solution, often causing convection [14,15]. Hydrodynamic flows associated with chemical wave propagation in a Belousov–Zhabotinsky solution excluding effects from evaporative cooling have been demonstrated [16]. In recent works we observed aperiodic oscillations during the chemical evolution of a closed unstirred cerium catalysed BZ system [17]. These aperiodic

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oscillations have been characterized as an example of transient chaos because they are sensitive to the initial conditions, the major distinctive feature of chaos [18]. The onset of chaos spontaneously starts by a Ruelle–Takens–Newhouse (RTN) scenario [19] as soon as convection motion couples to diffusion and local kinetics [17,18]. Further it has been shown that the medium viscosity is a controlling parameter of the system for the transition to chaos [20]. The increasing viscosity lowers the amplitude of convection and its coupling with diffusion and kinetics loses importance for the evolution of the system. We performed a series of experiments in order to assess the role of temperature in the evolution of a BZ system in an unstirred batch reactor. The cerium absorbance ($\lambda = 320$ nm) during 20 h of evolution was detected at different temperatures. In this Letter we will show that the temperature is another bifurcation parameter responsible for the transition periodicity to chaos by an RTN scenario of a closed unstirred BZ reaction.

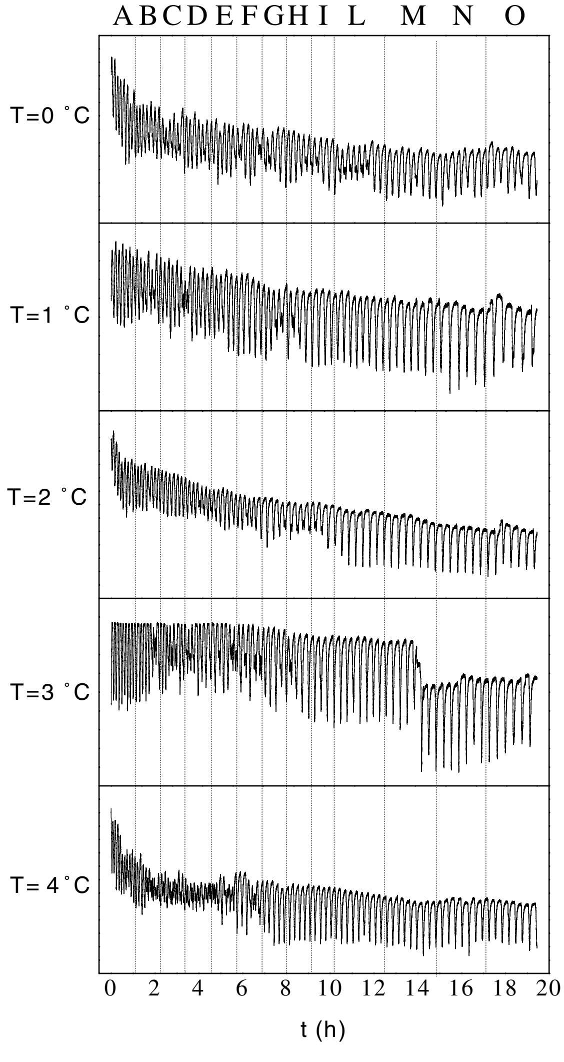

Fig. 1. Spectrophotometric recording ($\lambda = 320$ nm, sampling time $\tau_s = 1$ s) at 0°C $\leqslant T \leqslant$ 4°C. Capital letters denote the intervals of pseudo-stationary regime. From A to I the interval length is 4096 s; from L to O the length is 8192 s.

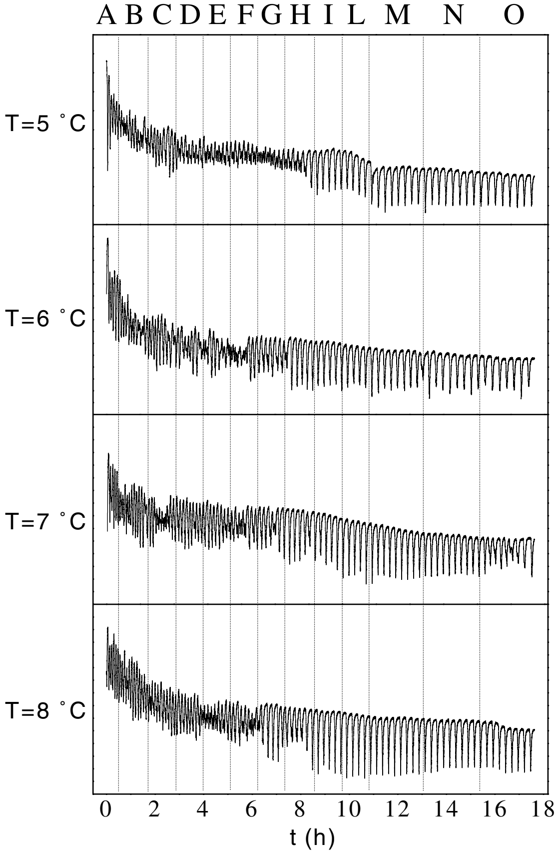

Fig. 2. Spectrophotometric recording ($\lambda = 320$ nm, sampling time $\tau_s = 1$ s) at 5°C $\leqslant T \leqslant$ 8°C. Capital letters denote the intervals of pseudo-stationary regime. The first interval length is 2048 s, from B to L the length is 4096 s and from M to O the length is 8192 s.

2. Experimental

All experiments were performed isothermally at temperatures varying between 0°C and 8°C in a batch reactor (spectrophotometer cuvette, 1 × 1× 4 cm^3). The dynamics were monitored by the solution absorbance at 320 nm using quartz UV grade spectrophotometer cuvettes. A double beam spectrophotometer (Varian, series 634) was used. All chemicals were of analytical quality and were used without further purification. The following concentrations of reactant stock solutions were used: $Ce(SO_4)_2$ 0.004 M, malonic acid 0.30 M, $KBrO_3$ 0.09 M; each stock solution was 1 M

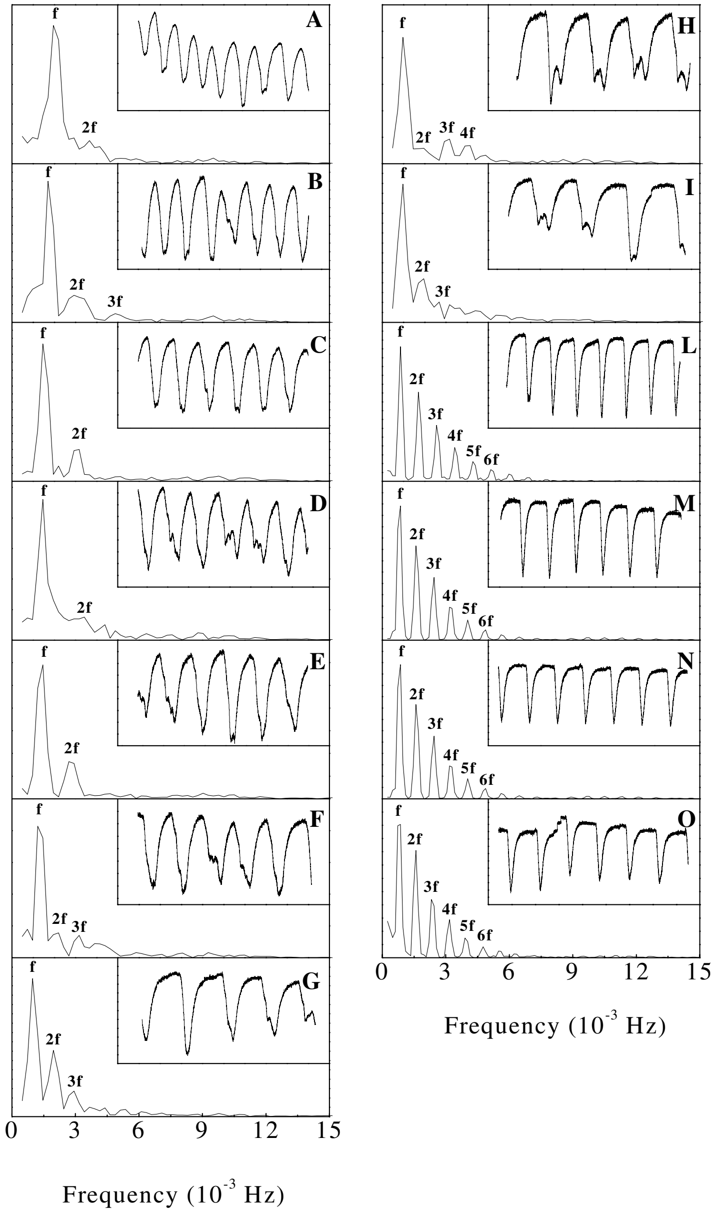

Fig. 3. Fast Fourier Transform of the intervals reported in Fig. 1 for $T = 3°C$. In the insets are reported the intervals.

H_2SO_4. The oscillator was started by mixing equal quantities of reactants in a flask. A thermostat has been used in order to keep the temperature constant in the cuvette; the uncertainty in temperature measurements was ±0.1°C. The solution was stirred for 5 min with a 1 cm length teflon-coated magnetic stirrer, at a constant high stirring rate, then was poured into the cuvette until the sample reached the top, and measurement of the signal began. The cross-sectional area of the spectrophotometer light beam was 30 mm^2. The volume spanned by the beam was 300 mm^3 (7.5% of the total volume) and was located 2 cm away from the liquid–air interface, 1 cm away from the bottom of the cuvette and about 0.4 cm away from the sides. The spectrophotometer was connected to an IBM compatible PC for data acquisition by an analogue to digital board converter with a 12 bit resolution. The absorbance was recorded with a $\tau_s = 1$ s sampling time. Time series points were recorded and stored in the computer for data analysis. Fast Fourier Transform was applied in order to characterize the signal.

3. Results and discussion

Spectrum series recorded at different temperatures between 0°C and 8°C are shown in Figs. 1 and 2. In order to study a stationary signal, every spectrum was divided into 13 intervals whose size was chosen in the range 2048–8192 s. The recurrence analysis [17,21–23] was made to choose the right size of the interval. In Fig. 3 are reported the

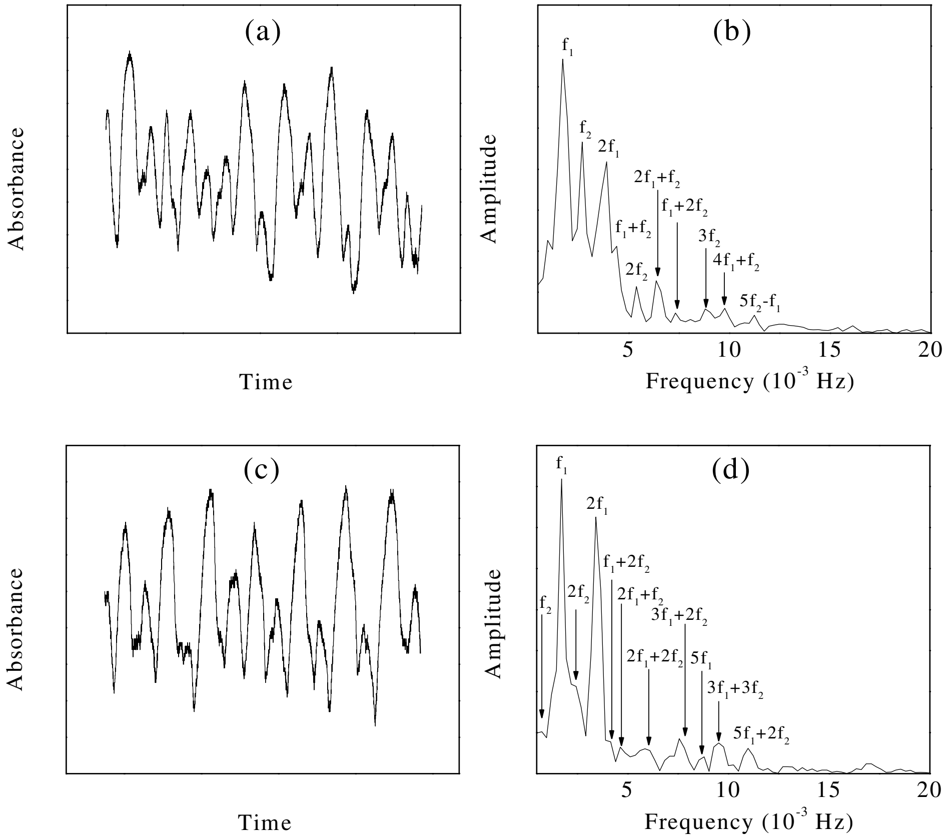

Fig. 4. Spectrophotometric recordings and FFTs of the two frequencies quasiperiodic interval for the acquisition at $T = 4°C$ (a,b) and $T = 5°C$ (c,d).

FFTs of the signal acquired at $T = 3$°C; the fundamental frequency and few harmonics are observed for every interval. This result shows that the dynamic regime is always periodic at this temperature. Nevertheless the frequency of the oscillations decreases in time as reagents are consumed. As a matter of fact our reactor is closed and the chemical reaction will reach thermodynamic

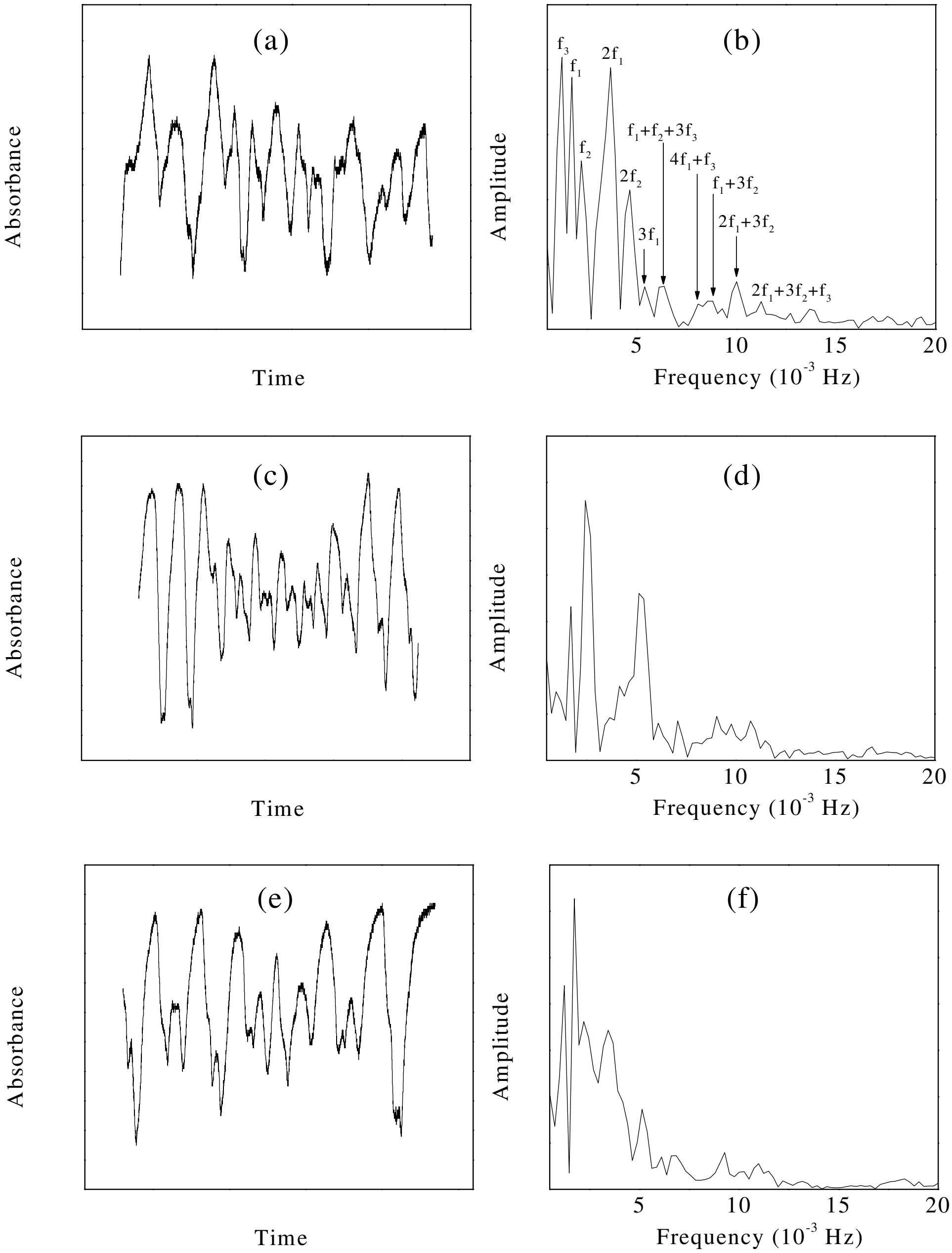

Fig. 5. Spectrophotometric recordings and FFTs of the 3 frequencies quasiperiodic interval for the acquisition at $T = 6$°C (a,b) and of the chaotic intervals at $T = 7$°C (c,d) and $T = 8$°C (e,f).

equilibrium. From a dynamical point of view the trajectory in phase space should be a slowly winding spiral. In a short period of time (about 4092 s) the signal is almost stationary and the trajectory is approximately a limit cycle in phase space. The same behaviour can be observed in the range 0–2°C. When the temperature reaches 4°C a new behaviour is observed. The FFTs show the fundamental frequency and few harmonics for every interval except for interval E where, as shown in Fig. 4b, two irrationally related frequencies were detected: $f_1 = 1.708 \times 10^{-3}$ Hz and $f_2 = 2.685 \times 10^{-3}$ Hz. The supposed attractor is a *2-fold torus* in phase space. The same quasiperiodic behaviour is observed when the temperature reaches 5°C (Fig. 4c,d). In this case the frequencies detected are $f_1 = 1.708 \times 10^{-3}$ Hz and $f_2 = 1.220 \times 10^{-3}$ Hz. When the experiment was performed at 6°C, three irrationally related frequencies were observed (Fig. 5b): $f_1 = 1.708 \times 10^{-3}$ Hz, $f_2 = 2.197 \times 10^{-3}$ Hz and $f_3 = 1.220 \times 10^{-3}$ Hz. The attractor should correspond to a *3-fold torus* in phase space. It is almost rare to find very convincing examples of a quasiperiodic system with a 3-fold torus, because the nonlinear coupling between the modes corresponding to the different frequencies tends to destroy quasiperiodicity and replace it by chaos [24]. Nevertheless in Fig. 5a,b we have a very good example of this type of system. A broadband spectrum, namely a chaotic regime, is observed when the temperature is over 7°C (Fig. 5d,f). These results allow us to identify an RTN transition to chaos as the temperature rises as reported below:

periodic oscillation (limit cycle)
$0°\mathrm{C} \leqslant T \leqslant 3°\mathrm{C}$
↓
quasiperiodic oscillation (2-fold torus)
$4°\mathrm{C} \leqslant \mathrm{T} \leqslant 5°\mathrm{C}$
↓
quasiperiodic oscillation (3-fold torus)
$T = 6°\mathrm{C}$
↓
chaotic oscillation (strange attractor)
$7°\mathrm{C} \leqslant T \leqslant 8°\mathrm{C}$

At higher temperatures until 25°C we always detect regions of chaotic regime as reported in other papers [17]. Temperature is an important control parameter for the transition to chaos for this system.

4. Conclusion

Our results prove unambiguously that the temperature is a bifurcation parameter of the closed unstirred BZ reaction. The dynamics can be explained by a Ruelle–Takens–Newhouse scenario where the system undergoes three Hopfs bifurcations.

Acknowledgements

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