Irregular behaviors of two chemical oscillators with a diffusion coupling

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Dynamic behaviors of two chemical oscillators coupled with a time delay were investigated at the border between regions of 1:1 and 2:1 entrainment. Chemical oscillators were realized by immersing cation exchange beads loaded with the ferroin catalyst in the Belousov-Zabotinskii reaction solution. On decreasing the distance d between two oscillators, subharmonic entrainment at commensurate frequency ratios such as 2:1, 3:2, and 4:3 occurred in that order. When d was further decreased, an irregular behavior was observed in the slower oscillator near the coupling region of 1:1. The time series for these states were characterized in terms of their power spectra, reconstructed attractors, and the largest Lyapunov exponent to confirm the feature of chaos. [S1063-651X(97)06502-1]

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I. INTRODUCTION

The coupling of nonlinear oscillators has been investigated to provide insight into the understanding of important features of biological oscillators such as coupled heart cells [1,2]. Many experimental studies have been carried out in the Belousov-Zabotinskii (BZ) reaction system using two or three continuous stirred tank reactors (CSTR's) [3–10]. A variety of interesting dynamic phenomena have been observed depending on the flow rate: entrainment, phase locking, propagation failure, and chaotic behaviors. These behaviors have been theoretically explained using various coupled oscillator models [11–18]. Very recently, we have investigated the properties of coupling in the discrete BZ reaction system different from the CSTR's [19]. This system is similar to that described by Maselko and Showalter, in which the ferroin catalyst is immobilized in cation exchange beads with spatial size of the same order as living cells [20–22]. The features of coupling in this system are peculiar compared with those of CSTR's. For example, the coupled frequency becomes higher than the natural frequency of the faster oscillator. In addition, the coupling is inherently accompanied by a time delay, since it is due to a mass diffusion. Such a time-delayed coupling is commonly seen in the information transmission between biological oscillators. This system can be easily extended to large populations of coupled oscillators and may serve as a realistic model for intercellular communication. It is now interesting to clarify whether or not this type of coupled oscillator exhibits chaotic behaviors as observed in CSTR's.

In this report we investigate dynamic aspects of the transition between two coupled states by using the discrete BZ reactor described above. The time series for dynamic behaviors are analyzed in terms of power spectra and reconstructed attractors. Furthermore, the largest Lyapunov exponent is calculated to confirm the existence of chaos. To our knowledge, there are no experimental reports on chaotic behaviors of coupled chemical oscillators of submillimeter size.

II. EXPERIMENT

The initial composition of BZ reaction solution was as follows: $[NaBrO_3]=0.49M$, $[NaBr]=0.07M$, $[CH_2(COOH)_2]=0.14M$, and $[H_2SO_4]=0.67M$. Water was twice distilled from deionized water and filtered through a 0.1-μm membrane filter. These materials were reagent grade and used without further purification. The cation exchange beads (DOWEX 50W-4X) of about 500 μm in diameter were loaded with ferroin ($[\text{ferroin}]=1.7\times10^{-5}$ mol/g beads). When ferroin-loaded beads were immersed in the BZ solution, the circular wave propagating on the bead surface appeared. The features of the redox reaction confined to the bead surface were monitored through a charge-coupled device (CCD) camera attached to a microscope and recorded on a video tape recorder. The change between blue and red colors was transformed into the change in light intensity by the imaging system (Avionics, Excel II), where the intensity was obtained by averaging the gray level of the fixed small area on the bead surface, corresponding to a grid of 3×3 pixels. Thus, we regarded the ferroin-loaded cation exchange bead as a chemical oscillator with a limit cycle. The period of the oscillation strongly depended on both the temperature and the composition of the BZ solution. Furthermore, the period rapidly and randomly decreased with time just after beads were immersed in the BZ solution. This is probably related to a dissolution of extra ferroin on the bead surface in the BZ solution. After a certain time, the rate of decrease became negligibly small and stationary. The period finally attained varied from bead to bead, even if bead sizes were almost the same. This is probably due to the difference in concentration of ferroin remaining on the bead surface without dissolving into the BZ solution. The ability to keep ferroin on the bead surface is considered to be influenced by the difference in structure of the bead surface. Thus, we obtained coupled oscillators with the frequency ratio up to about 3.7 by using a combination of beads with different natural frequencies. The temporal resolution for successive images was limited by the time required for data storage. The present system allowed examination of successive images at the time interval of 0.1 s.

The coupling strength was controlled by changing the distance d between two beads; the smaller the d, the larger the coupling strength. Here, d refers to the spacing between beads, so that $d=0$ means that beads are in contact with each other. Prior to a coupling experiment, many beads were im-

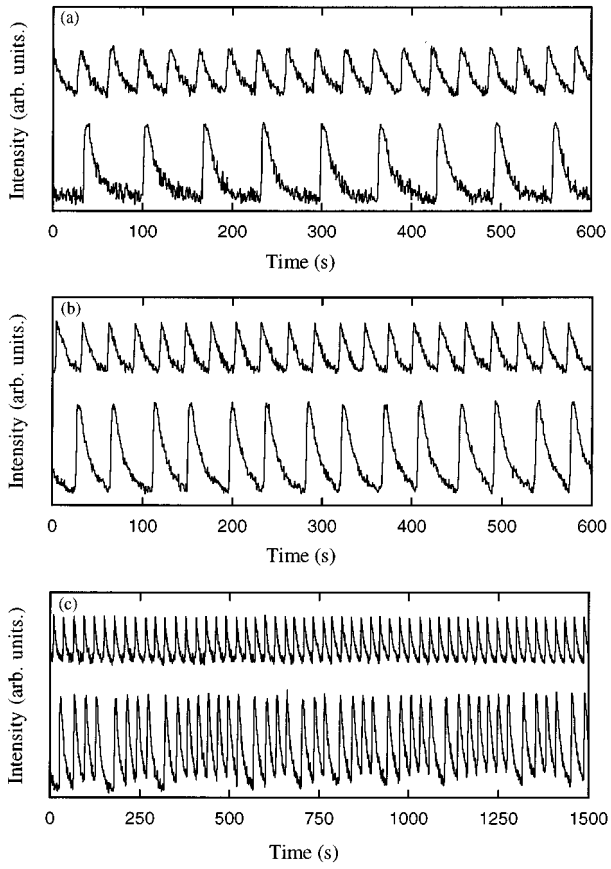

FIG. 1. Time series of light intensity from the two coupled oscillators with the natural frequency ratio of 2.3: (a) 2:1 entrainment, (b) 3:2 entrainment, and (c) irregular coupling.

mersed in the BZ solution until the oscillation became periodic. Then, two beads with the desired natural frequency ratio were transferred into the fresh BZ solution and coupled to each other. The coupled state depended on temperature, so that the temperature of the BZ solution was maintained at 23 ± 0.05 °C.

III. RESULTS AND DISCUSSION

We used two beads of almost the same size with the natural frequency ratio $\omega_2/\omega_1=2.3$, where ω_1 and ω_2 are the natural frequencies of slower and faster oscillators, respectively. Starting at the distance of 170 μm, we investigated the scenario of the transition from the coupled state of 2:1 to that of 1:1 while decreasing the distance d. This boundary region corresponds to the weak coupling region in the phase diagram obtained in our previous work [19]. Figure 1(a) shows the time courses from two oscillators under entrainment of 2:1, which was observed in the region of 80 μm$\leqslant d\leqslant$170 μm. Here, the oscillator bearing the upper trace plays the role of a pacemaker. In the region of 70 μm$\leqslant d\leqslant$80 μm, entrainment of 3:2 appeared, as shown in Fig. 1(b). In the vicinity of this region, a regular coexistence of 2:1 and 3:2, in addition to entrainment of 4:3, was also observed. As the coupling region of 1:1 was further approached, the coupling behavior depended more sensitively on d. Figure 1(c) shows time series of two coupled oscillators at $d=65$ μm, where, to maintain clarity in the figure, only a part of the data collected over 2400 s is represented. We can see irregular behaviors in both the period and the amplitude of the lower trace corresponding to the slower oscillator, i.e., an irregular occurrence of 1:1 entrainment. A closer inspection of the upper trace reveals that there also exist small irregularities of the same kind as those in the lower trace, but not pronounced as in the latter. This irregularity may be due to chaos, whose appearance was confined in only the very narrow region centered at 65 μm. Decreasing d below 60 μm, the stable entrainment of 1:1 appeared.

A sequence of transition phenomena was reproducible for coupled oscillators with the natural frequency ratio around 2:3. In contrast, at large ω_2/ω_1 above about 2:9, regions of subharmonic entrainment, as observed in this experiment, could not be clearly identified as functions of d. This is probably due to the condition that the boundary region between regions of 1:1 and 2:1 entrainment becomes rapidly narrow with an increase of ω_2/ω_1, according to the phase diagram of coupling states obtained in our previous work [19]. The threshold distance for each transition was dependent on the bead size and the temperature of the BZ solution. Irrespective of values of these variables, however, transition phenomena as described above were observed. The irregular behavior was observed only when the ratio of natural frequencies of the two oscillators, ω_2/ω_1, was large. This suggests that the ratio ω_2/ω_1 is an important quantity governing the appearance of the irregular behavior.

The question to be answered is whether or not the irregular behavior of the slower oscillator shown in Fig. 1(c) is truly due to chaos. Further information can be obtained by analyzing the time series in terms of Fourier spectra, the reconstructed attractor, and the Lyapunov exponent. Here, all the data obtained were used for a reliable estimate of these quantities. Figure 2(a) shows the power spectrum of the time series under entrainment of 2:1. The observed periodic oscillation results in the sharp peaks and associated harmonics. Under entrainment of 3:2, the number of peaks increases and the spectrum becomes complex, as shown in Fig. 2(b). However, the contribution of major peaks is seen to be sufficiently higher than the baseline noise. By contrast, the power spectrum of the irregular oscillation has no sharp peaks but a broadband characteristic of the chaotic state, as shown in Fig. 2(c). For further examination of this irregular oscillation, the three-dimensional phase portrait was constructed using the time-delay method. Figure 3 shows the case with a time delay $T=3.5$ s. Although the attractor includes some noise inherent in the optical detection of the redox reaction, it seems to be indicative of chaos. In addition to the attractor, the largest Lyapunov exponent λ was calculated with the method published by Wolf *et al.* [23] and $\lambda=0.14$ was obtained. The fact that the value of λ is positive, though small, implies the divergence of trajectories. Thus, these results suggest that the irregular behavior shown in Fig. 1(c) is chaotic. Chaotic behaviors in coupled chemical oscillators have been experimentally found in various types of systems: batch reactors [3], CSTR systems based on a mass exchange coupling [4,9], and electrical coupling [6,10]. These systems are all coupled without a time delay. Chaotic behaviors may be common features of the coupled reacting system irrespective of the presence of a time delay.

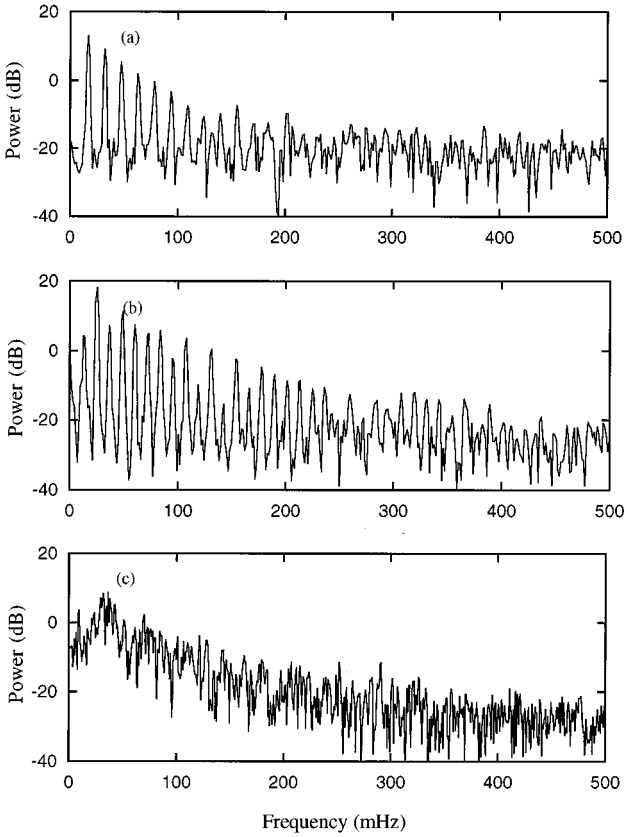

FIG. 2. Power spectra of time series of light intensity: (a) 2:1 entrainment (b) 3:2 entrainment, and (c) irregular coupling.

IV. CONCLUSION

We investigated the scenario of transition from 2:1 entrainment to 1:1 entrainment in time-delayed coupled oscillators of submillimeter size distributed spatially. On decreasing the distance between oscillators, we observed the sequence of subharmonic entrainment that can be described in terms of a Farey tree, taking 1:1 and 2:1 as the parent states. In the vicinity of the coupling region of 1:1, we observed the irregular coupling. This irregular behavior seems to be chaotic. Below the critical distance d_c, the stable entrainment of 1:1 necessarily appeared.

The appearance of the irregular behavior cannot be exactly explained at the present stage, but can be only speculated by making use of the idea of the frustration in a coupled Ising spin system [8,24,25]. The slower oscillator is more significantly perturbed by coupling than the faster oscillator. Then, coupling is supposed to exert two effects on the slower oscillator; one contributes to keeping the period of the slower oscillator at the intrinsic period, and the other contributes to forcing the period of the slower oscillator to harmonize with that of the faster oscillator. When natural frequencies of two oscillators differ greatly from each other, entrainment will certainly bring about some frustration to the slower oscillator entrained. This tendency will become more pronounced as the order of subharmonic entrainment becomes higher. Above d_c, corresponding to the weak coupling region, entrainment is not very stable. As a result, a release from entrainment will sometimes occur. This may be responsible for the appearance of irregular behaviors. Thus, irregular entrainment may be regarded as a sort of compensation action for the frustrated slower oscillator. Below d_c, on the other hand, the slower oscillator is completely entrained by the faster oscillator owing to a strong coupling, and as a consequence such a compensation action will no longer be able to occur. The present chaotic behavior arises from coupling and it is apparently different from that seen in the uncoupled oscillator system, in which bifurcation to chaos is controlled by the composition of a reaction solution.

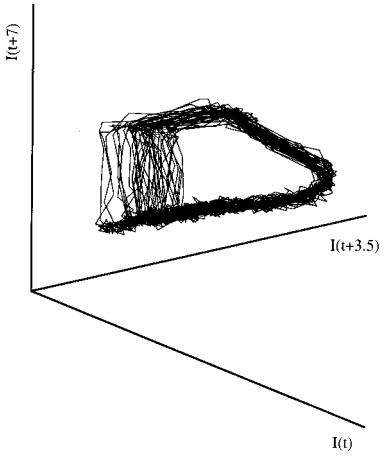

FIG. 3. Phase portrait for the irregular behavior of the slow oscillator. The trajectory is constructed in a three dimensional phase space using the time-delay method with a time delay $T=3.5$ s.

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