Pulse-coupled Belousov-Zhabotinsky oscillators with frequency modulation

Viktor Horvath, and Irving R. Epstein

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Coupling of oscillators can result in a variety of collective dynamical behaviors, in which the frequencies generally differ from those of the oscillators in isolation: inhibitory interactions lead to lower frequency, while excitatory interactions produce behaviors with increased frequency. Using numerical simulations, we explore the dynamics of two pulse-coupled Belousov-Zhabotinsky oscillators when frequency modulators (which can increase or decrease the frequency of the oscillators) are combined with coupling agents. New dynamical regimes emerge with a host of complex temporal patterns when frequency modulation (FM) is antagonistic to the natural frequency change resulting from excitatory or inhibitory coupling. We analyze the properties of the patterns and show the correlation between the frequency modulation strength and the pattern characteristics.

INTRODUCTION

The collective dynamics of coupled oscillatory systems comprised of bacterial cells, neurons, fireflies, wireless networks, and chemical oscillators has been extensively studied. Interaction between chemical oscillators may be implemented in a variety of ways, such as diffusion, electrical connections, mass transfer, pulses of light, or chemical pulses. A pair of pulse-coupled Belousov-Zhabotinsky (BZ) oscillators exhibits various synchronization modes, such as in-phase or out-of-phase synchronization, multipeak temporal patterns, and bursting. Systems consisting of a population of oscillators with different frequencies have been well-studied, and a variety of resonant, synchronized, partially synchronized, and chaotic modes can develop.

In this paper, we report the results of a numerical study of the dynamical behavior of two ferroin-catalyzed BZ oscillators coupled via chemical perturbations. We model perturbations by an activator (AgNO₃) or an inhibitor (KBr), combined with a frequency modulator (a strong acid or base). Excitatory perturbations cause the next cycle to be triggered, whereas inhibitory perturbations delay the next cycle. We have shown that ferroin-catalyzed BZ oscillators operated in a flow reactor do not behave as simple phase oscillators when perturbed by KBr: the period increases and then returns to the unperturbed value only after several cycles. This recovery exhibits exponential decay with a time constant close to the flow rate ($k_0$) used in the experiments, and the initial deviation from the relaxed frequency depends on the strength of inhibition.

Previously, the magnitude and the direction of this effect were not controllable: it was a consequence of the perturbations, and the magnitude depended on the strength of the coupling. We were motivated to investigate the dynamics of coupled oscillators when the frequency modulation (FM) is controlled independently. The frequency of the oscillations in the BZ reaction shows strong dependence on the acidity of the medium. Thus, by adding a strong acid or base to the perturbing solution, the transient changes of the frequency can be modulated. The magnitude of the frequency change depends both on the amount of the frequency modulator and also on how often the perturbations occur. Therefore, not only does the modulation affect the collective behavior of the coupled oscillators, but their collective dynamics also causes a feedback in the frequency change. Such modification to
pulse-coupling enables us to examine several interesting scenarios, in which the FM can be synergistic or antagonistic to the excitatory or inhibitory coupling.

METHODS

Our model of pulse-coupled BZ oscillators represents a slight modification of our previous work.21 We introduce an additional variable \( h \), which corresponds to the acidity of the reaction medium in an experiment, i.e., \([H^+]\). In order to avoid the slowdown of the numerical integration, we neglect terms associated with the mass action kinetics of \( H^+ \) consumption. This approximation is justified by the fact that any changes in \([H^+]\) due to the chemical reaction are very small compared to the total amount of acid in the reaction mixture

\[
\frac{dx}{dt} = -k_1 hxy + k_2 h^2 ay - 2k_3 x^2 + k_4 hax \zeta(z) - k_0 x, \quad (1)
\]

\[
\frac{dy}{dt} = -k_1 hxy - k_2 h^2 ay + k_0 vz + k_{11} p - k_{diff} yAg - k_0 y, \quad (2)
\]

\[
\frac{dz}{dt} = 2k_4 hax \zeta(z) - k_0 vz - k_{10} bz - k_0 z, \quad (3)
\]

\[
\frac{dv}{dt} = 2k_1 hxy + k_2 h^2 ay + k_3 x^2 - k_0 vz - k_{13} vz - k_0 v, \quad (4)
\]

\[
\zeta(z) = \frac{z_{max} - z}{z_{max} - z + k_{ref} \sqrt{3k_4 k_{10} z_{max}}}, \quad (5)
\]

\[
\frac{dh}{dt} = (h_0 - h)k_0, \quad (6)
\]

\[
\frac{dAg}{dt} = -k_{diff} yAg - k_0 Ag, \quad (7)
\]

\[
\frac{dp}{dt} = -k_{11} p - k_0 p, \quad (8)
\]

\[
\frac{da}{dt} = -k_2 h^2 by - k_4 hax \zeta(z) + (a_0 - a)k_0. \quad (9)
\]

The variables \( x, y, z, v, h, Ag, p, \) and \( a \) correspond to the concentrations of \( HBrO_2, Br^- \), ferrin (the oxidized form of the ferroin catalyst), bromomalonic acid (BrMA), hydrogen ion, silver ion, bromide ion-releasing intermediate (see below), and bromate ion, respectively. The model parameters are: \( k_1 = 2 \times 10^6 \) M\(^{-2}\) s\(^{-1}\), \( k_2 = 2 \) M\(^{-3}\) s\(^{-1}\), \( k_3 = 3000 \) M\(^{-1}\) s\(^{-1}\), \( k_4 = 42 \) M\(^{-2}\) s\(^{-1}\), \( k_0 = 20 \) M\(^{-1}\) s\(^{-1}\), \( k_{10} = 5 \times 10^{-2} \) M\(^{-1}\) s\(^{-1}\), \( k_{13} = 5 \times 10^{-3} \) s\(^{-1}\), \( k_0 = 5 \times 10^6 \) M\(^{-1}\) s\(^{-1}\), \( k_{11} = 2 \times 10^{-2} \) s\(^{-1}\), and \( k_{diff} = 5 \times 10^9 \) M\(^{-1}\) s\(^{-1}\). The following feed concentrations, \( a_0 = [NaBrO_3]_0 = 0.2 \) M, \( b = [MA] = 0.1 \) M, \( z_{max} = [ferroin]_0 = 2 \times 10^{-3} \) M, \( h_0 = [H^+]_0 = 0.333 \) M, and flow rate, \( k_0 = 1.25 \times 10^{-3} \) s\(^{-1}\), are used unless stated otherwise. These generate an unperturbed cycle length of 143.8 s. We have previously introduced a bromide ion-releasing intermediate (the exact chemical entity is still to be identified) to capture the long-term relaxation dynamics of the limit cycle when inhibitory perturbations are used. This modification also mimics the low sensitivity to intermediate KBr additions around the peaks.21 Each oscillator is modeled using a separate set of differential equations integrated using the ode15s variable order solver for stiff problems included in MATLAB.26 An absolute tolerance of \( 10^{-12} \) and a relative tolerance of \( 10^{-6} \) were used. Unless otherwise stated, oscillators 1 and 2 were initially 29.17 s and 102.08 s, respectively, into their cycles, ensuring that the calculations do not start at a peak.

High amplitude peaks in variable \( z \) are detected when \( z \) increases through the threshold, \( 1.5 \times 10^{-3} \). The coupling mimics the synaptic connections between neurons: when one oscillator produces a peak, the other oscillator receives a perturbation (after a time delay \( \tau \)) and vice versa. Parameters \( z, v, p, \) and \( h \) correspond to perturbations to variables \( Ag, p, \) and \( h \) respectively. When we model additions of a strong acid, \( \mu \) is positive; when we model additions of a base, it is negative; the values of \( \mu \) correspond to the acid or base concentration in mol/l. To stress the numerical nature of our results, we omit the concentration units in figures and in the text for numerical results, but note that the units of our model variables as well as the coupling parameters are mol/l.

Perturbations are implemented as additions (or subtractions for \( \mu < 0 \)) to the corresponding variable: for example \( h_2^+ (t_1^+ + t_{1-2}) = h_2(t_1^- + t_{1-2}) + \mu_{1-2} \) where \( h_2^+ (t_1^+ + t_{1-2}) \) refers to the value of variable \( h \) of oscillator 2 immediately after the perturbation that takes place with a delay of \( t_{1-2} \) after the peak of oscillator 1 at \( t_1^- \). In this paper, we explore behaviors when coupling is symmetric, that is, when the parameters for perturbations to oscillator 2 triggered by peaks of oscillator 1 are identical to those for perturbations to oscillator 1 triggered by peaks of oscillator 2. For example, perturbations in symmetrical excitation coupling with positive FM and a 15 s time delay can be described as follows: \( e_{1-2} = e_{2-1} = 0, u_{1-2} = u_{2-1} > 0, \mu_{1-2} = \mu_{2-1} > 0, \) and \( t_{1-2} = t_{2-1} = 15 \) s. Since the parameters are identical in the \( 1 \to 2 \) and \( 2 \to 1 \) directions, we only report a single value for the non-zero coupling parameters; thus, the previous example can be written as \( z > 0, \tau = 15 \) s.

RESULTS AND DISCUSSION

Frequency dependence on \( h_0 \)

The frequency of the ferroin-catalyzed BZ reaction exhibits strong dependence on the concentration of \( H^+ \) when the reaction is run in a batch reactor.25 We surveyed the unperturbed frequency of the oscillator in our model by varying the \( h_0 \) parameter while keeping the other parameters fixed. Our results confirm that the period depends strongly on \([H^+]\) in the reactant feed. The correlation appears to be log-log, similar to a previous report25 for batch oscillations (Fig. 1).

FM of a single pulse-perturbed oscillator

We exploit the strong dependence on the acid concentration to introduce FM: if perturbations are made with a higher acid concentration than \( h_0 \), the acid concentration in the mixture should increase slightly and recover as the flow restores \( h \) to its initial level. If perturbations are made periodically, the acid concentration should increase slightly and recover as the flow restores. If the perturbations are linked to
the dynamics of the oscillator, i.e., if they are triggered by the peaks, then the acid concentration will also depend on the frequency-modulating effect.

We modeled the dynamics of one oscillator perturbed after each peak (with $h_0$ set at 0.333) to study the effect of regular perturbations of the variable $h$. Figure 2 shows the dynamics of a single oscillator when perturbations to $h$ were carried out 10 s after each peak ($l_1 = 0.01$, $s_1 = 10$ s, and $e = 0$, $x = 0$).

The value of $h$ increased after each perturbation, and it oscillated between 0.4025 and 0.4125 when the quasi-stationary state was achieved. The period gradually decreased from the initial 143.8 s to 107.4 s when the perturbations were stopped at 8500 s. Recovery to the initial period was completed after about 4000 s ($\approx 5$ times the reactor’s residence time, $k_0^{-1}$).

When perturbations are triggered by the peaks of the perturbed oscillator, a positive FM ($\mu > 0$) generates an indirect positive feedback on $h$: an increase in $h$ results in an increase in the frequency at which perturbations take place, which in turn further increases $h$. At high $\mu$, this can cause an explosive frequency increase, which is experimentally unfeasible, because pulse-perturbations cause dilution (less than 1% of the total volume per perturbation), which is compensated for by the flow only if the time between two perturbations is long enough. When perturbations occur too frequently, i.e., the flow created by them is greater than the inflow of the reactants, the reaction mixture becomes depleted of the reactants, and the oscillations cease. (Based on a flow rate of $1.25 \times 10^{-3}$ s$^{-1}$ and a dilution factor of 0.67%, perturbations occurring more frequently than every 5.3 s will produce this effect.)

In order to ascertain the maximum feasible FM value, we modeled the dynamics of a single pulse-perturbed oscillator when perturbations of different magnitudes take place 2 s after each peak. When the quasi-stationary state was reached (the standard deviation of the frequency of the last 10 cycles was less than $10^{-4}$ s), we took the time-average of $h$ during the last cycle (Fig. 3).

Strong positive feedback caused by the FM is clearly apparent when $\mu > 0.01$. We had difficulty in reaching the quasi-stationary state at the required precision above $\mu = 0.0233$, and the limit cycle collapsed above 0.025 (Supplementary material Fig. 1.) These FM limits may be higher when two oscillators are coupled, because the intrinsic delay between the two peaks will lower the frequency of the perturbations.

**Inhibitory coupling and FM**

When two BZ oscillators are coupled using symmetrical inhibitory pulses and the perturbations immediately follow the peaks ($\tau = 0$ s), the oscillators synchronize anti-phase (AP), or display an oscillatory-suppressed state (OS) (high amplitude peaks in $z$ no longer appear for one of the oscillators). When the coupling is inhibitory ($e > 0$) and FM is positive ($\mu > 0$), complex temporal patterns develop in a large region between the AP and OS domains as shown in Fig. 4.

Besides the 1:N and N:M patterns that we reported previously for pulse-coupled oscillators with unequal inhibitory coupling, we find two additional pattern types: N:N AF (N > 1) and Nx(1:M) AF (N > 1, M > 1) [Figs. 5(a) and 5(b)].

The N:N AF type patterns (AF signifies that the peaks of the two oscillators align at the frame borders) appear at
higher \( \mu \) values, and the number of cycles, \( N \), for each oscillator in these patterns increases as \( e \) increases and decreases as \( l \) increases. The fine structure of some of the \( N:N \) AF patterns that appear at lower \( e \) is interesting as well: all the \( N \) peaks appear in aligned frames, and the periods of the two oscillators display symmetry. For example, the complex \( 22:22 \) AF pattern [Fig. 5(a)] can be written as a sequence of simpler patterns: \([10:1 \ 4:1 \ 3:1 \ 1:1] \ || \ [1:10 \ 1:4 \ 3:1 \ 1:1] \), where \( || \) indicates where the preceding sequence starts to repeat with the \( N \) and \( M \) numbers reversed. Patterns such as this one exhibit the following general structure: \([N(1):M(1) \ N(2):M(2) \ ... \ N(x):M(x)] \ || \ [M(1):N(1) \ M(2):N(2) \ ... \ M(x):N(x)]\), where the numbers in parenthesis are the indices of the simple patterns that the complex pattern is comprised of. This pattern is particularly interesting, because the sequence \( 10:1 \ 4:1 \ 3:1 \ 1:1 \) contains \( N:N \) and \( N:M \) elements, where the oscillator with the higher number of cycles is not always oscillator 1. During this sequence, the two oscillators converge to a state \((1:1)\) that can produce the complementary \(1:10 \ 1:4 \ 3:1 \ 1:1\) sequence. The alternation of the two oscillators is a consequence of having identical coupling parameters, and thus, the oscillators can take turns displaying the same sequence of patterns. Similar structures appear in other \( N:N \) patterns that are located closer to the \( 1:1 \) AF domain. On the other hand, the \( N:N \) AF patterns which are located close to the OS domain typically form simpler structures such as \([1:N-1] \ || \ [N-1:1] \), or \([1:1] \ || \ [1:N-2] \ || \ [1:1] \ || \ [N-2:N]\).

High resolution scanning at a fixed coupling strength over a wider range of \( l \) reveals an abrupt change from \( N:M \) AF patterns to \( 1:1 \) AF patterns as the strength of the FM is increased. We summarize this in an \( M/N \) ratio vs. \( l \) plot [Fig. 6(a)].

The cycle number ratio \( M/N \) for \( N:M \) patterns (where \( N < M \)) generally shows a gradual decrease between rational values, with a sudden drop from \( M/N = 4 \) to \( M/N = 1 \) between \( \mu = 2.42 \times 10^{-2} \) and \( \mu = 2.43 \times 10^{-2} \). This sudden drop is, however, only apparent. While \( M/N = 1 \) at \( \mu = 2.43 \times 10^{-2} \), the actual pattern is \( 85:85 \) AF, with an intricate structure of \([1:1] \ || \ [4:1]_{14} \ || \ [1:12] || \ [1:1] || \ [1:4]_{14} || \ [12:1] \). The prevalence of \( 1:4 \) and \( 4:1 \) patterns within the larger \( N:N \) pattern indicates that there is still a strong \( N/M = 4 \) character.
to the pattern, but it is interrupted by other N:M (and corresponding M:N), and 1:1 patterns. When \( \mu \) is further increased, patterns display the general form [1:1 | (4:1)\( n \) | 1:12] | 1:1] | (1:4)\( n \) | 12:1], with equal numbers of 1:4 and 4:1 repetitions, and as \( \mu \) increases \( n \) decreases [Fig. 6(b)]. Thus, the sharp change from M/N = 4 to M/N = 1 only appears at the complex pattern level, but in fact, there is a gradual trend of losing 1:4 (and 4:1) sequences as \( \mu \) is increased. All of these N:N AF patterns satisfy \( N = 5 \times M \), where M is between 17 and 2. Between these patterns, other N:N AF type patterns may appear with pattern structures different from that of the 5 \( \times \) M subtype. At the end of this sequence, a 19:19 AF pattern is found with a substructure of [1:1 | 1:11 | 1:4 || 1:1 | 11:1 | 4:1], which still contains 1:4 (and 4:1), but does not fit into the previous sequence.

The M \( \times \) (1:N) AF type patterns are interspersed with other N:M AF patterns in the \( e - \mu \) phase plane. Here, we show only the lengthy 5:25 AF pattern, but shorter strings such as 3:9 AF or 2:10 AF were also observed. Generally, M increases with \( e \) and N increases with \( \mu \).

Temporal patterns with such intricate structures may require strict control of the parameters and the initial conditions, which is possible in numerical calculations, but might be challenging in experiments. In order to test the sensitivity of patterns to initial conditions, we repeated our calculations for patterns in the \( e - \mu \) phase plane (Fig. 4) at \( e = 4.6 \times 10^{-4} \), but varied the initial phases of the oscillators (supplementary material Fig. 2). When the initial phase difference is close to zero, the oscillators synchronize in-phase. 1:N, N:M and N \( \times \) (1:M) type patterns develop under virtually any initial conditions for which \( \phi _1 (0) \neq \phi _2 (0) \). However, N:N patterns display higher sensitivity to the initial phase difference: they appear interspersed with in-phase synchronization or form islands. Although the 5:25 pattern is complex and only appears in a narrow range of \( \mu \), it is not sensitive to the initial conditions. There is also a small domain of stable antiphase synchronization at the highest \( \mu \) values and initial phase differences close to 0.5.

When there is no delay between the peaks and perturbations, we observe a rich dynamical behaviour. However, if a delay \( 0.03 T < \tau < 0.5 T \) is introduced between peaks and perturbations, in-phase synchronization of the oscillators takes place, and the complex patterns vanish. The delay vs. FM phase plane (supplementary material Fig. 3) at \( e = 4.6 \times 10^{-4} \) shows that short delays (\( \tau < 0.01 T \)) do not affect the patterns, but delays longer than 5 s (\( \tau > 0.03 T \)) cause all patterns to be replaced by in-phase behavior. Patterns that appear at lower \( \mu \) are more resilient to such delays. This result is in striking contrast to our previous observations with unequal inhibitory coupling (no FM), where we observed that the area in which patterns appeared in the \( e_1 - e_2 \) plane increased several fold when a short delay was introduced.

Initial frequency differences between nonidentical oscillators generate resonances and temporal patterns when BZ oscillators are coupled by chemical pulses. We tested if the patterned behavior generated by our identical oscillators is a result of convergence to frequency ratios dictated by the patterns. We looked at the N:M AF type patterns, because they have the largest domains in the \( e - \mu \) phase plane. We performed a high resolution parameter sweep in the region defined by \( 2 \times 10^{-3} \leq \mu \leq 2.5 \times 10^{-2} \), \( 3.2 \times 10^{-4} \leq \varepsilon \leq 5.2 \times 10^{-4} \). We selected a time series that produced stable N:M AF type patterns and calculated the time average of \( h \) for each oscillator for the last two pattern instances (e.g., for a 1:3 pattern, we examined the last 2 cycles for oscillator 1 and the last 6 cycles of oscillator 2). Then, we used the T vs. \( h_0 \) fit in Fig. 1 to evaluate the period of each oscillator as if it had the calculated mean \( h \) value as its \( h_0 \) parameter. Finally, we calculated the ratio of the periods \( \rho = T_2 / T_1 \), and plotted \( \rho \) as a function of \( \mu \) for each pattern in Fig. 7.

If the oscillators simply assume the frequencies required for an N:M resonance to occur, \( \rho \) should be close to N/M; however, Fig. 7 shows that all \( \rho \) values are significantly lower than dictated by the resonance. There is a surprising linear correlation between the frequency ratio and the FM strength, which prevails in all N:M AF patterns that we looked at. All fits appear to converge to \( \rho = 1 \), which means that when there is no frequency modulation patterns should not develop; only synchronization should occur. Although we only tested positive FM here, these results agree with our previous findings: it is the long-term effect of inhibitory coupling that causes the temporal patterns to occur.

Interestingly, the only fitted parameter, \( k \), is a linear function of N/M in the N:M patterns, as shown in the inset of Fig. 7. This implies that the smaller the N/M ratio the smaller the domain of the N:M AF pattern. This observation is consistent with the fact that N:M AF patterns with lower N/M ratios are less frequent in our parameter sweep, because they have a smaller chance to fall onto the grid points of the sweep.

Another interesting feature of this scan is that the N:N AF or 1:1 AF patterns all have \( \rho = 1 \), irrespective of \( \mu \). The continuation of the fit of \( k(N/M) \) does not include this value. The simple explanation is that when \( N \neq M \) then there is an inequality in the number of perturbations. The higher this

FIG. 7. Estimated unperturbed frequency ratio \( \rho \) vs. FM strength \( \mu \) calculated for 1:N type patterns. Solid lines: corresponding fits of \( \rho = 1 + k \times \mu \). Inset: parameter \( k \) as a function of N/M in the N:M AF patterns. Dashed line fit: \( k = -30.54 \times N/M + 25.99 \).
disparity, the steeper is the $\rho$ vs. $\mu$ function, and the higher is $k$. On the other hand, when $N = M$, there is no difference in the number of perturbations; therefore, $k = 0$.

**Excitatory coupling and FM**

Two pulse-coupled BZ oscillators with symmetrical excitatory coupling can generate in-phase synchronization, phase-lag synchronization, fast anti-phase oscillations, and bursting. To explore the dynamics of this system with FM, we performed a parameter scan similar to the one with inhibitory coupling to detect domains where the dynamics is affected.

When there is no delay between peaks and perturbations, FM has little effect on the behavior type. We found only in-phase synchronization in the excitatory coupling strength ($x$) vs. $\mu$ parameter plane. When the oscillators synchronize in-phase with excitatory coupling there is a “leader” and a “follower” oscillator. Peak splitting in the oscillatory traces of the “leader” can occur. These appear to be super-threshold peaks that do not trigger perturbations (supplementary material Fig. 4). Stronger FM can cause irregular long term dynamics: the period of the coupled system collapses to zero, and the oscillations cease, followed by a recovery and another crash (supplementary material Fig. 5). Excitatory coupling tends to shorten the period of both oscillators by triggering the next cycle. When combined with the increase in excitability due to the concomitant increase in $h$ from FM, the period may decrease to the point where peaks no longer trigger perturbations.

The activator also extends the duration of the oxidized state. As a result, higher $x$ values counteract the synergistic effect of FM and activation, causing the period to increase with $x$ at identical FM (Fig. 8).

Delay between peaks and perturbations is a crucial parameter for the coupled system to exhibit fast anti-phase oscillations and bursting. The latter requires the delay to have an intermediate value, so that each perturbation can trigger the next cycle, but this trigger can become ineffective when the sensitivity of the oscillators to perturbation by Ag$^+$ decreases during bursting. We explored the system’s dynamics at a delay of 15 s (Fig. 9), which without FM produces phase-lagged synchronization and fast anti-phase oscillations as well as bursts, depending on the coupling strength.

With negative $\mu$, FM brings about new types of bursting behaviors that form a new domain in the coupling strength range $3.0 \times 10^{-4} < x < 4.5 \times 10^{-4}$. Within this domain at small negative $\mu$, bursting is stable and regular; the number of spikelets for both oscillators is equal. At intermediate FM, a domain of burst groups appears in which the bursts form more complex patterns, and finally at large negative $\mu$ oscillations synchronize with a phase lag. An illustrative example of a burst group comprised of 2:2, 3:3, and 4:4 bursts with the sequence [(2:2)2 3:3 4:4] is shown in Fig. 5(c). This phenomenon is similar to the fine structure of the N:N patterns when the coupling is inhibitory and the FM is positive: simpler organized patterns combine to form larger complex patterns.

The burst group composition strongly depends on $x$ and $\mu$. As the FM becomes more negative, the composition shifts to higher numbers of bursts with fewer spikelets. More positive FM results in regular bursts, eventually transitioning into fast anti-phase behavior. We calculated the fraction of peaks that belong to a particular burst type in a repeating burst group for the burst groups that appear at $x = 3.75 \times 10^{-5}$ using the following equation:

$$\Phi = \frac{n \times N}{\sum_{i} M_i},$$

where $n$ and $N$ are the number of repetitions and the number of peaks of the burst of interest, respectively, $E$ is the number of elements in the burst group, and $M_i$ is the number of peaks in the $i$th element in the burst group. For example, for the [(2:2)2 3:3 4:4] burst group $\Phi(2:2) = 2 \times (2 \times 2) / (2 \times (2 \times 2) + 2 \times 3 + 2 \times 4) = 0.36$. We found that an increase in

![FIG. 8. Period of oscillator 1 after 15 000 s of integration vs. $\mu$ with increasing excitatory coupling strength ($x$); limit cycles collapse at $\mu = 0.03$, and $10^{-4} < x < 3 \times 10^{-4}$.](image1)

![FIG. 9. Domains of bursts, burst groups, and synchronization modes in the $x$-$\mu$ phase plane.](image2)
FM strength causes a gradual transition to higher spikelet numbers per burst in a burst group (Fig. 10).

As the strength of the FM increases, the fraction of peaks that belong to the 2:2 bursts in the repeated pattern groups increases, while that of 4:4 decreases. The peak fraction of 3:3 reaches a maximum at about $\mu = -0.015$, where the majority of the spikelets belong to this burst type. Thus, weak negative FM breaks up fast anti-phase oscillations to produce regular bursts. Then, at stronger negative FM, the bursts start to form burst groups. Eventually, at very strong negative FM, the oscillators synchronize with a phase lag. This tendency reflects the decrease in excitability as $h$ is decreased due to more negative $\mu$ values. Bursting or fast anti-phase oscillations occur only if there is sensitivity to excitatory perturbations. By decreasing the excitability, the sensitivity decreases and these behaviors fail to develop.

CONCLUSIONS

We have shown that frequency modulation concomitant to pulse perturbations has a significant effect on the dynamics of pulse-coupled chemical oscillators. We found new dynamical regimes when the coupling was symmetrical excitatory or inhibitory.

The temporal patterns for inhibitory coupling and positive FM are the results of dynamical processes acting on two different time scales: oscillations at the faster time scale (on the order of 100 s), and recovery from FM (repeated perturbations to the $h$ variable) on the slower time scale (on the order of 1000 s). Significant time delay between peaks and perturbations eliminates temporal patterns, and in-phase synchronization becomes typical. Our results highlight the importance of the matching of time-scales necessary for some behaviors, such as leap-frog (LF) synchronization of neurons. LF synchronization occurs when inhibitory coupling is combined with positive frequency modulation and the relaxation dynamics has a time constant close to the oscillator’s natural period. Our system only produces LF synchronization as a transient under inhibitory coupling and positive FM, which indicates time scale mismatch.

The dynamics of the system with excitatory coupling and negative FM is governed by three time scales: the fastest is the oscillatory dynamics. Regular bursting is produced when the sensitivity of the oscillators to excitatory perturbation undergoes periodic changes. The time scale of this process depends on the delay between peaks and perturbations as well as the excitatory coupling strength. The third and slowest timescale is that of the recovery from FM, which allows for burst group formation.

Oscillators with adaptive frequencies have been shown to be able to match the frequency of external forcing signals, depending on the coupling strength. Pulse-coupled BZ oscillators display only marginal changes in their intrinsic frequency as a result of frequency modulation when coupled, even though the frequency of the collective dynamics is significantly different than in the uncoupled state.

Our preliminary experimental results, to be explored in more detail elsewhere, agree with the basic assumptions required for the frequency modulation. We also see qualitative agreement with the numerical results reported here, and further systematic study of this system is underway. Finding regular patterns with complex structures such as N:N AF patterns and the burst groups poses a greater challenge in experiment. Due to the presence of noise, these may appear only as transients, as occurred in our previous experimental observations with higher N:M patterns.

SUPPLEMENTARY MATERIAL

See supplementary material for Figs. S1–S5 additional details referred to in the text.

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