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Chemical Resonance, Beats, and Frequency Locking in Forced Chemical Oscillatory Systems

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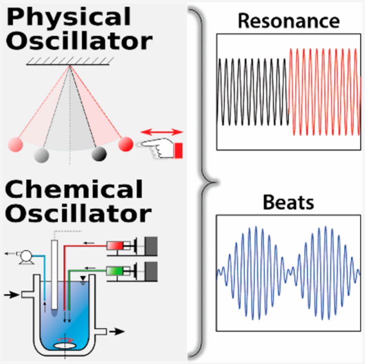
ABSTRACT: Resonance, beats, and synchronization are general and fundamental phenomena in physics. Their existence and their in-depth understanding in physical systems have led to several applications and technological developments shaping our world today. Here we show the existence of chemical resonance, chemical beats, and frequency locking phenomena in periodically forced pH oscillatory systems (sulfite−hydrogen peroxide and sulfite−formaldehyde−gluconolactone pH oscillatory systems). Periodic forcing was realized by a superimposed sinusoidal modulation on the inflow rates of the reagents in the continuous-flow stirred tank reactor. The dependence of the time period of beats follows the relation known from classical physics for forced physical oscillators. Our developed numerical model describes qualitatively the resonance and beat phenomena experimentally revealed. Application of periodic forcing in autonomously oscillating systems can provide new types of oscillators with a controllable frequency and new insight into controlling irregular chemical oscillation regimes.



System chemistry deals with the interaction of reaction networks and the emergent system-level properties.[1] Open chemical systems in a continuous-flow stirred tank reactor (CSTR) are good candidates for such investigations because the system itself is far from the thermodynamic equilibrium, and non-equilibrium structures may emerge under these conditions.[2−4] In almost all studies that have investigated the temporal or spatiotemporal dynamics of the open chemical systems, only constant inflow rates have been applied for the reagents.[5−7] Only a few experimental and theoretical studies have been attempted, in which time-dependent inflow rates were applied.[8−13] In an open and damped oscillatory system in the Belousov−Zhabotinsky (BZ) reaction,[14] the authors provided the first evidence for the chemical resonance using periodically changing inflow rates.[8] Other types of periodic forcing (for example, periodic irradiation) have been introduced and used in various chemical systems [e.g., in the Briggs−Rauscher reaction with a periodic illumination,[15] in electrochemical cells,[16] in BZ reaction (existence of the stochastic resonance),[17] and in the Turing pattern (controlling Turing structures with a periodic illumination[18])].

In physics, including mechanics, acoustics, optics, electronics, and atomic physics, resonance and beats are basic, well-known, and well-understood phenomena. These two phenomena always accompany each other. In chemistry, especially in oscillating open chemical systems, experimental evidence of the beat phenomenon is lacking. In mechanical systems, such as pendulums and masses connected to springs, the resonance occurs when the frequency at which a force is periodically applied is equal or close to the natural frequency of the system. This periodic forcing generates oscillations with greater amplitude than in the absence of periodic driving and when periodic forcing is applied at other frequencies. Moreover, when the frequency of periodic forcing is close to the natural frequency of the systems, the beat phenomenon emerges. The manifestation of this phenomenon is that the envelopes of the response curve have periodic character. Applications based on resonance and beats are widely used in physics (e.g., Doppler radar), medicine (Doppler pulse detection and Doppler pulse probe), and even chemistry (NMR and Mössbauer spectroscopy).[19−21]

The main aim of this study is to systematically investigate the effect of periodic forcing of the inflow rates on the pH oscillators in open chemical systems. We present the existence of the chemical resonance, beats, and frequency locking in such systems and show that chemical resonance and beats are internal properties of chemical oscillatory systems with periodic forcing. Additionally, we propose several applications of these phenomena.

In our study, we used the sulfite−hydrogen peroxide pH oscillator (see the Supporting Information) in a continuous-flow stirred tank reactor (CSTR).[22,23] The solutions of reagents were allowed to flow simultaneously with the same flow rate into the reactor using two programmable syringe

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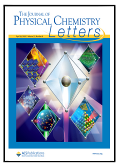

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pumps. The sketch in Figure S1 summarizes our experimental setup. In a constant inflow mode, the sulfite−hydrogen peroxide system exhibits sustained and undamped pH oscillations with a time period of ∼1 min. To investigate the chemical resonance and beats thus forcing the chemical oscillatory system, we superimposed a sinusoidal modulation on the inflow: $k_f = k_0[1 + \alpha \sin(\omega_f t)]$, where k_0, α, and ω_f are the constant inflow rate, the relative amplitude of the inflow rate, and the angular frequency of the forcing, respectively.

In a constant-flow mode ($\alpha = 0$) at a k_0 of 15.5 μL/s, the pH oscillator shows stable undamped oscillations with a time period of 62 ± 0.5 s (the natural time period) and amplitude of pH ∼0.7. When the sinusoidal forcing was applied at the natural frequency, the system immediately changed to higher- and constant-amplitude oscillations (Figure 1). The amplitude of the resonant oscillations linearly depends on the relative amplitude of the forcing (α) (Figure S2). At the maximum amplitude of the forcing ($\alpha = 0.968$), the observed pH amplitude in resonant oscillations was ΔpH ∼ 1.1, which is an ∼50% increase in amplitude.

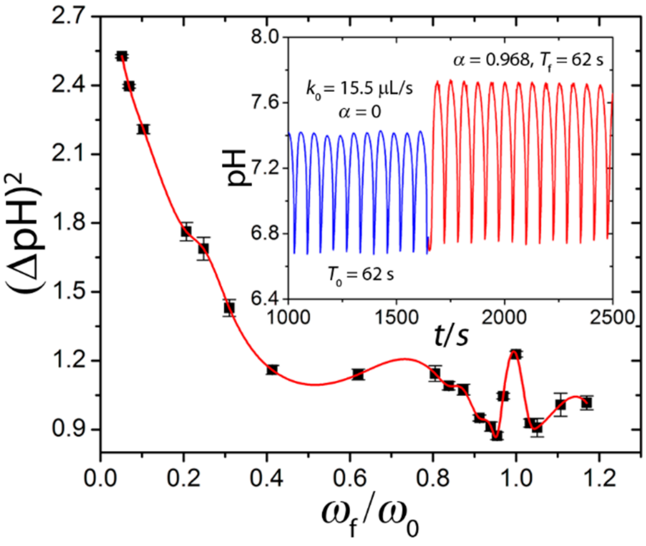

Figure 1. Chemical resonance curve in the sulfite−hydrogen peroxide pH oscillatory system using a sinusoidal periodic forcing of the inflow rate of the reagents (k_0 = 15.5 μL/s, and α = 0.968). ΔpH is the peak-to-peak amplitude of the oscillation. The inset shows the oscillations in the unforced case (blue line) with a time period of 62 s and the oscillations when a sinusoidal periodic forcing is applied (red line) with the natural frequency of the oscillatory system. Close to the natural frequency, where beat phenomena appeared, the amplitude of the oscillations was calculated as an average amplitude corresponding to the one period of beat.

Upon variation of the forcing frequency, ω_f (fixing k_0 and α), the average peak-to-peak amplitude of the pH oscillations changes, having a local maximum at unity relative forcing frequency (ω_f/ω_0), where ω_0 is the natural angular frequency of the oscillatory system (Figure 1). In contrast to the forced mechanical oscillators, the amplitude of the pH oscillations increases monotonically (up to ΔpH = 1.6) when the relative frequency goes to zero (i.e., the time period of forcing goes to infinity). This observation is in good agreement with the findings observed in a forced BZ reaction.[8]

When the forcing frequency was close to the natural frequency of the pH oscillator, the beat phenomenon appeared (Figure 2 and Figure S3). The beats manifest in the periodic change of the upper envelope of the pH oscillations. The time period of beats depends on the forcing frequency, and most importantly, this dependence is in perfect agreement with the relation known in forced physical oscillators; namely, the frequency of the beats (f_b) is equal to the absolute value of the difference of the forcing (f_f) and natural (f_0) frequencies $f_b = |f_f - f_0|$, or expressing with time periods, the time period of beats is $T_b = |1/[(T_f)^{-1} - (T_0)^{-1}]|$ (Figure 3a). This observation shows that all forced systems regardless of their nature share this fundamental characteristic. Interestingly, the beat phenomenon not only appears at a higher strength of forcing but also emerges at smaller amplitudes of forcing [α = 0.048 (Figure S4)].

To support our experimental findings, we used the Brusselator[24,25] and a kinetic model of the sulfite−hydrogen peroxide pH oscillator (see the Supporting Information).[23] The Brusselator model is a widely used chemical mechanism showing sustainable oscillations in CSTR and spatial patterns in reaction−diffusion systems.[24,25] We applied a sinusoidal periodic forcing to the reagents in both models. Similar to the experiments, in the absence of forcing, both systems provide undamped oscillations. Importantly, when a sinusoidal periodic forcing for the reagents was applied, the employed models predict chemical resonance and beats (Figure 3b and Figures S5−S7).

Another important aspect of the forcing is that the driven chemical oscillator emulates the frequency of the forcing within an error of 3% at the maximum amplitude of the forcing (Figure 4a and Figure S8). In other words, the oscillator is synchronized by the forcing. This phenomenon is called the frequency locking phenomenon when the period of an oscillator becomes identical with that of the external periodic forcing.[26] The period of the oscillator does not perfectly match the period of the external forcing if the difference in the periods is greater than a threshold value. Additionally, this threshold depends on the strength of the external forcing (i.e., if the forcing is weak, there is no synchronization). The frequency locking and beat phenomenon in chemical oscillatory systems have been reported only in the Briggs−Rauscher reaction.[15] In this study, the forcing was realized by using periodic irradiation, and the frequency locking occurred only when the periods of the oscillator and forcing were almost the same. Additionally, the period of oscillations was different from that of the external periodic forcing when the beating phenomenon emerged. In contrast to these observations, in our case, the period of the chemical oscillator was identical (synchronized) to the period of the external periodic forcing in a wide frequency range at the maximum amplitude of the forcing (Figure 4a), and in the case of beats, the time period of the oscillations was identical to the time period of the forcing. This behavior is also in contradiction with the behavior of an undamped forced pendulum, in which the frequency of the oscillations differs from the forcing frequency (and differs from the natural frequency, as well). The frequency locking is evident in our system;[26] in the case of resonant oscillations ($\omega_f/\omega_0 = 1$), the system was synchronized at all amplitudes of periodic forcing because the forcing frequency is equal to the natural frequency (Figure 4b). However, when ω_f/ω_0 was set to greater or less than unity, the synchronization occurred only if the amplitude of periodic forcing was greater than a given value; below it, the synchronization did not occur. Farther from the resonance, the greater amplitude of the forcing should be used to synchronize the system (Figure 4b). We carried out

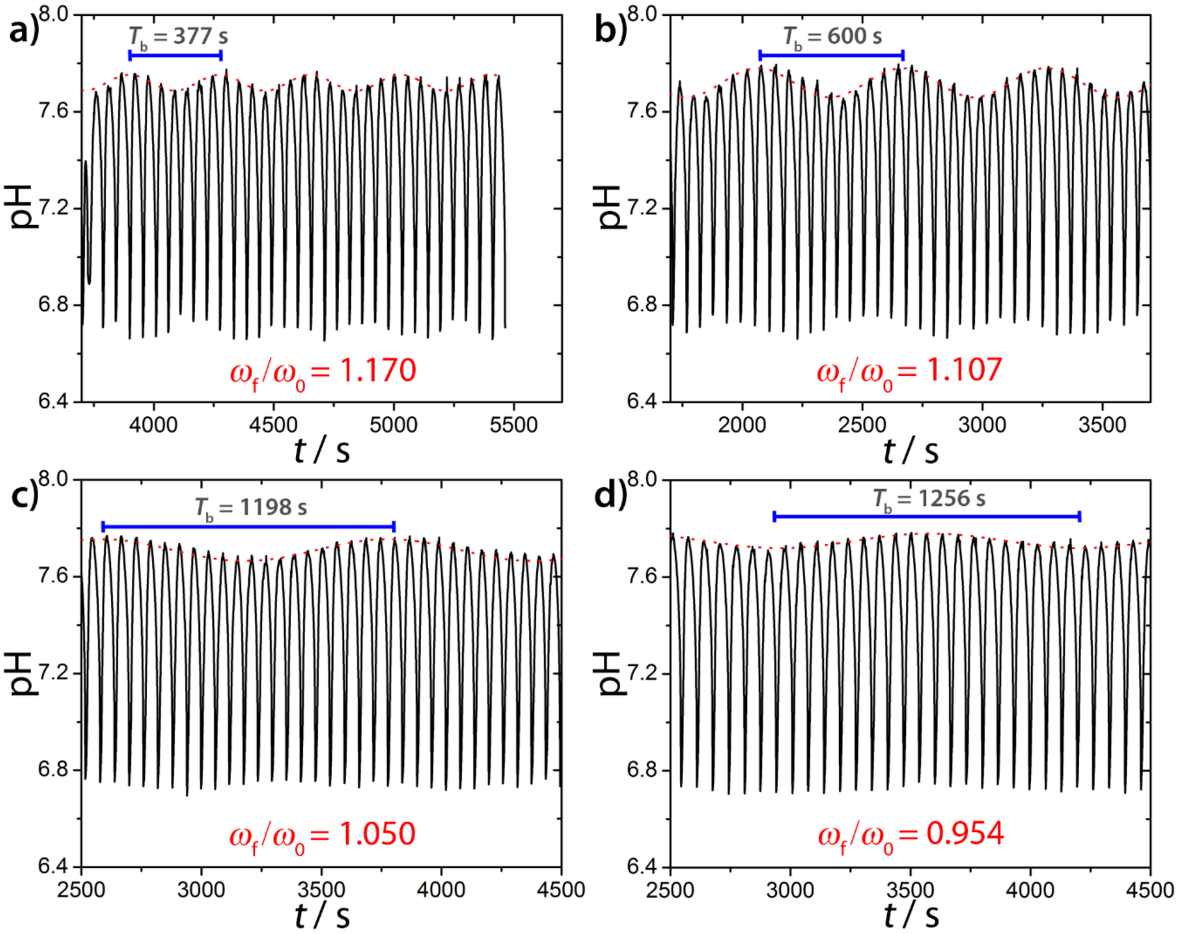

Figure 2. Existence of the chemical beats in the sulfite−hydrogen peroxide pH oscillatory system using sinusoidal periodic forcing of the inflow of the reagents with various driving frequencies (k_0 = 15.5 μL/s, and α = 0.968): (a) T_f = 53 s, (b) T_f = 56 s, (c) T_f = 59 s, and (d) T_f = 65 s. The natural time period of the system is 62 s. The dotted red lines are the fitted sinusoidal curves to the upper envelope of the oscillations.

several experiments to investigate other Arnold tongues (resonant behavior) in which the ratios of forcing frequencies to natural frequency were small integer ratios. We found no resonance at ω_f/ω_0 = 2/1, 3/1, and 1/2. In our system, the Arnold tongue was observed only at the resonance at ω_f/ω_0 = 1/1.

Above the natural time period, using a high amplitude of forcing (α = 0.968), the beat phenomenon gradually disappears and changes into constant-amplitude oscillation. During this transition, the time period of the beats (T_b) decreases (asymptotically approaches zero) and the amplitude of the beats decreases, as well. Once the time period of forcing is commensurate with the time period of the beats, because the oscillatory system emulates the frequency of the forcing, the beat phenomenon can no longer be resolved. The observed effects have far-reaching consequences in terms of further applications. First, these experimental findings can lead us to design oscillators with a given and controllable time period. The original system has a time period of 62 s; however, using a periodic forcing, the time period of the oscillator can be extended to 1500 s (Figure 4a), and the time period of the oscillations is identical to the time period of the forcing. This is a 20-fold increase (more than an order of magnitude) in the time period. At longer time periods of forcing, the oscillations have a constant and larger amplitude (Figure 1) compared to that of the original unforced system. It is important to note that the sinusoidal driving oscillations are in phase with the resulting pH oscillations irrespective of the forcing frequency (Figure S9), and the oscillator is synchronized within one period irrespective of the initial phase difference between the unforced oscillator and periodic forcing (Figure S10).

Another application of periodic forcing can be driving the system out of the aperiodic/irregular oscillation regime to a periodic one. In the sulfite−peroxide pH oscillator, the system provides stable and large-amplitude oscillation only at a given window of the inflow rate (between 15 and 16 μL/s). At larger and smaller values of k_0, the oscillatory system exhibits irregular oscillations with various amplitudes. However, when a periodic forcing is applied, the oscillator becomes periodic with the time period of forcing (Figure S11). It is particularly important in the regulation of chaotic/irregular oscillatory regimes in chemistry and medicine.[27,28] For instance, epileptic seizures can be modeled by using a network of coupled chaotic oscillators, and controlling the chaotic regime with an appropriate algorithm can drive the system into a periodic regime.[29] Chaos control, especially in chemical oscillatory systems,[30] is a complex procedure and is based on time-delay feedback, linearization of the Poincaré map, and periodic excitation of the system.[31] The latest method can be called nonfeedback control, which has been used to stabilize the unstable equilibrium in several systems. Our findings confirm that a periodic excitation method, similar to methods used in the physical systems, can be successfully used to regulate aperiodic/irregular chemical oscillations.

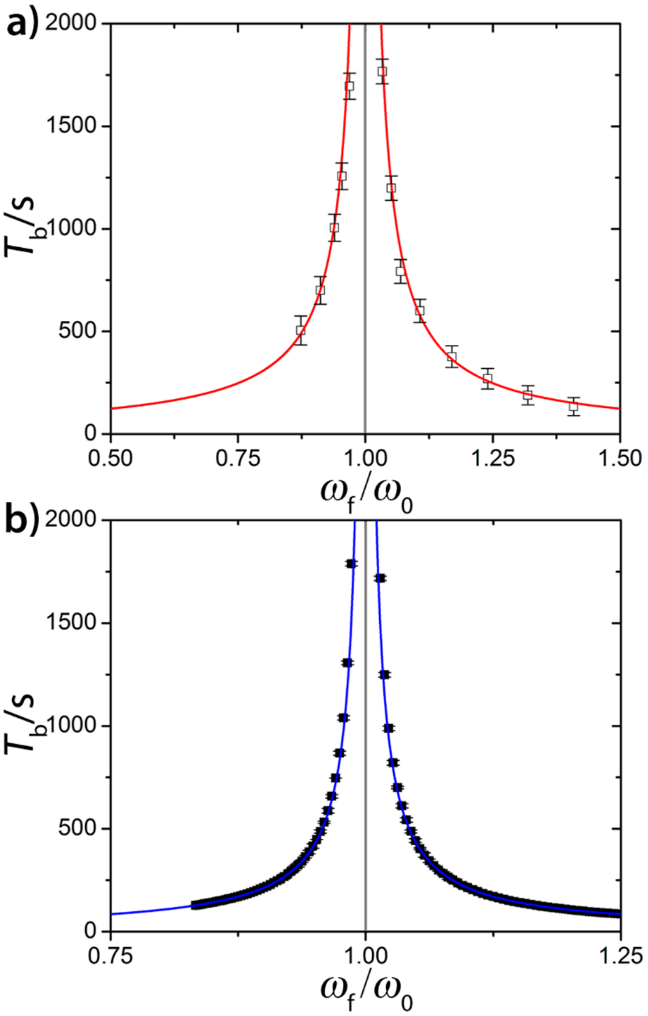

Figure 3. Dependence of the time period of the chemical beats on the relative forcing frequency (a) in experiments (k_0 = 15.5 μL/s, and α = 0.968) and (b) in numerical simulations using the Brusselator model (α_{num} = 0.015). The solid lines represent the theoretically calculated curves from the relation $f_b = |f_f - f_0|$.

Our third example of the application of periodic forcing in chemical systems is the determination of the natural frequency of the oscillatory chemical system. As we mentioned above, varying the inflow rate of the reagents (k_0), we could identify aperiodic/irregular oscillation regimes with different average amplitudes. First, we applied a periodic forcing with a given time period (T_f = 62 s) to an irregular oscillation [k_0 = 11.0 μL/s (Figure S12)]; as we demonstrated above, the irregular oscillations transformed into regular oscillations. The resulting oscillation exhibits a beat phenomenon with a well-defined time period/frequency [in our case, T_b = 252 s (Figure S12)]. From the determined beat frequency and from knowing the forcing frequency, the natural frequency of the system can be easily derived. It is evident that if the forcing frequency is the same as the natural frequency of the system, the resonance phenomenon should emerge (and the beats should disappear, i.e., the time period of the beats goes to infinity), resulting in constant-amplitude oscillations. When we applied a periodic forcing to the chemical oscillatory system with the natural frequency calculated (T_f = T_0 = 82 s), as it is expected, we found a constant-amplitude resonant oscillation (Figure S12). It is worth mentioning that the obtained natural frequency of the irregular unforced oscillation is very close to the highest time period component (T = 80 s) obtained from the Fourier spectrum of the unforced oscillation regime.

To look deeper into this behavior, first, we determined the main components of the time periods from the Fourier spectrum of the unforced aperiodic oscillation regime. Then we applied periodic forcing to the system using these obtained specific time periods. As we expected, at shorter time periods of forcing, the oscillations became regular and the beat phenomenon was evident (Figure S13). However, when we applied periodic forcing with the longest time period from the Fourier spectrum, the beat phenomenon vanished (Figure S13). This indicates that the lowest-frequency/longest-time period component obtained from the Fourier transformation can be associated with the natural frequency/time period of the aperiodic oscillations.

Finally, to verify and prove that chemical resonance and beats are not limited to and not specific to the sulfite−hydrogen peroxide pH oscillator, we chose another pH oscillator, namely the sulfite−formaldehyde−gluconolactone system (see the Supporting Information).[32,33] This is the only pH oscillator discovered, which operates in alkaline state, for which the oscillation range lies between pH ∼7 and ∼10.[33] The system oscillates with the time period of 85 s at a k_0 of 11.0 μL/s. When we applied a periodic forcing with the natural frequency of the unforced system, we observed a resonance with a shift of ΔpH from 2.5 to 3.0 (20% increase) (Figure S14a). Additionally, when the forcing frequency differed from the natural frequency, the beat phenomenon appeared to be similar to that of the sulfite−hydrogen peroxide system (Figure S14b).

It has been demonstrated in many studies that chemical oscillators, especially pH oscillators, can be successfully used to control the self-assembly of various building blocks (DNA,[34] nanoparticles,[35,36] fatty acids,[37] diblock copolymers,[38] and pH responsive gels[39]) and create non-equilibrium structures.[4] One of the key control parameters in these studies is that the time period of the chemical oscillator (the lifetime of a given pH state) should be in the same range as the duration of the assembly/disassembly process.[40−43] In some cases, the kinetics of the assembly is relatively slow, especially if the building blocks are larger than the regular ions and molecules.[40] The time period of the oscillations in the sulfite−formaldehyde−gluconolactone is between ∼70 and ∼100 s,[33] and it can be just slightly controlled by the flow rate and the concentrations of the reagents and provides only a limited degree of freedom to vary the time period. Using a periodic forcing, we could design oscillations (≤400 s, almost 5-fold longer oscillation compared to that of the unforced system) with arbitrarily chosen time periods because the time period of the oscillations can be tuned by the time period of the forcing (Figure S15).

We present the existence of chemical resonances and beats in forced chemical oscillatory systems. On the basis of experimental results and numerical model simulations, we show that these behaviors are internal properties of chemical oscillatory systems. We successfully applied periodic forcing of the inflow rates of reagents for controlling aperiodic oscillation regimes, designing oscillators with arbitrary time periods, and determining the natural frequency of irregular chemical oscillations. The results confirm the universality of the resonance and beat phenomena. Our chemical system (oscillations in a CSTR coupled to periodic forcing of the inflow rates of the reagents) is a counterpart of the forced

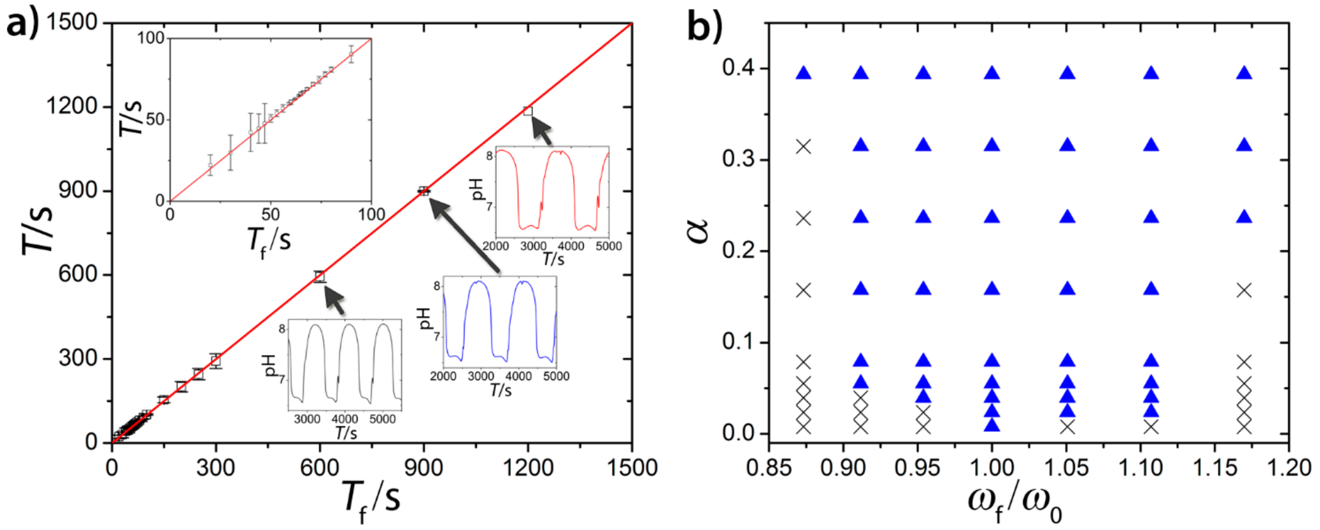

Figure 4. (a) Synchronization of the sulfite−hydrogen peroxide pH oscillatory system by periodic forcing. Dependence of the time period of the pH oscillations on the time period of a sinusoidal forcing in experiments (k_0 = 15.5 μL/s, and α = 0.968). The inset shows the enlarged view at shorter time periods of forcing. (b) Frequency locking in the sulfite−hydrogen peroxide pH oscillatory system (k_0 = 15.5 μL/s) using periodic forcing of the inflow of the reagents with various driving frequencies (ω_f/ω_0) and the amplitude of the forcing (α). Blue triangles and times signs correspond to the synchronization and nonsynchronization, respectively, of the oscillatory system by periodic forcing.

oscillators known form classical mechanics (e.g., driven pendulum), in which instead of application of a periodic external driving force, the periodically changing chemical potential drives the open oscillatory systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c00586.

> Description of the sulfite−hydrogen peroxide and sulfite−formaldehyde−gluconolactone pH oscillatory systems, description of the Brusselator and sulfite−hydrogen peroxide kinetic models, supporting figures (Figures S1−S15), and a supporting table (Table S1) (PDF)

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Notes

The authors declare no competing financial interest.

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