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Experimental, numerical, and mechanistic analysis of the nonmonotonic relationship between oscillatory frequency and photointensity for the photosensitive Belousov–Zhabotinsky oscillator

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The oscillation frequency of a nonlinear reaction system acts as a key factor for interaction and superposition of spatiotemporal patterns. To control and design spatiotemporal patterns in oscillatory media, it is important to establish the dominant frequency-related mechanism and the effects of external forces and species concentrations on oscillatory frequency. In this work, we identify the essential mechanistic step of the I–F relationship: the previously proposed photoreaction $\text{Ru}^{3+} + \text{Ru}^{2+} + \text{BrO}_3^- + 3\text{H}^+ \rightarrow \text{HBrO}_2 + 2\text{Ru}^{3+} + \text{H}_2\text{O}$, which has both effects of frequency-shortening and frequency-lengthening. The concentrations of species can shift the light intensity that produces the maximum frequency, which we simulate and explain with a mechanistic model. This result will benefit studies of pattern formation and biomimetic movement of oscillating polymer gels. © 2015 AIP Publishing LLC

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The oscillation frequency is an important factor for pattern structuring and wave interaction in nature. However, for specific oscillatory chemical reactions, e.g., the classical photosensitive Belousov–Zhabotinsky reaction, there has been no detailed investigation of the oscillation frequency and the factors that influence it. In this work, we establish the essential mechanistic step for the nonmonotonic relationship between photointensity and oscillator frequency (I–F) in the photosensitive Belousov–Zhabotinsky system. We also show that species concentrations can shift the maximum of the I–F curve. This result will have wide applications for designing spatiotemporal patterns and controlling the shape and movement of active matter.

I. INTRODUCTION

Spatiotemporal patterns in oscillatory distributed systems are generated by oscillators interacting through transport phenomena, such as diffusion and convection.1,2 The spatial distribution of oscillation frequency plays an essential role in pattern structuring and traveling wave interaction. The competition between oscillators with different intrinsic frequencies determines the final evolution of traveling waves, which can be high- or low-frequency dominant. For example, in heterogeneous oscillatory media, pulse waves from different sources compete, and the ultimate propagation direction is determined by the highest frequency source(s) of oscillation.3–5 In a capillary containing a self-oscillating gel that hosts the photosensitive Belousov–Zhabotinsky reaction (BZR), mechanical oscillations of the gel under nonuniform illumination, which controls the spatial distribution of oscillation frequency, can cause either photophobic or phototropic movement of the gel as a result of this mechanism.6 For rotating spiral waves, frequency dominance depends on the direction of motion perpendicular to the spiral rotation; outwardly and inwardly rotating spiral waves show high- and low-frequency dominance,2,7–10 respectively. When oscillators are arranged along a tube with continuous variation of species concentrations in a diffusion-fed gel,11 multiple-scale growth instabilities of pulse wave propagation are generated, which is caused by the decrease in frequency along the tube.

In oscillatory media, two- (or possibly three)12 frequency oscillators can be produced by external periodic forcing13 or internal system dynamics.14,15 Complex patterns are produced by the interaction between external forcing and intrinsic oscillators,16 which can create oscillatory clusters,17 labyrinthine patterns,18 bubble-shaped structures,16 hexagonal patterns,19 and soliton waves.20 Moreover, a second frequency can occur in a three-variable reaction–diffusion system, resulting in superposed structure waves, such as superspirals and over-targeted spirals, under appropriate conditions.14,15

In this study, we focus on the widely used photosensitive $\text{Ru(bipy)}_3^{2+}$-catalyzed BZR.21–24 Among the factors influencing the oscillatory dynamics, the reactant concentrations

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and the illumination intensity are the most convenient control parameters for studying the homogeneous kinetics and spatiotemporal patterns. On the one hand, photoinhibition25 and photoinduction26–28 of oscillations have been analyzed in the Ru(bipy)₃²⁺-catalyzed BZR through the photoexcited reaction of Ru(II). In a recent study,3 we accidentally discovered a nonmonotonic relationship between the imposed light intensity and the oscillation frequency, which manifested as a maximum frequency in the light intensity–oscillation frequency (I–F) curve. On the other hand, because bromate and malonic acid (MA, CH₂(COOH)₂) can change the individual reaction rates, the species concentrations also affect the oscillation frequency. The overall BZ reaction involves the oxidation and bromanion of malonic acid by acidified bromate in the presence of a catalyst.29

\[ 3\text{CH}_2(\text{COOH})_2 + 4\text{BrO}_3^- = 4\text{Br}^- + 9\text{CO}_2 + 6\text{H}_2\text{O}, \]  
(1)

\[ 3\text{H}^+ + 5\text{CH}_2(\text{COOH})_2 + 3\text{BrO}_3^- = 3\text{Br}_2\text{CH}(\text{COOH})_2 + 2\text{HCOOH} + 4\text{CO}_2 + 5\text{H}_2\text{O}. \]  
(2)

In this work, we perform experiments to uncover the dominant mechanism of the nonmonotonic I–F relationship in the photosensitive BZ reaction and explain the effect of species concentrations, which will have wide applications for pattern formation, photoinduced shape reconfiguration, and movement of oscillating polymer gels.

II. EXPERIMENT AND SIMULATION

A. Experiment

The Ru(bipy)₃²⁺-catalyzed BZ reaction was conducted in a quartz reactor with total volume 10 ml and thermostated at 22.0 ± 0.1°C. A LED source (wavelength maximum at 460 nm) was used to illuminate the reactor, and the light intensity was controlled by a digital control unit calibrated by a photometer (Model 1L1400A, International Light Newburyport, MA, USA). The reactor had an optical path length of 2 cm and was stirred with a Teflon-coated magnetic stirrer at 300 rpm. In general, oscillations can last for more than 10 h, and stable values of the oscillatory frequency and amplitude can persist for several hours, depending on the reaction conditions. After stable oscillations in the absence of illumination were obtained, the light intensity was adjusted every 10 min to obtain the average oscillatory period at each light intensity. Raw data were acquired with an e-coder (eDAQ, Australia) attached to a redox electrode (Thermo Fisher).

B. Mechanistic model and simulation method

A modified photosensitive Oregonator model is presented here, which is based on a four-variable model proposed by Amemiya et al.28 The chemical steps are

\[ \text{A + Y + 2H} \rightarrow \text{X + V}, \]  
(O1)

\[ \text{X + Y + H} \rightarrow \text{2V}, \]  
(O2)

\[ \text{A + X + H} \rightarrow \text{2X + 2Z}, \]  
(O3)

\[ 2\text{X} \rightarrow \text{A + V + H}, \]  
(O4)

\[ \text{B + Z} \rightarrow \text{H}, \]  
(O5)

\[ \text{V + Z} \rightarrow \text{Y}, \]  
(O6)

\[ \text{V} \rightarrow \text{products}, \]  
(O7)

\[ \text{E + V + H} \rightarrow \text{Y + Z}, \]  
(L1)

\[ \text{E + A + 3H} \rightarrow \text{X + 2Z}, \]  
(L2)

where A, B, H, V, X, Y, Z, and E denote the species BrO₃⁻, MA, H⁺, BrMA, HBrO₂, Br⁻, Ru(bipy)₃²⁺, and Ru(bipy)₃²⁺⁺, respectively. Ru(bipy)₃²⁺⁺ is the strongly reducing excited state of the reduced form of the catalyst, ruthenium-tris(2,2’-bipyridyl). For simplicity, these symbols also stand for the concentrations of the corresponding species in this work.

In this model, processes O1–O6 represent a modified version of the Oregonator model that explicitly takes into account malonic acid, and processes L1 and L2 represent the photosensitive reactions. To analyze the promotion effect of malonic acid on the oscillatory frequency, the organic substrate in the model was expanded into the two species B and V (malonic and bromomalonic acids), which replace the single reaction step and phenomenological stoichiometric factor f used for the organic species in the classical Oregonator model. The two separate steps (O5 and O6) are consistent with the Field–Körös–Noyes (FKN) mechanism of the BZ reaction.29 Step O7 removes BrMA without producing bromide ions.28,30 The concentrations of BrO₃⁻ (A), H⁺ (H), and MA (B) are taken to be constant, so the corresponding ordinary differential equations (ODEs) reduce to a four-variable model

\[ \frac{dV}{dt} = V_{O1} + 2V_{O2} + V_{O4} - V_{O6} - V_{O7} - rp_1, \]  
(1)

\[ \frac{dX}{dt} = V_{O1} - V_{O2} + V_{O3} - 2V_{O4} + rp_2, \]  
\[ \frac{dZ}{dt} = 2V_{O3} - V_{O5} - V_{O6} + rp_1 + 2rp_2, \]  
\[ \frac{dY}{dt} = -V_{O1} - V_{O2} + V_{O6} + rp_1, \]  
(1)

where \( V_{O1} = k_1H_2O_AY, \) \( V_{O2} = k_2H_2OXY, \) \( V_{O3} = k_3H_2O_AX, \) \( V_{O4} = k_4X^2, \) \( V_{O5} = k_5(B_0 - V)Z, \) \( V_{O6} = k_6VZ, \) \( rp_1 = H_0V/ (k_{L0}k_{L1} + H_0V + (k_{L2}k_{L3})\Phi A_0), \) \( rp_2 = (k_{L2}k_{L3})H_0^2A_0\Phi/k_{L0}k_{L1} + H_0V + (k_{L2}k_{L3})\Phi A_0), \) \( \Phi \) denotes the light flux, which is linearly proportion to the light intensity (I).31 The expressions for the rates of the photochemical reactions, \( rp_1 \) and \( rp_2, \) result from applying the steady state approximation to the excited state catalyst concentration, and \( k_{L0} \) is the rate constant of the reverse reaction of Ru(II)-excitation, as described by Amemiya et al.28 The ODEs were numerically integrated using an explicit fourth-order Runge–Kutta method and integration time step \( \Delta t = 0.001. \) We discarded the first 1.2 × 10⁶ steps and used the subsequent 6.0 × 10⁶ steps to compute the oscillatory frequency. Species concentrations A, B, and H served as the parameters with fixed values \( A_0, B_0, \) and \( H_0, \) respectively. The kinetic parameters \( k_1-k_4 \) were chosen from the work of Keener and Tyson:32 \( k_1 = 2.0 \times [H^+]^2 \text{M}^{-2} \text{s}^{-1}, \) \( k_2 = (1.0 \times 10^8) [H^+] \text{M}^{-2} \text{s}^{-1}, \) \( k_3 = 40.0 \times [H^+] \text{M}^{-2} \text{s}^{-1}, \) and \( k_4 = 2.0 \times 10^6 \text{M}^{-1} \text{s}^{-1} \). \( k_3 \) and \( k_6 \) were reported33 to be 0.2 M⁻¹s⁻¹ and
With these values of $k_5$ and $k_6$, we obtained complex (mixed-mode and quasiperiodic) oscillations and chaos, which were not observed in our experiments. Here, we use $0.1 \text{ M}$ and $1 \text{ M}$ for $k_5$ and $k_6$, which are of the same order of magnitude as the reported values, to qualitatively explain the nonmonotonic $I$–$F$ relationship. The kinetic parameter $k_7$ was arbitrarily assigned in this work as $k_7 = 2.0 \times 10^{-2} \text{ s}^{-1}$. The photochemical parameters were $k_{L0} = 0.0329 \text{ M}^{-2}$ and $k_{L1} = 5.54 \text{ M}^{-1} \text{ s}^{-1}$.

III. RESULTS AND DISCUSSION

A. Nonmonotonic $I$–$F$ Relationship

Figure 1 shows a typical nonmonotonic $I$–$F$ relationship observed in both experiment and simulation. The oscillatory frequency in each $I$–$F$ curve rapidly increases before gradually decreasing with increasing photointensity, which we refer to as photopromotion and photoinhibition of oscillatory frequency, respectively. Each $I$–$F$ curve has a peak, i.e., a point of maximum frequency separating the photopromotion and photoinhibition regions. Photopromotion of the frequency occurred in a small region of light intensity ranging from zero to this peak. Photoinhibition occurred in a broad region ranging from the peak to $>2000 \mu \text{Wcm}^{-2}$. The numerical results obtained from Eq. (1) qualitatively agree with the experimental curve.

B. Effect of species concentrations on the $I$–$F$ relationship

The light intensity, $I_{\text{max}}$ (corresponding to the light flux, $\Phi_{\text{max}}$), that yielded the maximum frequency, $F_{\text{max}}$, varied in response to changes of the initial species concentrations. In this section, we examine the dependence of the $I$–$F$ relationship on the initial concentrations of bromate ion, hydrogen ion, and MA by both experiments and Eq. (1) simulations.

1. Effect of bromate concentration

First, we investigated the $I$–$F$ relationship with different initial concentrations of bromate ion. The initial concentrations, $[\text{MA}]_0 = 0.08 \text{ M}$ and $[\text{H}^+]_0 = 0.7 \text{ M}$, were fixed in the experiments. The initial concentration of bromate was varied from 0.12 to 0.17 M at 0.01 M intervals. The numerical simulations used the same concentrations.

Figure 2 shows the effect of initial bromate concentration on the $I$–$F$ relationship. The maximum moved toward lower light intensity with increasing bromate concentration. With increasing concentration from 0.12 to 0.17 M, $I_{\text{max}}$ decreased from 392.0 to 17.4 $\mu \text{Wcm}^{-2}$ in the experiments (Fig. 2(b)), and $F_{\text{max}}$ from $2.50 \times 10^{-5}$ to $7.05 \times 10^{-6} \text{ M s}^{-1}$ in the numerical simulations (Fig. 3(b)). In addition, the maximum frequency of oscillations (i.e., $F_{\text{max}}$) changed, with a linear increase from 0.0251 to 0.0364 s$^{-1}$ in the experiments, and from 0.0223 to 0.0260 s$^{-1}$ in the simulations, as shown in Figs. 2(c) and 3(c), respectively. Moreover, as shown in Figs. 2(a) and 3(a), in the different light intensity regions, the oscillatory frequencies showed opposite tendencies with increasing bromate concentration: the frequency increased and decreased under low and high light intensity conditions, respectively.
2. Effect of acid concentration

Figure 4(a) shows the variation of the nonmonotonic I–F curves when the initial concentration of nitric acid was varied from 0.6 to 1.0 M at 0.1 M intervals with fixed concentrations of \([\text{MA}]_0 = 0.08 \text{ M}\) and \([\text{NaBrO}_3]_0 = 0.135 \text{ M}\). Over this range of \([\text{H}^+]\), \(I_{\text{max}}\) decreased from 142.6 to 17.4 \(\text{l W cm}^{-2}\) in the experiments (Fig. 4(b)), and \(U_{\text{max}}\) from 2.95 \(\times 10^{-10}\) to 3.0 \(\times 10^{-6}\) \(\text{Ms}^{-1}\) in the simulations (Fig. 5(b)). In addition, the maximum oscillation frequency linearly increased from 0.0243 to 0.0350 \(\text{s}^{-1}\) in the experiments (Fig. 4(c)), and from 0.0211 to 0.0314 \(\text{s}^{-1}\) in the simulations (Fig. 5(c)). With increasing acid concentration, the oscillation frequency increased and decreased in the low and high light intensity regions, respectively. Overall, the effect of acid concentration showed a trend similar to that of bromate concentration, which will be discussed later.

3. Effect of malonic acid concentration

Finally, we investigated the dependence of the I–F relationship on the initial concentration of MA, which we varied from 0.055 to 0.08 M at intervals of 0.005 M with \([\text{HNO}_3]_0 = 0.7 \text{ M}\) and \([\text{NaBrO}_3]_0 = 0.12 \text{ M}\). Figures 6(a) and 7(a) show experimental and numerical results, respectively, for the I–F relationships at different initial concentrations of MA. The results exhibit two different trends compared with the effects of bromate and nitric acid. The first trend is that \(I_{\text{max}}\) moved toward higher light intensity with increasing MA concentration. As \([\text{MA}]_0\) increased from 0.055 to 0.080 M, \(I_{\text{max}}\) changed from 73.5 to 392.0 \(\mu\text{W cm}^{-2}\) in the experiments (Fig. 6(b)) and \(U_{\text{max}}\) from 1.31 \(\times 10^{-10}\) to 2.60 \(\times 10^{-6}\) \(\text{Ms}^{-1}\) in the simulations (Fig. 7(b)). The oscillatory frequency generally increased with increasing MA concentration over the whole range of illumination intensity. The maximum oscillation frequency increased from 0.0218 to 0.0251 \(\text{s}^{-1}\) in the experiments (Fig. 6(c)) and from 0.0182 to 0.0223 \(\text{s}^{-1}\) in the simulations (Fig. 7(c)) when \([\text{MA}]_0\) changed from 0.055 to 0.08 M.

C. Mechanistic analysis

1. Reaction mechanism

As shown in Fig. 8, oscillations in the BZ reaction can be analyzed using the nullclines of the two-variable Oregonator model, \(^{32}\) i.e., the curves of \(du/dt = 0\) and \(dv/\text{d}t = 0\) in the \(u-v\) plane. Points a, b, c, and d correspond to feature points of the oscillation cycle. When the \(v\) nullcline crosses the \(u\) nullcline at a point on the bd branch, it will...
FIG. 5. Simulated curves of oscillatory frequency versus light intensity as a function of initial hydrogen ion concentration ($H_0$). Other parameters and concentrations are the same as in Fig. 1 except $A_0 = 0.135$ M.

FIG. 6. Curves of oscillatory frequency versus illumination intensity for different MA concentrations. Concentrations of the other species are the same as in Fig. 1.

FIG. 7. Simulated curves of oscillatory frequency versus light intensity as a function of initial MA concentration ($B_0$). Other parameters and concentrations are the same as in Fig. 1.
generate a limit cycle (dotted lines in Fig. 8). In the BZ reaction, the period preceding fullblown HBrO2 autocatalysis is the slowest part of the cycle, which evolves along the ab branch of the limit cycle (Fig. 8).

Time series of the variables for one oscillation cycle in our simulations are shown as solid lines in Fig. 9(a), where points a, b, c, and d in the time series for bromide ion (Y) are the same as in Fig. 8. The slow growth period leading up to HBrO2 autocatalysis is in the ab region, where the concentration of Y increases from point a (when X is at its minimum after a rapid drop), reaches a maximum and then decreases to b, the critical value, $Y_{cr}$, which can be determined from the ODEs of the model. When $Y$ falls below this critical value, process B of the FKN mechanism begins, which results in the autocatalytic increase in HBrO2 (X). The switch from the slow growth period to the autocatalytic process occurs at point b, where the rates of O2 and O3 are approximately equal, so the equation for critical the value of the bromide ion concentration is

$$Y_{cr} = k_3A_0/k_2.$$  (2)

In this work, we use $Y$ to estimate the oscillatory period rather than using the concentration of oxidized catalyst ($Z$), as is often done. The slow evolution of bromide ion concentration during the a-b period consumes most of the cycle, and thus $t_{ab}$ is roughly equal to the total period.

2. Intrinsic photoreaction for promotion and inhibition of oscillation frequency

In the present model, the photochemical reaction consists of two reaction steps, namely, L1 and L2, which were identified as photoinhibition and photoinduction processes, respectively.28 On the one hand, the photochemical reaction produces the inhibitor Br-, which is primarily generated from the reaction between Ru(II)* and BrMA:

$$\text{Ru}^{\text{II}}/C_3 + \text{BrMA} + H^+ \rightarrow \text{Br}^-/C_0 + \text{Ru}^{\text{III}}/C_3 + \text{products}. \quad \text{(R3)}$$

This promotes the autocatalytic process, reaction step O3, by consuming the inhibitor of Br- through reaction step O2, which accelerates the oscillation.28 Here, we investigate the effects of the photochemical reaction steps and their generated species through detailed simulations.
To analyze the dependence of the $I$–$F$ relationship on steps L1 and L2, we simulated the model under three scenarios: only L1 occurs, only L2 occurs, and both steps occur. With only the L1 step, the $I$–$F$ relationship is a monotonically decreasing function (solid line in Fig. 10). However, with only the L2 step, the $I$–$F$ curve shows both regions of photopromotion and photoinhibition of oscillatory frequency (dashed line in Fig. 10). Considering the results shown in Fig. 10, we can safely conclude that reaction L2 has both frequency increasing and frequency decreasing effects and is the key step that generates the nonmonotonic $I$–$F$ relationship. Reaction L1 has only an inhibitory effect on the oscillations; it is able to shift the position of $\Phi_{\text{max}}$ but it is not the crucial factor for the nonmonotonic $I$–$F$ relationship. Previous work has suggested that reaction L2 has only a photoinduction effect on the oscillations, but this analysis shows that it has both photopromotion and photoinhibition effects. Furthermore, it is step L2 that results in the maximum in the $I$–$F$ curve for the whole model with both reactions L1 and L2 (dotted line in Fig. 10). Based on the above discussion, we can simplify our investigation of the nonmonotonic $I$–$F$ relationship and focus on step L2 in the model simulation and analysis.

3. Effects of evolution rate and critical concentration of bromide on the oscillation frequency

A typical time series of bromide concentration is shown as the solid line in Fig. 9(a). The change of Y obeys the following ODE:

$$\frac{dY}{dt} = -k_1H_0^2A_0Y - k_2H_0XY + k_6VZ. \tag{3}$$

Equation (3) shows that the change of $Y$ is composed of contributions from reactions O1, O2, and O6, where O1 and O2 consume bromide and O6 produces bromide. During the growth period (a-b curve) leading up to autocatalysis, the combined effects of these steps result in the concentration of $Y$ undergoing a fast rise and a slow drop, as shown in Fig. 9(a). In the following, we analyze the effect of photoreaction L2 on the consumption of $Y$, which affects the duration of the a-b period. The effects of the photoproduction of X and Z by step L2 on the oscillation period are shown in Figs. 9(a) and 9(b), respectively. The time series of species concentrations [HBrO$_2$], [Br$^-$], [Ru(III)], and [BrMA] was plotted at different light intensities: no light, light intensity at 3.0 $\times$ 10$^{-5}$ M s$^{-1}$, and high light intensity, as shown in Fig. 9(b). This phenomenon can be attributed to the larger amount of photoproduced Z that generates more Y though reaction step O6 is at higher light intensity. Moreover, the critical value of $Y$ increases very slowly from 3.0 $\times$ 10$^{-5}$ to 9.0 $\times$ 10$^{-5}$ M s$^{-1}$. Therefore, at light intensities above $\Phi_{\text{max}}$, photoproduction of Z plays a dominant role in prolonging the induction period, which results in reduction of the oscillatory frequency.

In summary, the increase and decrease in the oscillatory frequency along the $I$–$F$ curves result from the photoproduction of X and Z, respectively. Photogeneration of X increases the critical value of $Y$ for autocatalysis (Eq. (4)), resulting in an increase in the frequency. Photogeneration of Z slows the consumption of Y, causing a decrease in the frequency. The two opposite effects compete, and the dominant effect depends on the magnitude of the light intensity.

D. Quasi-analytical approach

To supplement our direct numerical simulation of the $I$–$F$ relationship, we develop a quasi-analytical approach to further understand the relationship and the effect of species concentrations.

1. Key reactions in the oscillatory period

First, we need to determine which reaction steps are important for controlling the oscillatory period. Figure 9(a) shows that the a–b segment of the oscillation cycle, i.e., the time for Br$^-$ to increase rapidly then fall to its critical level that allows HBrO$_2$ autocatalysis, accounts for most of the
cycle time. During this portion of the cycle, the concentration of X is very low ($\sim 10^{-7}$–$10^{-6}$ M), so the rates of reaction steps O3 and O4 can be neglected. We have previously noted that step L1 does not play a role in determining the nonmonotonic character of the I-F curve. Thus, we approximate the oscillatory period as the time for the $a \rightarrow b$ process and solve the rate equations corresponding to reaction steps O1, O2, O5, O6, and L2 during this interval.

2. Quasi-analytical solution for the oscillatory period

The ODEs for the path $a \rightarrow b$ are then

$$\frac{dX}{dt} = k_1A_0YH_0^2 - k_2YH_0X + r_{p2}(\Phi)$$

$$\frac{dY}{dt} = -k_1H_0^2A_0Y - k_2H_0XY + k_6VZ$$

$$\frac{dZ}{dt} = -(k_5(B_0 - V) + k_6V)Z + 2r_{p2}(\Phi)$$

$$\frac{dV}{dt} = k_1A_0YH_0^2 + 2k_2YH_0X - k_6VZ - k_7V. \tag{5}$$

We obtain quasi-analytical solutions as follows. In each of the equations (5) for the rate of change of $X$, $Z$, and $V$, we treat the other variables as constant, thereby obtaining a set of linear first-order homogeneous differential equations, which can be solved analytically. The solution of $Z$ is then inserted into the equation for $dY/dt$, which was solved analytically to obtain $Y$. The quasi-analytical solutions are

$$X = K_1 + C_1e^{-F_1t},$$

$$Y = K_2(\Phi) + C_2e^{-F_2t} + K_3e^{-F_3t},$$

$$Z = K_4(\Phi) + C_3e^{-F_3t},$$

$$V = K_5 + C_4e^{-F_4t}, \tag{6}$$

where

$$F_1 = \frac{k_1A_0YH_0^2 + r_{p2}(\Phi)}{F_x},$$

$$F_2(\Phi) = \frac{k_1VCK_4(\Phi)}{F_y},$$

$$F_3 = \frac{k_6V}{F_y - F_Z},$$

$$F_4(\Phi) = \frac{2r_{p2}(\Phi)}{F_z},$$

$$K_5 = (k_1A_0H_0^2 + 2k_2YH_0)Y/(k_6Z + k_7),$$

and the $C_i$ depends on the initial values of the variables, e.g., $C_1 = X(0) - K_1$.

In Fig. 11, we show the results of implementing this approach to calculate the period. We chose our default concentrations $A_0$, $B_0$, and $H_0$ as 0.12 M, 0.08 M, and 0.7 M, respectively. The initial values of the variables were taken as the values at point a in Fig. 9 at zero light intensity: $X_{ini} = 1.685 \times 10^{-7}$ M, $Y_{ini} = 1.48 \times 10^{-3}$ M, $Z_{ini} = 7.29 \times 10^{-3}$ M, $V_{ini} = 8.14 \times 10^{-3}$ M. We note that the concentrations at point a are nearly independent of $\Phi$ in our simulations. We then used the expressions in Eq. (6) to sequentially update each concentration at 0.01 s intervals, recalculating the parameters $C_i$ and $K_i$ as well as the concentrations after each step, until $Y(t)$ reached the critical value, $Y_{cr}(\Phi)$. The results are shown in Fig. 11(a).

In a sense, the above procedure is an intuitively based approach to numerically integrate the rate equation (5). More interesting, perhaps, is the quasi-analytical solution for $Y$, Eq. (7), because it affords a chemical interpretation of the competing processes that lead to the nonmonotonic I-F relationship

$$Y(t) = C_2e^{-F_2t} + K_3e^{-F_3t} + 2k_6Vrp_{p2}(\Phi)/(F_x,F_z). \tag{7}$$

Of the three terms on the right hand side, the first represents the consumption of $Y$ through steps O1 and O2, the second corresponds to the production of $Y$ through step O6, and the third expresses the indirect generation of $Y$ from photoproduced $Z$.

3. Nonmonotonic I-F relationship determined from the quasi-analytical solution

We used Eq. (6) to calculate the kinetic curves of $Y$ at different light intensities, as shown in Fig. 11(b). Each curve starts from $Y_{ini}$ and ends when it reaches the critical value, $Y_{cr}(\Phi)$. The curves display two characteristic features. First, particularly at high light intensity, the curve levels off at longer times, which results from the third term in Eq. (7) becoming dominant. Second, $Y_{cr}(\Phi)$ increases with increasing light intensity, which has been discussed above. These two factors work together to determine the endpoints of the curves, i.e., the oscillation period. In Fig. 11(b), from line A to line C, the time to the endpoint decreases, because the increase in $Y_{cr}(\Phi)$ exceeds the change in the kinetic curve due to the increased light intensity. From line C to line E, the time increases, because the leveling off of the $Y$ concentration predominates over the increase in $Y_{cr}(\Phi)$. For curve F, there is no endpoint, because the $Y$ concentration never decreases to the corresponding $Y_{cr}(\Phi)$ value, so the oscillation period becomes infinite, i.e., the system ceases to oscillate. We thus obtain a nonmonotonic relationship between the light intensity and the oscillatory period, as plotted in the inset of Fig. 11(b), which shows a steep increase before a gradual decrease with increasing light intensity.

Our analytical results show that the nonmonotonic I-F relationship comes about for two reasons. First, the photogenerated species X increases $Y_{cr}(\Phi)$. Secondly, the photo-generated species Z slows the consumption of Y through reaction O6 during the second half of the $a \rightarrow b$ process. Under low intensity illumination, the increase in $Y_{cr}(\Phi)$ shortens the kinetic curves. The effect of photoproduced Z...
on the kinetic curves is still weak, so the oscillatory period decreases. At high light intensity, although \( Y_{cr} \) still slowly increases, a stronger effect from photoproduced \( Z \) distorts the curves and makes them decrease more slowly, so the period increases. This result reproduces both the experimental and numerical \( I-F \) relationships.

4. Effect of species concentrations on the \( I-F \) relationship from the analytical solution

The experimental and numerical results show that adjusting the species concentrations shifts the position of \( \Phi_{max} \) and the peak oscillatory frequency. In this section, we investigate whether Eq. (6), combined with the effect of light intensity on \( Y_{cr}(\Phi) \) (Eq. (4)), can account for the response of the \( I-F \) relationship to changes in the concentrations of bromate ion, nitric acid, and MA.

\( a. \) Effect of bromate concentration. With increasing initial concentration of bromate, the maximum point of the \( I-F \) relationship shifted toward lower light intensity, as shown in Fig. 12(a). The oscillatory frequency increased and decreased under low and high light intensities, showing the same trend as the experimental and numerical results (Figs. 2 and 3).

\( b. \) Effect of acid concentration. With increasing initial hydrogen ion concentration, \( \Phi_{max} \) shifted toward lower light intensity, as shown by the analytical results in Fig. 12(b). The changes in the oscillatory frequency with increasing acidity showed two opposite tendencies. The oscillatory frequency increased and decreased in the regions of low and

FIG. 11. Quasi-analytical results. (a) Time series of variables during the a-b period from Eq. (6) (light intensity set at \( 5.0 \times 10^{-6} \text{ M s}^{-1} \)). (b) Kinetic curves and oscillatory period from quasi-analytical solutions at different light intensities. Each curve of \( Y \) starts from \( Y_{ini} \) and goes to endpoint \( Y_{cr} \). The endpoint of each curve (A–E) is marked, with the critical value of \( Y \) indicated at the right. Curve F shows a high light intensity where no oscillation occurs. The duration of each curve dominates the oscillation frequency, and the corresponding results are shown in the inset as a nonmonotonic relationship between oscillatory frequency and light intensity.

FIG. 12. Quasi-analytical results showing the effect of species concentrations on the \( I-F \) relationship. (a) Bromate concentration \( (A_0) \). (b) Initial concentration of hydrogen ion \( (H_0) \). (c) MA concentration \( (B_0) \). The symbol “\( x \)” denotes the maximum oscillatory frequency.
high light intensity, respectively. This analytical result shows the same trend as both the experimental and numerical results, which are shown in Figs. 4 and 5.

c. Effect of MA concentration. With increasing initial MA concentration, $\Phi_{\text{max}}$ shifted toward higher light intensity, as shown in Fig. 12(c), and the oscillatory frequencies increased under all light intensities. The same trend was also observed in the experimental and numerical results as shown in Figs. 6 and 7, respectively.

At $\Phi_{\text{max}}$, the promotion and inhibition of oscillation frequency are balanced. When we increase the MA concentration at $I_{\text{max}}$, $Y$ decreases in Eq. (7), because $F_1$ increases, which results in promotion overcoming inhibition. Increasing the light intensity (i.e., $rp_2$) increases the inhibition in Eq. (7) to reach a new equilibrium between promotion and inhibition, which shifts $\Phi_{\text{max}}$ to higher light intensity. In contrast, increasing the concentrations of bromate or hydrogen ion raises the concentration of BrMA, which enhances the inhibition of bromide, resulting in the increase in $Y$ in Eq. (7), i.e., a shift of $\Phi_{\text{max}}$ to lower light intensity.

IV. CONCLUSION

In the Ru(bipy)$_2^{2+}$-catalyzed BZ reaction, the nonmonotonic $I$–$F$ relationship, which is composed of fast photopromotion and slow photoinhibition regions, was obtained from experimental, numerical, and analytical results. The results revealed that L2 is the key photochemical reaction step to generate the nonmonotonic $I$–$F$ relationship. The photogeneration of HBrO$_2$ dominates the shortened oscillatory period in the region of low light intensity, and photogeneration of Ru(III) indirectly results in increase in the oscillatory period in the high light intensity region. The maximum in the $I$–$F$ curve can be shifted by changing the species concentrations. The experiments, simulations, and mechanistic analyses showed the same tendency for the effect of species concentrations on the $I$–$F$ relationship. Our analysis reveals that MA expands the photopromotion region of oscillatory frequency by consuming photogenerated Ru(III), so $I_{\text{max}}$ shifts toward high light intensity. For hydrogen and bromate ions, increased production of BrMA reduces the promotion region by generating more bromide ions in step O6, so $I_{\text{max}}$ shifts toward lower light intensity.

The nonmonotonic $I$–$F$ relationship that we have explored here will be useful for the design of photocontrolled pattern formation and oscillating gel movement related to competition between oscillatory frequencies in systems that host the photosensitive BZ reaction. In addition, similar nonmonotonic $I$–$F$ relationships are likely to arise in other nonlinear chemical systems, such as pH and electrochemical oscillators.

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