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Periodical forcing for the control of chaos in a chemical reaction

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Control of the chaotic behavior of a chemical system can be achieved perturbing periodically some control parameters of the system. This procedure based on external forcing, which is based on the phenomenon of resonance, can change a chaotic behavior into a periodical one by means of the application of a sinusoidal perturbation. In this paper, the influence of a periodical modulation added to the parameter controlling the oxygen adsorption rate in a cellular automaton (CA) model studying CO oxidation is analyzed. This CA model considers the oxidation reaction of CO on a catalytic surface, taking into account the catalyst temperature variation in order to analyze the reaction time oscillatory behavior. Simulations of the CA model exhibit chaotic and quasiperiodical behaviors, and it can be shown that the periodical forcing strategy can suppress the chaotic dynamics by means of the stabilization of periodical solutions. © 2006 American Institute of Physics.

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I. INTRODUCTION

Periodical forcing of the kinetics of a reaction by means of the variation of some external parameters such as, for example, the rate of a chemical process or the bath temperature, is one of the most commonly used tools in basic and applied studies of heterogeneous catalytic reactions.¹ Thus, in experiments focused on the study of catalytic oscillatory reactions, periodic perturbations are used to stabilize oscillations of period 1 (P1). This can be easily achieved if the external and internal frequencies coincide. In fact, chemical reactions showing P1 oscillations can exhibit complex behavior, including a double period and an irregular kinetics, when external forcing is applied, which points out that the external and internal frequencies are not the same. The aim of the external forcing method is to stabilize unstable periodical orbits contained in the chaotic attractors of the system.

Oxidation of CO by O on catalytic metal, of the type Pt or Pd, is one of the most frequently studied catalytic reactions. This reaction, as a good example of a system far from thermodynamic equilibrium, exhibits kinetic phase transitions, bistability, and therefore hysteresis associated with it, and a rich variety of oscillatory behavior ranging from periodical form to quasiperiodical and chaotic ones.

Most models proposed to describe oscillatory evolutions in CO oxidation involve nonlinearities of a different nature. So there are models in which the catalyst temperature can stay at a value different from the room temperature, due to the reaction heats generated on the catalytic surface on which the reaction taking place can spread on this surface more quickly than the heat dissipated to the room, which results in an increase in the catalyst temperature. These oscillations are called thermokinetic—so that they can be distinguished from the isothermal ones, in which the temperature of the surface is constant—and are produced by a strong nonlinear depen-

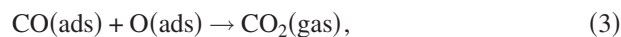
dence on the reaction rate on surface temperature. These changes in temperature in a reaction can be taken into account just by means of the addition of an equation describing the time surface temperature change.

The study of the oscillatory behavior of the CO reaction, including temperature as a dynamical variable, was performed in previous works by means of simulations carried out in a cellular automaton (CA),^{2,3} obtaining chaotic and quasiperiodical states.

In this paper we want to show the influence that the periodical variations in the oxygen adsorption rate have on the oscillatory behavior of the CO reaction, analyzing the results of simulations performed with the CA. In Sec. II, the model of the reaction and a set of preliminary results are described, in order to analyze, in Sec. III, the periodical modulation imposed on the system. Finally, in Sec. IV, some conclusions are summarized.

II. THE MODEL

The model assumes that the reaction takes place according to three elemental mechanisms:



where (ads) denotes that the particle is adsorbed on the surface. Two adjacent sites are needed for an oxygen molecule to be adsorbed. When a molecule is adsorbed on the surface, it remains fixed, and, therefore, surface diffusion is ignored in this model.

The rate constants k_i are chosen, for each of the mechanism quoted above ($i=1, 3$), in the Arrhenius form:

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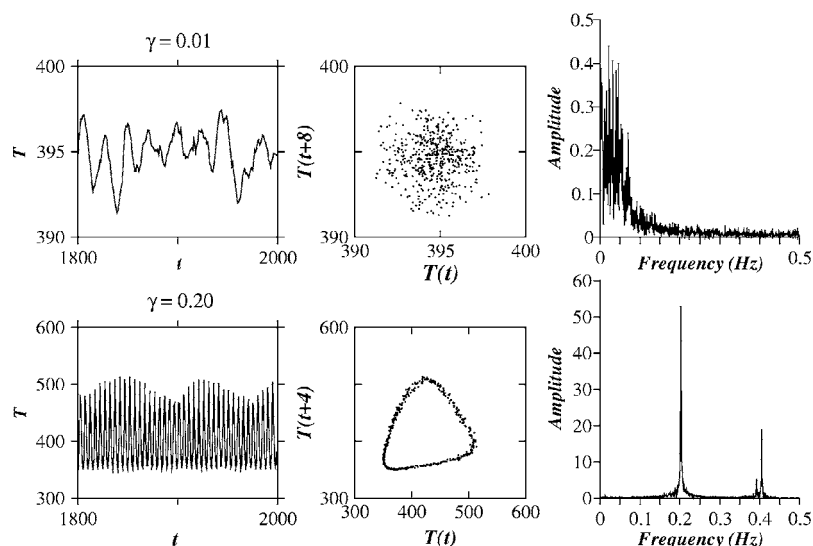


FIG. 1. Time series typical of autonomous oscillations (without forcing) of the surface temperature T for two values of the parameter γ . These series, obtained by simulations of the CA, represent a chaotic regime and a quasiperiodic one, as it can be observed in the Poincaré maps and the Fourier spectra attached. For $\gamma=0.01$, the regime is chaotic: the frequency spectrum is continuous and we can see the disperse filling of the Poincaré map. For $\gamma=0.20$, the Poincaré map represents a quasiperiodic behavior with two fundamental frequencies: $f_0=0.20264$ Hz and $f_1=0.39258$ Hz, the third peak corresponding to a harmonic of the first fundamental frequency, $2f_0=0.40527$ Hz.

$$k_i = A_i \exp\left(-\frac{E_i}{k_B T}\right), \quad (4)$$

where A_i are the preexponential factors, k_B is the Boltzmann constant, T denotes the surface temperature, and E_i are the activation energies of the three elemental processes.

In order to study the oscillatory behavior of the reaction, the model must be complemented by adding an equation describing the change of the surface temperature due to the adsorption and reaction processes:

$$\frac{dT}{dt} = -\gamma(T - T_B) + \sum_{i=1}^3 h_i p_i, \quad (5)$$

where γ is the relaxation rate of T towards the room temperature T_B , h_i are the reaction heats of the processes (1)–(3), and p_i are the number of processes of type i that take place per area unit.

The model can generate time oscillatory evolution for certain values of the set of parameters $\{A_i, E_i, h_i, \gamma, T_B\}$.

We have set the values $A_1=5 \times 10^{-2}$, $A_2=4 \times 10^5$, $A_3=1$, $E_1=0$, $E_2/k_B=6 \times 10^3$ K, $E_3=0$, $h_1=150$, $h_2=300$, $h_3=0$, and $T_B=300$ K as room temperature, γ being the control parameter. The previous results obtained from simulations of the CA are as follows.

- For $0 < \gamma \leq 0.004$ there is a state poisoned by oxygen at T_B .
- For $0.005 \leq \gamma \leq 0.09$ there is an aperiodical regime, in which the surface temperature fluctuates around a value greater than room temperature, $T > T_B$.
- For $0.10 \leq \gamma \leq 0.27$ there is a quasiperiodic regime, in which the surface temperature fluctuates around a value greater than room temperature, $T > T_B$.
- For $\gamma \geq 0.28$ there is a state poisoned by CO at T_B .

Thus, the CA model can describe a variety of behaviors: quasiperiodical and chaotic regimes, and two states poisoned.

III. RESULTS OF SIMULATIONS OF THE CA FOR THE CONTROL OF CHAOS

The CA uses a square lattice with 256×256 sites. Both the procedure and the transition rules of the automaton are described in Refs. 2 and 3. The transition probabilities of the CA depend on the molar fractions of the gaseous reactives, $y_{CO}=k_1/(k_1+k_2)$ and $y_O=k_2/(k_1+k_2)$, being $y_{CO}+y_O=1$. Reaction probabilities between pairs CO–O, process (3), is assumed to be 1.

In order to control chaos, a perturbation in the frequency factor A_2 of the rate of oxygen adsorption on the catalyst surface [Eq. (2)] is introduced. We use the sinusoidal function with only one frequency,

$$A_{2p} = A_2[1 + A \cos(\omega t)], \quad (6)$$

where A is the normalized amplitude and ω is the angular frequency of the perturbation. Obviously enough, the modulation of variable A_2 produces changes in all the surface processes.

A systematic variation of A and ω will allow us to draw the kinetic phase diagram of the model, which will show the dynamical system states and their possible bifurcation points.

In this paper we want to analyze the influence of the harmonic variations of the oxygen adsorption rate on the chaotic behavior of the reaction. As a result, the previous knowledge of the chaotic regions that the CA model presents are important. Thus, first, we choose the values of the parameters $\{A_i, E_i, h_i, T_B\}$ given in Sec. II. Secondly, and taking into account that our working parameters are A and ω , we must select a range for these parameters.

Figure 1 shows two time series typical of nonperturbed oscillations of the surface temperature T in the chaotic region ($\gamma=0.01$) and in the quasiperiodic one ($\gamma=0.20$). The Poincaré maps are built out of the average mutual information included in the mathematical program visual recurrence analysis (VRA):^{4,5} the mutual information between the measurement $T(t+\tau)$ and the measurement $T(t)$ is the quantity

known by $T(t+\tau)$ about $T(t)$ for some t . The program VRA has implemented the study of time series out of the construction of recurrence graphics and the quantification of magnitudes typical of nonlinear dynamics, such as the Shannon entropy, the maximum Lyapunov exponent, or the spatiotemporal entropy. For $\gamma=0.01$, the regime is chaotic: we find a disperse filling of the Poincaré map. However, for $\gamma=0.20$, the points place themselves over the same perfectly defined closed curve, indicating thereby a quasiperiodic regime. The Fourier spectra are obtained in the regular way. We show a continuous frequency spectrum, such as that corresponding to the chaotic case, and a discrete spectrum, with three clearly defined peaks, corresponding to the quasiperiodic case. This case presents two fundamental frequencies, $f_0=0.20264$ Hz and $f_1=0.39258$ Hz, since the third peak corresponds to a harmonic of f_0 , 0.40527 Hz ($2f_0$).

To begin with our study we equal the frequency of the perturbation [Eq. (6)] with the natural frequency corresponding to the highest peak in the Fourier spectrum of the quasiperiodic case. That is, as $\omega=2\pi f$, the reference frequency is $\omega_0=2\pi f_0=1.27322$ rad s^{-1} . (Another possibility is advanced by Kraus *et al.*,⁶ who chose as frequency that one corresponding to the highest peak of the Fourier spectrum for the chaotic case). Since we want to know if we are able to get a system out of its chaotic regime, we choose $\gamma=0.01$, without changing the values of the following parameters: $A_1=5 \times 10^{-2}$, $A_2=4 \times 10^5$, $A_3=1$, $E_1=0$, $E_2/k_B=6 \times 10^3$ K, $E_3=0$, $h_1=150$, $h_2=300$, $h_3=0$, and $T_B=300$ K. On the other hand, since A can range from 0 to 1 and the frequency from high values to low ones of the nonperturbed frequency ω_0 , we choose regions of low frequency from the phase diagram in the model, with $\omega_0=1.27322$ rad s^{-1} , A and ω being the two control parameters, in order to analyze the behavior of the system in the chosen area.

The simulation is carried out in the regular way: we begin with an empty lattice of 256×256 cells with periodic boundary conditions, four different series of random numbers are used in each simulation to make sure that the results are valid, and we obtain the output data for each iteration

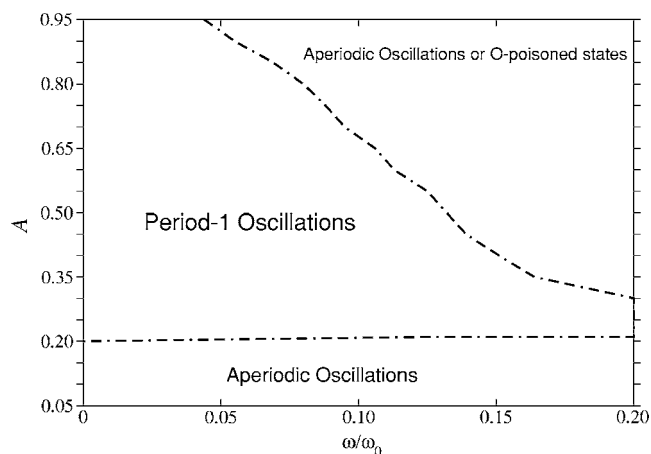


FIG. 2. Kinetic phase diagram obtained by means of periodic forcing of CA for the oxidation of CO. $\gamma=0.01$ and $\omega_0=1.27322$ rad s^{-1} .

(time step) carried out for the whole lattice. The output data represent the temperature of the catalytic surface, T ; the fractions of coverage of CO and O, n_{CO} and n_O ; and the production of CO_2 , R , that is, the number of CO–O pairs that are formed per area unit and that leave the surface immediately after their formation. For each pair of values A and ω , we took 5000 time steps to better visualize the oscillations that occurred at low frequencies.

In order to achieve our goal, we choose a unique output variable, surface temperature T , as it is the biggest one and, therefore, the one easiest to control. We discard the 500 first points in order to eliminate the transitory regime with complete certainty in all cases, and with the rest we calculate the time average of the temperature and its fluctuation, so that $T=\langle T \rangle + \theta$. The analysis of the results is performed over the fluctuation of temperature θ . Here we have also used the program VRA. This program, through the construction of recurrence graphics, qualitatively detects changes in the state of the evolution of a system.

The kinetic phase diagram of the model is shown in Fig. 2. Here period 1 oscillatory states can be seen along other

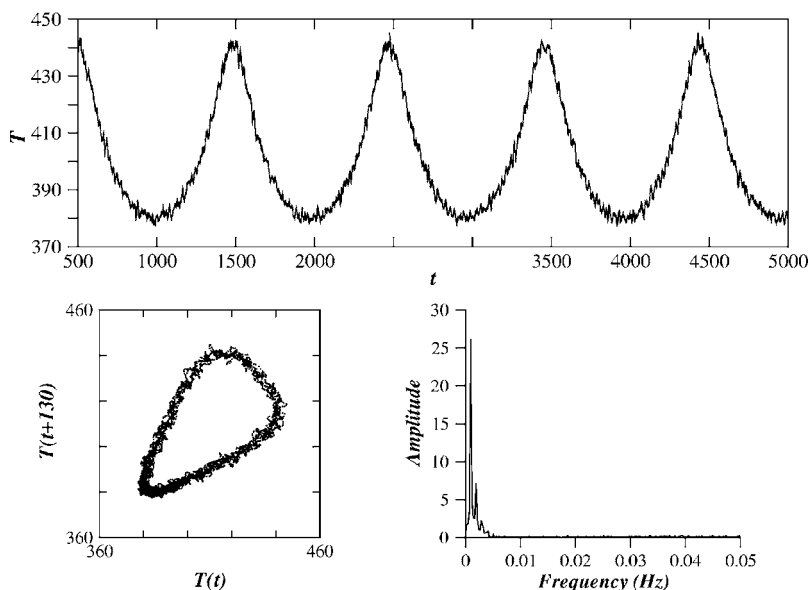


FIG. 3. Time evolution of the surface temperature, Poincaré map, and amplitude spectrum, obtained by means of the conventional technique of the Fourier transform, corresponding to the state of $\gamma=0.01$, $\omega_0=1.27322$ rad s^{-1} , $A=0.80$, and $\omega/\omega_0=0.005$. At this point, the system shows periodic oscillations of period 1 induced by an external harmonic perturbation.

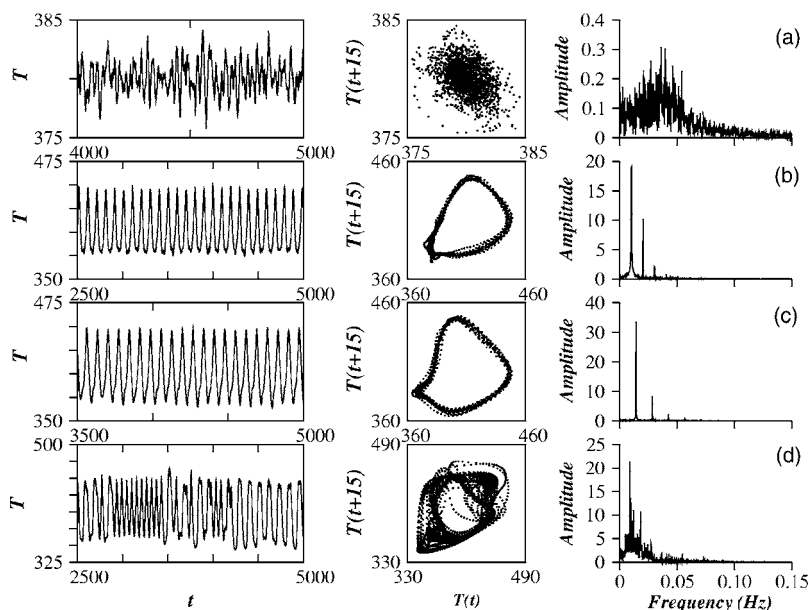


FIG. 4. Time series typical of the surface temperature T and its corresponding iterative maps and Fourier spectra for different values of the external frequency. (a) $\omega=0$, autonomous oscillations (without forcing) that represent a chaotic behavior: continuous frequency spectrum. (b) $\omega=0.05\omega_0$, harmonic waves train: stable orbit at a low frequency. The system presents a discrete frequency spectrum, with only a fundamental frequency. (c) $\omega=0.07\omega_0$, P1 oscillations: stable limit cycle. (d) $\omega=0.09\omega_0$, irregular and chaotic response. $\gamma=0.01$, $\omega_0=1.273\ 22\ \text{rad s}^{-1}$, and $A=0.80$. The evolutions of the Poincaré maps and the Fourier spectra show how the aperiodic behavior of the system in (a) gets stabilized in the orbits of period 1 in (b) and (c), showing, finally, an irregular behavior when the external frequency is increased [case (d)].

behaviors. The smaller the perturbation normalized amplitude, the bigger the range of the external resonant frequencies with the dynamic system. Thus, between the bands $A=0.25$ and $A=0.30$ we find P1 states for all the analyzed range of frequencies. If the normalized amplitude decreases the system goes into chaotic behavior at very low frequencies.

In order to analyze in detail how the reaction oscillatory behavior is altered when external modulation changes, we choose one of the bands typical in the phase diagram (Fig. 2), $A=0.80$, so that now ω remains as the sole control parameter.

In Fig. 3 we show the temporal series of T for $\omega=0.005\omega_0$: we only have to impose a low frequency to get the system to show P1 behavior. Oscillations of temperature with big amplitudes (around 80 K) can be observed, as well as, of course, big oscillation periods. The iterative map of the temperature of the surface T in function of a certain temporal delay is shown as well, along with the amplitude spectrum obtained through the conventional technique of the Fourier

transform. For $\omega/\omega_0=0.005$, the biggest amplitude peak takes place at 0.000 98 Hz, although its harmonic at 0.001 95 Hz can be observed too.

Figure 4 shows some time series typical of the temperature of the surface, T , and the corresponding Poincaré maps (for the same time delay) and the Fourier spectra for different external frequency values. (a) $\omega=0$, autonomous oscillations (without forcing) that represent chaotic behavior: erratic trajectories and a continuous frequency spectrum. (b) $\omega=0.05\omega_0$, stable orbit at a low frequency of period 1: trajectories are projected on the same closed curve. (c) $\omega=0.07\omega_0$, stable limit cycle (P1). Characteristic peaks are observed both in (b) and in (c) when the external perturbation frequency is resonant with the dynamic system. Resonant peaks occur in (b), the maximum amplitude peak being 0.010 25 Hz, and 0.020 26, 0.030 27, and 0.040 53 Hz its harmonics. For $\omega/\omega_0=0.07$ [case (c)], the most intense peak occurs at a frequency of 0.014 16 Hz. Its harmonics 0.028 32, 0.042 48, and 0.056 64 Hz can also be observed. Both amplitude spectra correspond to P1 oscillations, as they

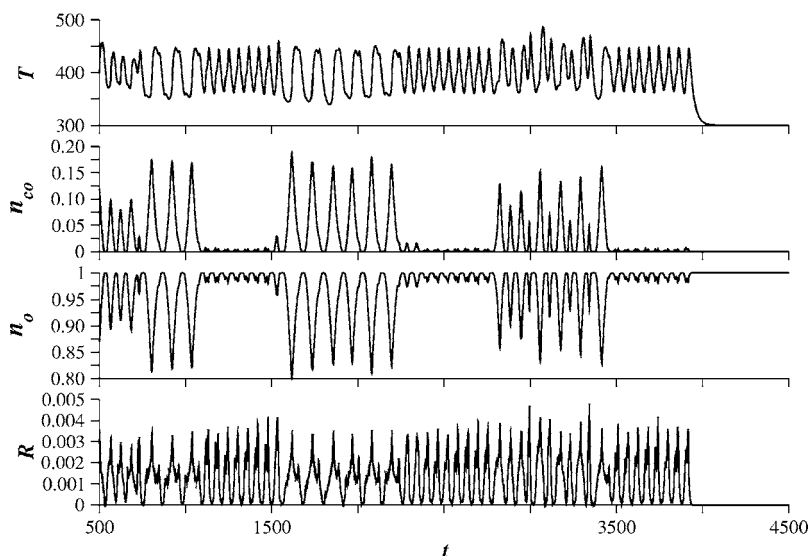


FIG. 5. Time evolution of the surface temperature, densities of CO and O, and production of CO_2 for $\omega/\omega_0=0.085$ and $A=0.80$, being $\gamma=0.01$ and $\omega_0=1.273\ 22\ \text{rad s}^{-1}$. After regular and irregular behaviors, the surface gets poisoned with oxygen atoms and the temperature of the surface relaxes until it reaches the room temperature, which ends the reactive process.

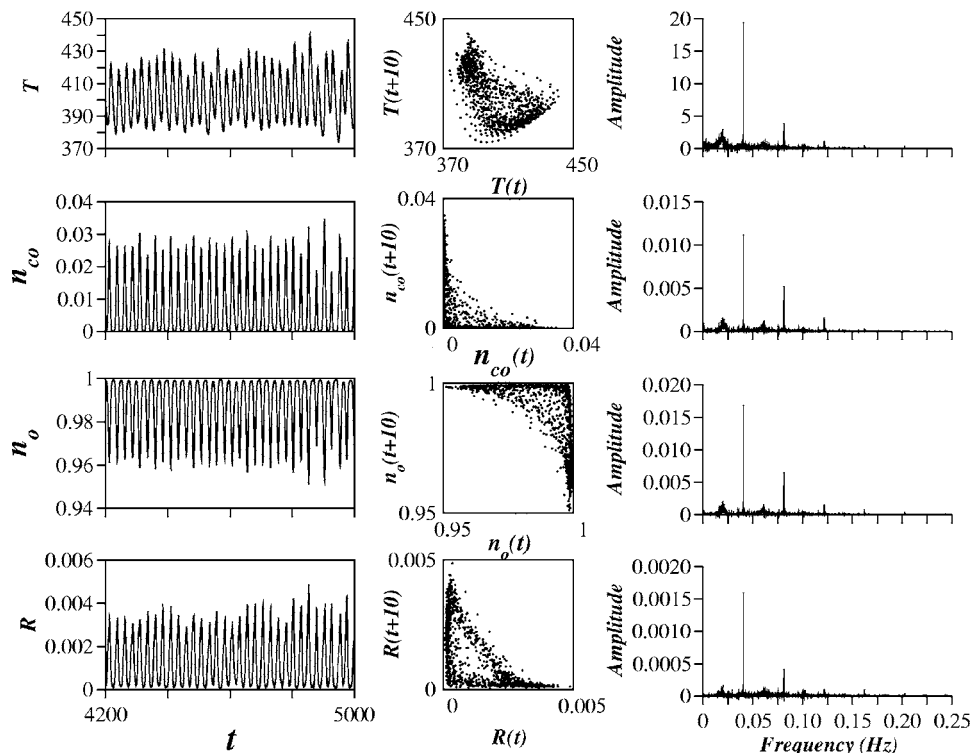


FIG. 6. Kinetic irregular oscillations of the surface temperature, densities of CO and O, and production of CO_2 , observed by the imposition of the external frequency $\omega=0.20\omega_0$, with $A=0.80$, being $\gamma=0.01$ and $\omega_0=1.273\ 22\ \text{rad s}^{-1}$. Also shown are the chaotic attractor and the frequency spectrum corresponding to the state indicated.

have only one fundamental frequency (submultiple of $f_0=0.202\ 64\ \text{Hz}$) and its corresponding harmonics. For $\omega=0.09\omega_0$ [case (d)], the response is irregular and chaotic. The evolutions of the Poincaré sections and the amplitude spectra show how the aperiodic behavior of the system in (a) gets stabilized in the orbits of P1 in (b) and (c), showing, finally in (d), an irregular behavior when the external frequency is increased. These results are in qualitative accord with the experiments and theoretical studies on nonlinear forced oscillations in the catalytic oxidation of CO.

Along the chosen band, $A=0.80$, and after the P1 range, we find alternation in the behavior of the system. As we increase ω , the system either shows an irregular response or the catalytic surface gets poisoned with oxygen atoms and the surface temperature relaxes to room temperature T_B , the reactive process thereby stopping. The transition to the poisoned state is shown in Fig. 5, corresponding to $\omega/\omega_0=0.085$. However, as ω increases, the system enters again a chaotic dynamic. Figure 6 shows the system chaotic behavior for $\omega/\omega_0=0.20$ and its corresponding iterative maps obtained for variables T , n_{CO} , n_{O} , and R from a certain time delay. The maximum Lyapunov exponent obtained is $0.149\ 798$, positive exponent as it should be in a chaotic behavior. It can also be observed that, although the Fourier spectrum corresponds to a chaotic case, frequency peaks corresponding to f_0 are still maintained. As Kraus *et al.*⁶ indicated, this last chaotic spectrum can be found next to a region of period 1 because it maintains a big amplitude peak ($0.040\ 53\ \text{Hz}$) and its harmonics ($0.081\ 05$, $0.121\ 58$, and $0.162\ 11\ \text{Hz}$) in the continuous frequency spectrum. In fact, if the Fourier spectrum in a chaotic state had two or more fundamental peaks (two or more independent frequencies), the period forcing method would likely coincide with the chaotic state of a periodic

state of periodicity bigger than 1. We have found in the phase diagram chaotic states of this kind that will have to be perturbed with two frequencies.

IV. CONCLUSIONS

In this paper we have shown, starting with the results obtained from the simulations carried out with the CA, that the forcing periodic method is able to control chaos by means of its conversion to periodic and predictable movements. We also show that a perturbing harmonic function of only one frequency is enough to transform the chaotic state of the system in periodic states of periodicity 1.

The simplicity of the external forcing method, in contrast to other chaos control methods such as that of Pyragas, which requires the redefinition of the feedback constant of the system, makes us go deeper into the oscillatory behavior of the reaction. The construction of the phase diagram can be extended for other regions of the amplitude and the frequency of the external perturbing function, using the technique of periodic forcing. Furthermore, a similar analysis can be performed when the temperature of the room where the reaction takes place (T_B) is perturbed, although the results taken from the literature show that they are similar to the ones obtained when the rate or the pressure of the oxygen adsorption process is perturbed. These two aspects are being currently analyzed by means of simulations carried out in the CA model for the study of the reaction of CO, using the forcing technique.

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