PHYSCON 2011, León, Spain, September, 5–September, 8 2011

PERIODIC FORCING ON THE OSCILLATORY BEHAVIOR OF A REACTION SIMULATED BY MONTE CARLO

F. E. Gálvez
Meteorological State Agency (AEMET)
Seville
Spain
fgalvezl@aemet.es

M. C. Lemos
Department of Condensed Matter Physics
University of Seville
Spain
lemos@us.es

A. Córdoba
Department of Condensed Matter Physics
University of Seville
Spain
cordoba@us.es

Abstract

In this paper we study the reaction $N_2O + H_2$ catalyzed on a Ir (110) surface by Monte Carlo (MC) simulation, focusing our study on the temporal evolution of the system. Bifurcation diagram of the model, which represents the surface density of adsorbed species as a function of a parameter, shows three distinct regions: an oscillatory region, which exhibits P1 (period-1, one maximum) oscillations, between two stable steady regions. Results obtained are in good agreement with experiments conducted in the reaction. At a later stage and to analyze the stability of the P1 oscillations observed, we apply harmonic disturbances on the MC model. To do this we perturb the P1 autonomous oscillations by periodic modulation of the partial pressure of one of the reactants. From the perturbed MC model interesting conclusions are drawn: when the external frequency is a half-integer of the natural frequency the behavior becomes aperiodic and quasiperiodic. In view of these results, we can think the existence of the Ruelle-Takens-Newhouse route to chaos in the perturbed MC model since it is observed that the chaotic state is obtained by breaking the quasiperiodic state.

Key words

Monte Carlo simulations; oscillatory kinetics; periodic forcing; model of surface reaction.

1 Introduction

Nitrous oxide is an important greenhouse gas and it participates in cyclic reactions that lead to ozone destruction [Ravishankara, 2009]. That is why it is necessary to supply to the industries of catalytic processes that diminish the nitrous oxide emitted in the atmosphere. In addition, the interest in N_2O reduction is not only practical but also theoretical. Catalytic systems are systems of many particles far from thermodynamic equilibrium, in which one can see a great variety of non-linear phenomena like kinetic phase transitions, oscillations, chaos or the formation of spatio-temporal patterns. Hysteresis and bistability have also been observed when external control parameters of the reaction (partial pressures or temperature) vary.

Autonomous isothermal oscillations in the reaction rates of the reaction $N_2O + H_2$ on the Ir(110) surface were observed experimentally by Carabineiro and Nieuwenhuys [Carabineiro and Nieuwenhuys, 2001] and Carabineiro, van Noort and Nieuwenhuys [Carabineiro, van Noort and Nieuwenhuys, 2002] under ultra-high vacuum conditions. The products of the reaction are N_2 and H_2O. The rate oscillations are found in a narrow range of temperature between 460 and 464 K, for ratios between partial pressures p_{H_2}/p_{N_2O} close to 1. The period of the oscillations is nearly 60 seconds. The oscillatory behavior in this system is special due to the unusual phase difference in the kinetic oscillations of the reaction products. Thus, N_2 oscillates in counter-phase with reactant N_2O and the oscillations maxima for H_2O are "delayed" compared to the maxima of N_2 oscillations. Later, Peskov *et al.* [Peskov, Slinko, Carabineiro and Nieuwenhuys, 2005] developed, successfully enough, a mean field (MF) model that describes the oscillatory behavior experimentally observed in the reaction. They demonstrated that as the origin of oscillations as the unusual phase difference between the oscillations of the reaction products can be explained on the basis of the character of the lateral interactions between the adsorbed species.

In the other way, periodic forcing of the kinetics of a reaction by the variation of some external control parameter such as, for example, the pressure of one of the reactants or the temperature of the gas, is one of the frequently used tools in the study of heterogeneous catalytic processes [Zhdanov, 2004]. The results obtained in this field refer generally to perturbations of P1 autonomous oscillations. In experiments focused on the study of the complex behavior in oscillatory catalytic reactions, the technique of the periodic perturbation is used as for stabilizing P1 oscillations, which is achieved if both external and internal frequencies coincide, as for generating quasiperiodic oscillations or to control chaos. In this case, one intends to stabilize the unstable periodic orbits contained in the chaotic attractors of the system. Too one of the goals of applying periodic perturbations on a reaction is to see whether these perturbations can be used to improve the performance of the reaction, for example, increasing the amount of resultant products.

The effect of periodic perturbations on the oscillatory kinetics of the reaction was analyzed by Lemos and Córdoba [Lemos and Córdoba, 2008]. These authors used the MF model of Peskov *et al.* [Peskov, Slinko, Carabineiro and Nieuwenhuys, 2005] to illustrate the stability of the P1 natural oscillations with regard to periodic perturbations. The goal was focused on the conversion of P1 natural oscillations to P1 oscillations with the imposed frequency. For this conversion, simultaneous periodic perturbations of both reactant pressures were found to be much more efficient compared to perturbation of one of the pressures. Quasiperiodic and chaotic states were not observed in the perturbed model.

The purpose of our study is double. First, we want to analyze the reaction through Monte Carlo (MC) simulations with special emphasis on the oscillatory behavior. To the best of our knowledge no work has been reported before for the $N_2O + H_2$ on the Ir(110) surface by MC simulations. In general, the study of the oscillatory behavior of a reaction is useful because the results of calculations for several models demonstrate that, for some cases, it is possible to reach a net reaction rate greater and/or better selectivity operating in an oscillatory regime than in a steady one. After, we want to show the influence that the periodic forcing of the pressure of one of the reactants has on the oscillatory behavior of the reaction, analyzing the results of the perturbed model simulated by MC.

2 Model and Monte Carlo simulation

The mechanism of the reaction includes the following steps: adsorption/desorption of N_2O and H_2, dissociation of N_2O, and formation of H_2O. We assume that the reaction products N_2 and H_2O are immediately desorbed after their formation on the catalytic surface.

$$\mathrm{N_2O\ (g)} + V \xrightarrow{k_1} \mathrm{N_2O\ (ads)}\ , \tag{1}$$

$$\mathrm{N_2O\ (ads)} \xrightarrow{k_{-1}} \mathrm{N_2O\ (g)} + V\ , \tag{2}$$

$$\mathrm{H_2\ (g)} + 2V \xrightarrow{k_2} \mathrm{H\ (ads)} + \mathrm{H\ (ads)}\ , \tag{3}$$

$$\mathrm{H\ (ads)} + \mathrm{H\ (ads)} \xrightarrow{k_{-2}} \mathrm{H_2\ (g)} + 2V\ , \tag{4}$$

$$\mathrm{N_2O\ (ads)} \xrightarrow{k_3} \mathrm{N_2\ (g)} + \mathrm{O\ (ads)}\ , \tag{5}$$

$$\mathrm{O\ (ads)} + 2\mathrm{H\ (ads)} \xrightarrow{k_4} \mathrm{H_2O\ (g)} + 3V\ , \tag{6}$$

where (g) indicates the gaseous phase, (ads) denotes an adsorbed particle on the surface, and V is a vacant site in the lattice. N_2O and H_2 are adsorbed on different vacant sites: the model assumes as well that N_2O and H_2 are adsorbed on separate sublattices. The adsorption is not competitive. The rate constants k_i $(i = \pm1, \pm2, 3, 4)$ are assumed in the Arrhenius form:

$$k_i = k_i^0 \exp[-\frac{E_i}{RT}],$$

where k_i^0 are the preexponential factors, R is the gas constant, T denotes the surface temperature, and E_i are the activation energies of the six elemental processes.

Lateral interactions between adatoms must be introduced into the model to obtain oscillations. It follows from the analysis of thermal desorption spectra that oxygen greatly modifies the desorption and dissociation rates of N_2O accelerating them. Accordingly, a contribution to the activation energy from the dependence of the rate constants k_{-1} and k_3 on the surface coverage of oxygen is introduced into the model:

$$\begin{aligned} k_{-1} = k_{-1}^0 \exp[-\frac{E_{-1}}{RT}] \exp[\frac{T_0}{T} e_{-1} n_O] = \\ = k_{-1}^* \exp[\frac{T_0}{T} e_{-1} n_O], \\ k_3 = k_3^0 \exp[-\frac{E_3}{RT}] \exp[\frac{T_0}{T} e_3 n_O] = \\ = k_3^* \exp[\frac{T_0}{T} e_3 n_O], \end{aligned}$$

with T_0 = 460 K, being n_O the O coverage.

The values of the preexponential factors and activation energies of various steps of the reaction mechanism used in the simulations are shown in Table 1. These values are equal to those of the MF model of Peskov *et al.* [Peskov, Slinko, Carabineiro and Nieuwenhuys, 2005]. Those were selected so that they produce the most similarity between the solutions of the MF model and the experimental data. At $T = T_0$ = 460 K, being

$Reaction\ \ step, i$	$k_i^0\ \ (s^{-1})$	$E_i\ \ (cal\ \ mol^{-1})$
1	6.2×10^4 mbar^{-1}	0
-1	10^{12}	31500
2	8.3×10^5 mbar^{-1}	0
-2	2.58×10^8	23000
3	5.0×10^{22}	51700
4	3.04×10^6	15000

Table 1. Kinetic parameters used in the model.

the gas constant R equal to 1.986 $cal\ \ K^{-1}\ \ mol^{-1}$, the values of the parameters of the model are:

$$\begin{aligned} k_1 = 6.2 \times 10^4\ \ s^{-1}\ \ mbar^{-1} &\quad , k_{-1}^* = 0.001\ \ s^{-1} \\ k_2 = 8.3 \times 10^5\ \ s^{-1}\ \ mbar^{-1} &\quad , k_{-2} = 0.003\ \ s^{-1} \\ k_3^* = 0.014\ \ s^{-1} &\quad , k_4 = 0.225\ \ s^{-1}. \end{aligned}$$

The nonlinearity, which is necessary to obtain oscillations, is accounted for through the dimensionless parameters of lateral interactions e_{-1} and e_3. It is also demonstrated that parameter e_{-1} practically does not affect the location and the width of the oscillatory interval for a value of e_3 fixed, that is, the critical parameter for oscillations is e_3.

2.1 Algorithm

The surface contains two kinds of sites. The molecules are adsorbed on the lattice sites and remain there until they desorb or react, without diffusion. The H_2 are adsorbed on one kind of site and the N_2O on a second type. The gas phase is a mixture of N_2O and H_2 molecules with partial pressures p_{N_2O} and p_{H_2}, respectively.

The lattice is square. Thus, each node has four nearest neighbors of a different kind to its and as second neighbors, four of the same kind. Only a square lattice is considered. The nodes of the lattice are labeled with two subscripts i and j, so that if $(i+j)$ is even the site belongs to the sublattice of O and if $(i+j)$ is odd, belongs to the sublattice of H.

The probability of an event is inferred from the relationship between the rate constants. They are defined as:

$$\begin{aligned} Norm = p_{N_2O}k_1 + k_{-1} + p_{H_2}k_2 + k_{-2} + k_3 + k_4 \\ p_{adsN_2O} &= p_{N_2O}k_1/Norm \\ p_{desN_2O} &= k_{-1}/Norm \\ p_{adsH_2} &= p_{H_2}k_2/Norm \\ p_{desH_2} &= k_{-2}/Norm \\ p_{disN_2O} &= k_3/Norm \\ p_{reac} &= k_4/Norm. \end{aligned}$$

In our simulations we have worked with a lattice 1000×1000 with boundary conditions. A Monte Carlo step (MCS) has been given when one performs so many elementary events as sites of the lattice. In our case, a MCS is to carry out 10^6 elementary events so that, on average, each site will have been visited once.

In the simulations carried out 1000 MCS have been made in cases in which the system does not oscillate and the density of adsorbed particles reaches a steady state, and up to 10000 MCS to study the system in the region of self-sustained oscillations.

The algorithm simulating each elementary event according to the proposed mechanisms is initiated by selecting a random lattice site:

> a) If the site belongs to the sublattice O ($i+j$, even) it may occur:
> a.1) If it is empty, N_2O can be adsorbed.
> a.2) If it contains a N_2O it can:
> a.2.1) to be desorbed or,
> a.2.2) to be dissociated. In this case, N_2 is desorbed immediately and O remains adsorbed.
> a.3) If it contains a O and there are two adjacent sites H on the H sublattice, the reaction of formation of a molecule H_2O can take place. The molecule formed is immediately desorbed leaving three vacant sites.
> b) If the site belongs to the sublattice H ($i+j$, odd) it may occur:
> b.1) If it is empty and there is at least one vacancy among the nearest neighbors on the sublattice of H, then a molecule H_2 can be adsorbed, being dissociated in two adsorbed H, each occupying the above empty positions.
> b.2) If it contains a H and there is at least another H between its nearest neighbors, then it can be combined to form a molecule H_2 that automatically desorbs leaving two empty sites.

The steps of adsorption, desorption, dissociation and reaction will be viable on the sites chosen according to the probabilities of each processes defined above.

2.2 Results of the autonomous model

At T = 460 K, $p_{N_2O} = 10^{-6}$ *mbar*, $p_{H_2} = 1.2 \times 10^{-6}$ *mbar*, and $e_{-1} = 4$, the results of MC simulations show that for certain values of the lateral interaction

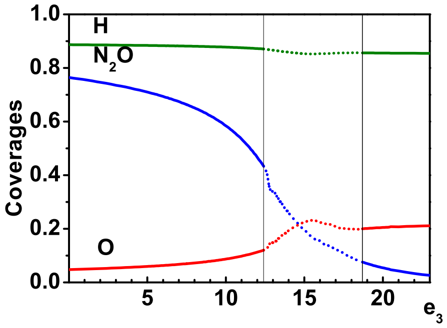

Figure 1. Bifurcation diagram for adsorbed species coverages as a function of the parameter e_3. The diagram shows an oscillatory region (dotted lines) between two steady regions (continuous lines). The system becomes oscillatory if the values of e_3 are between 12.7 and 18.7. The points inside oscillatory region indicate the time average of oscillation amplitudes for each value of e_3.

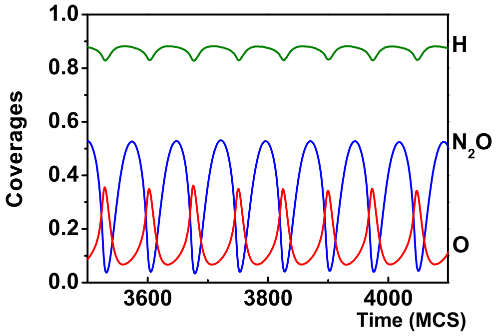

Figure 2. Time series of P1 (period-1, one maximum) autonomous oscillations of the adsorbed species coverages.

parameter e_3, constant values for the densities of adsorbed particles are reached. But there is a range of values of e_3 where self-sustained oscillations appear. These aspects are reflected in the bifurcation diagram of Figure 1 showing the three distinct regions: two stable steady regions (continuous lines) on both sides of an intermediate region where the system exhibits self-sustained oscillations (dotted lines). This last region is represented by the average value of the amplitude of the oscillation.

A first result that emerges from our study is that the oscillatory region is wider (the oscillations are observed for values of e_3 ranging between 12.7 and 18.7) than that obtained by Peskov *et al.* [Peskov, Slinko, Carabineiro and Nieuwenhuys, 2005] with the mean field equations (here, the oscillatory region is observed for values of e_3 between 10 and 11).

An oscillatory state that shows the temporal evolution of the density of adsorbed particles, for $e_3 = 13$, is shown in Figure 2. The oscillation period is 74 MCS. The model also shows the results that indicate that the signals of N_2O and H oscillate practically in counterphase in relation to that of O, and the maxima of the signals of N_2O are slightly delayed compared with the maxima of oscillations of H. The mechanism of the oscillations can be explained as follows: starting from a clean surface, hydrogen immediately occupies all the sites in the sublattice and, therefore, it plays a minor role in the appearance of oscillations. The concentration of N_2O on the surface keeps growing. Due to the dissociation of N_2O, the concentration of adsorbed oxygen increases as well. Oxygen accelerates dissociation of N_2O and surface concentration decreases drastically, while the oxygen coverage increases in an autocatalytic way. However, concentration of surface oxygen begins to diminish because of its reaction with hydrogen. The decrease of the concentration of oxygen leads to an increase of the surface concentration of N_2O. As a result of this process the dissociation rate of N_2O increases again, leading to an increase of the surface concentration of oxygen. Oxygen accelerates the dissociation rate of N_2O again and the cycle of oscillations begins anew. The rate oscillations for the reaction are related to periodic transitions between O-rich and O-poor surfaces.

MF equations obtained by direct application of mass-action law have very limited validity, because ignore the non-ideality of the adsorbed layer, considering the surface as homogeneous and without lattice structure, do not take into account correlations, assuming that the particles are randomly distributed on the surface, nor the elementary reaction mechanism. To resolve certain problems, it is common to obtain the MF equations in a simple approximation, approximation of sites, obtained from an extension of mass-action law and to incorporate the non-ideal factors (e. g., lateral interactions between adsorbed particles) via the dependence of the activation energies on coverage for some of the elementary steps. Model of Peskov *et al.* [Peskov, Slinko, Carabineiro and Nieuwenhuys, 2005] has been done at this last level: oscillatory kinetics is related to adsorbate-adsorbate lateral interactions. These generic approaches are reasonable in many cases and especially in situations in which rate processes on the adsorbed layer are not accompanied, for example, by adsorbate-induced surface restructuring. This is thus because experimental studies indicate that the kinetic oscillations often result from the interplay of rapid chemical reaction steps and relatively slow complementary processes such as adsorbate-induced surface restructuring and, therefore, oscillations are observed in a relatively small range of parameters of the system. Thus, strictly speaking, the conventional MF equations used to describe oscillations on homogeneous surfaces are not applicable on heterogeneous surfaces.

The difficulty of introducing into the kinetic equations some specific characteristics of both, the catalytic surface considered (restructuring of the catalytic surface, specific distribution of active sites, different adsorption levels, etc.) as well the particles involved in the reactive processes (adsorbate-adsorbate lateral interactions, mobility of the particles, etc.) can be avoided by using an alternative MC algorithm. The implementation of this method does not need to make approaches on the distribution of adsorbed particles on the surface and facilitates the knowledge of it. In particular, the MC method is indispensable for simulations of oscillatory patterns on the nanometre scale. On the other hand, due to computational limitations, it cannot be used in the situations where the range of the rate constants is very wide. For example, MC simulations of patterns on the micrometre or millimetre scales are still a challenge. In these cases, the MF theory is often more suitable. Thus, the MF and MC approaches are complementary.

It is convenient to notice, therefore, that qualitative agreement of the MC model with that predicted by using the MF model of Peskov *et al.* [Peskov, Slinko, Carabineiro and Nieuwenhuys, 2005], and earlier experimentally observed by Carabineiro and Nieuwenhuys [Carabineiro and Nieuwenhuys, 2001] is, of course, not a merit of the MC model, because physically the model was based on the ideas borrowed from the MF model, which in turn were based on the experimental data, and accordingly the agreement with experiment is neither surprising. However, MC model allows to follow the spatial evolution of the system, a possibility that MF models do not offer. In this sense, MC method is superior to MF one, because it allows us to incorporate into a model all the essential ingredients of the MF model and in addition to explore others non-ideal factors that are difficult to treat analytically. Although the aim of our study is to analyze the temporal evolution of the system without stopping to observe the distribution of the adsorbed species on the surface, in other problems the information that is extracted from the spatial structures is the key to understanding the behavior of the reaction. Thus, to complete our study, we include snapshots of a (100×100) fragment of the (1000×1000) lattice when the system exhibits oscillatory behavior. These surface snapshots were generated during the MC run shown in the Figure 2 and are represented in Figure 3. Pictures of the spatial distributions of the adsorbed N_2O (blue), O (red), H (yellow) and vacant sites (green) are shown for four different times when the N_2O coverage is: maximum (MCS = 3721); between the maximum and minimum (MCS = 3737); minimum (MCS = 3753); and between minimum and maximum (MCS = 3775). Random distributions, without island formation, were obtained in all cases.

2.3 Route to chaos

In a subsequent study, using the same experimental procedure, Carabineiro *et al.* [Carabineiro, van Noort and Nieuwenhuys, 2003] obtained an oscillatory behavior of the reaction at constant temperature and tried to alter this behavior. So, once the oscillations started, they showed that an attempt to change the pressure of H_2 involved the loss of the oscillation. By contrast, small variations in the pressure of N_2O caused changes in the oscillatory behavior. Thus, from a P1 oscillatory regime, they observed a number of duplications of period that ended in an aperiodic regime. These duplications of period observed for extremely small pressure differences indicated a Feigenbaum route to chaos in the reaction. Also P3 (period-3, three maxima) oscillations and P5 (period-5, five maxima) oscillations were observed. Pn indicates oscillations of period-n with n-maxima by period.

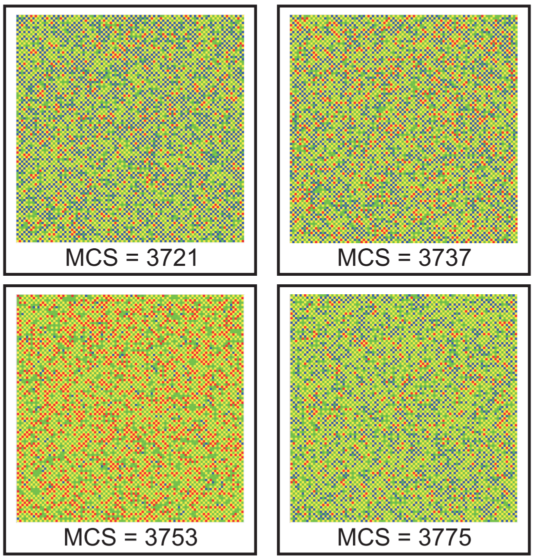

Figure 3. Snapshots of a (100×100) fragment of the (1000×1000) lattice at four different stages of oscillations of the MC run shown in the Figure 2. N_2O, O, H adsorbed particles and vacant sites correspond to blue, red, yellow and green colors, respectively. MCS = 3721 corresponds to a maximum in fraction of N_2O adatoms; MCS = 3737, between maximum and minimum; MCS = 3753, minimum; and, MCS = 3775, between minimum and maximum.

Our next step was to introduce into the MC simulation model the experimental values of pressures and temperature provided by Carabineiro *et al.* [Carabineiro, van Noort and Nieuwenhuys, 2003] in order to see if we got a route to chaos or the periodicity of the oscillations changes. But we did not get any of those results. It should be noted that in the study where this behavior appeared [Carabineiro, van Noort and Nieuwenhuys, 2003], the values of experimental pressures and temperature were slightly different from the values that Peskov *et al.* [Peskov, Slinko, Carabineiro and Nieuwenhuys, 2005] used in mean-field model, values that also we use in our simulation model.

To gain insight in the oscillatory behavior of the system and to see if it exhibits different oscillations to P1 ones or a route to chaos, we proceed in the next section to disturb the reaction harmonically. As there are experimental observations showing a route to chaos with period duplications, as well as P3 and P5 oscillations, as it is stated above, we expect that the periodic forcing technique allows us to observe chaotic, quasiperiodic or periodic with different periodicities behaviors.

3 Monte Carlo simulation of the perturbed model

To test the stability of the oscillations found by MC simulations of the reaction model, we apply a perturbation in the partial pressure of nitrous oxide, using a sinusoidal function of a single frequency:

$$p_{N_2O} = (p_{N_2O})_0(1 + A\sin(2\pi f t)) \ , \qquad (7)$$

where A and f are the normalized amplitude and frequency of disturbance, respectively, and $(p_{N_2O})_0$ corresponds to the partial pressure of N_2O used in the autonomous system (without forcing).

To simplify the calculations, we choose the coverage of oxygen, n_O, as the only output variable. Of the 5000 points that comprise each series, we ignored the 904 first to remove the transient regime and with the remaining ones we calculate the time average of the oxygen coverage and its fluctuation. We do the analysis of results on the fluctuation of n_O. At this point, we analyzed the time series obtained, finding, among others, the Fourier transform or the next-maximum map.

Figure 4 shows a self-sustained oscillation at T = 460 K, $(p_{N_2O})_0 = 10^{-6}$ $mbar$, $p_{H_2} = 1.4 \times 10^{-6}$ $mbar$, $e_{-1} = 4$ and $e_3 = 13$, keeping constant the other parameters listed in Section 2. The state oscillates with a natural frequency $f_0 = 0.01221$ MCS^{-1} (period equal to 82 MCS). Figure 4 shows the temporal evolution of O coverage at the top, along with its Fourier spectrum (in the middle) and next-maximum map (at the bottom). In the discrete Fourier spectrum the fundamental frequency and its harmonics are observed. It is known that the next-maximum map shows 1, 2, 3,..., or n points depending on the periodic oscillations are P1, P2, P3,..., or Pn, respectively, hence P1 oscillations are represented on the next-maximum map with one point in Figure 4. This P1 oscillatory state is that which we seek to disturb.

3.1 Results of the perturbed model

We analyze the response of the perturbed system for four values of the external frequency: $f_1 = f_0 = 0.01221$ MCS^{-1}, $f_2 = 1.5f_0 = 0.01831$ MCS^{-1}, $f_3 = 2f_0 = 0.02442$ MCS^{-1}, and $f_4 = 2.5f_0 = 0.03052$ MCS^{-1}. For each value of f, the normalized amplitude of the disturbance has been varied from $A = 0.1$ to $A = 1$, with a step of 0.1.

In cases where the external frequency is a integer multiple of the natural frequency (cases $f_1 = f_0$ and $f_3 = 2f_0$), the responses of the system are P1 oscillations, except for $f_3 = 2f_0$ and $A = 0.4$ in which the P1 natural oscillation is transformed into P3 one. In all these cases the system responds with an output frequency equal to the natural one.

Most interesting behaviors are observed in cases where the external frequency is a half-integer of the natural frequency (cases $f_2 = 1.5f_0$ and $f_4 = 2.5f_0$). Thus, for $f_2 = 1.5f_0$ and at low disturbance amplitudes, the behavior is quasiperiodic. By increasing the value of A, the system becomes chaotic ($A = 0.3$), and quasiperiodic later. For values of $A \geq 0.7$ the system exhibits P1 forced oscillations with an output frequency that equals the external one, that is, $f_{out} = f_2 \neq f_0$. When $f_4 = 2.5f_0$, the results are similar to the previous case, except that does not appear any chaotic state.

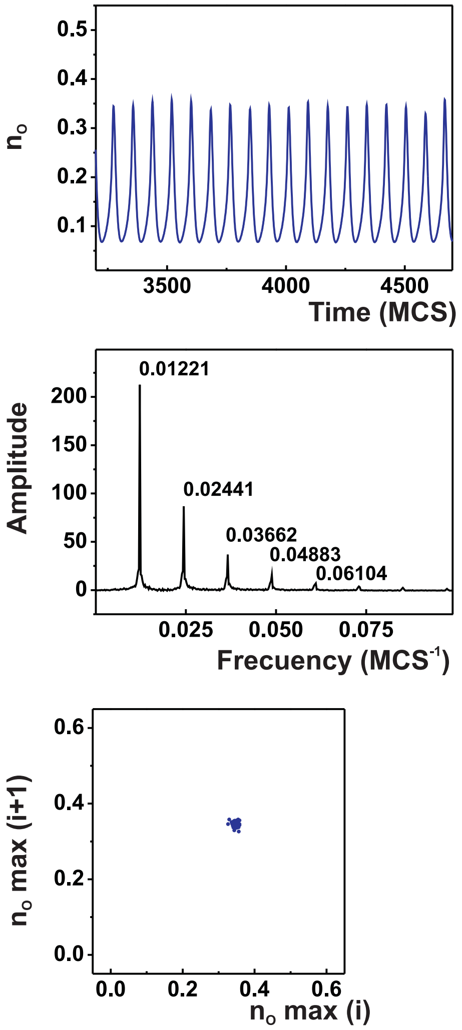

Figure 4. Typical time series of autonomous oscillations (without forcing). This series represents P1 oscillations of O coverage, as it can be observed in the Fourier spectrum and the next-maximum map attached. This map shows one point if the periodic oscillations are P1. The Fourier spectrum is discrete with one fundamental frequency, $f_0 = 0.01221$ MCS^{-1}. Its harmonics can also be seen.

Figure 5 shows the time evolutions of O coverage, the Fourier spectra and the next-maximum maps for $f_2 = 1.5f_0$ and $A = 0.3$ (left), and $f_2 = 1.5f_0$ and $A = 0.4$ (right). These series represent chaotic and quasiperiodic regimes, respectively. It can be observed that the temporal evolution of the quasiperi-

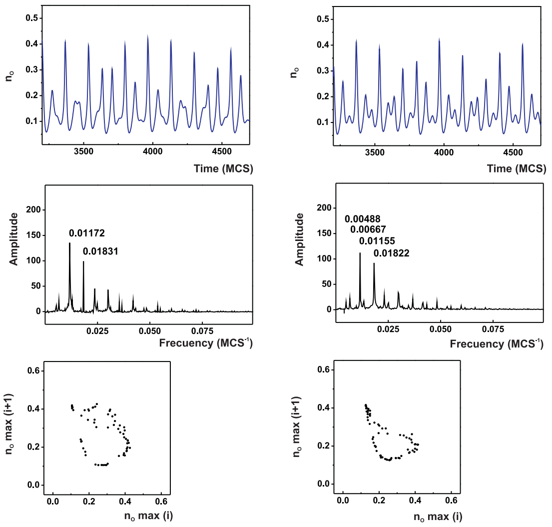

Figure 5. Time series of the forced oscillations of O coverage and its corresponding Fourier spectra and next-maximum maps, for different values of external normalized amplitude and $f = 1.5f_0 = 0.01831\, MCS^{-1}$. (Left) $A = 0.3$, forced oscillations that represent a chaotic behavior: time evolution is aperiodic and the next-maximum map is represented by open lines. (Right) $A = 0.4$, forced oscillations that represent a quasiperiodic state: the next-maximum map shows points place themselves over the same perfectly defined closed curve. In addition, the frequency spectrum shows two incommesurable fundamental frequencies, $f_{1out} = 0.00488\, MCS^{-1}$ and $f_{2out} = 0.00667\, MCS^{-1}$.

odic state shows a regular pattern, while the chaotic state is completely aperiodic. In the quasiperiodic state, the points place themselves over the same perfectly defined closed curve in the next-maximum map; the chaotic state is represented by open lines. The Fourier spectrum corresponding to the quasiperiodic case shows two fundamental frequencies, $f_{1out} = 0.00488\ MCS^{-1}$, and $f_{2out} = 0.00667\ MCS^{-1}$, since, for example, $f_{3out} = 0.01155\ MCS^{-1}$ and $f_{4out} = 0.01822\ MCS^{-1}$ are expressed as combination of the incommesurable two fundamental frequencies: $f_{1out} + f_{2out} = f_{3out}$ and $f_{4out} = 2f_{3out} - f_{1out}$. Finally, there is no doubt about the chaotic character of the time series corresponding to $f_2 = 1.5f_0$ and $A = 0.3$. We have calculated, moreover, the maximum Lyapunov exponent and it results 0.003047, with positive sign, so confirming the chaotic nature of that state.

It is convenient to remember that several behaviors observed from MC simulations of the perturbed model can be awaited if one know the theory of the periodically perturbed oscillatory systems [Scott, 1991]. When forcing happens at low values of the normalized amplitude, these systems usually exhibit a region of quasiperiodic oscillations. Inside this region are incrusted a number of islands (the so-called Arnold tongues) of periodic oscillations that correspond to the cases in which the ratio between the forced and natural frequencies, f/f_0, is close to an integer or to one simple fraction (in the practice, only the major tongues can be located). As the normalized amplitude of the disturbance increases, it is possible sometimes to observe regular oscillations, which are oscillations modulated with a frequency significantly smaller than both natural and external frequencies. The regions where these periodic oscillations are observed are called synchronization bands between the system and the disturbance. The wideness of a synchronization band, that is, the range of frequency where the response of the perturbed system is periodical for a fixed value of the normalized amplitude, increases as this increases. Chaotic oscillations can be observed as well when the amplitude of the disturbance increases; in this case the transition to chaos takes place by means of the duplication of period. Finally, if the normalized amplitude increases, P1 oscillations with the external frequency are observed.

The results that we have obtained are qualitative: a complete classification including the Arnold tongues or other type of regime different of that shown here is outside of the aim of this paper because it would require testing an exhaustive range of values for A and f. Of course, a systematic variation of A and f will allow us to draw the kinetic phase diagram of the perturbed model, which will show the dynamical system states and their possible bifurcation points.

4 Conclusions

We have developed a model that treats the reaction $N_2O + H_2$ catalyzed on Ir (110) surface using Monte Carlo (MC) simulations. The surface where the reaction takes place is a square lattice containing, in turn, two sublattices, O sublattice and H sublattice. The transition probabilities of the different processes of adsorption, desorption, dissociation and reaction are chosen in the form of Arrhenius and the contributions to the activation energy of the substrate and the interaction between neighboring adsorbed species are distinguished. It is noted that lateral interactions between neighboring adsorbates are the origin of oscillatory behavior. The main feedback mechanism leading to oscillations is the dissociation of N_2O to O.

Bifurcation diagram that represents the surface coverage of adsorbed species H, N_2O and O as a function of a lateral interaction parameter, shows three clearly defined regions: an oscillatory region between two steady regions. This diagram is similar to that obtained by other authors using a model of mean field (MF), although the region where the oscillatory behavior is observed is wider in the MC model than in the MF model. It also reproduces the observations showing a delay in the maxima of N_2O with respect to those of H. In any case, the results obtained by MC simulation are in good agreement with experiments conducted in the reaction studied.

To analyze the stability of the P1 oscillations shown and try to reproduce some of the complex behaviors observed experimentally in the reaction, we perturb harmonically the MC model. This study draws interesting conclusions: a) When the external frequency equals the natural frequency, the oscillations are completely stable and do not change the type of periodicity: P1 oscillations remain. However, if the external frequency doubles the natural frequency, the behavior remains periodic but, in some cases, the type of periodicity of oscillations change and the transition from P1 to P3 oscillations is observed. b) When the external frequency is a half-integer of the natural frequency, aperiodic and quasiperiodic behaviors can be observed. We did not find the Feigenbaum route to chaos, although the sweep done in the range of the perturbing normalized amplitude and frequency is not accurate enough. But we can say, in view of the results, that the route to chaos of Ruelle-Takens-Newhouse is observed in the perturbed MC model: the chaotic state is obtained by breaking the quasiperiodic state.

Acknowledgements

This work is partially financed by the Project No. FIS2008-04120 of the Ministry of Science and Innovation of the Spanish Govern.

References

Carabineiro, S. A. and Nieuwenhuys, B. E. (2001) Reduction of N_2O by H_2 on the Ir(110) surface: oscillations in rate. *Surface Science*, **495**, pp. 1–7.

Carabineiro, S. A., van Noort, W. D. and Nieuwenhuys, B. E. (2002) A comparative study of the $N_2O - CO$ and $N_2O - H_2$ reactions on the Ir(110) surface with emphasis on the oscillatory behavior. *Catalysis Letters*, **84**, pp. 135–142.

Carabineiro, S. A., van Noort, W. D. and Nieuwenhuys, B. E. (2003) Oscillations in the $N_2O - H_2$ reaction over Ir(110). Route to chaos. *Surface Science*, **532-535**, pp. 96–102.

Lemos, M. C. and Córdoba, A. (2008) Sinusoidal Perturbation of the Oscillatory Kinetics of the N_2O+H_2 Reaction on Ir(110). *Catalysis Letters*, **121**, pp. 121–130.

Peskov, N. V., Slinko, M. M., Carabineiro, S. A. and Nieuwenhuys, B. E. (2005) Mathematical modeling of rate oscillations in N_2O reduction by H_2 and CO over the Ir(110) surface. *Catalysis Today*, **105**, pp. 223–233.

Ravishankara, A. R., Daniel, J. S. and Portmann, R. W. (2009) Nitrous Oxide (N_2O): The Dominant Ozone-Deplecting Substance Emitted in the 21st Century. *Science*, **326**, pp. 123–125.

Scott, S. K. (1991). *Chemical Chaos*. Clarendon Press. Oxford.

Zhdanov, V. P. (2004) Periodic perturbation of the kinetics of heterogeneous catalytic reactions. *Surface Science Reports*, **55**, pp. 1–48.