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# Synchronization in oscillatory surface reactions on single crystal surfaces

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In oscillatory surface reactions on single crystal surfaces the partial pressure variations that accompany the oscillations in the reaction rate represent a global interaction between the local oscillators. The NO+CO reaction on Pt(100) exhibits both synchronized and unsynchronized oscillatory behavior depending on the substrate phase. Unsynchronized oscillations occur on the  $1 \times 1$  phase but on the hex phase one finds synchronized oscillatory behavior. The mechanism leading to synchronization in the oscillations on Pt(100)-hex can be traced back to a critical dependence of the  $1 \times 1 \rightleftharpoons \text{hex}$  phase transition on the partial pressures of NO and CO. At both ends of the temperature window for rate oscillations one finds well-defined transitions to a stationary reaction rate. These bifurcations are discussed in terms of a transition from synchronized to unsynchronized behavior. In particular, the occurrence of deterministic chaos in connection with a Feigenbaum scenario is interpreted as being due to such a transition.

## I. INTRODUCTION

In heterogeneously catalyzed reactions exhibiting rate oscillations, the surface of the catalyst can be thought of as a large ensemble of individual oscillators which need to be synchronized in order to produce macroscopic variations of the reaction rate.<sup>1-3</sup> In oscillation experiments conducted at high pressure ( $p \approx 1-1000$  mbar), thermal coupling undoubtedly plays the dominant role in synchronization.<sup>4,5</sup> This mode is irrelevant in the single crystal experiments carried out under isothermal low pressure conditions ( $p < 10^{-3}$  mbar), because due to the extremely small reaction rate, these experiments can be regarded as perfectly isothermal.<sup>6</sup>

Under these conditions, spatial coupling of the different surface elements is provided by two basic mechanisms, surface diffusion of a mobile adsorbate and gas-phase coupling (GPC) via partial pressure variations of the reactants. The latter arise due to mass balance in the reaction and, depending on the experimental parameters, typically variations of the order of  $\approx 1\%$  are seen corresponding to conversion rates of the same magnitude.

While surface diffusion provides only a communication between neighboring surface elements, gas-phase coupling represents a global interaction since the reaction rate integrates over the whole surface area. The partial pressure variations which arise in a flow reactor can be described by the equation

$$\frac{dp}{dt} = \frac{p_0 - p}{\tau} + p^*(r_d - r_a)$$

in which  $p_0$  denotes the partial pressure without reaction,  $\tau$  the reactor residence time,  $p^*$  the pressure increase caused by desorption of one monolayer, and  $r_d$  and  $r_a$  are the desorption and the adsorption rate, respectively.

Since the UHV chamber represents a gradient-free flow reactor, all parts of the surface are affected by GPC in the same way and practically without delay ( $\tau < 1$  ms). In the simplest case one would therefore expect a homogeneously oscillating surface. Since, on the other hand, surface diffu-

sion gives rise to reaction fronts and various types of spatial patterns, two competing coupling mechanisms exist.

The purpose of this article is to demonstrate some mechanisms over which gas-phase coupling can achieve synchronization in an oscillatory surface reaction and to illustrate the various phenomena which can be observed in transitions from synchronized to unsynchronized oscillations. After briefly reviewing the role of GPC in catalytic CO oxidation, mainly the results of spatially resolved measurements of the NO+CO reaction on Pt(100) are discussed. Because both synchronized and unsynchronized behavior is found in this reaction, this system represents a nice example for demonstrating some of the more general phenomena which can occur in synchronized oscillatory systems.

## II. SYNCHRONIZATION IN CATALYTIC CO OXIDATION

The important role GPC plays in determining the stability and regularity of rate oscillations became evident through a comparison of the oscillations which occur in catalytic CO oxidation on Pt(100) and Pt(110).<sup>6</sup> While very regular and stable oscillations were found on Pt(110), the oscillations on Pt(100) were usually irregular and difficult to reproduce. The different character of the oscillations could be attributed to a highly efficient GPC mode in the case of Pt(110) and to the absence of this mode in the case of Pt(100). The strongly varying efficiency of gas-phase coupling on the two substrate orientations could in turn be traced back to the different extensions of the existence range for oscillations in parameter space which determines the sensitivity to partial pressure variations.<sup>6</sup>

Direct evidence demonstrating the influence of GPC was gained in experiments in which two Kelvin probes were used to record the  $\Delta\phi$  oscillations simultaneously at two different locations of the sample. Such experiments were started first with a flat Pt(110) sample and then continued with a Pt single crystal of cylindrical shape (axis  $\parallel [001]$ ) whose surface comprised all orientations of the  $[001]$ -zone.<sup>7,8</sup> The dominant role of gas-phase coupling in the oscillations on Pd(110) was

TABLE I. The influence of gas-phase coupling in oscillatory surface reactions.

Reaction system	Integral behavior	Spatial patterns	Gas-phase coupling
Pt/CO+O <sub>2</sub>	Rate oscillations	Homogeneous oscillations + wave patterns	Yes
Pt(100)-1×1/NO+CO	Stationary (excitable)	Wave trains	No
Pt(100)-hex/NO+CO	Rate oscillations	Homogeneous oscillations	Yes
Pt(100)-hex/NO+NH <sub>3</sub>	Rate oscillations	Homogeneous oscillations + wave patterns	Yes

demonstrated by cutting a Pd(110) single crystal in half and following the oscillations on the two halves with two Kelvin probes.<sup>9</sup>

With the introduction of photoemission electron microscopy (PEEM) as a method to image the locally varying adsorbate concentration with a high spatial resolution ( $\approx 1 \mu\text{m}$ ), the synchronizing influence of GPC could be made visible directly. In catalytic CO oxidation on Pt(110), a spectacular variety of spatiotemporal patterns were found.<sup>10</sup> In particular, the occurrence of standing waves seemed to be only explicable in terms of synchronization via the gas-phase. Although this interpretation is supported by simulations by Levine *et al.*<sup>11</sup> showing that standing waves can arise due to parametric resonance, their analysis is not fully consistent with the experimental findings and more work is required in order to clarify the origin of this interesting effect.

### III. SYNCHRONIZATION IN THE NO+CO REACTION ON Pt(100)

#### A. Unsynchronized oscillations on Pt(100)-1×1

The catalytic reduction of NO with either CO, H<sub>2</sub>, or NH<sub>3</sub> as reducing agent exhibits kinetic oscillations on a Pt(100) surface which have been studied in the  $10^{-9}$ – $10^{-5}$  mbar range with various methods.<sup>12–16</sup> All three oscillatory reactions exhibit similar dynamical behavior whose origin can be traced back to autocatalysis inherent in the chemical reaction network. The autocatalysis, which arises due to the vacant site requirement for NO dissociation, is considered to be the main driving force for the rate oscillations while presumably the surface phase transition (SPT) of Pt(100) plays only a minor role.

In the NO+CO reaction, two separate  $T$  windows for oscillatory behavior exist on Pt(100) which behave entirely differently with respect to synchronization.<sup>17–19</sup> In the lower-lying  $T$  window, the oscillations proceed unsynchronized on a 1×1 substrate, while in the upper-lying  $T$  window we observe a largely hex-reconstructed, uniformly oscillating surface due to synchronization via the gas phase. The two existence ranges for oscillations can thus be used to demonstrate the mechanisms of synchronization. An overview of synchronization in the NO+CO reaction and in other reaction systems of interest is given in Table I.

In the lower-lying  $T$  window, no sustained rate oscillations were found.<sup>13,17,19</sup> In PEEM, one observes periodic

wave trains, i.e., the surface is oscillating on a local scale. Averaged over a larger area, however, these local oscillations correspond to a stationary reaction rate. By applying a small synchronizing  $T$  jump, rate oscillations can be excited, corresponding to a uniformly oscillating surface. As the periodic wave trains again spread out over the surface, the rate oscillations decay within a small number of cycles.<sup>13</sup> Evidently, in this lower-lying  $T$  window for oscillations, gas-phase coupling is not strong enough to ensure a synchronized oscillating surface. In order to understand why gas-phase coupling is ineffective in the NO+CO reaction on Pt(100)-1×1, it is very instructive to compare this reaction with the CO+O<sub>2</sub> reaction on Pt surfaces where gas-phase coupling is known to dominate.

The effect of gas-phase coupling is shown in Fig. 1 for two systems, Pt(110)/CO+O<sub>2</sub> and Pt(100)-1×1/NO+CO, by means of their rate versus  $p_{\text{CO}}$  curves. The amplitude of rate oscillations is schematically represented in the two plots by bars with double arrows. These bars are not aligned vertically since due to mass balance in the reaction an increase in the reaction rate is accompanied by a corresponding decrease in  $p_{\text{CO}}$  (strongly exaggerated in the plots). Of course, the decrease in  $p_{\text{CO}}$  is also connected with a corresponding decrease of the other reactant, but for simplicity we neglect the pressure variations of the gas being present in excess (O<sub>2</sub> and NO, respectively).

In both reaction systems, one has a reactive state (denoted by A in the plots), characterized by a low adsorbate coverage so that the reactants can adsorb and dissociate freely, and an unreactive state (denoted by B), in which a high adsorbate coverage inhibits adsorption (O<sub>2</sub>) or dissociation (NO). In a simplified way, rate oscillations can be described as periodic transitions between these two states. Of decisive importance for the different efficiency of gas-phase coupling in the two reaction systems is that their existence ranges for oscillations are located on different sides of the rate maximum. In the CO+O<sub>2</sub> reaction, oscillations are only found to the right of the rate maximum, while in the NO+CO reaction oscillations occur mostly to the left of the rate maximum, i.e., with NO being present in excess.<sup>13,19</sup>

Considering first the CO+O<sub>2</sub> reaction, it is quite evident from the diagram in Fig. 1(a) that a positive feedback exists between the transitions from A to B and vice versa and the concomitant variations in  $p_{\text{CO}}$ . An increase in the reaction rate and hence a decrease in  $p_{\text{CO}}$  will favor the move towards the reactive state A because the CO coverage is low in A. In

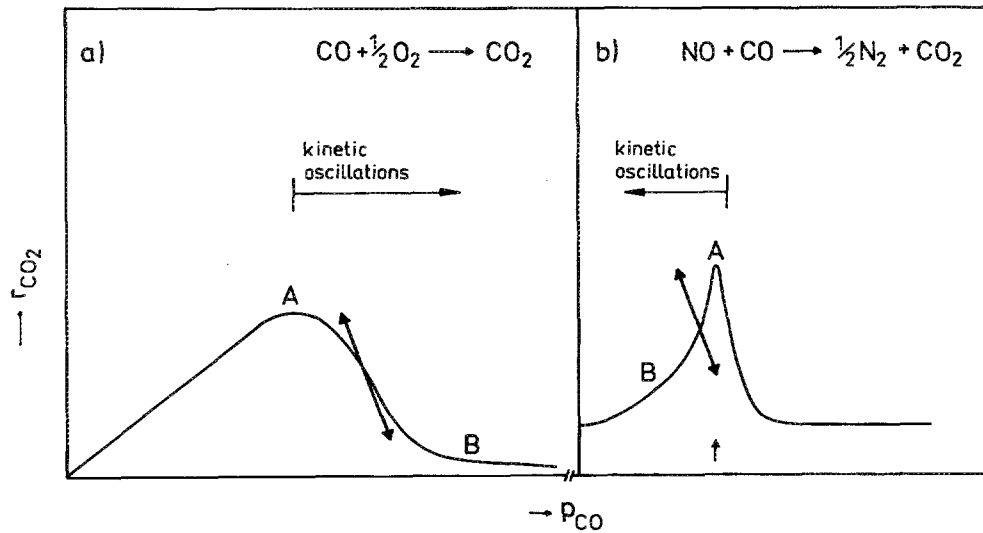


FIG. 1. Schematic diagrams explaining (a) the synchronizing and (b) desynchronizing influence of gas-phase coupling in two oscillatory surface reactions. The amplitude of the rate oscillations are represented by bold lines with double arrows. Their inclination angle with respect to the vertical direction indicates the  $p_{\text{CO}}$  variations that arise due to the finite pumping rate of the system. In the diagram these angles have been strongly exaggerated for the sake of clarity. A and B denote the reactive and unreactive state, respectively, in the rate vs  $p_{\text{CO}}$  curves. (a) Catalytic CO oxidation on Pt surfaces. The shape of the rate vs  $p_{\text{CO}}$  curve was taken from Ref. 3. (b) The NO+CO reaction on Pt(100)-1 $\times$ 1. The functional dependence of  $r_{\text{CO}_2}$  versus  $p_{\text{CO}}$  was taken from Ref. 13. The vertical arrow at A indicates a stoichiometric 1:1 ratio of  $p_{\text{NO}}/p_{\text{CO}}$ .

a similar way, a decrease in the reaction rate will raise  $p_{\text{CO}}$  and therefore enhance the tendency towards the unreactive CO covered surface. For the NO+CO reaction in Fig. 1(b), the simple diagram shows that just the opposite effects hold. A negative feedback exists between the changes in the state of the surface and the concomitant variations in  $p_{\text{CO}}$ . It thus becomes plausible that gas-phase coupling has no synchronizing effect for the oscillations in the NO+CO reaction on Pt(100)-1 $\times$ 1, while the opposite is true for catalytic CO oxidation on Pt(110).

Quite generally, it has been shown using simulation with the CGL equation that depending on the specific properties of a reaction system gas-phase coupling can either have a synchronizing or desynchronizing effect on the spatially homogeneous state.<sup>18,20</sup> In the latter case, a breaking apart into domains ("Ising-like") is predicted. However, these results, which were derived from the CGL equation, are strictly valid only for small-amplitude harmonic oscillations (i.e., in the vicinity of a Hopf bifurcation). Therefore, the application to a realistic system still needs to be worked out in detail.

## B. Synchronized oscillations on Pt(100)-hex

At higher temperature, around 480 K, a second  $T$  window for oscillatory behavior in the NO+CO reaction exists in which sustained rate oscillations occur on a largely hex reconstructed surface.<sup>18,19</sup> The corresponding bifurcation diagram is displayed in Fig. 2. This existence range for oscillations is located at the onset of the NO/CO-induced lifting of the hex reconstruction and the variations in the reaction rate are coupled to periodic structural transformations via the NO/CO-induced 1 $\times$ 1 $\rightleftharpoons$ hex SPT.<sup>13</sup> Since the oscillations proceed spatially uniformly as demonstrated by PEEM measurements, it is evident that synchronization must be

achieved via gas-phase coupling. At both ends of the oscillatory range one finds interesting transitions from synchronized to unsynchronized behavior, i.e., from rate oscillations to a macroscopically stationary reaction rate. Before discussing these transitions, the mechanism which presumably is responsible for synchronizing the oscillations is elucidated.

Both in the NO+H<sub>2</sub> and in the NO+NH<sub>3</sub> reaction one finds sustained rate oscillations under conditions very similar to those of the NO+CO reaction because these oscillations

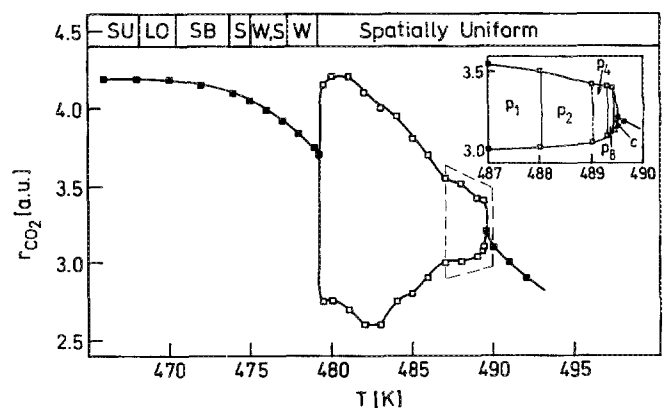


FIG. 2. Bifurcation diagram showing the amplitude of the rate oscillations (open squares) and the stationary states (filled squares) in the NO+CO reaction on Pt(100). The inset shows the Feigenbaum scenario which is found at the upper  $T$  boundary of the oscillatory range. The different types of wave patterns which have been observed with PEEM are indicated schematically: W=wave trains, WS=wave trains and spirals, S=spiral waves, SB=spiral breakup, LO=local outbursts, SU=spatially uniform. The experiment was conducted in the direction of decreasing temperature with  $p_{\text{NO}}=4\times 10^{-6}$  mbar and  $p_{\text{CO}}=4\times 10^{-6}$  mbar (Ref. 18).

also proceed on a largely hex reconstructed Pt(100) surface.<sup>14-16</sup> On the other hand, only unsynchronized oscillations occur in the NO+CO reaction on Pt(100)-1×1. These facts suggest that the 1×1-hex SPT is essential for the synchronization mechanism in the rate oscillations.

A plausible mechanism can be depicted in the following way.<sup>19</sup> The lifting of the hex reconstruction proceeds via the NO/CO-induced nucleation of 1×1 islands. The size of these islands which nucleate homogeneously as demonstrated by scanning tunneling microscopy is thereby well below 1 μm<sup>21</sup> [ $\theta_{CO,crit} \approx 0.05-0.08$  (Ref. 22).] The 1×1 islands nucleate as the NO/CO coverage on the hex phase exceeds a critical coverage. Under reaction conditions the adsorbate coverage on the rather unreactive hex phase is mainly determined by an adsorption/desorption equilibrium with the gas phase. Since  $p_{CO}$  and  $p_{NO}$  under oscillation conditions are chosen such that the adsorbate coverage on the hex phase is close to  $\theta_{crit}$ , it is evident that small partial pressure variations can have a strong influence on the surface reaction. These variations modify the nucleation rate of 1×1 islands, thereby synchronizing the local oscillators on the surface. According to this picture, the essential role of the SPT in obtaining rate oscillations in the NO reducing reactions on Pt(100) appears to lie less in creating an oscillatory reaction cycle but rather in synchronizing the different local oscillators.

#### IV. TRANSITIONS FROM SYNCHRONIZED TO UNSYNCHRONIZED BEHAVIOR

##### A. Breakdown of global coupling: The role of defects

As one adjusts sustained rate oscillations in the NO+CO reaction and then subsequently lowers the temperature, the amplitude of these oscillations collapses in a discontinuous transition at the low  $T$  boundary of the oscillatory range, at  $T_c$ , as depicted in Fig. 2.<sup>18,19</sup> Simultaneously with the dis-

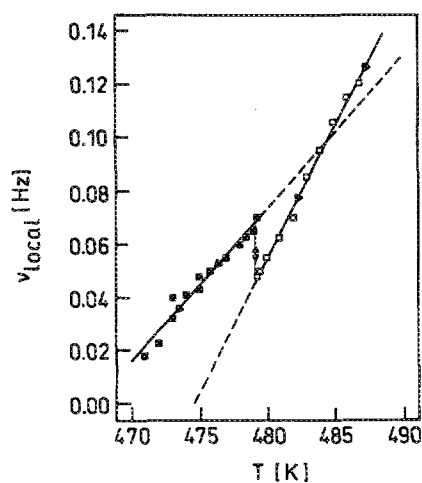


FIG. 3. Variation of the local oscillation frequency during the transition from synchronized oscillations to wave patterns as depicted in Fig. 2. The local oscillation frequency has been determined by integrating the PEEM intensity in a small spot of 20 μm×20 μm size (Ref. 18).

appearance of the rate oscillations at  $T_c$ , one observes in PEEM the formation of target patterns. Periodic wave trains start to emanate from a few defects of macroscopic size ( $\approx 1-5 \mu\text{m}$ ) until the imaged area is completely filled with the wave pattern. Macroscopically a stationary reaction rate results because the different local contributions to the reaction rate average out in the spatial integral of a wave pattern. With the vanishing of the rate oscillations, also gas-phase coupling is obviously no longer present. Accordingly, the transition from the uniformly oscillating surface to the wave pattern can be viewed as a breakdown of global coupling.<sup>18</sup>

Some insight into the mechanism leading to the breakdown of global coupling is gained by looking at the variation of the local oscillation frequency during this transition as depicted in Fig. 3. One observes a linear dependence on the temperature both above and below  $T_c$  but with two different slopes. At  $T_c$  the frequency nearly doubles in a discontinuous jump from the lower to the upper branch. Keeping in mind the observations with PEEM, we can assign the two slopes to two kinds of oscillators, the defect-free surface above  $T_c$  and the macroscopic defects below  $T_c$ . The interpretation of the transition at  $T_c$  is then as follows.

As seen in the diagram in Fig. 3, with decreasing temperature, the frequency gap between the two different oscillators increases continuously until it finally exceeds a certain threshold. At this point, complete synchronization is no longer possible, and the faster oscillating defects become trigger centers, sending out waves in the more slowly oscillating surrounding medium. The abruptness of the transition can be explained by the positive feedback between the spreading of the wave pattern and the vanishing of the rate oscillations, i.e., of global coupling. This interpretation was corroborated in a simulation with a modified complex Ginzburg-Landau (CGL) equation, demonstrating that the essential factor causing the breakdown of global coupling is in fact the existence of a defect with a frequency higher than the bulk frequency.<sup>18,20</sup> Defects thus have a very important role for synchronization of a system because they can act as nuclei for the breakdown of global coupling.

In the NO+NH<sub>3</sub> reaction on Pt(100), one also observes a similar transition from a spatially uniformly oscillating surface to a wave pattern.<sup>16</sup> This transition, however, exhibits some differences to the one discussed above, as demonstrated by the scheme reproduced in Fig. 4. In that reaction,

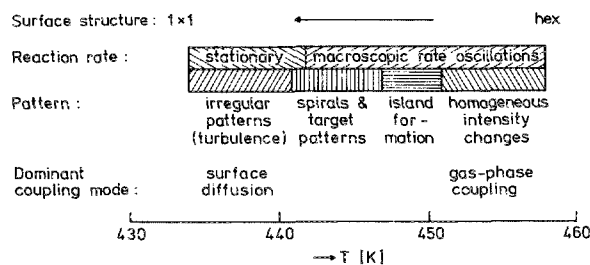


FIG. 4. Schematic overview of the temperature ranges in which macroscopic rate oscillations and different types of spatial patterns are observed in the NO+NH<sub>3</sub> reaction on Pt(100) (Ref. 16).

the breakdown of global coupling takes place less abruptly since spatial patterns coexist over a finite temperature range with the synchronized oscillating surrounding "background" area. The vanishing of the rate oscillations then carries the system directly into a regime of spatiotemporal turbulence. The occurrence of spatiotemporal chaos in an oscillatory surface reaction appears to be closely linked to the vanishing of global coupling. As demonstrated by simulations with the CGL equation, a variety of possible scenarios can be obtained but, in order to connect these calculations to the experimental results, an elaborate analysis of the experimental situation is required.<sup>20</sup>

## B. Deterministic chaos

At the upper  $T$  boundary of the oscillatory range, the rate oscillations terminate via a sequence of period doublings leading from regular period-1 oscillations to chaotic rate variations, i.e., a Feigenbaum scenario is observed. The chaotic behavior which occurs in such a transition is typically low-dimensional and therefore deterministic. In the course of this development, the oscillation amplitude decreases continuously until a stationary state is reached.<sup>18,19</sup> During this transition depicted in the inset of Fig. 2, PEEM shows a spatially uniformly oscillating surface within its resolution of  $\approx 1 \mu\text{m}$ . Since the spatial degrees of freedom play no role, one could expect to find an explanation for the occurrence of deterministic chaos in the dynamics of an individual oscillator as described by ordinary differential equations. Since three degrees of freedom have been shown to suffice to create chaotic behavior, such an approach seems to be reasonable. Following the reasoning given below, however, we favor a different explanation based on synchronization.<sup>19</sup>

Since a Feigenbaum scenario leading to deterministic chaos has also been found in the  $\text{NO} + \text{H}_2$  reaction on Pt(100), details of the specific chemistry of the reaction are apparently of minor importance for the development of deterministic chaos.<sup>15</sup> Common to both systems,  $\text{NO} + \text{CO}$  and  $\text{NO} + \text{H}_2$ , is the  $1 \times 1 \rightleftharpoons \text{hex}$  SPT of Pt(100) whose role supposedly is to synchronize the local oscillations. One could therefore expect that synchronization plays an essential role in the development of deterministic chaos leading to the following picture.

Starting with the stationary state at high  $T$ ,  $1 \times 1$  adsorbate islands randomly nucleate and dissolve on the hex phase. As with decreasing temperature the nucleation and growth rate of these islands increases, the fluctuating islands synchronize via partial pressure variations in the gas phase, as discussed in the previous section. Finally, a uniformly oscillating surface is reached which corresponds to sustained rate oscillations. The existence of a certain transition range in which complete synchronization is not yet fully established, can also be made plausible by the following consideration. Gas-phase coupling requires rate oscillations of finite amplitude and, since the oscillation amplitude in the  $\text{NO} + \text{CO}$  reaction grows continuously with decreasing  $T$ , it is evident that the rate oscillations have to develop from a state in which local oscillations take place unsynchronized.

Although it is not at all evident that the synchronization process depicted above might produce a Feigenbaum sce-

nario, some support for this idea comes from a cellular automaton study by Mikhailov *et al.* They demonstrated, that synchronizing a large number of randomly oscillating cells can, in fact, give rise to deterministic chaos and a Feigenbaum sequence.<sup>23</sup> Interestingly, in the chaotic state they observed that the system was reacting synchronously, i.e., spatially uniformly and only the temporal variation of the integral signal exhibited chaotic oscillations. In order to demonstrate that this synchronization mechanism really explains the occurrence of deterministic chaos in the  $\text{NO} + \text{CO}$  and  $\text{NO} + \text{H}_2$  reactions on Pt(100), simulations with a realistic model are required. Such calculations are currently under way, and first results look rather promising.

Although the oscillation mechanism in the  $\text{CO} + \text{O}_2$  reaction on Pt(110) is different from that of  $\text{NO}$  reduction on Pt(100), there are some indications that the mechanism giving rise to deterministic chaos in this system is also based on synchronization.<sup>24,25</sup> Similarly to the proposed scenario in the  $\text{NO} + \text{CO}$  reaction, a stationary state in the reaction rate exists, which on a local scale exhibits spatiotemporal turbulence.<sup>26</sup> This state is located in the vicinity of the rate maximum in the plot in Fig. 1(a). A sequence of period doublings occurs with a decreasing  $p_{\text{CO}}$  acting as bifurcation parameter, leading from regular period-1 oscillations to deterministic chaos which is seen on the way to the rate maximum [state A in Fig. 1(a).] Since the strength of gas-phase coupling in this system is essentially given by steepness of the rate versus  $p_{\text{CO}}$  curve, it is very plausible that the deterministic chaos just reflects the beginning of a desynchronizing process taking place as the amplitude of the rate oscillations falls below a certain threshold. It should be emphasized that this picture is still rather speculative and needs to be confirmed by experiments and simulations.

## V. CONCLUSIONS

In oscillatory surface reactions conducted under isothermal low-pressure conditions the local oscillators can synchronize via the gas phase. The  $\text{NO} + \text{CO}$  reaction on Pt(100) has been discussed as an example for both synchronized and unsynchronized behavior. Synchronization in this system can be traced back to the operation of the  $1 \times 1 \rightleftharpoons \text{hex}$  SPT of Pt(100) at higher  $T$ , while the absence of the SPT at lower  $T$  can be made responsible for the existence of unsynchronized oscillations. At higher  $T$ , one finds well-defined transitions from synchronized to unsynchronized oscillations with the latter corresponding macroscopically to a stationary reaction rate. The occurrence of deterministic chaos in connection with a Feigenbaum scenario at the high  $T$  boundary of the oscillatory range and the collapse of the rate oscillations at the low  $T$  boundary have been interpreted in terms of such a transition.

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