Forced Oscillations of a Self-Oscillating Surface Reaction

M. Eiswirth and G. Ertl
Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-1000 Berlin 33, West Germany
(Received 30 November 1987)

Harmonic resonance, subharmonic and superharmonic entrainment, as well as quasiperiodic behavior are among the effects observed if the catalytic oxidation of CO on a Pt(110) surface is carried out under conditions of stable, self-sustained kinetic oscillations and then subjected to low-amplitude periodic modulation of the oxygen partial pressure.

PACS numbers: 68.35.Rh, 82.65.Jv

Periodic forcing of a nonlinear, self-oscillating system can result in a large variety of phenomena, ranging from harmonic to chaotic response. More specifically, the system can respond in such a way that the ratio of the frequency of the resulting oscillation to that of the perturbation, ν_r/ν_p, is a rational number (entrainment), or that quasiperiodic or even chaotic behavior results. Effects of this type have been studied extensively in various physical systems such as Josephson junctions,[1-3] nonlinear electric conductors,[4] or hydrodynamic systems (Rayleigh-Bénard instability).[5,6] As far as oscillating chemical systems are concerned, most work has been dedicated to homogeneous reactions, both in theory[7-9] and in experiment.[10-13] Several previous studies with heterogeneous reactions suffered mainly from irregular behavior of the nonperturbed system.[14-18] The low-pressure oxidation of carbon monoxide on a Pt(110) single-crystal surface was, however, found to exhibit stable periodic oscillations of the rate of CO_2 formation under certain conditions of partial pressures and temperature[9] which renders this system a suitable candidate for a systematic study on periodic forcing of a self-oscillating surface reaction.

The reaction $Co+\frac{1}{2}O_2 \rightarrow CO_2$ catalyzed by platinum proceeds through a Langmuir-Hinshelwood mechanism by recombination of adsorbed CO and dissociatively adsorbed oxygen on the surface.[19] Isothermal temporal oscillations in the rate of CO_2 formation on a Pt(110) surface originate from a coupling between surface reaction steps and periodic structural transformations of the surface: If the CO coverage is high enough, the 1×2 reconstruction of the clean Pt(110) surface is lifted, and this transformation affects, in turn, the catalytic activity. By proper adjustment of the parameters (p_{CO}, p_{O_2}, T) the parallel development of step arrays leading to facet formation[20] can be suppressed so that regular autonomous oscillations can be sustained for long periods of time under constant conditions. Spatial self-organization is mediated through the very small ($<1\%$) variations of the partial pressures associated with the changing reaction rate. Because of this high sensitivity to changes of the partial pressures, periodic forcing of the system could be achieved by low-amplitude (about 1%) modulation of p_{O_2}. Variations of the reaction rate are paralleled by corresponding variations of the work function[20,21] which was used as a convenient probe for the dynamical response of the system.

The experiments were performed in a standard UHV system equipped with LEED and Auger-electron spectroscopy for surface characterization and operated under isothermal, gradient-free flow conditions.[21] Gases of the highest available grade were subjected to further purification in order to suppress surface contamination.[22] The sample (surface area about 30 mm^2) was prepared from

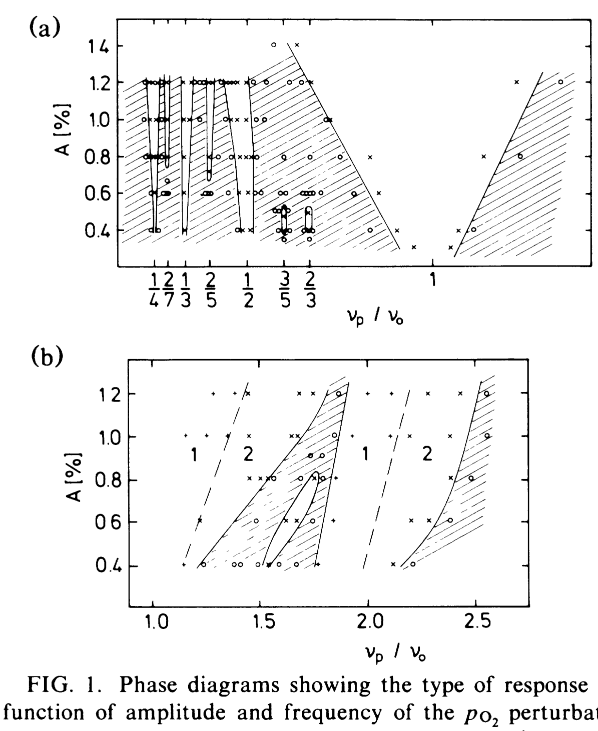

FIG. 1. Phase diagrams showing the type of response as a function of amplitude and frequency of the p_{O_2} perturbation. Data were taken at the points denoted by crosses (phase locking) and circles (quasiperiodic response). (a) $p_{O_2}=4.15\times10^{-5}$ Torr, $p_{CO}=2.1\times10^{-5}$ Torr, $T=530$ K, $\nu_0\approx0.25$ s^{-1}; (b) $p_{O_2}=3\times10^{-5}$ Torr, $p_{CO}=1.6\times10^{-5}$ Torr, $T=525$ K, $\nu_0\approx0.1$ s^{-1}. The numbers (1,2) refer to the periodicity of the response (see text). During the measurement ν_0 varied by up to 0.01 s^{-1}.

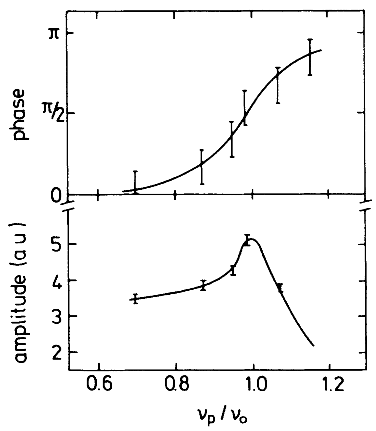

FIG. 2. Resonance behavior (amplitude and phase) in the harmonic entrainment band ($p_{O_2}=4\times10^{-5}$ Torr, $p_{CO}=2\times10^{-5}$ Torr, $T=530$ K, $\nu_0=0.17$ s^{-1}, forcing amplitude 1.2%).

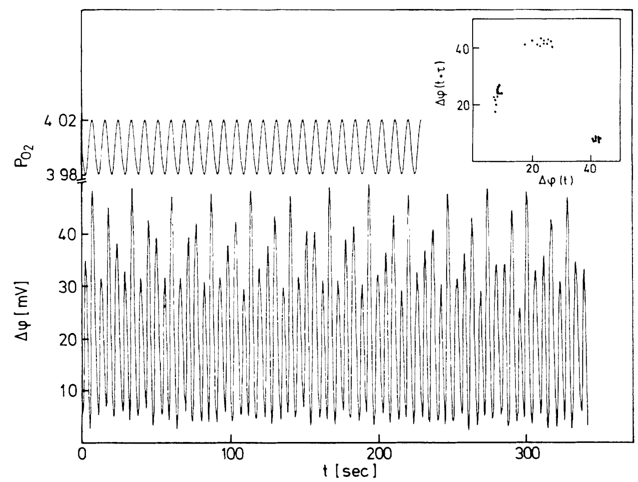

FIG. 3. Time series and stroboscopic plot of $\frac{5}{3}$ superharmonic entrainment ($p_{O_2}=4\times10^{-5}$ Torr, $p_{CO}=2\times10^{-5}$ Torr, $T=530$ K, $\nu_0=0.17$ s^{-1}, $\nu_p=0.11$ s^{-1}, $A=0.5\%$, $\tau-8.9$ s).

a single-crystal rod according to standard procedures.[20,21] A specially designed, feedback-controlled gas inlet system[17,22] served to establish constant partial pressures as well as to modulate them with frequencies up to 0.5 s^{-1} and relative amplitudes around 1%.

The general behavior of the system under the influence of a periodic modulation of p_{O_2} with amplitude A and frequency ν_p (scaled relative to the natural frequency ν_0) is schematically represented by the phase diagram shown in Figs. 1(a) and 1(b). The two sets of observations were made under somewhat different conditions for experimental reasons in order to establish clearly the respective features. The response of the system is either phase locked (entrained) or quasiperiodic, the boundaries between these two types of behavior being indicated by straight lines. The numbers (1,2) inserted in Fig. 1(b) denote the periodicity of the forced oscillations. The main effects observed are the following.

(i) *Harmonic entrainment.*—If ν_p is near ν_0, the system oscillates with the same frequency as the perturbation with a fixed phase difference (phase locking). The system behaves similarly to a linear oscillator, i.e., exhibits resonancelike behavior ("chemical resonance"[23]). Figure 2 shows the variation of the phase and amplitude with ν_p/ν_0 for an otherwise fixed set of parameters. The system response exhibits maximum amplitude (more precisely, variance) and $\pi/2$ phase shift for $\nu_p=\nu_0$ like a classical forced oscillator. Since our system is undamped, there also exist, of course, finite amplitudes outside the resonance region.

(ii) *Subharmonic and superharmonic entrainment.*—Outside the region of harmonic entrainment there exist other entrainment bands in which $\nu_r/\nu_p=l/k$, with $k,l=$integers. If $l/k<1$, the entrainment is denoted as subharmonic, and for $l/k>1$ it is called superharmonic. In total, two subharmonic ($\frac{2}{3},\frac{1}{2}$) and seven superharmonic ($\frac{4}{1},\frac{7}{2},\frac{3}{1},\frac{5}{2},\frac{2}{1},\frac{5}{3},\frac{3}{2}$) entrainment bands were discovered. An example of a time series for superharmonic entrainment ($\frac{5}{3}$) is shown in Fig. 3 together with its stroboscopic plot. The latter is constructed by plotting of the signal $\Delta\phi(t)$ versus $\Delta\phi(t+\tau)$ at intervals of the modulation period where τ is a suitable delay time.[10] (In principle, the value of τ may be arbitrary, but in order to minimize the effect of noise it was chosen in a way that the steepest changes in the experimental signal were circumvented.) For perfect entrainment, this plot should consist of k discrete points which condition was best fulfilled for low values of k and l. In the example shown there exists some variation in the heights of corresponding response amplitudes and therefore the stroboscopic plot exhibits some spreading of the data. While k is most conveniently derived from the stroboscopic plot, l is simply derived from the periodicity of the time series,[13] i.e., the system response consists of repeating patterns of l different amplitudes. In the case of harmonic ($l/k=\frac{1}{1}$) and subharmonic ($l/k=\frac{1}{2}$) entrainment, however, there may exist alternating oscillations with high and low amplitudes ("period doubling").

In theory, finite widths of the entrainment bands are expected as long as the forcing amplitude is nonvanishing.[7,24] In the present experiments, however, small bandwidths ($<2\%$ of ν_0) could not be resolved because of the limited constancy of the modulation frequency and noise ($\simeq0.1\%$) in the pressure-controlling gas inlet system.

(iii) *Quasiperiodic oscillations.*—Under conditions marked by the shaded regions of the phase diagram (Fig. 1) the system exhibits quasiperiodic conditions. There no longer exists a fixed phase relation between perturbation and response, but this changes continuously from period to period. As a consequence, the stroboscopic plot no longer consists of discrete points but of a closed curve

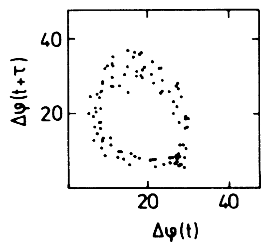

FIG. 4. Stroboscopic plot of quasiperiodic oscillations near the low-frequency $\frac{2}{1}$ entrainment edge ($p_{O_2}=4\times10^{-5}$ Torr, $p_{CO}=2\times10^{-5}$ Torr, $T=530$ K, $\nu_0=0.19$ s^{-1}, $\nu_p=0.09$ s^{-1}, $A=0.6\%$, $\tau=9$ s).

(Fig. 4) which the system passes once during the beat period which is the time required for the phase difference to return close to an initial value. The inverse of the beat period, the beat frequency, is thus the difference between the forcing and response frequencies.

An example for a section from a time series over a beat period near the $\frac{2}{1}$ entrainment edge is reproduced in Fig. 5. The response consists essentially of two peaks for each forcing period. Initially, the second peak is smaller but grows continuously in intensity while that of the first peak decreases, until the situation is reversed. After twelve forcing periods, one "extra" oscillation of the system is gained (25 instead of 24 in the case of $\frac{2}{1}$ superharmonic entrainment). More precisely, after completion of such a cycle the quasiperiodic response does not, of course, return *exactly* to the initial phase relation, but the small displacements are beyond experimental resolution.

With the example just shown the beat frequency can be determined quite easily. If the autonomous frequency ν_0 were not affected by switching on the periodic modulation with frequency ν_p, the beat frequency would in this case simply be given by $\nu_b=\nu_0-2\nu_p$. A systematic series of experiments revealed that ν_b was always smaller than predicted by this relation. (For example, for $\nu_p/\nu_0=0.45$, ν_b/ν_0 was 0.05 instead of 0.10.) This demonstrates that the frequency of the system is affected by the modulation frequency not only in the entrainment band, but also in the adjacent region of quasiperiodic behavior. This effect of "frequency pulling" is analogous to the observations made recently by Hudson, Lamba, and Mankin[13] with the Belousov-Zhabotinsky reaction.

(iv) *Transient behavior.*—If the modulation was switched on for conditions inside an entrainment band (and far enough away from its edges) the system responded rapidly and within a few cycles phase locking was established. The transition from a region of entrainment to conditions of unentrained behavior can be viewed as a sort of phase transition and consequently one might expect an increase of the relaxation time as the system approaches an entrainment edge.[24] This effect of "critical slowing down" was recently observed experimentally for the first time with a gas-phase combustion

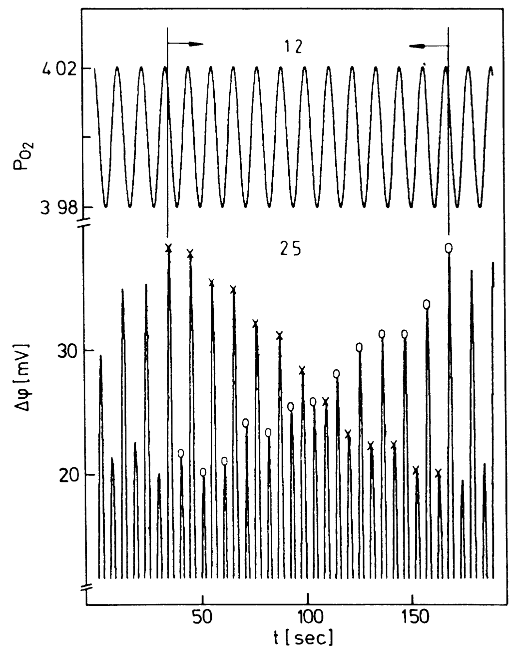

FIG. 5. Section of the time series corresponding to Fig. 4.

reaction.[12] Experiments performed with the present system near the $\frac{2}{1}$ entrainment edge qualitatively confirmed this effect. The number of modulation periods needed for establishing entrainment increased markedly (up to about 50!) upon approaching the entrainment edge, although quantitative analysis was not feasible.

The outlined experimental observations fit completely into the general features of periodic perturbations of chemical oscillators, as treated theoretically first by Kai and Tomita[7] for the Brusselator model. This is a three-variable model, while the present system is of higher order and requires at least four coupled differential equations for realistic modeling.[25] A general feature of the theoretical phase diagram for the Brusselator model is the increasing width of the entrainment bands with increasing amplitude and the occurrence of both subharmonic and superharmonic entrainment, separated by regions of quasiperiodic behavior. At larger forcing amplitudes, this model may even exhibit transition to chaos via a sequence of period doubling. While chaotic behavior was observed with homogeneous reactions periodically disturbed with *large* amplitude,[11,14,26] in the present investigation only *small* amplitudes could be applied without leaving the narrow range of control parameters for autonomous oscillations. Chaos originating from an interaction of resonances was predicted for driven circle maps[27] and has been identified in several physical systems,[1-5,28] but for the Brusselator model, on the other hand, no chaotic states were predicted when neighboring entrainment bands are covered by the fundamental one.[7]

With the present experimental system no evidence for chaotic behavior was obtained which could, however, if existent in narrow regions, have escaped detection because of limited experimental resolution or influence of noise. We would like to mention, however, that a well-defined transition to chaos via period doubling could be identified for *autonomous* oscillations of the present system upon variation of the control parameters.[29]

In conclusion, this work describes the first well-defined example of a heterogeneous surface reaction showing the features developed for self-oscillating chemical reactions under the influence of periodic perturbations.

[1]E. Ben-Jacob, Y. Braiman, R. Shainsky, and Y. Imry, Appl. Phys. Lett. **38**, 822 (1981).

[2]W. J. Yeh, D.-R. He, and Y. H. Kao, Phys. Rev. Lett. **52**, 480 (1984).

[3]P. Alstrøm, M. H. Jensen, and M. T. Levinsen, Phys. Lett. **103A**, 171 (1984).

[4]S. Martin and W. Marthiensen, Phys. Rev. Lett. **56**, 1522 (1986).

[5]J. Maurer and A. Libchaber, J. Phys. (Paris), Lett. **40**, L419 (1979), and **41**, L515 (1980).

[6]A. Libchaber and J. Maurer, in *Nonlinear Phenomena at Phase Transitions and Instabilities,* edited by T. Risle (Plenum, New York, 1982).

[7]T. Kai and K. Tomita, Prog. Theor. Phys. **61**, 54 (1979).

[8]I. G. Kevrekides, R. Aris, and L. D. Schmidt, Chem. Eng. Sci. **41**, 1549 (1986).

[9]R. Aris, in "Spatial Inhomogeneities and Transient Behavior in Chemical Kinetics," edited by G. Nicolis (to be published), and references therein.

[10]F. W. Schneider, Annu. Rev. Phys. Chem. **36**, 347 (1985).

[11]M. Dolnik, I. Schreiber, and M. Marek, Physica (Amsterdam) **21D**, 78 (1986).

[12]S. A. Pugh, M. Schell, and J. Ross, J. Chem. Phys. **85**, 868 (1986).

[13]J. L. Hudson, P. Lamba, and J. C. Mankin, J. Phys. Chem. **90**, 3430 (1986).

[14]M. Marek, in *Temporal Order,* edited by L. Rensing and N. I. Jaeger (Springer-Verlag, Berlin, 1985), p. 105.

[15]H. U. Onken and E. Wicke, Ber. Bunsenges. Phys. Chem. **90**, 976 (1986).

[16]S. C. Capsaskis and C. N. Kenney, J. Phys. Chem. **90**, 4631 (1986).

[17]R. J. Schwankner, M. Eiswirth, P. Möller, K. Wetzl, and G. Ertl, J. Chem. Phys. **87**, 742 (1987).

[18]N. I. Jaeger, P. J. Plath, and P. Svensoon, in "Spatial Inhomogeneities and Transient Behavior in Chemical Kinetics," edited by G. Nicolis (to be published).

[19]T. Engel and G. Ertl, Adv. Catal. **28**, 1 (1979).

[20]S. Ladas, R. Imbihl, and G. Ertl, Surf. Sci., to be published.

[21]M. Eiswirth and G. Ertl, Surf. Sci. **177**, 90 (1986).

[22]M. Eiswirth, R. Schwankner, and G. Ertl, Z. Phys. Chem. **144**, 59 (1985).

[23]T. Buchholtz and F. W. Schneider, J. Am. Chem. Soc. **105**, 7450 (1983).

[24]P. Rehmus and J. Ross, J. Chem. Phys. **78**, 3747 (1983).

[25]R. Imbihl, M. P. Cox, G. Ertl, H. Müller, and W. Brenig, J. Chem. Phys. **83**, 1578 (1985).

[26]P. Lamba and J. L. Hudson, Chem. Eng. Sci. **42**, 1 (1987).

[27]S. Ostlund, D. Rand, J. Sethna, and E. Siggia, Physica (Utrecht) **80**, 303 (1983); M. H. Jensen, P. Bak, and T. Bohr, Phys. Rev. A **30**, 1960 (1984).

[28]B. A. Huberman, J. P. Crutchfield, and N. H. Packard, Appl. Phys. Lett. **37**, 750 (1980).

[29]M. Eiswirth, K. Krischer, and G. Ertl, to be published.