TABLE I. Comparison of the experimental and calculated cross sections to the lower Rydberg states of acetone.

		One photon int.		Two photon int.	
Exc.	State	calc.[a]	obs., rel.[b]	calc.[a]	obs., rel.
3s	$1B_2$	0.04	4	3×10^{-57}	5×10^{-3}
3p	$2A_1$	0.01	0.25	3×10^{-51}	0.5
3p	$2A_2$	forb.	$=0$	4×10^{-52}	1.3
3p	$2B_2$	3×10^{-5}	1	6×10^{-52}	1.0

[a] Reference 1. Values given in the units of Ref. 1.
[b] R. H. Huebner, R. J. Celotta, S. R. Mielczarek, and C. E. Kuyatt, J. Chem. Phys. **59**, 5434 (1973).

similar equilibrium geometries to the ion are expected to be similar. Hence for transitions from the ground to the Rydberg states of acetone we expect the 2RMPI intensities to accurately reflect their 2 photon cross sections. Thus the comparisons presented in Table I are valid.

The comparison of the calculated and experimental 1 and 2 photon intensities of the first 4 Rydberg $\leftarrow X$ transitions of acetone presented in Table I indicates that the only accurately calculated intensity relation is that the 1 photon intensity to the 3s Rydberg state is approximately $4\times$ that of the strongest of the $3p\leftarrow X$ transitions. More specifically, neither of the two extreme results—that the 1 photon transition from the ground to the $2B_2$ Rydberg state is 10^{-3} the intensity of the other 1 photon transitions or that the 2 photon transition from the ground to the $1B_2$ Rydberg state is 10^{-5} the intensity of the other 2 photon transitions—is experimentally verified. We must, therefore, conclude that for both one and two photon transitions from the ground to the first 3 Rydberg states of acetone, the theoretical treatment presented in Ref. 1 does not satisfactorily reproduce experimental results.

[1] V. Galasso, J. Chem. Phys. (in press).
[2] R. McDiarmid and A. Sabljic, J. Chem. Phys. **89**, 6086 (1988).
[3] M. Lawson and A. B. F. Duncan, J. Chem. Phys. **12**, 329 (1944).

[4] Under our conditions the ionization of the 2 photon resonant state is assumed to be saturated. [P. Johnson, Acc. Chem. Res. **13**, 20 (1980)].

Chaos in the Showalter–Noyes–Bar-Eli model of the Belousov–Zhabotinskii reaction

David Lindberg[a)] and Jack S. Turner
Center for Statistical Mechanics and Department of Physics, University of Texas, Austin, Texas 78712
Dwight Barkley[b)]
Program in Applied and Computational Mathematics and Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544

(Received 19 October 1989; accepted 13 November 1989)

Ever since it was suggested that chaos arises in the reaction kinetics of the Belousov–Zhabotinskii (BZ) reaction, controversy has raged.[1–4] The controversy stems largely from disagreement between experiments and simulations on the issue of chaos. Several groups have reported chaos in continuous stirred tank reactor (CSTR) experiments on the BZ reaction,[2,3,5–7] and yet many simulations, which otherwise reproduce the kinds of mixed-mode states observed experimentally, do not produce the chaos recorded in experiments (e.g., Ref. 8). More precisely, simulations do show chaos, but often it is on small scales and is present over parameter ranges too small to be of experimental relevance.[2,4] This has led to the argument that the chaos observed in experiment, while genuine chaos, is not inherent in the chemical kinetics, but instead derives from other sources.[4]

The purpose of this note is to report the observation of *robust, large-scale* chaos in a BZ model which is commonly thought not to exhibit chaos to any significant degree. We stress the distinction between the high and low flow-rate regimes.

The model considered is that proposed by Showalter, Noyes, and Bar-Eli (SNB)[9]:

$$A+Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X+P, \quad X+Y \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2P,$$

$$A+X \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} 2W, \quad C+W \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} X+Z,$$

$$2X \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} A+P, \quad Z \overset{k_6}{\rightarrow} gY+C.$$

This kinetic scheme gives rise to differential equations for the chemical concentrations in a CSTR. The results we report have been obtained by integrating these equations (Gear method) with a one-step relative error of 10^{-10}.

 0021-9606/90/053238-02$03.00

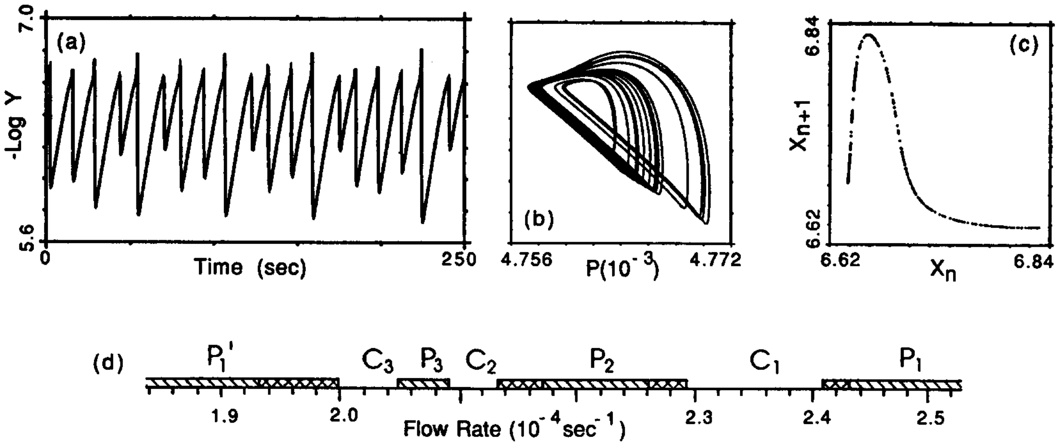

FIG. 1. (a) Time series, (b) phase portrait, and (c) next maximum map for the SNB model at flow rate $= 2.12\times10^{-4}$. To allow for comparison with experiment, $-\log Y$ is plotted in (a) and (b) (see Ref. 17 in Ref. 11). $x_n = n$th relative maximum of $-\log Y$. (d) Periodic–chaotic sequence for the SNB model. The notation is that of Ref. 6. Periodic regions are indicated with diagonal hatching. Cross-hatching indicates (approximately) regions of period-doubling cascades.

We use rate constants for the first five reactions essentially as given by SNB, except that here $[H^+] = 0.8$ M.

$$k_1 = 1.34 \qquad k_{-1} = 1.0\times10^4$$
$$k_2 = 1.6\times10^9 \qquad k_{-2} = 5.0\times10^{-5}$$
$$k_3 = 8.0\times10^3 \qquad k_{-3} = 2.0\times10^7$$
$$k_4 = 5.2\times10^5 \qquad k_{-4} = 2.4\times10^7$$
$$k_5 = 4.0\times10^7 \qquad k_{-5} = 1.6\times10^{-10}.$$

These are in $M^{-1}s^{-1}$. The other parameters used here are: $g = 0.462$, $k_6 = 7.0\ s^{-1}$, $A_0 = 0.06$ M, $C_0 = 1.25\times10^{-4}$ M, $Y_0 = 2.0\times10^{-6}$ M, where zero subscripts denote feed concentrations. Various flow rates are considered.

Figure 1(a)–(c) shows the model dynamics at one flow rate. The form of the oscillations and the shape of the one-dimensional map compare extremely well with those observed in the Texas experiments[3,6,7] *at low flow rates.* The oscillation period is, however, about an order of magnitude smaller than in experiment. We have integrated the model equations for 8 000 model seconds[10] [data shown in Fig. 1(c)], and we are confident that the state shown is a strange attractor and probably lies on a wrinkled torus.[2,11,12]

The importance of our observation is that we find robust chaos embedded in a sequence of periodic and chaotic states, as illustrated in Fig. 1(d). The width of the chaotic regimes are comparable with those found experimentally,[6] and as with experiment, there are periodic windows within the chaotic regions.[7] At other parameter values we find many states in the periodic–chaotic sequence[13]; for example, at $Y_0 = 5.0\times10^{-5}$, we find periodic states with up to nine oscillations per period.

Complex dynamics are found in experiments on the BZ reaction at both high and low flow rates. The simulations here correspond to low flow rates where there is not a great disparity between the large and small oscillations. Contrast the waveforms here with those in Refs. 5, 8, and 9, where there are two distinct types of oscillations: large and small amplitude. Simulations which fail to generate significant chaos *always* have a disparity between large and small oscillations. An explanation of the lack of chaos in such cases has been given.[14]

New values have been proposed for the rate constants[15] and we have attempted, without success, to reproduce the low-flow-rate dynamics with the new values. The only complex waveforms we find using the new rate constants in the SNB model are those seen in high-flow-rate experiments, i.e., the waveforms composed of large and small oscillations only. As expected, these are not chaotic. More study is needed to determine whether waveforms like those in the Texas experiments can be found using the new rate constants. The results reported here are, nevertheless, significant to the issue of chaos in the BZ reaction, and they should provide a good reference point for future investigations using the new rate constants.

Computing resources for this work were provided by the University of Texas Center for High Performance Computing.

[a] Supported by the Robert A. Welch Foundation.
[b] Supported by DARPA Grant No. N00014-86-K-0759 and NSF Grant No. ECS-8945600. Author to whom correspondence should be addressed.

[1] References 2–4 are recent reviews and contain complete references to the literature.
[2] F. Argoul, A. Arneodo, P. Richetti, and J. C. Roux, J. Chem. Phys. **86**, 3325, 3339 (1987).
[3] F. Argoul, A. Arneodo, P. Richetti, J. C. Roux, and H. L. Swinney, Acc. Chem. Res. **20**, 436 (1987).
[4] L. Gyorgyi and R. J. Field, J. Phys. Chem. **92**, 7079 (1988), and J. Phys. Chem. **93**, 2865 (1989).
[5] R. A. Schmitz, K. R. Graziani, and J. L. Hudson, J. Chem. Phys. **67**, 3040 (1977); J. L. Hudson, M. Hart, and D. Marinko, *ibid.* **71**, 1601 (1979).
[6] J. S. Turner, J. C. Roux, W. D. McCormick, and H. L. Swinney, Phys. Lett. **85A**, 9 (1981).
[7] K. Coffman, W. D. McCormick, and H. L. Swinney, Phys. Rev. Lett. **56**, 999 (1986).
[8] N. Ganapathisubramanian and R. M. Noyes, J. Chem. Phys. **76**, 1770 (1982).
[9] K. Showalter, R. M. Noyes, and K. Bar-Eli, J. Chem. Phys. **69**, 2514 (1978).
[10] Initial conditions close to the attractor are $P = 4.758\times10^{-3}$, $Y = 2.644\times10^{-7}$, $X = 7.816\times10^{-10}$, $W = 1.088\times10^{-8}$, $Z = 8.914\times10^{-8}$, and A and C given by the stoichiometric constraints in Ref. 12. The variable P changes slowly in general, and arbitrary initial conditions take a very long time to reach the attractor.
[11] D. Barkley, J. Chem. Phys. **89**, 5547 (1988).
[12] D. Barkley, J. Ringland, and J. S. Turner, J. Chem. Phys. **87**, 3812 (1987).
[13] D. Lindberg, Ph.D. thesis, University of Texas, Austin, Texas, 1988.
[14] D. Barkley, Phys. Lett. A **129**, 219 (1988); J. Ringland and M. Schell, Phys. Rev. A (in press).
[15] R. J. Field and H. D. Forsterling, J. Phys. Chem. **90**, 5400 (1986).