Nonlinear Phenomena in Light-Mediated Bromate−Hydroquinone−Benzoquinone Reactions

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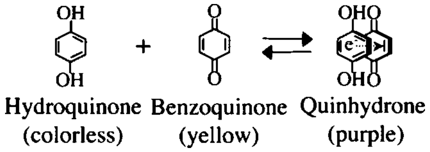
This study presents an experimental investigation of nonlinear dynamics in the photomediated bromate-1,4-benzoquinone-1,4-hydroquinone reaction, in which the copresence of hydroquinone and benzoquinone results in chemical oscillations taking place shortly after mixing all reagents together, which is in great contrast to the case of a few hours of induction time seen in the bromate−hydroquinone or bromate−benzoquinone photochemical oscillators. It is essential to keep the acid concentration low in order to achieve these oscillations. Measurements with mass spectrometry and UV/vis spectroscopy confirm the formation of hydroquinone−benzoquinone complexes. The results suggest that interactions of hydroquinone and benzoquinone can play a significant role in the kinetics of related chemical systems.

1. Introduction

Photochemical reactions are ubiquitous and play a vital role in nature.[1] For academic interests, photosensitive chemical reactions have been frequently employed in the study of nonlinear dynamics.[2–12] Photochemical effects of ultraviolet light in the cerium-catalyzed Belousov−Zhabotinsky (BZ) reaction, for instance, were studied nearly forty years ago, and the results showed that the oscillatory behavior depended on light intensity and chemical compositions.[2,3] Further research indicates that ruthenium-catalyzed BZ systems respond significantly to the illumination of visible light.[4,5] Since then, the ruthenium-catalyzed BZ reaction has been extensively employed to investigate perturbed nonlinear dynamics in both stirred and reaction-diffusion media.[6–12] These investigations have greatly helped researchers to understand a variety of complex behaviors that occur in nature such as stochastic resonance and synchronizations.[13,14]

1,4-Benzoquinone (Q), an aromatic dicarbonyl compound, has been commonly used in laboratory experiments for its photochemical properties.[15–18] Our group has recently explored nonlinear behavior in the light-mediated bromate−Q reaction.[19] In such a system, hydroquinone (H_2Q), a photoreduction product of Q, reacts with acidic bromate through an autocatalytic process, implementing a nonlinear feedback which reproduces Q.[17,20] The observed oscillatory behavior has an extremely long induction time (>3 h), which is similar to the induction time reported for other uncatalyzed bromate-based oscillators.[20–22] It is well documented in the literature that H_2Q and Q can readily form complexes.[23] It has also been confirmed in our laboratory that mixing yellow Q and colorless H_2Q together results in an immediate formation of black powder. Several chemical oscillators reported recently contain both H_2Q and Q as intermediates.[24–26] Whether the formation of H_2Q−Q complexes plays an important role in the kinetics of these chemical oscillations remains to be answered and could be critical in deciphering the mechanism of these chemical oscillators. In particular, these chemical oscillators have exhibited various interesting nonlinear behaviors which could not be interpreted based on the current mechanisms, such as the anomalous dispersion relationship in the ferroin−bromate−cyclohexanedione system.[25]

In this research, we attempted to explore the importance of the formation of H_2Q−Q complexes via studying the nonlinear dynamics in the illuminated bromate−H_2Q−Q reaction. Hydroquinone is a very strong reducing agent and is quickly oxidized by acidic bromate.[20] The investigation was pursued at low acidic conditions, where the autocatalytic oxidation of hydroquinone $H_2Q + 2BrO_2^{\bullet} \rightarrow Q + 2HBrO_2$ is slowed down through the influence of H^+ on the reaction $HBrO_2 + BrO_3^- + H^+ \rightarrow H_2O + 2\ BrO_2^{\bullet}$.[20] Therefore, under a low acid concentration, H_2Q shall have time to form complexes with Q before being oxidized. For the 1:1 H_2Q−Q complex, in the presence of light, an electron may be donated from the hydroquinone to the benzoquinone, forming a charge−transfer complex to give the characteristic purple color (see the following schematic illustration).[27]



As reported in the following, the coexistence of H_2Q and Q does induce qualitative changes in the reaction behavior, in which chemical oscillations that are quite different from those observed in the bromate−Q or bromate−H_2Q photochemical oscillators were achieved. The acid concentration also exhibits a great influence on the nonlinear phenomena, where the oscillatory behavior disappeared at high acid concentration (>0.2 M).

2. Experimental Procedure

All experiments were run in a 50 mL thermal-jacketed glass reactor under isothermal conditions at 25.0 ± 0.1 °C. The reaction temperature was maintained by using a circulation water bath (ThermoNesLab RTE 7). The reactor was mounted onto a magnetic stirrer, which was operated at approximately 750 rpm for all experiments. Throughout this study, the progress of the reaction was monitored with a platinum electrode coupled with

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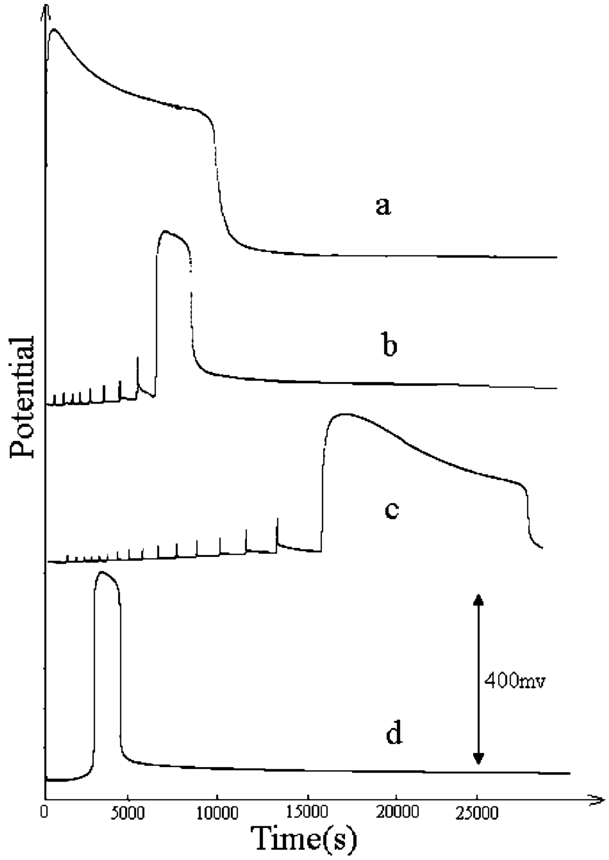

Figure 1. Reaction behavior under different concentrations of H_2Q: (a) 0.0 M, (b) 0.0025 M, (c) 0.005 M, and (d) 0.01 M. Other reaction conditions are [Q] = 0.015 M, $[NaBrO_3]$ = 0.06 M, $[H_2SO_4]$ = 0.1 M, and light intensity = 70 mW/cm^2.

a $Hg/Hg_2SO_4/K_2SO_4$ reference electrode (Radiometer Analytical XR200 and M231 Pt-9). The Pt potential was recorded through an eCorder 201 (eDAQ) data logger connected to a personal computer.

$NaBrO_3$ solution (Aldrich, 99%; 0.6 M) and sulfuric acid (Aldrich, 98%; 3 M) were prepared with doubly distilled water. 1,4-Benzoquinone (Aldrich, 99%) and 1,4-hydroquinone (Aldrich, 99%) were directly dissolved in the reaction mixture. A halogen lamp with dual bifurcated optic fibers and a continuous variable light level was used as the light source (Fisher Scientific, model DLS-100HD, 150 W). The light intensity was measured with an optical photometer from Newport (model 1815-C). Illumination was implemented by placing the two fibers on either the opposite or the same side of the reactor, and no difference in the reaction behavior was observed, implying that mixing was fast enough to generate a situation of homogeneous illumination. Despite the strong illumination, there was no temperature increase in the reaction solution.

3. Results and Discussion

Effects of H_2Q on the dynamics of the photomediated bromate−Q reaction are presented in Figure 1, where the concentration of H_2Q is increased gradually from (a) to (d). As shown in Figure 1a, the system only exhibits a very broad peak in the absence of H_2Q, in which the sudden decrease in the Pt potential at about 8000 s is consistent with the behavior observed in the bromate−Q photoreaction.[19] When 0.0025 M H_2Q is added, eight sharp peaks with increasing amplitudes are achieved (see Figure 1b), which are followed by a broad oscillation peak. A further increase of H_2Q concentration leads to more oscillation peaks (see Figure 1c). If the concentration of H_2Q is increased still, however, the system then stops exhibiting these sharp oscillations. Figure 1d shows that there is only one broad peak at 0.01 M H_2Q concentration. The above scenario illustrates that the presence of H_2Q, which is expected to form complexes with Q, can play a prominent kinetic role in the bromate−Q photochemical oscillator and, possibly, in the bromate−cyclohexanedione system as well.[21]

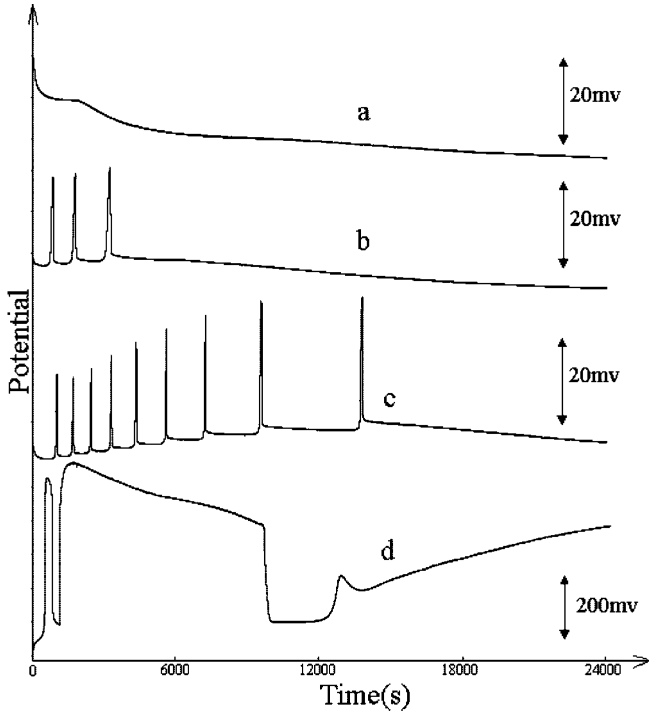

Figure 2. Reaction behavior under different sulfuric acid concentrations: (a) 0.03 M, (b) 0.06 M, (c) 0.08 M, and (d) 0.2 M. Other reaction conditions are [Q] = 0.015 M, $[H_2Q]$ = 0.005 M, $[NaBrO_3]$ = 0.06 M, and light intensity = 70 mW/cm^2.

The above experiments were carried out using 0.1 M H_2SO_4. As discussed earlier in the Introduction, the selection of a low acidic condition is desired in order to slow down the consumption of H_2Q so that it has time to interact with Q. Time series plotted in Figure 2 illustrate how the dynamics of the bromate−H_2Q−Q photoreaction responds to the change of H_2SO_4 concentration. Figure 2a shows that when the H_2SO_4 concentration is 0.03 M, the system does not exhibit any oscillatory behavior at all. In Figure 2b, 0.06 M H_2SO_4, the system exhibits three sharp oscillations. A further increase of sulfuric acid concentration leads to more sharp oscillations with increasing amplitude and decreasing frequency. This trend is likely due to that high acid concentration favors the nonlinear feedback loop implemented through the reactions $HBrO_2 + BrO_3^- + H^+ \rightarrow H_2O + 2\ BrO_2^\bullet$ and $H_2Q + 2BrO_2^\bullet \rightarrow Q + 2HBrO_2$.[20] However, as shown in Figure 2d, when the concentration of sulfuric acid is increased still (>0.2 M), only one sharp oscillation takes place before the broad peak. Notably, after the broad peak, there is another small amplitude oscillation at about 13 000 s in Figure 2d, and this small peak largely resembles the behavior seen in the bromate−Q photochemical oscillator.[19] We would like to point out that the broad peak seen in Figure 2c has also been observed at the conditions used in Figure 2b and c, but it does not occur until 11 h after the start of the reaction. To show these small peaks better, the broad peak is omitted from Figure 2b and c. The optimum H_2SO_4 concentration appeared to be around 0.1 M, in which a series

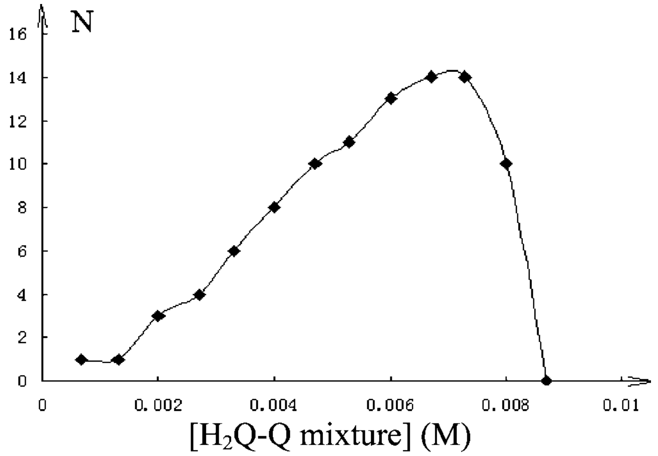

Figure 3. A plot of the number of peaks versus the concentration of the Q−H_2Q mixture. Other reaction conditions are [$NaBrO_3$] = 0.06 M, [H_2SO_4] = 0.1 M, and light intensity = 70 mW/cm^2.

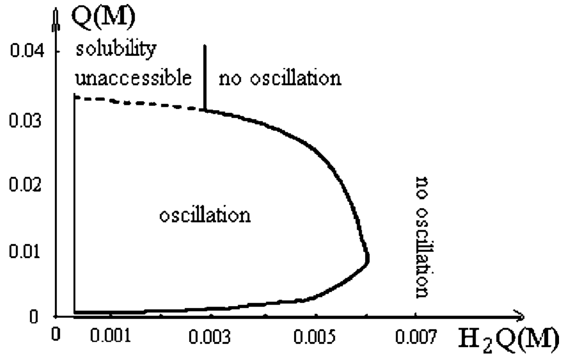

Figure 4. Phase diagram in the hydroquinone and benzoquinone concentration space. Other reaction conditions are [$NaBrO_3$] = 0.06 M, [H_2SO_4] = 0.1M, and light intensity = 70 mW/cm^2.

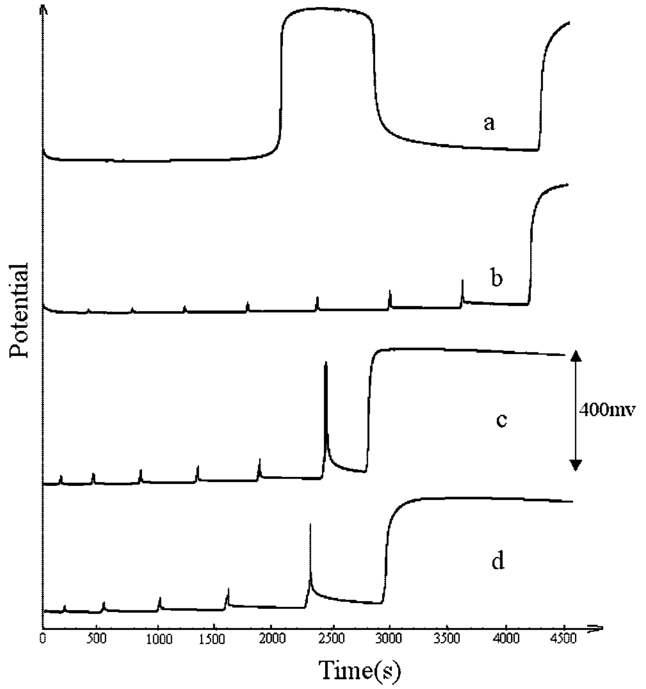

Figure 5. Time series obtained at different light intensities: (a) 30 mW/cm^2, (b) 50 mW/cm^2, (c) 70 mW/cm^2, and (d) 100 mW/cm^2. Other reaction conditions are [Q] = 0.008 M, [H_2Q] = 0.003 M, [H_2SO_4] = 0.1 M, and [$NaBrO_3$] = 0.06 M.

of small, sharp oscillations could be obtained. This result confirms the necessity of having a low acidic environment, which is presumably required by (1) the autocatalytic oxidation of H_2Q by bromine dioxide radicals, and (2) the formation of H_2Q and Q complexes.

An earlier theoretical investigation suggests that a 1:1 Q and H_2Q mixture forms a favorable dimer structure.[23] We prepared a solution containing 0.1 M Q and 0.1 M H_2Q and used different amounts of this solution to react with acidic bromate. Our experiments illustrate that when the concentration of this Q−H_2Q mixture is within 0.002 and 0.01 M, the illuminated bromate−H_2Q−Q reaction exhibits these sharp oscillations. The total number of oscillation peaks is plotted in Figure 3 as a function of the concentration of the Q−H_2Q mixture. It shows that the largest number of peaks is obtained at the concentration of 0.007 M.

Figure 4 summarizes the reaction behavior in the Q and H_2Q concentration plane. This phase diagram indicates that, regardless of the concentration of Q, there must be a small amount of H_2Q (>0.0003 M) for the system to exhibit the type of oscillatory behavior shown in Figure 1b. On the other hand, the oscillation phenomenon disappears when the concentration of H_2Q is too high. The threshold H_2Q concentration which separates the oscillatory and nonoscillatory parameter window increases first as the concentration of Q is increased. It then decreases with a further increase of Q concentration. Limited by the solubility of Q in water, we were unable to characterize the reaction behavior for Q concentrations above 0.035 M. Nevertheless, a domain with a nearly closed boundary is established here, which highlights the importance of the formation of H_2Q−Q complexes in the above observed nonlinear chemical kinetics.

When the bromate concentration was adjusted as the sole variable while other conditions were fixed at 0.015 M Q, 0.005 M H_2Q, 0.1 M H_2SO_4, and light intensity = 70 mW/cm^2, no oscillation could be achieved for bromate concentrations higher than 0.15 M or lower than 0.04 M. Within the oscillation parameter window, the number of oscillation peak increases until the bromate concentration reaches 0.09 M. The number of oscillations then declines with a further increase of bromate concentration. Increasing the bromate concentration also prolongs the induction time of the first oscillation peak. A pulse addition of bromide ions can completely quench the oscillations or prolong the time interval between two consecutive oscillations, implicating that nonlinear behavior in this light-mediated bromate−Q−H_2Q system is bromide-controlled.

Figure 5 presents the reaction behavior under different intensities of illumination: (a) 30 mW/cm^2, (b) 50 mW/cm^2, (c) 70 mW/cm^2, and (d) 100 mW/cm^2. Under low light intensity, the system only yields a broad peak after a long induction time (ca. 2000 s). As the light intensity is increased to 50 mW/cm^2, several small amplitude oscillations take place in the system. A further increase of the light intensity shortens the induction time of the first peak. In Figure 5d, the total number of oscillations becomes slightly less than that in Figure 5c, implying that the applied light intensity system is now above the optimum value. The above scene illustrates that, despite that interactions between H_2Q and Q are critical in achieving those oscillations, the system remains to be a photocontrolled chemical oscillator. Indeed, these oscillations would stop immediately upon turning off the light and revive upon resuming illumination.

Figure 6 presents a series of absorption spectra collected as the reaction evolves in time, in which the absorption peak at 290 nm mainly arises from H_2Q whereas the absorption at 250 nm is largely due to Q. This measurement shows that, at the

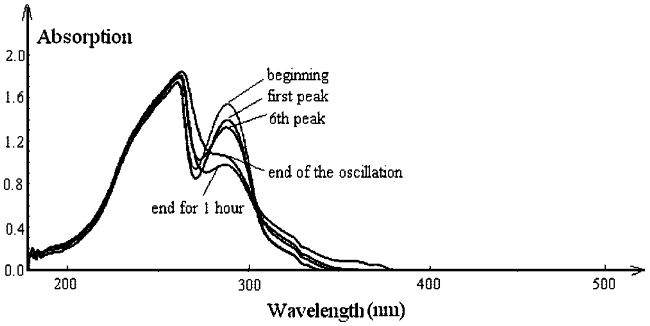

Figure 6. Absorption spectra of the photoilluminated bromate−Q−H_2Q reaction. Reaction conditions are [Q] = 0.015 M, [H_2Q] = 0.005 M, [H_2SO_4] = 0.1 M, [$NaBrO_3$] = 0.06 M, and light intensity = 70 mW/cm^2.

beginning of the reaction, the H_2Q concentration is at its highest value and then decreases in time. At the end of the oscillatory process, the H_2Q concentration reaches its lowest level. This UV/vis spectroscopic study provides further evidence that the copresence of H_2Q and Q is essential in the development of the above oscillatory behavior. The investigation presented in this figure was carried out by conducting the reaction in a 50 mL reactor, and then 0.5 mL of the reaction solution was taken out at the recorded time and diluted into 2.5 mL in the cuvette for the absorption measurements.

Mass spectrometry of the H_2Q−Q mixture was investigated with a 1200 L single quadrupole mass spectrometer (MS; Varian) using a direct insertion probe. The mass range was between 10 and 800 amu, and electron ionization was used as the ionization mode. The probe temperature was controlled independently and changed from 20 to 300 °C with the same steps and durations for all the MS measurements. The complexes were prepared via mixing H_2Q and Q powders in a 1:1 stoichiometric ratio. The mass spectra of all samples were recorded at 20 eV electron impact. In the spectrum, there are two intense ion peaks centered at 108 and 110 *m*/*e*, which correspond to hydroquinone and benzoquinone molecules, respectively. Although significantly less intense than the ones centered at 108 and 110 *m*/*e*, an ion peak centered at 218 *m*/*e* nevertheless can be clearly seen in the spectrum, which suggest the formation of the H_2Q−Q dimer.

4. Summary

Unlike the bromate−Q or bromate−H_2Q photomediated oscillator,[19] in which oscillations have a very long induction time (>3 h), here spontaneous oscillations commence shortly after the start of the reaction. Another important difference is the oscillation pattern. In this H_2Q−Q system, the redox potential of the system stays flat for a long time after each oscillation, forming a train of spikes. In contrast, in the bromate−Q system, oscillations in the Pt potential are continuous and there is no flat separation between neighboring peaks. The phase diagram in the Q−H_2Q concentration plane illustrates that the copresence of H_2Q and Q is critical for achieving these chemical oscillations. UV/vis absorption spectra further indicate that the disappearance of these sharp oscillations is related to the consumption of H_2Q. Our experiments further show that the system could exhibit oscillations within a broader range of bromate concentration when the initial concentration ratio of Q/H_2Q is 1:1.

Despite that the interactions of Q and H_2Q play a critical role in the above observed oscillatory behavior, it is important to point out that the studied system remains to be photocontrolled. The Pt potential of the reaction would stay constant in the absence of external illumination. Therefore, the core reaction mechanism of this bromate−H_2Q−Q system shall be the same as that of the bromate−Q photochemical oscillator. Mass spectrometry studies confirm the formation of Q and H_2Q dimer. Since dimers may act as a temporal storage of H_2Q, their formation could be responsible for the dramatic changes in the reaction behavior observed in this study. Several bromate-based oscillators discovered recently contain both H_2Q and Q as intermediates.[19–22] Various interesting nonlinear behaviors such as the anomalous dispersion relationship observed in those systems could not be reproduced with the existing mechanisms.[25] The kinetic role of the interactions of Q and H_2Q unveiled in this study could be important in understanding the dynamics of those oscillators, especially when those systems are performed at low acid concentrations.

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References and Notes

(1) Kruse, O.; Ruppercht, J.; Mussgnug, J. H.; Dismukes, G. C.; Hankamer, B. *Photochem. Photobiol. Sci.* **2005**, *4*, 957.
(2) Vavilin, V. A.; Zhabotinsky, A. M.; Zaikin, A. N. *Russ. J. Phys. Chem.* **1968**, *42*, 1649.
(3) Gaspar, V.; Bazsa, G.; Beck, M. T. *Z. Phys. Chem. (Leipzig)* **1983**, *264*, 43.
(4) Kuhnet, L.; Agladze, K.; Krinsky, V. *Nature* **1990**, *337*, 224.
(5) Sekiguchi, T.; Mori, Y.; Okazaki, N.; Hanazaki, I. *Chem. Phys. Lett.* **1993**, *211*, 1309.
(6) Kadar, S.; Amemiya, T.; Showalter, K. *J. Phys. Chem. A* **1997**, *101*, 8200.
(7) Kaminaga, A.; Hanazaki, I. *J. Phys. Chem. A* **1998**, *102*, 3307.
(8) Petroy, V.; Ouyang, Q.; Swinney, H. *Nature* **1997**, *388*, 655.
(9) Epstein, I. R.; Showalter, K. *J. Phys. Chem.* **1996**, *100*, 13132.
(10) Steinbock, O.; Zykov, V.; Muller, S. C. *Nature* **1993**, *366*, 322.
(11) Sorensen, P. G.; Lorenzen, T.; Hynne, F. *J. Phys. Chem.* **1996**, *100*, 19192.
(12) Trendl, L.; Knudsen, D.; Nakamura, T.; Inoue, T. M.; Jorgensen, K. B.; Rouff, P. *J. Phys. Chem. A* **2000**, *104*, 10783.
(13) Kádár, S.; Wang, J.; Showalter, K. *Nature* **1998**, *391*, 770.
(14) Roussel, M. R.; Wang, J. *J. Phys. Chem. A* **2000**, *104*, 11751.
(15) Ononye, A. I.; Mcintosh, A. R.; Bolton, J. R. *J. Phys. Chem.* **1986**, *90*, 6266.
(16) Cramer, W. A.; Zhang, H.; Yan, J.; Kurisu, G. *Biochem. Soc. Trans.* **2005**, *33*, 921.
(17) Gorner, H. *J. Phys. Chem. A* **2003**, *107*, 11587.
(18) Li, N.; Green, J. R.; Wang, J. *Chem. Phys. Lett.* **2007**, *447*, 241.
(19) Zhao, B.; Wang, J. *Chem. Phys. Lett.* **2006**, *430*, 41.
(20) Szalai, I.; Körös, E. *J. Phys. Chem. A* **1998**, *102*, 6892.
(21) Farage, V. J.; Janjic, D. *Chem. Phys. Lett.* **1982**, *88*, 301.
(22) Szalai, I.; Kurin-Csorgei, K.; Epstein, I. R.; Orban, M. *J. Phys. Chem. A* **2003**, *107*, 10074.
(23) Sundaram, K.; Purcell, W. P. *Int. J. Quantum Chem.* **1971**, *5*, 101.
(24) Zhao, J.; Chen, Y.; Wang, J. *J. Chem. Phys.* **2005**, *122*, 114514.
(25) Manz, N.; Steinbock, O. *Phys. Rev. E* **2004**, *70*, 66213.
(26) Kereszturi, K.; Szalai, I. *Chem. Phys. Lett.* **2006**, *428*, 288.
(27) Regeimbal, J.; Gleiter, S.; Trumpower, B. L.; Yu, C. A.; Diwakar, M.; Ballou, D. P.; Bardwell, J. C. A. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 13779.

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