4. N. G. Krishman, W. N. Delgass and W. D. Robertson, *Surf. Sci.*, **57**, 1 (1976).
5. D. F. Mitchell, P. B. Sewell and M. Cohen, *Surf. Sci.*, **61**, 355 (1976).
6. P. R. Notyon, T. L. Tapping and J. W. Goodale, *Surf. Sci.*, **65**, 13 (1977).
7. C. R. Brundle and H. Hopster, *J. Vac. Sci. Technol.*, **18(2)** 663 (1981).
8. P. H. Holloway, *J. Vac. Sci. Technol.*, **18(2)** 653 (1982).
9. C. R. Brundle, in "Aspects of the Kinetics and Dynamics of Surface Reactions". ed Uzi Landman. (American Institute of Physics, 1980) P. 57.
10. J. H. Boo, Thesis(M. S.) Sung Kyun Kwan Univ., 2 (1987).
11. S. K. Shi, J. M. White and R. L. Hannce, *J. Phys. Chem.*, **84** 244 (1980).
12. J. L. Gland, *Surf. Sci.*, **93** 487 (1980).
13. D. A. King and M. G. Wells, *Proc. R. Soc. London*, A **339**, 245 (1974).
14. G. Ertl, S. B. Lee and M. Weiss, *Surf. Sci.*, **114**, 515 (1982).
15. W. A. Steel, Interaction of Gases with Solid Surfaces Chapt. 2, Pergamon, New York (1974).
16. J. O. Hirschfelder, C. E. Curtis, and R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley&Sons, New York (1964).
17. A. B. Anderson, *J. Chem. Phys.*, **64**, 4046 (1976).
18. J. B. Benziger and E. Preston, *Surf. Sci.*, **141**, 567 (1984).

The Time Correlation Functions of Concentration Fluctuations in the Lotka Model near the Oscillatory Marginal Steady State

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Received October 20, 1987

The time correlation functions of concentration fluctuations due to the random forces near the steady state are evaluated for a general two-component nonlinear chemical system by solving the corresponding two dimensional Fokker-Planck equation. The approximate method of solving the Fokker-Planck equation is based on the eigenfunction expansion and the corresponding eigenvalues for both the linear and nonlinear Fokker-Planck operators are obtained near the steady state. The general results are applied to the Lotka model near the oscillatory marginal steady state and the comparison is made between linear and nonlinear cases.

Introduction

Various kinds of approximate methods[1-7], such as size expansion[1], time scaling[2-3], mode-mode coupling[4], dynamic renormalization[5] and etc.[6-7], have been used to discuss the dynamic phenomena for a single component nonlinear chemical system, starting from a Langevin equation, Fokker-Planck equation or other equations. It is, however, much more complicated to obtaine the dynamic properties for a multicomponent system than for a single component system.

The purpose of the present paper is to obtain the time correlation function of concentration fluctuations near a steady state for general two component nonlinear chemical system, assuming that chemical species obey a Langevin equation. The method to be used is the response theory[7-9], which is one of the most effective methods. Then, applying the general results to a specific reaction model with instability, that is, the Lotka model[10], we discuss the time correlation functions between the fluctuating parts of concentration near the oscillatory marginal stable steady state.

At first, we restrict ourselves to the linear Langevin equation. In order to discuss the time correlation function near a steady state(or equilibrium) we have to obtain the eigenvalue and probability distribution of the linear Fokker-Planck equation. The easiest method in our opinion is the operator method as in quantum mechanics.[7-8,11] We diagonalize the linear Langevin equation with the aid of a suitable eigenvector[3] and obtain the corresponding linear Fokker-Planck equation. We introduce a function so that the Fokker-Planck equation is transformed into a time-dependent Schrödinger equation.[7] Using the creation and annihilation operators[7,8,11], it can be shown that the probability distribution can be expressed in terms of the coupled Hermite polynomials. With the aid of the eigenfunction we may obtain the solvable recurrence formulae for the eigenvalues of the Fokker-Planck equation in any order of coupling. Then, we extend the linear theory to the nonlinear case to obtain the eigenvalue of the nonlinear Fokker-Planck equation. In the nonlinear case it is only possible to obtain the eigenvalue up to the first order of the coupling. Nevertheless, we may discuss the nonlinear effect on the time correlation functions near a steady state.

Finally, the general results for the correlation functions are applied to the Lotka model to obtain the correlation functions between the fluctuating parts due to the random forces at the oscillatory marginal steady state.

Theory

Let us consider a general nonlinear system of two variables, y_1 and y_2, which satisfies the following Langevin equation

$$\frac{d}{dt}(y_1, y_2)^T = \mathbf{M}(y_1, y_2)^T + y_1^2(f_1, g_1)^T + y_1 y_2 (f_2, g_2)^T + y_2^2(f_3, g_3)^T + (\xi_1, \xi_2)^T, \qquad (2.1)$$

where the matrix **M** is given as

$$\mathbf{M} = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \qquad (2.2)$$

and the random forces, ξ_i's, are assumed to satisfy the Gaussian conditions[14]

$$\langle \xi_i(t) \rangle = 0, \quad \langle \xi_i(t)\xi_j(t') \rangle = 2D_{ij}\delta_{ij}\delta(t-t'). \qquad (2.3)$$

The f_i's and g_i's are assumed constants, D_{ij} is the diffusion coefficient, δ_{ij} is the Kronecker delta, and $\delta(t\text{-}t')$ is the Dirac delta function. The Fokker-Planck equation for the probability distribution, $P(y_1, y_2, t)$, corresponding to eq.(2.1) is

$$\frac{\partial}{\partial t}P(y_1, y_2, t) = \Xi P(y_1, y_2, t) \; ;$$

$$\Xi P(y_1, y_2, t) = \sum_{i,j}\left[-\frac{\partial}{\partial y_i}(\Xi_i P) + D_{ij}\frac{\partial^2}{\partial y_i \partial y_j}P\right], \quad (i, j = 1 \text{ or } 2), \qquad (2.4)$$

where Ξ_i is the i-th component of the drift vector term in eq. (2.1). At a steady state or equilibrium we have

$$\frac{\partial}{\partial t}P_0(y_1, y_2) = \Xi P_0(y_1, y_2) = 0, \qquad (2.5)$$

where P_0 is the probability distribution at a steady state or equilibrium. The Fokker-Planck equation under the influence of an external perturbation may be described as[7-9]

$$\frac{\partial}{\partial t}P(y_1, y_2, t) = [\Xi + \Xi'(t)]P(y_1, y_2, t), \qquad (2.6)$$

where $\Xi'(t)$ is the perturbation term given as

$$\Xi'(t) = BF(t). \qquad (2.7)$$

Here, B is an operator with respect to y_1 and y_2 and $F(t)$ is a given function of time.

The system is assumed to be in a steady state or equilibrium at $t = -\infty$. To ensure the initial condition we switch on the perturbation at $t = -\infty$ adiabatically so that Ξ' at $t = -\infty$ is zero. If the perturbation is small, we may obtain up to the first order approximation as follows

$$P(y_1, y_2, t) = P_0(y_1, y_2) + \int_{-\infty}^{t} dt' \exp[\Xi(t-t')] \times BF(t')P(y_1, y_2, t). \qquad (2.8)$$

Using the first order approximation, the average value of an observable represented by a quantity A at time t is

$$\langle A(t) \rangle = \langle A \rangle_0 + \int_{-\infty}^{t} G_{AB}(t-t')F(t')\,dt', \qquad (2.9)$$

where $G_{AB}(t\text{-}t')$ is the retarded Green function or response function defined as

$$G_{AB}(t-t') = \theta(t-t')\,\langle A(y_1, y_2)\exp[\Xi(t-t')] \times B(y_1, y_2) \rangle_0, \qquad (2.10)$$

the Heaviside unit step function $\theta(x)$ being given as

$$\theta(x) = \begin{cases} 1 & \text{for } x > 0 \\ 0 & \text{for } x < 0, \end{cases} \qquad (2.11)$$

and $\langle \cdots \rangle_0$ is the equilibrium ensemble average over the distribution. Using the stationary assumption, the time correlation function between A and B, $C_{AB}(t)$, is related to the retarded Green function as follows:

$$G_{AB}(t) = \theta(t)\;C_{AB}(t). \qquad (2.12)$$

From the retarded Green function we may obtain the other dynamic properties. In order to obtain the explicit form of the time correlation function, we shall use the method to diagonalize eq.(2.1) and introduce the creation and annihilation operators. At first, we shall restrict ourselves to the linear case and then extend the linear result to the nonlinear case.

(A) Linear case

Let us consider the linear case of eq.(2.1) in this section. The linear stability of the system depends on the eigenvalue of the matrix, **M**:

(a) If all the real parts of the eigenvalues are negative, the system is stable.

(b) When at least one of the real parts of the eigenvalues is positive, the system is unstable.

(c) If a real part of an eigenvalue is zero, the system is at a state of marginal stability. When det **M** = 0, the state of marginal stability is called as the state of nonoscillatory marginal stability, while tr **M** = 0 and det **M**>0 is the condition for the state of oscillatory marginal stability. We shall consider the system at a stable state or the state of oscillatory marginal stability.

Let the eigenvalue of **M** and its corresponding right and left eigenvectors be $-\lambda_i$, $\underset{\sim}{\Psi}^i$ and $\underset{\sim}{\bar{\Psi}}^i$, respectively. Then, the eigenvalues and eigenvectors are given as[3]

$$\lambda_1 = \alpha + \beta, \quad \lambda_2 = \alpha - \beta, \quad (Re\,\lambda_i \geq 0),$$

$$\underset{\sim}{\Psi}^i = \frac{1}{2\beta}(1, \lambda_i + d)^T, \quad \underset{\sim}{\bar{\Psi}}^i = (1, \frac{-b}{\lambda_i + d}), \quad (i = 1 \text{ or } 2) \qquad (2.13)$$

where

$$\alpha = -\frac{1}{2}\,tr\,\mathbf{M} \geqq 0, \quad \beta = (\alpha^2 - det\,\mathbf{M})^{\frac{1}{2}}. \qquad (2.14)$$

It can be easily checked that the eigenvectors satisfy the orthonormalization conditions

$$\sum_{\alpha}\bar{\Psi}^i_\alpha \Psi^j_\alpha = \delta_{ij}, \quad \sum_{i}\bar{\Psi}^i_\alpha \Psi^i_\beta = \delta_{\alpha\beta}. \qquad (2.15)$$

With the aid of eq.(2.13), the linear part of eq.(2.1) reduces to

$$\frac{d}{dt}x_i = -\lambda_i x_i + \xi'_i, \quad (i = 1 \text{ or } 2), \qquad (2.16)$$

where

$$x_1 = y_1 - \frac{b}{\lambda_1 + d}y_2, \quad x_2 = y_1 - \frac{b}{\lambda_2 + d}y_2,$$

$$\xi'_1 = \xi_1 - \frac{b}{\lambda_1 + d}\xi_2, \quad \xi'_2 = \xi_1 - \frac{b}{\lambda_2 + d}\xi_2 \qquad (2.17)$$

The Fokker-Planck equation corresponding to eq.(2.16) becomes

$$\frac{\partial}{\partial t}P(x_1,x_2,t)=\Xi_0P(x_1,x_2t)=-\lambda P(x_1,x_2,t)\ ;$$

$$\Xi_0=\lambda_1\frac{\partial}{\partial x_1}x_1+\lambda_2\frac{\partial}{\partial x_2}x_2+d_{11}\frac{\partial^2}{\partial x_1^2}+d_{22}\frac{\partial^2}{\partial x_2^2}+2d_{12}\frac{\partial^2}{\partial x_1\partial x_2} \tag{2.18}$$

where

$$d_{11}=\langle\xi_1'(t)\,\xi_1'(t)\rangle=D_{11}+\left(\frac{b}{\lambda_1+d}\right)^2D_{22},$$

$$d_{12}=d_{21}=\langle\xi_1'(t)\,\xi_2'(t)\rangle=D_{11}+\frac{b^2}{(\lambda_1+d)\,(\lambda_2+d)}D_{22},$$

$$d_{22}=\langle\xi_2'(t)\,\xi_2'(t)\rangle=D_{11}+\left(\frac{b}{\lambda_2+d}\right)^2D_{22}. \tag{2.19}$$

Let us introduce a new function defined as[7-8]

$$\bar{P}(z_1,z_2,t)=\exp\left[\frac{1}{4}(z_1^2+z_2^2)\right]P(z_1,z_2,t), \tag{2.20}$$

where

$$z_i=\left(\frac{\lambda_i}{d_{ii}}\right)^{\frac{1}{2}}x_i \tag{2.21}$$

Then, eq.(2.18) becomes

$$\frac{\partial}{\partial t}\bar{P}(z_1,z_2,t)=\tilde{\Xi}_0\bar{P}(z_1,z_2,t)=-\lambda\bar{P}(z_1,z_2,t)\ ;$$

$$\tilde{\Xi}_0=\exp\left[\frac{1}{4}(z_1^2+z_2^2)\right]\Xi_0\exp\left[-\frac{1}{4}(z_1^2+z_2^2)\right], \tag{2.22}$$

Introducing the creation and annihilation operators with respect to z_1 and z_2 as[7-8,11]

$$\hat{a}=\frac{\partial}{\partial z_1}+\frac{1}{2}z_1,\quad \hat{a}^+=-\frac{\partial}{\partial z_1}+\frac{1}{2}z_1,$$

$$\hat{b}=\frac{\partial}{\partial z_2}+\frac{1}{2}z_2,\quad \hat{b}^+=-\frac{\partial}{\partial z_2}+\frac{1}{2}z_2, \tag{2.23}$$

we have

$$\tilde{\Xi}_0=-\lambda_1\hat{a}^+\hat{a}-\lambda_2\hat{b}^+\hat{b}+2\left[\frac{d_{12}^2\lambda_1\lambda_2}{d_{11}d_{22}}\right]^{\frac{1}{2}}\hat{a}^+\hat{b}^+. \tag{2.24}$$

The operators satisfy the following commutation relations:

$$[\hat{a},\hat{a}^+]=1,\ [\hat{b},\hat{b}^+]=1,\ [\hat{a}^+,\hat{b}]=[\hat{a}^+,\hat{b}^+]=[\hat{a},\hat{b}]$$

$$=[\hat{a},\hat{b}^+]=0. \tag{2.25}$$

Let the eigenfunctions of $\hat{a}^+\hat{a}$ and $\hat{b}^+\hat{b}$ be $\bar{P}_{n_1}(z_1)$ and $\bar{P}_{n_2}(z_2)$, respectively. Then, we have

$$\begin{aligned}\hat{a}\,\bar{P}_{n_1}(z_1)&=n_1^{\frac{1}{2}}\bar{P}_{n_1-1}(z_1),\\ \hat{a}^+\bar{P}_{n_1}(z_1)&=(n_1+1)^{\frac{1}{2}}\bar{P}_{n_1+1}(z_1),\\ \hat{b}\,\bar{P}_{n_2}(z_2)&=n_2^{\frac{1}{2}}\bar{P}_{n_2-1}(z_2),\\ \hat{b}^+\bar{P}_{n_2}(z_2)&=(n_2+1)^{\frac{1}{2}}\bar{P}_{n_2+1}(z_2),\end{aligned} \tag{2.26}$$

where n_i's are zero or positive integers and the eigenfunctions may be expressed in terms of the Hermite polynomials[8]

$$\bar{P}_n(z)=\frac{1}{[n!\,(2\pi)^{1/2}]^{1/2}}\exp\left(-\frac{1}{4}z^2\right)\mathrm{H}_n\left(\frac{z}{2^{1/2}}\right)\ ;$$

$$\mathrm{H}_n(z)=(-1)^n\exp\left(\frac{1}{2}z^2\right)\frac{d^n}{dz^n}\exp\left(-\frac{1}{2}z^2\right). \tag{2.27}$$

The solution of eq.(2.22) may be written as

$$\bar{P}(z_1,z_2,t)=\sum_{n_1,n_2=0}^{\infty}C_{n_1,n_2}$$

$$\times\exp(-\lambda_{n_1,n_2}t)\,\bar{P}_{n_1}(z_1)\,\bar{P}_{n_2}(z_2). \tag{2.28}$$

The above solution shows that the eigenfunctions are coupled each other through $C_{n1,n2}$ and $\lambda_{n1,n2}$. let N be n_1+n_2. Then, eq.(2.28) can be rewritten as

$$\bar{P}(z_1,z_2,t)=\sum_{N=0}^{\infty}\sum_{n=0}^{N}\mathrm{C}_n^N\exp(-\lambda_{N-n,n}t)\,\bar{P}_{N-n}(z_1)\,\bar{P}_n(z_2), \tag{2.29}$$

where

$$C_{N-n,n}=C_n^N\,(N\geqq n\geqq 0). \tag{2.30}$$

Now, let us obtain the eigenvalue of $\tilde{\Xi}_0$. Substitution of eqs.(2.24) and (2.29) into eq.(2.22) leads to

$$\begin{aligned}&\sum_{N=0}^{\infty}\sum_{n=0}^{N}[\{\lambda_1(N-n)+\lambda_2n-\lambda_{N-n,n}\}C_n^N\bar{P}_{N-n}(z_1)\,\bar{P}_n(z_2)\\ &-2\left(\frac{d_{12}^2\lambda_1\lambda_2}{d_{11}d_{22}}\right)^{\frac{1}{2}}\times\{(N+1-n)\,(n+1)\}^{\frac{1}{2}}\,C_{n+1}^{N+2}\\ &\times\bar{P}_{N+1-n}(z_1)\,\bar{P}_{n+1}(z_2)]=0.\end{aligned} \tag{2.31}$$

Assuming that N is the maximum order, we may split eq.(2.31) into two parts, that is,

$$[\lambda_1(N-n)+\lambda_2n-\lambda_{N-n,n}]C_n^N=0,\ \text{if } N \text{ is } 0 \text{ or } 1, \tag{2.32}$$

$$[\lambda_1(N-n)+\lambda_2n-\lambda_{N-n,n}]C_n^N-2\left(\frac{d_{12}^2\lambda_1\lambda_2}{d_{11}d_{22}}\right)^{\frac{1}{2}}$$

$$\times[(N-n+1)\,(n+1)]^{\frac{1}{2}}C_{n+1}^N=0, \tag{2.33}$$

when $N\geq 2$.

From eq.(2.32) we can see that $N=0$ describes the steady state or equilibrium of the system. As will be shown in the next section we do not have to consider the case of $N\geq 2$ to obtain the time correlation functions explicitly near a steady state. From eq.(2.32) we obtain the following eigenvalues for $N=1$

$$\lambda_{1,0}=\lambda_1,\ \lambda_{0,1}=\lambda_2. \tag{2.34}$$

We shall extend the linear theory to the nonlinear case in the next section.

(B) Nonlinear case

The Fokker-Planck equation given in eq.(2.4) may be given as, using eq.(2.17),

$$\frac{\partial}{\partial t}P(x_1,x_2,t)=\Xi P(x_1,x_2,t) \tag{2.35}$$

$$\Xi=\Xi_0+\Xi_N$$

where Ξ_0 is the linear operator already discussed and Ξ_N is the nonlinear operator given as follows

$$\Xi_N=-\frac{\partial}{\partial x_1}(f_1'x_1^2+f_2'x_1x_2+f_3'x_2^2)$$

$$-\frac{\partial}{\partial x_2}(g_1' x_1^2 + g_2' x_1 x_2 + g_3' x_2^2) \tag{2.36}$$

$$f_1' = [\frac{\lambda_1 + d}{\lambda_1 - \lambda_2}]^2 [f_1 + \frac{\lambda_2 + d}{b} f_2 + (\frac{\lambda_2 + d}{b})^2 f_3]$$

$$f_2' = -\frac{(\lambda_1 + d)(\lambda_2 + d)}{(\lambda_1 - \lambda_2)^2}[2f_1 + \frac{\lambda_1 + \lambda_2 + 2d}{b} f_2 + \frac{2(\lambda_1 + d)(\lambda_2 + d)}{b^2} f_3]$$

$$f_3' = (\frac{\lambda_2 + d}{\lambda_1 - \lambda_2})^2 [f_1 + \frac{\lambda_1 + d}{b} f_2 + (\frac{\lambda_1 + d}{b})^2 f_3]$$

and we may obtain g_i''s by replacing f_j by g_j. Using the same method as in the linear case, we have

$$\frac{\partial}{\partial t}\bar{P}(z_1, z_2, t) = \widetilde{\Xi}\bar{P}(z_1, z_2, t) = (\widetilde{\Xi}_0 + \widetilde{\Xi}_N)\bar{P}(z_1, z_2, t). \tag{2.37}$$

where $\widetilde{\Xi}_o$ corresponds to the result given in eq.(2.24) and $\widetilde{\Xi}_N$ is

$$\begin{aligned}\widetilde{\Xi}_N = &-(2f_1' + g_1')(\frac{d_{11}}{\lambda_1})^{\frac{1}{2}}(\hat{a}^+ + \hat{a}) - (f_2' + 2g_3')(\frac{d_{22}}{\lambda_2})^{\frac{1}{2}}(\hat{b}^+ + \hat{b}) \\ &+ (\frac{d_{11}}{\lambda_1})(\hat{a}^+ + \hat{a})^2\{(\frac{\lambda_1}{d_{11}})^{\frac{1}{2}} f_1' \hat{a}^+ + (\frac{\lambda_2}{d_{22}})^{\frac{1}{2}} g_1' \hat{b}^+\} \\ &+ (\frac{d_{11}d_{22}}{\lambda_1\lambda_2})^{\frac{1}{2}}(\hat{a}^+ + \hat{a})(\hat{b}^+ + \hat{b})\{(\frac{\lambda_1}{d_{11}})^{\frac{1}{2}} f_2' \hat{a}^+ + (\frac{\lambda_2}{d_{22}})^{\frac{1}{2}} g_2' \hat{b}^+\} \\ &+ (\frac{d_{22}}{\lambda_2})(\hat{b}^+ + \hat{b})^2\{(\frac{\lambda_1}{d_{11}})^{\frac{1}{2}} f_3' \hat{a}^+ + (\frac{\lambda_2}{d_{22}})^{\frac{1}{2}} g_3' \hat{b}^+\}.\end{aligned} \tag{2.38}$$

Assuming that the eigenfunction of eq.(2.37) is the same as that for the linear case, the eigenvalues for $N \leq 1$ are

$$\lambda_{0,0} = 0,\ \lambda_{1,0} = \lambda_1 + (\frac{d_{11}}{\lambda_1})^{\frac{1}{2}}(f_1' + \frac{\lambda_1 d_{22}}{\lambda_2 d_{11}} f_3'),\ \lambda_{0,1} = \lambda_2, \tag{2.39}$$

The time correlation function $C_{y_i y_j}(t)$ near the steady state may be evaluated from the following expression:

$$C_{y_i y_j}(t) = \langle y_i \exp(\Xi t) y_j \rangle_0 = \frac{\int_{-\infty}^{\infty} dy_1 dy_2 y_i \exp(\Xi t) y_j P_{0,0}(y_1, y_2)}{\int_{-\infty}^{\infty} dy_1 dy_2 P_{0,0}(y_1, y_2)} \tag{2.40}$$

The results become

$$C_{y_1 y_1}(t) = \frac{1}{(\lambda_1 - \lambda_2)^2}[(\lambda_1 + d)^2 (\frac{d_{11}}{\lambda_1})\exp(-\lambda_{1,0} t) + (\lambda_2 + d)^2 (\frac{d_{22}}{\lambda_2})\exp(-\lambda_{0,1} t)],$$

$$C_{y_1 y_2}(t) = C_{y_2 y_1}(t) = \frac{(\lambda_1 + d)(\lambda_2 + d)}{b(\lambda_1 - \lambda_2)^2}[(\lambda_1 + d)(\frac{d_{11}}{\lambda_1})\exp(-\lambda_{1,0} t) + (\lambda_2 + d)(\frac{d_{22}}{\lambda_2})\exp(-\lambda_{0,1} t)], \tag{2.41}$$

$$C_{y_2 y_2}(t) = [\frac{(\lambda_1 + d)(\lambda_2 + d)}{b(\lambda_1 - \lambda_2)}]^2 [\frac{d_{11}}{\lambda_1}\exp(-\lambda_{1,0} t) + \frac{d_{22}}{\lambda_2}\exp(-\lambda_{0,1} t)]$$

We can apply the results to any two-component chemical system. In the next section we will discuss the Lotka model which is a chemical reaction model with instability.

Application to the Lotka Model

The Lotka model is a model of chemical reaction mechanism showing the sustained oscillation, which is given by[15]

$$\begin{aligned} A + X_1 &\xrightarrow{k_1} 2X_1, \\ X_1 + X_2 &\xrightarrow{k_2} 2X_2, \\ X_2 &\xrightarrow{k_3} P \end{aligned} \tag{3.1}$$

where k_i's are the rate constants, the concentration of the reactant A is kept to be constant and X_1 and X_2 are the intermediates. The rate equations for the intermediates are

$$\begin{aligned} \frac{d}{dt}X_1 &= k_1 A X_1 - k_2 X_1 X_2 + \xi_1, \\ \frac{d}{dt}X_2 &= -k_3 X_2 + k_2 X_1 X_2 + \xi_2, \end{aligned} \tag{3.2}$$

with the nontrivial steady state value

$$X_1^0 = \frac{k_3}{k_2},\quad X_2^0 = \frac{k_1 A}{k_2}. \tag{3.3}$$

Expansion of eq.(3.2) in terms of $y_i(t) = X_i(t) - X_i^o$ leads to

$$\frac{d}{dt}(y_1, y_2)^T = \begin{pmatrix} 0 & -k_3 \\ Ak_1 & 0 \end{pmatrix}(y_1, y_2)^T + k_2 y_1 y_2 (-1, 1)^T + (\xi_1, \xi_2)^T. \tag{3.4}$$

The time correlation function for the Lotka model near the steady state can be obtained explicitly from eq.(2.40) to give

$$\begin{aligned} C_{y_1 y_1}(t) &= \frac{-id_{11}}{4w_0}[\exp(-\lambda_{1,0} t) - \exp(-\lambda_{0,1} t)], \\ C_{y_1 y_2}(t) &= \frac{d_{11}}{4k_3}[\exp(-\lambda_{1,0} t) + \exp(-\lambda_{0,1} t)], \\ C_{y_2 y_2}(t) &= \frac{-Ak_1}{k_3} C_{y_1 y_1}(t), \end{aligned} \tag{3.5}$$

where

$$\omega_0 = (Ak_1 k_3)^{\frac{1}{2}},\ d_{11} = \frac{Ak_1 D_{11} - k_3 D_{22}}{Ak_1} \tag{3.6}$$

At first, let us consider the linear case. The steady state of the Lotka model is marginally oscillatory. The eigenvalues for the linear case obtained in eq.(2.34) can be evaluated using eq.(3.4) and the corresponding time correlation functions are obtained as follows:

$$\begin{aligned} C_{y_1 y_1}(t) &= \frac{-d_{11}}{2\omega_0}\sin(\omega_0 t), \\ C_{y_1 y_2}(t) &= C_{y_2 y_1}(t) = \frac{d_{11}}{2k_3}\cos(\omega_0 t), \\ C_{y_2 y_2}(t) &= \frac{-Ak_1}{k_3} C_{y_1 y_1}(t), \end{aligned} \tag{3.7}$$

It is natural that the time correlation functions undergo sustained oscillation at the marginally stable steady state. As shown in the mechanism of the Lotka model, the intermediate X_1 is related to X_2 through the feedback step. Even though the feedback step has indirect influence on the correlation functions through the value of the steady state, it controls the ratio of $C_{y_2y_2}(t)$ over $C_{y_1y_1}(t)$ to be $-Ak_1/k_3$ at any time.

Including the nonlinear terms, we obtain the following eigenvalues:

$$\lambda_{1,0} = -\left(\frac{\omega_0 k_2^2 d_{11}}{8k_3^2}\right)^{\frac{1}{2}} + i\left[\omega_0 - \left(\frac{\omega_0 k_2^2 d_{11}}{8k_3^2}\right)^{\frac{1}{2}}\right],$$

$$\lambda_{0,1} = \lambda_2 = -i\omega_0. \qquad (3.8)$$

The effect of the nonlinear terms is to make one of the modes increase or decrease in an oscillatory fashion depending on the value of d_{11}. If $d_{11}>0$, the mode with $\lambda_{1,0}$ increases oscillatorily. It diverges as time goes to infinity. This means that we have to consider the higher order approximation to discuss the nonlinear effect. In the present paper, however, we have restricted ourselves to the first order approximation. Thus, we consider only the case of $d_{11}<0$. When $d_{11}<0$, the mode with $\lambda_{1,0}$ decreases oscillatorily and the time correlation functions after long time become

$$C_{y_1y_1}(t) = \frac{|d_{11}|}{4\omega_0}\exp\left[i\left(\omega_0 t - \frac{\pi}{2}\right)\right],$$

$$C_{y_1y_2}(t) = \frac{|d_{11}|}{4k_3}\exp\left[i\left(\omega_0 t - \pi\right)\right], \qquad (3.9)$$

$$C_{y_2y_2}(t) = \frac{-Ak_1}{k_3}C_{y_1y_1}(t).$$

The same argument for the linear system may be applied to the nonlinear case. We shall extend the present theory to describe the dynamic phenomena of negative(and positive) metabolic control circuits[12-13] in the forthcoming papers.

Acknowledgement. This work was supported by a grant from the Basic Science Research Institute Program, Ministry of Education of Korea, 1986.

References

1. N. G. van Kampen, *Can. J. Phys.* **19**, 551 (1961).
2. M. Suzuki, *J. Stat. Phys.* **16**, 11 (1977).
3. K. O. Han, D. J. Lee, J. M. Lee, K. J. Shin, and S. B. Ko, *Bull. Kor. Chem. Soc.* **7**, 224 (1986).
4. D. J. Lee, Unpublished.
5. J. R. Tucker and B. I. Halperin, *Phys. Rev.* **3**, 3768 (1971).
6. D. J. Lee, M. H. Ryu, and J. M. Lee, *Bull. Kor. Chem. Soc.* **6**, 295 (1985).
7. H. S. Kim and D. J. Lee, *Thesis Collection*(Chonbuk National Univ.) **26**, 494 (1984).
8. H. Risken, *The Fokker-Planck Equation*(Springer-Verlag, 1984).
9. R. Kubo, *J. Phys. Soc. Japan* **12**, 570 (1957).
10. K. J. Shin, in *Research Report for Nonlinear Phenomena and Their Theories*(Submitted to the Daewoo Foundation, 1982).
11. E. Merzbacher, *Quantum Mechanics*(John-Wiley, 1970).
12. N. MacDonald, *J. Theor. Biology* **65**, 727 (1977).
13. D. Allwright, *J. Math. Biology* **4**, 363 (1977).
14. *Selected Papers on Noise and Stochastic Processes*, ed. N. Wax(Dover, 1954).
15. P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations*(Wiley-Interscience, 1971).

The pH Dependence of Metal Tetrakis (4-sulfonato-phenyl) porphine Structure Probed by Raman Spectroscopy

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Received October 28, 1987

The pH dependence studies of Raman spectra are reported for water-soluble free-base, Zn, Co and Cu tetrakis (4-sulfonato-phenyl) porphine in pH 4, pH 7 and pH 13.9 aqueous solution. For free base porphine, the substantial differences are found in absorption and Raman spectra between pH 4 and pH 7 or pH 10 aqueous solutions due to the protonation at low pH. For Zn and Co porphyrins, the hydrolysis equilibrium constants are obtained by spectrophotometric titration experiments. The consistent shifts in Raman frequencies are found at high pH due to the hydrolysis. For Cu porphyrins, instead of hydrolysis the aggregation effect is detected at high pH through the absorption and Ramsn studies.

Introduction

For many years, the porphyrin has been one of the central interests in the photochemistry in view of its important roles in photosynthesis[1,2] and its potential utility as sensitizer in photochemical system for solar-energy conversion.[3] Water