5 June 1998

Chemical Physics Letters 289 (1998) 97–104

CHEMICAL PHYSICS LETTERS

Absorption line shape of impurity molecule driven by a fractal noise

Gautam Gangopadhyay [1], Yoshitaka Tanimura

Theoretical Studies Division, Institute for Molecular Science, Myodaiji, Okazaki-444, Japan

Received 29 January 1998; in final form 10 March 1998

Abstract

We have applied the quantum master equation to simulate a two-level system driven by a fractal noise in a dissipative environment. The fractal noise is assumed to be a two-state process with $\pm\Delta$ and characterized by its correlation function $1/\tau^{\beta}$ where $0<\beta<1$. Steady state absorption spectrum for the system is obtained analytically for a monochromatic laser excitation. A dramatic blue shift as well as a broadening of the absorption peak, due to the interference between the fractal noise and the natural damping, is observed. © 1998 Elsevier Science B.V. All rights reserved.

Recently a single molecule [1–5] as a guest on a solid host matrix environment reveals a very exciting system to test many fundamental models of molecular physics, solid state physics and quantum optics. The matrix in a very low temperature keeps the molecule fixed and therefore its zero phonon line is a simple isolated transition. Thus the molecular system can be represented as an electronic two-level system where the effect of vibrational dynamics can be made negligibly small. A resonant laser field interaction with the molecule can be approximately treated with parametrized Bloch equation. The very first observation of single molecule showed narrow homogeneous Lorentzian line shapes [2], saturation [3] and antibunching [4] due to optical nutation. The pump-probe experiments [5] showed light shift and Autler–Townes [6]-like structures when the pump is in resonant with the molecule.

There are two important points to understand the single molecule spectroscopy properly. The applicability of two-level model to the molecule, without considering the vibrational motion, may impair the use of Bloch equation. For example, a long lived vibrational mode in the electronic ground or excited state does not allow the nonlinear polarization to go up to the saturation intensity. Secondly, the presence of matrix as the environment can modify the Bloch equation picture where the vacuum and the gas phase environment is assumed.

The environment which basically induce a noise in the system can be of very short to very long correlation time depending on the properties of the material. The single molecular detection technique provides information about the nature of the noise with the ensemble average removed. An observable which has recently drawn

[1] On leave from S.N. Bose National Centre for Basic Sciences, JD Block, Sec-III, Salt Lake City, Calcutta-700 091, India; e-mail: gautam@boson.bose.res.in

PII S0009-2614(98)00377-7

attention in spectroscopic studies of single impurity molecule in host system is the modulation of their transition energies [1] with time. The energy fluctuations, which appear as spectral noise, can be described as spectral random walks. Such systems have been studied theoretically [7,8] using randomly distributed independent two-level systems, which follow the Anderson-Kubo processes [9]. Then Tanimura et al. [10] introduced the Ising spin glass model, whose properties have been extensively studied within the field of critical phenomena as the host lattice instead of using independent two-level systems. They calculated the fluctuations in the transition energies of impurity molecules, for different temperatures and various Ising parameters, and find that the spectral distribution of the fluctuations follow approximately a $1/f$ power law.

In this work we study the model of an impurity molecule by a stochastic theory, where the perturbation from the local environment is regarded as adiabatic stochastic process. We consider that the stochastic process $\xi(t)$ is a two state process taking the values $\pm\Delta$ and obeys a power law correlation function. The spectral properties of such random fluctuations are revealed in many circumstances when rather than being dominated by a narrow band of frequencies, spread themselves into a broad band spectrum, so that correlations persist from very short to very long time scales [11]. Such spectra when they are inverse power law, indicate fractal random time series [12] and could be generated either by colored noise or by the chaotic solutions of low dimensional deterministic systems. On the other hand, the statistics of the fluctuations are often found to deviate strongly from the normally expected central limit theorem. However, a generalized central limit theorem holds for this long correlated noise which satisfy a Levy stable distribution [11]. As this long correlated noise does not satisfy fluctuation-dissipation relation [13] one has to consider it as external rather than being an internal by which the back reaction of the noise on the system i.e, a pumping of infinite amount of energy into the system can be avoided.

In the present work we are interested in analyzing the effect of fractal noise which modulates the frequency of a two-state system and the system is also coupled to a thermal bath. We study the steady state probe absorption of the system. For such we investigate the coherence of the system as a function of detuning and intensity of the probe field in presence of fractal noise. We verify that the coherence of the system is sensible in its shape on the correlation time and the coupling strength of the noise. Even when the coherence of the initial density matrix does not exist, coherence appears asymptotically depending on the detuning, the intensity of the external field and on the parameters of fractal noise. Our central result is that in the presence of fractal noise the absorption spectra undergoes a blue shift and the amount of shift can be as large as of the order of homogeneous linewidth due to natural damping.

In what follows we first construct the generalized master equation of the reduced system. The asymptotic density matrix in presence of a driving field is then obtained to analyze the effect of long term memory of the noise process.

Let us consider an impurity molecule interacting with an external laser field and a matrix environment. The impurity molecule is described by a two-level system with the resonant frequency ω_0. The interactions between the impurity molecule and the matrix consist of two parts. One is the dissipation part denoted by the heat bath, and interaction between the molecule and the bath. This part corresponds to dissipation arises from the lattice fluctuation of the matrix molecules. The other one is the stochastic perturbation part which is expressed as the adiabatic perturbation on the two-level system. In the case of the pentacene doped p-terphenyl crystals, this perturbation corresponds to the noise arises from the motion of the phenyl ring in the terphenyl molecule [1]. The total Hamiltonian is then expressed as

$$H_{\mathrm{T}} = H_{\mathrm{s}}(t) + H_{\mathrm{B}} + V_1 + V_2(t), \tag{1}$$

where $H_{\mathrm{s}}(t)$ is the system Hamiltonian which includes the laser field interaction, and H_{B} and V_1 are the bath Hamiltonian and the system-bath interaction, respectively. The stochastic perturbation on the system is denoted by $V_2(t)$. The system Hamiltonian is expressed by the Pauli operators as

$$H_{\mathrm{s}}(t) = \frac{\hbar\omega_0}{2}\sigma_z + \hbar\left[E_0\sigma_+\ \mathrm{e}^{-i\omega t} + E_0\sigma_-\ \mathrm{e}^{i\omega t}\right], \tag{2}$$

where we assumed the laser field interaction with the amplitude E_0 and frequency ω in the rotating wave approximation (RWA) form. The heat bath Hamiltonian and the system–bath interaction are given by

$$H_{\mathrm{B}} = \sum_j \hbar \omega_j b_j^{\dagger} b_j, \tag{3}$$

$$V_1 = \hbar \sum_j g_j \left(\sigma_+ b_j + \sigma_- b_j^{\dagger} \right), \tag{4}$$

respectively, where $b_j(b_j\dagger)$ are annihilation (creation) operator of the phonon with frequency ω_j and g_j is the coupling strength between system and bath modes. The stochastic perturbation is assumed to be

$$V_2(t) = \hbar \xi(t) \sigma_z, \tag{5}$$

where $\xi(t)$ is some stochastic process with zero mean and its properties will be specified later.

Following the standard procedure to derive the equation of motion for the reduced density operator of two-level system [14], we obtain the quantum master equation in the form

$$\begin{aligned} \frac{\mathrm{d}\rho}{\mathrm{d}t} = &-\frac{i\omega_0}{2}[\sigma_z,\rho] - i[E(t)\sigma_+ + E^*(t)\sigma_-,\rho] - \frac{\gamma}{2}(1+\bar{n})(\sigma_+\sigma_-\rho - 2\sigma_-\rho\sigma_+ + \rho\sigma_+\sigma_-) \\ &-\frac{\gamma}{2}\bar{n}(\sigma_-\sigma_+\rho - 2\sigma_+\rho\sigma_- + \rho\sigma_-\sigma_+) - \int_0^t \mathrm{d}t' \{ [\sigma_z\sigma_z\rho(t') + \rho(t')\sigma_z\sigma_z - 2\sigma_z\rho(t')\sigma_z] W(t,t') \}, \end{aligned} \tag{6}$$

where $W(t,t')$ is given by

$$W(t,t') = \langle \xi(t) \xi(t') \rangle. \tag{7}$$

Here γ and $\bar{n}$ are defined as the natural damping rate $\gamma = 2\pi D(\omega_0)|g(\omega_0)|^2$ and the thermal average excitation number $\bar{n} = [\mathrm{e}^{\hbar\omega_0/kT} - 1]^{-1}$, where $D(\omega_0)$ denotes the spectral density function of the harmonic oscillator heat bath modes.

Note that Eq. (7) implies the two point correlation function $\langle \xi(t)\xi(t')\rangle$ depends only on the time difference $|t-t'|$ so the process is stationary. In the normal diffusion process there exists a microscopic time scale, defined by

$$\tau = \int_0^{\infty} \frac{\langle \xi(0)\xi(t')\rangle}{\langle \xi^2 \rangle} \mathrm{d}t'. \tag{8}$$

If the correlation function $\langle \xi(0)\xi(t)\rangle$ decays quickly enough to make τ finite, then one can explore the random walk process for times t very large compared to τ. The time scale separation between the random walk process and the fluctuations of the relevant variable allows the central limit theorem to work, thereby reaching a Gaussian diffusion process for the two-state model. On the other hand, in the case of $\tau \to \infty$ there is no time scale separation between the microscopic(diffusion) and the microscopic process of fluctuations, $\xi(t)$ which implies non-Gaussian statistics.

Here we consider a dichotomous stochastic process $\xi(t)$ taking the values $\pm\Delta$ and introduce the equilibrium correlation function $\Phi_{\xi}(t)$ defined by

$$\Phi_{\xi}(t) \equiv \frac{\langle \xi(0)\xi(t)\rangle}{\langle \xi^2 \rangle}, \tag{9}$$

which is the function used in the definition of the microscopic time rate in Eq. (8). Recently, Geisel et al. [15] established a connection between the stationary correlation function, and another important statistical function, the waiting time distribution $\psi(t)$ used in continuous time random walk model. This latter function determines the probability that $\xi(t)$ has made a transition between states in a time t. In the specific case where ξ is a dichotomous process, as in the case of present interest, this connection between $\Phi_\xi(t)$ and $\Psi(t)$ is exactly given by

$$\Phi_\xi(t) = \frac{\int_t^\infty (t-t')\psi(t')\mathrm{d}t'}{\int_0^\infty t'\psi(t')\mathrm{d}t'}. \tag{10}$$

West et al. [16] has considered a case of waiting time distribution which is an inverse power law to elucidate the behaviour of anomalous diffusion by giving an explicit solution of fractional diffusion equation. In the present study we consider the inverse power law waiting time distribution $\psi(t)$ as

$$\psi(t) = \frac{1}{t^{1+\alpha}}, \tag{11}$$

with

$$1 < \alpha < 2. \tag{12}$$

Using Eq. (11) in Eq. (10) we obtain

$$\Phi_\xi(t) \sim \frac{A}{t^\beta}, \tag{13}$$

for

$$0 < \beta < 1, \tag{14}$$

where

$$\beta = \alpha - 1. \tag{15}$$

Thus using the above correlation function in Eq. (13) we find the modified Bloch equation as follows

$$\langle \dot{\sigma}_+(t)\rangle = i\omega_0\langle\sigma_+(t)\rangle - \frac{iE_0}{2}\langle\sigma_z(t)\rangle \mathrm{e}^{i\omega t} - \frac{\gamma}{2}(1+2\bar{n})\langle\sigma_+(t)\rangle - A\int_0^t \frac{\langle\sigma_+(t')\rangle}{(t-t')^\beta}\mathrm{d}t', \tag{16a}$$

$$\langle \dot{\sigma}_-(t)\rangle = -i\omega_0\langle\sigma_-(t)\rangle + \frac{iE_0}{2}\langle\sigma_z(t)\rangle \mathrm{e}^{i\omega t} - \frac{\gamma}{2}(1+2\bar{n})\langle\sigma_-(t)\rangle - A\int_0^t \frac{\langle\sigma_-(t')\rangle}{(t-t')^\beta}\mathrm{d}t', \tag{16b}$$

$$\langle \dot{\sigma}_z(t)\rangle = -iE_0\left(\langle\sigma_+(t)\rangle \mathrm{e}^{-i\omega t} - \langle\sigma_-(t)\rangle \mathrm{e}^{i\omega t}\right) - \gamma(1+2\bar{n})\langle\sigma_z(t)\rangle - \gamma, \tag{16c}$$

where the parameter A is taken in place of $1/\langle\xi^2\rangle$.

Although these equations look deceptively simple, they are difficult to solve analytically. In the present study we calculate the asymptotic solution of equation of motion to investigate the steady state susceptibility.

By taking the slowly varying envelope approximation i.e, $\langle\sigma_+(t)\rangle = S_+ \mathrm{e}^{i\omega t}$, $\langle\sigma_-(t)\rangle = S_- \mathrm{e}^{-i\omega t}$ and $\langle\sigma_z(t)\rangle = S_z(t)$ and Laplace transformation of Eqs. (16), we obtain,

$$p\bar{S}_+ - S_+(0) = i\delta\bar{S}_+ - \frac{iE_0}{2}\bar{S}_z - \frac{\gamma}{2}(1+2\bar{n})\bar{S}_+ - A\bar{S}_+\bar{F}, \tag{17a}$$

$$p\bar{S}_- - S_-(0) = -i\delta\bar{S}_- + \frac{iE_0}{2}\bar{S}_z - \frac{\gamma}{2}(1+2\bar{n})\bar{S}_- - A\bar{S}_-\bar{F}^*, \tag{17b}$$

$$p\bar{S}_z - S_z(0) = -iE_0\left(\bar{S}_+ - \bar{S}_-\right) - \gamma(1+2\bar{n})\bar{S}_z - \frac{\gamma}{p}, \tag{17c}$$

where $\bar{F}$ is given by

$$\bar{F} = \frac{\Gamma(-\beta+1)}{(p+i\omega)^{-\beta+1}}, \tag{18}$$

with $\delta = (\omega_0 - \omega)$ and $S_{\bar{i}}$ denotes the Laplace transformed variable of $S_i(t)$.

Thus the asymptotic solution can be obtained as

$$S_z(t\to\infty) \equiv \mathrm{Lim}_{p\to 0}\, pS_{\bar z} = \frac{-\gamma}{\gamma(1+2\bar n) + (E_0^2/2)(x+x^*)}. \tag{19}$$

and

$$S_+(t\to\infty) = S_z(t\to\infty)\frac{-iE_0/2}{-i\delta + \gamma(1+2\bar n)/2 + A\bar F}. \tag{20}$$

Here $x+x^*$ is given by

$$x+x^* = \frac{\gamma(1+2\bar n) + 2Au}{(\delta - Av)^2 + [\gamma(1+2\bar n)/2 + Au]^2} \tag{21}$$

with

$$u = \frac{\Gamma(1-\beta)}{\omega^{1-\beta}}\cos\left(\frac{\pi(1-\beta)}{2}\right), \tag{22}$$

$$v = -\frac{\Gamma(1-\beta)}{\omega^{1-\beta}}\sin\left(\frac{\pi(1-\beta)}{2}\right). \tag{23}$$

To obtain the absorption line shape E, we need to calculate the rate at which quanta are absorbed from the external field (EF). This can be expressed as

$$E = \frac{1}{\epsilon_2 - \epsilon_1}\left\{\epsilon_2\left[\dot W_2(t)\right]_{\mathrm{EF}} + \epsilon_1\left[\dot W_1(t)\right]_{\mathrm{EF}}\right\} \equiv \langle \dot\sigma_z(t)\rangle_{\mathrm{EF}} \tag{24}$$

where $[\dot W_2(t)]_{\mathrm{EF}}$ ($[\dot W_1(t)]_{\mathrm{EF}}$) and ϵ_2 (ϵ_1) are the rate of change of occupation probabilities and energies of levels 2(1), respectively induced by the external field. Now in Schrodinger picture

$$[\langle \dot\sigma_z(t)\rangle]_{\mathrm{EF}} = iE_0\langle\sigma_+(t)\rangle \mathrm{e}^{-i\omega t} - iE_0\langle\sigma_-(t)\rangle \mathrm{e}^{i\omega t}. \tag{25}$$

Thus E becomes

$$E = -2|E_0|^2\,\mathrm{Im}\left(\frac{\langle\sigma_+(t)\rangle}{E_0}\mathrm{e}^{-i\omega t}\right). \tag{26}$$

The asymptotic value of the bandshape function E can be obtained as

$$E = \frac{\gamma(E_0^2/2)[\gamma(1+2\bar n)/2 + Au]}{\gamma(1+2\bar n)\left\{(\delta - Av)^2 + [\gamma(1+2\bar n)/2 + Au]^2\right\} + E_0^2[\gamma(1+2\bar n) + 2Au]/2} \tag{27}$$

where

$$Au = \frac{A}{\omega_0^{1-\beta}}\frac{1}{(1-\delta/\omega_0)^{1-\beta}}\cos\left(\frac{\pi(1-\beta)}{2}\right)\Gamma(1-\beta) \tag{28}$$

$$Av = -\frac{A}{\omega_0^{1-\beta}}\frac{1}{(1-\delta/\omega_0)^{1-\beta}}\sin\left(\frac{\pi(1-\beta)}{2}\right)\Gamma(1-\beta). \tag{29}$$

In the lineshape function, Eq. (27), the term E_0^2 in the denominator arises due to saturation effect induced by strong field and it affects the width of the lineshape. In presence of fractal noise this saturation effect increases as field strength increases. For low field strength, however, this effect due to fractal noise is negligibly small.

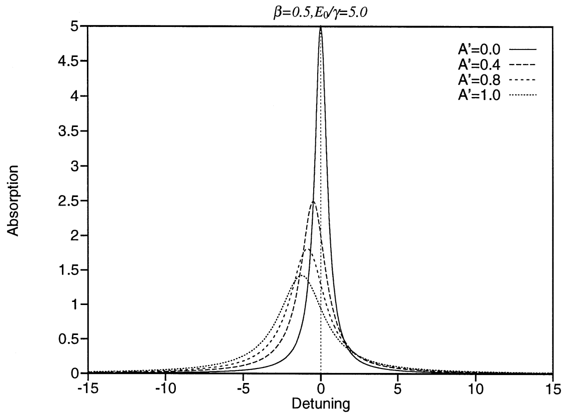

Fig. 1. Line shape function E/γ is plotted with detuning $(\omega_0-\omega)/\gamma$ with $E_0/\gamma=5.0$ and $\beta=0.5$ for different values of $A'=A/\gamma\omega_0^{1-\beta}=0.0$, 0.4, 0.8 and 1.0.

Near the resonance the term δ/ω_0 is very small, thus the contribution of detuning from these terms in Eqs. (28) and (29) is very small. Therefore even when E_0 is small there is a blue shift in absorption which is approximately given by

$$\frac{A}{\omega_0^{1-\beta}}\sin\left(\frac{\pi(1-\beta)}{2}\right)\Gamma(1-\beta).$$

Note that since β is in the range of $0<\beta<1$, the sin term is always positive and less than one.

The amount of shift and broadening due to fractal noise is proportional to the inverse of the magnitude $\omega_0^{1-\beta}$. Since β, A and ω_0 are coupled parameters, it is difficult to estimate the individual effects of them. In the following we define $A/\gamma\omega_0^{1-\beta}\equiv A'$, as a dimensionless quantity. In Fig. 1 we plot the absorption line shape as a function of detuning $\delta=\omega_0-\omega$ for different noise intensity A' with $\beta=0.5$. When A' increases the blue peak shift and the broadening is observed. Fig. 2 is for $\beta=0.9$. Except β, the other parameters are the same as in Fig. 1. The peak shift observed in Fig. 2 are about the same values as Fig. 1, whereas the broadening of the peak changes dramatically especially for large A'. Fig. 3 displays the absorption for different laser intensities. Although the peak height rises with the probe intensity, no other effect is observed in this case. In all cases we assume the thermal bath is at zero temperature, i.e, $\bar{n}=0$.

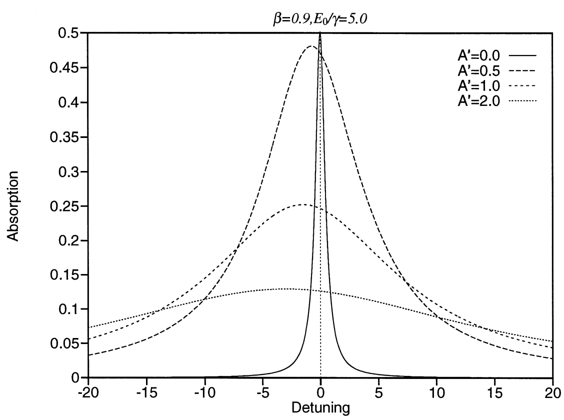

Fig. 2. Same as in Fig. 1 except $\beta=0.9$.

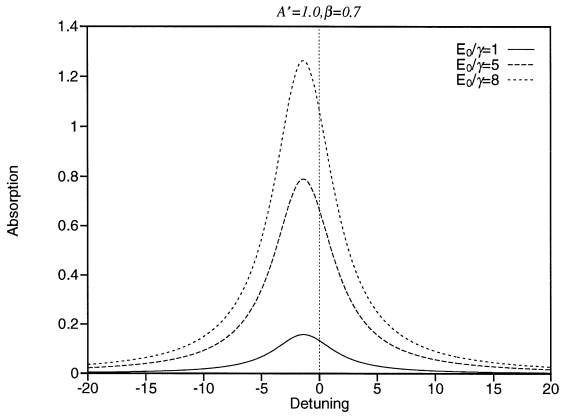

Fig. 3. Line shape function E/γ is plotted with detuning $(\omega_0 - \omega)/\gamma$ with $A' = 1.0$ and $\beta = 0.7$ for different values of $E_0/\gamma = 1.0$, 5.0 and 8.0.

To understand whether such peak shift and broadening are special character of the system driven by fractal noise, we also calculate the same model using the exponential decay noise $W(t-t') = \mathrm{e}^{-\Gamma(t-t')}$. We thus obtain

$$Au = \frac{A\Gamma}{(\omega_0 - \delta)^2 + \Gamma^2} \quad \text{and} \quad Av = \frac{-\omega_0 A}{(\omega_0 - \delta)^2 + \Gamma^2}.$$

Now for a weakly coupled noise and taking slow decay noise i.e, $\Gamma/\omega_0 \ll 1$, the shift would be of the order of $\frac{A}{\omega_0}\gamma$, whereas for the fractal noise case the shift is of the order of $\frac{A}{\omega_0^{1-\beta}}\gamma$. For the fractal noise case, if β is close to unity, the shifts can be very large, at least of the order of γ and can be seen clearly, whereas for the exponential decay noise , as $A/\omega_0 \ll 1$, the shift may not be observed. Note that this shift arises from the interference between the natural damping and the noise, and differs from blue shift observed for a two-level system driven by the Gaussian-Markovian bath at a finite temperature [17].

In this paper, we have applied the quantum master equation to study absorption spectra of a two-level system in a dissipative environment driven by a fractal noise. A dramatic blue shift as well as a broadening of absorption peak are observed due to the interference between the fractal noise and the natural damping. A lot of open questions are left to understand regarding the dynamical effect of this process which is now under investigation.

Acknowledgements

We are thankful to Japan Society for the Promotion of Science for the financial support in this work.

References

[1] W.P. Ambrose, W. Moerner, Nature 349 (1991) 225; T. Basche, W.E. Moerner, M. Orrit, U.P. Wild (Eds.), Single Molecule Optical Detection, Imaging and Spectroscopy, VCH, Weinheim, Germany.
[2] M. Orrit, J. Bernard, Phys. Rev. Lett. 65 (1990) 2716.
[3] T. Basche, W.E. Moerner, M. Orrit, H. Talon, Phys. Rev. Lett. 69 (1992) 1516.
[4] Ph. Tamarat, B. Lounis, J. Bernard, M. Orrit, S. Kummer, R. Kettner, S. Mais, T. Basche, Phys. Rev. Lett. 75 (1995) 1514.
[5] B. Lounis, F. Jelezko, M. Orrit, Phys. Rev. Lett. 78 (1997) 3673.

[6] S.H. Autler, C.H. Townes, Phys. Rev. 100 (1955) 703.
[7] P.D. Reilly, J.L. Skinner, J. Chem. Phys. 101 (1994) 959; 102 (1995) 1540.
[8] G. Zumofen, J. Klafter, Chem. Phys. Lett. 219 (1994) 303.
[9] R. Kubo, Adv. in Chem. Phys. 15 (1969) 101, and references therein.
[10] Y. Tanimura, H. Takano, J. Klafter, J. Chem. Phys. 108 (1998) 1851.
[11] E.W. Montroll, B.J. West, in: Fluctuation Phenomena, 2nd ed., North Holland, Amsterdam, 1987.
[12] B.B. Madelbrot, Fractals: Form, Chance and Dimensions, Freeman, San Fransisco, 1977; M.F. Shlesinger, J. Klafter, Y.M. Wong, J. Stat. Phys. 27 (1982) 499.
[13] G. Trefan, E. Floriani, B.J. West, P. Grigolini, Phys. Rev. E 50 (1994) 2564.
[14] G. Gangopadhyay, D.S. Ray, Phys. Rev. A 46 (1992) 1507.
[15] T. Geisel, J. Heldstab, H. Thomas, Z. Phys. B 55 (1984) 165.
[16] B.J. West, P. Grigolini, R. Metzler, T.F. Nonnenmacher, Phys. Rev. E 55 (1997) 99.
[17] Y. Tanimura, R. Kubo, J. Phys. Soc. Jpn. 58 (1989) 101.