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Photon statistical properties emitted from single molecule derived from generating function method

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Abstract. In this paper, we summarize the photon emission statistical properties of single molecule system, using the recently developed generating function method. Through the introduce of one or double "auxiliary" variables, we can investigate the first moment and second moment of photon emission statistics driven by different external fields, such as the line shapes and Mandel's Q parameters, the photon emission probabilities, the probability distribution of time between successive emission, the waiting time and the waiting time distribution, the cross correlation, the joint probabilities, etc. Among,the first moment of photon statistics and the experimental results of optical amplification are in good agreement.

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Key words: Two-Level System, Generating Function, Photon Counting Statistics.

1 Introduction

Single molecule technology has been used for the research of condensed phase systems in multiple areas [1–5] and has developed rapidly for the several decades. There are a large number of experimental studies [6–10]. Correspondingly, there are several developed theoretical methods [11–15] about single molecule fluorescence photon, including Master equation method, Wiener-Khintchine method, quantum jumping method, generating function and Levy-walk method and so on. Among, the generating function method has studied many single molecule systems and gives some photon emission statistical properties [16–26]. Also, this method can get the high-order moments, the bunching and anti-bunching effect of single molecule emission photon distribution.

We study the photon emission of this dissipative two-level system under different external fields and give the photon emission statistical properties of single molecules

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system, using the recently developed generating function method. First of all, the time-dependent Hamiltonian of single molecule under pump-probe field can be written as:

$$\mathcal{H}(t)=\hbar\omega_g|g\rangle\langle g|+\hbar\omega_e|e\rangle\langle e|-\mu_{ge}\cdot E(t)(|g\rangle\langle e|+|e\rangle\langle g|). \tag{1}$$

The external field can be expressed as [27], and has a variety of forms. The different forms will be displayed in the flowing, corresponding to the related figures. The dynamical evolution of density element satisfies the quantum Liouville-Von Neumann equation $\partial\rho/\partial t=-i[H,\rho]/\hbar$ [1,28]. The density matrix elements have four parts $\rho_{ee}(t)$,$\rho_{gg}(t)$,$\rho_{ge}(t)$ and $\rho_{eg}(t)$. The above equations can be rewritten as $\dot{\rho(t)}=L_0(t)\rho(t)+L_1(t)\rho(t)$. Within the optical Bloch frame, we can resolve the density operator into the manner $\rho(t)=\sigma^{(0)}(t)+\sigma^{(1)}(t)+\sigma^{(2)}(t)+\cdots$. Here $\sigma^{(n)}(t)=(\sigma_{ee}^{(n)}(t),\sigma_{gg}^{(n)}(t),\sigma_{ge}^{(n)}(t),\sigma_{eg}^{(n)}(t))^{\dagger}$. The $\sigma^{(n)}(t)$ is the part of the density matrix and is corresponding to n photons have been emitted. So, we can defined the generating functions as

$$\begin{aligned}
G_{ee}(s,t)&\equiv\sum_{n=0}^{\infty}\sigma_{ee}^{(n)}(t)s^n;\\
G_{gg}(s,t)&\equiv\sum_{n=0}^{\infty}\sigma_{gg}^{(n)}(t)s^n;\\
G_{ge}(s,t)&\equiv\sum_{n=0}^{\infty}\sigma_{ge}^{(n)}(t)s^n;\\
G_{eg}(s,t)&\equiv\sum_{n=0}^{\infty}\sigma_{eg}^{(n)}(t)s^n.
\end{aligned} \tag{2}$$

In the rotating wave approximation (RWA), we derive the evolution differential equations of the generalized Bloch vectors $\mathcal{U}(s,t)$, $\mathcal{V}(s,t)$, $\mathcal{W}(s,t)$, and $\mathcal{Y}(s,t)$ as

$$\begin{aligned}
\mathcal{U}(s,t)&\equiv\frac{1}{2}(\mathcal{G}_{ge}e^{-i\omega_L t}+\mathcal{G}_{eg}e^{i\omega_L t}),\\
\mathcal{V}(s,t)&\equiv\frac{1}{2i}(\mathcal{G}_{ge}e^{-i\omega_L t}-\mathcal{G}_{eg}e^{i\omega_L t}),\\
\mathcal{W}(s,t)&\equiv\frac{1}{2}(\mathcal{G}_{ee}-\mathcal{G}_{gg}),\\
\mathcal{Y}(s,t)&\equiv\frac{1}{2}(\mathcal{G}_{ee}+\mathcal{G}_{gg}).
\end{aligned} \tag{3}$$

Following, we enumerate the photon emission statistical properties of single molecules system, Such as the line shapes and Mandel's Q parameters, the photon emission probabilities, the probability distribution of time between successive emission, the waiting time and the waiting time distribution, the cross correlation, the joint probabilities.

2 Theory and numerical results

2.1 The line shapes and Mandel's Q parameters

The first, second and m order moments are respectively

$$\begin{aligned}
&\langle N\rangle(t)=2\frac{\partial}{\partial s}\mathcal{Y}(s,t)|_{s=1},\\
&\langle N^2\rangle(t)=2\frac{\partial^2}{\partial s^2}\mathcal{Y}(s,t)|_{s=1}+2\frac{\partial}{\partial s}\mathcal{Y}(s,t)|_{s=1},\\
&\langle N^{(m)}\rangle(t)=\langle N(N-1)\cdots(N-m+1)\rangle(t)\\
&\qquad=2\frac{\partial^m}{\partial s^m}\langle\mathcal{Y}(s,t)\rangle|_{s=1}.
\end{aligned}\tag{4}$$

The line shape of single molecules I can be got from the correlation function's fourier transformation of electric dipole moment, as follows

$$I=\lim_{t\to\infty}\frac{\partial\langle N\rangle(t)}{\partial t}.\tag{5}$$

And we also can get the Mandel's Q parameters and can be defined [29]:

$$Q=\frac{\langle N^2\rangle(t)-\langle N\rangle^2(t)}{\langle N\rangle(t)}-1.\tag{6}$$

The single dibenzanthanthrene (DBATT) molecule in hexadecane (HD) was extensively studied in experiment [30, 31]. The external fields are a laser and an electric radio frequency (rf) field. To compare our theoretical results with experimental results, we here consider the same conditions as in experiment. The line shapes of photon statistics and the experimental results of optical amplification are in good agreement [18, 19]. There is the obvious rf Rabi resonance when $\omega_{rf}=60$MHz, while the multi-rf-photon resonances are found at lower rf frequencies. Further, the control of photon emission from single quantum system driven simultaneously by a resonant or detuning driving field and a tunable probe field is investigated, shown in Fig. 2. In the two figures, we all observe sub-Poissonian behaviors associated with photon antibunching.

2.2 The photon emission probabilities

The probability that n photons have been spontaneously emitted by time t can be calculated via [16, 32]

$$p_n(t)=\frac{2}{n!}\frac{\partial^n}{\partial s^n}\mathcal{Y}(s,t)|_{s=0}.\tag{7}$$

For the super-Gaussian rf pulse, we can optimize the laser field and rf field to emit single photon from the single molecule source. For clearly, the corresponding average

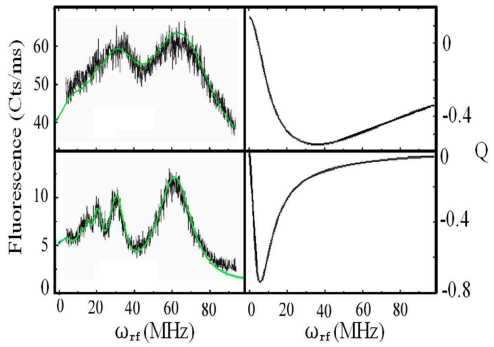

Figure 1: (Color online) Fluorescence and the Mandel's Q parameter of a single molecule as a function of the Pumpprobe applied rf frequency ω_{rf} for two laser Rabi frequencies: $\Omega=0.5\Gamma$, 2Γ. The laser detuning is fixed at $\delta=3\Gamma$, $\Omega_{rf}=4.5\Gamma$ ($\Gamma/2\pi=20$MHz). All the parameters we used are the same with the experiment by Orrit *et al.* [30], no fit parameter was introduced.

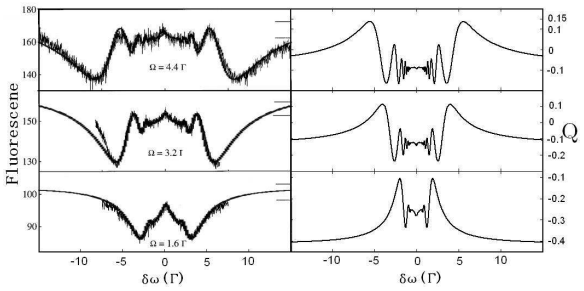

Figure 2: Average emission photon numbers and the Mandel's Q parameter for different pump-probe fields as the function of frequency difference. $\Omega=4.4\Gamma$, 3.2Γ, 1.6Γ.

photon number, single and two photons emission probabilities are shown in Fig. 3. In this case, the single molecule can be thought as the single photon source. The single photon emission probability p_1 can reach to 0.73 and two photons emission probability is also exhibited.

2.3 Probability distribution of time between successive emission

From the generating function, the probability distribution of time between successive emission events $w(t)$ be calculated via

$$w(t)\equiv-\frac{d}{dt}p_0(t)=-2\frac{d}{dt}\mathcal{Y}(s,t)|_{s=0}. \tag{8}$$

For the case of laser zero detuning, the probability distribution for different rf modulation indexes are shown in Fig. 4. For the weak laser field, there is no obvious Rabi oscillation. The oscillation appears obviously as the enhancement of rf field strength.

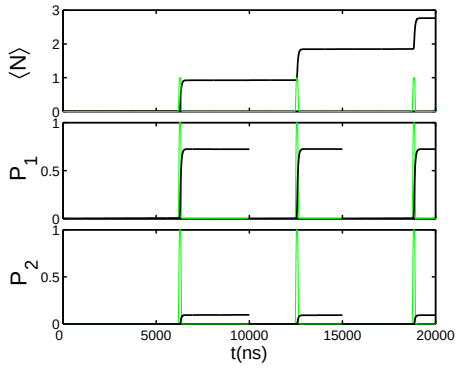

Figure 3: (Color online) The average emission photon number $\langle N \rangle$ and probabilities of single and double photons emitted when the rf pulses are imposed on the single molecule under continuous laser field. The parameters are $\Gamma/2\pi = 20$MHz, $\Omega = 53$MHz, $\delta = 4000$MHz, $\omega_{rf} = 1$MHz, $\tau_p = 68$ns, $\varepsilon_0 = \delta$.

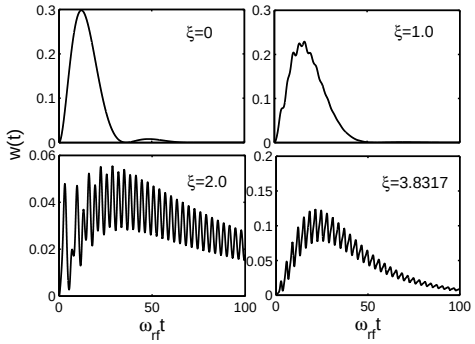

Figure 4: Probability distribution $w(t)$ of the time between successive emission events as a function of time for different rf field modulation indexes. $\delta = 0$, $\Omega = \Gamma$, $\omega_{rf} = 5\Gamma$ and the different ξ are shown in the figure.

The Rabi oscillations disappear and the waiting time between two successive photon emission events becomes longer as rf field is gradually increased. This presents the modulation effects of rf field on the excited state of single molecule system. There is an rf-induced antibunching and the emission time intervals are the longest when the rf field modulation indexes are the roots of the zeroth order Bessel function $J_0(\xi) = 0$.

2.4 Waiting time and the waiting time distribution

The dynamics of fluorescence intermittency is corresponding to the transformation between the ON state and the OFF state in blinking statistics. Some found that the distribution for the sojourn time on ON state or OFF state followed the power law form [33]. The time-dependent dynamics equation about the single biological system can be shown

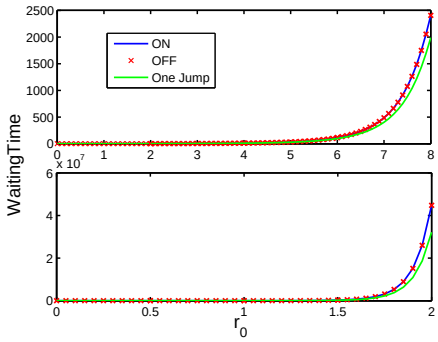

Figure 5: (Color online) The waiting time of the OFF state jumping and ON state jumping as the function of r_0, while the blinking rates are fast or slow. The parameters used are from Ref. [34]: $K_{eq}=2.0$, $\lambda=1.0$, $\kappa=5.0$ and $\theta=5.0$ (for fast case); $K_{eq}=2.0$, $\lambda=1.0$, $\kappa=0.2$ and $\theta=0.2$ (for slow case).

$$ON \underset{k_{ON}(t)}{\overset{k_{OFF}(t)}{\rightleftharpoons}} OFF\,. \tag{9}$$

Once the generating function is gotten, we can extract some statistical quantities of blinking jumping behaviors. The waiting time respectively for OFF state jumping and ON state jumping

$$\begin{aligned}\langle\tau\rangle_{OFF} &= \int_0^\infty \langle\mathcal{P}(s_1,s_2,t)\rangle|_{s_1=0,s_2=1}dt,\\ \langle\tau\rangle_{ON} &= \int_0^\infty \langle\mathcal{P}(s_1,s_2,t)\rangle|_{s_1=1,s_2=0}dt,\end{aligned} \tag{10}$$

Fig. 5 shows the waiting time as a function of ligand radius r_0, respectively for the fast (left column) and slow (right column) blinking rates. The waiting time for ON state jumping and OFF state jumping are identical, and greater than jumping without direction. The distribution as the r_0 and the relation between the OFF state and the ON state are consistent with the reaction-diffusion process. For the relatively small radius r_0, the binding of ligand to the protein can easily happen and don't wait for long time, corresponding to the smaller waiting time for ON state jumping and OFF state jumping. With the increase of ligand radius, the waiting time for the passage through the bottleneck drastically gets long. This variation tendency of waiting time as the ligand radius r_0 is according to our common understanding.

2.5 The cross correlation

The cross correlation of the blinking jumping times for the OFF state and the ON state

$$\langle N_{s_1} N_{s_2}\rangle = \frac{\partial^2}{\partial s_1 \partial s_2}\langle\mathcal{P}(s_1,s_2,t)\rangle|_{s_1=s_2=1}. \tag{11}$$

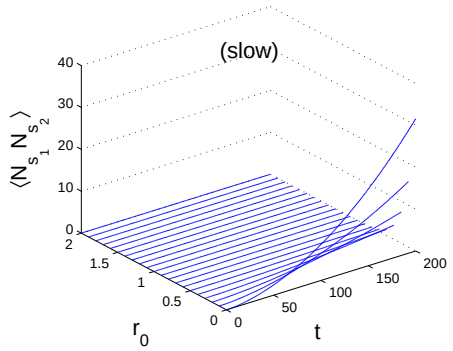

Figure 6: The cross correlation as functions of r_0, while the rate blinking is slow. The parameters are the same as to the Fig. 5.

The cross correlation $\langle N_{s_1} N_{s_2} \rangle$ of the blinking jumping times for different directions is calculated by using Eq. (11). The cross correlation for the slow rate blinking is shown in the Fig. 6. We take the calculation time $t = 200$ for slow case. Relatively small r_0 can induces the strong correlation between the ON state jumping and the OFF state jumping. As the increasing of r_0, the cross correlation gradually tends to be less correlation. This is because the effect of bottleneck is very strong for small radius r_0. But there is hardly jumping event for the relatively big r_0.

2.6 The joint probabilities

The joint probability of the times for OFF and ON states jumping is shown by

$$P_{n_1 n_2} = \frac{1}{n_1! n_2!} \frac{\partial^{(n_1+n_2)}}{\partial s_1^{n_1} \partial s_2^{n_2}} \langle \mathcal{P}(s_1, s_2, t) \rangle |_{s_1=s_2=0}, \tag{12}$$

The joint probability of the jumping times for the OFF state and ON state. In the Fig. 7, the different joint probabilities P_{10} and P_{11} are shown as the function of r_0 and time t, for the fast rate blinking. As the increasing of r_0, the probability maximum of P_{10} and P_{11} appears more and more late in time. For the fast rate blinking, the maximums of probabilities P_{10} and P_{11} have a fluctuation. Firstly reach a peak, and then rapidly drop to zero at big value of r_0. The middle radius also can induce the big P_{11} or P_{10}, similar to the very small radius r_0. The larger radius makes against the passage through the bottleneck and there is hardly jumping event.

3 Conclusion

In conclusion, we discuss the statistical properties of single molecule two-level system under different external fields. Using the generating function method, we introduce the

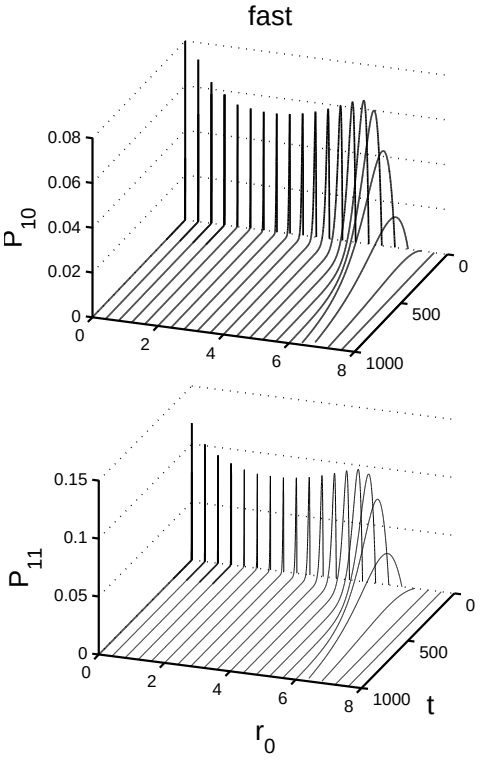

Figure 7: (Color online) The joint probability for the jumping times as the function of r_0 and time t, while the blinking rates are fast. The parameters are the same as to the Fig. 5.

one "auxiliary" variable s or two "auxiliary" variables s_1 s_2. Then the line shape and Mandel' Q parameter of single molecule can be got by the derivation of generalized Bloch vectors. The line shape we given and the experimentally measured result are in good agreement. And that the Mandel' Q parameters show the bunching and anti-bunching effect in different field conditions. By the modulation of the pump and probe field parameters, we can control the photon emission of single molecule. Using the modified model, we considered the properties behaviors for the blinking jumping events comprehensively, from the waiting time distribution to the cumulants of jumping times. Also we gave the joint probability and cross correlation of blinking events, indicating the correlation degree between the times for ON state jumping and OFF state jumping. In addition, this theoretical method can solve the photon statistics of quantum dot in the following study. And this paper provides a good theoretical basis.

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