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Photon distribution function in blinking fluorescence of individual molecules

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ABSTRACT

A photon distribution function $w_N(T)$ for blinking fluorescence with bright on- and dark off-intervals is derived. The function $w_N(T)$ is expressed via few Poissonian functions each of which relates to corresponding exponential process in quantum dynamics of a given individual molecule. The distribution of photons is calculated for short, middle and long time intervals as compared to off-intervals. The distributions are much broader than Poissonian distribution and have rather complicated shape. If time resolution of an experiment does not permit us to see off-interval and, therefore, fluorescence looks like CW emission, the distribution of photons gives a signal about existence of hidden off- intervals in such CW fluorescence.

1. Introduction

Fluorescence of single molecules enables one to obtain important information concerning quantum dynamics of individual molecules embedded in a solid matrix. The information can be extracted from a random sequence of fluorescence photons emitted by a molecule driven by CW laser field. Fluorescence of such a molecule looks like CW radiation because data acquisition time (bin time), as a rule, is much longer as compared with the time interval between two photons of fluorescence. Nevertheless, the number N of photons counted during bin time T will fluctuate in such CW fluorescence. Distribution of photon numbers N measured in time interval T is described by a function, $w_N(T)$. Although the photon distribution looks like a Poissonian function $P_N(\langle N\rangle) = \langle N\rangle^N \exp(-\langle N\rangle)/N!$, where $\langle N\rangle$ is an average number of photons, the distribution is narrower as compared to the Poissonian function $P_N(\langle N\rangle)$, i.e. the photon distribution is of sub-Poissonian type. Exact expression for such sub-Poissonian distribution of photons in CW fluorescence was derived in Refs. [1,2].

However, fluorescence of many individual complex organic molecules has blinking character, i.e. the fluorescence interrupted by pauses without light. Organic molecules have, as a rule, a triplet level situated between the ground electronic level and the first excited singlet electronic level. The molecule driven by CW laser field emits photons jumping from the excited to the ground singlet level. If the molecule gets to triplet state, the fluorescence is interrupted although the molecule is irradiated by light. After transition to the ground electronic state, fluorescence emerges again. Such fluorescence consisting of alternating bright on-intervals and dark off-intervals has blinking character. Obviously, quantum dynamics of such three-level molecule will be more complex than quantum dynamics of two-level molecule with CW fluorescence. Therefore, the photon distribution function $w_N(T)$ in blinking fluorescence will be more complex. An expression for $w_N(T)$ is derived and discussed in the present paper.

2. General formulas for photon distribution function

From theoretical point of view, there are three methods of photon counting in single molecule fluorescence. All three methods have been recently considered in Ref. [3]. For brevity, they have been named methods M, Z and O in accordance with the fact that the method M was considered in Refs. [4,5] and the methods O and Z were considered in Refs. [1,2,6], respectively. Results of Ref. [3] show that theoretical expressions for various methods of photon counting are different. Nevertheless, this problem did not discuss at all in the works [7–17] in which photon statistics was studied. One can suppose that authors of the works believed that their expressions relate to the method M proposed by Mandel [4]. However, the theoretical method based, for instance, on "generating function" [11–14] does not relate to the method M. In the method M, the starting and stopping dates of interval T, in which we count photons, are not specified. On the contrary, in the methods Z and O they are specified. The method M is more convenient for implementation in an experiment and therefore, one is in common use in experiment. Therefore, we shall consider theoretical expressions solely for the method M.

In accordance with Refs. [5,6] photon distribution function, $w_N(T)$ is an N-fold integral. The integral is expressed via a single function, $s(t)$. This function describes correlation of two consecutive

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photon emission events and therefore was named start–stop correlator [18,19]. Cohen-Tannodji and Dalibard [20] called this function "delay function $w_2(t)$".

In accordance with the expression

$$dS(t) = s(t)dt \tag{1}$$

for the probability of finding the second photon at time interval (t, $t + dt$), if the first photon was emitted at $t = 0$, start–stop correlator $s(t)$ describes the density probability of photon emission at time moment t.

A photon distribution function $w_N(T)$ can be expressed solely via start–stop correlator. Laplace transform of the photon distribution function looks as follows [3,5,17]:

$$w_N(\lambda) = \frac{1}{\lambda^2\tau_0}[1 - s(\lambda)]^2 s(\lambda)^{N-1} \quad (N \geqslant 1) \tag{2}$$

Here

$$\tau_0 = \int_0^\infty dt[1 - \int_0^t s(x)dx] = \int_0^\infty dt[1 - S(t)] \tag{2a}$$

is an average time interval between two consecutive photon emission events. In accordance with Eq. (1) the function $S(t) = \int_0^t s(x)dx$ determines the probability of finding the second photon by time moment t, if the first photon was emitted at $t = 0$. The probability of finding an interval T with no photons in the method M is given by [3]:

$$w_0(T) = \frac{1}{\tau_0}\int_0^\infty dt[1 - S(T + t)]. \tag{3}$$

The derivation of Eqs. (2) (3) was carried out with no addressing to any microscopic model for the quantum system. Therefore, they can be used both for two-level molecule with CW fluorescence and for three-level molecule with blinking fluorescence. Results for CW fluorescence of two-level nanoparticle have already been reported in short communication [3]. However, distribution of photons in blinking fluorescence is more complex as compared to CW fluorescence, because photons of various on-intervals can contribute to the distribution function. Blinking fluorescence is considered in the present paper.

Making use the inverse Laplace transformation in Eq. (2), we arrive at the following final expressions for the photon distribution function:

$$w_N(T) = \frac{1}{\tau_0}\int_0^T (T - t)\{[s(\lambda)^{N-1}]_t - 2[s(\lambda)^N]_t + [s(\lambda)^{N+1}]_t\}dt, \quad (N \geqslant 2) \tag{4}$$

Eq. (4) can be used for fluorescence of single molecules with various quantum dynamics. All details of the physical system are described by the start–stop correlator.

3. Quantum dynamics of three-level molecule

First of all, we need to find a theoretical expression for the start–stop correlator for three-level molecule. It was shown in Refs. [2,18,19] that the start–stop correlator is determined by the following formula: $s(t) = W_1(t)/T_1$ in which the population $W_1(t)$ of the excited state is a solution of the following rate equations [2]

$$\begin{aligned}\dot{W}_1 &= -(k + G + 1/T_1 + A)W_1 + kW_0,\\ \dot{W}_0 &= (k + G)W_1 - kW_0 + aW_2,\\ \dot{W}_2 &= AW_1 - aW_2,\end{aligned} \tag{5}$$

This set of equation relates to the scheme of transitions shown in Fig. 1.

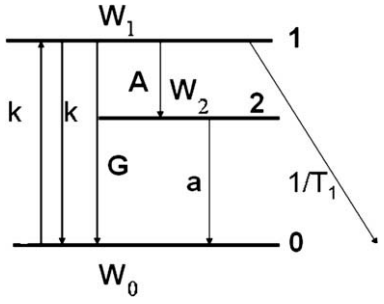

Fig. 1. Energy diagram for a three-level nanoparticle with "dark" state 2.

The molecule making jump from the level 1 to the level 0 emits a photon of fluorescence. G is the rate of non-radiative transitions from the excited level 1 to the ground state 0. A and a are rate constants for transitions to and from dark state 2. Dark state 2 can emerge by various reasons. For instance, a lowest triplet state serves as dark state in many organic molecules. If a molecule gets to triplet level 2 its fluorescence is interrupted and off-interval in fluorescence emerges. Average duration of on- and off-intervals is given by [19]

$$\frac{1}{\tau_{on}} = \frac{kA}{A + G + 2k + 1/T_1}, \quad \frac{1}{\tau_{off}} = a \tag{6}$$

Carrying out Laplace transformation

$$\int_0^\infty dtW(t)e^{i(\omega+i0)t} = W(i\omega) = W(\lambda)$$

in the set of Eq. (5), and by solving algebraic equations for Laplace transforms with the initial condition $W_0(0) = 1$, we arrive, as it is shown in Appendix, at the following expression for the Laplace transform of the start–stop correlator:

$$\begin{aligned}s(\lambda) = W_1(\lambda)/T_1 &= \frac{k(a - \lambda)/T_1}{(\lambda_0 - \lambda)(\lambda_1 - \lambda)(\lambda_2 - \lambda)}\\ &= \lambda_1\lambda_2\frac{\lambda_0}{a}\frac{(a - \lambda)}{(\lambda_0 - \lambda)(\lambda_1 - \lambda)(\lambda_2 - \lambda)}\end{aligned} \tag{7}$$

Here λ_i are roots of the equation $Det_W = 0$ determined in Appendix. We took into account an expression $-ka/T_1 = -\lambda_0\lambda_1\lambda_2$ that follows from the properties of roots of the algebraic equation, $Det_W = 0$.

By carrying out the inverse Laplace transformation of Eq. (7), we find the following equation for the start–stop correlator:

$$\begin{aligned}s(t) &= \lambda_1\lambda_2 \times\frac{\lambda_0}{a}\left[\frac{(a - \lambda_0)e^{-\lambda_0 t}}{(\lambda_2 - \lambda_0)(\lambda_1 - \lambda_0)} - \frac{(a - \lambda_1)e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)(\lambda_1 - \lambda_0)} + \frac{(a - \lambda_2)e^{-\lambda_2 t}}{(\lambda_2 - \lambda_1)(\lambda_2 - \lambda_0)}\right]\\ &= \sum_{j=0}^{2} s_j \exp(-\lambda_j t)\end{aligned} \tag{8}$$

In accordance with Eq. (6) the following set of constants

$$\begin{aligned}&k = 10^5\ \mathrm{s}^{-1} \quad 1/T_1 = 10^8\ \mathrm{s}^{-1} \quad G = 10^7\ \mathrm{s}^{-1}\\ &A = 3.7 \times 10^5\ \mathrm{s}^{-1} \quad \text{and} \quad a = 200\ \mathrm{s}^{-1}\end{aligned} \tag{9}$$

yields values $\tau_{on} = 3 \times 10^{-3}$ s and $\tau_{off} = 5 \times 10^{-3}$ s measured for single DiI molecule in Ref. [21]. Start–stop correlator shown in Fig. 2 has been calculated by means of Eq. (8) with the set of parameters (9).

An exponential behavior in logarithmic time scale looks like smooth step covering one order of magnitude of time. We see three smooth steps relating to three exponential functions in the start–stop correlator. The exponential function with $\lambda_2 \cong 1/T_1 = 10^8 c^{-1}$

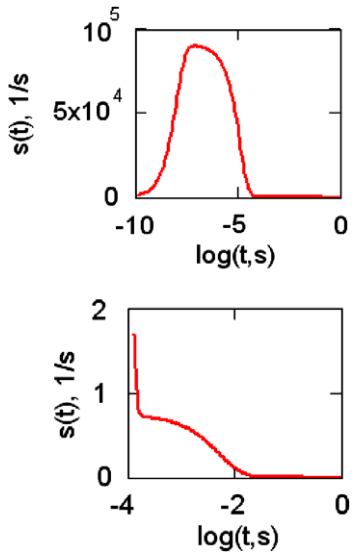

Fig. 2. Start–stop correlator calculated by means of Eq. (8) with the set of parameters (9).

determines growth of $s(t)$ in time scale of order of 10^{-8} s. The exponential functions with $\lambda_1 \cong k = 10^5\ \mathrm{s}^{-1}$ and $\lambda_0 \cong a = 200\ \mathrm{s}^{-1}$ determine two time scales in which the start–stop correlator $s(t)$ goes down to zero. These three relaxation times manifest themselves in the photon distribution functions. It is shown in the next section.

4. Photon distribution in blinking fluorescence

If we carry out the inverse Laplace transformation of Eq. (2) we arrive at N-fold integrals. Results of Refs. [5,6] was presented in the form of such N-fold integrals. Numerical calculation of such integrals has not been realized in practice. However, N-fold integral can be expressed via one or two integrals of few Poissonian functions. It was shown first in Ref. [1] for two-level molecule. This fact facilitate numerical calculation of the distribution functions as it was shown in Refs. [1,2] for various models. In this section, we express photon distribution functions $w_N(T)$ for blinking fluorescence via Poissonian functions.

By using Eq. (7), we can write

$$s(\lambda)^N = \lambda_1\lambda_2\left(\frac{\lambda_0}{a}\right)^N\left(\frac{a-\lambda}{\lambda_0-\lambda}\right)^N\frac{\lambda_1^{N-1}}{(\lambda_1-\lambda)^N}\frac{\lambda_2^{N-1}}{(\lambda_2-\lambda)^N} \tag{10}$$

Two last ratios are Laplace transforms $P_{N-1}^{\lambda_i}(\lambda) = \lambda_i^{N-1}/(\lambda_i-\lambda)^N$ of Poissonian function $P_N(\lambda_i t) = (\lambda_i t)^N\exp(-\lambda_i t)/N!$. The second ratio can be presented in the following form

$$\left(\frac{a-\lambda}{\lambda_0-\lambda}\right)^N = \left(1+\frac{a-\lambda_0}{\lambda_0}\frac{\lambda_0}{\lambda_0-\lambda}\right)^N = \sum_{m=0}^{N}\frac{N!}{m!(N-m)!}\left(\frac{a-\lambda_0}{\lambda_0}\right)^m\left(\frac{\lambda_0}{\lambda_0-\lambda}\right)^m \tag{11}$$

This sum over m is an expansion in power series of small parameter $(a-\lambda_0)/\lambda_0$ because value of λ_0 is close to the value of parameter a. The parameter $(a-\lambda_0)/\lambda_0$ is always positive and less than unit. By using the set of parameters (9) we find the following values for roots: $\lambda_0 = 199.221\,\mathrm{s}^{-1} \cong a$, $\lambda_1 = 9.085\times10^4\ \mathrm{s}^{-1} \cong k$, $\lambda_2 = 1.105\times10^8\ \mathrm{s}^{-1} \cong 1/T_1$ with the help of Eqs. (3A)–(5A) of Appendix. Hence, we find, $(a-\lambda_0)/\lambda_0 = 3.91\times10^{-3}$, i.e. the parameter is very small indeed. Inserting Eq. (10) to Eq. (11), we arrive at the following expression:

$$\begin{aligned} s(\lambda)^N &= \lambda_1\lambda_2\left(\frac{\lambda_0}{a}\right)^N\frac{\lambda_1^{N-1}}{(\lambda_1-\lambda)^N}\frac{\lambda_2^{N-1}}{(\lambda_2-\lambda)^N} \\ &\times\lambda_0\sum_{m=0}^{N}C_N^m\left(\frac{a-\lambda_0}{\lambda_0}\right)^m\frac{\lambda_0^{m-1}}{(\lambda_0-\lambda)^m} = \lambda_1\lambda_2\left(\frac{\lambda_0}{a}\right)^N \\ &\times\left[P_{N-1}^{\lambda_1}(\lambda)P_{N-1}^{\lambda_2}(\lambda)+\lambda_0\sum_{m=1}^{N}C_N^m\left(\frac{a-\lambda_0}{\lambda_0}\right)^m\right. \\ &\left.\times P_{m-1}^{\lambda_0}(\lambda)P_{N-1}^{\lambda_1}(\lambda)P_{N-1}^{\lambda_2}(\lambda)\right] \end{aligned} \tag{12}$$

This expression includes solely Laplace transformation of Poissonian functions. Carrying out the inverse Laplace transform in Eq. (12) we arrive at the following expression:

$$\begin{aligned} [s(\lambda)^N]_t &= \lambda_1\lambda_2\left(\frac{\lambda_0}{a}\right)^N\left\{\int_0^t dx P_{N-1}[\lambda_1(t-x)]P_{N-1}[\lambda_2 x]+\lambda_0\right. \\ &\times\sum_{m=1}^{N}C_N^m\left(\frac{a-\lambda_0}{\lambda_0}\right)^m\int_0^t dx P_{m-1}[\lambda_0(t-x)] \\ &\left.\times\int_0^x dy P_{N-1}[\lambda_1(x-y)]P_{N-1}[\lambda_2 y]\right\} \end{aligned} \tag{13}$$

This very expression enables one to avoid N-fold integration in the photon distribution function described by Eq. (4). This fact facilitates considerably calculation of the photon distribution function. Eq. (13) reveals also an important relation existing between quantum dynamics of the nanoparticle and its photon distribution function. *Each exponential process with rate λ_i in the start–stop correlator $s(t)$ manifests itself via Poissonian function $P_N(\lambda_i x)$ in the expression for the photon distribution function.*

Let us find now the probability $w_0(T)$ to detect time interval with no photons. This probability is described by Eq. (3). Consider dependence of this probability on T. It is obvious that

$$\int_0^\infty s(t)dt = \sum_{j=0}^{2}\frac{s_j}{\lambda_j} = 1 \tag{14}$$

This formula has simple physical meaning. In accordance with Eq. (1) last equation shows that probability of emitting the second photon by time moment $t=\infty$ equal unit. By inserting Eq. (8) to Eq. (3) and allowing for Eq. (14), we arrive at the following expressions for the probability of finding interval with no photons:

$$w_0(T) = \left[\sum_{j=0}^{2}\frac{s_j}{(\lambda_j)^2}\right]^{-1}\sum_{j=0}^{2}\frac{s_j}{(\lambda_j)^2}\exp(-\lambda_j T), \tag{15}$$

The probability was calculated with the set of parameters (9). Result is shown in Fig. 3. If time interval T increases the probability decreases with two relaxation times $T \cong 10^{-5}$ s and $T \cong 5\times10^{-3}$ s relating to two relaxation constants: $1/\lambda_1 \cong 1/k$, and $1/\lambda_0 \cong 1/a$.

Eqs. (4) and (13) enable one to calculate photon distribution function for time intervals T of various duration. It was carried out for the set of parameters (9). The result is shown in Fig. 4.

Fig. 4a shows distribution of photons for short time interval $T = 1$ ms. This interval is less than τ_{on} and τ_{off}. Authors of Ref.

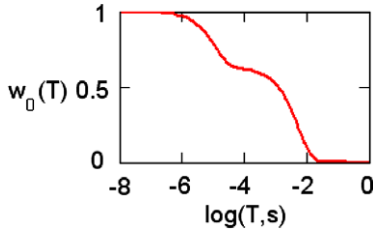

Fig. 3. Decrease of the probability $w_0(T)$ with growth of time interval T.

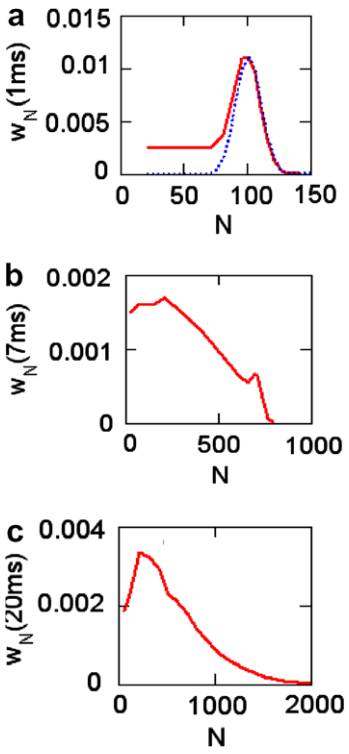

Fig. 4. Distribution of photons in blinking fluorescence calculated for various time intervals. Dashed line shows a Poissonian distribution. Average values of on- and off-interval are $\tau_{on} = 3$ ms and $\tau_{off} = 5$ ms.

[8,15] postulated a Poissonian distribution of photons emitted from electronic excited state of a two-level molecule. However, we see that distribution function $w_N(1\text{ ms})$ in blinking fluorescence has both a Poissonian peak and a tail extended to small values of N. The appearance of this tail can be understood if we take into account that some time intervals will coincide with the end of on-intervals. The intervals of such type will include small number of photons. Hence, the probability of finding time intervals with small numbers of photons will not be negligible.

Fig. 4b shows distribution of photons for time interval $T = 7$ ms. Duration of this interval is comparable with τ_{on} and τ_{off}. Therefore, photons from various on- intervals will be detected in this case. The Poissonian peak becomes very small and the tail is considerably increased. Shape of the distribution is strongly of non-Poissonian type. Fig. 4c shows distribution of photons for long time interval $T = 20$ ms. The Poissonian peak disappears.

Maximum of the broad distribution corresponds to $N \cong 100$. This value of maximum in the distribution function can be obtained from the following estimation. $k\tau_{on} = 10^5\ \text{s}^{-1} \times 3\ \text{ms} = 300$ is an average number of photons in on-interval. However, these photons will be detected only on $\tau_{on}/(\tau_{off} + \tau_{on}) = 3/8$ part of whole time scale. Therefore, we shall detect $300 \times 3/8 \approx 100$ events on the time interval T.

The function $w_N(T)$ takes into account photons emitted in various on-intervals. This fact manifests itself in Eq. (13) via factor $(\lambda_0/a)^N$ and a sum over m. For two-level nanoparticle with CW fluorescence, the sum over m is absent because a relation $\lambda_0 = a$ holds true. Then the only first term exists in figure brackets of Eq. (13).

If time interval T is increased the tail in the photon distribution function is increased as well. Calculations reveal that the tail ranging to small N in Fig. 4a emerges due to the factor, $(\lambda_0/a)^N$. Influence of the sum over m is still negligible. However, if duration of time interval T becomes comparable with average value of off-intervals, the contribution from the sum over m existing in Eq. (13) increases, and this sum begins to play important role. Fig. 4b and c demonstrate influence of this sum. Due to the sum over m the tail dominates.

Narrow Poissonian peak describes contribution from photons that are emitted in one on-interval. Contribution of this peak to the photon distribution functions is diminished for long time intervals. The peak almost disappears at $T = 7$ ms as Fig. 4b shows. The photon distribution function is of super-Poissonian type, i.e. one is broader as compared to the Poissonian distribution.

There is a bin time T in real experiments. Therefore, fluctuations of the intensity in blinking fluorescence can be described by the following expression

$$I(t,T) = \frac{1}{T}\int_t^{t+T} J(\tau)d\tau \tag{16}$$

A function $J(\tau)$ describes fluctuations of on- and off-intervals. This function calculated for $\tau_{on} = 3$ ms and $\tau_{off} = 5$ ms is shown in Fig. 5a. Increase of bin time will influence on view of fluorescence. Fig. 5b–d demonstrates how value of bin time influences on view of fluorescence.

Intensity of fluorescence predetermines how short bin time can be chosen in an experiment. In fact, bin time determines time

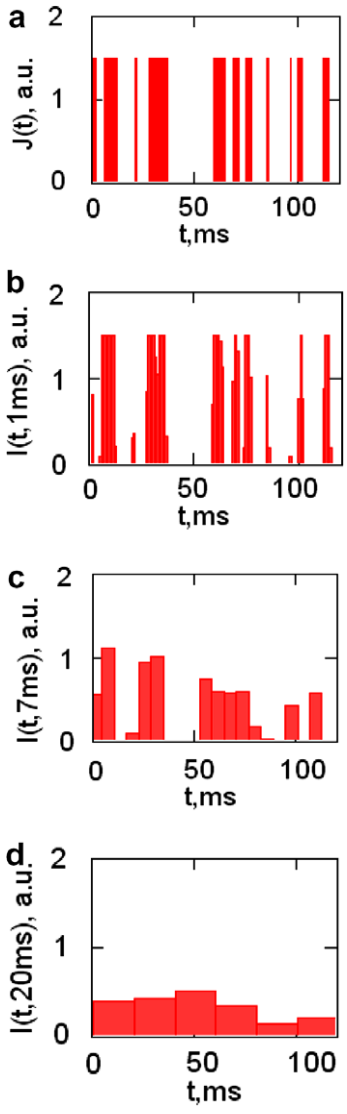

Fig. 5. Fluctuations of the fluorescence intensity at various values of bin time.

resolution of the experiment. If average duration of off-intervals is much shorter as compared with bin time, the fluorescence of a nanoparticle will look like CW emission. Indeed, we do not see off-intervals in Fig. 5d. However, existence of hidden off-intervals can be revealed even in such situation because photon distribution measured in such CW fluorescence will be much broader than Poissonian distribution, and the distribution will look as Fig. 4c shows. This distribution is of super-Poissonian type. In true CW fluorescence, without hidden off-intervals, the distribution of photons will be of sub-Poissonian type, i.e. it will be narrower than Poissonian distribution. Such distribution has been calculated in Ref. [1].

5. Conclusions

It was found simple mathematical expressions Eqs. (4) and (13) for the photon distribution function $w_N(T)$ enabling us to avoid N-fold integration. These equations are convenient for use in practice. Fig. 4 proves this statement. Eq. (13) establishes very important fact that each exponential process in quantum dynamics of a single nanoparticle manifests itself via corresponding Poissonian function in the expression for $w_N(T)$.

The distribution function $w_N(T)$ for blinking fluorescence has complicated shape because of photon contribution from various on-intervals.

If bin time exceeds duration of off-intervals, the fluorescence will look like CW emission. However, we are able to reveal off-intervals masked by long bin time, if we measure photon distribution function, $w_N(T)$. The distribution will differ considerably from that in true CW fluorescence.

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Appendix A

Carrying out Laplace transformation in Eq. (5) and using initial condition $W_j(0) = \delta_{j0}$ we arrive at the following set of equations:

$$\begin{aligned}&(\lambda - k - G - 1/T_1 - A)W_1 + kW_0 = 0,\\ &(k+G)W_1 + (\lambda - k)W_0 + aW_2 = -1,\\ &AW_1 + (\lambda - a)W_2 = 0.\end{aligned} \tag{1A}$$

The equation, $Det_W = 0$ with the determinant of Eq. (1A) looks as follows:

$$\begin{aligned}Det_W = {}&[\lambda - (A + k + 1/T_1 + G)](\lambda - k)(\lambda - a)\\ &- \lambda k(k+G) + ka(A + k + G) = 0\end{aligned} \tag{2A}$$

By solving this cubic equation we arrive at the following formulas for roots:

$$\lambda_0 = M - \frac{2}{3}\sqrt{P}\cos\left[\frac{1}{3}a\cos\left(\frac{-Q}{2P^{1.5}}\right)\right], \tag{3A}$$

$$\lambda_1 = M - \frac{2}{3}\sqrt{P}\sin\left[\frac{1}{3}a\sin\left(\frac{Q}{2P^{1.5}}\right)\right], \tag{4A}$$

$$\lambda_2 = M + \frac{2}{3}\sqrt{P}\sin\left[\frac{1}{3}a\sin\left(\frac{Q}{2P^{1.5}}\right) + \frac{\pi}{3}\right], \tag{5A}$$

Here

$$\begin{aligned}P = {}&A^2 + A[k - a + 2(1/T_1 + G)] + 4k^2 - k(2a - 1/T_1 - 4G)\\ &+ a^2 - a(1/T_1 + G) + (1/T_1 + G)^2,\end{aligned} \tag{6A}$$

$$M = \frac{A + 2k + a + 1/T_1 + G}{3} \tag{7A}$$

$$\begin{aligned}Q = {}&2A^3 + 3A^2[k - a + 2(1/T_1 + G)] + 3A[2k^2 - k(7a - 2/T_1 - 5G)\\ &- a^2 - 2(a - 1/T_1 - G)(1/T_1 + G)] + 16k^3\\ &- 6k^2(2a - 1/T_1 - 4G) - 3k[2a^2 + 2a(2G - 1/T_1)\\ &- (1/T_1)^2 - G(5/T_1 + 4G)] + (a + 1/T_1 + G)[2a^2\\ &- 5a(1/T_1 + G) + 2(1/T_1 + G)^2].\end{aligned} \tag{8A}$$

The solution of Eq. (1A) looks as follows:

$$W_1(\lambda) = \frac{k(a - \lambda)}{(\lambda_0 - \lambda)(\lambda_1 - \lambda)(\lambda_2 - \lambda)} \tag{9A}$$

where $\lambda_0\lambda_1\lambda_2 = ka/T_1$.

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