

Manifestation of single macromolecule quantum dynamics in photon distribution function of blinking fluorescence

I. S. Osad'ko^{1,2,a)} and V. V. Fedyanin²

¹*Lebedev Physical Institute, RAS, 119991 Moscow, Russia*

²*Moscow State Pedagogical University, 119889 Moscow, Russia*

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Distribution function $w_N(T)$ for photons created by three-level nanoparticle in time interval T under cw laser excitation is calculated for various methods of photon counting. It is found that each exponential process $\exp(-\lambda_i t)$ in quantum dynamics of three-level nanoparticle manifests itself via Poissonian function $P_N(\lambda_i t) = (\lambda_i t)^N \exp(-\lambda_i t) / N!$ in the photon distribution function $w_N(T)$. The distribution function $w_N(T)$ is expressed via two or three integrals of two or three Poissonian functions $P_N(\lambda_i t)$. The simple mathematical expression for $w_N(T)$ enables one to calculate photon distribution in blinking fluorescence with on and off intervals. A scaling between photon distribution function $w_N(T)$ and photoelectric pulse distribution function $w_n(T)$ is found. Comparison of the theoretical distribution $w_n(T)$ and the distribution measured in blinking fluorescence of single polymer molecule dPPV-PPyV and complex organic molecule 1,1'-didodecyl-3,3,3',3'-tetramethylindocarbocyanine perchlorate (DiI) is carried out. The theoretical distributions are able to describe those found in an experiment. © 2009 American Institute of Physics.

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I. INTRODUCTION

Single polyatomic nanoparticles excited by cw laser light reveal, as a rule, blinking fluorescence with bright on intervals and dark off intervals. Blinking fluorescence was observed in single polymer molecules,¹⁻⁴ single dendrimer molecules,⁵⁻⁷ single protein molecules,⁸⁻¹⁰ single light harvesting systems (LH2),¹¹ and single semiconductor nanocrystals.¹²⁻¹⁵ Hence, blinking fluorescence is a typical phenomenon for a single nanoparticle and therefore it deserves to be considered in detail.

Instants of single nanoparticle photon emission are distributed randomly in time scale. These instants contain information concerning quantum dynamics of the nanoparticle excited by cw laser light. Photons emitted at these random time moments are collected into a bin during time interval T of the order of 1 or 10 ms. Therefore the whole time scale consists of short bin times and the number of photons stored at a bin time is a fluctuating function $I(t)$ called quantum trajectory of intensity (QTI). QTI contains information concerning quantum dynamics of the nanoparticle excited by cw laser light. After statistical treating of QTI one can find distribution of on and off intervals and photon statistics in fluorescence, i.e., photon distribution function $w_N(T)$ for time interval T . Although photon statistics of single molecules was studied in many works,¹⁶⁻²⁴ a photon distribution function $w_N(T)$ was not calculated in those works and photon statistics was studied with the help of the method of moments offered by Mandel²⁵ or methods of the so-called generating function.^{18,19}

Distribution of intensity in QTI measured for single polymer molecules can exhibit a few maxima.^{1,2} One of the

reasons leading to such distribution of intensity is connected with the possibility of complex organic systems to emit light from few excited quantum states.^{24,26,27} Berezhkovski *et al.*²⁶ proposed a method to calculate jumps between two fluorescent states. Molski²⁸ used their result to consider photon distribution in fluorescence of single polymer molecule as doubly stochastic Poisson process. Similar approach based on Poissonian distribution for photons emitted from each fluorescent state has also been used for calculation of the intensity distribution in fluorescence of a single donor-acceptor pair²⁴ and for the distribution of turnovers in a simple model proposed for conformational changes.²⁹

The assumption that distribution of photons emitted from each fluorescent state is of Poissonian type is not quite correct. It will be shown in the present paper in which photon distribution function is calculated exactly for a three-level nanoparticle. If fluorescence has a blinking character, the distribution function for photons emitted even from one fluorescent state differs from the Poissonian function.

In order to calculate the photon distribution function in fluorescence of a polymer molecule, we shall use a method developed in Ref. 30 for a two-level molecule. The method permits us to reduce multiple integrals in photon distribution function^{31,32} to one or two integrals of a few Poissonian functions. The method has already been used to calculate the distribution function in both continuous fluorescence³⁰ and blinking fluorescence.^{33,34}

The method enables one to find a simple relation between quantum dynamics of a single molecule driven by cw laser field, on one hand, and photon statistics of its fluorescence on the other hand. It was found that each exponential process in quantum dynamics generates a Poissonian func-

^{a)}Electronic mail: osadko@sci.lebedev.ru.

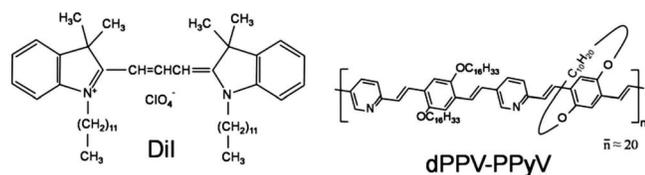


FIG. 1. Structure of 1,1'-didodecyl-3,3,3',3'-tetramethylindocarbocyanine perchlorate (DiI) molecule and a molecule of conjugated polymer dPPV-PPyV (Ref. 36).

tion with the same relaxation constant in photon distribution function found within various possible methods of photon counting.³⁵

The main goals of the present paper are (i) to calculate the photon distribution functions related to various methods of photon counting, (ii) to find a relation between a distribution of photons, on one hand, and a distribution of electric pulses in photomultiplier tube on the other hand, and (iii) to compare calculated photon distributions with photon distributions measured in Ref. 36 for blinking fluorescence of a single polymer molecule dPPV-PPyV and a complex organic molecule 1,1'-didodecyl-3,3,3',3'-tetramethylindocarbocyanine perchlorate (DiI). The structure of these molecules is shown in Fig. 1. The all three announced problems are new and they have not been solved yet in the literature on single molecule spectroscopy.

II. GENERAL THEORETICAL FORMULAS

From a theoretical point of view, photons in single molecule fluorescence excited by cw laser light can be counted by various methods. They have been considered in Refs. 30–33. For brevity they will be called method *O*, method *Z*, and method *M*. The photon distribution functions $w_N^O(T)$, $w_N^Z(T)$, and $w_N^M(T)$ for these methods will be different.

Time intervals related to these methods are shown in Fig. 2. In method *O* we take into account all intervals of duration T opened and closed by emitted photon. Such method of photon counting has also been considered by Yang and Cao.¹⁶ In method *Z*, a field of events is formed from all intervals of duration T opened by emitted photon.³¹ In method *M* used by Mandel,²⁵ the starting and stopping dates of interval T are not specified. Cao and Silbey³⁷ called the probabilities found in methods *Z* and *M* as event-averaged and time-averaged probabilities, respectively. From experimental point of view, method *M* is the most convenient in experimental implementation, whereas method *O* is more difficult. However, from theoretical point of view, method *O* is the simplest and the theoretical expression for method *M*

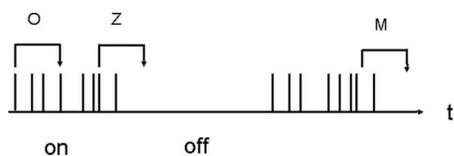


FIG. 2. Time interval taken into account in methods *O*, *Z*, and *M* of photon counting.

is the most cumbersome. Therefore, we consider in Appendix A the all three methods of photon counting starting from the simplest method *O*.

Derivation of the expressions for these three methods of photon counting is given in the Appendix A. The following expressions for three distribution functions were found.

For method *O*,

$$w_N^O(T) = [s(\lambda)^{N+1}]_T / \sum_{N=0}^{\infty} [s(\lambda)^{N+1}]_T. \quad (1)$$

For method *Z*,

$$w_N^Z(T) = \int_0^T dt \{ [s(\lambda)^N]_t - [s(\lambda)^{N+1}]_t \} \quad (N \geq 1), \quad (2a)$$

$$w_0^Z(T) = 1 - \int_0^T s(t) dt. \quad (2b)$$

For method *M*,

$$w_N^M(T) = \frac{1}{S} \int_0^T (T-t) \{ [s(\lambda)^{N-1}]_t - 2[s(\lambda)^N]_t + [s(\lambda)^{N+1}]_t \} dt \quad (N \geq 1), \quad (3a)$$

$$w_0^M(T) = \frac{1}{S} \int_0^{\infty} \left[1 - \int_0^{T+t} s(x) dx \right] dt, \quad (3b)$$

$$S = \int_0^{\infty} \left(1 - \int_0^t s(x) dx \right) dt.$$

Here $s(\lambda)$ is the Laplace transform of the function $s(t)$. The function $s(t)$ is equivalent to the function $w_2(t)$ considered by Cohen-Tannoudji and Dalibard³⁸ and the function $\varphi(t)$ introduced by Gopich and Szabo.²⁹ The density probability $s(t)$ determines the correlation between two consecutively emitted photons. Therefore, $s(t)$ was named as the start-stop correlator.^{39,40} S is the average time interval between two consecutively emitted photons.

We see that the all three distribution functions are expressed solely via degrees of $s(\lambda)$. Transition to $s(t)$ in Eqs. (1), (2a), (2b), (3a), and (3b) with the help of inverted Laplace transformation yields N -fold integrals. Numerical calculations of these N -fold integrals have not been realized in practice. However it can be carried out with help of new approach proposed in Ref. 30

This approach to calculation of Eqs. (1), (2a), (2b), (3a), and (3b) enables one to avoid N -fold integration. The approach is based on the idea that the function $[s(\lambda)^N]_t$ can be expressed via a single integral of two Poissonian functions for a two-level nanoparticle and via a double integral of three Poissonian functions for a three-level nanoparticle with blinking fluorescence.^{33,35} Such transition to Poissonian functions is shown in Appendix B.

At first glance, transition from the start-stop correlator to Poissonian functions looks like purely technical operation. However, this transition provides an insight to an important relation existing between nanoparticle dynamics, on one hand, and photon statistics in single nanoparticle fluores-

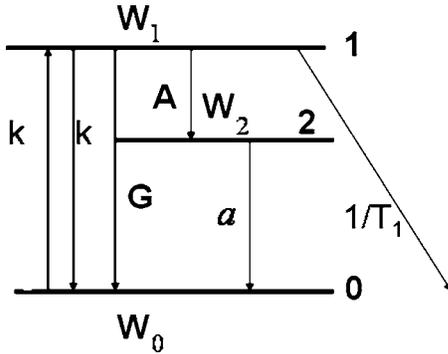


FIG. 3. Energy scheme for the nanoparticle with “bright” states 0 and 1 and “dark” state 2.

cence on the other hand. The relation demonstrates that each exponential process $\exp(-\lambda_i t)$ in the start-stop correlator manifests itself via a Poissonian function $(\lambda_i t)^N \exp(-\lambda_i t)/N!$ in the photon distribution function. Shortly speaking, it has established the relation

$$\exp(-\lambda_i t) \rightarrow (\lambda_i t)^N \exp(-\lambda_i t)/N! \quad (4)$$

between dynamics of the nanoparticle and statistics of its fluorescence. We show in this paper that this relation is true for all the three types of the distribution functions $w_N^O(T)$, $w_N^Z(T)$, and $w_N^M(T)$.

A. Start-stop correlator for a three-level model

Since formulas for photon statistics depend solely on start-stop correlator, we should find this correlator for a three-level nanoparticle with blinking fluorescence. A method of finding equations for start-stop correlator of two-level molecule is discussed in detail in Sec. 2.6 of the book³⁹ and in Ref. 40. It was shown that $s(t) = W_1(t)/T_1$. Here $W_1(t)$ is a probability of finding the molecule in the excited electronic state before spontaneous emission of a photon happened; $1/T_1$ is the rate of spontaneous emission. The theory^{39,40} takes into account coherent effects described by off-diagonal elements of the density matrix. However, if we consider low intensity of excitation, we can use rate equations. It is shown in Ref. 30. Applying the method of finding $W_1(t)$ to a three-level molecule we arrive at the following set of rate equations:³³

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

$$\dot{W}_2 = AW_1 - aW_2.$$

Here W_0 and W_1 are probabilities of finding a nanoparticle in the ground and the excited singlet electronic states of the nanoparticle. This set of equations relates to the scheme of transitions shown in Fig. 3. Here k is the rate of light-induced emission and absorption of laser photons and G is the rate of radiation-free transitions from the excited level 1 to the ground state 0 taking part in fluorescence. A and a are rate transitions to and from dark state 2. $1/T_1$ is the rate of spontaneous emission.

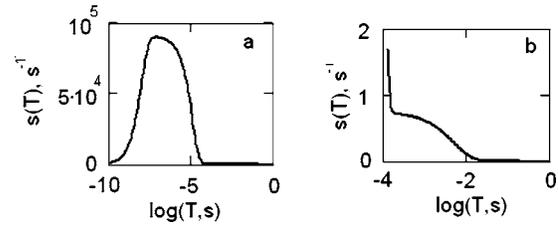


FIG. 4. Start stop correlator calculated by means of Eq. (8) with the set of parameters (9).

Dark state 2 can emerge in various reasons. For instance, the lowest triplet state serves as a dark state in a molecule DiI. 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^{36,39}

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

However, the mechanism of fluorescence interruption in a polymer molecule is of another type. It results from charge separation in traps existing in a polymer chain. A quantum level of a trap can play the role of a dark state.^{41–43} Consequently, Eq. (5) can describe various physical situations.

Carrying out Laplace transformation in Eq. (5) and solving algebraic equations for Laplace transforms with the initial condition $W_0(0) = 1$, we arrive at the following expression for the Laplace transform of the start-stop correlator:

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

Here λ_i are roots of the equation $\text{Det}_W = 0$ found in Appendix B. In accordance with the properties of the roots of the cubic algebraic equation $\text{Det}_W = 0$, we took into account the expression $-ka/T_1 = -\lambda_0 \lambda_1 \lambda_2$.

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

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

We shall choose values of parameters in Eq. (8) by taking into account the experimental data for DiI. In accordance with Eq. (6) the following set of constants

$$k = 10^5 \text{ s}^{-1}, \quad 1/T_1 = 10^8 \text{ s}^{-1}, \quad G = 10^7 \text{ s}^{-1}, \quad (9)$$

$$A = 3.7 \times 10^5 \text{ s}^{-1}, \quad \text{and} \quad a = 200 \text{ s}^{-1}$$

yields values $\tau_{\text{on}} = 3 \times 10^{-3} \text{ s}$ and $\tau_{\text{off}} = 5 \times 10^{-3} \text{ s}$ measured for a single molecule DiI.³⁶ The start-stop correlator shown in Fig. 4 has been calculated by means of Eq. (8) with the set of parameters (9).

Exponential behavior in the logarithmic time scale looks like a smooth step covering one order of magnitude of time. We see three smooth steps relating to three exponential functions in start-stop correlator. The exponential function with $\lambda_2 \cong 1/T_1 = 10^8 \text{ s}^{-1}$ determines the growth of $s(t)$ in time scale of the order of 10^{-8} s. The exponential functions with $\lambda_1 \cong k = 10^5 \text{ s}^{-1}$ and $\lambda_0 \cong a = 200 \text{ s}^{-1}$ determine the two time scales in which start-stop correlator $s(t)$ goes down to zero. These three relaxation times manifest themselves in the photon distribution functions. Indeed, it is shown in Appendix B that the function

$$[s(\lambda)^N]_t = \lambda_1 \lambda_2 \left(\frac{\lambda_0}{a}\right)^N \left\{ \int_0^t dx P_{N-1}[\lambda_1(t-x)] P_{N-1}[\lambda_2 x] + \lambda_0 \sum_{m=1}^N C_N^m \left(\frac{a-\lambda_0}{\lambda_0}\right)^m \int_0^t dx P_{m-1}[\lambda_0(t-x)] \times \int_0^x dy P_{N-1}[\lambda_1(x-y)] P_{N-1}[\lambda_2 y] \right\} \quad (10)$$

in Eqs. (1), (2a), (2b), (3a), and (3b) is expressed via Poissonian functions with the same rate constants. Statistics of blinking fluorescence was considered in Ref. 28 as “doubly stochastic Poisson process.” Our exact Eq. (10) shows that three Poissonian functions contribute to the photon distribution functions (1), (2a), (2b), (3a), and (3b) in case of blinking fluorescence. This very expression enables one to avoid N -fold integration in the photon distribution function. This fact facilitates considerably the calculation of the photon distribution function. Equations (8) and (10) reveal also an important relation (4) 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.

B. Numerical calculation of the distribution functions

Consider now the probability to detect time interval with no photons. The function $w_0^Z(T)$ determines the probability of finding no photon in semiclosed time interval $[0, T)$ that is opened by an emitted photon. The function $w_0^M(T)$ determines the probability of finding time interval T with no photon in the method M of photon counting. These probabilities are described by Eqs. (2b) and (3b).

Consider the dependence of these probabilities on T . It is obvious that

$$\int_0^\infty s(t) dt = \sum_{j=0}^2 \frac{s_j}{\lambda_j} = 1. \quad (11)$$

This formula has a simple physical meaning. Equation (11) shows that the probability of emitting the second photon by time moment $t = \infty$ equals unit. By inserting Eq. (8) into Eqs. (2b) and (3b) and allowing for Eq. (11), we arrive at the following expressions for both probabilities:

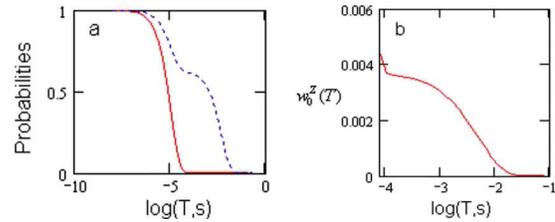


FIG. 5. (Color online) Decrease in the probability $w_0^Z(T)$ (solid line) and the probability $w_0^M(T)$ (dotted line) with growth of time interval T .

$$w_0^Z(T) = \sum_{j=0}^2 \frac{s_j}{\lambda_j} \exp(-\lambda_j T), \quad (12)$$

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

Both probabilities were calculated with the set of parameters (9). The result is shown in Fig. 5. Both probabilities approach unit if time interval approaches zero. If time interval T increases, both probabilities decrease with two relaxation times $T \cong 10^{-5}$ s and $T \cong 5 \times 10^{-3}$ s relating to two relaxation constants $1/\lambda_1 \cong 1/k$ and $1/\lambda_0 \cong 1/a$.

Consider photon distribution in blinking fluorescence for the set of parameters (9) for DiI molecule. The photon distribution function depends strongly on duration T of the interval. Figure 6 shows the values of average on and off intervals and four time intervals a , b , c , and d of various durations. Bin time was 1 ms in Ref. 36. By inserting Eq. (10) into Eqs. (1), (2a), (2b), (3a), and (3b) we calculated the distribution functions $w_N^M(T)$, $w_N^Z(T)$, and $w_N^O(T)$ for time intervals a , b , c , and d shown in Fig. 6. The result is shown in Fig. 7.

First of all, the photon distribution functions $w_N^M(T)$, $w_N^Z(T)$, and $w_N^O(T)$ have various shapes. This result differs considerably from that obtained in Ref. 35 for cw fluorescence emitted by a two-level nanoparticle. In cw fluorescence all three distributions are similar if time interval is so long that the average number of photons $\langle N \rangle$ exceeds 5.

The authors in Refs. 22 and 28 postulated a Poissonian distribution of photons emitted from the excited electronic state. Only the photon distribution function $w_N^O(T)$ in Fig. 7(a) satisfies this assumption approximately. However, the distribution functions $w_N^M(T)$ and $w_N^Z(T)$ in Fig. 7(a) have tails ranging from small N . Hence, these distributions differ from the Poissonian distribution. These tails are not a noise but they are a signal. The appearance of this signal can be explained by means of the scheme shown in Fig. 2

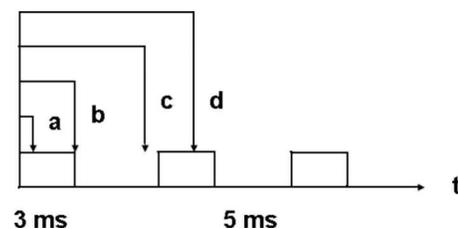


FIG. 6. Average on and off intervals and four time intervals T for which the distribution functions in Fig. 7 are calculated.

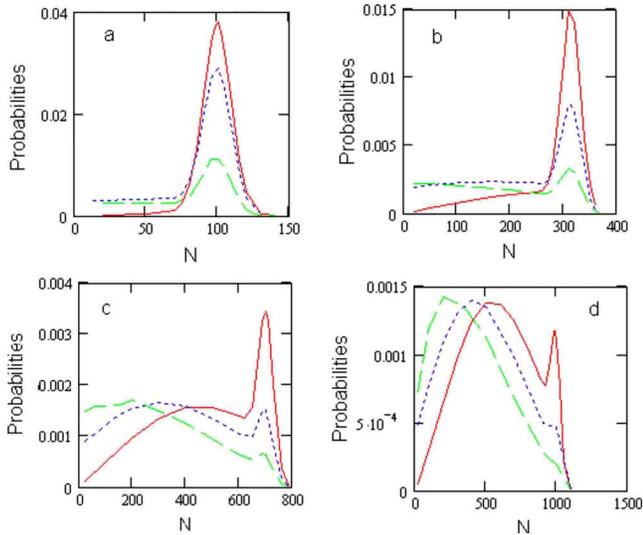


FIG. 7. (Color online) Probabilities $w_N^O(T)$ (solid line), $w_N^Z(T)$ (dotted line), and $w_N^M(T)$ (dashed line) calculated for the set of parameters (9) at (a) $T = 1$ ms, (b) 3 ms, (c) 7 ms, and (d) 10 ms.

Interval O cannot cover off interval even partially because the interval O is opened and closed by a photon emission. In contrast to interval O , intervals Z and M can cover off interval partially. Therefore, if time interval T exceeds considerably the average interval $1/k$ between two photons, as it is shown in Fig. 2, the probability of finding one photon in the method O of photon counting equals zero. However, the probability of finding at least one photon on long interval T is not zero if we use method Z or method M of photon counting. Tails in the functions $w_N^M(T)$ and $w_N^Z(T)$ are manifestations of these nonzero probabilities.

The functions $w_N^O(T)$, $w_N^M(T)$, and $w_N^Z(T)$ take into account the photons emitted in various on intervals. This fact manifests itself in Eq. (10) via factor $(\lambda_0/a)^N$ and a sum over m . For a 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. (10).

If time interval T is increased, the tails in the photon distribution functions are increased as well, as Fig. 7(b) shows. Calculations reveal that the tails ranging from small N in Figs. 7(a) and 7(b) emerge due to the factor $(\lambda_0/a)^N$. The influence of the sum over m is still negligible. However, if the duration of time interval T becomes comparable with the average value of off intervals, the contribution from the sum over m staying in Eq. (10) increases and this sum begins to play an important role. Figure 7(c) demonstrates the influence of this sum. Due to the sum over m the contribution of photons from various on intervals begins to play an important role and tails dominate in all three photon distribution functions. The difference between functions $w_N^M(T)$, $w_N^Z(T)$, and $w_N^O(T)$ is very large. A narrow Poissonian peak describes the contribution from photons that are emitted in one on interval. The contribution of this peak to the photon distribution functions is diminished for large time intervals. The peak almost disappears at $T = 10$ ms, as Fig. 7(d) shows. These photon distribution functions result from the sum over m .

Although this sum is a power series of small parameter

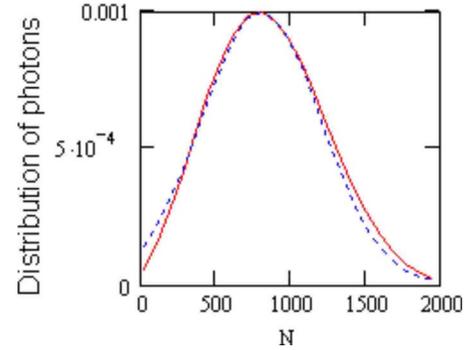


FIG. 8. (Color online) Photon distribution function $w_N^Z(20 \text{ ms})$ (solid line) calculated with the set of parameters (9) and Gaussian function with $\sigma = \langle N^2 \rangle - \langle N \rangle^2 = 200 \langle N \rangle$ (dotted line).

$(a - \lambda_0)/\lambda_0$, the value of coefficients C_N^m increases if m approaches to $N/2$. Nevertheless, the value of the product $C_N^m (a - \lambda_0)^m / \lambda_0^m$ becomes negligible at $m > 12$ even for $T = 10$ ms. We see that if time interval T exceeds the value of the sum of the average on and off intervals, the distribution function is much broader as compared with Poissonian distribution, i.e., the photon distribution is of super-Poissonian type. The shape of the photon distributions differs from Poissonian distribution considerably.

The intensity of fluorescence predetermines how short bin time can be chosen. Bin time determines time resolution of an experiment. If an average duration of off intervals is much shorter as compared with bin time the fluorescence of a nanoparticle will look like cw emission. We shall not see off intervals. However, the existence of off intervals can be revealed even in such situation.

In order to explain how off intervals can be revealed in such situation, we consider fluorescence with average on and off intervals shown in Fig. 6. However, now we take long bin time $T = 20$ ms. It exceeds off intervals considerably, and therefore, fluorescence will look like cw emission. Figure 8 shows distribution of photons at such long bin time. The distribution can be approximated by Gaussian function with the same maximum and half width. Gaussian function

$$e^{-(N - \langle N \rangle)^2 / 2\sigma} / \sqrt{2\pi\sigma} = G_N[\sigma, \langle N \rangle] \quad (13)$$

fits this photon distribution function well. It is well known that Poissonian function $P(\langle N \rangle) = \langle N \rangle^N \exp(-\langle N \rangle) / N!$ is determined completely by the average number of photons $\langle N \rangle$. The average number of photons determines both the position of maximum and the value of the variance

$$\sigma = \langle N^2 \rangle - \langle N \rangle^2 = \langle N \rangle. \quad (14)$$

The variance in the Gaussian function shown in Fig. 8 is 200 times larger as compared with the variance of Poissonian function for the same value of $\langle N \rangle$. Such super-Poissonian distribution is a clear sign of hidden off intervals in fluorescence that looks like cw emission.

III. APPLICATION TO EXPERIMENT

It is interesting how the theoretical formulas derived from this paper are able to describe the photon distributions

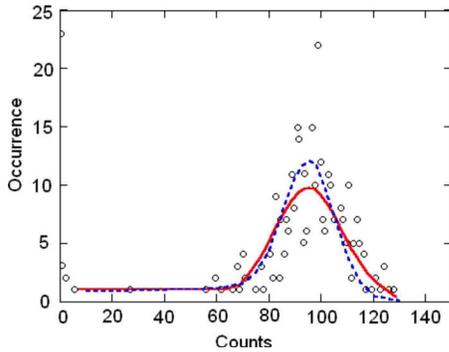


FIG. 9. (Color online) Distribution of the fluorescence intensity in QTI of a single molecule dPPV-PPyV measured in Ref. 36 (circles) and the histogram of this distribution (solid line). The dashed line shows the function $400w_N^Z(96 \text{ ms})$ calculated by means of Eqs. (2) and (10) at the following values of parameters: $k=10^3 \text{ s}^{-1}$, $A=3.7 \times 10^5 \text{ s}^{-1}$, $a=5 \text{ s}^{-1}$, $1/T_1=10^8 \text{ s}^{-1}$, and $G=10^7 \text{ s}^{-1}$.

measured in blinking fluorescence of a single molecule DiI and a single molecule of conjugated polymer dPPV-PPyV.^{1,36}

A. Molecule dPPV-PPyV

Single molecules of this polymer exhibit blinking fluorescence with on and off intervals on the order of a hundred milliseconds. Bin time was 100 ms in Ref. 1 and 10 ms in Ref. 36. The exponential distributions of on and off intervals were measured. Average value of off-interval τ_{off} was 200 ms. The value τ_{on} of average on interval depended on the intensity of excitation. It varied from 150 ms at large intensity to 650 ms for small intensity.

Some of the molecules dPPV-PPyV demonstrate on-intervals with two levels of light intensity: moderate and strong. Photon distribution in fluorescence of such molecules reveals two maxima. A more complex model than the model presented in Fig. 2 is needed to describe the photon distribution with two maxima. Such a model was considered in Ref. 27. However, some of molecules dPPV-PPyV reveal a photon distribution with one maximum. Such photon distributions can be compared with photon distributions calculated with the help of our theory.

The comparison of theory and experiment is shown in Fig. 9. Unfortunately, the authors in Refs. 1 and 36 did not tell which of the three possible methods of photon counting was used in their works. The dashed line shows the distribution function w_N^Z calculated by means of Eqs. (2a) and (10) at bin time $T \cong 0.1 \text{ s}$. Values $\tau_{\text{on}}=300 \text{ ms}$ and $\tau_{\text{off}}=200 \text{ ms}$ correspond to the set of parameters $k=10^3 \text{ s}^{-1}$, $A=3.7 \times 10^5 \text{ s}^{-1}$, $a=5 \text{ s}^{-1}$, $1/T_1=10^8 \text{ s}^{-1}$, and $G=10^7 \text{ s}^{-1}$. These very values of τ_{on} and τ_{off} were measured in the experiment.¹ Value $\tau_{\text{off}}=200 \text{ ms}$ is 20 times larger than the triplet state lifetime in a polymer molecule. Therefore, triplet states are not responsible for blinking in fluorescence of a polymer molecule.

The physical picture of blinking fluorescence in a polymer molecule can look as follows. An electron-hole pair created by cw laser light in a polymer chain moves along the chain and electron is captured by a trap. This electron capture hampers electron-hole recombination and emission is suppressed. Therefore, dark states in a polymer chain are

formed by traps existing in the chain.^{36,41–43} Modulation of fluorescence intensity by external ac electric field proves that the blinking character of fluorescence in a polymer chain is caused by ionization-neutralization processes in a polymer chain.^{41–43} This situation is similar to that existing in semiconductor nanocrystals. The ionization-neutralization processes are the main reason for blinking fluorescence in single semiconductor nanocrystals CdSe. A mechanism of relaxation of electron-hole pairs in single nanocrystals and the ionization-neutralization processes in CdSe nanocrystals were considered in detail in Refs. 44 and 45. In such physical picture for fluorescence blinking, parameter A in Fig. 3 describes the rate of capture of charge by a trap (or rate of charge capture by a trap). Parameter a describes the rate of escape of electron from the trap (or the rate of electron escape from the trap).

The value of constant $k=10^3 \text{ s}^{-1}$ utilized for calculation of the theoretical curve in Fig. 9 deserves to be commented. At first sight, this value seems to be too small because the rate of photon absorption reported in Ref. 36 is two orders of magnitude larger. However, we must take into account that not all photons emitted by a single molecule get to photodetector and cause photoelectric pulse. If 10% of photons get to photodetector and 10% of them cause photoelectric pulses we arrive at the conclusion that the number of photoelectric pulses will be two orders of magnitude smaller than the number of photon absorptions. If the rate of photon absorption is 10^5 s^{-1} , the on interval of 100 ms will include 10^4 photon emissions and 100 photoelectric pulses, as Fig. 9 shows. Henceforth, taking $k=10^3 \text{ s}^{-1}$ we allow for losses of photons emitted by a single molecule.

Let us write the Poissonian distribution of photons in the following form:

$$P_N(T) = (kT)^N \exp(-kT)/N! = w_N(k, T). \quad (15)$$

Let $1/q$ be a deal of photons detected by a photodetector. It is obvious that losses in photons can be compensated by increased time interval T for this distribution function, i.e.,

$$w_N(k, T) = w_N\left(\frac{k}{q}, Tq\right). \quad (16)$$

We may say that some kind of scaling exists. This scaling in Poissonian distribution is not surprising because the Poissonian distribution depends on the product kT , as Eq. (15) shows. However, photon distribution function $w_N^Z(T)$ for blinking fluorescence is described by complex Eqs. (2a) and (10) and therefore it will differ from the electric pulse distribution function $w_n^Z(T)$. The inequality $w_N(T) \neq w_n(T)$ will take place for all the three methods of photon counting. However, can the distribution function, for instance, $w_N^Z(T)$, reveal some kind of scaling?

In order to answer this question we rewrite the photon distribution function in the following form: $w_N^Z(T) \equiv w_N^Z(k, \tau_{\text{on}}, \tau_{\text{off}}, T)$. Our calculations show that the following relation holds true:

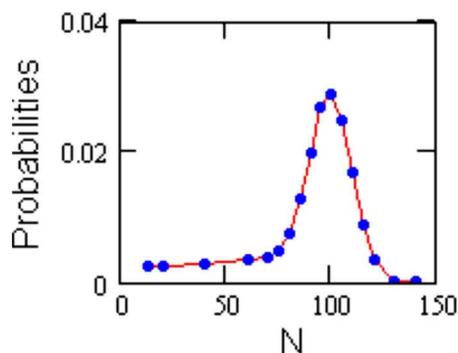


FIG. 10. (Color online) Probability $w_N^Z(10^4 \text{ s}^{-1}, 0.03 \text{ s}, 0.02 \text{ s}, 0.01 \text{ s})$ (points) and probability $w_N^Z(10^3 \text{ s}^{-1}, 0.3 \text{ s}, 0.2 \text{ s}, 0.1 \text{ s})$ (solid line) calculated with the help of Eqs. (2a) and (10).

$$w_N^Z(k, \tau_{\text{on}}, \tau_{\text{off}}, T) \cong w_N^Z\left(\frac{k}{q}, \tau_{\text{on}}q, \tau_{\text{off}}q, Tq\right). \quad (17)$$

Figure 10 proves this relation for $q=10$. Hence, some kind of scaling exists even in complex expression for $w_N^Z(T)$ if parameters τ_{on} and τ_{off} are included in the set of parameters scaled. The photon distribution function can be calculated if electric pulse distribution and photon losses are known.

The comparison of the histogram shown in Fig. 9 with the theoretical distribution reveals that our theory is able to describe the existence of a Poissonian peak and a broad wing. The theory can explain why the broad photon wing emerges.

B. DiI molecule

Blinking fluorescence of DiI molecule was measured in Ref. 36. The fluorescence is characterized by shorter values of τ_{on} and τ_{off} as compared with dPPV-PPyV fluorescence. These values are $\tau_{\text{on}}=3 \text{ ms}$ and $\tau_{\text{off}}=5 \text{ ms}$. These very values we used to calculate the distribution functions shown in Fig. 7.

It was shown in Ref. 36 that the dark state in DiI molecule is of triplet nature. Therefore, constant A in Fig. 3 describes the rate of intersystem crossing and constant a describes the inverse lifetime of the triplet level 2. The triplet character of dark state in DiI molecule was established in the course of the experiments with artificial saturation of the sample by O_2 . Saturation by oxygen decreases lifetime of triplet level, i.e., increases rate a of triplet-singlet transitions. For instance, addition of oxygen to the sample diminished τ_{off} by a factor of 20.

Figure 11 shows a histogram of the intensity distribution in QTI of a single DiI molecule at a maximal saturation of the sample by oxygen. Taking this fact into account we took rate a of triplet decay ten times larger as compared with $a=200 \text{ s}^{-1}$ used in the set of parameters (9). The histogram measured in the experiment and the theoretical distribution calculated with the help of Eqs. (3a) and (10) are shown in Fig. 11.

The theoretical distribution corresponds to blinking fluorescence with $\tau_{\text{on}}=3 \text{ ms}$ and $\tau_{\text{off}}=0.33 \text{ ms}$. The theoretical distribution function is able to describe deviation from Poissonian distribution, i.e., tail ranging from small N .

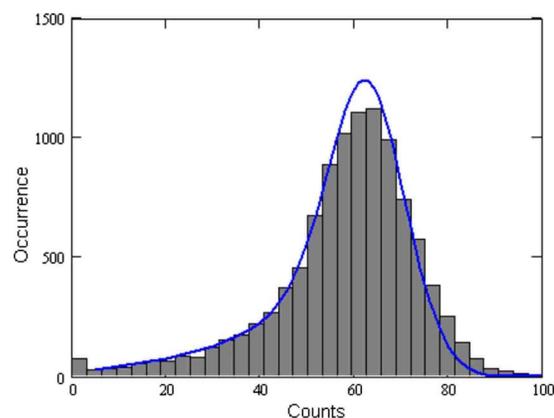


FIG. 11. (Color online) Histogram of the intensity distribution in blinking fluorescence of a single DiI molecule at maximal saturation by oxygen (Ref. 36). The solid line shows the distribution function $4 \times 10^4 w_N^M(1 \text{ ms})$ calculated by means of Eqs. (3) and (10) at $k=7 \times 10^4 \text{ s}^{-1}$, $A=5.3 \times 10^5 \text{ s}^{-1}$, $a=3000 \text{ s}^{-1}$, $1/T_1=10^8 \text{ s}^{-1}$, and $G=10^7 \text{ s}^{-1}$.

IV. CONCLUSIONS

Three methods O , Z , and M of photon counting in fluorescence of a single nanoparticle have been considered. Three photon distribution functions $w_N^M(T)$, $w_N^Z(T)$, and $w_N^O(T)$ relating to these methods have been expressed via a few Poissonian functions for blinking fluorescence of a single nanoparticle. Equations (1), (2a), (2b), (3a), (3b), and (10) are the main theoretical results of this work.

Photon distribution functions presented in Fig. 7 show that distribution of photons in blinking fluorescence can have rather complicated shape with a narrow peak and broad distribution because of photon contribution from various intervals. A view of the photon distribution function depends strongly on the method of photon counting.

The comparison of the photon distribution functions calculated with the photon distribution functions measured in blinking fluorescence of a single dPPV-PPyV molecule and a single DiI molecule reveals that our theory is able to explain all details of measured distributions.

The expression of the photon distribution functions via Poissonian functions reveals a relation between quantum dynamics of the nanoparticle described by start-stop correlator, on one hand, and distribution of photons in its fluorescence on the other hand. Each exponential process in quantum dynamics manifests itself via Poissonian function in the photon distribution. This relation, expressed by Eq. (4), was found first in Ref. 30 for a two-level nanoparticle with two exponential dynamics and here for a three-level nanoparticle in which quantum dynamics is described by three exponential functions.

The physical model considered in the present paper is characterized by exponential distribution of on and off intervals. However, blinking fluorescence of single semiconductor nanocrystals exhibits power-law distribution of on and off intervals.¹³⁻¹⁵ Therefore, the question arises: can the relation between exponential dynamical process, on one hand, and Poissonian function in the photon distribution function, on the other hand, be extended to the systems with power-law statistics? We cannot give a definite answer to this question

yet. However, one of the authors⁴⁴ has recently shown that experimental data on power-law statistics can be explained if we take into account that quantum dynamics of CdSe nanocrystal with ZnS shell is described by six exponents related to surface states in a core shell. This result enables one to hope that the method developed in the present paper can be applied in the future to the systems with power-law statistics.

ACKNOWLEDGMENTS

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APPENDIX A: VARIOUS METHODS OF PHOTON COUNTING

1. Method *O* of photon counting

Let

$$dS(t) = s(t)dt \quad (\text{A1})$$

be a probability of finding a photon in time interval $(t, t + dt)$ if preceding photon was emitted at $t=0$. The function $s(t)$ is the density of the probability. The function $s(t)$ determines the correlation between two consecutively emitted photons. Therefore, one was named as the start-stop correlator.^{39,40} It is obvious that the function

$$S(T) = \int_0^T s(t)dt \quad (\text{A2})$$

determines the probability to find the second photon by time moment T . Hence, the integrals

$$s_1(T) = \int_0^T s(T-t_1)s(t_1)dt_1, \quad (\text{A3})$$

$$s_2(T) = \int_0^T s(T-t_2)s_1(t_2)dt_2, \dots, s_N(T) \\ = \int_0^T s(T-t_N)s_{N-1}(t_N)dt_N, \dots$$

determine the densities of the probability of finding 1, 2, ..., N so-called intermediate photons in time interval $[0, T]$ opened and closed by a photon. The density of the probability of finding N intermediate photons is expressed via a single function $s(T)$,

$$s_N(T) = \int_0^T dt_N \int_0^{t_N} dt_{N-1} \dots \int_0^{t_2} dt_1 s(T-t_N) \\ \times s(t_N-t_{N-1}) \dots s(t_2-t_1)s(t_1). \quad (\text{A4})$$

Consider an infinite sum

$$p(T) = s(T) + \sum_{N=1}^{\infty} s_N(T) \quad (\text{A5})$$

that determines the density of the probability of finding any number of intermediate photons between the photon in the onset and in the end of time interval $[0, T]$. The function

$p(T)$ determines the correlation between two photons in the onset and in the end of time interval independently on the number of intermediate photons in the interval $[0, T]$. Therefore, the function $p(T)$ was named as full two-photon correlator.^{39,40}

Full two-photon correlator $p(T)$ and the start-stop correlator $s(T)$ are related by the following integral equation:

$$p(T) = s(T) + \int_0^T s(T-t)p(t)dt. \quad (\text{A6})$$

This integral equation can be easily derived with the help of Eqs. (A3) and (A5). Since correlator $p(T)$ takes into account the intervals with any number of intermediate photons, the following ratios

$$w_0^O(T) = \frac{s(T)}{p(T)}, \quad w_N^O(T) = \frac{s_N(T)}{p(T)} \quad (\text{A7})$$

can be considered as the probabilities of finding interval $[0, T]$ with no intermediate photon and with N intermediate photons. The sum of all probabilities equals unit

$$\sum_{N=0}^{\infty} w_N^O(T) = 1. \quad (\text{A8})$$

2. Method *Z* of photon counting

In this method we deal with semiopen time intervals $[0, T)$ opened by an emitted photon. The probability of finding time interval with no photon is given by

$$w_0^Z(T) = 1 - S(T). \quad (\text{A9})$$

The probability of finding interval $[0, T)$ with one photon and with N photons is given by

$$w_1^Z(T) = \int_0^T dt_1 w_0^Z(T-t_1)s(t_1), \quad (\text{A10})$$

$$w_N^Z(T) = \int_0^T dt_N \int_0^{t_N} dt_{N-1} \dots \int_0^{t_2} dt_1 w_0^Z(T-t_N) \\ \times s(t_N-t_{N-1}) \dots s(t_2-t_1)s(t_1).$$

These probabilities are expressed solely via the start-stop correlator. The sum of all probabilities equals unit

$$\sum_{N=0}^{\infty} w_N^Z(T) = 1. \quad (\text{A11})$$

3. Method *M* of photon counting

Consider first an auxiliary method. It differs from method *Z* because now we are interested in the probability of finding a photon in time interval $(t_0, T+t_0)$, whose onset was separated by time t_0 from the moment $t=0$ in which a photon was emitted. This situation is shown in Fig. 12.

The probability of finding a photon in the interval $(t_0, T+t_0)$ at the additional condition (conditional probability) that a preceding photon was emitted at time moment $t=0$ is given by

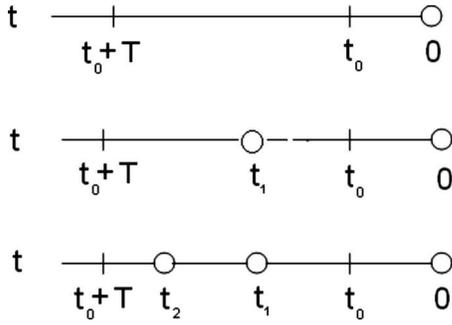


FIG. 12. Time intervals with photons (circles).

$$\begin{aligned} \rho_1(T+t_0, t_0|0) &= \int_{t_0}^{T+t_0} \left(1 - \int_{t_1}^{T+t_0} s(t-t_1) dt\right) s(t_1) dt_1 \\ &= \int_{t_0}^{T+t_0} dt_1 w_0^Z(T+t_0-t_1) s(t_1). \end{aligned} \quad (\text{A12})$$

The conditional probability of finding two and N photons in time interval $(t_0, T+t_0)$ is given by

$$\begin{aligned} \rho_2(T+t_0, t_0|0) &= \int_{t_0}^{T+t_0} dt_2 w_0^Z(T+t_0-t_2) \int_{t_0}^{t_2} dt_1 \\ &\quad \times s(t_2-t_1) s(t_1), \end{aligned} \quad (\text{A13})$$

$$\begin{aligned} \rho_N(T+t_0, t_0|0) &= \int_{t_0}^{T+t_0} dt_N w_0^Z(T+t_0-t_N) \int_{t_0}^{t_N} dt_{N-1} \\ &\quad \times s(t_N-t_{N-1}) \cdots \int_{t_0}^{t_2} dt_1 s(t_2-t_1) s(t_1) \\ &= \int_0^T dx_N \int_0^{x_N} dx_{N-1} \cdots \int_0^{x_2} dx_1 \\ &\quad \times w_0^Z(T-x_N) s(x_N-x_{N-1}) \cdots s(x_2-x_1) \\ &\quad \times s(x_1+t_0). \end{aligned} \quad (\text{A14})$$

The conditional probability $\rho_N(T+t_0, t_0|0)$ can be written in the following form:

$$\rho_N(T+t_0, t_0|0) = w_N(T+t_0, t_0) \rho_0(t_0|0), \quad N \geq 1. \quad (\text{A15})$$

Here $\rho_0(t_0|0) = 1 - S(t_0)$ is a probability of finding no photons in time interval $(0, t_0)$ and $w_N(T+t_0, t_0)$ is a probability of finding N photons in time interval $(t_0, T+t_0)$ independently on the photon history preceded time moment t_0 . Therefore, we shall call $w_N(T+t_0, t_0)$ as unconditional probability. By operating in the same fashion, we can write the following expression for the probability $\rho_0(T+t_0|0) = 1 - S(T+t_0)$ of finding no photon in the interval $(0, T+t_0)$ if preceding photon was emitted at $t=0$:

$$\rho_0(T+t_0|0) = w_0(T+t_0, t_0) \rho_0(t_0|0). \quad (\text{A16})$$

Here $w_0(T+t_0, t_0)$ is an unconditional probability of finding

interval $(t_0, T+t_0)$ with no photons.

The expression for $w_N(T+t_0, t_0)$ can be written in the following form:

$$w_0(T+t_0, t_0) = \frac{\rho_0(T+t_0|0)}{\rho_0(t_0|0)} = \frac{1 - S(T+t_0)}{1 - S(t_0)} = \frac{w_0^Z(T+t_0)}{1 - S(t_0)}. \quad (\text{A17})$$

By using Eq. (A14), we can derive the following expression for the sum of conditional probabilities

$$\sum_{N=1}^{\infty} \rho_N(T+t_0, t_0|0) = S(T+t_0) - S(t_0). \quad (\text{A18})$$

By deriving this equation we took into account that

$$\int_{t_0}^{T+t_0} dt_1 \int_{t_1}^{T+t_0} dt \cdots = \int_{t_0}^{T+t_0} dt \int_{t_0}^t dt_1 \cdots$$

Making use of Eqs. (17A) and (18A) we arrive at the following law of conservation for the unconditional probabilities:

$$\frac{1 - S(T+t_0)}{1 - S(t_0)} + \sum_{N=1}^{\infty} \frac{\rho_N(T+t_0, t_0|0)}{1 - S(t_0)} = \sum_{N=0}^{\infty} w_N(T+t_0, t_0) = 1. \quad (\text{A19})$$

At $t_0=0$, these probabilities coincide with the probabilities $w_N^Z(T)$, i.e., $w_N(T+0, 0) = w_N^Z(T)$.

If we detect photons with the help of method M , we find time interval $(0, t_0)$ with no photons with the following density of probability:

$$P(t_0) = \frac{1 - S(t_0)}{\int_0^{\infty} (1 - S(t_0)) dt_0} = \frac{1 - S(t_0)}{S}. \quad (\text{A20})$$

Here S is the average interval between two consecutively emitted photons. Therefore, the probability of finding interval T with N photons is determined by the following expression:

$$\begin{aligned} w_N^M(T) &= \int_0^{\infty} w_N(T+t_0, t_0) P(t_0) dt_0 \\ &= \frac{1}{S} \int_0^{\infty} \rho_N(T+t_0, t_0|0) dt_0. \end{aligned} \quad (\text{A21})$$

This is the photon distribution function for method M of photon counting. Making use of Eqs. (A19) and (A21), we arrive at the law of the probability conservation $\sum_{N=0}^{\infty} w_N^M(T) = 1$.

By summing up we can write the following expressions for the probabilities $w_N^O(T)$, $w_N^Z(T)$, and $w_N^M(T)$:

$$\begin{aligned} w_N^i(T) &= \int_0^T dt_N \int_0^{t_N} dt_{N-1} \cdots \int_0^{t_2} dt_1 P^i(t_N, t_{N-1}, \dots, t_1), \\ N &\geq 1. \end{aligned} \quad (\text{A22a})$$

Here $i=O, Z, M$ and

$$P^O(t_N, t_{N-1}, \dots, t_1) = \frac{s(T-t_N)^{N-1}}{p(T)} \prod_{j=1}^{N-1} s(t_{j+1}-t_j)s(t_1),$$

$$w_0^O(T) = s(T)/p(T), \quad (\text{A22b})$$

$$P^Z(t_N, t_{N-1}, \dots, t_1) = w_0^Z(T-t_N) \prod_{j=1}^{N-1} s(t_{j+1}-t_j)s(t_1),$$

$$w_0^Z(T) = 1 - S(T), \quad (\text{A22c})$$

$$P^M(t_N, t_{N-1}, \dots, t_1) = \frac{w_0^Z(T-t_N)^{N-1}}{S} \prod_{j=1}^{N-1} s(t_{j+1}-t_j)w_0^Z(t_1),$$

$$w_0^M(T) = \frac{1}{S} \int_0^\infty dt_0 w_0^Z(T+t_0), \quad (\text{A22d})$$

$$w_1^M(T) = \frac{1}{S} \int_0^T w_0^Z(T-t)w_0^Z(t)dt.$$

Carrying out Laplace transformation $\int_0^\infty dt F(t)e^{i(\omega+i0)t} = F(i\omega) = F(\lambda)$ in Eq. (A22a), we arrive at the following equations:

$$(w_0^O p(T))_\lambda = s(\lambda)^{N+1}, \quad w_0^Z(\lambda) = \frac{1}{-\lambda} [1 - s(\lambda)]s(\lambda)^N,$$

$$w_0^M(\lambda) = \frac{1}{\lambda^2 S} [1 - s(\lambda)]^2 s(\lambda)^{N-1} \quad (N \geq 1). \quad (\text{A23})$$

All the three Laplace transforms are expressed via the Laplace transform of the start-stop correlator. The expression for $w_0^M(\lambda)$ coincides with Eq. (3.6) derived from Ref. 29.

If we know the expression for the function $[s(\lambda)^N]_t$, then after the inverted Laplace transformation in Eq. (A23) we arrive at the following expressions. For method *O*,

$$w_0^O(T) = [s(\lambda)^{N+1}]_T / p(T). \quad (\text{A24})$$

For method *Z*,

$$w_0^Z(T) = \int_0^T dt \{ [s(\lambda)^N]_t - [s(\lambda)^{N+1}]_t \} \quad (N \geq 1), \quad (\text{A25a})$$

$$w_0^Z(T) = 1 - \int_0^T s(t)dt. \quad (\text{A25b})$$

For method *M*,

$$w_0^M(T) = \frac{1}{S} \int_0^T (T-t) \{ [s(\lambda)^{N-1}]_t - 2[s(\lambda)^N]_t + [s(\lambda)^{N+1}]_t \} dt \quad (N \geq 1), \quad (\text{A26a})$$

$$w_0^M(T) = \frac{1}{S} \int_0^\infty \left[1 - \int_0^{T+t} s(x)dx \right] dt. \quad (\text{A26b})$$

APPENDIX B: EXPRESSION OF START STOP CORRELATOR VIA POISSONIAN FUNCTIONS

By using Eq. (7) we can write

$$s(\lambda)^N = \lambda_1 \lambda_2 \left(\frac{\lambda_0}{a} \right)^N \left(\frac{a-\lambda}{\lambda_0-\lambda} \right)^N \frac{\lambda_1^{N-1}}{(\lambda_1-\lambda)^N} \frac{\lambda_2^{N-1}}{(\lambda_2-\lambda)^N}. \quad (\text{B1})$$

Here λ_i are the roots of the equation $\text{Det}_w = 0$. The determinant of Eq. (5) looks as follows:

$$\text{Det}_w = [\lambda - (A + k + 1/T_1 + G)](\lambda - k)(\lambda - a) - \lambda k(k + G) + ka(A + k + G) = 0. \quad (\text{B2})$$

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

$$\lambda_0 = M - \frac{2}{3} \sqrt{P} \cos \left[\frac{1}{3} a \cos \left(\frac{-Q}{2P^{1.5}} \right) \right], \quad (\text{B3a})$$

$$\lambda_1 = M - \frac{2}{3} \sqrt{P} \sin \left[\frac{1}{3} a \sin \left(\frac{Q}{2P^{1.5}} \right) \right], \quad (\text{B3b})$$

$$\lambda_2 = M + \frac{2}{3} \sqrt{P} \sin \left[\frac{1}{3} a \sin \left(\frac{Q}{2P^{1.5}} \right) + \frac{\pi}{3} \right]. \quad (\text{B3c})$$

Here

$$P = A^2 + A[k - a + 2(1/T_1 + G)] + 4k^2 - k(2a - 1/T_1 - 4G) + a^2 - a(1/T_1 + G) + (1/T_1 + G)^2, \quad (\text{B4})$$

$$M = \frac{A + 2k + a + 1/T_1 + G}{3}, \quad (\text{B5})$$

$$Q = 2A^3 + 3A^2[k - a + 2(1/T_1 + G)] + 3A[2k^2 - k(7a - 2/T_1 - 5G) - a^2 - 2(a - 1/T_1 - G)(1/T_1 + G)] + 16k^3 - 6k^2(2a - 1/T_1 - 4G) - 3k[2a^2 + 2a(2G - 1/T_1) - (1/T_1)^2 - G(5/T_1 + 4G)] + (a + 1/T_1 + G) \times [2a^2 - 5a(1/T_1 + G) + 2(1/T_1 + G)^2]. \quad (\text{B6})$$

Two last ratios in Eq. (B1) are Laplace transforms $P_{N-1}^{\lambda_i}(\lambda) = \lambda_i^{N-1}/(\lambda_i - \lambda)^N$ of Poissonian function $P_N(\lambda; t) = (\lambda_i t)^N \exp(-\lambda_i t)/N!$. The second ratio can be presented in the following form:

$$\left(\frac{a-\lambda}{\lambda_0-\lambda} \right)^N = \left(1 + \frac{a-\lambda_0}{\lambda_0} \frac{\lambda_0}{\lambda_0-\lambda} \right)^N = \sum_{m=0}^N \frac{N!}{m!(N-m)!} \left(\frac{a-\lambda_0}{\lambda_0} \right)^m \left(\frac{\lambda_0}{\lambda_0-\lambda} \right)^m. \quad (\text{B7})$$

This sum over m is an expansion in power series of small parameter $(a-\lambda_0)/\lambda_0$ because the value of λ_0 is close to the value of a . The parameter is always positive and less than the unit. By using the set of parameters (9) we find the following values for roots $\lambda_0 = 199.221 \text{ s}^{-1} \cong a$, $\lambda_1 = 9.085 \times 10^4 \text{ s}^{-1} \cong k$, and $\lambda_2 = 1.105 \times 10^8 \text{ s}^{-1} \cong 1/T_1$. Hence we find $(a-\lambda_0)/\lambda_0 = 3.708 \times 10^{-3}$, i.e., the parameter is very small indeed. Inserting Eq. (B7) into Eq. (B1), we arrive at the

following expression:

$$s(\lambda)^N = \lambda_1 \lambda_2 \left(\frac{\lambda_0}{a} \right)^N \sum_{m=0}^N C_N^m \left(\frac{a - \lambda_0}{\lambda_0} \right)^m \lambda_0 \frac{\lambda_0^{m-1}}{(\lambda_0 - \lambda)^m} \frac{\lambda_1^{N-1}}{(\lambda_1 - \lambda)^N} \frac{\lambda_2^{N-1}}{(\lambda_2 - \lambda)^N}$$

$$= \lambda_1 \lambda_2 \left(\frac{\lambda_0}{a} \right)^N \left[P_{N-1}^{\lambda_1}(\lambda) P_{N-1}^{\lambda_2}(\lambda) + \lambda_0 \sum_{m=1}^N C_N^m \left(\frac{a - \lambda_0}{\lambda_0} \right)^m P_{m-1}^{\lambda_0}(\lambda) P_{N-1}^{\lambda_1}(\lambda) P_{N-1}^{\lambda_2}(\lambda) \right]. \quad (\text{B8})$$

This expression includes solely the Laplace transforms of Poissonian functions. Carrying out the inverted Laplace transformation in Eq. (B8), we arrive at the following expression:

$$[s(\lambda)^N]_t = \lambda_1 \lambda_2 \left(\frac{\lambda_0}{a} \right)^N \left\{ \int_0^t dx P_{N-1}[\lambda_1(t-x)] P_{N-1}[\lambda_2 x] \right.$$

$$+ \lambda_0 \sum_{m=1}^N C_N^m \left(\frac{a - \lambda_0}{\lambda_0} \right)^m \int_0^t dx P_{m-1}[\lambda_0(t-x)]$$

$$\left. \times \int_0^x dy P_{N-1}[\lambda_1(x-y)] P_{N-1}[\lambda_2 y] \right\}. \quad (\text{B9})$$

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