

# Influence of conformational changes in complex molecules on photon statistics of single molecule fluorescence

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(Received 4 February 2011; published 28 June 2011)

A single complex molecule with conformational changes (conformations 0 and 2) is considered. When such a molecule is irradiated by cw-laser light it can randomly change the intensity or polarization of its fluorescence due to jumps from one conformation to another. In fact, the molecule manifests itself either like the 0-type or the 2-type emitter. An expression for the matrix  $s_{\alpha\beta}(t)$  called the start-stop correlator (waiting time distribution) in which  $\alpha = 0, 2$  and  $\beta = 0, 2$  is derived. An expression for the matrix  $p_{\alpha\beta}(t)$  called the full correlator is derived as well. It determines the density of the probability of finding an event of  $\alpha$  type and an event of  $\beta$  type separated by time interval  $t$ . A relation between matrices  $s_{\alpha\beta}(t)$  and  $p_{\alpha\beta}(t)$  is found. A mathematical expression for the distribution  $w_N(T)$  of events measured in time interval  $T$  is derived. It is expressed solely via the matrix  $s_{\alpha\beta}(t)$ . Numerical calculations of the event distribution function for various rates of intra- and interconformational jumps are carried out with the help of the formula for  $w_N(T)$  and by the Monte Carlo method. Both methods of the calculation yield identical distributions. Fluctuating fluorescence intensity  $I(t)$  for a bin time of 5 ms is calculated for slow and fast interconformational jumps. A relation is found between the autocorrelation function  $g^{(2)}(t)$  of fluorescence measurable in experiments and the matrix  $p_{\alpha\beta}(t)$  calculated theoretically.

DOI: 10.1103/PhysRevA.83.063841

PACS number(s): 42.50.Ar, 82.37.—j

## I. INTRODUCTION

For the last decade, single molecule spectroscopy revealed itself as an effective tool for studying both local environmental conditions of guest molecules embedded in polymer films and organic glasses [1–9] and quantum dynamics of complex organic molecules embedded in condensed matter [10–17].

It is known that complex organic molecules such as the polymer chain can change their conformations [11,12], [14–17]. Such conformational changes are accompanied by changes in polarization or intensity of single molecule fluorescence excited by cw-laser light. Jumps in fluorescence intensity of a single molecule can serve as an important source of information about conformational changes in the molecule. If we measure fluorescence from an ensemble of molecules this source of information is lost because of the summation of photons emitted by all molecules.

Absorption and emission bands of single molecules measured at room temperature are very broad due to strong electron-phonon interaction [11–13]. Therefore the measurement of the band shape gives us extremely little information about the quantum dynamics of the molecule. Therefore spectral methods are ineffective at room temperature. However, even first measurements of whole single polymer molecule fluorescence integrated over the frequency revealed blinking of the fluorescence intensity [11,12]. By now, blinking in single organic molecule fluorescence has become a routine phenomenon.

Quantum dynamics of the single molecule manifest via blinking fluorescence. We can find this dynamic if we are able to relate fluctuations in fluorescence with this dynamic. Blinking fluorescence measured by the Barbara group [11,12] reveals two levels of intensity: strong and moderate. This fact

can be related to the existence of two types of conformations in the polymer molecule. A theoretical model for single molecule fluorescence from two types of conformation has been discussed in Ref. [18]. The model was able to describe many facts found by the Barbara group in the experiment. A number of rate constants governing dynamics of the molecule with two types of fluorescence have been found. However, the functions for the distribution of photons and waiting time distributions have not been found in Ref. [18].

Recently, an expression for the photon distribution function  $w_N(T)$  for a single molecule with two types of fluorescence has been derived by Gopich and Szabo [16]. Their theory was based on the Mandel formula [19]:

$$w_N(T) = \int_0^\infty P(W|T) \frac{W^N}{N!} e^{-W} dW, \quad (1)$$

for the photon distribution function. Fast emission processes in both conformations were described by two Poisson functions. Slow interconformational transitions were described by the probability  $P(W|T)$ . The probability  $P(W|T)$  has been found with the help of the two-level model. Such an approach is certainly an approximation.

Jumps of absorption lines of a guest single molecule embedded in a polymer film observed in a frequency scale at low temperature [8,9] can also be considered as a manifestation of conformational changes in the spectrum of an impurity center (robust guest molecule with flexible surrounding environment). Conformational changes of such type in the impurity center are considered within the scope of the two-level system (TLS) model. The rate of jumps in TLS can be in the millisecond time scale, i.e., it can be comparable with the rate of photon emission. Such a system cannot be described by the theory for slow conformational changes.

It must be noted that the first studies on quantum jumps in single atom fluorescence excited by cw-laser light [20–22]

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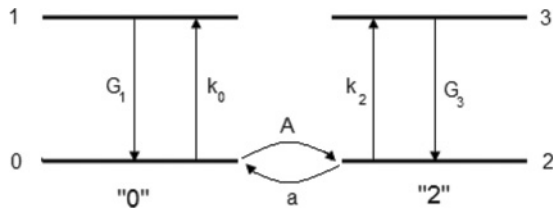


FIG. 1. Quantum states of the molecule with conformations “0” and “2”.

were carried out without addressing Eq. (1). They used the probability density function (PDF) that exactly  $N$  photons are emitted at times  $t_1, t_2, \dots, t_N$  by the atom in the time interval  $t$ . Unfortunately, this approach generates  $N$ -fold integration if we try to find the photon distribution function. In later works, the method using the PDF function  $f(t, t_N, t_{N-1}, \dots, t_1)$  was modified so that the photon distribution function  $w_N(T)$  was expressed via two- and threefold integrals [23–26].

Until recently, solely systems in which the PDF function  $f(t, t_N, t_{N-1}, \dots, t_1)$  is factorized have been discussed [20–26]. In these systems the PDF function is a product of  $N$  elementary densities of the probabilities  $s(t_j - t_{j-1})$  called “waiting time distribution” [21] or the start-stop correlator [3,7].

Very recently, the authors of Ref. [27] have discussed moments of the distribution function for the systems in which the PDF function  $f(t, t_N, t_{N-1}, \dots, t_1)$  is not factorized. These systems were called the “systems with memory.” A molecule with two types of conformation has been classified in Ref. [27] to a system with memory.

The main goal of the paper is to derive the distribution functions for single molecule fluorescence with two types of emitted photons and without any restrictions on the rate of interconformational jumps. This means that the task for two types of photons modulated by interconformational jumps has to be solved exactly. It will be done in this paper by a method not using Eq. (1).

## II. DYNAMICS OF THE MOLECULE WITH TWO CONFORMATIONS

It has been pointed out in the Introduction that complex organic molecules can have several conformational forms. This is especially typical for open-chain molecules such as the polymer molecule. This molecule is able to jump spontaneously from one conformation to another. Some physical properties of the molecule can be different for different conformations. For instance, intensity or polarization of fluorescence in various conformational forms can be different. In this case, a change of conformation can be detected with the help of single molecule fluorescence.

Consider a single molecule which can change its conformation being in the ground electronic state. Such a molecule can be described by the energy scheme shown in Fig. 1.

Here 0 and 1 mark the ground and the excited state of the molecule in conformation “0,” and 2 and 3 mark the ground and the excited states of the molecule in conformation “2.”  $k_0$  and  $k_2$  are rates of light absorption,  $G_1$  and  $G_3$  are rates of light emission in conformations “0” and “2,” and  $A$  and  $a$  are rates of interconformational transitions.

The number of photons emitted in each time interval of duration  $T$  will fluctuate because of the random character of photon creation instants. It is obvious that the number of emitted photons exceeds the number of photoelectric pulses created in a photomultiplier tube (PMT), i.e., detected events. In fact, the distribution function  $w'_N(T)$  of emitted photons, the distribution function  $w'_N(T)$  of photons arrived at the PMT, and, finally, the distribution function  $w_N(T)$  of photoelectric pulses created in the PMT are different. A relation between  $w''_N(T)$  and  $w'_N(T)$  was found in Refs. [25,26]. The expression for  $w'_N(T)$  can be calculated if we are able to calculate the expression for  $w''_N(T)$ . A relation between moments of the distributions  $w'_N(T)$  and  $w_N(T)$  was found by introducing a coefficient  $\eta$  of the quantum efficiency of the PMT [19,21].

Another approach for finding a relation between  $w'_N(T)$  and  $w_N(T)$  was used in Ref. [28]. A molecule and PMT were considered as two parts of the united dynamical system in which the PMT is characterized by the probability  $\alpha$  of photoeffect and by dead time  $1/\beta$ . The theory presented in Ref. [28] enabled one to find relations between  $w'_N(T)$  and  $w_N(T)$  for “fast,” “moderately fast,” and “slow” PMTs. The distribution of detected events depended on both rate constants of the molecule and rate constants  $\alpha$  and  $\beta$  of the PMT. For a “fast” PMT we have found the following relation:  $w_N(T) \cong w'_N(T)$ . Then, the distribution of detected events in fluorescence of a single molecule having only one conformation can be described by the following expression [28]:

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

$$w_0(T) = \frac{1}{\tau_0} \int_0^\infty \left[ 1 - \int_0^{T+t} s(x) dx \right] dt. \quad (2b)$$

The distribution is expressed via a single function,  $s(t)$ . Here  $s(\lambda) = s(i\omega) = \int_0^\infty s(t) e^{i(\omega+i0)t} dt$  is the Laplace transform of the start-stop correlator. The function  $[s(\lambda)^N]_t$  means the inverse Laplace transformation of  $s(\lambda)^N$ . The function  $s(t)$  describes the correlation between two consequently created photoelectric pulses. Therefore it was called the photoelectric start-stop correlator because

$$dS(t) = s(t) dt \quad (3)$$

describes the probability of finding the second event in the time interval  $(t, t+dt)$ , if the preceding event was detected at  $t=0$ . Hence,  $s(t)$  describes the density of the probability of finding two adjacent photoelectric pulses separated by time interval  $t$  (waiting time distribution). The constant

$$\tau_0 = \int_0^\infty \left[ 1 - \int_0^t s(x) dx \right] dt = \int_0^\infty t s(t) dt \quad (4)$$

determines an average time interval between adjacent events.

The start-stop correlator  $s(t)$  can be found from dynamical equations for the system [23,25,26,28]. Therefore, one can suppose that if we know dynamical equations for the molecule

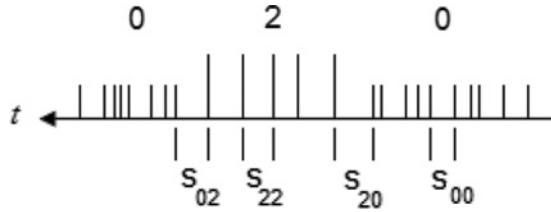


FIG. 2. Sequence of detected events. Random time moments of detected events of 0 type are shown by short vertical segments and events of 2 type by long vertical segments.

having two conformations, we can find the start-stop correlator  $s(t)$  and use Eq. (2a). However, this assumption will be wrong.

As a matter of fact, the molecule described by the energy scheme shown in Fig. 1 has two electronic transitions,  $1 \rightarrow 0$  and  $3 \rightarrow 2$ , accompanied by photon emission. We shall call photons emitted from conformation “0” and “2” as photons of 0 and 2 type. Therefore the PMT will detect events of 0 and 2 type. Schematically the situation looks as Fig. 2 shows.

In accordance with Fig. 2 there are four types of adjacent events. Four start-stop correlators  $s_{\alpha\beta}(t)$  in which  $\alpha$  and  $\beta$  can be 0 or 2 form a matrix. They are shown in Fig. 2. Hence, instead of Eq. (3) we have the following equation in the matrix form:

$$dS_{\alpha\beta}(t) = s_{\alpha\beta}(t) dt. \quad (5)$$

Here  $dS_{\alpha\beta}(t)$  determines the probability of finding an event of  $\alpha$  type in time interval  $(t, t + dt)$ , if the preceding event of  $\beta$  type was detected at  $t = 0$ .

If events of 0 and 2 type differ by some physical parameter, for instance by polarization, we can detect events solely of one type. Then short or long vertical segments will be absent in Fig. 2. and the matrix  $s_{\alpha\beta}(t)$  is reduced to a single start-stop correlator, say  $s_{00}(t)$ . In this case we may use Eq. (2a) with  $s(t) = s_{00}(t)$ . However, if events of 0 and 2 types are indistinguishable, we are forced to use whole matrix  $s_{\alpha\beta}(t)$ . In this case Eq. (2a) should be substituted by another expression. This expression is derived in Appendix A.

### III. MATRIX FOR THE START-STOP CORRELATORS

In “fast” PMT, times  $1/\alpha$  and  $1/\beta$  are shorter as compared with the average time of the order of  $1/k$  between adjacent absorption events. In this case, the distribution of photoelectric pulses created in the PMT is similar to the distribution of photons arrived at the PMT [28]. However, the distribution of photons arrived at the PMT can be calculated if we know the losses of fluorescence photons [25,26]. Therefore our task is reduced to calculating the distribution of emitted photons. This distribution is determined by quantum dynamics of a single molecule excited by cw-laser light. Dynamics of the molecule described by the energy scheme shown in Fig. 1 are determined by the following set of equations:

$$\begin{aligned} \dot{\rho}_0 &= -(k_0 + A)\rho_0 + G_1\rho_1 + a\rho_2, \\ \dot{\rho}_1 &= k_0\rho_0 - G_1\rho_1, \\ \dot{\rho}_2 &= A\rho_0 - (k_2 + a)\rho_2 + G_3\rho_3, \\ \dot{\rho}_3 &= k_2\rho_2 - G_3\rho_3. \end{aligned} \quad (6)$$

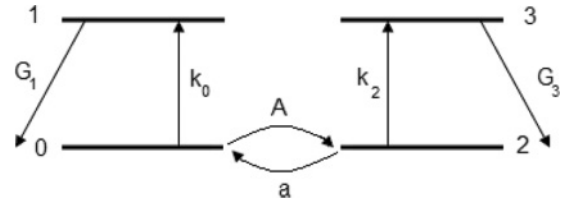


FIG. 3. Quantum states and transitions in an open system from which photons of two types can leave.

Here  $\rho_j$  is the probability of finding the molecule in a quantum state  $j$ . The physical meaning of all rate constants has already been explained.

The set of Eq. (6) describes a so-called closed system in which full probability is conserved because  $\dot{\rho}_0 + \dot{\rho}_2 + \dot{\rho}_1 + \dot{\rho}_3 = 0$ . However, start-stop correlators can be found from a set of equations for a so-called open system in which fluorescence photons leave the system. Therefore, full probability in the open system is not conserved. The energy scheme with possible transitions for the open system from which photons of two types leave looks as Fig. 3 shows.

Here inclined arrows show the photons going to the PMT. The set of equations for this scheme looks as follows:

$$\begin{aligned} \dot{W}_0 &= -(k_0 + A)W_0 + aW_2, \\ \dot{W}_1 &= k_0W_0 - G_1W_1, \\ \dot{W}_2 &= AW_0 - (k_2 + a)W_2, \\ \dot{W}_3 &= k_2W_2 - G_3W_3. \end{aligned} \quad (7)$$

Here  $W_j$  is the probability of finding an open system in a quantum state  $j$ . We find from Eq. (7) the following equation:

$$\sum_{j=0}^3 \dot{W}_j = -G_1W_1 - G_3W_3. \quad (8)$$

The terms  $G_1W_1$  and  $G_3W_3$  describe the rate of counted events of 0 and 2 types, respectively.

If an event of 0 type happened at  $t = 0$ , the system reached state 0. Therefore

$$W_0(0) = 1, W_2(0) = W_1(0) = W_3(0) = 0. \quad (9)$$

By carrying out the Laplace transformation in Eq. (7) we arrive at the following set of algebraic equations:

$$\begin{aligned} (\lambda - k_0 - A)W'_0 + aW'_2 &= -1, \\ k_0W'_0 + (\lambda - G_1)W'_1 &= 0, \\ AW'_0 + (\lambda - k_2 - a)W'_2 &= 0, \\ k_2W'_2 + (\lambda - G_3)W'_3 &= 0. \end{aligned} \quad (10)$$

The Laplace transform of the start-stop correlator  $s_{00}$  corresponding to two adjacent events of 0 type looks as follows:

$$s_{00}(\lambda) = G_1W'_1(\lambda). \quad (11)$$

The Laplace transform of the start-stop correlator  $s_{20}$  corresponds to the situation in which after an event of 0 type

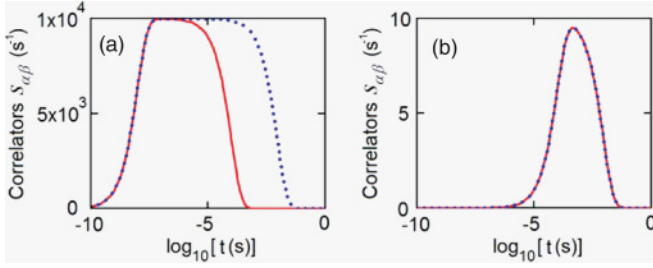


FIG. 4. (Color online) Four start-stop correlators for the molecule with two conformations. (a)  $s_{00}$  (solid line),  $100s_{22}$  (dotted line); (b)  $50s_{20}$  (solid line),  $s_{02}$  (dotted line)

the next event is of 2 type. This correlator is described by the following equation:

$$s_{20}(\lambda) = G_3 W_3'(\lambda). \quad (12)$$

Consider a situation in which the molecule reached state 2, i.e., the molecule emitted photons of 2 type at  $t = 0$ . This fact corresponds to the following initial condition:

$$W_2(0) = 1, W_0(0) = W_1(0) = W_3(0) = 0. \quad (13)$$

By carrying out the Laplace transformation in Eq. (7) we arrive at the following set of algebraic equations:

$$\begin{aligned} (\lambda - k_0 - A)W_0'' + aW_2'' &= 0, \\ k_0W_0'' + (\lambda - G_1)W_1'' &= 0, \\ AW_0'' + (\lambda - k_2 - a)W_2'' &= -1, \\ k_2W_2'' + (\lambda - G_3)W_3'' &= 0. \end{aligned} \quad (14)$$

The Laplace transform of the start-stop correlator  $s_{22}$  corresponding to two adjacent events of 2 type looks as follows:

$$s_{22}(\lambda) = G_3 W_3''(\lambda). \quad (15)$$

The Laplace transform of the start-stop correlator  $s_{02}$  corresponds to the situation in which after an event of 2 type the next event is of 0 type. This correlator is described by the following equation:

$$s_{02}(\lambda) = G_1 W_1'(\lambda). \quad (16)$$

Laplace transforms marked by one prime and two primes can be found from Eqs. (10) and (14) with the same determinant but with a different right-hand side.

By solving the set of Eqs. (10) and (14) we arrive at the following matrix for the start-stop correlator:

$$\begin{aligned} \hat{s}(\lambda) &= \begin{pmatrix} s_{00}(\lambda) & s_{02}(\lambda) \\ s_{20}(\lambda) & s_{22}(\lambda) \end{pmatrix} \\ &= \frac{1}{(G_1 - \lambda)(G_3 - \lambda)(\lambda_0 - \lambda)(\lambda_2 - \lambda)} \\ &\quad \times \begin{pmatrix} \bar{s}_{00}(\lambda) & \bar{s}_{02}(\lambda) \\ \bar{s}_{20}(\lambda) & \bar{s}_{22}(\lambda) \end{pmatrix}. \end{aligned} \quad (17)$$

Here

$$\begin{aligned} \bar{s}_{00}(\lambda) &= (G_3 - \lambda)G_1k_0(k_2 + a - \lambda), \\ \bar{s}_{02}(\lambda) &= (G_3 - \lambda)G_1k_0a, \\ \bar{s}_{20}(\lambda) &= (G_1 - \lambda)G_3k_2A, \\ \bar{s}_{22}(\lambda) &= (G_1 - \lambda)G_3k_2(k_0 + A - \lambda), \end{aligned} \quad (17a)$$

and roots of the equation  $\text{Det}_s = 0$  look as follows:

$$\begin{aligned} \lambda_{1,3} &= G_{1,3}, \quad \lambda_{0,2} = \frac{k_0 + A + k_2 + a}{2} \\ &\quad \pm \sqrt{\left(\frac{k_0 + A - k_2 - a}{2}\right)^2 + aA}. \end{aligned} \quad (18)$$

After an inverse Laplace transformation we find the following expressions for the start-stop correlators:

$$\begin{aligned} s_{00}(t) &= \frac{G_1k_0(k_2 + a - \lambda_0)}{(G_1 - \lambda_0)(\lambda_2 - \lambda_0)}e^{-\lambda_0 t} + \frac{G_1k_0(k_2 + a - \lambda_2)}{(G_1 - \lambda_2)(\lambda_0 - \lambda_2)}e^{-\lambda_2 t} \\ &\quad + \frac{G_1k_0(k_2 + a - G_1)}{(\lambda_0 - G_1)(\lambda_2 - G_1)}e^{-G_1 t}, \end{aligned} \quad (19a)$$

$$\begin{aligned} s_{20}(t) &= k_2AG_3 \left[ \left( \frac{e^{-\lambda_0 t}}{G_3 - \lambda_0} - \frac{e^{-\lambda_2 t}}{G_3 - \lambda_2} \right) \frac{1}{(\lambda_2 - \lambda_0)} \right. \\ &\quad \left. + \frac{e^{-G_3 t}}{(\lambda_0 - G_3)(\lambda_2 - G_3)} \right], \end{aligned} \quad (19b)$$

$$\begin{aligned} s_{22}(t) &= \frac{G_3k_2(k_0 + A - \lambda_0)}{(G_3 - \lambda_0)(\lambda_2 - \lambda_0)}e^{-\lambda_0 t} + \frac{G_3k_2(k_0 + A - \lambda_2)}{(G_3 - \lambda_2)(\lambda_0 - \lambda_2)}e^{-\lambda_2 t} \\ &\quad + \frac{G_3k_2(k_0 + A - G_3)}{(\lambda_0 - G_3)(\lambda_2 - G_3)}e^{-G_3 t}, \end{aligned} \quad (19c)$$

$$\begin{aligned} s_{02}(t) &= k_0aG_1 \left[ \left( \frac{e^{-\lambda_0 t}}{G_1 - \lambda_0} - \frac{e^{-\lambda_2 t}}{G_1 - \lambda_2} \right) \frac{1}{(\lambda_2 - \lambda_0)} \right. \\ &\quad \left. + \frac{e^{-G_1 t}}{(\lambda_0 - G_1)(\lambda_2 - G_1)} \right]. \end{aligned} \quad (19d)$$

The correlators calculated with the help of these formulas for the following set of parameters,

$$\begin{aligned} k_0 &= 10^4 s^{-1}, \quad k_2 = 10^2 s^{-1}, \quad a = 10 s^{-1}, \quad A = 20 s^{-1}, \\ G_1 &= G_3 = 10^8 s^{-1}, \end{aligned}$$

are shown in Fig. 4.

Consider first diagonal elements  $s_{00}$  and  $s_{22}$  of the matrix for the start-stop correlators. In accordance with Fig. 4(a) we may conclude that the correlator  $s_{00}$  equals zero at  $t > 10^{-3}$  s, whereas the correlator  $s_{22}$  is nonvanishing in this time region. However, such a conclusion will not be true. This proves Fig. 5.

Both the correlator  $s_{00}$  and the correlator  $s_{22}$  are nonvanishing at  $t > 10^{-3}$  s. However, they differ strongly by value in this time domain. The probability of finding two adjacent events of 0 type separated by  $t > 10^{-3}$  s is  $5 \times 10^3$  times less as compared to two adjacent events of 2 type. On the contrary, the probability of finding two adjacent events of 0 type separated by  $t < 10^{-3}$  s is  $k_0/k_2 = 100$  times larger as compared to two adjacent events of 2 type.

The correlators  $s_{20}$  and  $s_{02}$  differ from zero in the same time domain as Fig. 4(b) shows. However, the correlator  $s_{02}$  is  $G_1k_0a/G_3k_2A = 50$  times larger as compared to the correlator  $s_{20}$ . This ratio is already seen from Eqs. (19b) and (19d).

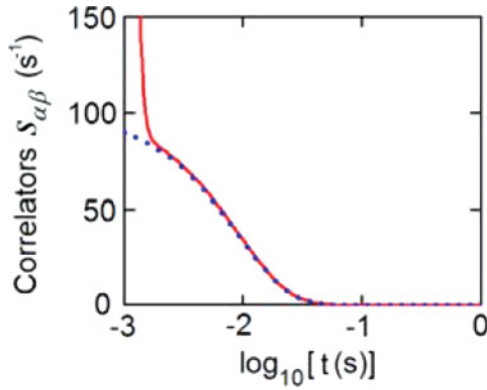


FIG. 5. (Color online) Comparison of the correlator  $s_{00}$  multiplied by  $5 \times 10^3$ , (solid line) with the correlator  $s_{22}$  (dotted line) at long time.

After integration of Eq. (5) we arrive at the following functions of time  $t_0$ :

$$S_{\alpha\beta}(t_0) = \int_0^{t_0} s_{\alpha\beta}(t) dt. \quad (20)$$

They determine the probability of finding an event of  $\alpha$  type prior to time moment  $t_0$  if the preceding event of  $\beta$  type happened at  $t = 0$ . It is obvious that the function

$$S_{\beta}(t_0) = \int_0^{t_0} \sum_{\alpha} s_{\alpha\beta}(t) dt \quad (21)$$

determines the probability of finding the second event of any type prior to time moment  $t_0$  if the preceding event of  $\beta$  type happened at  $t = 0$ . By using Eqs. (19a)–(19d) we find the following relation:

$$S_{\beta}(\infty) = 1. \quad (22)$$

#### IV. MATRIX OF FULL CORRELATOR

So far we have considered solely start-stop correlators, i.e., pairs of adjacent events separated by time interval  $t$ . However, one can consider pairs of any events separated by time interval  $t$  not taking into account how many events happened between the two events of this pair. Then  $dP(t) = p(t) dt$  determines the probability of finding an event in time interval  $(t, t + dt)$  after the first event happened at  $t = 0$ . Correlation of events in such a pair has been called full correlator  $p(t)$  [3,7]. Full correlator  $p(t)$  plays an important role in the fluorescence of single molecules. For fluorescence from the molecule without conformational changes, the autocorrelation function  $g^{(2)}(t)$  can be expressed via  $p(t)$  as follows [22,29]:

$$g^{(2)}(T) = \frac{\langle I(t)I(t+T) \rangle}{\langle I(t) \rangle^2} = \frac{p(T)}{p(\infty)}. \quad (23)$$

It is obvious that if fluorescence consists of photons of 0 and 2 types we can consider four full correlators  $p_{\alpha\beta}(t)$ . They correspond to four possible pairs of events. Full correlators can be found from the set of Eq. (6) for a closed system.

If an event of 0 type happened at  $t = 0$  the probability of finding the molecule in state 0 equals 1. Therefore we can write:

$$\rho_0(0) = 1, \quad \rho_2(0) = \rho_1(0) = \rho_3(0) = 0. \quad (24)$$

By carrying out the Laplace transformation in Eq. (6) we arrive at the following set of algebraic equations:

$$\begin{aligned} (\lambda - k_0 - A)\rho'_0 + G_1\rho'_1 + a\rho'_2 &= -1, \\ k_0\rho'_0 + (\lambda - G_1)\rho'_1 &= 0, \\ A\rho'_0 + (\lambda - k_2 - a)\rho'_2 + G_3\rho'_3 &= 0, \\ k_2\rho'_2 + (\lambda - G_3)\rho'_3 &= 0. \end{aligned} \quad (25)$$

Laplace transform of the correlator  $p_{00}$  corresponding to two events of 0 type is given by

$$p_{00}(\lambda) = G_1\rho'_1(\lambda). \quad (26)$$

The correlator  $p_{20}$  corresponds to the situation in which the first event was of 0 type and the second event was of 2 type. Therefore the Laplace transform of this correlator is given by the following formula:

$$p_{20}(\lambda) = G_3\rho'_3(\lambda). \quad (27)$$

If an event of 2 type happened at  $t = 0$  the probability of finding the molecule in state 2 equals 1. Therefore we can write:

$$\rho_2(0) = 1, \quad \rho_0(0) = \rho_1(0) = \rho_3(0) = 0. \quad (28)$$

By carrying out the Laplace transformation in Eq. (6) we arrive at the following set of algebraic equations:

$$\begin{aligned} (\lambda - k_0 - A)\rho''_0 + G_1\rho''_1 + a\rho''_2 &= 0, \\ k_0\rho''_0 + (\lambda - G_1)\rho''_1 &= 0, \\ A\rho''_0 + (\lambda - k_2 - a)\rho''_2 + G_3\rho''_3 &= -1, \\ k_2\rho''_2 + (\lambda - G_3)\rho''_3 &= 0. \end{aligned} \quad (29)$$

The correlator  $p_{22}$  corresponds to two events of 2 type. Its Laplace transform is given by

$$p_{22}(\lambda) = G_3\rho''_3(\lambda). \quad (30)$$

The correlator  $p_{02}$  corresponds to the situation in which the first event was of 2 type and the second event was of 0 type. Therefore the Laplace transform of this correlator is given by the following formula:

$$p_{02}(\lambda) = G_1\rho''_1(\lambda). \quad (31)$$

Equations (25) and (29) have the same determinant but a different right-hand side in accordance with different initial conditions.

By solving Eqs. (25) and (29) and by using Eqs. (26) and (27), and Eqs. (30) and (31), we find four elements of the

matrix  $\hat{p}$  for the full correlator:

$$\hat{p}(\lambda) = \begin{pmatrix} p_{00}(\lambda) & p_{02}(\lambda) \\ p_{20}(\lambda) & p_{22}(\lambda) \end{pmatrix} = \frac{1}{-\lambda(\Lambda_1 - \lambda)(\Lambda_2 - \lambda)(\Lambda_3 - \lambda)} \times \begin{pmatrix} \bar{p}_{00}(\lambda) & \bar{p}_{02}(\lambda) \\ \bar{p}_{20}(\lambda) & \bar{p}_{22}(\lambda) \end{pmatrix}. \quad (32)$$

Here

$$\begin{aligned} \bar{p}_{00}(\lambda) &= \bar{s}_{00}(\lambda) - k_0 k_2 G_1 G_3, & \bar{p}_{02}(\lambda) &= \bar{s}_{02}(\lambda), \\ \bar{p}_{20}(\lambda) &= \bar{s}_{20}(\lambda), & \bar{p}_{22}(\lambda) &= \bar{s}_{22}(\lambda) - k_0 k_2 G_1 G_3. \end{aligned} \quad (32a)$$

Here  $0, \Lambda_1, \Lambda_2,$  and  $\Lambda_3$  are roots of the equation  $\text{Det}_\rho = 0$ , in which  $\text{Det}_\rho$  is the determinant of Eqs. (25) and (29). This determinant can be written in the following form:

$$\begin{aligned} \text{Det}_\rho &= \text{Det}_s - G_1(\lambda - G_3)k_0(\lambda - k_2 - a) - G_3 \\ &\times (\lambda - G_1)k_2(\lambda - k_0 - A) + k_0 k_2 G_1 G_3. \end{aligned} \quad (33)$$

Here  $\text{Det}_s$  is the determinant of Eqs. (10) and (14) for finding the start-stop correlator. It is given by the following expression:

$$\text{Det}_s = (G_1 - \lambda)(G_3 - \lambda)(\lambda_0 - \lambda)(\lambda_2 - \lambda). \quad (34)$$

By using Eqs. (32) and (17) we arrive at the following relation between matrices  $\hat{p}$  and  $\hat{s}$  for the full correlator and the start-stop correlator:

$$\hat{p}(\lambda) = \frac{\hat{s}(\lambda)}{1 - \hat{s}(\lambda)}. \quad (35)$$

By carrying out an inverse Laplace transformation in Eq. (35) we arrive at the following equation for the matrices  $\hat{p}(t)$  and  $\hat{s}(t)$ :

$$\hat{p}(t) = \hat{s}(t) + \int_0^t \hat{s}(t-x)\hat{p}(x) dx. \quad (36)$$

By carrying out an inverse Laplace transformation of matrix elements in Eq. (32) we find the following expression

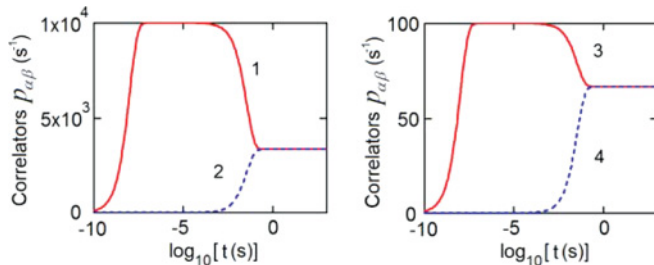


FIG. 6. (Color online) Full correlators for fluorescence of the molecule with two conformations and for the following set of parameters:  $k_0 = 10^4 \text{ s}^{-1}$ ,  $k_2 = 10^2 \text{ s}^{-1}$ ,  $a = 10 \text{ s}^{-1}$ ,  $A = 20 \text{ s}^{-1}$ ,  $G_1 = G_3 = 10^8 \text{ s}^{-1}$ ;  $p_{00}(1), p_{02}(2), p_{22}(3), p_{20}(4)$ .

for  $p_{\alpha\beta}(t)$ :

$$\begin{aligned} p_{\alpha\beta}(t) &= \frac{\bar{p}_{\alpha\beta}(0)}{\Lambda_1 \Lambda_2 \Lambda_3} + \frac{\bar{p}_{\alpha\beta}(\Lambda_1) e^{-\Lambda_1 t}}{-\Lambda_1(\Lambda_2 - \Lambda_1)(\Lambda_3 - \Lambda_1)} \\ &+ \frac{\bar{p}_{\alpha\beta}(\Lambda_2) e^{-\Lambda_2 t}}{-\Lambda_2(\Lambda_1 - \Lambda_2)(\Lambda_3 - \Lambda_2)} \\ &+ \frac{\bar{p}_{\alpha\beta}(\Lambda_3) e^{-\Lambda_3 t}}{-\Lambda_3(\Lambda_1 - \Lambda_3)(\Lambda_2 - \Lambda_3)}. \end{aligned} \quad (37)$$

These full correlators calculated for a set of parameters used also in Fig. 4 for the start-stop correlators are shown in Fig. 6.

In contrast to start-stop correlators, full correlators approach constant values at long times. These values are determined by the following formulas:

$$\begin{aligned} p_{00}(\infty) &= p_{02}(\infty) = \frac{G_1 G_3 k_0 a}{\Lambda_1 \Lambda_2 \Lambda_3}, \\ p_{20}(\infty) &= p_{22}(\infty) = \frac{G_1 G_3 k_2 A}{\Lambda_1 \Lambda_2 \Lambda_3}. \end{aligned} \quad (38)$$

Here  $\Lambda_1 \Lambda_2 \Lambda_3 = G_1 G_3(a + A) + G_1 k_2 A + G_3 k_0 a$ . Decrease of the correlators  $p_{00}(t), p_{22}(t)$  at short times of the order of  $1/G_1, 1/G_3 \cong 10^{-8} \text{ s}$  reveals antibunching of events. Decrease of the correlators  $p_{00}(t), p_{22}(t)$  at long times of the order of  $1/A, 1/a$  describes bunching of events. The correlators approach  $p_{00}(\infty) = p_{02}(\infty)$  and  $p_{20}(\infty) = p_{22}(\infty)$  at long times. Bunching of events is well pronounced at  $k_0/k_2 = 100$ , used in Fig. 6.

## V. DISTRIBUTION OF PHOTONS

If fluorescence consists of photons of two types we cannot use Eqs. (2a) and (2b) because we have four start-stop correlators  $s_{\alpha\beta}(t)$ . Therefore, derivation of the expression for the distribution function  $w_N(T)$  should be carried out anew.

Operating with photons of two types presents a new problem. Indeed, if a photon was detected in time interval  $T$  we do not know exactly what type of photon this is. We can only say the photon could be of 0 type with the probability  $n_0$  or of 2 type with the probability  $n_2$ . Obviously,  $n_0 + n_2 = 1$ .

The probabilities  $n_0$  and  $n_2$  must depend on both rates  $k_0$  and  $k_2$  of events and the duration that the molecule stays in conformations 0 and 2. Intervals of staying in conformations 0 and 2 are seen in Fig. 2. Their average durations are determined by values  $1/A$  and  $1/a$ . Allowing for these reasons we take the probabilities in the following form:

$$\begin{aligned} n_0 &= \frac{k_0/A}{k_0/A + k_2/a} = \frac{k_0 a}{k_0 a + k_2 A}, \\ n_2 &= \frac{k_2 A}{k_0 a + k_2 A}. \end{aligned} \quad (39)$$

It is obvious that the following scalar function,

$$s(t) = \sum_{\alpha,\beta} s_{\alpha\beta}(t) n_\beta = (1, 1) \hat{s}(t) \begin{pmatrix} n_0 \\ n_2 \end{pmatrix} = \langle \vec{1} | \hat{s}(t) | \vec{n} \rangle, \quad (40)$$

determines the density of the probability of finding an event of any type at time  $t$  if the preceding event of any type happened

at  $t = 0$ . The preceding event can be of 0 type or of 2 type with the probability  $n_0$  or  $n_2$ . Therefore the scalar function

$$S(t_0) = \int_0^{t_0} s(t) dt, \quad (41)$$

determines the probability of finding an event of any type prior to time moment  $t_0$  if the preceding event of any type happened at  $t = 0$ . By using Eqs. (21) and (22) we arrive at the following formula:

$$S(\infty) = 1, \quad (42)$$

which expresses the law of conservation of total probability.

In accordance with Eq. (A25) of Appendix A the distribution of photons of any type in time interval  $T$  is given by the following expression:

$$w_N(T) = \frac{1}{\tau_0} \langle \bar{1} | \int_0^T dx_N \int_0^{x_N} dx_{N-1} \cdots \int_0^{x_2} dt_1 \hat{s}(x_N - x_{N-1}) \times \hat{s}(x_{N-1} - x_{N-2}) \cdots \hat{s}(x_2 - x_1) \hat{w}(x_1) - \int_0^T dx \int_0^x dx_N \int_0^{x_N} dx_{N-1} \cdots \int_0^{x_2} dx_1 \hat{s}(x - x_N) \times \hat{s}(x_N - x_{N-1}) \cdots \hat{s}(x_2 - x_1) \hat{w}(x_1) | \vec{n} \rangle, N \geq 1 \quad (43)$$

$$w_0(T) = \frac{1}{\tau_0} \int_0^\infty \left[ 1 - \int_0^{T+t_0} s(t) dt \right] dt_0. \quad (43a)$$

Here

$$\tau_0 = \int_0^\infty [1 - S(t)] dt = \int_0^\infty ts(t) dt \quad (44)$$

is an average time interval between photons;  $s(t)$  is determined by Eq. (40). The matrix  $\hat{w}(x)$  looks as follows:

$$\hat{w}(x) = \hat{S}(\infty) - \hat{S}(x). \quad (45)$$

Existence of  $N$ -fold integrals in Eq. (43) is a serious obstacle for numerical calculation. However we can solve this problem by using the method developed in Refs. [23,25,26]. Let us carry out a Laplace transformation  $\int_0^\infty dt F(t) e^{i(\omega+i0)t} = F(i\omega) = F(\lambda)$  of both sides of Eq. (43). We arrive at the following equation:

$$w_N(\lambda) = \frac{1}{-\lambda \tau_0} \langle \bar{1} | [\hat{s}(\lambda)^{N-1} - \hat{s}(\lambda)^N] \hat{w}(\lambda) | \vec{n} \rangle. \quad (46)$$

The following relation,

$$\hat{S}(\infty) | \vec{n} \rangle = | \vec{n} \rangle, \quad (47)$$

is shown in Appendix B. Therefore, by carrying out the Laplace transformation of both sides of Eq. (45) we arrive at the following equation:

$$\hat{w}(\lambda) | \vec{n} \rangle = \frac{1 - \hat{s}(\lambda)}{-\lambda} | \vec{n} \rangle. \quad (48)$$

After substitution of Eq. (48) into Eq. (46) we find

$$w_N(\lambda) = \frac{1}{\lambda^2 \tau_0} \langle \bar{1} | \hat{s}(\lambda)^{N-1} - 2\hat{s}(\lambda)^N + \hat{s}(\lambda)^{N+1} | \vec{n} \rangle. \quad (49)$$

After an inverse Laplace transformation in Eq. (49) we arrive at the following final expression for the photon distribution

function:

$$w_N(T) = \frac{1}{\tau_0} \int_0^T (T-t) \langle \bar{1} | \{ [\hat{s}(\lambda)^{N-1}]_t - 2[\hat{s}(\lambda)^N]_t + [\hat{s}(\lambda)^{N+1}]_t \} | \vec{n} \rangle dt, (N \geq 1). \quad (50)$$

Equation (50) is an analog of Eq. (2a). However, Eq. (50) can be used for calculation of photon distribution in fluorescence with several types of photons.

The function  $\langle \bar{1} | [\hat{s}(\lambda)^{N+1}]_t | \vec{n} \rangle$  depends on time; it can be written in the following form:

$$\langle \bar{1} | [\hat{s}(\lambda)^{N+1}]_t | \vec{n} \rangle = \int_0^t dt_N \int_0^{t_N} dt_{N-1} \cdots \times \int_0^{t_2} dt_1 f(t, t_N, t_{N-1}, \dots, t_1). \quad (51)$$

Here  $f$  is PDF, which has already been discussed in the Introduction. For the molecule with several conformational forms PDF looks as follows:

$$f(t, t_N, t_{N-1}, \dots, t_1) = \langle \bar{1} | \hat{s}(t - t_N) \hat{s}(t_N - t_{N-1}) \cdots \times \hat{s}(t_2 - t_1) \hat{s}(t_1) | \vec{n} \rangle. \quad (52)$$

The function  $\langle \bar{1} | [\hat{s}(\lambda)^{N+1}]_t | \vec{n} \rangle$  has a simple physical meaning. It determines the probability of finding  $N$  events in time interval  $(0, t)$ . The interval is open and closed by an event of any type. Equation (50) describes so-called time-averaged probability and Eq. (51) describes so-called event-averaged probability [30]. The function  $f(t, t_N, t_{N-1}, \dots, t_1)$  is not factorized. However this fact does not stem from some kind of memory. It is a consequence of the matrix character of the start-stop correlator.

Equation (50) differs considerably from Eq. (2a) for fluorescence with a single type of emitted photon. However, Eqs. (43a) and (44), and Eqs. (2b) and (4) look similar to each other. The difference stems from the equation  $s(t) = \sum_{\alpha, \beta} s_{\alpha\beta}(t) n_\beta$  for the start-stop correlator. This very sum must be used in Eqs. (43a) and (44). The sum includes four start-stop correlators whereas  $s(t)$  in Eqs. (2b) and (4) includes only one function, say  $s_{00}(t)$ .

The method developed in Refs. [23,25,26] for calculation of  $w_N(T)$  consists in expression of the function  $\langle \bar{1} | [\hat{s}(\lambda)^{N+1}]_t | \vec{n} \rangle$  via the product of Poisson functions without transition to Eq. (51). However substitution of the function  $s(t)$  by the matrix  $\hat{s}(t)$  creates a new problem because we have to calculate the  $N$ th degree of the matrix  $\hat{s}(\lambda)$ . The difficulties can be overcome with the help of the Silvester formula for the degree of a matrix. Calculation of  $\hat{s}(\lambda)^N$  is presented in Appendix C.

Consider a single molecule in which interconformational transitions are two orders of magnitude less as compared with rates of photon emission. The photon distribution in fluorescence of such a molecule was considered by Gopich and Szabo [16] with the help of Eq. (1). Results of our calculation with the help of Eq. (50) in which the event-averaged probabilities  $\langle \bar{1} | [\hat{s}(\lambda)^N]_t | \vec{n} \rangle$  are determined by Eqs. (C26) and (C27) are shown in Fig. 7 by solid lines.

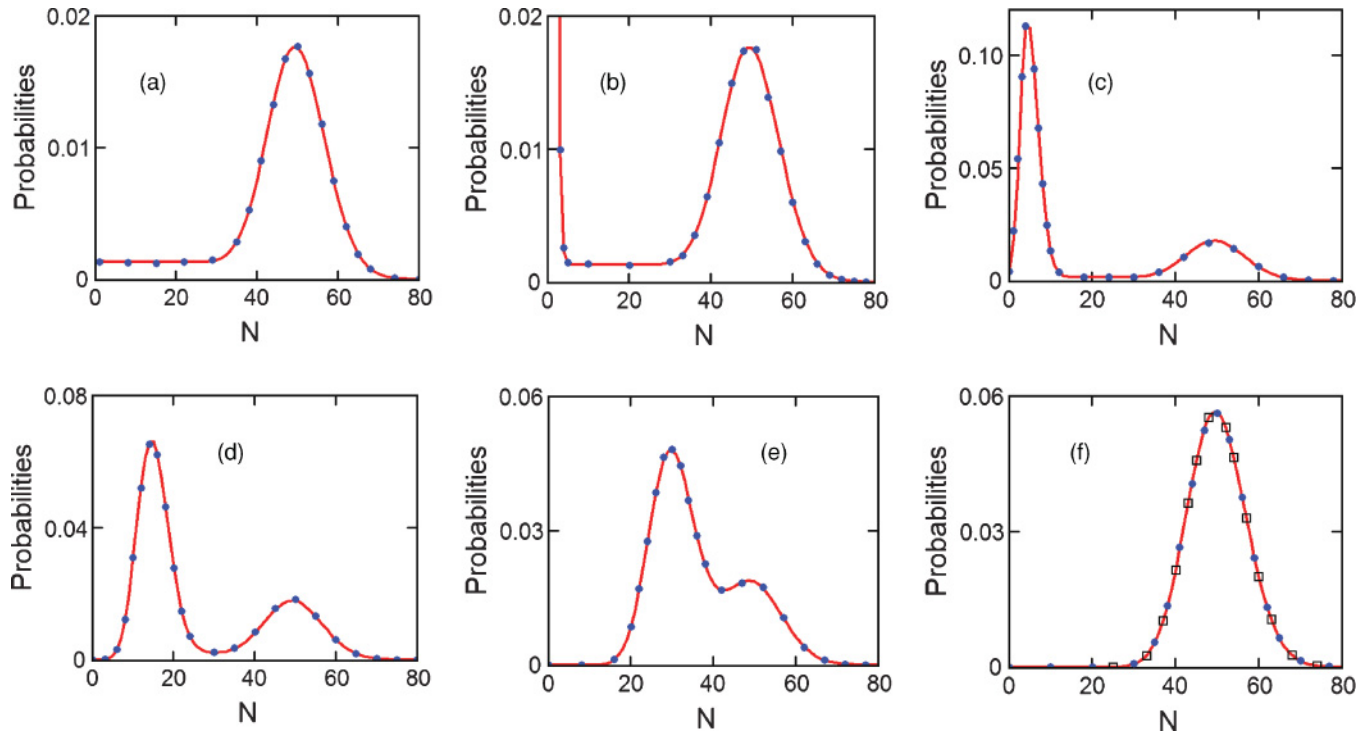


FIG. 7. (Color online) Distribution of photons  $w_N(5 \text{ ms})$  calculated with the help of Eq. (50), (solid lines) and by the Monte Carlo method (circles), at  $k_0 = 10^4 \text{ s}^{-1}$ ,  $A = 20 \text{ s}^{-1}$ ,  $a = 10 \text{ s}^{-1}$ , and  $G_1 = G_3 = 10^8 \text{ s}^{-1}$  and for various intensity of fluorescence from conformation 2: (a)  $k_2 = 0 \text{ s}^{-1}$ , (b)  $10^2 \text{ s}^{-1}$ , (c)  $10^3 \text{ s}^{-1}$ , (d)  $3 \times 10^3 \text{ s}^{-1}$ , (e)  $6 \times 10^3 \text{ s}^{-1}$ , and (f)  $10^4 \text{ s}^{-1}$ . Squares show Poisson distribution.

In this case of slow conformational changes our result coincides with the result obtained with the help of the Gopich and Szabo formula [16].

Figure 7(a) shows the distribution of events in fluorescence when the molecule in conformation 2 does not fluoresce. In this case we shall see on and off intervals as Fig. 8 shows. The distribution of events in Fig. 7(a) is of super-Poisson type, i.e., it is broader as compared with Poisson distribution. The distribution has a narrow peak and a broad wing extended to small values of  $N$ . Distributions of such type have been already discussed in Refs. [25,26] for three methods of photon counting. Appearance of a narrow peak and a broad wing can be easily explained with the help of Fig. 8.

Some intervals of time will fall into on intervals entirely. We will count many events in these intervals. These intervals form a narrow peak in the distribution function. However, some intervals will cover the end or the beginning of on intervals as Fig. 8 shows. We will count few events in these intervals. These intervals form a broad wing extended to small values of  $N$ .

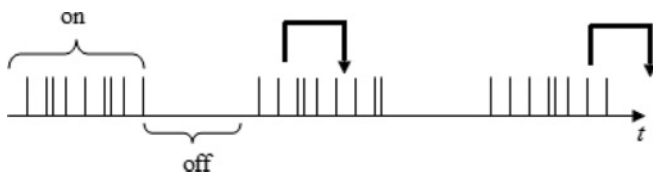


FIG. 8. Sequence of events in blinking fluorescence and two types of intervals of time in which events are counted.

If the molecule fluoresces in conformation 2, off intervals will be filled by photons. The distribution of events in such fluorescence is shown in Fig. 7. If intensity of fluorescence from the conformation 2 increases, the second peak at small values of  $N$  emerges. Maximum of this peak approximately equals  $k_2 T$ . For Fig. 7(d) we find the following position of the maximum:  $N_{\max} = k_2 T = 3 \times 10^3 \times 5 \times 10^{-3} = 15$ . At  $k_2 = k_0$  the distribution of events looks as Fig. 7(f) shows. It is of Poisson type as shown by squares in Fig. 7(f).

Consider now how the photon distribution presented in Fig. 7(c) is transformed if the frequency of interconformational jumps is increased and approaches the frequency of photon emission. This situation cannot be considered on the basis of the Gopich-Szabo formula. Results of our calculation are shown in Fig. 9.

In order to verify our calculations with the help of Eq. (50) we carried out independent calculations by the Monte Carlo method with the utilization of four constants:  $k_0 + A$ ,  $G_1$ ,  $k_2 + a$ , and  $G_3$ . Our Monte Carlo method of calculation was similar to that used by Budini [31] for calculation of the start-stop correlator.

The molecule leaves state 0 with the rate  $k_0 + A$  for state 2 or state 1. It reaches state 2 with the probability  $A/(k_0 + A)$  and state 1 with the probability  $k_0/(k_0 + A)$ . Leaving state 1, the molecule reaches state 0 with the rate  $G_1$ . By leaving state 2 with the rate  $k_2 + a$ , the molecule reaches state 0 with the probability  $a/(k_2 + a)$  or state 3 with the probability  $k_2/(k_2 + a)$ . Leaving state 3, the molecule reaches state 2 with the rate  $G_3$  and so on. By considering  $10^6$  of such steps we find the sequence of random events shown in Fig. 10.



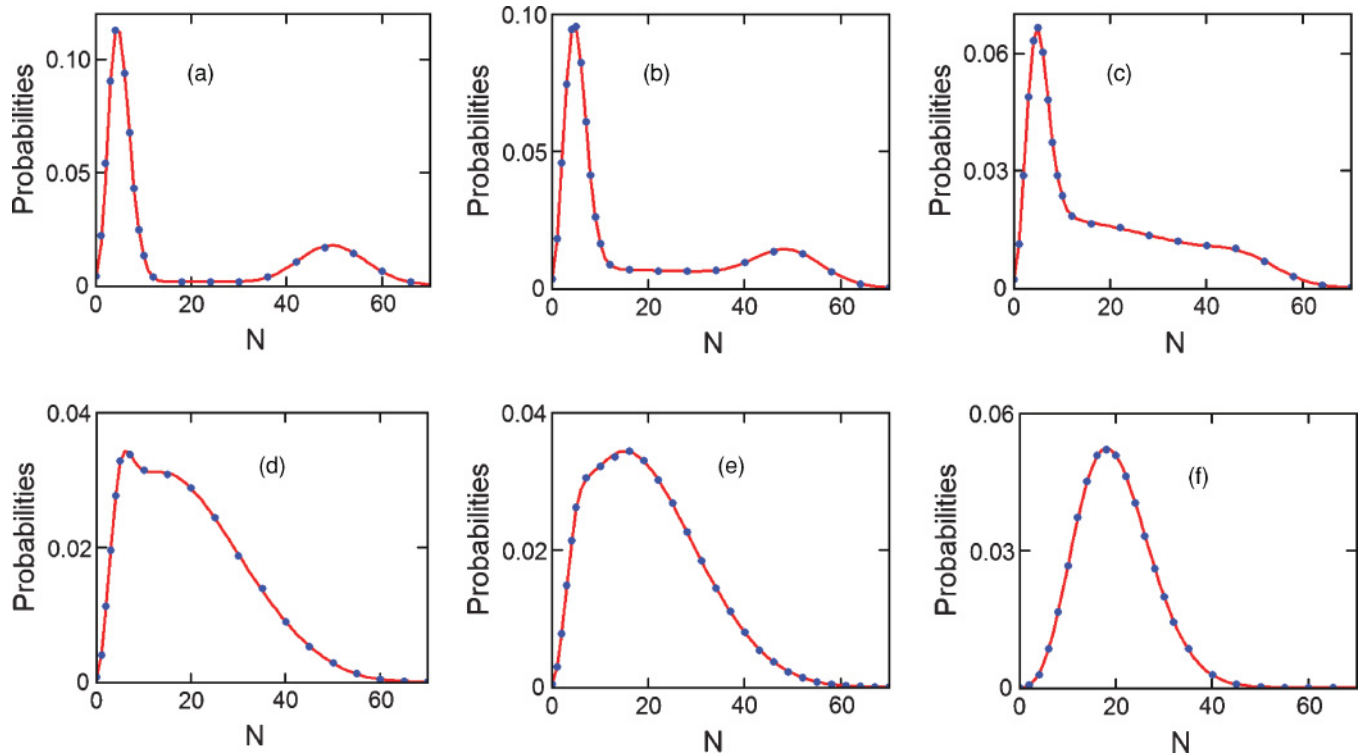


FIG. 9. (Color online) Changes in the photon distribution function  $w_N$  (5 ms) with an increase of the rate of interconformational transitions. (a)  $k_0 = 10^4 \text{ s}^{-1}$ ,  $k_2 = 10^3 \text{ s}^{-1}$ ,  $G_1 = G_3 = 10^8 \text{ s}^{-1}$ , and  $A = 20 \text{ s}^{-1}$ ,  $a = 10 \text{ s}^{-1}$ ; (b)  $A = 100 \text{ s}^{-1}$ ,  $a = 50 \text{ s}^{-1}$ ; (c)  $A = 300 \text{ s}^{-1}$ ,  $a = 150 \text{ s}^{-1}$ ; (d)  $A = 800 \text{ s}^{-1}$ ,  $a = 400 \text{ s}^{-1}$ ; (e)  $A = 10^3 \text{ s}^{-1}$ ,  $a = 5 \times 10^2 \text{ s}^{-1}$ ; (f)  $A = 3 \times 10^3 \text{ s}^{-1}$ ,  $a = 1.5 \times 10^3 \text{ s}^{-1}$ . Calculations were made with Eq. (50) (solid lines) and the Monte Carlo method (circles).

Intervals of 0 type with frequent events alternate intervals of 2 type with infrequent events as Fig. 10(a) shows. The duration of these intervals shown in Fig. 10(a) is much longer as compared with intervals between adjacent events. In this case frequent intraconformational jumps and infrequent interconformational jumps can be considered separately as Gopich and Szabo did. However, if the frequency of interconformational jumps increases we cannot consider intra- and

interconformational jumps separately. This is clearly seen in Fig. 10(f); it corresponds to the case in which the frequency of interconformational jumps is comparable with the frequency of intraconformational jumps in conformation 2.

The sequence of events shown in Fig. 10 enabled us to calculate the distribution of events without using Eq. (50). For this purpose the whole time axis was covered by equal time intervals of  $5 \times 10^{-3} \text{ s}$ . We counted the number of events in

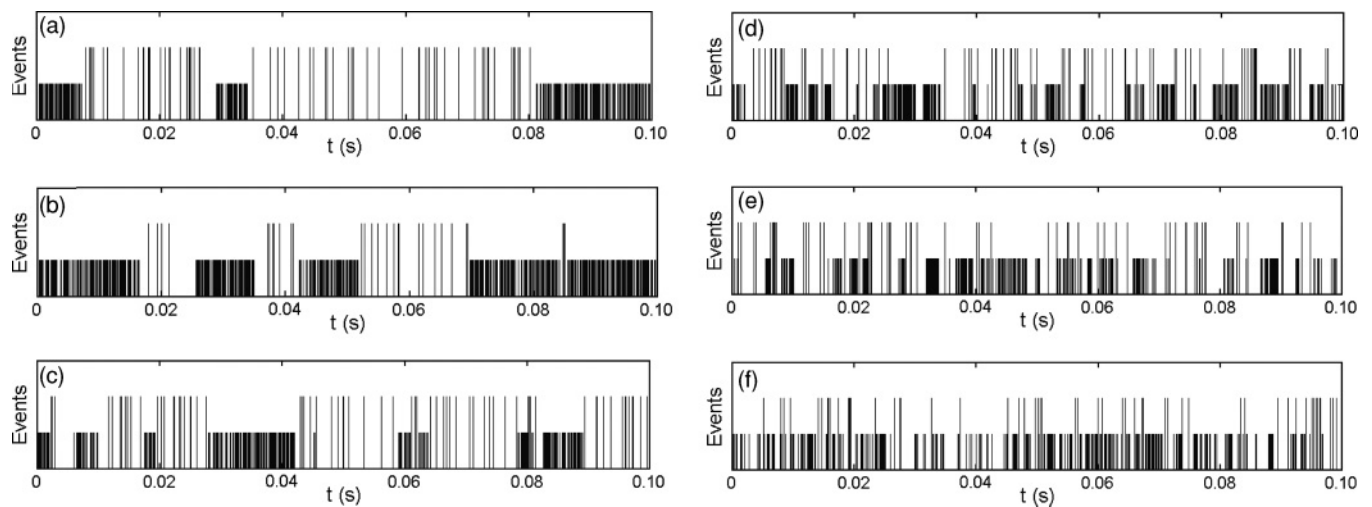


FIG. 10. Sequence of random events of 0 type (short segments), and of 2 type (long segments) calculated by the Monte Carlo method, with rate constants  $k_0 = 10^4 \text{ s}^{-1}$ ,  $G_1 = G_3 = 10^8 \text{ s}^{-1}$ , and  $k_2 = 10^3 \text{ s}^{-1}$ , and with rates of conformational transitions  $A$  and  $a$  relating to the photon distributions shown in Figs. 9(a)–9(f)

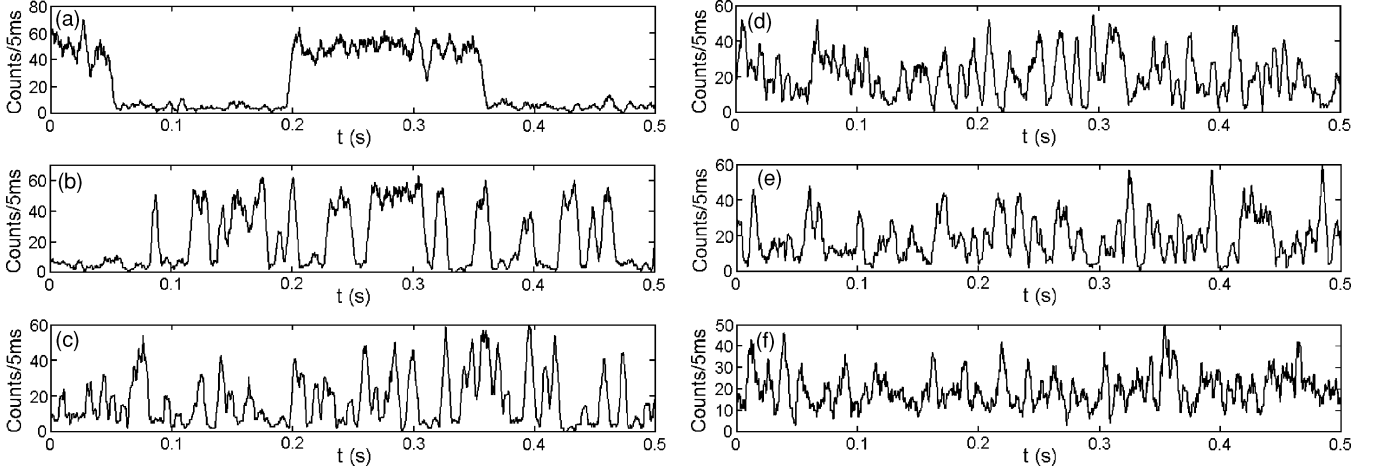


FIG. 11. Fluctuations of fluorescence intensity at bin time of 5 ms obtained with the help of sequences of events like those shown in Figs. 10(a)–10(f) and with the same set of parameters.

each time interval. The distribution of counted events in all time intervals is shown in Figs. 7 and 9 by circles. There is a coincidence of circles with solid lines. This coincidence proves the accuracy of both methods of calculation.

The distribution of events presented in Fig. 10 can be related to an experiment if experimental conditions permit us to count each event. If all counted events are stored at a bin we shall measure chaotic fluctuations of fluorescence intensity. For a bin time of 5 ms, the sequences of events like those shown in Fig. 10 are transformed to fluctuations of fluorescence intensity shown in Fig. 11.

The ratio  $k_0/k_2$  equals 10 for all tracks shown in Fig. 11. However, values of constants  $A$  and  $a$  responsible for interconformational jumps increase within two orders of magnitude if we move from Fig. 11(a) towards Fig. 11(f).

Figures 11(a), 10(a), and 7(c) show fluctuations of events and the distribution of events for the case of infrequent interconformational jumps. Fluorescence shown in Fig. 11(a) still has the so-called “on-off structure”. “On-off structure” disappears if we increase the rate of interconformational jumps. Figure 11(f) demonstrates this fact clearly.

## VI. AUTOCORRELATION FUNCTION OF FLUORESCENCE

Measurement of autocorrelation function  $g^{(2)}(t)$  of fluorescence (AF) is a standard treatment of experimental data in works dealing with fluctuating fluorescence. In accordance with Mandel [32], the second factorial moment of the photon distribution is expressed via  $g^{(2)}(t)$  as follows:

$$\begin{aligned} \langle N(N-1) \rangle_t &= \int_0^t dt_2 \int_0^{t_2} dt_1 \langle \hat{I}[\hat{I}(t_2)\hat{I}(t_1)] \rangle \\ &= 2\langle I \rangle^2 \int_0^t dt_2 \int_0^{t_2} dt_1 g^{(2)}(t_2 - t_1). \end{aligned} \quad (53)$$

On the left-hand side of Eq. (23) we see the function  $g^{(2)}(t)$  measurable in experiment. On the right-hand side of Eq. (23) we see the function which can be calculated theoretically for a given microscopic model. However, Eq. (23) was derived for fluorescence with a single type of photon. If the full correlator

is substituted by the matrix, Eq. (23) is not correct. How can we modify Eq. (23) for fluorescence with several types of emitted photons?

In order to derive an analog of Eq. (23) we shall use Eq. (53). Equation (53) is rather general and can be used for the distribution of events of various types. Carrying out the Laplace transformation in Eq. (53) we arrive at the following expression:

$$\langle N(N-1) \rangle_\lambda = 2\langle I \rangle^2 g^{(2)}(\lambda)/\lambda^2. \quad (54)$$

However, the left-hand side of Eq. (54) can be calculated with the help of the following formula:

$$\langle N(N-1) \rangle_\lambda = \sum_{N=0}^{\infty} N(N-1)w_N(\lambda). \quad (55)$$

Here  $w_N(\lambda)$  is determined by Eq. (49). After substitution of Eq. (49) into Eq. (55) we arrive at the following expression:

$$\begin{aligned} \langle N(N-1) \rangle_\lambda &= \frac{1}{\lambda^2 \tau_0} \sum_{N=0}^{\infty} N(N-1) \langle \vec{1} | \hat{s}(\lambda)^{N-1} - 2\hat{s}(\lambda)^N + \hat{s}(\lambda)^{N+1} | \vec{n} \rangle. \end{aligned} \quad (56)$$

After calculations of sums over  $N$  we arrive at the following simple equation:

$$\langle N(N-1) \rangle_\lambda = \frac{2}{\lambda^2 \tau_0} \langle \vec{1} | \frac{\hat{s}(\lambda)}{1 - \hat{s}(\lambda)} | \vec{n} \rangle = \frac{2}{\lambda^2 \tau_0} \langle \vec{1} | \hat{p}(\lambda) | \vec{n} \rangle. \quad (57)$$

Comparing the right-hand sides of Eqs. (54) and (57) we find

$$g^{(2)}(\lambda) = \frac{1}{\tau_0 \langle I \rangle^2} \langle \vec{1} | \hat{p}(\lambda) | \vec{n} \rangle. \quad (58)$$

Because

$$1/\tau_0 = \langle I \rangle = \langle \vec{1} | \hat{p}(t = \infty) | \vec{n} \rangle \quad (59)$$

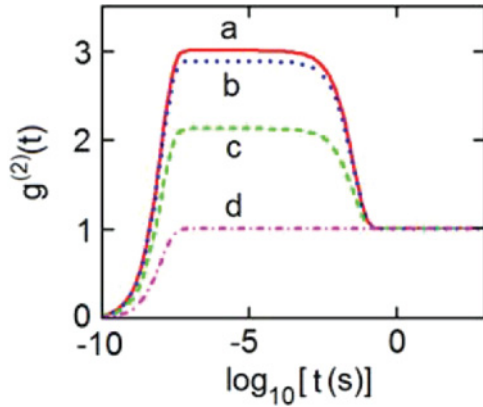


FIG. 12. (Color online) Autocorrelation function of fluorescence with two types of photons at  $k_0 = 10^4 \text{ s}^{-1}$ ,  $A = 20 \text{ s}^{-1}$ ,  $a = 10 \text{ s}^{-1}$ , and  $G_1 = G_3 = 10^8 \text{ s}^{-1}$ , and for various values of the ratio (a)  $k_2/k_0 \cdot k_2 = 0 \text{ s}^{-1}$ , (b)  $10^2 \text{ s}^{-1}$ , (c)  $10^3 \text{ s}^{-1}$ , (d)  $10^4 \text{ s}^{-1}$ .

is an average fluorescence intensity we find after the Laplace transformation of the left- and right-hand sides of Eq. (58) this final expression:

$$g^{(2)}(T) = \frac{\langle \vec{1} | \hat{\rho}(T) | \vec{n} \rangle}{\langle \vec{1} | \hat{\rho}(\infty) | \vec{n} \rangle}. \quad (60)$$

The formula establishes a relation between the function  $g^{(2)}(T)$  measurable in the experiment and the matrix  $\hat{\rho}(t)$  of the full correlator. This matrix can be calculated for given microscopic model. Figure 12 shows the autocorrelation function calculated with the help of Eq. (60) for various ratios of intensity of fluorescence from conformations 0 and 2.

First of all, antibunching is inherent in all curves. The curve ‘‘a’’ corresponds to blinking fluorescence with on and off intervals. It demonstrates bunching of events. Bunching disappears if the intensity of fluorescence from conformation 2 approaches the intensity of fluorescence from conformation 0. In fact, the curve ‘‘d’’ corresponds to fluorescence of a two-level molecule.

## VII. CONCLUSION

We have studied fluorescence of single complex molecules or a single impurity center with two conformations (0 and 2) excited by cw-laser light. Such a molecule can emit light from each conformation with different intensity or polarization. The molecule being in conformation 0 (2) emits photons of 0 (2) type.

A theory for the photon distribution function for a single molecule, revealing itself like two emitters (emitter 0 and 2), has been already developed by Gopich and Szabo [16] with an approximation in which the rates of intra- and interconformational transitions have been considerably different.

We have used another approach and developed a theory which is free of such approximation. Figure 9 demonstrates this fact. The theory for fluorescence consisting of photons of two types has a complicated character as compared with the theory for fluorescence with emitted photons of a single type. All mathematical difficulties have been overcome and details can be found in the three following Appendixes.

After the microscopic model was formulated, our theory enabled one to (i) calculate the matrix  $s_{\alpha\beta}(t)$  for the start-stop correlator (waiting time distributions), (ii) calculate the matrix  $p_{\alpha\beta}(t)$  for the full correlator and to find a relation between autocorrelation function  $g^{(2)}(t)$  and the matrix  $p_{\alpha\beta}(t)$ , (iii) calculate the distribution function  $w_N(T)$  for events measured in time interval  $T$ , (iv) calculate fluctuations of fluorescence intensity relating to the formulated microscopic model.

In order to verify our calculations with the help of Eq. (50) we carried out independent calculations of the distribution functions by the Monte Carlo method. Both methods of calculations yield identical distributions as Figs. 7 and 9 show.

By starting from the microscopic model we arrived at fluctuating fluorescence as Fig. 11(c) shows. The fluctuations of such type could indeed be measured in a real experiment. Can information about the microscopic model be extracted from such a method? We hope that our theory in which such method is related to the distribution function shown in Fig. 9(c) and to a definite microscopic model can help researchers to find a positive answer to this question.

## ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research via Grant No. 10-02-90047.

## APPENDIX A: DERIVATION OF THE FUNCTION FOR THE DISTRIBUTION OF EVENTS

Matrix elements  $[\hat{s}(t)]_{\alpha\beta} = s_{\alpha\beta}(t)$  of the start-stop correlator determine the density of the probability of finding adjacent events of  $\alpha$  and  $\beta$  type separated by time interval  $t$ . Then matrix elements

$$[\hat{S}(t_0)]_{\alpha\beta} = S_{\alpha\beta}(t_0) = \int_0^{t_0} s_{\alpha\beta}(t) dt \quad (A1)$$

determine the probability of finding an event of  $\alpha$  type prior to time moment  $t_0$  if the preceding event of  $\beta$  type happened at  $t = 0$ . Then

$$S_{\beta}(t_0) = \int_0^{t_0} \sum_{\alpha} s_{\alpha\beta}(t) dt \quad (A2)$$

describes the probability of finding an event of any type prior to time moment  $t_0$ . It is obvious that

$$\begin{aligned} S(t_0) &= (1, 1) \hat{S}(t_0) \begin{pmatrix} n_0 \\ n_2 \end{pmatrix} \\ &= \langle \vec{1} | \hat{S}(t_0) | \vec{n} \rangle = \int_0^{t_0} s(t) dt \end{aligned} \quad (A3)$$

is the probability of finding an event of any type prior time moment  $t_0$  if the preceding event happening at  $t = 0$  was an event of 0 or 2 type with the probability  $n_0$  or  $n_2$ , respectively. Equation (A3) looks like that in the case of fluorescence consisting of photons of a single type [25,26]. However, for the molecule emitting photons of various types, the expression for  $s(t)$  looks as follows:

$$s(t) = \sum_{\alpha, \beta} s_{\alpha\beta}(t) n_{\beta} = (1, 1) \hat{s} \begin{pmatrix} n_0 \\ n_2 \end{pmatrix} = \langle \vec{1} | \hat{s} | \vec{n} \rangle. \quad (A4)$$

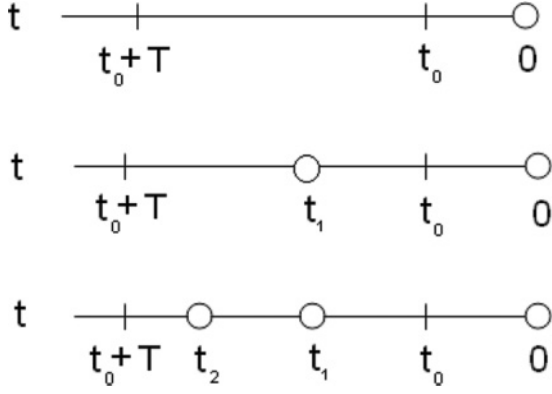


FIG. 13. (a) Time interval without events and with one and two events (circles).

Consider the probability of not finding any event in time interval  $(t_0, T + t_0)$  whose onset is separated by time  $t_0$  from an event that happened at  $t = 0$ . The situation is shown in the first line in Fig. 13. It is obvious the function

$$w(t_0) = 1 - S(t_0) \tag{A5}$$

is the probability of finding no event in time interval  $(0, t_0)$  if an event happened at  $t = 0$ . Then, the probability of not finding an event in time interval  $(0, T + t_0)$ , if an event happened at  $t = 0$ , will be given by the following expression:

$$w(T + t_0) = w_0(T + t_0, t_0)w(t_0). \tag{A6}$$

The probability

$$w_0(T + t_0, t_0) = \frac{w(T + t_0)}{w(t_0)} = \frac{1 - S(T + t_0)}{1 - S(t_0)} \tag{A7}$$

determines the absence of an event in time interval  $(t_0, T + t_0)$ . In contrast to the conditional probability  $w(t)$  the probability  $w_0(T + t_0, t_0)$  is of the nonconditional type. It does not depend on the time history prior to time  $t_0$ .

It is obvious that the function

$$P(t_0) = w(t_0) / \int_0^\infty w(t_0) dt_0 = w(t_0) / \tau_0 \tag{A8}$$

is the density of the probability of not finding an event in time interval  $(0, t_0)$ . Here the constant

$$\tau_0 = \int_0^\infty w(t) dt = \int_0^\infty ts(t) dt \tag{A9}$$

is the average time interval between two adjacent events. The probability of finding time interval  $T$  without events can be found with the help of Eqs. (A7) and (A8) as follows:

$$\begin{aligned} w_0(T) &= \int_0^\infty w_0(T + t_0, t_0)P(t_0) dt_0 = \frac{1}{\tau_0} \int_0^\infty w(T + t_0) dt_0 \\ &= \frac{1}{\tau_0} \int_T^\infty w(x) dx. \end{aligned} \tag{A10}$$

Consider now the second line in Fig. 13. Here we see a single event in time interval  $(t_0, T + t_0)$ . The probability of finding any event in time interval  $(t_0, T + t_0)$  if the preceding

event at  $t = 0$  was an event of  $\beta$  type is given by

$$\begin{aligned} &[\rho_1(T + t_0, t_0|0)]_\beta \\ &= \int_{t_0}^{T+t_0} dt_1 \left\{ \left[ 1 - \int_{t_1}^{T+t_0} dt \sum_\alpha s_{\alpha 0}(t - t_1) \right] s_{0\beta}(t_1) \right. \\ &\quad \left. + \left[ 1 - \int_{t_1}^{T+t_0} dt \sum_\alpha s_{\alpha 2}(t - t_1) \right] s_{2\beta}(t_1) \right\}. \end{aligned} \tag{A11}$$

Expressions in the square brackets determine the probability of finding no event in time interval  $(t_1, T + t_0)$ . Since an event of  $\beta$  type can happen at  $t = 0$  with the probability  $n_\beta$ , the function

$$\begin{aligned} \rho_1(T + t_0, t_0) &= \sum_\beta [\rho_1(T + t_0, t_0|0)]_\beta n_\beta \\ &= \langle \vec{1} | \int_{t_0}^{T+t_0} dt_1 \hat{s}(t_1) - \int_{t_0}^{T+t_0} dt_1 \\ &\quad \times \int_{t_1}^{T+t_0} dt \hat{s}(t - t_1) \hat{s}(t_1) | \vec{n} \rangle \end{aligned} \tag{A12}$$

will describe the probability of finding any event in time interval  $(t_0, T + t_0)$  if the preceding event of any type happened at  $t = 0$ .

Using a similar line of reasoning, we can derive the probability of finding two events of any type in time interval  $(t_0, T + t_0)$  if the preceding event of any type happened at  $t = 0$ :

$$\begin{aligned} &\rho_2(T + t_0, t_0|0) \\ &= \langle \vec{1} | \int_{t_0}^{T+t_0} dt_2 \int_{t_0}^{t_2} dt_1 \hat{s}(t_2 - t_1) \hat{s}(t_1) - \int_{t_0}^{T+t_0} dt_2 \\ &\quad \times \int_{t_2}^{T+t_0} dt \int_{t_0}^{t_2} dt_1 \hat{s}(t - t_2) \hat{s}(t_2 - t_1) \hat{s}(t_1) | \vec{n} \rangle. \end{aligned} \tag{A13}$$

Such situation is shown in the third line of Fig. 13.

It is obvious that for the probability of finding  $N$  events in time interval  $(t_0, T + t_0)$  we find the following expression:

$$\begin{aligned} &\rho_N(T + t_0, t_0|0) \\ &= \langle \vec{1} | \int_{t_0}^{T+t_0} dt_N \int_{t_0}^{t_N} dt_{N-1} \dots \\ &\quad \times \int_{t_0}^{t_2} dt_1 \hat{s}(t_N - t_{N-1}) \hat{s}(t_{N-1} - t_{N-2}) \dots \\ &\quad \times \hat{s}(t_2 - t_1) \hat{s}(t_1) - \int_{t_0}^{T+t_0} dt_N \int_{t_N}^{T+t_0} dt \\ &\quad \times \int_{t_0}^{t_N} dt_{N-1} \dots \int_{t_0}^{t_2} dt_1 \hat{s}(t - t_N) \\ &\quad \times \hat{s}(t_N - t_{N-1}) \dots \hat{s}(t_2 - t_1) \hat{s}(t_1) | \vec{n} \rangle. \end{aligned} \tag{A14}$$

If we take into account

$$\int_{t_0}^{T+t_0} dt_N \int_{t_N}^{T+t_0} dt \dots = \int_{t_0}^{T+t_0} dt \int_{t_0}^t dt_N \dots, \tag{A15}$$

Equation (A14) can be rewritten in the following form:

$$\begin{aligned}
 \rho_N(T + t_0, t_0|0) &= \langle \vec{1} | \int_{t_0}^{T+t_0} dt_N \int_{t_0}^{t_N} dt_{N-1} \cdots \\
 &\times \int_{t_0}^{t_2} dt_1 \hat{s}(t_N - t_{N-1}) \hat{s}(t_{N-1} - t_{N-2}) \cdots \\
 &\times \hat{s}(t_2 - t_1) \hat{s}(t_1) - \int_{t_0}^{T+t_0} dt \int_{t_0}^t dt_N \int_{t_0}^{t_N} dt_{N-1} \cdots \\
 &\times \int_{t_0}^{t_2} dt_1 \hat{s}(t - t_N) \hat{s}(t_N - t_{N-1}) \cdots \\
 &\times \hat{s}(t_2 - t_1) \hat{s}(t_1) | \vec{n} \rangle, \quad (N \geq 1). \quad (\text{A16})
 \end{aligned}$$

By using Eq. (A16) we arrive at the following equation:

$$\sum_{N=1}^{\infty} \rho_N(T + t_0, t_0|0) = \int_{t_0}^{T+t_0} dt_1 s(t_1) = S(T + t_0) - S(t_0). \quad (\text{A17})$$

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

$$\rho_N(T + t_0, t_0|0) = w_N(T + t_0, t_0) w(t_0), \quad N \geq 1. \quad (\text{A18})$$

Here  $w(t_0) = 1 - S(t_0)$  is the probability of finding no event in time interval  $(0, t_0)$  if an event happened at  $t = 0$ , and  $w_N(T + t_0, t_0)$  is the nonconditional probability of finding  $N$  events in time interval  $(t_0, T + t_0)$ . It does not depend on time history prior to  $t_0$ .

By using Eq. (A17) and Eq. (A18), we find the following expression for the sum of nonconditional probabilities:

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

Making use of Eq. (A19) and Eq. (A7) we arrive at the law of conservation of full nonconditional probability:

$$\sum_{N=0}^{\infty} w_N(T + t_0, t_0) = 1. \quad (\text{A20})$$

From Eq. (A18) we can derive the following expression for nonconditional probability of finding  $N$  events in time interval  $(t_0, T + t_0)$ :

$$w_N(T + t_0, t_0) = \frac{\rho_N(T + t_0, t_0|0)}{w(t_0)}, \quad N \geq 1. \quad (\text{A21})$$

With the help of this equation and Eq. (A8) we arrive at the following expression for the probability of finding time interval  $T$  with  $N$  events of any type:

$$\begin{aligned}
 w_N(T) &= \int_0^{\infty} w_N(T + t_0, t_0) P(t_0) dt_0 \\
 &= \frac{1}{\tau_0} \int_0^{\infty} \rho_N(T + t_0, t_0|0) dt_0. \quad (\text{A22})
 \end{aligned}$$

By making substitution  $t_j = x_j + t_0$  of variables in Eq. (A16) for  $\rho_N(T + t_0, t_0|0)$  we arrive at the following expression:

$$\begin{aligned}
 w_N(T) &= \frac{1}{\tau_0} \langle \vec{1} | \int_0^T dx_N \int_0^{x_N} dx_{N-1} \cdots \int_0^{x_2} dt_1 \\
 &\times \hat{s}(x_N - x_{N-1}) \hat{s}(x_{N-1} - x_{N-2}) \cdots \hat{s}(x_2 - x_1) \\
 &\times \int_0^{\infty} dt_0 \hat{s}(x_1 + t_0) - \int_0^T dx \int_0^x dx_N \\
 &\times \int_0^{x_N} dx_{N-1} \cdots \int_0^{x_2} dx_1 \hat{s}(x - x_N) \\
 &\times \hat{s}(x_N - x_{N-1}) \cdots \hat{s}(x_2 - x_1) \int_0^{\infty} dt_0 \hat{s}(x_1 + t_0) | \vec{n} \rangle. \quad (\text{A23})
 \end{aligned}$$

Allowing for the equation

$$\begin{aligned}
 \int_0^{\infty} dt_0 \hat{s}(x_1 + t_0) &= \int_0^{\infty} \hat{s}(z) dz - \int_0^{x_1} \hat{s}(z) dz \\
 &= \hat{S}(\infty) - \hat{S}(x_1) = \hat{w}(x_1), \quad (\text{A24})
 \end{aligned}$$

we can transform Eq. (A23) for the probability of finding time interval  $T$  with  $N$  events to the final form:

$$\begin{aligned}
 w_N(T) &= \frac{1}{\tau_0} \langle \vec{1} | \int_0^T dx_N \int_0^{x_N} dx_{N-1} \cdots \int_0^{x_2} dt_1 \\
 &\times \hat{s}(x_N - x_{N-1}) \hat{s}(x_{N-1} - x_{N-2}) \cdots \hat{s}(x_2 - x_1) \hat{w}(x_1) \\
 &- \int_0^T dx \int_0^x dx_N \int_0^{x_N} dx_{N-1} \cdots \int_0^{x_2} dx_1 \\
 &\times \hat{s}(x - x_N) \hat{s}(x_N - x_{N-1}) \cdots \\
 &\times \hat{s}(x_2 - x_1) \hat{w}(x_1) | \vec{n} \rangle, \quad N \geq 1. \quad (\text{A25})
 \end{aligned}$$

By using this equation we find

$$\begin{aligned}
 \sum_{N=1}^{\infty} w_N(T) &= \frac{1}{\tau_0} \int_0^T \langle \vec{1} | \hat{w}(x) | \vec{n} \rangle dx \\
 &= \frac{1}{\tau_0} \int_0^T w(x) dx, \quad (\text{A26})
 \end{aligned}$$

Taking into account Eq. (A10) for  $w_0(T)$  we arrive at the law of conservation of full probability:

$$\begin{aligned}
 \sum_{N=0}^{\infty} w_N(T) &= \frac{1}{\tau_0} \int_0^T w(x) dx \\
 &+ \frac{1}{\tau_0} \int_T^{\infty} w(x) dx = 1. \quad (\text{A27})
 \end{aligned}$$

## APPENDIX B: DERIVATION OF THE EQUATION

$$\hat{S}(\infty) | \vec{n} \rangle = | \vec{n} \rangle$$

By using Eqs. (20) and (22) we can write the matrix  $\hat{S}(\infty)$  in the following form:

$$\hat{S}(\infty) = \begin{pmatrix} 1 - S_{20}(\infty) & S_{02}(\infty) \\ S_{20}(\infty) & 1 - S_{02}(\infty) \end{pmatrix}. \quad (\text{B1})$$

Here

$$S_{20}(\infty) = \int_0^{\infty} s_{20}(t) dt, \quad S_{02}(\infty) = \int_0^{\infty} s_{02}(t) dt. \quad (\text{B2})$$

Inserting Eqs. (19b) and (19d) for start-stop correlators into the integrals and performing the integration we find

$$S_{02}(\infty) = k_0 a / \lambda_0 \lambda_2, \quad S_{20}(\infty) = k_2 A / \lambda_0 \lambda_2. \quad (\text{B3})$$

Here  $\lambda_0$  and  $\lambda_2$  are determined by Eq. (18). Allowing for these formulas and Eq. (39) we arrive at the following equation:

$$\begin{aligned} \hat{S}(\infty) |\vec{n}\rangle &= \begin{pmatrix} 1 - S_{20}(\infty) & S_{02}(\infty) \\ S_{20}(\infty) & 1 - S_{02}(\infty) \end{pmatrix} \begin{pmatrix} n_0 \\ n_2 \end{pmatrix} \\ &= \begin{pmatrix} [1 - S_{20}(\infty)]n_0 + S_{02}(\infty)n_2 \\ S_{20}(\infty)n_0 + [1 - S_{02}(\infty)]n_2 \end{pmatrix} \\ &= \begin{pmatrix} n_0 \\ n_2 \end{pmatrix} = |\vec{n}\rangle. \end{aligned} \quad (\text{B4})$$

**APPENDIX C: CALCULATION OF THE PROBABILITY  $\langle \vec{1} | [\hat{s}(\lambda)^N]_t | \vec{n} \rangle$  OF FINDING  $N-1$  EVENTS IN TIME INTERVAL  $(0, t)$**

We shall do calculations neglecting antibunching, i.e., we set  $G_1/(G_1 - \lambda) = 1$  and  $G_3/(G_3 - \lambda) = 1$ . Then the Laplace transform of the start-stop correlator takes the following form:

$$\hat{s}(\lambda) = \frac{\hat{M}(\lambda)}{(\lambda_0 - \lambda)(\lambda_2 - \lambda)}. \quad (\text{C1})$$

Here

$$\hat{M}(\lambda) = \begin{pmatrix} k_0(k_2 + a - \lambda) & k_0 a \\ k_2 A & k_2(k_0 + A - \lambda) \end{pmatrix}. \quad (\text{C2})$$

In order to calculate the matrix  $\hat{M}(\lambda)^N$  we shall use the Silvester formula:

$$\begin{aligned} \hat{M}(\lambda)^N &= \frac{M_2^N - M_0^N}{M_2 - M_0} \hat{M}(\lambda) \\ &\quad - M_0 M_2 \frac{M_2^{N-1} - M_0^{N-1}}{M_2 - M_0}. \end{aligned} \quad (\text{C3})$$

Here  $M_0$  and  $M_2$  are roots of the equation  $\text{Det}(\hat{M} - M) = 0$ :

$$\begin{aligned} M_{0,2} &= \frac{2k_0 k_2 + k_0 a + k_2 A - (k_0 + k_2)\lambda}{2} \\ &\quad \mp \sqrt{\left(\frac{k_0 a - k_2 A - (k_0 - k_2)\lambda}{2}\right)^2 + k_0 k_2 a A}. \end{aligned} \quad (\text{C4})$$

The variable  $\lambda$  staying under the square root sign complicates the inverse Laplace transformation in Eq. (C3). However,  $u = M_0 + M_2$  and  $v = M_0 M_2$  do not include the square root. In order to make the transition to new variables we rewrite Eq. (C3) in the following form:

$$\hat{M}(\lambda)^N = Q_{N-1}(u, v) \hat{M}(\lambda) - v Q_{N-2}(u, v). \quad (\text{C5})$$

Here

$$Q_N(u, v) \equiv \frac{M_2^{N+1} - M_0^{N+1}}{M_2 - M_0} = \sum_{q=0}^N M_0^q M_2^{N-q}. \quad (\text{C6})$$

We can derive the following recurring relations for even and odd values of  $N$ :

$$\begin{aligned} Q_{2n}(u, v) &= u^{2n} \\ &\quad - \sum_{q=1}^n v^q (C_{2n}^q - C_{2n}^{q-1}) Q_{2(n-q)}(u, v), \end{aligned} \quad (\text{C7})$$

$$\begin{aligned} Q_{2n+1}(u, v) &= u^{2n+1} \\ &\quad - \sum_{q=1}^n v^q (C_{2n+1}^q - C_{2n+1}^{q-1}) Q_{2(n-q)+1}(u, v). \end{aligned} \quad (\text{C8})$$

Here  $C_i^j$  are binomial coefficients. The functions  $Q_{2(n-q)}$  and  $Q_{2(n-q)+1}$  can be rewritten as polynomials of the new variables:

$$Q_{2n}(u, v) = \sum_{q=0}^n (-v)^q D_{qn-q}^0 u^{2(n-q)}, \quad (\text{C9})$$

$$Q_{2n+1}(u, v) = \sum_{q=0}^n (-v)^q D_{qn-q}^1 u^{2(n-q)+1}. \quad (\text{C10})$$

Coefficients  $D_{ij}^0$  and  $D_{ij}^1$  are determined by recurring relations:

$$D_{ij}^0 = \sum_{k=1}^i (C_{2(i+j)}^k - C_{2(i+j)}^{k-1}) D_{i-kj}^0 (-1)^{k+1}, \quad (\text{C11})$$

$$D_{0j}^0 = 1,$$

$$D_{ij}^1 = \sum_{k=1}^i (C_{2(i+j)+1}^k - C_{2(i+j)+1}^{k-1}) D_{i-kj}^1 (-1)^{k+1}, \quad (\text{C12})$$

$$D_{0j}^1 = 1,$$

New variables depend on  $\lambda$  as follows:

$$u(\lambda) = (k_0 + k_2)(\bar{\lambda} - \lambda), \quad (\text{C13})$$

$$v(\lambda) = k_0 k_2 (\lambda_0 - \lambda)(\lambda_2 - \lambda). \quad (\text{C14})$$

Here  $\bar{\lambda} = \frac{2k_0 k_2 + k_0 a + k_2 A}{k_0 + k_2}$  and  $\lambda_{0,2}$  are determined by Eq. (18). After insertion of Eqs. (C9) and (C10) into Eq. (C5) we arrive at the following formulas for  $\hat{s}(\lambda)^N$ :

$$\begin{aligned} \hat{s}(\lambda)^{2n} &= (k_0 k_2)^{2n} \sum_{q=0}^{n-1} (-1)^q \left[ D_{qn-1-q}^1 \frac{u(\lambda)^{2(n-q)-1}}{v(\lambda)^{2n-q}} \hat{M}(\lambda) \right. \\ &\quad \left. - D_{qn-1-q}^0 \frac{u(\lambda)^{2(n-q)-2}}{v(\lambda)^{2n-q-1}} \right], \end{aligned} \quad (\text{C15})$$

$$\begin{aligned} \hat{s}(\lambda)^{2n+1} &= (k_0 k_2)^{2n+1} \left[ \sum_{q=0}^n (-1)^q D_{qn-q}^0 \frac{u(\lambda)^{2(n-q)}}{v(\lambda)^{2n-q+1}} \hat{M}(\lambda) \right. \\ &\quad \left. - \sum_{q=0}^{n-1} (-1)^q D_{qn-1-q}^1 \frac{u(\lambda)^{2(n-q)-1}}{v(\lambda)^{2n-q}} \right]. \end{aligned} \quad (\text{C16})$$

A method permitting us to reduce such expressions to a product of the Poisson function was developed in Refs. [23,25,26]. Existence of the variable  $\lambda$  in the numerator of the ratios complicates the inverse Laplace transformation in

Eqs. (C15) and (C16). This obstacle can be overcome by using the following expression,

$$\begin{aligned} \left(\frac{\bar{\lambda} - \lambda}{\lambda_0 - \bar{\lambda}}\right)^l &= \left(1 + \frac{\bar{\lambda} - \lambda_0}{\lambda_0} \frac{\lambda_0}{\lambda_0 - \lambda}\right)^l \\ &= \sum_{s=0}^l C_l^s \left(\frac{\bar{\lambda} - \lambda_0}{\lambda_0}\right)^s \left(\frac{\lambda_0}{\lambda_0 - \lambda}\right)^s, \end{aligned}$$

in ratios staying in Eqs. (C15) and (C16). Then we arrive at

$$\begin{aligned} \frac{u(\lambda)^l}{v(\lambda)^m} &= \frac{(k_0 + k_2)^l}{(k_0 k_2)^m} \sum_{s=0}^l C_l^s \left(\frac{\bar{\lambda} - \lambda_0}{\lambda_0}\right)^s \\ &\times \frac{\lambda_0^s}{(\lambda_0 - \lambda)^{m-l+s}} \frac{1}{(\lambda_2 - \lambda)^m}, \end{aligned} \quad (C17)$$

$$\begin{aligned} \frac{u(\lambda)^l}{v(\lambda)^m} \hat{M}(\lambda) &= \frac{(k_0 + k_2)^l}{(k_0 k_2)^m} \sum_{s=0}^l C_l^s \left(\frac{\bar{\lambda} - \lambda_0}{\lambda_0}\right)^s \\ &\times \frac{\lambda_0^s}{(\lambda_0 - \lambda)^{m-l+s}} \frac{\hat{M}(\lambda)}{(\lambda_2 - \lambda)^m}. \end{aligned} \quad (C18)$$

The second ratio in Eq. (C18) can be transformed to the following expression:

$$\begin{aligned} \frac{\hat{M}(\lambda)}{(\lambda_2 - \lambda)^m} &= \frac{\hat{M}(\lambda_2)}{(\lambda_2 - \lambda)^m} + \begin{pmatrix} k_0 & 0 \\ 0 & k_2 \end{pmatrix} \\ &\times \frac{1}{(\lambda_2 - \lambda)^{m-1}}. \end{aligned} \quad (C19)$$

By substituting Eq. (C19) into Eq. (C18) we can express Eqs. (C17) and (C18) via the Laplace transform  $P_m^{\lambda_i}(\lambda) = \lambda_i^m / (\lambda_i - \lambda)^{m+1}$  of Poisson functions:

$$\frac{u(\lambda)^l}{v(\lambda)^m} = \frac{(k_0 + k_2)^l}{(k_0 k_2)^m \lambda_0^{m-l-1} \lambda_2^{m-1}} \sum_{s=0}^l C_l^s \left(\frac{\bar{\lambda} - \lambda_0}{\lambda_0}\right)^s P_{m-l+s-1}^{\lambda_0}(\lambda) P_{m-1}^{\lambda_2}(\lambda), \quad (C20)$$

$$\begin{aligned} \frac{u(\lambda)^l}{v(\lambda)^m} \hat{M}(\lambda) &= \frac{(k_0 + k_2)^l}{(k_0 k_2)^m \lambda_0^{m-l-1} \lambda_2^{m-2}} \sum_{s=0}^l C_l^s \left(\frac{\bar{\lambda} - \lambda_0}{\lambda_0}\right)^s \left[ \frac{\hat{M}(\lambda_2)}{\lambda_2} P_{m-l+s-1}^{\lambda_0}(\lambda) P_{m-1}^{\lambda_2}(\lambda) \right. \\ &\left. + \begin{pmatrix} k_0 & 0 \\ 0 & k_2 \end{pmatrix} P_{m-l+s-1}^{\lambda_0}(\lambda) P_{m-2}^{\lambda_2}(\lambda) \right]. \end{aligned} \quad (C21)$$

Making an inverse Laplace transform in Eqs. (C20) and (C21) we find the following expressions:

$$\left[ \frac{u(\lambda)^l}{v(\lambda)^m} \right]_t = \frac{(k_0 + k_2)^l}{(k_0 k_2)^m \lambda_0^{m-l-1} \lambda_2^{m-1}} \sum_{s=0}^l C_l^s \left(\frac{\bar{\lambda} - \lambda_0}{\lambda_0}\right)^s \int_0^t P_{m-l+s-1}[\lambda_0(t-x)] P_{m-1}[\lambda_2 x] dx \quad (C22)$$

$$\begin{aligned} \left[ \frac{u(\lambda)^l}{v(\lambda)^m} \hat{M}(\lambda) \right]_t &= \frac{(k_0 + k_2)^l}{(k_0 k_2)^m \lambda_0^{m-l-1} \lambda_2^{m-2}} \sum_{s=0}^l C_l^s \left(\frac{\bar{\lambda} - \lambda_0}{\lambda_0}\right)^s \left\{ \frac{\hat{M}(\lambda_2)}{\lambda_2} \int_0^t P_{m-l+s-1}[\lambda_0(t-x)] P_{m-1}[\lambda_2 x] dx \right. \\ &\left. + \begin{pmatrix} k_0 & 0 \\ 0 & k_2 \end{pmatrix} \int_0^t P_{m-l+s-1}[\lambda_0(t-x)] P_{m-2}[\lambda_2 x] dx \right\}. \end{aligned} \quad (C23)$$

Here  $P_M(\lambda, x) = (\lambda x)^M \exp(-\lambda x) / M!$ . Allowing for  $\langle \vec{1} | \vec{n} \rangle = 1$ ,  $\langle \vec{1} | \frac{\hat{M}(\lambda_2)}{\lambda_2} | \vec{n} \rangle = \lambda_0 - (k_0 n_0 + k_2 n_2)$  and  $\langle \vec{1} | \begin{pmatrix} k_0 & 0 \\ 0 & k_2 \end{pmatrix} | \vec{n} \rangle = (k_0 n_0 + k_2 n_2)$  we can transform Eqs. (C22) and (C23) to the following form:

$$\langle \vec{1} | \left[ \frac{u(\lambda)^l}{v(\lambda)^m} \right]_t | \vec{n} \rangle = \frac{(k_0 + k_2)^l}{(k_0 k_2)^m \lambda_0^{m-l-1} \lambda_2^{m-1}} \sum_{s=0}^l C_l^s \left(\frac{\bar{\lambda} - \lambda_0}{\lambda_0}\right)^s \int_0^t P_{m-l+s-1}[\lambda_0(t-x)] P_{m-1}[\lambda_2 x] dx, \quad (C24)$$

$$\begin{aligned} \langle \vec{1} | \left[ \frac{u(\lambda)^l}{v(\lambda)^m} \hat{M}(\lambda) \right]_t | \vec{n} \rangle &= \frac{(k_0 + k_2)^l}{(k_0 k_2)^m \lambda_0^{m-l-1} \lambda_2^{m-2}} \sum_{s=0}^l C_l^s \left(\frac{\bar{\lambda} - \lambda_0}{\lambda_0}\right)^s \left\{ [\lambda_0 - (k_0 n_0 + k_2 n_2)] \int_0^t P_{m-l+s-1}[\lambda_0(t-x)] \right. \\ &\left. \times P_{m-1}[\lambda_2 x] dx + (k_0 n_0 + k_2 n_2) \int_0^t P_{m-l+s-1}[\lambda_0(t-x)] P_{m-2}[\lambda_2 x] dx \right\}. \end{aligned} \quad (C25)$$

For the function  $\langle \vec{1} | [\hat{s}(\lambda)^N]_t | \vec{n} \rangle$  with even and odd  $N$  we arrive at the following expressions:

$$\langle \vec{1} | [\hat{s}(\lambda)^{2n}]_t | \vec{n} \rangle = (k_0 k_2)^{2n} \sum_{q=0}^{n-1} (-1)^q \left\{ D_{qn-1-q}^1 \langle \vec{1} | \left[ \frac{u(\lambda)^{2(n-q)-1}}{v(\lambda)^{2n-q}} \hat{M}(\lambda) \right]_t | \vec{n} \rangle - D_{qn-1-q}^0 \langle \vec{1} | \left[ \frac{u(\lambda)^{2(n-q)-1}}{v(\lambda)^{2n-q}} \right]_t | \vec{n} \rangle \right\}, \quad (C26)$$

$$\langle \vec{1} | [\hat{s}(\lambda)^{2n+1}]_t | \vec{n} \rangle = (k_0 k_2)^{2n+1} \left\{ \sum_{q=0}^n (-1)^q D_{qn-q}^0 \langle \vec{1} | \left[ \frac{u(\lambda)^{2(n-q)}}{v(\lambda)^{2n-q+1}} \hat{M}(\lambda) \right]_t | \vec{n} \rangle - \sum_{q=0}^{n-1} (-1)^q D_{qn-1-q}^1 \langle \vec{1} | \left[ \frac{u(\lambda)^{2(n-q)-1}}{v(\lambda)^{2n-q}} \right]_t | \vec{n} \rangle \right\}. \quad (\text{C27})$$

Equations (C24)–(C27) express the function  $\langle \vec{1} | [\hat{s}(\lambda)^N]_t | \vec{n} \rangle$  via onefold integrals of two Poisson functions. These equations enable one to carry out numerical calculations with the help of Eq. (50). Rate constants  $\lambda_0$  and  $\lambda_2$  in the Poisson functions determine both quantum dynamics

of the emitter [see expression for  $s_{\alpha\beta}(t)$ ] and photon statistics of its fluorescence. Hence, the quantum dynamics of the system manifests itself in photon statistics via rate constants  $\lambda_0$  and  $\lambda_2$  staying in the Poisson functions.

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