

Super-Poissonian statistics of on-off jumps in blinking fluorescence of single molecules

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Blinking fluorescence of a single guest molecule embedded in a polymer matrix and excited by cw laser light is considered. Such fluorescence exhibits quantum jumps from bright on-intervals to dark off-intervals, i.e., so-called on→off jumps. A system with one type of on-intervals and with two types of off-intervals is studied. A distribution function $w_N(T)$ for the number N of on→off jumps in a time interval T is derived. The distribution function is expressed via a threefold integral of three Poissonian functions, each of which relates to the corresponding exponential process in the quantum dynamics of a fluorescent impurity center. Numerical calculations of the distribution function $w_N(T)$ for four time intervals T of various durations are carried out. The distribution function $w_N(T)$ is broader as compared with the Poissonian one and has two maxima, one of which relates to observed time intervals without on→off jumps. © 2009 American Institute of Physics.
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I. INTRODUCTION

Quantum jumps detected in fluorescence of single ions have already been the subject of extensive works both in experiments^{1–3} and in the theory^{4–8} 20 years ago. The first experiments with single guest molecules embedded in a polymer matrix^{9,10} have also revealed quantum jumps in fluorescence of these molecules. These jumps can serve as a tool for studying local quantum dynamics of the guest molecule interacting with its local environment.

Fluorescence of single organic molecules embedded in a polymer matrix, excited by a cw laser field has, as a rule, a blinking character, i.e., time intervals with fluorescence (on-intervals) alternate with dark intervals with no fluorescence (off-intervals).^{11–15} These “dark” quantum states with no fluorescence can be of various physical origins. Triplet states of organic molecules,^{12,13} or quantum states with separated electrons and holes, as in polymer molecules,^{16–18} can play a role of dark states.

However, there is still one important physical mechanism for the appearance of blinking fluorescence. Indeed, many individual organic molecules embedded in a polymer matrix exhibit quantum jumps of optical lines.^{19,20} An example of these jumps detected in experiments with a scanned laser frequency is given in Fig. 1. These fluctuations of the resonant frequency emerge due to tunneling transitions in a polymer matrix in the vicinity of a guest molecule.

The fluorescence excitation spectrum shown in Fig. 1 was obtained with the help of a scanned laser frequency. It consists of two black vertical bands (trails) with interruptions in time. Each trail consists of on-intervals with fluorescence and off-intervals without fluorescence. However, each on-interval in both trails has an additional structure expressed by small white spots. The size of these spots in time is about

hundred milliseconds. These small white spots in the black part of the trail reveal short off-intervals related to short-living dark states of the guest molecule.

Let us imagine that the laser frequency is not scanned, and it coincides with the frequency of the right trail in Fig. 1. Then the left trail disappears and we have only the trail with long off-intervals of order of 50 s and short off-intervals (small white spots) of order of 0.2 s. The main goal of the present paper is to derive a mathematical expression for the distribution function $w_N(T)$ for on→off jumps in blinking fluorescence with two types of off-intervals like those shown in the right trail in Fig. 1, and to carry out numerical calculations with the mathematical expression found for $w_N(T)$.

Statistics of on→off jumps can be studied in the same way that the photon distribution was studied in a number of works.^{21–24} Indeed, by counting the photons of fluorescence, we count, in fact, the number of $e \rightarrow g$ quantum jumps from the excited to the ground state of a molecule driven by a cw laser field. The expression

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

was found in Refs. 21, 22, and 24 for the Laplace transform of the photon distribution function. Here $s(\lambda)$ is the Laplace transform of the function $s(t)$. The function $s(t)$ is the probability density of finding a fluorescence photon at time t if the preceding photon was emitted at $t=0$. τ_0 is an average time interval between two successively emitted photons. The expressions for τ_0 and for the probability $w_0(T)$ of finding an interval T without photons were found in Ref. 24,

$$w_0(T) = \frac{1}{\tau_0} \int_0^\infty \left[1 - \int_0^{T+t} s(\tau) d\tau \right] dt,$$

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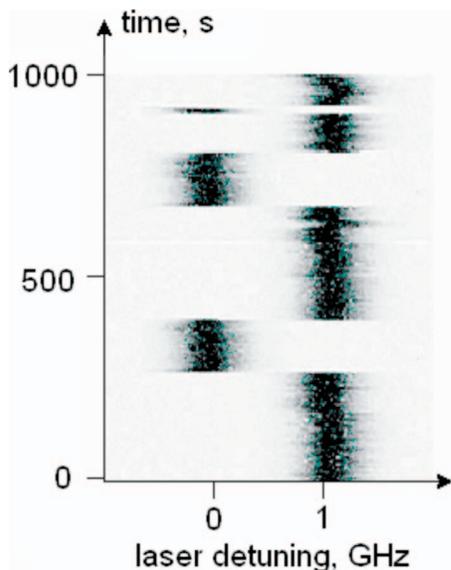


FIG. 1. Jumps of optical line of tetra-tert-butylterrylene molecule embedded in polyisobutylene at 7 K (Ref. 20). Duration of each laser scan was 8 s.

$$\tau_0 = \int_0^\infty \left[1 - \int_0^t s(\tau) d\tau \right] dt. \quad (2)$$

In accordance with Eqs. (1) and (2), the photon distribution function is expressed via a single function $s(t)$. This function has a clear physical meaning: it describes the correlation between two successively emitted photons. Therefore, the function $s(t)$ was named the start-stop correlator in Refs. 25 and 26. Since quantum $e \rightarrow g$ jumps and quantum on \rightarrow off jumps can be considered on equal footing, Eqs. (1) and (2) can serve as starting expressions for the consideration of on \rightarrow off jumps as well. In this case the function $s(t)$ describes the correlation between two successive on \rightarrow off jumps.

II. DISTRIBUTION FUNCTION FOR ON \rightarrow OFF JUMPS

In order to use Eqs. (1) and (2) we need to formulate a physical model for the calculation of the start-stop correlator.

A. Physical model

In accordance with the modern view on amorphous solids such as polymers and glasses, spontaneous reorientations of the groups of atoms happening over a wide time scale are typical phenomena in these solids. The transition from one type of atomic configuration to another is a quantum jump. The transition has a tunneling character because the lifetime of the unstable atomic configuration can range from milliseconds to hundreds of seconds. Since the energy of electronic excitation in a guest molecule depends on the type of the atomic configuration in the vicinity of the guest molecule, the quantum jump resulting from the atomic reorientation manifests itself as a jump of the resonant frequency of the guest molecule, i.e., as jump of the optical line. Figure 1 shows these jumps of the absorption line.

Anderson *et al.*²⁷ and Phillips²⁸ describe pairs of various atomic configurations in an amorphous solid with the help of

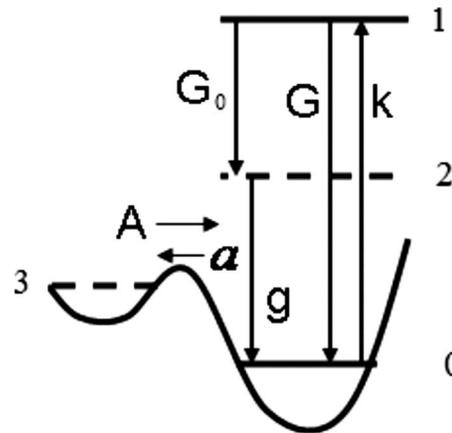


FIG. 2. Scheme for the electronic states of the guest molecule with blinking fluorescence interrupted by short and long off intervals.

double-well potentials with one level in each well. This simple two-level system (TLS) models two unstable atomic configurations with transitions from one configuration to another. The TLS model can describe almost all low temperature anomalies in the physical properties of amorphous solids. TLSs manifest themselves also in experiments with single molecules embedded in an amorphous solid, as Fig. 1 shows.

It is obvious that there are many TLSs in amorphous matrix. Influence of the atomic configuration on the optical spectra of a guest molecule can be considered as a result of an interaction of the optical electron of the guest molecule with TLS. Interaction of a guest molecule with many TLSs was considered by Geva and Skinner²⁹ and by Osad'ko.²⁶ However, experiment shows^{19,20} that interaction with only a few TLSs in the nearest vicinity of the guest molecule primarily contributes to the optical spectrum of the guest molecules. For instance, Fig. 1 shows the influence of a single TLS on the optical spectrum. Such situations will be considered further in the paper.

If the laser frequency is not scanned and it permanently coincides with the maximum of the absorption band in the right trail, the left trail in Fig. 1 disappears. Then long off-intervals emerge due to a shift in the electronic frequency from the laser frequency. Reorientation of the atomic group in the vicinity of this guest molecule is the physical reason for the appearance of this detuning. If we take into account that the electronic system of the guest organic molecule can be described by a three-level energy scheme in which a triplet level is situated between the ground and the excited singlet electronic levels, we arrive at the model described by the energy scheme shown in Fig. 2.

Here 0 and 3 are singlet levels of the guest molecule in two types of ground states relating to two unstable atomic configurations near the guest molecule. The levels 0 and 3 describe TLS in the ground electronic state of the guest molecule. The level 1 and the level 2 relate to the excited singlet state and to a triplet state of the molecule, respectively. Here k describes the rate of light absorption via frequency of the right trail in Fig. 1, $G = k + 1/T_1 + \Gamma$ is the rate of light-induced k and spontaneous $1/T_1$ emission and radiation free transitions Γ to the ground state 0 of the molecule, G_0 is the

rate of the singlet-triplet transitions in the excited electronic state, and g is the rate of triplet state decay. a and A determine the rate of transitions between the two types of ground states. The states 2 and 3 denoted by dashed lines in Fig. 2 are dark states. They result in short and long off-intervals, respectively.

B. Equations for the start-stop correlator

Consider the rate equations for the population of the electronic levels in the energy scheme shown in Fig. 2,

$$\begin{aligned}\dot{n}_1 &= -(G + G_0)n_1 + kn_0, \\ \dot{n}_0 &= Gn_1 - (k + a)n_0 + gn_2 + An_3, \\ \dot{n}_2 &= G_0n_1 - gn_2, \\ \dot{n}_3 &= an_0 - An_3.\end{aligned}\quad (3)$$

The rate constant G is of order of 10^8 s^{-1} . It describes the fastest process. This rate constant is at least two orders of magnitude larger as compared with the other rate constants. This constant is responsible for the dynamics in the nanosecond time scale. Since singlet-triplet transitions and jumps between trails are slower processes, we may consider these processes within steady-state approximation, i.e., $\dot{n}_1 = 0$. Then we find the relation

$$n_1 = \frac{k}{G + G_0} n_0 \ll 1 \quad (4)$$

from the first equation of Eq. (3). Fluorescence exists if the system occupies states 1 and 0. Therefore, we may write $n_1 + n_0 = n_{\text{on}}$ for the population of on-state. By using Eq. (4) we arrive at the following relations:

$$n_1 = \frac{k}{k + G + G_0} n_{\text{on}}, \quad n_0 = \frac{G + G_0}{k + G + G_0} n_{\text{on}}. \quad (5)$$

After insertion of Eq. (5) to three equations (3) we arrive at the following set of equations:

$$\begin{aligned}\dot{n}_{\text{on}} &= -Kn_{\text{on}} + gn_2 + An_3, \\ \dot{n}_2 &= K_k n_{\text{on}} - gn_2, \\ \dot{n}_3 &= K_a n_{\text{on}} - An_3.\end{aligned}\quad (6a)$$

Here

$$\begin{aligned}K_k &= k \frac{G_0}{k + G + G_0} \ll k, \quad K_a = a \frac{G + G_0}{k + G + G_0} \cong a, \\ K &= K_k + K_a.\end{aligned}\quad (6b)$$

Although Eq. (6) describes the slow dynamics of the system, it cannot be used directly to study the statistics of on \rightarrow off jumps. Since the detected event is a jump from the on-state, we, in accordance with the results of Refs. 22, 23, 25, 26, and 30, should omit the terms which describe transitions to the on-state from the dark states 2 and 3 in Eq. (6). This method of finding equations for statistics of quantum

jumps for two successively emitted photons was found in Refs. 25 and 26. It was generalized for more complicated event structures in Refs. 22 and 23.

Omitting terms $K_k n_{\text{on}}$ and $K_a n_{\text{on}}$ in Eq. (6), we arrive at equations

$$\begin{aligned}\dot{W}_{\text{on}} &= -KW_{\text{on}} + gW_2 + AW_3, \\ \dot{W}_2 &= -gW_2, \\ \dot{W}_3 &= -AW_3\end{aligned}\quad (7)$$

for the new probabilities W . Although these equations were obtained from Eq. (6) by omitting some terms, nevertheless Eq. (7) is an exact equation for finding the start-stop correlator for the system under consideration. Equation (7) describes the so-called start-stop dynamics of the system.^{25,26}

By taking into account the way the expression for the start-stop correlator was found in Chap. 2 of the book in Ref. 26 for photon emission events, we find that the start-stop correlator for on \rightarrow off jumps will be determined by the term that describes leaving the on-state for the off-state.³⁰ Hence, the start-stop correlator will be described by the following expression:

$$s(t) = KW_{\text{on}}(t). \quad (8)$$

The probability $W_{\text{on}}(t)$ should be found from Eq. (7) with a definite initial condition. In the case of a single off-state, for instance state 2, such initial condition should be $W_2(0) = 1$, because after the on-interval terminates, the molecule reaches state 2 with the probability equal to 1. This very initial condition was used in Ref. 31 in which a system with a single type of dark state was considered. However our system has two types of off-intervals. We do not know exactly which type (2 or 3) of dark state is occupied after the fluorescence ends. However we can find the probabilities of on \rightarrow off jumps to 2 and 3 states,

$$p_2 = K_k/K, \quad p_3 = K_a/K. \quad (9)$$

These probabilities satisfy the following condition: $p_2 + p_3 = 1$. Therefore, the initial condition should be taken by the following form:

$$W_2(0) = p_2, \quad W_3(0) = p_3, \quad W_{\text{on}}(0) = 0. \quad (10)$$

This initial condition means that after the on-interval terminates, the system can occupy dark states 2 and 3 with the probabilities p_2 and p_3 , respectively.

By solving Eq. (7) with this initial condition, we arrive at the following equation for the start-stop correlator:

$$s(t) = \sum_{j=1}^3 s_j \exp(-\lambda_j t). \quad (11a)$$

Here

$$\lambda_1 = K, \quad \lambda_2 = g, \quad \lambda_3 = A, \quad (11b)$$

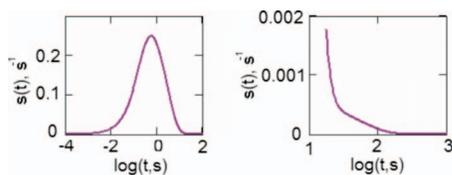


FIG. 3. Start-stop correlator calculated with the help of Eq. (11) and with set of rate constants (12).

$$s_1 = -(s_2 + s_3), \quad s_2 = \frac{-Kp_2\lambda_2}{\lambda_2 - \lambda_1}, \quad s_3 = \frac{-Kp_3\lambda_3}{\lambda_3 - \lambda_1}. \quad (11c)$$

The choice of parameter values will be made in such a way that they could provide values of average on- and off-intervals in accordance with those in the right trail in Fig. 1. The set of parameters

$$k = 10^4 \text{ s}^{-1}, \quad G_0 = 3 \times 10^3 \text{ s}^{-1}, \quad G = 10^8 \text{ s}^{-1}, \\ g = 5 \text{ s}^{-1}, \quad a = 0.01 \text{ s}^{-1}, \quad A = 0.02 \text{ s}^{-1} \quad (12)$$

results in the following set of values for average time intervals:

$$\tau_{\text{on}}^T = 1/K = 3.226 \text{ s}, \quad \tau_{\text{off}}^T = 1/g = 0.2 \text{ s}, \\ \tau_{\text{on}}^{\text{TLS}} = 1/a = 100 \text{ s}, \quad \tau_{\text{off}}^{\text{TLS}} = 1/A = 50 \text{ s}. \quad (13)$$

Short time intervals τ_{on}^T and τ_{off}^T result from the existence of the triplet state in the guest molecule. Long time intervals $\tau_{\text{on}}^{\text{TLS}}$ and $\tau_{\text{off}}^{\text{TLS}}$ result from the right trail, i.e., from the existence of TLS. Average time intervals (13) correspond to the right trail and small white spots shown in Fig. 1.

The start-stop correlator calculated with the help of Eq. (11) and with the set (12) is shown in Fig. 3. The average time interval between two successive on \rightarrow off jumps is given by $\tau_0 = 5.03 \text{ s}$. Exponential functions with exponents λ_1 , λ_2 , and λ_3 manifest themselves in Fig. 3 as three smooth steps extended over one order of magnitude in time scale. The start-stop correlator increases as $1 - \exp(-\lambda_2 t)$ with increasing time. Decrease in the start-stop correlator shown in Fig. 3 is determined by $\exp(-\lambda_1 t)$ and $\exp(-\lambda_3 t)$.

The consequence of on- and off-intervals of average duration is shown in Fig. 4. Triplet state 2 is responsible for the appearance of short off-intervals. Jumps in TLS are responsible for the appearance of long off-intervals. In the real system, the duration of all intervals fluctuates. However, the statistics of on \rightarrow off jumps depends on the relation between average values of on- and off-intervals and value of time interval T of the observation.

In fact, each on-interval consists of a finite number of points relating to time instants of photon emission. Carrying out the transition from Eq. (3) to Eq. (6a) we neglect this fine structure of on-interval. We believe that light is emitted con-

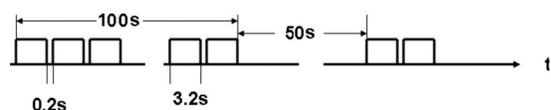


FIG. 4. Consequence of on- and off-intervals. Numerals show the average duration of on/off intervals.

tinuously within the on-interval. This approximation is correct because the average time interval between two successively emitted photons is of order of $1/k = 10^{-4} \text{ s}$. It is three orders of magnitude shorter as compared with the average value of 0.2 s for short off-intervals and four orders of magnitude shorter as compared with the average value of 3.2 s for on-intervals.

C. Calculation of the distribution function

Consider now the transition to functions of time for the Laplace transform described by Eq. (1). It looks as follows:

$$w_N(T) = \frac{1}{\tau_0} \int_0^T dx(T-x) ([s(\lambda)^{N-1}]_x - 2[s(\lambda)^N]_x \\ + [s(\lambda)^{N+1}]_x). \quad (14)$$

Transition to the function $s(t)$ in the expression $[s(\lambda)^N]_t = (1/2\pi i) \int_{-i\infty}^{i\infty} s(\lambda)^N \exp(-\lambda t) d\lambda$ yields N -fold integrals. This step will create problems for numerical calculations of the distribution function $w_N(T)$. There is software for numerical inverse Laplace transformation. However, if we shall use a numerical inverse Laplace transformation of Eq. (1) directly we miss a very important physical relation existing between dynamics of the system and its statistics. This relation can be read as follows: each exponential process in the start-stop correlator creates Poissonian function with the same rate constant in the final expression for the distribution function $w_N(T)$.

Indeed by using a method found first in Ref. 32 and then successfully used in Refs. 24, 31, and 33 we can express the function $[s(\lambda)^N]_t$ via a few Poissonian functions. The way this transformation can be carried out is shown in the Appendix, in which the following equation is derived:

$$[s(\lambda)^N]_t = \lambda_1 \lambda_2 Q^N \left\{ \int_0^t dx P_{N-1}[\lambda_1(t-x)] P_{N-1}[\lambda_2 x] \right. \\ \left. + \lambda_3 \sum_{m=1}^N C_N^m \left(\frac{L - \lambda_3}{\lambda_3} \right)^m \int_0^t dx P_{m-1}[\lambda_3(t-x)] \right. \\ \left. \times \int_0^x dy P_{N-1}[\lambda_1(x-y)] P_{N-1}[\lambda_2 y] \right\}. \quad (15a)$$

Here

$$P_N[ax] = (ax)^N \exp(-ax) / N!, \quad Q = \frac{A + p_2(g - A)}{g}, \\ L = \frac{A}{Q}. \quad (15b)$$

We see that each exponential process $\exp(-\lambda_j t)$ in the start-stop correlator manifests itself via the Poissonian function $P_N[\lambda_j x]$ with the same rate constant λ_j in the distribution function $w_N(T)$ for on \rightarrow off jumps. This very relation will be lost in any numerical inverse Laplace transformation.

Consider the distribution of on \rightarrow off jumps in time intervals T of various durations. Consider first the probability $w_0(T)$ to measure time interval without on \rightarrow off jump. After

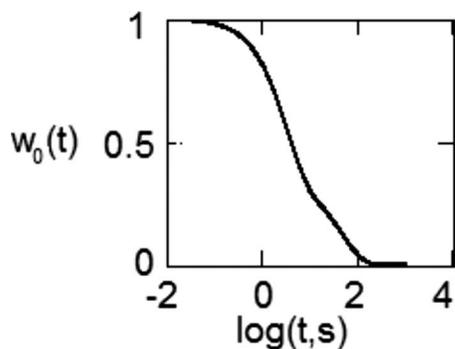


FIG. 5. The probability of finding time interval T without on \rightarrow off jumps.

the insertion of Eq. (11a) for the start-stop correlator into Eq. (2) we arrive at the following simple equation:

$$w_0(T) = \frac{1}{\tau_0} \sum_{j=1}^3 \frac{s_j}{\lambda_j^2} \exp(-\lambda_j T), \quad \tau_0 = \sum_{j=1}^3 \frac{s_j}{\lambda_j^2}. \quad (16)$$

By deriving these equations we allowed the following equation:

$$\int_0^\infty s(t) dt = \sum_{j=1}^3 (s_j / \lambda_j) = 1. \quad (17)$$

This equation means that the total probability of finding the second on \rightarrow off jump by infinite time moment after the first on \rightarrow off jump equals 1. Dependence of the probability $w_0(T)$ on the duration T of time interval is shown in Fig. 5. Decrease in this probability has two phases: fast and slow. It is described by two exponential functions $\exp(-\lambda_2 t) = \exp(-t/\tau_{\text{off}}^T)$ and $\exp(-\lambda_3 t) = \exp(-t/\tau_{\text{off}}^{\text{TLS}})$. The first decrease starts if $T > \tau_{\text{off}}^T = 1/g = 0.2$ s. The second stage of decrease starts if $T > \tau_{\text{off}}^{\text{TLS}} = 1/A = 50$ s.

After insertion of Eq. (15a) into Eq. (14) the latter includes only two- and threefold integrals. Therefore, the distribution function can be calculated numerically for various duration of T interval. The result is shown in Fig. 6.

These four time intervals T should be compared with the on-intervals shown in Fig. 4.

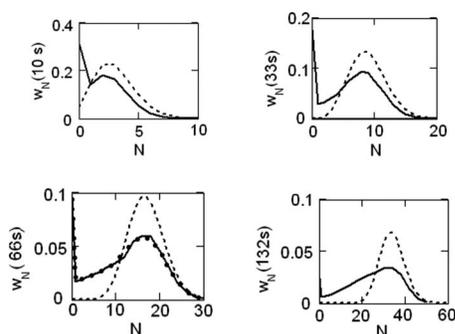


FIG. 6. The distribution of on \rightarrow off jumps in time intervals of various durations (solid lines). Poissonian functions with the same positions of maximum (dashed lines). $w_N(0.032, 0.002, 1, 0.5, 0.66)$ (points). See discussion concerning scaling in the text.

III. DISCUSSION OF RESULTS

The distributions of on \rightarrow off jumps differ considerably from the Poissonian distribution $P_N(\langle N \rangle) = \langle N \rangle^N \exp(-\langle N \rangle) / N!$ with the same position of the maximum. Since the position of the maximum in the Poissonian function coincides with the average number $\langle N \rangle$ of events, we may conclude that the average number $\langle N \rangle$ of on \rightarrow off jumps in our system is smaller than that for Poissonian distribution with the same position of maximum.

The position of the maximum of the broad peak in Fig. 6 is close to the average number T/τ_{on}^T of on \rightarrow off jumps in time intervals T , i.e., $10/3.2=3.1$, $33/3.2=10.3$, $66/3.2=20.6$, and $132/3.2=41.2$. The probability $w_0(T)$ of finding time interval T without photons is high enough for time intervals of 10, 33, and 66 s. The narrow peak in the left side of Fig. 6 demonstrates this fact. The distribution $w_N(T)$ is broader than the Poissonian distribution. Hence, the Mandel parameter $Q(T)$ (Ref. 34) will be positive, and we are facing super-Poissonian statistics of on \rightarrow off jumps.

Consider now the contribution of the various terms of Eq. (15a) for determining the complex shape of the distribution functions shown in Fig. 6. At $a=0$ we find $\tau_{\text{on}}^{\text{TLS}} = \infty$. This means that jumps to dark state 3 disappear and, hence, on-interval of 100 s duration shown in Fig. 4 approaches infinity. This long on-interval will be interrupted by short off-intervals related to small white spots in Fig. 1. Solely on \rightarrow off jumps to triplet state 2 exist in this case. The sum over m in Eq. (15a) disappears and the onefold integral with two Poissonian functions remains. In this case, the distribution of on \rightarrow off jumps described by Eq. (14) is narrower as compared with the Poissonian distribution with the same $\langle N \rangle$. Such sub-Poissonian distribution has been already considered in Ref. 31. It was also shown that such distribution can describe the distribution of on \rightarrow off jumps in blinking fluorescence of Hg^{2+} ion measured in Ref. 35.

Terms in the sum over m take into account influence of dark state 3 on the distribution function. The resonant frequency can make a jump of order of 1 GHz to state 3, as Fig. 1 shows. Influence of dark state 3 increases in long time intervals T . This influence manifests itself in the tail of the function $w_N(T)$ extended to smaller values of N .

Poissonian distribution with $\langle N \rangle = kT$, i.e., $P_N(T) = kT^N \exp(-kT) / N!$, demonstrates some kind of scaling. Indeed, if the rate of absorption k diminishes by a factor of q and time interval T increases by a factor of q , the Poissonian distribution is not changed. This scaling can be written in the following form:

$$w_N(k, T) = w_N(k/q, Tq). \quad (18)$$

The scaling is not surprising for a Poissonian function in which k and T are included as the product $\langle N \rangle = kT$.

In the case under consideration in this paper the distribution function depends on many physical parameters and can be written as $w_N(k, G, G_0, T_1, a, A, T)$. Therefore, the distribution function has a rather complex shape. It is difficult to hope that some kind of scaling exists in the case under consideration. However, we have recently found³⁶ that some kind of scaling can exist in the photon distribution function

of complex shape for blinking fluorescence. Figure 10 in Ref. 36 shows this scaling. Such scaling exists also in the distribution function for on→off jumps shown in Fig. 6. Indeed, if we rewrite $w_N(k, G, G_0, T_1, a, A, T)$ in the form of $w_N(\tau_{\text{on}}^T, \tau_{\text{off}}^T, \tau_{\text{on}}^{\text{TLS}}, \tau_{\text{off}}^{\text{TLS}}, T)$, which includes solely parameters measured experimentally, we can write the following equation:

$$w_N(\tau_{\text{on}}^T q, \tau_{\text{off}}^T q, \tau_{\text{on}}^{\text{TLS}} q, \tau_{\text{off}}^{\text{TLS}} q, Tq) \cong w_N(\tau_{\text{on}}^T, \tau_{\text{off}}^T, \tau_{\text{on}}^{\text{TLS}}, \tau_{\text{off}}^{\text{TLS}}, T). \quad (19)$$

This scaling is fulfilled with good accuracy. For instance, in accordance with Eq. (19) the distribution functions calculated for $q=0.01$, i.e., for average values,

$$\tau_{\text{on}}^T = 1/K = 0.032 \text{ s}, \quad \tau_{\text{off}}^T = 1/g = 0.002 \text{ s}, \\ \tau_{\text{on}}^{\text{TLS}} = 1/a = 1 \text{ s}, \quad \tau_{\text{off}}^{\text{TLS}} = 1/A = 0.5 \text{ s}, \quad (20)$$

will coincide for time intervals $T=0.1, 0.33, 0.66$, and 1.32 s with the distribution functions presented in Fig. 6. Indeed the distribution function $w_N(0.032, 0.002, 1, 0.5, 0.66)$ shown by points in Fig. 6 coincides with the distribution function $w_N(3.2, 0.2, 100, 50, 66)$ shown by solid line in Fig. 6.

IV. CONCLUSIONS

Figure 1 shows experimental data in which two types of off-intervals manifest themselves. Short off-intervals of hundred millisecond duration look like small white spots. Long-lived dark state emerges due to fluctuations of the resonant frequency of the guest molecule embedded in a polymer matrix. Such experimental data have not yet been analyzed theoretically. For the theoretical analysis we had to solve the following tasks:

- (1) First of all we had to find the way the start-stop correlator can be calculated for the case in which a detected event, i.e., on-off jump, cannot be related to a definite type of quantum transition. This situation is new and it differs considerably from the situation in which each photon emission event relates definitely to the transition from the excited electronic state to the ground electronic state. The way out was found by solving the four-level scheme (3) in which the probabilities of jumps to the state 2 and the state 3 were used as the initial conditions (10).
- (2) We had to find the way the distribution function for on-off jumps can be calculated. To solve this problem we used a method found by Osad'ko³³ for calculation of the photon distribution function in blinking fluorescence. The method enables one to derive Eqs. (14) and (15a) for the distribution function for on-off jumps analogous to the derivation of an expression for photon distribution function in blinking fluorescence.
- (3) Equations (14) and (15a) enable one to calculate numerically the distribution functions for on-off jumps for time intervals of various duration.

It has to be mentioned that the inverse Laplace transformation of Eq. (1) can be carried out by various methods, for instance, by numerical methods. However, the numerical

treatment is a rather complex procedure. At least it has not been carried out yet and reported in literature. Moreover, the main shortcoming of the numerical treatment is that it misses the important relation between quantum dynamics of the system and statistics of on-off jumps. Equations (14) and (15) enable one to find the relation $\exp(-\lambda_j t) \rightarrow (\lambda_j t)^N \exp(-\lambda_j t) / N!$. The relation shows that each exponential process in quantum dynamics of the system manifests itself via a Poissonian function with the same rate constant λ_j in the distribution function for on-off jumps. This relation is new and it has not yet been discussed in the literature on on-off jumps.

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APPENDIX: TRANSFORMATION OF $s(\lambda)^N$

Carrying out the Laplace transformation $\int_0^\infty dt W(t) e^{i(\omega+i0)t} = W(i\omega) = W(\lambda)$ in Eq. (7) and solving algebraic equations, we find the following expression for the Laplace transform of the start-stop correlator:

$$s(\lambda) = KW_{\text{on}}(\lambda) = K(p_2g + p_3A) \frac{(L - \lambda)}{(\lambda_1 - \lambda)(\lambda_2 - \lambda)(\lambda_3 - \lambda)}. \quad (A1)$$

Here $L = Ag / (p_2g + p_3A)$ and $\lambda_1 = K$, $\lambda_2 = g$, $\lambda_3 = A$. By using Eq. (A1) we can write

$$s(\lambda)^N = \lambda_1 \lambda_2 Q^N \left(\frac{L - \lambda}{\lambda_3 - \lambda} \right)^N \frac{\lambda_1^{N-1}}{(\lambda_1 - \lambda)^N} \frac{\lambda_2^{N-1}}{(\lambda_2 - \lambda)^N}. \quad (A2)$$

Here $Q = (p_2g + p_3A) / g$.

Two last ratios in Eq. (A2) are Laplace transforms $P_{N-1}^{\lambda_i}(\lambda) = \lambda_i^{N-1} / (\lambda_i - \lambda)^N$ of the Poissonian function $P_N(\lambda_i t) = (\lambda_i t)^N \exp(-\lambda_i t) / N!$. The first ratio can be rewritten in the following form:

$$\left(\frac{L - \lambda}{\lambda_3 - \lambda} \right)^N = \left(1 + \frac{L - \lambda_3}{\lambda_3} \frac{\lambda_3}{\lambda_3 - \lambda} \right)^N \\ = \sum_{m=0}^N \frac{N!}{m! (N-m)!} \left(\frac{L - \lambda_3}{\lambda_3} \right)^m \left(\frac{\lambda_3}{\lambda_3 - \lambda} \right)^m. \quad (A3)$$

This sum over m is an expansion in power series of small parameter $(L - \lambda_3) / \lambda_3$ because the value of λ_3 almost equals to the value of L . The parameter is always positive and it is less than 1. By using the set of parameters (12) we find the following values for roots: $\lambda_1 = K = 0.31 \text{ s}^{-1}$, $\lambda_2 = g = 5 \text{ s}^{-1}$, $\lambda_3 = A = 0.02 \text{ s}^{-1}$, and $L = 0.0207$; we find $(L - \lambda_3) / \lambda_3 = 0.035$, i.e., the parameter is very small indeed. Inserting Eq. (A3) into Eq. (A2), we arrive at the following expression:

$$\begin{aligned}
s(\lambda)^N &= \lambda_1 \lambda_2 Q^N \sum_{m=0}^N C_N^m \left(\frac{L - \lambda_3}{\lambda_3} \right)^m \\
&\quad \times \lambda_3 \frac{\lambda_3^{m-1}}{(\lambda_3 - \lambda)^m} \frac{\lambda_1^{N-1}}{(\lambda_1 - \lambda)^N} \frac{\lambda_2^{N-1}}{(\lambda_2 - \lambda)^N} \\
&= \lambda_1 \lambda_2 Q^N \left[P_{N-1}^{\lambda_1}(\lambda) P_{N-1}^{\lambda_2}(\lambda) \right. \\
&\quad \left. + \lambda_3 \sum_{m=1}^N C_N^m \left(\frac{L - \lambda_3}{\lambda_3} \right)^m P_{m-1}^{\lambda_3}(\lambda) P_{N-1}^{\lambda_1}(\lambda) P_{N-1}^{\lambda_2}(\lambda) \right].
\end{aligned} \tag{A4}$$

This expression includes solely Laplace transforms of Poissonian functions. Carrying out the inverse Laplace transformation in Eq. (A4), we arrive at Eq. (15).

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