

Single Nanoparticle Quantum Dynamics Studied by the Photon Distribution Function

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Abstract—The blinking fluorescence of a single nanoparticle excited by CW laser radiation was studied. In the case of a low time resolution setup, blinking fluorescence appears to be a continuous emission. Blinking can nevertheless be established if we measure the photon distribution function in such quasi-continuous fluorescence.

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INTRODUCTION

Measuring the fluorescence of single molecules and semiconducting nanocrystals (single nanoparticles) offers new possibilities for studying the quantum dynamics of these nanoparticles. This is shown clearly in the blinking of the fluorescence intensity of a single nanoparticle excited by CW laser light [1–4]. The fluorescence time scale consists of alternate *on* intervals with light and *off* intervals without light. Such blinking does not reveal itself in the total radiation of an assembly of nanoparticles, due to the averaging of random *on* and *off* intervals in the radiation of each molecule.

The presence of *off* intervals means that among quantum states there are some that cause fluorescence to stop when a nanoparticle appears in them. Such dark states can vary in their physical nature [4–6]. The transition from the *on* state to the *off* state (*on* → *off* jumps) is visible to the unaided eye through a luminescent microscope as a blinking glow. At frequent jumps, it cannot be noticed by the unaided eye. It can, however, be detected by a photodetector that accumulates the signal over a short period T . This time is limited by the intensity of the fluorescence of a single nanoparticle and is usually about 10^{-2} to 10^{-4} s. If signal accumulation time T is greater than the average time of blinking, the photodetector will perceive the blinking fluorescence as continuous; i.e., no *on* → *off* dynamics will be detected.

We show below that *on* → *off* jumps can also be detected in fluorescence perceived by a photodetector as continuous, since these *on* → *off* jumps are manifested in the distribution function of fluorescence photons $w_N(T)$, i.e., in the fluctuation number of photons N measured over the interval T .

THEORETICAL

A fluorescent nanoparticle in the dark state can be described with a three-level energy scheme in which optical transitions occur, e.g., between levels 0 and 1, and level 2 corresponds to the dark state. The physical nature of these three states can differ. For example, levels 0 and 1 can correspond to the ground and the excited singlet states of a molecule, while level 2 (located between 0 and 1) corresponds to triplet state of a molecule [4]. In a long polymer chain, the $0 \rightarrow 1$ transition can be a response to the generation of coupled electron–hole pairs (excitons), while “dark” state 2 can result from electron capture by a trap existing in the polymer chain [4–6].

The slow kinetics of a nanoparticle associated with *on* → *off* jumps can be considered on the basis of rate equations

$$\begin{aligned}\dot{\rho}_1 &= -(G + k + 1/T_1 + A)\rho_1 + k\rho_0, \\ \dot{\rho}_0 &= (G + k + 1/T_1)\rho_1 - k\rho_0 + a\rho_2, \\ \dot{\rho}_2 &= A\rho_1 - a\rho_2.\end{aligned}\quad (1)$$

Here, ρ_j is the probability of detecting the nanoparticle in quantum state $j = 0, 1, \text{ or } 2$, and constants k , $1/T_1$ and G are, respectively, the rates of induced, spontaneous, and nonradiative transitions between optically active states 0 and 1. Constants A and a describe the rate of the transition to “dark” state 2 and the rate of turning back.

A nanoparticle radiated by continuous laser light fluoresces, making jumps between states 0 and 1 at random time instants, radiating one photon upon jump. When the nanoparticle transitions from state 1 to “dark” state 2, the radiation stops despite the continuous radiation of the nanoparticle by laser light, i.e., we observe an *off* interval. After the molecule

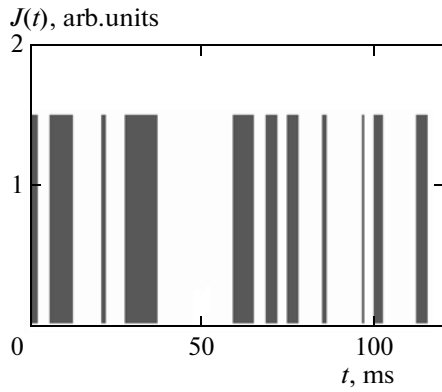


Fig. 1. Blinking fluorescence with average values $\tau_{on} = 3$ ms and $\tau_{off} = 5$ ms for *on* and *off* intervals.

jumps from state 2 to state 0, the *off* interval ends and the fluorescence appears again.

As was shown in [7, 8], the equations for finding the probability density for *on* and *off* intervals of a definite length can be found with two equations,

$$\dot{\rho}_{on} = -\rho_{on}/\tau_{on}, \quad \dot{\rho}_{off} = -\rho_{off}/\tau_{off}, \quad (2)$$

stemming from system of Eqs. (1). Here, $\rho_{on} = \rho_1 + \rho_0$, $\rho_{off} = \rho_2$, and

$$\frac{1}{\tau_{on}} = k \frac{AT_1}{1 + (2k + G + A)T_1} = kY, \quad 1/\tau_{off} = a, \quad (3)$$

where Y is the quantum yield to the “dark” state. The probability densities determined from system (2) are the exponents

$$P_{on,off} = \frac{1}{\tau_{on,off}} \exp\left(-\frac{t}{\tau_{on,off}}\right), \quad (4)$$

normalized integrally to unit, while τ_{on} and τ_{off} are the average lengths of *on/off* intervals. Using formulas (4), we can calculate random moments t_n of *on* \rightarrow *off* jumps with the following equation:

$$rnd(n) = \int_0^{t_n} P_{on,off}(\tau) d\tau. \quad (5)$$

Here, $rnd(n)$ is a random number between 0 and 1 that can be found, e.g., with the random number generator in the Mathcad program.

Using formula (5), the calculations for random instants of time t_n were performed in [9] for functions (4) with $\tau_{on} = 3$ ms and $\tau_{off} = 5$ ms. With these random instants of time for *on* \rightarrow *off* and *off* \rightarrow *on* jumps, we can construct the fluctuating fluorescence intensity. The result is shown in Fig. 1.

During experiments, however, a particular time T of signal accumulation was always used. In other words, the time axis is divided into equal time periods

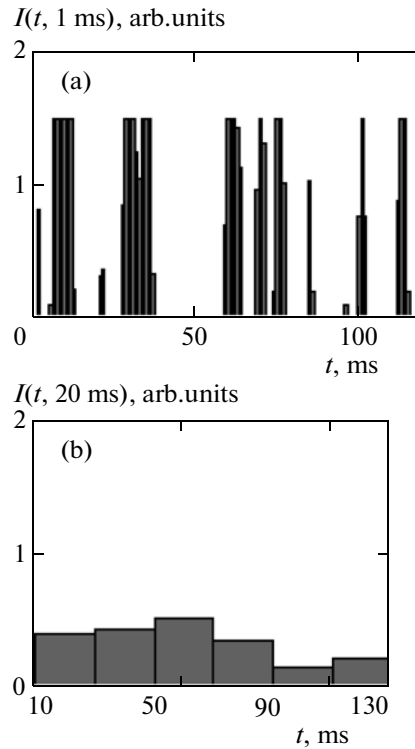


Fig. 2. Fluctuations of fluorescence intensity at short (a) and long (b) signal accumulation times.

T , and the number of photons counted in each time interval T is plotted on the Y axis. The fluctuating intensity can be found with the following formula:

$$I(t, T) = \frac{1}{T} \int_t^{t+T} J(\tau) d\tau, \quad (6)$$

where $J(t)$ is the fluctuation function shown in Fig. 1. For short periods of signal accumulation (1 ms) and long periods (20 ms), we can find the fluorescence fluctuation using formula (6) (Fig.2).

We can see that if the time of signal accumulation is appreciably shorter than the average values $\tau_{on} = 3$ ms and $\tau_{off} = 5$ ms of the *on* and *off* intervals, the fluctuations of fluorescence intensity are still clear (Fig. 2a), and we are able to find the distribution of *on* and *off* intervals according to their length. At signal accumulation times exceeding these average values, the fluorescence becomes quasi-continuous (Fig. 2b). This makes impossible to establish the presence of *on* and *off* intervals in the fluorescence. We must then measure the photon distribution.

CALCULATION OF THE PHOTON DISTRIBUTION FUNCTION

The formula derived in [10, 11] for photon distribution function $w_N(T)$ over the intervals T covering the

time axis has the following form:

$$w_N(T) = \frac{1}{\tau_0} \int_0^T (T-t) \{ [s(\lambda)]_t^{N-1} - 2[s(\lambda)]_t^N + [s(\lambda)]_t^{N+1} \} dt, \quad (N \geq 1), \quad (7)$$

$$w_0(T) = \frac{1}{\tau_0} \int_0^{\infty} \left[1 - \int_0^{T+t} s(x) dx \right] dt. \quad (8)$$

Here,

$$\tau_0 = \int_0^{\infty} \left[1 - \int_0^t s(x) dx \right] dt \quad (9)$$

is the average time interval between two photons of fluorescence, emitted one after another. We can see that the photon distribution function $w_N(T)$ is expressed by a single function $s(t)$ or via its Laplace transform:

$$s(\lambda) = s(i\omega) = \int_0^{\infty} s(t) e^{i(\omega+i0)t} dt. \quad (10)$$

Function $s(t)$, referred to as the two-photon start–stop correlator, determines the dynamics of a nanoparticle excited by continuous laser light. It is determined by the following expression:

$$dW(t) = s(t) dt, \quad (11)$$

where $dW(t)$ is the probability of the emission of a fluorescence photon in time interval $(t, t + dt)$, under the condition that the preceding photon of fluorescence was emitted at $t = 0$. Since $W(\infty) = 1$, start–stop correlator $s(t)$ is integrally normalized to one. This describes the distribution of time intervals between consecutively emitted photons.

It is obvious that the explicit form of the start–stop correlator depends on the type of nanoparticle emitting the light. As was shown in [7, 11], the equations for determining the start–stop correlator can be obtained from system (1) if we omit term ρ_1/T_1 in the second equation. System (1) is then transformed into

$$\begin{aligned} \dot{W}_1 &= -(k + G + 1/T_1 + A)W_1 + kW_0, \\ \dot{W}_0 &= (k + G)W_1 - kW_0 + aW_2, \\ \dot{W}_2 &= AW_1 - aW_2. \end{aligned} \quad (12)$$

As was shown in [7], the start–stop correlator is determined by the formula

$$s(t) = W_1(t)/T_1, \quad (13)$$

where $W_1(t)$ is the solution for system (12) at initial condition $W_0(0) = 1$, $W_1(0) = W_2(0) = 0$. In other words, the nanoparticle emits a fluorescence photon at the time moment zero.

Performing a Laplace transformation in both parts of system (12), we arrive at the following system of algebraic equations:

$$\begin{aligned} [\lambda - (k + G + 1/T_1 + A)]W_1 + kW_0 &= 0, \\ (k + G)W_1 + (\lambda - k)W_0 + aW_2 &= -1, \\ AW_1 + (\lambda - a)W_2 &= 0. \end{aligned} \quad (14)$$

Equating the determinant of this system to zero, we obtain the following equation for finding the roots of system (14):

$$\begin{aligned} \text{Det}_W &= [\lambda - (A + k + 1/T_1 + G)](\lambda - k)(\lambda - a) \\ &\quad - \lambda k(k + G) + ka(A + k + G) = 0. \end{aligned} \quad (15)$$

Solving system (14) leads to the following expression for the Laplace transform of the start–stop correlator:

$$\begin{aligned} s(\lambda) &= W_1(\lambda)/T_1 = \frac{k(a - \lambda)/T_1}{(\lambda_0 - \lambda)(\lambda_1 - \lambda)(\lambda_2 - \lambda)} \\ &= \lambda_1 \lambda_2 \frac{\lambda_0}{a} \frac{(a - \lambda)}{(\lambda_0 - \lambda)(\lambda_1 - \lambda)(\lambda_2 - \lambda)}. \end{aligned} \quad (16)$$

Here, λ_j are the roots of Eq. (15). At $k = 10^5 \text{ s}^{-1}$, $1/T_1 = 10^8 \text{ s}^{-1}$, $G = 10^7 \text{ s}^{-1}$, $A = 3.7 \times 10^5 \text{ s}^{-1}$, and $a = 200 \text{ s}^{-1}$, we find the following values for roots $\lambda_2 = 1.105 \times 10^8 \text{ s}^{-1} \cong 1/T_1 = 10^8 \text{ s}^{-1}$, $\lambda_1 = 9.085 \times 10^4 \text{ s}^{-1} \cong k = 10^5 \text{ s}^{-1}$, $\lambda_0 = 199.261 \text{ s}^{-1} \cong a = 200 \text{ s}^{-1}$ and arrive at the following values for the average lengths of *on* and *off* intervals: $\tau_{\text{on}} = 3 \text{ ms}$ and $\tau_{\text{off}} = 5 \text{ ms}$.

Performing an inverse Laplace transformation in (16), we obtain the following expression for the start–stop correlator:

$$\begin{aligned} s(t) &= \lambda_1 \lambda_2 \frac{\lambda_0}{a} \left[\frac{(a - \lambda_0)e^{-\lambda_0 t}}{(\lambda_2 - \lambda_0)(\lambda_1 - \lambda_0)} \right. \\ &\quad \left. - \frac{(a - \lambda_1)e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)(\lambda_1 - \lambda_0)} + \frac{(a - \lambda_2)e^{-\lambda_2 t}}{(\lambda_2 - \lambda_1)(\lambda_2 - \lambda_0)} \right] = \\ &= \sum_{j=0}^2 s_j \exp(-\lambda_j t). \end{aligned} \quad (17)$$

The three exponential processes manifested in the start–stop correlator correspond approximately to the rate of spontaneous fluorescence, $1/T_1 = 10^8 \text{ s}^{-1}$; the rate of light absorption by a nanoparticle, $k = 10^5 \text{ s}^{-1}$; and the rate of the transition from the dark state to the ground electron state of the nanoparticle, $a = 200 \text{ s}^{-1}$.

Raising to the N -th power the Laplace transform of the start–stop correlator we arrive at the following expression:

$$s(\lambda)^N = \lambda_1 \lambda_2 \left(\frac{\lambda_0}{a} \right)^N \left(\frac{a - \lambda}{\lambda_0 - \lambda} \right)^N \frac{\lambda_1^{N-1}}{(\lambda_1 - \lambda)^N} \frac{\lambda_2^{N-1}}{(\lambda_2 - \lambda)^N}. \quad (18)$$

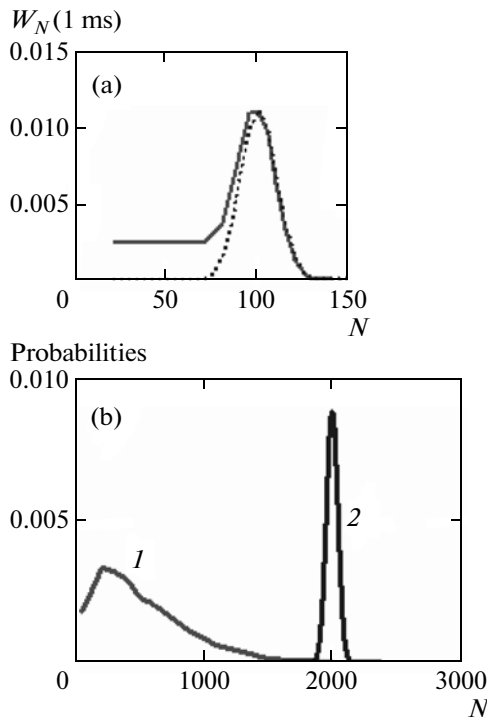


Fig. 3. Photon distribution in the blinking fluorescence shown in Fig. 2a at an accumulation time of 1 ms (a), and in the quasi-continuous fluorescence shown in Fig. 2b at an accumulation time of 20 ms (b). The dashed line shows the Poisson distribution; line 2 shows the photon distribution in the true continuous fluorescence.

Here, the two last ratios are the Laplace transforms of the Poisson function $P_N(\lambda, t) = (\lambda, t)^N \exp(-\lambda, t)/N!$. Considering that

$$\begin{aligned} \left(\frac{a-\lambda}{\lambda_0-\lambda}\right)^N &= \left(1 + \frac{a-\lambda_0}{\lambda_0} \frac{\lambda_0}{\lambda_0-\lambda}\right)^N \\ &= \sum_{m=0}^N \frac{N!}{m!(N-m)!} \left(\frac{a-\lambda_0}{\lambda_0}\right)^m \left(\frac{\lambda_0}{\lambda_0-\lambda}\right)^m, \end{aligned} \quad (19)$$

we can express the N th power of the Laplace transforms of the start-stop correlator via the Laplace transforms of three Poisson functions:

$$\begin{aligned} s(\lambda)^N &= \lambda_1 \lambda_2 \left(\frac{\lambda_0}{a}\right)^N \\ &\times \sum_{m=0}^N C_N^m \left(\frac{a-\lambda_0}{\lambda_0}\right)^m \lambda_0 \frac{\lambda_0^{m-1}}{(\lambda_0-\lambda)^m} \frac{\lambda_1^{N-1}}{(\lambda_1-\lambda)^N} \frac{\lambda_2^{N-1}}{(\lambda_2-\lambda)^N} \\ &= \lambda_1 \lambda_2 \left(\frac{\lambda_0}{a}\right)^N \left[P_{N-1}^{\lambda_1}(\lambda) P_{N-1}^{\lambda_2}(\lambda) + \lambda_0 \right. \\ &\left. \times \sum_{m=1}^N C_N^m \left(\frac{a-\lambda_0}{\lambda_0}\right)^m P_{m-1}^{\lambda_0}(\lambda) P_{N-1}^{\lambda_1}(\lambda) P_{N-1}^{\lambda_2}(\lambda) \right]. \end{aligned} \quad (20)$$

After inverse Laplace transformation to a function of time, arrive at the following expression:

$$\begin{aligned} [s(\lambda)^N]_t &= \lambda_1 \lambda_2 \left(\frac{\lambda_0}{a}\right)^N \left\{ \int_0^t dx P_{N-1}[\lambda_1(t-x)] P_{N-1}[\lambda_2 x] \right. \\ &+ \lambda_0 \sum_{m=1}^N C_N^m \left(\frac{a-\lambda_0}{\lambda_0}\right)^m \int_0^t dx P_{m-1}[\lambda_0(t-x)] \\ &\left. \times \int_0^x dy P_{N-1}[\lambda_1(x-y)] P_{N-1}[\lambda_2 y] \right\}. \end{aligned} \quad (21)$$

By substituting this expression in formula (7) for the photon distribution function, we can calculate the photon distribution at various times T of photon accumulation. To accomplish this, we must first calculate triple integrals from the Poisson functions.

Formula (21) reveals an important connection between the dynamics of a nanoparticle and the statistics of its radiation: Each exponential process with relaxation constant λ_j in the dynamics of the nanoparticle is expressed through a Poisson function with the same relaxation constant in the photon distribution function.

In [9], the photon distribution functions for various times of photon accumulation were calculated using formulas (7) and (21). The results for the photon distribution functions calculated for photon distribution times of 1 and 20 ms are presented in Fig. 3.

The photon distributions presented in Fig. 3 were measured in fluorescence whose intensity of fluctuations is shown in Fig. 2. The photon distribution in Fig. 3a has a plateau extending to small values of N . The appearance of nonzero probability at small values of N can be explained by certain intervals of time T falling only partially in *on* intervals with fluorescence photons when *off* intervals are present, as a large number of them fall in *off* intervals without photons. This is why the probability of measuring a small number of photons in an interval T exceeding the average interval between photons is not infinitely low, as the plateau in the distribution in Fig. 3a shows.

With long photon accumulation times, the fluorescence will appear to be continuous (without *off* intervals), as is shown in Fig. 2b. However, the photon distribution in such continuous fluorescence is described by the wide distribution 1 (Fig. 3b). This photon distribution differs greatly from the one described by function 2 in Fig. 3b, which would be measured in true continuous fluorescence without alternating *on* and *off* intervals. Measuring distribution 1 instead of 2 would thus be a signal that the seemingly continuous fluorescence measured by a photodetector is in fact not continuous. On the contrary, it consists of *on* and *off* intervals invisible to an observer because of the low time resolution of the setup.

CONCLUSIONS

We have shown that studies of the blinking fluorescence of single nanoparticles offer new possibilities for investigating the quantum dynamics of a nanoparticle excited by continuous laser light. When fluorescence blinking is not manifested, i.e., when the fluorescence appears to be a continuous glow, our theory of the functions of fluorescence photon distribution allows us to determine the dynamics of a nanoparticle as exhibited in *on* \rightarrow *off* jumps invisible to an observer because of the low time resolution of the setup. It is enough to compare distributions 1 and 2 in Fig. 3b to establish the presence of *on* \rightarrow *off* - dynamics in fluorescence that appears to be a continuous glow.

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