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Distribution of Photons in Single Quantum Dot Intermittent Photoluminescence with Power-Law Distribution of On/Off Intervals

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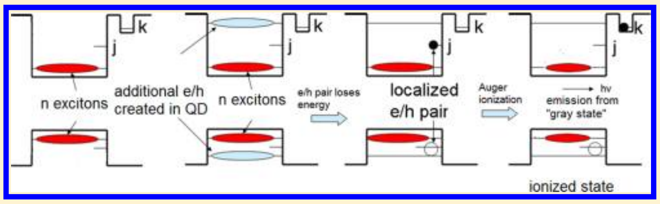
ABSTRACT: Monte Carlo simulation is used to calculate random time instants of photon emission in single core–shell quantum dot fluorescence with power-law distribution of on and off intervals. Simulation is based on the rate equations which describe a model proposed earlier by the author (*JETP Lett.* **2004**, *79*, 416) for the quantum dots with many doorways for ionization. After statistical treating of random instants of photon emission, the on/off distributions obeying $1/t^{1+m}$ law with $0 < m \leq 0.8$ are found. The value of m informs us about the character of the distribution of surface levels in the core and trap levels in the shell near the core–shell interface. Probabilities $w_N(t)$ of finding N photons in time interval t in fluorescence with power-law distribution of on and off intervals are calculated for a few values of bin time t. The distribution $w_N(t)$ of photon counts in quantum dot photoluminescence with rather intensive fluorescence from so-called "gray states" and with background light is calculated as well. It agrees well with the distribution of counts found in the experiment with blinking fluorescence of CdSe/ZnS single quantum dots.



1. INTRODUCTION

Intermittent photoluminescence (PL) of single colloidal semiconductor quantum dots (QDs) has been the subject of considerable interest for the past decade.[1−4] Early studies[5−11] were aimed to explain the power-law distributions of on/off intervals. Later, considerable attention was paid to the fast dynamics of emission from on and off states of QDs[12−17] and to the fine structure of PL bands of excitons, biexcitons, and trions.[18,19] It was found[12,13] that weak PL does exists in so-called off states of QD. Off states with weak PL were named "gray states".[16]

However, despite many facts discovered during the past decade in PL of single QDs, many details of a theoretical model for intermittent PL of single QDs are still a subject for discussion. Therefore, the use of new experimental methods in studying intermittent PL of QDs and theoretical calculations related to these methods are desirable.

It is to be noted that intermittent PL emerges not only in single semiconductor QDs. Many types of single complex molecules, for instance, polymer molecules, exhibit blinking PL as well.[20,21] The dynamics of on/off jumps in PL of a single molecule is determined by lifetimes of "dark states" inherent to the molecule. Dark states in complex molecules can have various physical origins.[21,22]

The experimental and theoretical study of blinking PL of complex molecular systems revealed high efficiency of the method based on the measure and the calculation of the probability $w_N(t)$ of finding N photons in bin time t.[23−25] For instance, the shape of the function $w_N(t)$ enables one to get information concerning very fast on/off jumps even in a situation when these jumps are not visible in the PL track because of low time resolution.[25] Therefore, measurement and theoretical treatment of the photon distribution function $w_N(t)$ in intermittent PL of single QDs are desirable indeed.

Unfortunately, experimental data on the photon distribution $w_N(t)$ for PL of single QDs are very scarce.[26,27] Theoretical analysis of these data has not been carried out so far. Therefore, the main tasks of this paper are as follows: (i) the formulation of the theoretical model for QDs with PL from gray states and the calculation of random time instants of photon emission by using the Monte Carlo technique, (ii) the calculation of the distribution of on/off intervals, (iii) the calculation of the photon distribution function $w_N(t)$ for PL with power-law distribution of on/off intervals, (iv) the comparison of the calculated distributions $w_N(t)$ with the measured ones in ref 26.

2. A MICROSCOPIC MODEL FOR FLUORESCENCE INTERMITTENCY IN QD

First of all, we should pick out such a theoretical model which is able to describe power-law distribution for on/off intervals and explain the appearance of PL from the gray states. For the basis of our model, we choose the mechanism of ionization/neutralization of QDs proposed by Efros and Rosen.[28] Such a model was substantially modified in refs 29 and 30, in which the core surface levels were considered to explain power-law distribution of on intervals. By now, the important role of the core surface levels is already recognized. Chemical and physical methods of manipulation with shell levels including "giant" QDs are used to increase PL quantum yield.[31−34]

The authors of ref 34 believe the following: "Although details (*of the QD model I.O.*) are still unclear, a consensus has emerged that PL blinking is fundamentally caused by extra charges in nanocrystal that greatly enhance nonradiative decay

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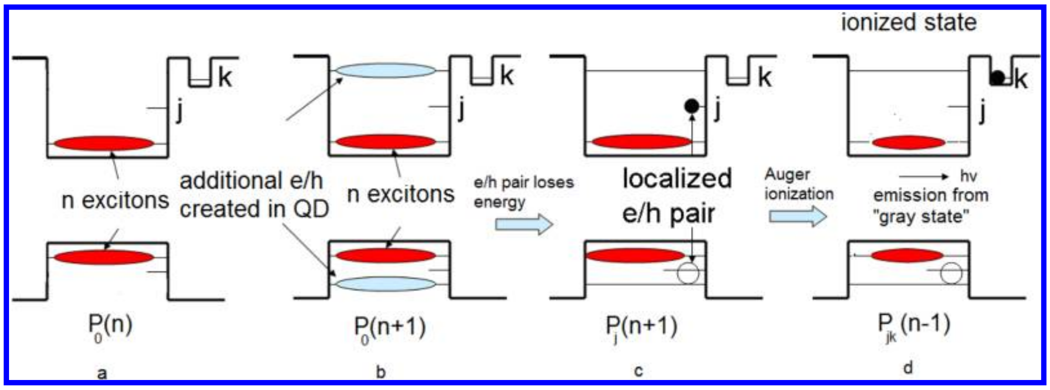

Figure 1. Process of ionization in core−shell QDs. (a) There are $n = 1, 2$ excitons in a core of QD excited by CW laser light. These excitons create fluorescence. (b) An additional electron−hole pair is created after the absorption of one laser photon. (c) This electron−hole pair loses energy due to the electron−phonon interaction, and its electron can occupy localized state j on the surface of the core. (d) In the process of the Auger ionization, one exciton annihilates and its energy is transferred to the electron in state j. This electron is ejected from the core with the rate $1/t_{A_j}$ and gets trap k in the shell. The intensity of PL from this ionized state is reduced. These states are called "gray states".

rates". In our model[29,30] based on this idea, the process of ionization in QD looks as it is shown in Figure 1.

The main result of the ionization of QD is the reduction of the quantum yield of photoluminescence from QD. The theories[28−30] assumed that fluorescence stops in the ionized state. Therefore, off states were considered as nonemissive states. Now we assume the ionized states can emit weak PL.

If we take into account that the state shown in Figure 1d can emit weak light, we will detect photons of two types: photons emitted from off states (gray states) and photons emitted from on states. The number of photons emitted from gray states is considerably less as compared to the number of photons emitted from on states. Nevertheless, photons emitted from gray states will contribute to the photon distribution function $w_N(t)$. It will be shown further.

The diagram depicted in Figure 2 is able to explain the appearance of PL from on states and from gray states.

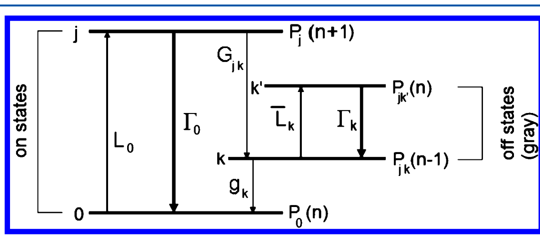

Figure 2. Core−shell QD excited by CW laser light with the ionization going via the jth surface level and with few trap levels in the shell numbered by k.

The diagram shown in Figure 2 is the diagram for the quantum states but not the diagram for the energy levels. Therefore, there is no contradiction with Figure 1 in which trap level k is shown higher as compared with doorway level j. Here $P_0(n)$ is the probability of finding $n = 1,2$ e−h pairs in QD. $P_j(n + 1)$ is the probability of finding n e−h pairs simultaneously with the jth localized e−h pair whose electron can escape the core, $P_{jk}(n - 1)$ is the probability of finding QD after the jth electron is transferred to the kth shell trap because of Auger ionization, and $P_{jk'}(n)$ is the probability of finding the ionized QD with n e−h pairs. $P_0(n)$ and $P_j(n + 1)$ relate to the neutral QD with bright fluorescence. $P_{jk}(n - 1)$ and $P_{jk'}(n)$ relate to the ionized form of QD with weak fluorescence (fluorescence from so-called "gray" states). $\Gamma_0 = \gamma_{em} + \gamma_0$ and $\Gamma_k = \gamma_{em} + \gamma_k$. Here γ_{em} is the rate of light emission and γ_0 and γ_k are the rates of nonradiative transitions in the neutral state and in ionized states, respectively. $L_0 = L\gamma_{em}/\Gamma_0$, $\overline{L_k} = L\gamma_{em}/\Gamma_k$, and L is the rate of light absorption.

In accordance with this diagram, the ionization of the core in core/shell QD is realized via jth localized electronic states situated in the surface of the core in the core/shell interface. States j are populated by an electron from the electron/hole pairs created permanently by laser light. States j are doorways for the core ionization. G_{jk} is the rate of the jth electron transition to the kth trap, and g_k is the rate of deactivation of the kth trap.

The diagram presented in Figure 2 was built up by using the charging model. However, it can describe also the multiple recombination centers (MRC) model[31] based, in fact, on the two-level system (TLS) model with fluctuating nonemissive transitions with rates γ_k. More details of the model sketched in Figure 2 are depicted in Figure 3.

In accordance with the diagram shown in Figure 2, we can write the following set of equations for the QD emitter

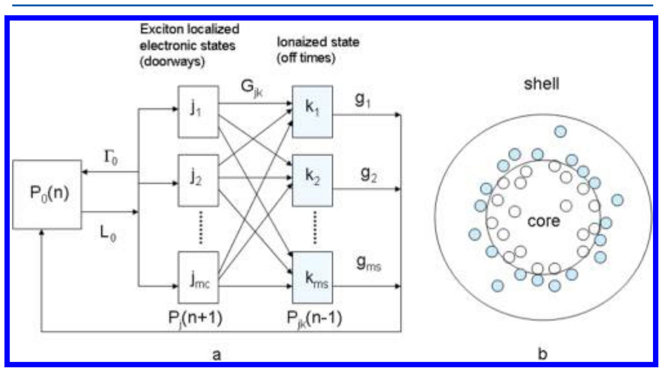

Figure 3. (a) Transitions between neutral and ionized forms of QDs. White squares relate to the on states of QD. Gray squares depict gray states with weak PL. (b) Doorway states j (open circles) and traps k (gray circles) The most localized states situated in the immediate region of the core−shell interface. Few doorways and traps are shifted inside the core and shell, respectively.

$$\begin{aligned}\dot{P}_j(n+1) &= -(\Gamma_0 + \sum_k G_{jk})P_j(n+1) + L_0 P_0(n)\\ \dot{P}_0(n) &= \Gamma_0 P_j(n+1) - L_0 P_0(n) + \sum_k g_k P_{jk}(n-1)\\ \dot{P}_{jk}(n-1) &= G_{jk}P_j(n+1) - (g_k + \overline{L}_k)P_{jk}(n-1) + \Gamma_k P_{jk'}(n)\\ \dot{P}_{jk'}(n) &= \overline{L}_k P_{jk}(n-1) - \Gamma_k P_{jk'}(n)\end{aligned} \tag{1}$$

These equations enable one to calculate both the distribution of on/off intervals and the distribution of photons in PL. Indexes j and k run over all doorways and traps.

PL of a neutral QD is rather bright. Such a state will be called the "bright state" or on state. It has been found later[12,13] that the states with weak emission exist in QD as well. Such states were named "gray states".[16] Rates γ_k of nonradiative transitions from gray states are larger as compared to the rate γ_0 of nonradiative transition in the on state.

The PL intensity from gray states is given by

$$\overline{L}_k = \frac{L_0\gamma_{\mathrm{em}}}{\gamma_{\mathrm{em}} + \gamma_k} \ll L_0 \tag{2}$$

The decay of PL from each kth gray state is of the exponential type with the following relaxation time:

$$t_k = (\gamma_{\mathrm{em}} + \gamma_k)^{-1} \tag{3}$$

If the nonradiative rate γ_k takes a few values (fluctuates), the intensity $\overline{L}_k$ and time t_k of PL decay will fluctuate as well. Fluctuations of $\overline{L}_k$ will correlate with fluctuations of t_k: the weaker the intensity $\overline{L}_k$ is, the faster the decay of fluorescence with time t_k is. This result of our model is in agreement with experimental findings.[12,13] Further, we shall call bright and gray states on and off states.

3. DISTRIBUTION OF ON AND OFF INTERVALS

First of all, we must show that our model results in power-law distributions of on/off intervals. It will be shown in two ways: (A) We derive theoretical expressions for the distribution of on/off intervals directly from eq 1. (B) We find the distribution of on/off intervals applying the Monte Carlo technique to rate equations. Both ways will be used.

(A) In accordance with Figure 2, we can write the following equations for the probabilities of finding QD in on or off states:

$$P_j^{\mathrm{on}} = P_0 + P_j, \quad P_{jk}^{\mathrm{off}} = P_{jk} + P_{jk'} \tag{4}$$

Fast dynamics are governed by the largest rate constants Γ_0 and Γ_k. If we want to consider slower on−off dynamics, we can neglect fast dynamics by setting

$$\dot{P}_j = \dot{P}_{jk'} = 0 \tag{5}$$

Then, we can find the following relations

$$P_j = \frac{L_0}{\Gamma_0 + \sum_k G_{jk}}P_0, \quad P_{jk} = \frac{\Gamma_k}{\overline{L}_k}P_{jk'} \tag{6}$$

from the first and fourth lines of eq 1. By inserting eq 6 into eq 4, we arrive at the following relations:

$$P_j = \frac{L_0}{L_0 + \Gamma_0 + \sum_k G_{jk}}P_j^{\mathrm{on}}, \quad P_{jk} = \frac{\Gamma_k}{\Gamma_k + \overline{L}_k}P_{jk}^{\mathrm{off}} \tag{7}$$

Summing up the two first lines and the two last lines in eq 1, we arrive at the following two equations:

$$\begin{aligned}\dot{P}_j^{\mathrm{on}} &= -\sum_k G_{jk}P_j + \sum_k g_k P_{jk}\\ \dot{P}_{jk}^{\mathrm{off}} &= -g_k P_{jk} + G_{jk}P_j\end{aligned} \tag{8}$$

By inserting eq 7 into eq 8, we can transform eq 8 into the following form:

$$\begin{aligned}\dot{P}_j^{\mathrm{on}} &= -\frac{1}{\tau_{\mathrm{on}}^j}P_j^{\mathrm{on}} + \underline{\sum_k \frac{1}{\tau_{\mathrm{off}}^k}P_{jk}^{\mathrm{off}}}\\ \sum_k \dot{P}_{jk}^{\mathrm{off}} &= \underline{\frac{1}{\tau_{\mathrm{on}}^j}P_j^{\mathrm{on}}} - \sum_k \frac{1}{\tau_{\mathrm{off}}^k}P_{jk}^{\mathrm{off}}\end{aligned} \tag{9}$$

Here

$$\begin{aligned}\frac{1}{\tau_{\mathrm{on}}^j} &= L_0\frac{\sum_k G_{jk}}{L_0 + \Gamma_0 + \sum_k G_{jk}} = L_j\\ \frac{1}{\tau_{\mathrm{off}}^k} &= g_k\frac{\Gamma_k}{\Gamma_k + \overline{L}_k} \cong g_k\end{aligned} \tag{10}$$

Equation 9 describes jumps from on states to off states and back; i.e., it describes the dynamics of mutual conversations of on/off intervals. In order to find the dynamics of on or off states, we need to omit the underlined terms. Then, we can arrive at new equations:

$$\dot{p}_{\mathrm{on}}^j = -\frac{1}{\tau_{\mathrm{on}}^j}p_{\mathrm{on}}^j \qquad \dot{p}_{\mathrm{off}}^k = -\frac{1}{\tau_{\mathrm{off}}^k}p_{\mathrm{off}}^k \tag{11}$$

Here $p_{\mathrm{off}}^k = \sum_j p_{jk}^{\mathrm{off}}$ describes the probability of finding QD with an electron in the kth trap. The following solutions

$$w_{\mathrm{on}}^j(t) = \exp(-t/\tau_{\mathrm{on}}^j)/\tau_{\mathrm{on}}^j \qquad w_{\mathrm{off}}^k(t) = \exp(-t/\tau_{\mathrm{off}}^k)/\tau_{\mathrm{off}}^k \tag{12}$$

of eq 11 describe the probability density of finding an on interval of duration t in a sequence of on intervals with the average duration τ_{on}^j and an off interval of duration t in a sequence of off intervals with the average duration τ_{off}^k.

The distribution of all on and off intervals can be described by the following equations:

$$\begin{aligned}w_{\mathrm{on}}(t) &= \frac{1}{N_0}\sum_{j=1}^{N_0} w_{\mathrm{on}}^j(t) = \frac{1}{N_0}\sum_{j=1}^{N_0} L_j \mathrm{e}^{-L_j t}\\ w_{\mathrm{off}}(t) &= \frac{1}{N_t}\sum_{k=1}^{N_t} w_{\mathrm{off}}(t) = \frac{1}{N_t}\sum_{k=1}^{N_t} g_k \mathrm{e}^{-g_k t}\end{aligned} \tag{13}$$

Here N_0 is the number of doorways for the electron escape from the core and N_t is the number of traps accessible for the electron after its escape from the core of QD. If the power-law statistics for on intervals and off intervals range over 3 orders of the magnitude in time scale, these sums must include terms with rate constants ranging at least in 3 orders of magnitude.

Let us assume that the QD shell has three types of traps with lifetime $1/g_k$; that is, index k runs 1, 2, and 3. Analogously to the situation with traps, the QD core has three types of doorways for ionization; that is, index j runs 1, 2, and 3 as well.

We also set $G_{jk} = G_j$. This is an approximation. In this approximation, the distribution of on intervals will not correlate with the distribution of off intervals. Hence, we have three rates G_1, G_2, and G_3 of ionization and three rates g_1, g_2, and g_3 of neutralization of QD.

Strictly speaking, the number of surface levels and traps in the core/shell interface is certainly more than three, i.e., numbers N_0 and N_t in eq 13 exceed 3 considerably. Therefore, eq 13 can be rewritten in the following form:

$$w_{\rm on}(t) = \sum_{j=1}^{3} u_j L_j e^{-L_j t} \qquad w_{\rm off}(t) = \sum_{k=1}^{3} v_k g_k e^{-g_k t} \tag{14}$$

It is obvious that u_j can be considered as the probability of finding a doorway for the ionization with rate L_j, and v_k is the probability of finding the trap with lifetime $1/g_k$. The probabilities must satisfy the natural condition $u_1 + u_2 + u_3 = v_1 + v_2 + v_3 = 1$. It is obvious, u_j is proportional to the population of surface levels which governs the ionization with rate L_j. The probability v_k is proportional to the number of traps with lifetime $1/g_k$. The simple equations in eq 14 are able to describe the power-law distribution of on/off intervals. It will be shown further.

(B) Consider now a statistical method. Equation 14 enables us to calculate the distribution of on/off intervals that have been derived from eq 1 by neglecting the fast photon dynamics. Indeed, photons of bright and gray PL fill up on and off intervals, respectively. Equation 5 means that we neglect fast dynamics; i.e., we neglect the photon sequence in on intervals. Slow dynamics are described by $0 \to j$, $j \to k$, and $k \to 0$ transitions depicted in Figures 2 and 3. Therefore, slow dynamics of on−off and off−on jumps can be described by the scheme shown in Figure 4.

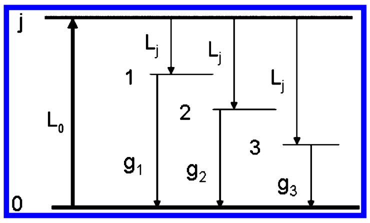

Figure 4. Scheme describing the dynamics of $0 \to j$, $j \to k$, and $k \to 0$ jumps.

Here L_j and g_k are defined by eq 10. They describe rates of ionization and neutralization, respectively. In accordance with Figure 4, the dynamics of on−off jumps can be described by the following rate equations:

$$\dot{P}_j = -3L_jP_j + L_0P_0$$
$$\dot{P}_0 = -L_0P_0 + \sum_{k=1}^{3} g_kP_k$$
$$\dot{P}_k = L_jP_j - g_kP_k \tag{15}$$

Applying the Monte Carlo technique to eq 15, we can find random values of on and off intervals. After statistical treatment of these random values of intervals, we find the distribution of on/off intervals. We can compare these distributions with the distributions calculated with the help of eq 14.

On Intervals. Time intervals between $0 \to j$ and $j \to k$ transitions are on intervals. They have been calculated with the following set of parameters:

$$L_0 = 10^4\ {\rm s}^{-1}, \quad g_1 = 10^3\ {\rm s}^{-1}, \quad g_2 = 10^2\ {\rm s}^{-1}, \quad g_3 = 10^1\ {\rm s}^{-1}, \quad L_1 = 10^2\ {\rm s}^{-1}, \quad L_2 = 10\ {\rm s}^{-1}, \quad L_3 = 10^0\ {\rm s}^{-1} \tag{16}$$

Probabilities u_j of finding doorway j are not included in eq 15. We must take into account that eq 15 is realized with the probability u_j at CW laser excitation. Hence, probabilities u_j should be taken into account in the course of our Monte Carlo simulation. The result for on intervals simulated with parameters (eq 16) and with the probabilities

$$u_1 = 0.7, \quad u_2 = 0.2, \quad u_3 = 0.1 \tag{17}$$

is presented in Figure 5.

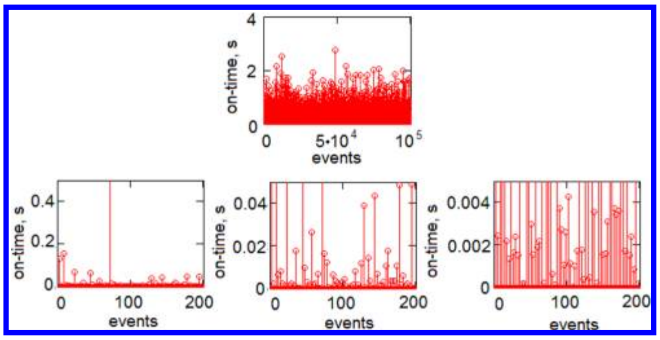

Figure 5. All on intervals found between $0 \to j$ and $j \to k$ transitions shown in Figure 4 (upper panel) and first 200 on intervals calculated by the Monte Carlo method (lower panels). On intervals shown in the lower panels are distinguished from each other by 1 and 2 orders of the magnitude.

Statistical treating of all on intervals shown in the upper panel of Figure 5 with the binning time of 10 ms results in the on interval distribution shown in Figure 6.

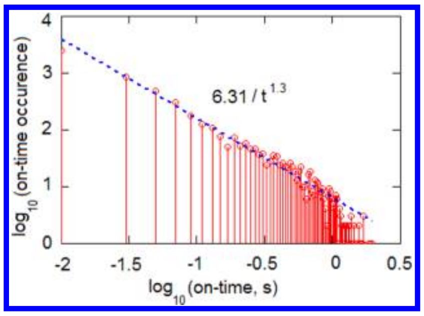

Figure 6. Distribution of on intervals obtained by statistical treating of on intervals simulated at $u_1 = 0.7$, $u_2 = 0.2$, and $u_3 = 0.1$ and shown in the upper panel of Figure 5. $t_{\rm bin} = 10$ ms.

This power-law distribution differs considerably from the exponential distribution predicted by the Efros−Rosen theory[28] that took into account only excitons for Auger ionization and ignores the important role of surface levels of the core in the ionization of QD.

It would be interesting to clarify the role of the probabilities u_j in the formation of the exponent value in the on time power law. Figure 7 shows the on time distribution calculated by the same method but with use of equal probabilities, $u_1 = u_2 = u_3 = 1/3$, of finding the jth doorway for ionization.

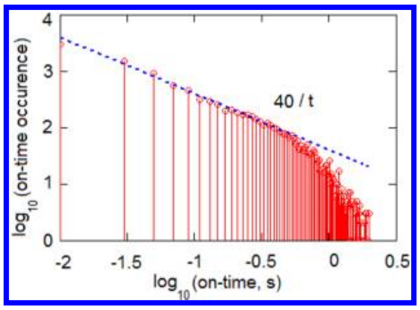

Figure 7. Same as in Figure 6 but with $u_1 = u_2 = u_3 = 1/3$.

The comparison of Figure 7 with Figure 6 allows us to make such conclusions. (1) The nearer the distribution of the probabilities u_j to homogeneous, the less the exponent of the power law is. (2) The time interval in which the power law holds is shorter for a homogeneous distribution of u_j.

The distribution $u_1 = 0.7$, $u_2 = 0.2$, and $u_3 = 0.1$ used for calculation of the distribution depicted in Figure 6 manifests a very important feature: the doorway for the fastest ionization has the most weight in the distribution u_j. It will be natural to suppose that the fastest ionization is realized via core surface states localized on atoms situated immediately in the core−shell interface. The probability of finding such states is $u_1 = 0.7$. It can be supposed that slower ionization is realized via levels j which belong to atoms slightly shifted inside the core. The number of such doorways is certainly less. Therefore, we have $u_2 = 0.2$ and $u_3 = 0.1$ for such levels, respectively. Such a distribution of doorway atoms is shown in Figure 3b.

Hence, the slope of the power law for on times informs us about the degree of localization of doorways for ionization near the core−shell interface: the more degree of localization of levels j near the core−shell interface is, the more value of m in the distribution $1/t^{1+m}$ occurs. The distribution shown in Figure 6 can be described also by simple eq 14 with L_j described by eq 16 and the parameters $u_1 = 0.7$, $u_2 = 0.2$, and $u_3 = 0.1$. Hence, the theoretical formulas (eq 14) and the distribution found from eq 15 with the help of the Monte Carlo method give similar results.

Off Intervals. The scheme depicted in Figure 4 and eq 15 can be used for finding the distribution of off intervals. An off interval begins by $j \to k$ transition, and it ends by $k \to 0$ transition. Here $k = 1$, 2, or 3 are numbers of trap levels. Off intervals simulated with the help of eq 15 and parameters

$$L_0 = 10^4\ \mathrm{s}^{-1}, \quad L_1 \cong 10^2\ \mathrm{s}^{-1}, \quad L_2 \cong 10\ \mathrm{s}^{-1},$$
$$L_3 \cong 10^0\ \mathrm{s}^{-1}, \quad g_1 = 10^3\ \mathrm{s}^{-1}, \quad g_2 = 10^2\ \mathrm{s}^{-1},$$
$$g_3 = 10^1\ \mathrm{s}^{-1}, \quad u_1 = 0.7, \quad u_2 = 0.2, \quad u_3 = 0.1,$$
$$\nu_1 = \nu_2 = \nu_3 = 1/3 \tag{18}$$

are depicted in Figure 8.

After statistical treating of all off intervals with a binning time of 1 ms, we arrive at the distribution shown in Figure 9.

The distribution of off intervals shown in Figure 9 can be described also by eq 14 with $\nu_1 = \nu_2 = \nu_3 = 1/3$, i.e., at a homogeneous distribution of traps. It does not depend on the distribution of on times. The slope of power-law distribution increases if the probability ν_1 of finding traps with the shortest

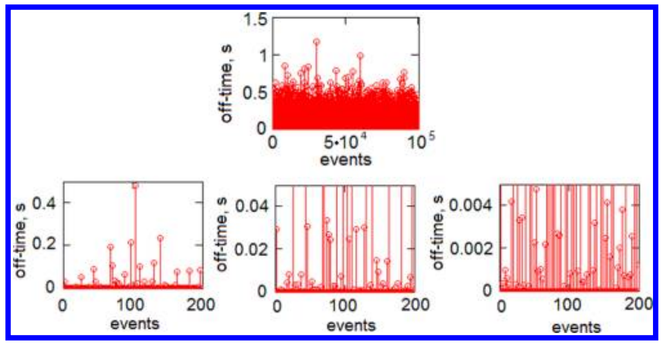

Figure 8. Same as in Figure 5 but only for off intervals (times between $j \to k$ and $k \to 0$ transitions shown in Figure 4).

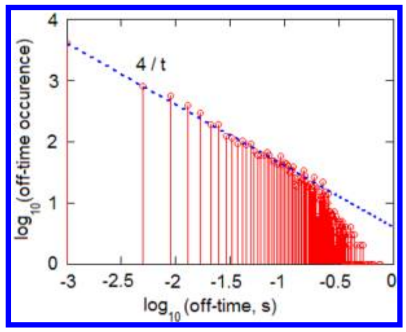

Figure 9. Distribution of off intervals obtained by statistical treatment of all off intervals shown in Figure 8.

lifetime is increased as well. We can suppose that the traps with the shortest lifetime are situated on the core−shell interface, and the traps with longer lifetime are shifted inside the shell. It will be natural if we assume that the number of traps on the shell surface exceeds the number of traps inside the shell.

Figure 10 shows the distribution of off intervals, calculated with the help of eq 14 and with various distributions for probabilities ν_k.

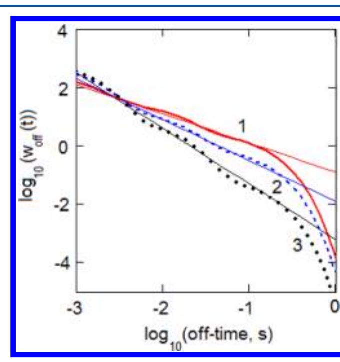

Figure 10. Distribution of off intervals calculated with the help of eq 14 at $\nu_1 = \nu_2 = \nu_3 = 1/3$ (1), $\nu_1 = 0.7$, $\nu_2 = 0.2$, $\nu_3 = 0.1$ (2), and $\nu_1 = 0.9$, $\nu_2 = 0.09$, $\nu_3 = 0.01$ (3) . Straight lines show power laws: $10^{0.9}/t$ (1), $10^{-1.9}/t^{1.4}$ (2), and $10^{-3.2}/t^{1.9}$ (3).

We may conclude that the slope of the power law in off distribution informs us about the degree of localization of traps near the core−shell interface: the more degree of localization of traps near the core−shell interface is, the steeper slope of the power-law distribution occurs.

The power-law distributions of on/off intervals observed in Figures 6 and 10 show that the distribution of on/off times becomes exponential beyond the time interval of two to three decades. Tang and Marcus[35] offered a "diffusion-controlled electron-transfer" mechanism for explanation of the power-law distribution for on/off intervals extended for more decades. However, eq 14 with more terms in the sums over j and k can provide the power-law distribution of on/off intervals ranging over 5 orders of magnitude in time scale. Figure 5 in ref 30 shows this fact. Extension of the time interval t with the power law for on/off distribution can be determined by the values of the average on/off time intervals $\tau^{\text{on,off}}$ as follows: min $\tau^{\text{on,off}} < t <$ max $\tau^{\text{on,off}}$. The distribution acquires an exponential shape beyond this interval.

If we try to find distributions of on/off intervals with the help of statistical treatment of the measured PL track, we are faced with the choice of the threshold intensity of PL which enables us to refer a given interval to on or off type. It is a so-called "threshold intensity problem". Our Monte Carlo simulation for on/off intervals is free of such a problem.

4. DISTRIBUTION OF PHOTONS IN FLUORESCENCE OF QD

The photon distribution function $w_N(t)$ is a more informative characteristic of intermitted fluorescence as compared to the distribution of on and off intervals because it avoids the "threshold intensity problem". The probability $w_N(t)$ of finding N photons in time interval t can be measured and calculated if we have found random time instants of photon emission with the help of the Monte Carlo technique applied to eq 1. These random instants have been found with the help of the following set of parameters:

$$L_0 = 10^4\ \text{s}^{-1}, \quad \Gamma_0 = 10^{10}\ \text{s}^{-1}, \quad g_1 = 10^3\ \text{s}^{-1}, \quad g_2 = 10^2\ \text{s}^{-1}, \quad g_3 = 10^1\ \text{s}^{-1}, \quad G_1 = 10^8\ \text{s}^{-1}, \quad G_2 = 10^7\ \text{s}^{-1}, \quad G_3 = 10^6\ \text{s}^{-1}, \quad u_1 = 0.7, \quad u_2 = 0.2, \quad u_3 = 0.1 \tag{19}$$

which have already been used in section 3 in connection with the calculation of the distributions of on and off intervals shown in Figures 5 and 8. These random instants of photon detection are depicted in Figure 11.

The time scale is increased 10 times if we move from the upper panel in Figure 11 downward. We clearly see three time scales for on and off intervals like Kuno et al observed.[6]

We can calculate the PL track applying the Monte Carlo technique to eq 1. Taking a bin time of 1 ms and the following set of parameters

$$L_0 = 2 \times 10^4\ \text{s}^{-1}, \quad \Gamma_0 = 10^{10}\ \text{s}^{-1}, \quad G_1 = 2 \times 10^7\ \text{s}^{-1}, \quad G_2 = 2 \times 10^6\ \text{s}^{-1}, \quad G_3 = 2 \times 10^5\ \text{s}^{-1}, \quad \bar{L}_1 = 5 \times 10^3\ \text{s}^{-1}, \quad \bar{L}_2 = 3 \times 10^3\ \text{s}^{-1}, \quad \bar{L}_3 = 2 \times 10^3\ \text{s}^{-1}, \quad g_1 = 10^3\ \text{s}^{-1}, \quad g_2 = 10^2\ \text{s}^{-1}, \quad g_3 = 10\ \text{s}^{-1}, \quad u_1 = 0.7, \quad u_2 = 0.2, \quad u_3 = 0.1 \tag{20}$$

we arrive at the PL track shown in Figure 12. It includes PL from gray states.

Rates L_j found with the help of eq 10 with the set of parameters (eq 20) are $L_1 = 120\ \text{s}^{-1}$, $L_2 = 12\ \text{s}^{-1}$, and $L_3 = 1.2\ \text{s}^{-1}$. The narrow peak at small N in the photon distribution function shows the contribution from gray PL to the photon distribution function.

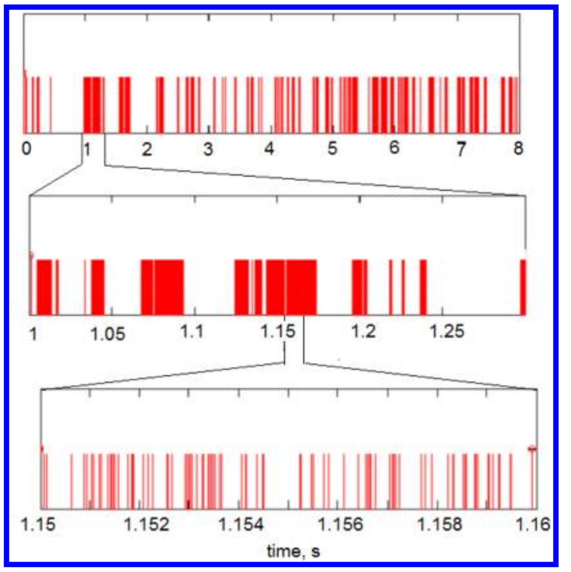

Figure 11. Random time instants of photon detection (without gray PL) calculated by the Monte Carlo technique for the emitter described by eq 1 and with parameters (eq 19).

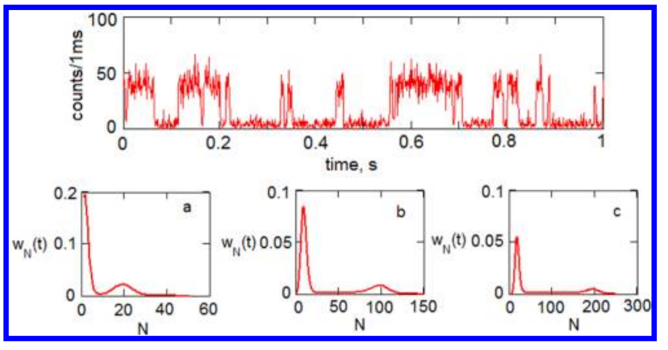

Figure 12. PL track allowing for light emitted from three gray states and the photon distribution function measured in this track with binning times 1 ms (a), 5 ms (b), and 10 ms (c).

If we measure the probability $w_N(t)$ of finding N photons in time interval t, we avoid the problem of "threshold intensity" indeed; however, the problem of background light emerges. Background light does not change the shape of the photon distribution function if the intensity of gray PL exceeds the intensity of background light. However, if the intensity of background light exceeds the intensity of gray PL, background light will change the shape of the photon distribution function considerably.

Background light does not correlate with the emission from QD. Photon statistics of light emitted from few uncorrelated emitters has been considered in ref 36. We can use the results of this paper. Considering background light as Poisson light from an independent emitter (noise), we can use the following equation for the distribution function for signal + noise:[36]

$$w_N^{s+n}(t) = \sum_{M=0}^{N} w_{N-M}(t) \frac{(qt)^M}{M!} \exp(-qt) \tag{21}$$

The upper panel of Figure 13 shows pure photon distribution functions calculated with the help of parameters (eq 20) without gray PL. The distributions are of strongly non-Poisson

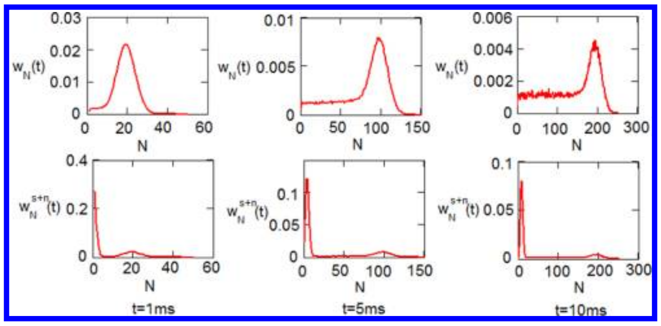

Figure 13. Distribution of photons calculated with parameters (eq 20) without background light (upper row) and with background light of the intensity of $q = 10^3 cps$ (lower row). The distributions in each column are calculated for the bin times shown at the bottom.

type. The lower panel of Figure 13 shows the distribution function for signal + noise.

Here the narrow peak shows the contribution from background light. The comparison of the photon distribution functions shown in Figures 12 and 13 shows that the contributions from background light and from gray PL are similar to each other: both result in a narrow peak at small N in the photon distribution function.

It would be interesting to compare the calculated photon distribution with the distribution of photons measured in an experiment. Unfortunately, experimental data on the photon distribution in fluorescence of single QD are scarce. Margolin et al.[26] discussed the role of Levy walk processes in the formation of the power law in on/off distributions in fluorescence of single QD. It would be interesting to see what type of photon distribution function can be produced by Levy walk processes in single core/shell CdSe/ZnS QDs. However, such a calculation has not been carried out in ref 26. The authors of this work pointed out that the shape of the distribution varies from one dot to another.

The two-peak distribution shown in Figure 2 of ref 26 looks similar to the two-peak distribution presented in Figure 12 of this work. The one-peak distribution presented in Figure 2 of ref 26 is shown here in Figure 14.

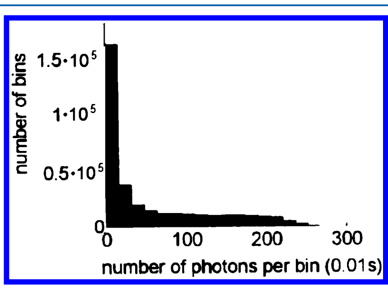

Figure 14. Distribution of photons in fluorescence of single CdSe/ZnS QDs measured at t = 10 ms.[26]

The typical features of measured distributions are a large narrow peak at small N and a flat distribution over the whole range of N. The theory enables one to calculate the distribution of events allowing for background fluorescence. Six parameters, $u_1 = 0.7$, $u_2 = 0.2$, $u_3 = 0.1$, $G_1 = 10^8\ s^{-1}$,$G_2 = 10^7\ s^{-1}$, $G_3 = 10^6\ s^{-1}$, needed for such a calculation can be found from the distribution of on intervals. Another six parameters, $g_1 = 6.3 \times 10^3\ s^{-1}$, $g_2 = 6.3 \times 10^2\ s^{-1}$, $g_3 = 63\ s^{-1}$, $\nu_1 = \nu_2 = \nu_3 = 1/3$, can be found from the distribution of off intervals. The rate $L_0 = 2 \times 10^4\ s^{-1}$ of photon counts is determined by the end of the photon distribution. The rate $q = 10^3\ s^{-1}$ of background emission is determined by the position of the narrow peak in Figure 14. The result of the calculation with these parameters is shown in Figure 15.

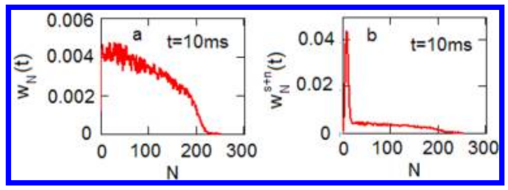

Figure 15. Distributions of photons with $L_0 = 2 \times 10^4\ s^{-1}$, $q = 0$ (a) and with $L_0 = 2 \times 10^4\ s^{-1}$, $q = 10^3\ s^{-1}$ (b).

The calculated distribution depicted in panel b of Figure 15 is similar in shape to the distribution of photons shown in Figure 14. The narrow peak in Figure 15b results from background light. However, it can originate from gray PL. If we had more detailed experimental data, we could distinguish these two cases.

5. CONCLUSION

Photon statistics in intermittent PL of single QDs with a power-law distribution of on/off intervals has been the main goal of the paper. Intermittent PL has been considered on the basis of the theoretical model described by eq 1 and Figures 2 and 3.

The theoretical model predicts the existence of intermittent PL with bright on intervals and off intervals with light of reduced intensity. The distributions of both on and off intervals are described by power laws with various slopes.

These power-law distributions of on/off intervals were obtained in section 3 in two ways: (i) with the help of the theoretical eq 14 that was derived directly from eq 1 and (ii) by a statistical method based on Monte Carlo simulation applied to eq 1. Both methods yield similar results for on/off interval distributions. Figure 10 calculated with the help of eq 14 enables one to relate the slope of the power law for an on/off distribution to the degree of localization of doorways and traps situated near a core−shell interface.

After we were convinced our model is able to explain the power-law distribution of on/off intervals, we have calculated in section 4 (i) tracks for PL allowing for bright and gray PL and (ii) the photon distribution functions $w_N(t)$ for three bin times t = 1, 5, and 10 ms. The influence of background light on the photon distribution function has been considered, and the distribution functions for signal and for signal + noise are shown in Figure 13.

The photon distribution function calculated in this paper is able to describe the photon distribution measured in ref 26. The necessary theoretical parameters can be found from the measured distribution of on/off intervals.

The scheme of quantum states depicted in Figure 2 can be considered as a modified version of the so-called charged model for QDs with intermittent PL.[28−30] However, recently a multiple recombination centers (MRC) model has been proposed in ref 31 for the explanation of intermittent PL from single QDs as an alternative model to the charged model. The MRC model is based, in fact, on the two-level-system (TLS) approach to QDs with intermittent PL.

However, if we determine off states in Figure 2 as dark states of TLS, QD dynamics in the frame of the MRC model can be described by Figure 2 as well. If "dark" states of TLS are related to the ionized core of QD, there will not be the difference in both models discussed. Unfortunately, photon statistics cannot distinguish which of the two models forms intermittent PL. Therefore, the question can be formulated as follows: Is charging or spectral diffusion the reason for the appearance of gray states in QDs? It is to be noted that experiments with an electrostatic microscope[37,38] demonstrate the existence of charge in QDs with intermittent PL.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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