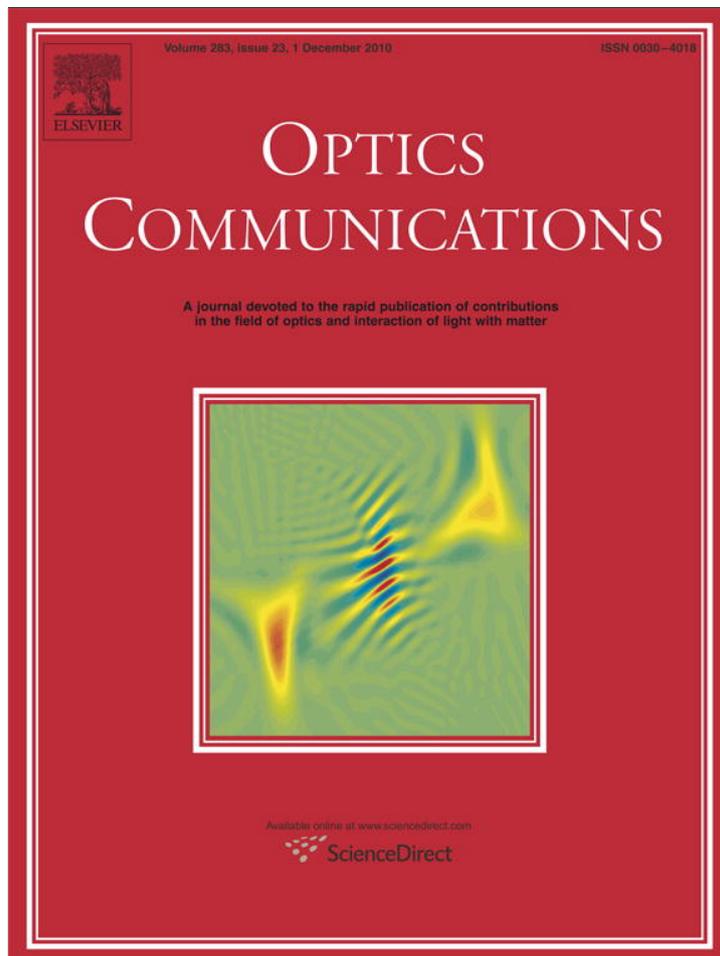


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Dynamical theory for photon and photoelectric pulse distributions in single molecule fluorescence

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ABSTRACT

A single two-level molecule driven by CW-laser field and a photomultiplier tube (PMT) are considered as two parts of the united dynamical system connected with each other by photons of molecular fluorescence. Each PMT is characterized by a rate α of photo-effect and by a rate β of PMT recovery. A theory for the photon distribution function $w_N(t)$ and for the photoelectric pulse distribution function $f_n(t)$ for such a system is built up. If times $1/\alpha$ and $1/\beta$ characterizing PMT are much shorter as compared to the average time interval $1/k$ between two successively emitted photons of fluorescence, the photon and the photoelectron distribution functions coincide with each other, i.e. $f_n(t) \cong w_N(t)$. A relation between $w_N(t)$ and $f_n(t)$ is studied in detail for the case in which PMT works slower as compared to the rate k of photon emission, i.e. at $1/\alpha, 1/\beta \geq 1/k$.

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1. Introduction

Development of the molecular ensemble spectroscopy towards single molecule spectroscopy [1,2] discovers new possibilities for studying the dynamics of electronic excitations in the molecules. These possibilities emerge due to detection of fluorescence photons emitted solely by a single molecule. These photons are emitted at random time moments but with the definite probability. The probability is determined by the dynamics of the molecular excited state. Therefore we are able to study the molecular dynamics by measuring the distribution of emitted photons in time. This new possibility disappears due to ensemble average if we deal with fluorescence of a molecular ensemble [3].

Consider fluorescence of a single molecule excited by CW-laser light. Such a molecule jumps from the ground electronic state to the excited electronic state by emitting photons at random time moments. Therefore the number N of photons emitted in equal time intervals of duration T will fluctuate. These fluctuations are described by the probability $w_N(T)$ of finding N photons at time interval T . The distribution $w_N(T)$ of emitted photons is narrower as compared with the Poissonian distribution, i.e. the distribution is of sub-Poissonian type [4–6].

However not each photon emitted by a single molecule arrives at a photo-multiplier tube (PMT). Therefore the distribution function $\bar{w}_N(T)$ of photons arrived at PMT will differ from the distribution

function $w_N(T)$ of emitted photons. A relation between $w_N(T)$ and $\bar{w}_N(T)$ was discussed in Ref. [7].

It is obvious that a photoelectric pulse created in PMT is an event detected, and not each photon arriving at PMT will create a photoelectric pulse. Therefore the distribution function $f_n(T)$ of photoelectric pulses can differ considerably from the distribution function $\bar{w}_N(T)$ of photons arrived at PMT. Earlier, a relation between photons arrived at PMT and photoelectric pulses created in PMT was considered by comparing the first and second moments of both distributions [8]. These moments describe average number of events and width of the distributions. In the present paper, we derive a mathematical expression for the distribution function $f_n(T)$ relating to the distribution functions $\bar{w}_N(T)$ and $w_N(T)$.

In order to realize such derivation we use a method found by the author for consideration the photon distribution functions [5–7,9]. It was found that each exponential process $\exp(-\lambda_j t)$ in the molecular quantum dynamics manifests itself via Poissonian function $P_N(\lambda_j t) = (\lambda_j t)^N \exp(-\lambda_j t) / N!$ in the photon distribution function $w_N(T)$. The main idea of the present work is to extend this relation existing between molecular dynamics and statistics of photons over more complicated system and to consider a molecule and PMT as two parts of the united dynamical system connected with each other by photons emitted by the molecule and arriving at the PMT. This idea is used in the paper to derive expression for the photoelectric pulse distribution function $f_n(T)$.

2. Photon distribution function

Consider now how we can calculate photon distribution function by using dynamical model for a molecule. It was shown in Ref. [5,6]

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that the photon distribution function $w_N(t)$ for a two-level molecule can be calculated on the basis of the dynamical scheme shown in Fig. 1.

Here W_1 and W_0 are the probabilities of finding the molecule in the excited and the ground electronic state without spontaneously emitted photon. K , $1/T_1$ and G are the rates of light-induced, spontaneous and radiation free transitions in the molecule, respectively. The inclined arrow shows that after spontaneous emission of a photon, the system gets new quantum state consisting of the molecule in the ground state and one photon of fluorescence.

The dynamics of the system is described by the following rate equations

$$\begin{aligned} \dot{W}_1 &= -(K + G + 1/T_1)W_1 + KW_0, \\ \dot{W}_0 &= (K + G)W_1 - KW_0. \end{aligned} \tag{1}$$

If a photon was emitted at $t=0$ we must take into account that $W_0(0) = 1$. This value can be considered as initial condition for Eq. (1). The rate of spontaneous emission is described by

$$\dot{W}_0 + \dot{W}_1 = -W_1/T_1 = -s_{ph}(t). \tag{2}$$

The function

$$dW_{ph}(t) = s_{ph}(t)dt \tag{3}$$

describes the probability of finding the next photon at the time interval $(t, t + dt)$ if the preceded photon was emitted at $t=0$. The function $s_{ph}(t)$ describes the distribution of time intervals between two successively emitted photons. Therefore it was called “the two-photon start–stop correlator” [10], “the waiting time distribution” [11], or “the time distribution function between adjacent events” [12].

By solving Eq. (1) with initial condition $W_0(0) = 1$ we arrive at the following equation

$$s_{ph}(t) = \frac{\bar{\lambda}_1 \bar{\lambda}_2}{\bar{\lambda}_2 - \bar{\lambda}_1} \left[e^{-\bar{\lambda}_1 t} - e^{-\bar{\lambda}_2 t} \right]. \tag{4}$$

Here $\bar{\lambda}_{1,2} = (2K + G + 1/T_1) / 2 \mp \sqrt{(2K + G + 1/T_1)^2 / 4 - K/T_1}$. Two exponential functions describe the dynamics of the molecule excited by CW-laser with rate K and emitting spontaneously photons with rate $1/T_1$.

The two-photon start–stop correlator plays a decisive role in single molecule photon statistics because the photon distribution function $w_N(T)$ depends solely on $s_{ph}(t)$. This fact shows the following equation

$$w_N(T) = \frac{1}{T_0} \int_0^T dt (T-t) \{ [s_{ph}(\lambda)]^{N-1} \}_t - 2 [s_{ph}(\lambda)]^N \}_t + [s_{ph}(\lambda)^{N+1} \}_t, \quad (N \geq 1) \tag{5}$$

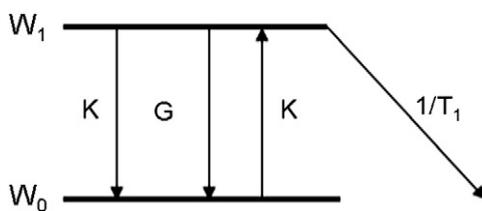


Fig. 1. Two-level scheme for molecular dynamics.

derivation of which can be found in Ref. [7,9]. Here $s_{ph}(\lambda) = s_{ph}(i\omega) = \int_0^\infty s_{ph}(t) e^{i(\omega + i0)t} dt$ is Laplace transform of the two-photon start–stop correlator. The constant

$$\tau_0 = \int_0^\infty s_{ph}(t) dt = \int_0^\infty dt \left[1 - \int_0^t s_{ph}(x) dx \right] \tag{6}$$

determines the average value of time interval between two successively emitted photons. The function of time $[s_{ph}(\lambda)^N]_t$ describes inverse Laplace transform of the function $s_{ph}(\lambda)^N$.

The problem of finding the expression for $[s_{ph}(\lambda)^N]_t$ can be solved for a single molecule with rather complicated quantum dynamics [7,9]. For the two-level molecule this expression looks as follows [5,6]:

$$[s_{ph}(\lambda)^N]_t = \frac{1}{\bar{\lambda}_1 \bar{\lambda}_2} \int_0^t P_{N-1}[\bar{\lambda}_1(t-x)] P_{N-1}[\bar{\lambda}_2 x] dx. \tag{7}$$

Here $P_N(ax) = (ax)^N \exp[-ax] / N!$. Eqs. (4), (5) and (7) demonstrate that the rate of each exponential process in quantum dynamics manifests itself in the photon distribution function via Poissonian function. Distributions of photons calculated with the help of Eqs. (5) and (7) are given in Fig. 2.

At comparable values of rate constants $\bar{\lambda}_2$ and $\bar{\lambda}_1$, the distribution of photons is of sub-Poissonian type, i.e. it is narrower as compared with Poissonian one. The curve 1 demonstrates this fact. However if the difference in values of $\bar{\lambda}_2$ and $\bar{\lambda}_1$ is large the shape of the photon distribution approaches to Poissonian function as curve 2 shows. At $\bar{\lambda}_2 / \bar{\lambda}_1 > 10$ we find $\bar{\lambda}_1 \cong K$ and $\bar{\lambda}_2 \cong 1/T_1$. Therefore taking curve 2 into account we may write for the distribution of photons created by single molecule under CW-laser excitation the following expression:

$$w_N(t) \cong P_N(\bar{\lambda}_1 t) \cong P_N(Kt). \tag{8}$$

However not all photons created by a molecule under CW-excitation arrive at PMT. The number N of photons arriving at PMT will be ξ times smaller as compared to the number N of photons created by the molecule. Allowing for this factor and Eq. (8) we arrive at the following relation between the distribution of photons created by the molecule and the distribution of photons arriving at PMT:

$$\bar{w}_N(t) = w_N(t / \xi). \tag{9}$$

3. Dynamics of the system consisting of a molecule and PMT

Scheme in Fig. 1 and Eq. (1) define the dynamics of a molecule emitting photons of fluorescence. If we want to consider photoelectric pulses we have to add dynamical characteristics of PMT. There are two processes inside PMT: creation of a photoelectron with the help of

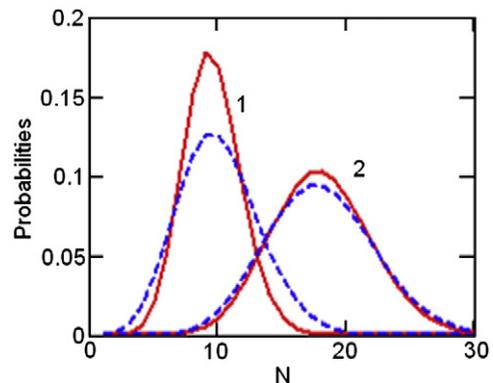


Fig. 2. The distribution of photons $w_N(20 / \bar{\lambda}_1)$ at $\bar{\lambda}_2 / \bar{\lambda}_1 = 1$ (1) and 10 (2) (solid lines). Poissonian distributions with the same average number of photons (dashed lines).

photo-effect and renewal of the possibility to new photoelectron creation. Scheme shown in Fig. 3 includes these two additional processes.

Here $k=K/\xi$ defines how many photons arrive at PMT per second, α is the rate of photoelectron creation, and β is the rate of renewal of the possibility to new photoelectron creation. The probabilities relating to the molecule and to PMT will be denoted by letters M and P , respectively. Four probabilities shown in Fig. 3 can be written in the following form:

$$W = M_0 P_0^*, \quad W_0 = M_0 P_0, \quad W_1 = M_0^* P_0, \quad w = M_1 P_0. \quad (10)$$

Here P_0^* is the probability of finding an ionized state after photoelectron creation, P_0 is the probability of finding PMT to be ready for new photoelectron creation. M_0 and M_0^* define the probabilities of finding the molecule in the ground and the excited electronic state, respectively. Initial condition, $W(0) = 1$, means that first photoelectric pulse is created at $t = 0$. After photon emission with rate $1/T_1$ the molecule gets to the ground electronic state. M_1 is the probability of finding the molecule in the ground electronic state with one spontaneously emitted photon. The lower index "1" shows the number of spontaneously emitted photons. The following set of equations relates to the scheme shown in Fig. 3:

$$\begin{aligned} \dot{W}_1 &= -(k + G + 1/T_1)W_1 + kW_0, \\ \dot{W}_0 &= (k + G)W_1 - kW_0 + \beta W, \\ \dot{W} &= -\beta W, \\ \dot{w} &= W_1/T_1 - \alpha w. \end{aligned} \quad (11)$$

The sum

$$\dot{W}_0 + \dot{W}_1 + \dot{W} + \dot{w} = -aw(t) = -s_{el}(t) \quad (12)$$

describes the rate of the creation of the second photoelectric pulse if the preceded photoelectric pulse was created at $t = 0$. Analogously to Eq. (3) we may write the following expression

$$dW_{el}(t) = s_{el}(t)dt \quad (13)$$

for the probability of finding the second photoelectric pulse in time interval $(t, t + dt)$ if the first pulse was created at $t = 0$. Obviously, the correlator $s_{el}(t)$ defines the correlation between two successively created electric pulses. Therefore this function can be named the two-electron start-stop correlator analogously to the two-photon start-stop correlator discussed earlier.

Carrying out Laplace transformation in the set of Eq. (11) we arrive at the following set of algebraic equations:

$$\begin{aligned} (\lambda - k - G - 1/T_1)W_1 + kW_0 &= 0, \\ (k + G)W_1 + (\lambda - k)W_0 + \beta W &= 0, \\ (\lambda - \beta)W &= -1, \\ W_1/T_1 + (\lambda - \alpha)w &= 0. \end{aligned} \quad (14)$$

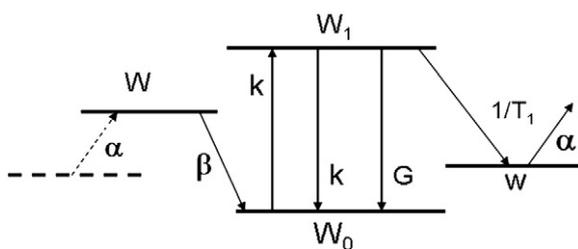


Fig. 3. Scheme of quantum states in the molecule + PMT system.

Here the initial condition $W(0) = 1$ was used. By solving this set of equations we arrive at the following expression for the two-electron start-stop correlator:

$$aw(\lambda) = s_{el}(\lambda) = \frac{\alpha \beta \lambda_1 \lambda_2}{\alpha - \lambda \beta - \lambda \lambda_1 - \lambda \lambda_2 - \lambda}. \quad (15)$$

Here rate constants

$$\lambda_{1,2} = (2k + G + 1/T_1)/2 \mp \sqrt{(2k + G + 1/T_1)^2/4 - k/T_1}. \quad (16)$$

determine the dynamics of the molecule irradiated by CW-laser light and rate constants α and β determine the dynamics of PMT. Carrying out inverse Laplace transformation in Eq. (15) we arrive at the final expression for the two-electron start-stop correlator:

$$s_{el}(T) = s_\alpha e^{-\alpha T} + s_\beta e^{-\beta T} + s_1 e^{-\lambda_1 T} + s_2 e^{-\lambda_2 T}, \quad (17)$$

Here coefficients

$$\begin{aligned} s_\alpha &= \frac{\alpha \beta \lambda_1 \lambda_2}{(\beta - \alpha)(\lambda_1 - \alpha)(\lambda_2 - \alpha)}, \\ s_\beta &= \frac{\alpha \beta \lambda_1 \lambda_2}{(\alpha - \beta)(\lambda_1 - \beta)(\lambda_2 - \beta)}, \\ s_1 &= \frac{\alpha \beta \lambda_1 \lambda_2}{(\alpha - \lambda_1)(\beta - \lambda_1)(\lambda_2 - \lambda_1)}, \\ s_2 &= \frac{\alpha \beta \lambda_1 \lambda_2}{(\alpha - \lambda_2)(\beta - \lambda_2)(\lambda_1 - \lambda_2)}, \end{aligned} \quad (18)$$

depend solely on four rate constants which determine the quantum dynamics of the system consisting of the molecule and PMT.

An expression for the photoelectric pulse distribution $f_n(T)$ can be derived the way the expression for the photon distribution $w_N(T)$ has been derived in Ref. [6,7,9]. The derivation in Ref. [7,9] has been realized, in fact, for the detected random events. If we consider emission of a photon in the capacity of such random detected event, we arrive at Eq. (5) with the two-photon start-stop correlator $s_{ph}(t)$. However if we consider creation of a photoelectric pulse in the capacity of such random detected event we may use expression (5) with the substitution of the two-photon start-stop correlator $s_{ph}(t)$ by the two-electron start-stop correlator $s_{el}(t)$. After such substitution we arrive at the following expression for the electric pulse distribution:

$$f_n(T) = \frac{1}{\tau_0} \int_0^T dt (T-t) \{ [s_{el}(\lambda)]^{n-1} \Big|_t - 2[s_{el}(\lambda)]^n \Big|_t + [s_{el}(\lambda)^{n+1}] \Big|_t \}, \quad (n \geq 1). \quad (19)$$

Here

$$\tau_0 = \int_0^t s_{el}(t) dt = \int_0^\infty dt \left[1 - \int_0^t s_{el}(x) dx \right] \quad (20)$$

is the average time interval between two adjacent electric pulse creations.

The Laplace transform of $n + 1$ -th degree of the two-electron start-stop correlator takes the form of the product of four Laplace transforms of Poissonian functions:

$$\begin{aligned} s_{el}(\lambda)^{n+1} &= \alpha \beta \lambda_1 \lambda_2 \\ &\times \frac{\alpha^n}{(\alpha - \lambda)^{n+1}} \frac{\beta^n}{(\beta - \lambda)^{n+1}} \frac{\lambda_1^n}{(\lambda_1 - \lambda)^{n+1}} \frac{\lambda_2^n}{(\lambda_2 - \lambda)^{n+1}}. \end{aligned} \quad (21)$$

Therefore, after inverse Laplace transformation of Eq. (21) we arrive at the following expression:

$$[s_{el}(\lambda)^{n+1}]_t = \alpha\beta\lambda_1\lambda_2 \int_0^t dx P_n[\alpha(t-x)] \times \int_0^x dy P_n[\beta(x-y)] \int_0^y dz P_n[\lambda_1(y-z)] P_n(\lambda_2 z) \quad (22)$$

with four Poissonian functions $P_n(ax) = (ax)^n \exp(-ax)/n!$. It has to notice the all four rate constants α , β , λ_1 , and λ_2 of the two-electron start–stop correlator manifest themselves in four Poissonian functions included in the distribution function. In other words Eqs. (19) and (22) show that each exponential process in quantum dynamics of the

complicated system consisting of a single molecule and PMT manifests itself via Poissonian function in the photoelectron distribution function. Poissonian functions with α and β describe the influence of PMT characteristics on statistics of photoelectric pulses.

4. Comparison of photon and photoelectron distributions

Consider now the two-electron start–stop correlator $s_{el}(t)$ and the distribution function $f_n(T)$ of photoelectric pulses by taking the following set of rate constants

$$1/T_1 = 10^8 \text{ s}^{-1}, \quad G = 10^7 \text{ s}^{-1}, \quad k = 10^6 \text{ s}^{-1}, \quad (23)$$

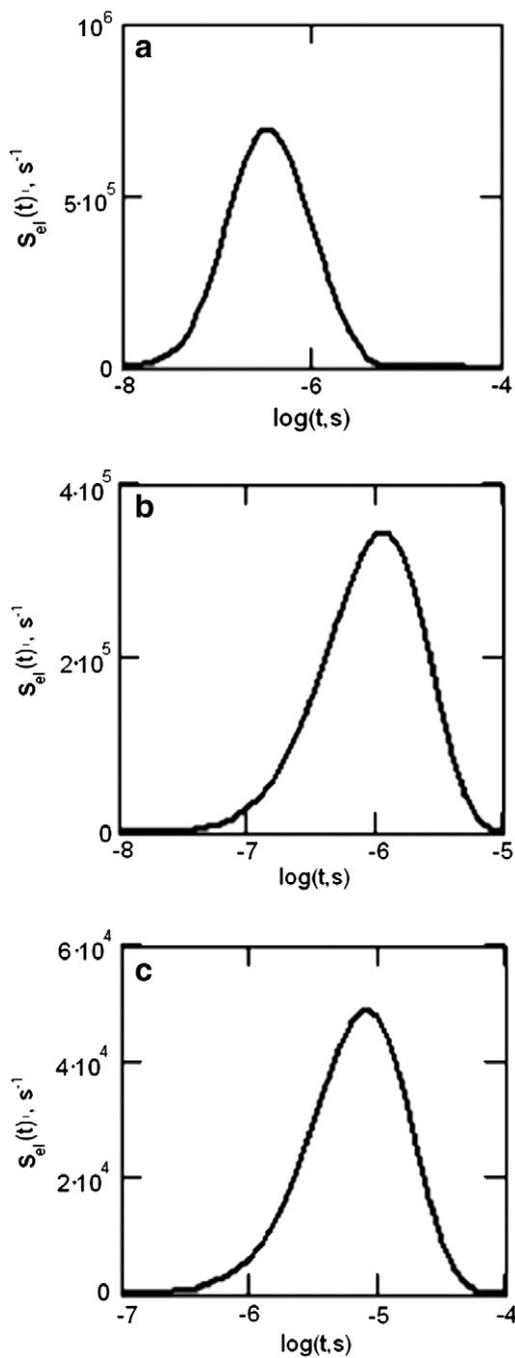


Fig. 4. The distribution of times between adjacent photoelectric pulses for fast (a), moderately fast (b) and slow (c) PMT.

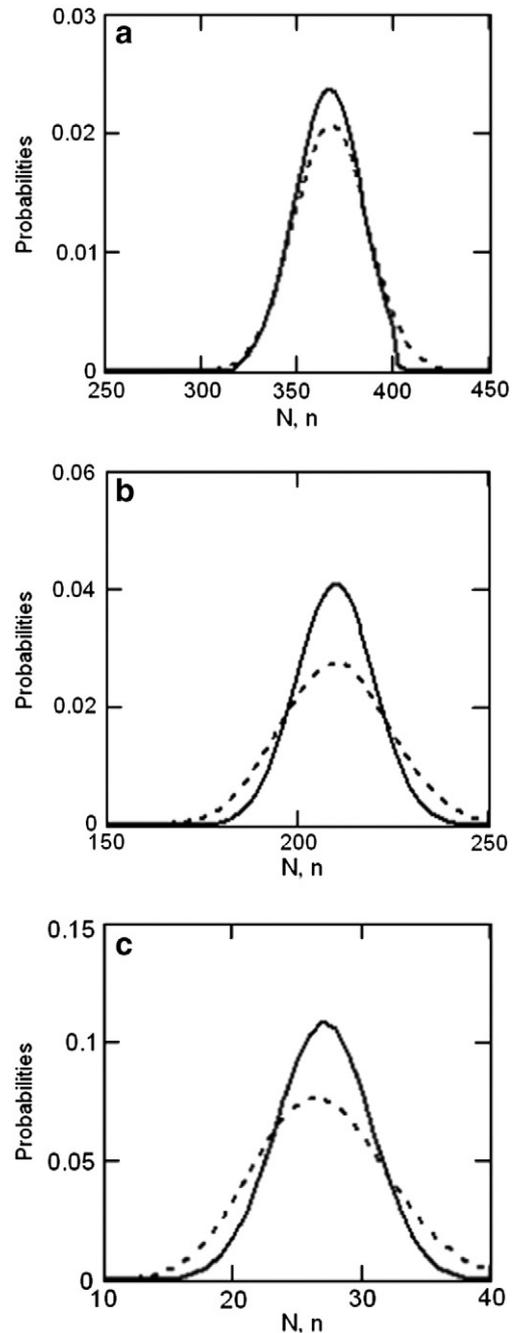


Fig. 5. The photoelectric pulse distribution functions $f_n(0.44 \text{ ms})$ (solid lines) and Poissonian functions for the same average number of events (dashed lines) for fast (a), moderately fast (b) and slow (c) PMT. The dashed line in a shows the distribution function $\bar{w}_N(0.44 \text{ ms})$ of photons arriving at PMT.

for molecular dynamics and varying values of rate constants α and β for PMT as follows:

- Fast PMT* ($1/\alpha = 10^{-7}$ s, $1/\beta = 5 \times 10^{-8}$ s). Time of PMT operation is ten times shorter as compared to the average time interval $1/k = 10^{-6}$ s between adjacent photons.
- Moderately fast PMT* ($1/\alpha = 10^{-6}$ s, $1/\beta = 10^{-7}$ s). Time of PMT operation equals to the average time interval $1/k = 10^{-6}$ s between adjacent photons.
- Slow PMT* ($1/\alpha = 10^{-5}$ s, $1/\beta = 5 \times 10^{-6}$ s). Dead time of PMT is five times longer as compared to the average time interval $1/k = 10^{-6}$ s between adjacent photons.

The distribution of times between adjacent photoelectric pulses can be calculated with the help of Eq. (17). The result is shown in Fig. 4. It demonstrates that the slower the operations of PMT the longer the distribution of times between adjacent photoelectric pulses.

The photoelectric pulse distribution functions $f_n(T)$ for three types of PMT have been calculated with the help of Eq. (19) and Eq. (22). The result is presented in Fig. 5.

Fig. 5a shows the following relation $f_n(T) \cong \bar{w}_N(T)$ for fast PMT, i.e. the photoelectric pulse distribution function almost coincides with the distribution of photons arriving at PMT. Fig. 5b demonstrates the photoelectric pulse distribution in case in which the rate of arrival of photons is comparable with the rate of PMT operation. Such moderately fast PMT will miss some photons. Therefore the rate of photoelectric counts will be reduced as Fig. 5b shows. The maximum of the function $f_n(0.44$ ms) corresponds to 210 counts whereas the maximum of the function $\bar{w}_N(0.44$ ms) corresponds to 370 photons. Value $210/370 = 0.57$ is the quantum efficiency of the moderately fast PMT.

Since the rate $\alpha = 10^6$ s $^{-1}$ of the operation of the moderately fast PMT coincides with the rate $k = 10^6$ s $^{-1}$ of photon arrival, the photoelectric pulse distribution is of sub-Poissonian type as Fig. 5b shows. It is surprising because the distribution function $w_N(0.44$ ms) for photons arriving at PMT is described by Poissonian function as dashed line in Fig. 5a shows. Hence, the shapes of $f_n(0.44$ ms) and $\bar{w}_N(0.44$ ms) can differ with each other for the moderately fast PMT.

Dead time $1/\beta = 5 \times 10^{-6}$ s in the slow PMT is five times longer as compared to the average time $1/k = 10^{-6}$ s between adjacent photons. This fact leads to considerable reducing of quantum efficiency. Indeed,

the ratio of the maximum of dashed line in Fig. 5a corresponds to 370 counts whereas the maximum of the solid curve in Fig. 5c corresponds only to 28 counts. Therefore quantum efficiency of the slow PMT is $28/370 = 0.076$. Only one of thirteen photons creates photoelectric pulse in the slow PMT. Since the rate α of photo-effect is comparable with the rate β of the PMT recovery, the photoelectric pulse distribution will be of sub-Poissonian type as Fig. 5c shows. This fact is due to solely PMT characteristics and it has nothing to do with the molecular dynamics.

5. Conclusions

Our approach based on the consideration of a single molecule and PMT within the frame of the united dynamical system enabled one to find theoretical expressions for the distribution function $\bar{w}_N(t)$ for photons arriving at PMT and for the photoelectric pulse distribution function $f_n(t)$. Theoretical expressions for $\bar{w}_N(t)$ and for $f_n(t)$ enabled one to calculate numerically both distributions to compare them with each other for PMT operating slow and fast. In the case of fast PMT, the distributions $\bar{w}_N(t)$ and $f_n(t)$ coincide with each other. However in the case of slow operating PMT, they differ considerably in the rate of counts and in the shape of the distributions.

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