Photon statistics in single molecule fluorescence with Rabi oscillations

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A B S T R A C T

An expression for the distribution function of photons detected in non-resonant single molecule fluorescence excited by CW-laser light is derived. Numerical calculations of the photon distribution for fluorescence whose autocorrelation function exhibits Rabi oscillations are carried out. It is found that phase memory does not influence noticeably on the photon distribution function in non-resonant fluorescence.

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1. Introduction

Number of the molecules excited by a short laser pulse depends on a dose of laser light absorbed by the molecules. Intensity of fluorescence is proportional to the number of excited molecules. If intensity of laser light is high, the dependence of fluorescence intensity on a dose of laser light manifests Rabi oscillations. The fluorescence intensity is maximal for so-called π-pulse, 3π-pulse and so on [1,2]. Rabi oscillations in fluorescence mean that the effects of phase memory play an important role and we must use optical Bloch equations to describe such a system.

In fluorescence of single molecules driven by strong CW-laser field, Rabi oscillations manifest themselves in autocorrelation function $g^{(2)}(t)$. It was shown in the first experiments with single atoms [3,4]. Very recently Rabi oscillations have been observed in the autocorrelation function measured in fluorescence of single protein molecules [5]. Rabi oscillations of fluorescence mean that the probability of finding a molecule in the excited state oscillates as well. Hence, the probability of photon emission will oscillate and this fact can influence a photon distribution function measured in experiment.

By now the photon distribution function was calculated for a single molecule excited by weak CW-laser field so that the rate k of light-induced transitions in a molecule was less as compared to the rate $1/T_1$ of spontaneous photon emission [6,7]. If $k \ll 1/T_1$, we may use rate equations instead of Bloch equations to describe the dynamics of the molecule driven by CW-laser field. The photon distribution function $w_N(t)$ for fluorescence of a two-level molecule was expressed via an integral of two Poissonian functions [6]. The photon distribution function $w_N(t)$ for blinking fluorescence of a three-level molecule was expressed via two

integrals of three Poissonian functions [7]. These formulas for $w_N(t)$ enabled one to calculate the photon distribution function numerically. However, a question: how the photon distribution function $w_N(t)$ will look for fluorescence with an oscillating autocorrelation function is still open.

In this paper, we apply an approach developed in Refs. [6,7] to calculate the photon distribution in single molecule fluorescence excited by strong CW-laser field. We cannot use rate equations to describe the dynamics of such a molecule and we have to use equations for the density matrix with off-diagonal elements.

2. Photon distribution functions for various methods of photon counting

It was found in the papers of various authors [6–12] that the photon distribution function can be expressed via a single function, $s(t)$. The function determines a correlation between two sequentially detected photons in accordance with the following equation

$$dW(t) = s(t)dt. \tag{1}$$

Here $dW(t)$ is the probability of finding the second photon in time interval $(t, t + dt)$ if preceded photon was emitted at $t = 0$. Therefore, the density of the probability $s(t)$ was named the start–stop correlator [13].

Various methods of photon counting are possible. The simplest method for experimental implementation was named the method M in Refs. [14,15]. In this method, time axis is covered by equal time intervals t. The onset and the end of the interval t are not related to any event. The number of events is counted on each interval t and the distribution function $w_N^M(t)$ of events can be found. In contrast to the method M, an alternative method of photon counting was considered in Refs. [6,16]. In this method, time intervals t of another type are considered. Each time interval t is opened and closed by an event. In this case the distribution function $w_N^O(t)$ of so-called intermediate events which happened between two events in the onset and the end of the time interval t can be found.

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The following expression for the distribution function $w_N^0(t)$ was found in Refs. [6,14,15]:

$$w_0^O(t) = s(t)/p(t), \quad w_N^O(t) = s^{(N)}(t)/p(t). \qquad (2)$$

Here

$$s^{(N)}(t) = \int_0^t dt_N s(t-t_N) \int_0^{t_N} dt_{N-1} s(t_N - t_{N-1}) \cdots \int_0^{t_2} dt_1 s(t_2 - t_1) s(t_1),$$

$$p(t) = s(t) + \sum_{N=1}^{\infty} s^{(N)}(t). \qquad (3)$$

The start–stop correlator $s(t)$ describes the correlation between two sequentially detected photons separated by the time interval t. The correlator $s^{(N)}(t)$ describes the correlation of two events separated by the time interval t with N intermediate events in between. Hence, the correlator $p(t)$ describes the correlation of two events separated by the time interval t with arbitrary number of intermediate events in this time interval. Therefore, the function $p(t)$ can be named full correlator [13].

The following formulas for the distribution function $w_N^M(t)$ were derived in Refs. [14,15]:

$$w_0^M(t) = \frac{1}{\tau_0} \int_0^{\infty} w(t+\tau) d\tau,$$

$$w_N^M(t) = \frac{1}{\tau_0} \int_0^t dt_N w(t-t_N) \int_0^{t_N} dt_{N-1} s(t_N - t_{N-1}) \cdots \int_0^{t_2} dt_1 s(t_2 - t_1) w(t_1). \qquad (4)$$

Here

$$w(t) = 1 - \int_0^t s(x) dx \qquad (4a)$$

is the probability of not detecting the second event by the time moment t if the first event was detected at $t = 0$.

$$\tau_0 = \int_0^{\infty} w(t) dt \qquad (4b)$$

is an average time interval between two sequentially detected events. Eqs. (2) and (4) have been derived without addressing any definite microscopic model for the system.

3. Physical model

Consider a single molecule with two electronic levels and vibronic levels. The molecule is excited via pure electronic transition $1 \leftarrow 0$ by CW-laser field as it is shown in Fig. 1. The whole fluorescence of the molecule will consist of the resonant fluorescence relating to pure electronic transition $0 \leftarrow 1$ and non-resonant fluorescence relating to transitions to vibronic levels. This non-resonant fluorescence is described by transitions $2 \leftarrow 1$ in our model.

Here k is the rate of light-induced transitions, G is the sum of spontaneous non-radiative and radiative transitions $0 \leftarrow 1$, g is
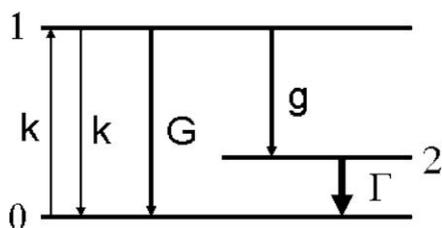
the rate of non-resonant fluorescence, Γ is the rate of fast vibronic relaxation to the ground electronic state 0.

The molecule driven by CW-laser light will jump from the ground electronic state to the excited one and back as it is shown in Fig. 2. Instants of photon absorption and instants of photon emission are random. However, they are characterized by the probabilities which can be found from the equations for quantum dynamics of the system.

Each quantum jump is a random event. However, not each jump can be detected experimentally. In fact, we cannot detect the instant of light absorption, i.e. $1 \leftarrow 0$ jump, because the disappearance of one photon from a huge number of laser photons cannot be detected in incident light. We cannot detect photon of resonant fluorescence either for the same reason. However, by using a color filter for absorption of laser light, we can detect photons of non-resonant fluorescence, i.e. $2 \leftarrow 1$ transitions. Detected events are shown by arrows in Fig. 2. The rate of detected events is denoted g. Because of the random character of photon detections instants the number of detected events in various time intervals T of the same duration will fluctuate. The distribution of these fluctuations can be measured.

4. Start–stop correlator and full correlator

The quantum dynamics of the system described by the scheme shown in Fig. 1 is determined by the following set of equations for the density matrix of the molecule:

$$\begin{aligned}
\dot{\rho}_{10} &= -i(\Delta - i/T_2)\rho_{10} + \chi(\rho_1 - \rho_0), \\
\dot{\rho}_{01} &= i(\Delta + i/T_2)\rho_{01} + \chi(\rho_1 - \rho_0), \\
\dot{\rho}_1 &= -(G+g)\rho_1 - \chi(\rho_{10} + \rho_{01}), \\
\dot{\rho}_0 &= G\rho_1 + \chi(\rho_{10} + \rho_{01}) + \Gamma\rho_2, \\
\dot{\rho}_2 &= g\rho_1 - \Gamma\rho_2.
\end{aligned} \qquad (5)$$

Here Δ is the difference between laser frequency and resonant frequency of $1 \leftarrow 0$ transition, $\chi = \mathbf{E}\mathbf{d}/\hbar$ is Rabi frequency depending on electric vector $\mathbf{E}$ of laser field and dipole moment $\mathbf{d}$ of electronic transition of the molecule. The rate $1/T_2$ determines the decay of phase memory, i.e. optical dephasing.

If we detected all photons of spontaneous fluorescence, full correlator $p(t)$ would be described by the following formula: $p(t) = \rho_1(t)/T_1$. It is shown in detail in Chapter 3 of the book [17]. Here $\rho_1(t)$ is the probability of finding the molecule in the fluorescent excited state after the jump to the ground state at $t = 0$. $1/T_1$ is the rate of spontaneous fluorescence. However, we detect solely photons of non-resonant fluorescence. Therefore, the formula for full correlator should look as follows:

$$p(t) = g\rho_1(t). \qquad (6)$$

Here $\rho_1(t)$ is the solution of Eq. (5) at initial condition $\rho_2(0) = 1$ and g is the rate of non-resonant fluorescence. This initial condition means that a photon of non-resonant fluorescence was emitted at $t = 0$.

Fig. 1. Energy scheme with two electronic levels 0 and 1 and with the set of vibronic levels described by level 2.
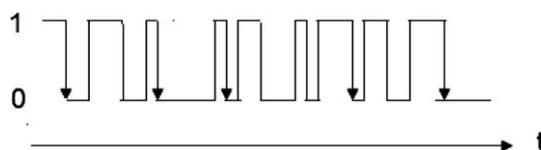

Fig. 2. Quantum jumps of the molecule accompanied by absorption and emission of photons. Arrows mark radiation of non-resonant fluorescence photons, i.e. detected events.

By carrying out Laplace transformation $\int_0^\infty dt F(t) e^{i(\omega+i0)t} = F(i\omega) = F(\lambda)$ of the left and right parts of Eq. (5), we arrive at the following equations for Laplace transforms:

$$(\lambda - i\Delta - 1/T_2)\rho_{10} + \chi(\rho_1 - \rho_0) = 0,$$
$$(\lambda + i\Delta - 1/T_2)\rho_{01} + \chi(\rho_1 - \rho_0) = 0,$$
$$-\chi(\rho_{10} + \rho_{01}) + (\lambda - G - g)\rho_1 = 0,$$
$$\chi(\rho_{10} + \rho_{01}) + G\rho_1 + \lambda\rho_0 + \Gamma\rho_2 = 0,$$
$$g\rho_1 + (\lambda - \Gamma)\rho_2 = -1.$$
(7)

By solving this set of equations we find the following expression for Laplace transform of the full correlator:

$$p(\lambda) = \frac{2\chi^2 g\Gamma(\lambda - 1/T_2)}{Det_\rho}.$$
(8)

Here Det_ρ is the determinant of Eq. (7). For resonance case $\Delta = 0$ the determinant will look as follows:

$$Det_\rho = \lambda(\lambda - 1/T_2)\{(\lambda - \Gamma)[(\lambda - 1/T_2)(\lambda - G - g) + 4\chi^2] - 2\chi^2 g\}.$$
(9)

After insertion of this determinant to Eq. (8) we arrive at the following expression:

$$p(\lambda) = \frac{2\chi^2 g\Gamma}{-\lambda(\Lambda_1 - \lambda)(\Lambda_2 - \lambda)(\Lambda_3 - \lambda)}.$$
(10)

Here Λ_j are the roots of the equation, $(\lambda - \Gamma)[(\lambda - 1/T_2)(\lambda - G - g) + 4\chi^2] - 2\chi^2 g = 0$. Expressions for the roots Λ_j can be found in the Appendix.

Carrying out inverse Laplace transformation in Eq. (10) we arrive at the final expression for the full correlator:

$$p(t) = p_0 + p_1 e^{-\Lambda_1 t} + p_2 e^{-\Lambda_2 t} + p_3 e^{-\Lambda_3 t}.$$
(11)

Here

$$p_0 = \frac{2\chi^2 g\Gamma}{\Lambda_1 \Lambda_2 \Lambda_3}, \quad p_1 = \frac{2\chi^2 g\Gamma}{\Lambda_1(\Lambda_1 - \Lambda_2)(\Lambda_3 - \Lambda_1)},$$
$$p_2 = \frac{2\chi^2 g\Gamma}{\Lambda_2(\Lambda_2 - \Lambda_1)(\Lambda_3 - \Lambda_2)}, \quad p_3 = \frac{2\chi^2 g\Gamma}{\Lambda_3(\Lambda_3 - \Lambda_1)(\Lambda_2 - \Lambda_3)}.$$
(12)

A method of finding equations for the start–stop correlator with the help of the equations for quantum dynamics of the system was found in Refs. [11–13]. The equations for the start–stop correlator can be derived from the equations for the quantum dynamics, i.e. from Eq. (5) in our case, by omitting the term that describes the rate of detectable events, i.e. by omitting the term $g\rho_1$ in the fifth equation of the set (5). Then we arrive at the following set of equations:

$$\dot{W}_{10} = -i(\Delta - i/T_2)W_{10} + \chi(W_1 - W_0),$$
$$\dot{W}_{01} = i(\Delta + i/T_2)W_{01} + \chi(W_1 - W_0),$$
$$\dot{W}_1 = -(G + g)W_1 - \chi(W_{10} + W_{01}),$$
$$\dot{W}_0 = GW_1 + \chi(W_{10} + W_{01}) + \Gamma W_2,$$
$$\dot{W}_2 = -\Gamma W_2.$$
(13)

Eq. (13) should be solved with the initial condition $W_2(0) = 1$. This condition means that the first detectable event happened at $t = 0$. Eq. (13) describe evolution of the system before the second detectable event happens. The start–stop correlator is described by the following formula:

$$s(t) = gW_1(t).$$
(14)

This very expression should be inserted to Eq. (1) for the probability $dW(t)$ of finding the second event in time interval $(t, t + dt)$.

By carrying out Laplace transformation in the left and the right hand sides of Eq. (13), we arrive at the following equations for Laplace transforms:

$$(\lambda - i\Delta - 1/T_2)W_{10} + \chi(W_1 - W_0) = 0,$$
$$(\lambda + i\Delta - 1/T_2)W_{01} + \chi(W_1 - W_0) = 0,$$
$$-\chi(W_{10} + W_{01}) + (\lambda - G - g)W_1 = 0,$$
$$\chi(W_{10} + W_{01}) + GW_1 + \lambda W_0 + \Gamma W_2 = 0,$$
$$(\lambda - \Gamma)W_2 = -1.$$
(15)

By solving this set of equations, we find the following expression for Laplace transform of the correlator start–stop:

$$s(\lambda) = \frac{2\chi^2 g\Gamma(\lambda - 1/T_2)}{Det_W}.$$
(16)

In resonance case, i.e. at $\Delta = 0$, the determinant of Eq. (15) is given by

$$Det_W = (\lambda - \Gamma)(\lambda - 1/T_2)\{\lambda[(\lambda - G - g)(\lambda - 1/T_2) + 4\chi^2] - 2\chi^2 g\}.$$
(17)

By inserting this determinant to Eq. (16), we arrive at the following expression:

$$s(\lambda) = \frac{\Gamma\lambda_1\lambda_2\lambda_3}{(\Gamma - \lambda)(\lambda_1 - \lambda)(\lambda_2 - \lambda)(\lambda_3 - \lambda)}.$$
(18)

Here we used the relation $\lambda_1\lambda_2\lambda_3 = 2\chi^2 g$ for the roots of the following algebraic equation: $\lambda[(\lambda - G - g)(\lambda - 1/T_2) + 4\chi^2] - 2\chi^2 g = 0$. Expressions for the roots λ_j are shown in the Appendix.

After carrying out the inverse Laplace transformation in Eq. (18) we arrive at the final expression for the correlator start–stop of the system:

$$s(t) = se^{-\Gamma t} + s_1 e^{-\lambda_1 t} + s_2 e^{-\lambda_2 t} + s_3 e^{-\lambda_3 t}.$$
(19)

Here

$$s = \frac{\Gamma\lambda_1\lambda_2\lambda_3}{(\lambda_1 - \Gamma)(\lambda_2 - \Gamma)(\lambda_3 - \Gamma)}, \quad s_1 = \frac{\Gamma\lambda_1\lambda_2\lambda_3}{(\Gamma - \lambda_1)(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)},$$
$$s_2 = \frac{\Gamma\lambda_1\lambda_2\lambda_3}{(\Gamma - \lambda_2)(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2)}, \quad s_3 = \frac{\Gamma\lambda_1\lambda_2\lambda_3}{(\Gamma - \lambda_3)(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)}.$$
(20)

Consider rate constants in Eq. (15). Here G and g are of order of inverse fluorescence life time T_1; $1/T_2 = 1/2T_1 + \gamma$ describes optical dephasing rate in which γ is a contribution from electron–phonon interaction. At low temperature, γ is of order of pure dephasing rate $1/2T_1$. The rate constant Γ describes fast decay of vibration excitations. We shall calculate the start–stop correlator and the full correlator with the help of Eqs. (11) and (19) for the following set of parameters:

$$G = 10^8 \text{ s}^{-1}, \quad 1/T_2 = 1.5 \times 10^8 \text{ s}^{-1}, \quad g = 10^8 \text{ s}^{-1},$$
$$\Gamma = 10^{12} \text{ s}^{-1}$$
(21)

and $\chi = 5 \times 10^8 \text{ s}^{-1}$. We shall use the set of parameters (21) throughout in the present paper varying solely χ. Roots λ_j for the set (21) of physical parameters are: $\lambda_1 = 4.92 \cdot 10^7 \text{ s}^{-1}$, $\lambda_2 = (1.50 - 9.96i) \cdot 10^8 \text{ s}^{-1}$ and $\lambda_3 = (1.50 + 9.96i) \cdot 10^8 \text{ s}^{-1}$. The start–stop correlator and the full correlator for the set (21) of physical parameters are shown in Fig. 3.

Since Rabi frequency χ exceeds the optical dephasing rate $1/T_2$, the probability of finding a molecule in the electronic excited state oscillates. However, Rabi oscillations disappear at $t > T_2$. The full correlator $p(t)$ demonstrates this fact. These very oscillations manifest themselves in the autocorrelation function because the fluorescence autocorrelation function and the full correlator are related with each other as follows [17–19]:
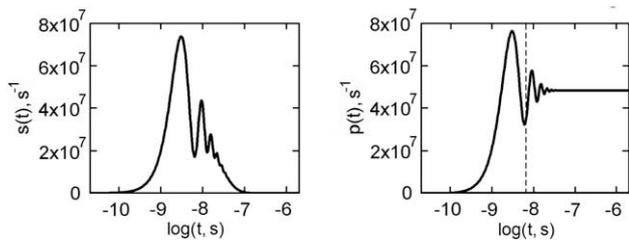
Fig. 3. Manifestation of Rabi oscillations in the start–stop correlator and in the full correlator at $\chi T_2 = 3.33$ (strong excitation). Vertical dashed line shows optical dephasing time $T_2 = 6.66 \times 10^{-9}$ s.

$$g^{(2)}(T) = \frac{<I(t)I(t+T)>}{<I(t)I(t+\infty)>} = \frac{p(T)}{p(\infty)}. \tag{22}$$

In accordance with Fig. 3 both correlators oscillate in nanosecond time scale. Hence, in accordance with Eq. (1) the probability of finding the second photon after the emission of the preceded photon will oscillate as well.

5. Distribution of emitted photons

Eqs. (2) and (4) enable one to calculate the photon distribution function for two methods of photon counting. Fig. 4 shows the probabilities $w_0^O(t)$ and $w_0^M(t)$ of finding no photon and the probabilities $w_1^O(t)$, $w_1^M(t)$ and $w_2^O(t)$, $w_2^M(t)$ of finding one photon and two photons in fluorescence of the system whose correlator start–stop is shown in Fig. 3.

The probability of finding no photon approaches zero as time interval increases over few nanoseconds. The decrease of $w_0^O(t)$ and $w_0^M(t)$ is accompanied by the increase of the probabilities of one and two photon observation. It is interesting that Rabi oscillations do not manifest themselves in the probability of finding an interval with no photon and with one and two photon if we use method M of photon counting although the autocorrelation function of fluorescence oscillates as Fig. 3 shows. Fig. 4b shows this fact. Rabi oscillations disappear in the probability of finding an interval with two photons for both methods of photon counting. In fact we see: $w_2^O(t) \cong w_2^M(t)$. Independence of the probabilities on the method of photon counting is a typical fact for the probabilities with $N \geqslant 2$ found in Ref. [14]. However, this conclusion is not correct for the molecules with blinking fluorescence [15].

What is the reason to various behavior of the probabilities with $N = 0$ and $N = 1$ measured by the method O and the method M? The onset and the end of time interval in the method O coincide with the instant of photon emission. Therefore, $w_N^O(t)$ is the distribution of intermediate photons which were emitted between events in the onset and the end of the time interval $(0,t)$. The probability $w_0^O(t) = s(t)/p(t)$ is, in fact, the probability of finding two sequentially emitted photons separated by the time interval $(0,t)$.
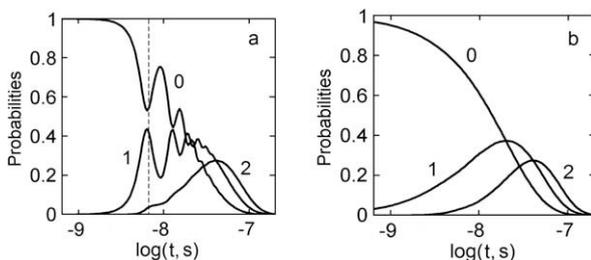

Fig. 4. Probabilities of fining no photon (0) and one (1) and two (2) photons when using the method. O (a) and the method M (b) of photon counting. $\chi T_2 = 3.33$. Vertical dashed line shows optical dephasing time $T_2 = 6.66 \times 10^{-9}$ s.

This probability will oscillate as curve 0 in Fig. 4a shows because the probability of finding the molecule in the excited state after emission of the first photon oscillates. In the method M, time axis is covered by equal time intervals $(0,t)$. The onset and the end of the interval $(0,t)$ are not related to photon emission. Therefore, the probability of finding time interval without photon will depend solely on the average time interval between two sequentially emitted photons. Rabi oscillations will not manifest themselves in the value of the average interval. Therefore, curve 0 in Fig. 4b does not oscillate. As to the probabilities $w_N^O(t)$ and $w_N^M(t)$ with $N > 2$, they are multiple integrals of the start–stop correlator $s(t)$. Such integration suppresses oscillations originating from $s(t)$.

Unfortunately, the calculation with the help of Eqs. (2)–(4) for long time intervals in which average number of photons $\langle N \rangle$ is more than 5 is impossible because we are forced to calculate N-fold integrals. A method for transformation of N-fold integrals to a few integrals of two or three Poissonian functions was found in Ref. [6,7,15], i.e. Eqs. (2) and (4) can be transformed to the following form [15]:

$$w_N^O(t) = [s(\lambda)^{N+1}]_t / p(t), \tag{23}$$

$$w_N^M(t) = \frac{1}{\tau_0} \int_0^t (t-\tau)\Big\{[s(\lambda)^{N-1}]_\tau - 2[s(\lambda)^N]_\tau + [s(\lambda)^{N+1}]_\tau\Big\} d\tau, \quad (N \geqslant 1). \tag{24}$$

Since $a^N/(a-\lambda)^{N+1}$ is Laplace transform $P_N^a(\lambda)$ of Poissonian function $P_N(at) = (at)^N \exp(-at)/N!$, we can express Nth degree of $s(\lambda)$ via Poissonian functions:

$$s(\lambda)^N = \Gamma \lambda_1 \lambda_2 \lambda_3 P_{N-1}^\Gamma(\lambda) P_{N-1}^{\lambda_1}(\lambda) P_{N-1}^{\lambda_2}(\lambda) P_{N-1}^{\lambda_3}(\lambda). \tag{25}$$

Carrying out the inverse Laplace transformation in Eq. (25), we arrive at the following expression:

$$[s(\lambda)^N]_t = \Gamma \lambda_1 \lambda_2 \lambda_3 \int_0^t dx P_{N-1}[\Gamma(t-x)] \int_0^x dy P_{N-1}[\lambda_1(x-y)]$$
$$\times \int_0^y dz P_{N-1}[\lambda_2(y-z)] P_{N-1}(\lambda_3 z). \tag{26}$$

This formula takes into account all relaxation processes shown in Fig. 1. The processes are described by four exponential functions in Eq. (19) for the start–stop correlator. Each exponential function manifests itself in Eq. (26) via Poissonian function with the same relaxation constant. This fact reveals an important relation between the quantum dynamics of the system, on the one hand, and photon statistics of fluorescence, on the other hand.

Eq. (26) can be simplified. Since rate Γ of vibronic relaxation is few orders of magnitude greater as compared to other relaxation constants, λ_j, we can approximately set $\Gamma/(\Gamma - \lambda) = 1$ in Eq. (18). After such simplification we arrive at the following formula instead of Eq. (26):

$$[s(\lambda)^N]_t = \lambda_1 \lambda_2 \lambda_3 \int_0^t dx P_{N-1}[\lambda_1(t-x)] \int_0^x dy P_{N-1}[\lambda_2(x-y)] P_{N-1}(\lambda_3 y). \tag{26a}$$

Rabi oscillations emerge if Rabi frequency χ exceeds the dephasing rate, $1/T_2$. In this case, root λ_1 of the equation $Det_W = 0$ is real and $\lambda_2 = \lambda_3^*$, i.e. $\lambda_2/\lambda_1 = c - ir$, $\lambda_3/\lambda_1 = c + ir$. By introducing dimensionless variables, $T = \lambda_1 t$, $X = \lambda_1 x$, $Y = \lambda_1 y$ we can rewrite integral (26a) in the following form:

$$[s(\lambda)^N]_t = \lambda_1 (c^2 + r^2)^N e^{-T} \int_0^T dX \frac{(T-X)^{N-1}}{(N-1)!} e^{(1-c)X}$$
$$\times \int_0^X dY \frac{(X-Y)^{N-1}}{(N-1)!} \frac{Y^{N-1}}{(N-1)!} \cos[r(2Y-X)]. \tag{27}$$

We can calculate the photon distribution with the help of Eqs. (23), (24) and (26a) for various values for Rabi frequency by varying time interval so that $\langle N \rangle$ would be the same. The result is shown in Fig. 5.

First of all we see that $w_N^O(T) \cong w_N^M(T)$, i.e. the photon distribution does not depend on the method of counting. Fig. 5c shows the photon distribution under strong excitation at $\chi T_2 = 3.33$. In this case, the photon distribution coincides with the Poissonian one. This fact was found earlier in Ref. [20]. Fig. 5b shows the photon distribution for the case when Rabi frequency is comparable with the rate of optical dephasing, i.e. at $\chi T_2 = 0.6$. In this case, the photon distribution is narrower as compared to the Poissonian one, i.e. the photon distribution is of sub-Poissonian type. If we decrease laser intensity more, we find that at $\chi T_2 = 0.2$, the photon distribution approaches the Poissonian distribution again. Fig. 5a shows this fact.

Fig. 5 shows that Rabi oscillations do not reveal themselves in the distribution function measured for given time interval. Perhaps they can reveal themselves in the moments of the distribution if we shall measure the distribution for various time intervals. In order to clarify this problem we shall use the Mandel parameter $Q = [\langle N(N-1) \rangle - \langle N \rangle^2]/<N>$ taken in the following form [21]:

$$Q(t) = \langle I \rangle \left[\frac{2}{t} \int_0^t dx \int_0^x dy g^{(2)}(y) - t \right] \tag{28}$$

in which we use $\langle I \rangle = 1/\tau_0$ and Eq. (22) for the autocorrelation function. We have calculated the Mandel parameter $Q(t)$ for the set of parameters (21) and for three values of Rabi frequency. Result is shown in Fig. 6.

Here the curves a,b and c relate to the distribution functions shown in Fig. 5a, b and c, respectively. Negative value of the Mandel parameter proves sub-Poissonian character of the photon distribution. Sub-Poissonian character of the distribution is pronounced most clearly in Fig. 5b. The curve b in Fig. 6 demonstrates the greatest value of the negative Mandel parameter for this case. It is interesting that Rabi oscillations can reveal themselves in the Mandel parameter. The curve c shows Rabi oscillations in the Mandel parameter for $\chi T_2 = 3.33$.

6. Conclusion

We have calculated numerically the distribution of photons $w_N^O(t)$ and $w_N^M(t)$ in non-resonant fluorescence detected by the method O and the method M under strong CW-laser excitation. The distribution of photons does not almost depend on the method of photon counting. Squares and lines in Fig. 5 reveal this fact.

If the rate of laser excitation exceeds the rate of optical dephasing, Rabi oscillations manifest themselves in fluorescence autocorrelation function and in the Mandel parameter. Fig. 3 shows this fact. However, we have shown that Rabi oscillations do not manifest themselves in the photon distribution function. They manifest themselves solely in the probability $w_0^O(t)$ and
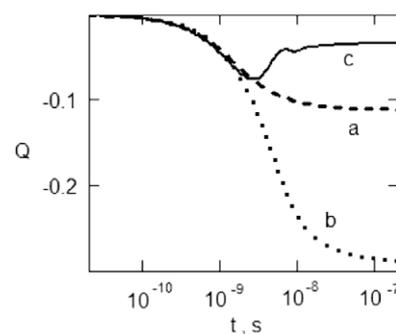

Fig. 6. Mandel parameter $Q(t)$ for $\chi T_2 = 0.2$ (a), 0.6 (b), 3.33 (c) and set (21) of physical parameters.

the probability $w_1^O(t)$ if the method O of photon counting is used. The method M of photon counting in non-resonant fluorescence is insensitive to the coherence in molecular polarization. Hence, the effects of molecular phase memory do not play noticeable role in photon statistics.

Appendix A

Roots of the equation $(\lambda - \Gamma)\left[(\lambda - 1/T_2)(\lambda - G - g) + 4\chi^2\right] - 2\chi^2 g = 0$ look as follows:

$$\Lambda_1 = M - \frac{2}{3}\sqrt{P}\sin\left[\frac{1}{3}a\sin\left(\frac{Q}{2P^{1.5}}\right)\right], \tag{A1}$$

$$\Lambda_2 = M - \frac{2}{3}\sqrt{P}\cos\left[\frac{1}{3}a\cos\left(\frac{-Q}{2P^{1.5}}\right)\right], \tag{A2}$$

$$\Lambda_3 = M + \frac{2}{3}\sqrt{P}\sin\left[\frac{1}{3}a\sin\left(\frac{Q}{2P^{1.5}}\right) + \frac{\pi}{3}\right]. \tag{A3}$$

Here

$$P = (G + \Gamma + 1/T_2 + g)^2 - 3(4\chi^2 + \Gamma(G+g) + (G + \Gamma + g)(1/T_2)), \tag{A4}$$

$$M = \frac{G + \Gamma + 1/T_2 + g}{3}, \tag{A5}$$

$$Q = -9(G + \Gamma + 1/T_2 + g)(4\chi^2 + \Gamma(G+g) + (G + \Gamma + g)(1/T_2)) + 27(2\chi^2(g + 2\Gamma) + \Gamma(1/T_2)(G+g)) - 2(G + \Gamma + 1/T_2 + g)^3. \tag{A6}$$
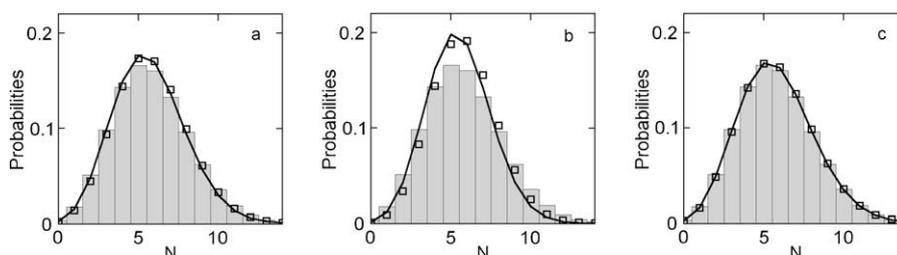

Fig. 5. Probabilities: $w_N^O(t)$ (solid line), $w_N^M(t)$ (squares) and Poissonian function (histogram) at the set of constants (21) and $\chi = 3 \times 10^7$ s^{-1}, $t = 1.2 \times 10^{-6}$ s (a), $\chi = 9 \times 10^7$ s^{-1}, $t = 2 \times 10^{-7}$ s (b), $\chi = 5 \times 10^8$ s^{-1}, $t = 1.2 \times 10^{-7}$ s (c). $\langle N \rangle = 5.8$.

Solution of the equation $\lambda\left[(\lambda - G - g)(\lambda - 1/T_2) + 4\chi^2\right] - 2\chi^2 g = 0$ is described by Eqs. (A1), (A2) and (A3) as well. However, we should insert now in Eqs. (A1), (A2) and (A3) the following formulas:

$$P = (G + 1/T_2 + g)^2 - 3(4\chi^2 + (G + g)(1/T_2)), \qquad (A7)$$

$$M = \frac{G + 1/T_2 + g}{3}, \qquad (A8)$$

$$Q = -2(G + 1/T_2 + g)^3 - 9(G + 1/T_2 + g)(4\chi^2 + (G + g)(1/T_2))$$
$$+ 27(2\chi^2 g). \qquad (A9)$$

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