

NONLINEAR AND QUANTUM OPTICS

From Quantum Light Emitted by Single Molecule to Classical Light Emitted by Molecular Ensemble

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Abstract—Fluorescence from an ensemble of noninteracting molecules excited by continuous laser radiation is considered as a glow of M individual molecules. The expression that governs the autocorrelation function (ACF) of fluorescence from M molecules is derived based on the theoretical expression that governs the ACF of fluorescence from a single-molecule. Fluctuations of blinking fluorescence and its statistical properties are analyzed using a computer simulation. The results of statistical analysis of the computer experiment are in good agreement with the derived formula that governs the ACF of fluorescence from several molecules.

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INTRODUCTION

Fluorescence from an ensemble of molecules excited by a continuous-wave (cw) laser radiation consists of a flow of photons and represents classical incoherent light of constant intensity. At the same time, the fluorescence of a single molecule represents a quantized light. Because each molecule emits photons at random moments in time, the intensity of fluorescence $I(t) = N/t$ or the number of photons N detected during the bin time t will fluctuate. The second-order autocorrelation function (ACF) defined as [1, 2]

$$g^{(2)}(T) = \frac{\langle I(t)I(t+T) \rangle}{\langle I(t)I(t+\infty) \rangle} = \frac{\langle I(t)I(t+T) \rangle}{\langle I \rangle^2} \quad (1)$$

can be measured for this fluctuating fluorescence. The numerator in (1) represents the sum over all overlapping products of two fluctuating fluorescence intensities shifted by time interval T and $\langle I \rangle$ is the mean fluorescence intensity.

The intensity in formula (1) can be measured experimentally. Obviously, the ACF dependence on T is determined by the dynamics of quantum jumps between ground electronic state 0 and excited electronic state 1 of each molecule, i.e., the microscopic model of the molecular ensemble. Hence, the derivation of the theoretical formula that relates $g^{(2)}(T)$ to the microscopic model of the emitter is an important practical task. Finding the solution would allow one to determine how the quantum properties of light disappear with an increase in the number of molecules in an ensemble.

AUTOCORRELATION FUNCTION OF SINGLE-MOLECULE FLUORESCENCE

First, we outline the possible ways of finding a theoretical expression that governs the ACF of single-molecule fluorescence. To this end, consider the general expression governing probability $w_N(T)$ of detecting N photons within time interval T , which was first obtained by Mandel [1, 2], as follows:

$$w_N(T) = \left\langle \left\langle \hat{T} : \frac{1}{N!} \left[\int_t^{t+T} dx \hat{I}(x) \right]^N \exp \left[- \int_t^{t+T} dx \hat{I}(x) \right] : \right\rangle \right\rangle. \quad (2)$$

This formula represents the quantum-statistical average of the time-ordered normal product of operators $\hat{I}(x)$ of electromagnetic field intensity. The formula is applicable to fluorescence from both an ensemble of molecules and a single molecule. Calculating the second-order factorial moment of distribution function (2), we obtain the known expression

$$\begin{aligned} \langle N^{(2)}(T) \rangle &= \sum_{N=0}^{\infty} N(N-1)w_N(T) \\ &= \int_t^{t+T} dt_2 \int_t^{t+T} dt_1 \left\langle \left\langle \hat{T} : \hat{I}(t_1)\hat{I}(t_2) : \right\rangle \right\rangle \\ &= 2 \int_0^T dx \int_0^x dy \left\langle \left\langle \hat{I}(x)\hat{I}(y) : \right\rangle \right\rangle = 2 \langle I \rangle^2 \int_0^T dx \int_0^x dy g^{(2)}(x-y). \end{aligned} \quad (3)$$

Performing Laplace transformation

$$f(\lambda) = f(i\omega) = \int_0^{\infty} f(t)e^{i(\omega+i0)t} dt$$

of both sides of formula (3), we have

$$\langle N^{(2)}(\lambda) \rangle = 2\langle I \rangle^2 g^{(2)}(\lambda)/\lambda^2. \quad (4)$$

Alternatively, the second-order factorial moment of the distribution of photons emitted by a single molecule can be calculated using the expression for the function $w_N(T)$ that describes the distribution of fluorescence photons emitted by a single molecule excited by continuous light; a detailed derivation of this expression can be found in [3, 4]. The Laplace transform of this probability is described by the following formula [3–6]:

$$w_N(\lambda) = [1 - s(\lambda)]^2 s(\lambda)^{N-1} / \tau_0 \lambda^2. \quad (5)$$

This formula describes the distribution function of the fluorescence photons from a single molecule in terms of Laplace transform $s(\lambda)$ of the so-called start–stop correlator. The physical meaning of the start–stop correlator is defined by the formula $dW_s(t) = s(t)dt$, where $dW_s(t)$ is the probability of detecting the second fluorescence photon in the $(t, t + dt)$ time interval, provided the preceding photon was emitted at $t = 0$. Obviously, the start–stop correlator is the probability of detecting two successively emitted photons separated by time interval t . For this reason, $s(t)$ is also called the waiting time distribution [5–7]. Specific form of the start–stop correlator is determined by the microscopic model of the single photon emitter.

Quantity

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

is the mean duration of the interval between two successively emitted photons [3, 4]. Obviously, this time is related to the average intensity of fluorescence by the following simple formula:

$$1/\tau_0 = \langle I \rangle. \quad (7)$$

Next, we calculate the second-order factorial moment of the distribution function $w_N^M(T)$; the Laplace transform of the latter is defined by formula (5). The calculations are performed using Laplace components as follows:

$$\begin{aligned} \langle N^{(2)}(\lambda) \rangle &= \sum_{N=0}^{\infty} N(N-1)w_N(\lambda) \\ &= \frac{[1 - s(\lambda)]^2}{\tau_0 \lambda^2} \sum_{N=0}^{\infty} N(N-1)s(\lambda)^{N-1} = \frac{2s(\lambda)}{\tau_0 \lambda^2 [1 - s(\lambda)]}. \end{aligned} \quad (8)$$

The obtained expression can be significantly simplified by introducing the so-called full two-photon correlator $p(t)$ defined as

$$dW_p(t) = p(t)dt, \quad (9)$$

where $dW_p(t)$ is the probability of detecting two photons separated by time interval t for arbitrary number of additional photons emitted within this interval. As was shown in detail in [8, 9], the full correlator and the start–stop correlator are related by the integral expression

$$p(t) = s(t) + \int_0^t s(t-x)p(x)dx.$$

Carrying out a Laplace transformation, we obtain the following formula for Laplace components:

$$s(\lambda)/[1 - s(\lambda)] = p(\lambda).$$

The substitution of this relation into (8) yields

$$\langle N^{(2)}(\lambda) \rangle = 2p(\lambda)/\tau_0 \lambda^2 = 2\langle I \rangle p(\lambda)/\lambda^2. \quad (10)$$

Equating the right-hand sides of (4) and (10) leads to the following expression governing Laplace transform of the fluorescence ACF:

$$g^{(2)}(\lambda) = p(\lambda)/\langle I \rangle. \quad (11)$$

Recall that $dW_p(t) = p(t)dt$ is the probability of observation of the second photon in the $(t, t + dt)$ interval, provided that the first photon was emitted at $t = 0$. The correlation between the two photons vanishes if the time interval t is fairly long. Then,

$$dW_p(\infty) = p(\infty)dt = \langle I \rangle dt,$$

which means that the probability of observation of a photon in interval $(t, t + dt)$ is determined by the product of average intensity of the glow and the length of the time interval. Taking into account that $\langle I \rangle = p(\infty)$ and switching to functions of time in (11), we finally have

$$g^{(2)}(T) = p(T)/p(\infty). \quad (12)$$

This formula relates the experimentally measurable ACF of fluorescence with the full two-photon correlator, which can be calculated for a given model of the single emitter. Equation $g^{(2)}(\infty) = 1$ means the lack of correlation between the two photons emitted with a long delay with respect to each other.

AUTOCORRELATION FUNCTION OF FLUORESCENCE FROM A MOLECULAR ENSEMBLE

Next, we consider the fluorescence from two independent molecules. In this case, we deal with a sequence of photons emitted by both molecules. If the

spectral bands of fluorescence of molecules 1 and 2 are different, photons emitted by each of the molecules can be detected separately by using spectral filters. Figure 1 shows the sequence of photons emitted by two molecules whose absorption rates k differ by a factor of three. Photons emitted by molecules 1 and 2 are indicated by short and long vertical lines, respectively. Apparently, in this case, we can measure four types of probabilities, i.e.,

$$dW_{nm}(t) = p_{nm}(t)dt, \quad (13)$$

where the first index $n = 1, 2$ denotes the number of the molecule that emitted a photon at time zero, while the second index $m = 1, 2$ denotes the number of the molecule that emitted a photon in the time interval $(t, t + dt)$. Formula (13) represents a generalization of formula (9) for the case of light emission by two molecules. The probabilities $p_{11}(t) = p_1(t)$ and $p_{22}(t) = p_2(t)$ of the events where both photons were emitted by molecule 1 or molecule 2, are termed the full correlators of molecules 1 and 2, respectively. Probabilities $p_{12}(t)$ and $p_{21}(t)$, which correspond to the events where the first and the second photons were emitted by different molecules, are referred to as ‘‘cross correlators.’’

Since the molecules emit fluorescence photons independently, the following relations apparently take place:

$$p_{11}(\infty) = p_{21}(\infty) = p_1(\infty), \quad p_{22}(\infty) = p_{12}(\infty) = p_2(\infty). \quad (14)$$

Recall that the first index corresponds to the number of the molecule that emits the first photon in the pair, while the second index corresponds to the number of the molecule emitting the second photon. Formula (14) states that the correlation between any two photons is absent at long delays.

Because of the quantum nature of fluorescence from a single molecule, two fluorescence photons cannot be emitted simultaneously, i.e., $p_{11}(0) = p_{22}(0) = 0$. This effect is called photon antibunching. However, antibunching is absent for photons emitted by different molecules because

$$p_{21}(0) = p_1(\infty), \quad p_{12}(0) = p_2(\infty). \quad (15)$$

Combining (14) and (15), we have

$$p_{21}(0) = p_{21}(\infty) = p_{21}(\tau) = p_1(\infty),$$

$$p_{12}(0) = p_{12}(\infty) = p_{12}(\tau) = p_2(\infty).$$

Consequently, there is no correlation between any pair of photons 1 and 2, and the corresponding cross-correlator is determined by the photons count rate of closing time interval τ .

Obviously,

$$P_1 = p_1(\infty)/[p_1(\infty) + p_2(\infty)],$$

$$P_2 = p_2(\infty)/[p_1(\infty) + p_2(\infty)]$$

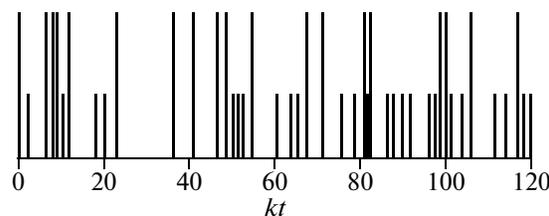


Fig. 1. Distribution of fluorescence photons emitted by molecule 1 (short lines) and molecule 2 (long lines) over a time interval.

are the probabilities of seeing photon 1 and photon 2 in the combined sequence of photons shown in Fig. 1. Consequently, the coefficient

$$p_{(2)}(\tau) = P_1[p_{11}(\tau) + p_{12}(\tau)] + P_2[p_{22}(\tau) + p_{21}(\tau)] \quad (16)$$

$$= p_1[p_1(\tau) + p_2]/(p_1 + p_2) + p_2[p_2(\tau) + p_1]/(p_1 + p_2)$$

represents the count rate of pairs of any photons separated by time interval τ in the combined fluorescence from two molecules. The abbreviated notations $p_1(\infty) = p_1$ and $p_2(\infty) = p_2$ were used above. Consequently, the ACF of fluorescence from two molecules, which equals unity when time tends to infinity, is determined by the following formula

$$g_{(2)}^{(2)}(\tau) = p_{(2)}(\tau)/p_{(2)}(\infty)$$

$$= [p_1(\tau)p_1 + p_2(\tau)p_2 + 2p_1p_2]/(p_1 + p_2)^2 \quad (17)$$

$$= [p_1^2g_1^{(2)}(\tau) + p_2^2g_2^{(2)}(\tau) + 2p_1p_2]/(p_1 + p_2)^2.$$

The latter formula expresses ACF of fluorescence from two molecules in terms of ACF of fluorescence from each of them.

Formulas (16) and (17) can be easily generalized to the case of fluorescence from M independent molecules:

$$p_{(M)}(\tau) = \sum_{j=1}^M \left[p_j p_j(\tau) + \sum_{k=1}^M (1 - \delta_{jk}) p_j p_k \right] / \sum_{j=1}^M p_j, \quad (18)$$

$$g_{(M)}^{(2)}(\tau) = \sum_{j=1}^M \left[p_j^2 g_j^{(2)}(\tau) + \sum_{k=1}^M (1 - \delta_{jk}) p_j p_k \right] / \left(\sum_{j=1}^M p_j \right)^2. \quad (19)$$

These formulas express the full two-photon correlator and the ACF of fluorescence from M different noninteracting molecules in terms of full two-photon correlator $p_j(\tau)$ and ACF of fluorescence $g_j^{(2)}(\tau)$ of each of the M molecules.

FULL TWO-PHOTON CORRELATOR OF BLINKING FLUORESCENCE

The full two-photon correlator of fluorescence from a single molecule can be calculated, provided a microscopic model that describes a single molecule excited by a continuous light source and emitting flu-

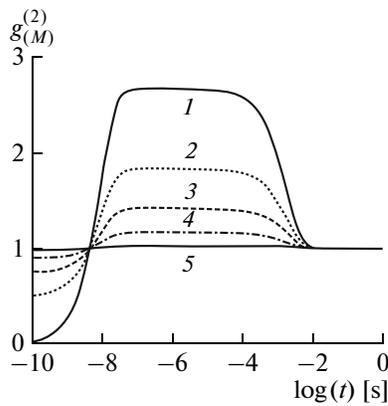


Fig. 2. Autocorrelation function of fluorescence from one (1), two (2), four (3), ten (4) and sixty (5) identical molecules calculated based on formulas (19) and (21) with set of parameters (23).

orescence photons is available. As an example, we consider a molecule with a triplet state that emits fluorescence photons under cw light illumination. The molecule can be described by a three-level energy diagram, where optical transitions occur between singlet electronic states 0 and 1, with triplet level 2 located between them.

Processes in this molecule can be analyzed using kinetic equations

$$\begin{aligned}\dot{\rho}_1 &= -(G + k + 1/T_1 + A)\rho_1 + k\rho_0, \\ \dot{\rho}_0 &= (G + k + 1/T_1)\rho_1 - k\rho_0 + a\rho_2, \\ \dot{\rho}_2 &= A\rho_1 - a\rho_2.\end{aligned}\quad (20)$$

Here, ρ_j is the probability of finding the molecule in quantum state $j = 0, 1$, or 2 . Constants k , $1/T_1$, and G represent the rates of induced, spontaneous, and non-radiative transitions between optically active states 0 and 1. Constants A and a describe the rate of transitions to and from dark state 2, in which the molecule's fluorescence stops. In particular, a triplet state often plays the role of the dark state.

The molecule illuminated by a cw laser radiation emits fluorescence accompanied by random jumps of the molecule between states 0 and 1, whereby the molecule emits one photon in each jump from state 1 to state 0. The time interval within which the molecule jumps between states 0 and 1 is called the on interval. When a nanoparticle makes a transition from state 1 to dark state 2, its emission stops, despite continuing laser illumination, i.e., the off interval begins. Fluorescence recovers and the off interval ends when the molecule jumps from state 2 to state 0. The presence of the on and off intervals is the second piece of evidence that demonstrates the quantum nature of fluorescence emitted by a single molecule.

As was shown in [8], the full two-photon correlator is defined by the formula $p(t) = \rho_1(t)/T_1$, where $\rho_1(t)$ is

the solution of set of equations (20) with initial conditions $\rho_0(0) = 1$, $\rho_1(0) = \rho_2(0) = 0$. In the process of registering spontaneous fluorescence photons, at time zero, the probabilities have the aforementioned values. Solving set of equations (20), we find that

$$p(t) = \frac{k}{T_1} \left[\frac{a}{\gamma_0^2 - R^2} + \left(1 - \frac{a}{\gamma_0 - R} \right) \frac{e^{-(\gamma_0 - R)t}}{2R} - \left(1 - \frac{a}{\gamma_0 + R} \right) \frac{e^{-(\gamma_0 + R)t}}{2R} \right], \quad (21)$$

where

$$\begin{aligned}\gamma_0 &= (1/T_1 + G + A + 2k + a)/2, \\ R &= \sqrt{[(1/T_1 + G + A + 2k - a)/2]^2 - kA}.\end{aligned}\quad (22)$$

Substituting (21) into (12), we obtain an expression that governs the ACF of blinking fluorescence from a single molecule. The result of calculations using this formula with the following set of relaxation constants:

$$\begin{aligned}k &= 10^5, \quad G = 10^7, \quad 1/T_1 = 10^8, \\ a &= 200, \quad A = 3.7 \times 10^5 \text{ s}^{-1}\end{aligned}\quad (23)$$

is presented in Fig. 2 by a line that corresponds to $M = 1$. The drop in fluorescence to zero at short times is due to the photon antibunching effect, which has a purely quantum nature, as was mentioned above. Inequality $g^{(2)}(t) > 1$ shows that photons are emitted in groups (photon bunching), i.e., during the on intervals.

Also shown in Fig. 2 are the ACF of fluorescence from 2, 4, 10, and 60 identical molecules calculated according to (19). Evidently, as the number of molecules increases, the effects of both antibunching and bunching disappear; i.e., fluorescence from several molecules attains the features of a classical light, although radiation of each molecule has quantum nature.

DISTRIBUTION OF THE ON AND OFF INTERVALS

Next, we numerically simulate blinking fluorescence, which consists of on and off intervals. The molecule illuminated by cw laser radiation makes jumps between singlet states 0 and 1 at random moments in time, emitting a photon in each jump from state 1.

Equations Governing On States

These equations can be obtained from (20) by omitting the term $a\rho_2$ that describes transition of molecule from triplet to singlet state in the second equa-

tion. We get the following set of equations governing the dynamics of the on states:

$$\begin{aligned}\dot{\rho}_1 &= -(G + k + 1/T_1 + A)\rho_1 + k\rho_0, \\ \dot{\rho}_0 &= (G + k + 1/T_1)\rho_1 - k\rho_0.\end{aligned}\quad (24)$$

The formula that governs the distribution of the on intervals will have a simple form if we take into account that the mean time interval between the jumps between states 1 and 0 is significantly shorter than the duration of the on interval. For such frequent jumps between states 0 and 1, probability of the molecule to be in the on state can be determined from the formula $\rho_{\text{on}} = \rho_0 + \rho_1$, which coincides with the probability that the molecule is in a singlet state. Hence, adding two equations of set (24), we have

$$\dot{\rho}_{\text{on}} = -A\rho_1. \quad (25)$$

When the time of accumulation of photons is significantly longer than the mean interval between two emitted photons, the fluorescence emitted during the on interval is perceived as a continuous glow. In this case, a quasi-stationary approximation can be used; for $\dot{\rho}_1 = 0$, the first equation of set (24) yields

$$\rho_1 = \frac{kT_1}{1 + (k + A + G)T_1} \rho_0.$$

Using this formula and formula $\rho_{\text{on}} = \rho_0 + \rho_1$, it can be expressed in terms of ρ_{on} :

$$\rho_1 = \frac{kT_1}{1 + (2k + G + A)T_1} \rho_{\text{on}}.$$

Substituting this relation into (25), we obtain the following simple equation that governs the probability of finding a molecule in the on state:

$$\dot{\rho}_{\text{on}} = -\rho_{\text{on}}/\tau_{\text{on}}, \quad (26)$$

where

$$1/\tau_{\text{on}} = kAT_1/[1 + (2k + G + A)T_1] = kY_{\text{ISC}}.$$

Here, Y_{ISC} is the quantum yield of intersystem crossing. The solution of Eq. (26) has the form

$$\rho_{\text{on}}(t) = c_{\text{on}} \exp(-t/\tau_{\text{on}}), \quad (27)$$

where c_{on} is an arbitrary coefficient (for now). However, this function can be regarded as the density of the probability of finding an on interval of duration t , provided that the arbitrary coefficient is chosen to satisfy the probability normalization condition

$$\int_0^{\infty} P(t) dt = 1. \quad (28)$$

Substituting (27) into (28), we find that $c_{\text{on}} = 1/\tau_{\text{on}}$. Consequently, the distribution function of the on interval has the form

$$P_{\text{on}} = (1/\tau_{\text{on}}) \exp(-t/\tau_{\text{on}}). \quad (29)$$

Obviously, τ_{on} is the mean duration of the on interval.

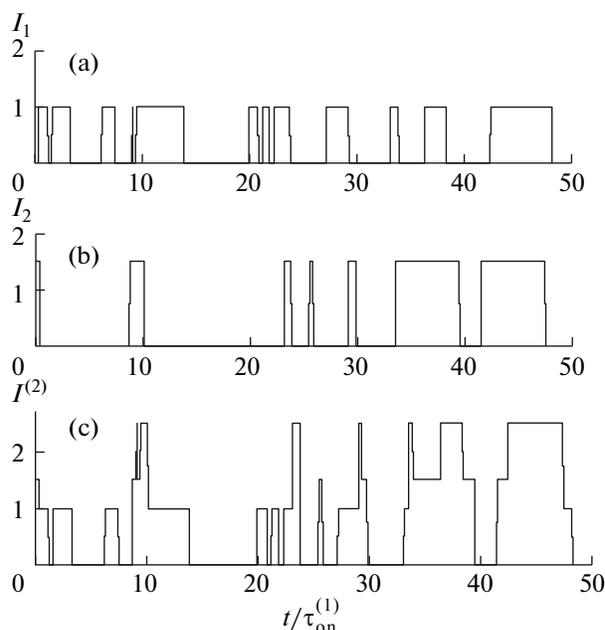


Fig. 3. Quantum trajectory of fluorescence intensity from two noninteracting molecules (a) and (b) and the combined fluorescence from these two molecules (c).

Equation Governing Off States

When a molecule is in a triplet state, its fluorescence stops. Consequently, $\rho_{\text{off}} = \rho_2$ determines the probability of the molecule being in the off state. The equation that governs the probability of detecting a molecule in the off state can be found from (20) if the term $A\rho_1$, which describes the arrival of the molecule to the off state from the on state in the third equation, is omitted. Consequently, the dynamics of the off state is described by the equation $\dot{\rho}_{\text{off}} = -a\rho_{\text{off}}$. Reiterating the arguments used when deriving formula (29), the following expression governing the probability of finding a molecule in the off state can be obtained:

$$P_{\text{off}} = a \exp(-at), \quad (30)$$

where $\tau_{\text{off}} = 1/a$ is the mean duration of the off interval.

QUANTUM TRAJECTORY OF INTENSITY OF FLUORESCENCE FROM TWO MOLECULES

Jumps from the on state to the off state and back occur at random moments in time with the probabilities given by (29) and (30). To determine these random moments, we can use the equation

$$\text{rnd}(t) = \int_0^t P(\tau) d\tau, \quad (31)$$

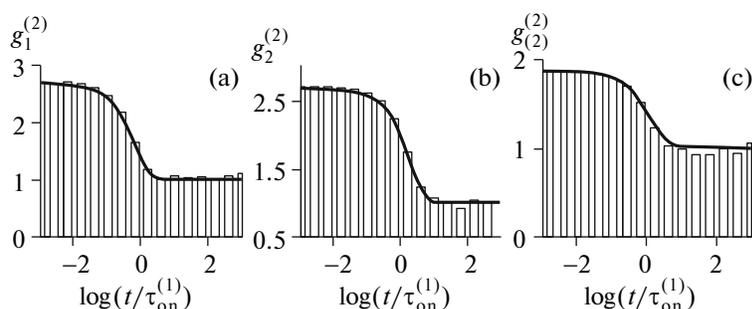


Fig. 4. Histograms of correlation functions of fluorescence from a molecule measured from quantum trajectories of intensity shown in Figs. 3a–3c, respectively. Solid lines are ACF calculated based on formulas (32) and (17).

where the function $rnd(t)$ defines a random number between 0 and 1 with a constant density of probability. The values of t found from Eq. (31) are the sought random moments in time, which are distributed with the density of probability $P(t)$.

The random moments of fluorescence stop and recovery, i.e., intensity fluctuations of the fluorescence from two different molecules calculated using formula (31), are shown in Figs. 3a and 3b. Figure 3a presents the model fluorescence with parameters (23) for which the ratio of mean durations of the on and off intervals is $\tau_{on}^{(1)}/\tau_{off}^{(1)} = 3/5$. Figure 3b illustrates the fluorescence that would be emitted by a molecule with longer mean intervals: $\tau_{on}^{(2)} = 3\tau_{on}^{(1)}$ and $\tau_{off}^{(2)} = 3\tau_{off}^{(1)}$. Because these molecules do not interact with each

other, fluctuations of fluorescence from each molecule are independent. Hence, fluctuations of combined fluorescence from two molecules are simply added, as can be seen from Fig. 3c. As a result, some of the off intervals disappear. Consequently, fluorescence from even several molecules does not reveal any off intervals and becomes continuous, as is usually observed in the case of a molecular ensemble.

The rate $1/T_1$ of spontaneous fluorescence is the largest in the set of constants (23). Expanding the expression that governs R in (22) in a power series with respect to small parameter kAT_1^2 , we obtain the following expressions for the exponents in (21):

$$\gamma_0 + R \cong 1/T_1, \quad \gamma_0 - R \cong 1/\tau_{on} + 1/\tau_{off}.$$

If the temporal resolution in the experiment is lower than the mean time interval between two successively emitted photons, after averaging over the time interval that corresponds to the available temporal resolution, the second exponential in (21) vanishes and formula (21) takes the form

$$p(t) = k \left\{ \frac{1/\tau_{off}}{1/\tau_{on} + 1/\tau_{off}} - \frac{1/\tau_{on}}{1/\tau_{on} + 1/\tau_{off}} \exp[-t(1/\tau_{on} + 1/\tau_{off})] \right\}.$$

Substituting the latter expression into (12), we obtain the following simple formula that describes the ACF of fluorescence from a single molecule:

$$g^{(2)}(t) = 1 + (\tau_{off}/\tau_{on}) \exp[-t(1/\tau_{on} + 1/\tau_{off})]. \quad (32)$$

The ratio τ_{off}/τ_{on} is called the contrast.

Applying formula (1), which is usually used for the statistical processing of experimentally measured fluorescence, we can measure the ACF of the blinking fluorescence shown in Fig. 3. The result is presented as a histogram in Fig. 4. Solid lines show the results of the calculation of ACF of fluorescence from single molecules based on formulas (19), (32) with $M = 1$ (Figs. 4a, 4b) and $M = 2$ (Fig. 4c). Rather good agreement between the curves and the histograms

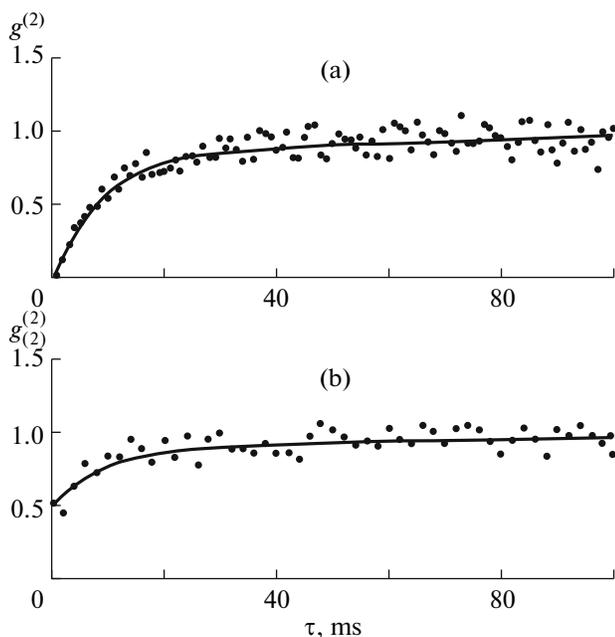


Fig. 5. Autocorrelation function of fluorescence from one (a) and two (b) Hg^+ ions measured in [10] (dots) and calculated based on formulas (12) and (17) (solid lines).

proves the validity of formula (19), which governs the ACF of fluorescence from several molecules.

Formula (17) can be compared with the ACF of fluorescence from one and two Hg^+ ions measured in [10]. The result is shown in Fig. 5. The theory yields satisfactory agreement with the experiment. The suppression of antibunching and the decrease of contrast in fluorescence from two ions are clearly seen, which indicates that fluorescence from two ions acquires the properties of classical light.

CONCLUSIONS

If each molecule excited by cw laser radiation exhibits blinking fluorescence, fluorescence from an ensemble of several molecules will continue to blink, but will be smoothed. Nevertheless, statistical analysis can be applied to this fluorescence with smoothed blinking to find its ACF. In the present work, we theoretically derived the expression that governs the ACF of fluorescence from an ensemble of molecules and expressions that govern the distribution functions of the on and off intervals. We conducted a computer experiment to simulate fluctuations of the blinking fluorescence and to perform statistical processing of the simulated fluorescence using formula (1) usually used for processing the experimentally measured fluctuations. The agreement of the histograms with the

curves in Fig. 4 proves the validity of both the theoretically derived formulas and the computer simulations.

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