Looking at a blinking quantum emitter through time slots: The effect of blind times

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Most experimental observations of physical processes are naturally accompanied by "blind" ("dead") times, which in principle can distort the result of measurements. Here we analyze how the presence of blind times in measurements changes the measured statistics of blinking fluorescence of single quantum dots. We show that information can be extracted even for blinking processes with characteristic times longer than both blind times and time slots between them.

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Many experiments in various fields cannot be designed without "blind" times—periods when observation is interrupted, and no information about the process under investigation can be acquired. These blind times are separated by time slots between them, periods when observation is carried out. In other words, during time slots we can "see" the process, whereas during blind times we cannot. They follow each other repeatedly in a regular manner, with definite durations. The question of how blind times affect the result of an experimental observation (statistical regularities) of dynamical processes is quite general in natural science and has already been under discussion for a long time. For example, in [1] authors went as far as analyzing the contribution of eyewink to experimental errors. In modern experiments, this problem may appear because of dead time of detection systems, intermittence of continuous observation due to the necessity for data transfer, influence of additional interfering processes, e.g., earth rotation impeding continuous observation of astronomical objects, etc. Similar problems of restoring full data from separate bits are known in statistics [2], signal processing [3], etc. A deep understanding of this problem can have applied (sometimes unexpected) significance, for example, a novel biometric approach for human identification using eye blinking [4] or the dynamics of blinking vortices [5]. The question of blind times is also naturally applied in pump-probe spectroscopy with pulsed lasers.

One of the most important fields where statistical analysis of dynamical processes is very important and blind times are inevitable is the modern spectroscopy of single quantum objects and nanostructures (molecules, semiconductor and dielectric quantum dots, emitting sites of macromolecules, etc.) [6–9]. The study of such emitters has a strongly marked interdisciplinary character and opens great prospects for their broad application: as luminescent labels in life and material sciences [10,11], nonclassical light sources in quantum computing systems [12,13], nanosensors [14,15], and elements of nanophotonic devices [16,17]. Super-resolution microscopy based on single emitter fluorescence was awarded the Nobel Prize in Chemistry in 2014 [18,19].

An important property of single quantum objects is blinking of their fluorescence [20–28]. The photoluminescence intensity trajectory (time track of the number of photons emitted per bin time, t_{bin}) consists in this case of alternating intervals of various intensity levels when the emitter is excited by a cw laser. The simplest case of a two-level system with one "dark" (of) state is shown in Fig. 1. Blinking times are orders of magnitude longer than the excited state lifetime (intervals between successive photons in an on-interval).

The durations of on- and off-intervals in the simplest case are distributed exponentially, with the probability density $f_{\mathrm{on,off}}(t)$ to encounter an on,off-interval of duration t equal to

$$f_{\mathrm{on,off}}(t) = (1/t_{\mathrm{on,off}})\exp(-t/t_{\mathrm{on,off}}). \tag{1}$$

Here $t_{\mathrm{on,off}}$ are the characteristic times of bright and dark states, respectively. The analysis of experimental on- and off-distributions gives the opportunity to find the characteristic times $t_{\mathrm{on,off}}$ [20,21]. Note, however, that the off-intensity is nonzero in real measurements due to background fluorescence and dark counts. Moreover, as recent measurements show [29,30], many quantum emitters manifest transitions into "grey" states, which are slightly fluorescent but can be recognized as off-states. As a result, the analysis is subjected to errors caused by thresholding.

Another way is to analyze the photon distribution function (PDF), which is the distribution for the number of fluorescence photons per bin time [31–33]. In the simplest case [Fig. 1(c)], the PDF consists of two distinct on- and off-peaks. The heights of those peaks are proportional to the average on,off-interval durations. Besides, the height and the shape of the plateau between them are connected to the relations of $t_{\mathrm{on,off}}$ to the bin time [34]. So, if experimental PDFs, such as that in Fig. 1(c), are at our disposal, it is basically possible to determine $t_{\mathrm{on,off}}$, as it was done in [35], avoiding the notorious problem of how to establish the threshold between on,off-intervals.

Our aim here is to analyze the influence of blind times on the blinking time constants, which we extract from fluorescence trajectories. Is it necessary to introduce any modifying factors to determine the "real" parameters in this case? In this paper we present computer simulations, experimental results, and analytical considerations on this issue.

We have simulated 10^4 different samples of blinking fluorescence trajectories with one off-state. Two characteristic cases out of them are analyzed in Fig. 2 (simulation 1

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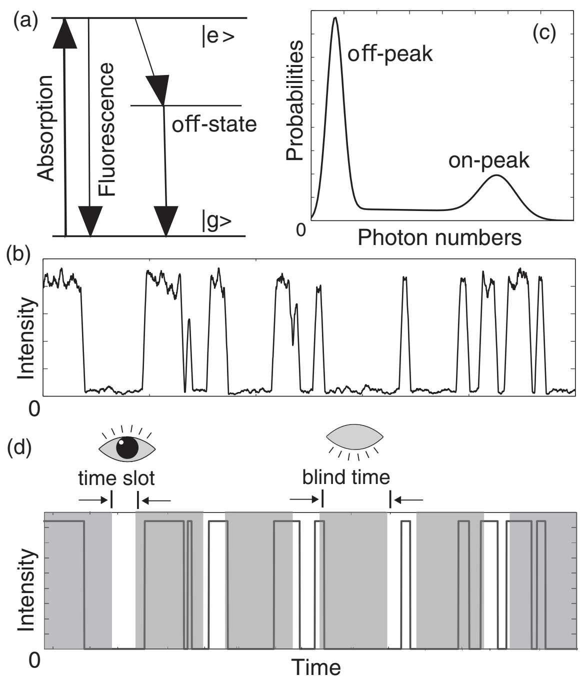

FIG. 1. Fluorescence trace of a single two-level emitter with one dark state. (a) Energy scheme of the emitter, (b) simulated fluorescence intensity trajectory with on,off-intervals, and (c) distribution of fluorescence photon number per bin time for the simulated trajectory. (d) An intensity trajectory of single emitter blinking fluorescence observed through time slots. Information during blind times (grey areas) is lost. Importantly, the time slots are shorter than the characteristic on-off-times. The blind times are longer than the time slots and comparable to the average blinking times.

and simulation 2). Random on,off-intervals were distributed exponentially, both types with equal average durations $t_{on} = t_{off} = 10$ s. The simulated trajectories were 10^4 s long. Fluctuations within on,off-intervals were smoothed out, and background fluorescence was neglected, since we wanted to focus on on-off-durations [Fig. 1(d)]. Then equal regular time slots of 1.5 s and blind times of 8.5 s [grey rectangles in Fig. 1(d)] were introduced. Thus, the relation of the times was as follows: time slot duration (1.5 s) < blind time duration (8.5 s) < average blinking times (10 s). In this case we seemingly lose too much information. But we prove that even in this extreme case the distortion of the parameters is (with great probability) slight.

We calculated the relations of time cumulatively spent in the on-state to the total observation time (on-time relations) for continuous and interrupted observation (r and r' hereafter). A factor to be taken into account was the length of the intensity trajectory. To study shorter trajectories, we "cut" the ones we have and treat their pieces: 0–10 s, 0–20 s, and 0–10^4 s. We count the on-relations r and r' for these pieces of various lengths. Expectedly, when only a short piece is at our disposal, fluctuations are great. For long trajectories, r and r' both approach the value $t_{on}/(t_{on} + t_{off}) = 10\text{ s}/(10\text{ s} + 10\text{ s}) = 0.5$ [such a case is presented in the upper panel of Fig. 2(a), simulation 1]. However, there are cases when r' deviated from r even for full trajectory length, 10^4 s [the lower panel of Fig. 2(a), simulation 2]. In a single experiment the first case would give us an idea of some nonstochastic pattern, though we can see through a number of simulated experiments that this pattern does not actually take place.

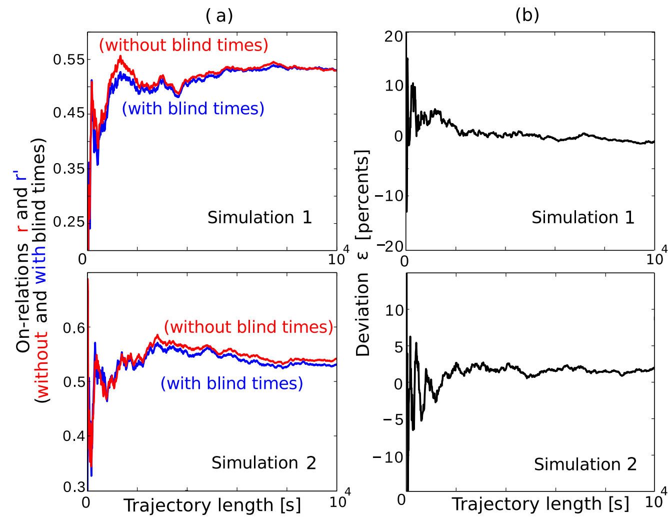

FIG. 2. (Color online) Results for two simulated intensity trajectories out of 10^4. (a) On-time relations r and r' without and with blind times; (b) deviation between these relations, $\varepsilon = [(r - r')/r] \times 100\%$.

We also wanted to establish the limits of the deviation ε between r and r' due to blind times. In Fig. 2(b), the relative deviation in percents is presented: $\varepsilon = [(r - r')/r] \times 100\%$. The longer the trajectory is, the closer to zero the deviation is.

The frequency of occurrence of the deviation was calculated throughout all the 10^4 simulations. The result is presented in Fig. 3: for full trajectory duration, 10^4 s [Fig. 3(a)] and for a short piece, 500 s [Fig. 3(b)].

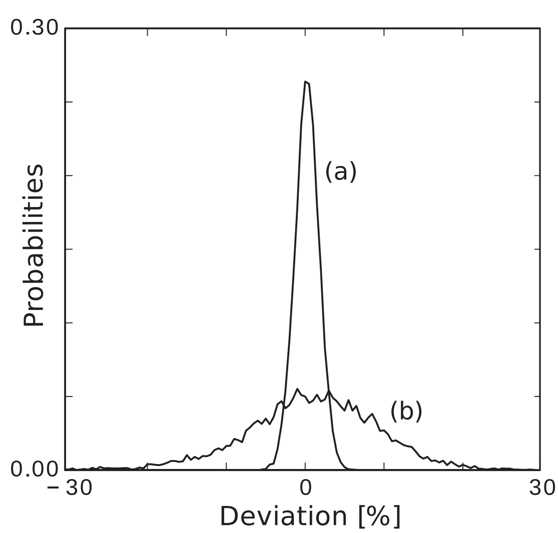

FIG. 3. Distribution of deviations $\varepsilon = [(r - r')/r] \times 100\%$ between on-time relations r and r' of continuous and interrupted observation for (a) full trajectory length, 10^4 s (Gaussian shape) and (b) pieces of trajectories of 500 s.

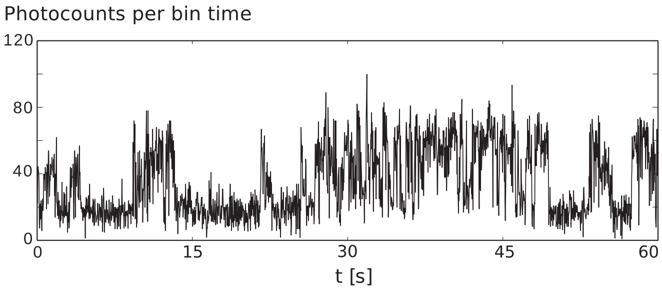

FIG. 4. A piece of fluorescence intensity trajectory of a single quantum dot CdSe/ZnS.

As can be seen in Fig. 3(b), the majority of cases demonstrate the deviation within a range of 20% to 30% for short trajectories. Larger deviations, even over 100%, can also occur, but their probability is negligibly small (one occurrence of $\varepsilon = 120\%$ in 10^4 trajectories). As for long trajectories [Fig. 4(a)], the deviation does not exceed 5% with an overwhelming probability (and is of Gaussian shape). Thus, the introduction of time slots does not distort the result, but causes more statistical uncertainty. It holds true even when characteristic processes are several times longer than time slots.

Let us now demonstrate an experimental example: fluorescence of a single quantum dot (QD) CdSe/ZnS (Lumidot 610 nm, size is 5.2 nm without ligands). QDs were placed on a cover glass by dilute toluene solution spin-coating. Their excitation was performed by a tunable dye laser Coherent CR-599. Fluorescence images and intensity trajectories of single QDs were acquired with a custom-built luminescence microscope and highly sensitive cooled CCD PCO Sensicam EM at room temperature. The bin time was 30 ms. The trajectory was 10 000 bins long, or 300 s. The general description of the setup is presented in [10]. The data on single QD fluorescence were extracted with specially developed software for the procession of single emitter experiments [11].

We have chosen a single QD with pronounced blinking (see Fig. 4, where a piece of a fluorescence intensity trajectory is presented). Blinking times here have multiexponential, and not single-exponential, distribution and vary from about 0.5 s to about 5 s, which is typical for this kind of QD [36]. Thus, it is more convenient to study the PDF, which is presented in Fig. 5(a). We see on- and off-peaks [compare to Fig. 1(c)].

The regular blind times were introduced into the experimental trajectory and its pieces were deliberately "cut out" to see what distortion the presence of blind times brings. Blind times were chosen to be 0.18 s (six times longer than the bin time), and time slots 0.06 s (twice the bin time). So, here the relation is again the following: time slot duration (0.06 s) $<$ blind time duration (0.18 s) $<$ average blinking times (0.5–5 s). Time slots are several times less than characteristic on-off-times.

The PDF of this "discontinuously observed" trajectory is plotted in Fig. 5(b). As can be seen, the effect reduces only to more statistical uncertainty. The uncertainty increases, as the total observation time was reduced from 10 000 bins (300 s) to 2500 bins (75 s).

Now let us come back to the full experimental trajectory with 10 000 bins and pick 2500 randomly placed bins from it. Thus, we have another set of the same size, but the positions of the recorded bins are not regular, but random. The distribution for this set is shown in Fig. 5(c). Again, the shape of the distribution and the heights of the peaks are not principally distorted. The distribution only becomes noisier. It means that basically the same parameters ($t_{\mathrm{on,off}}$) would be extracted from the experimental results in the three cases: (1) from the continuously observed trajectory, (2) from the trajectory with regular time slots, and (3) from the trajectory with randomly observed bits. Let us once again emphasize that it holds true even when $t_{\mathrm{on,off}}$ are several times longer than time slots.

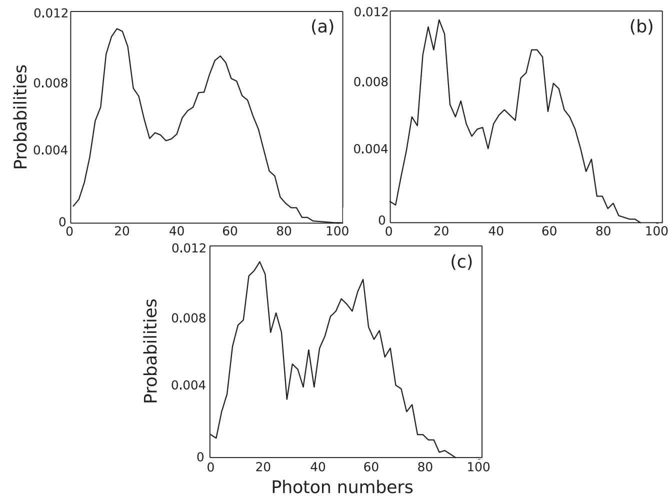

FIG. 5. Fluorescence photon distribution function (a) for a full intensity trajectory, (b) for the same trajectory with regular deliberately "cut out" blind times and time slots, and (c) for the same trajectory with random time slots.

The total observation time defines the accuracy with which the parameters can be determined. It should be much bigger than the time of the characteristic process. If this condition is satisfied, seemingly, no matter how short the time slots are in comparison to blinking on-off-times, the conclusion made above about the reliability of the acquired data still holds. This can justify the same reasoning for the case of QDs with a wider range of on-off-times than those in the experiment described above.

It is worth mentioning that this result can also be applied to the case of single blinking quantum objects excited by pulsed lasers. In such an experiment, blind times (between pulses) are inevitable. Time slots then coincide with pulse durations, which can be considerably short. Nevertheless, as we show in the present paper, even if the pulse duration is shorter than the characteristic time of the process under consideration, the photon statistics correctly reflects this process if we acquire enough cumulative pulse time. "Enough" here means that the total cumulative observation time should be much longer than the characteristic time of the process of interest. Note that the problem discussed in the present paper become more important in the case of slowly varying processes and/or nonergodic systems (see, e.g., [37]).

We have also developed the analytical approach for the case of blind times and time slots intermittence, which is outlined here. First, it is necessary to derive the expressions for the distributions $f(r)$ and $f(r')$ of the on-relations r and r' for continuous and interrupted observation.

Let us consider an observation interval of a given duration t_{obs}. The on-relation of value r means that the emitter cumulatively spends time $t_{obs}r$ in the on-state. This cumulative time can be realized as a sum of an arbitrary number of exponentially distributed on-intervals of t duration, $f_{on}(t) = (1/t_{on})\exp(-t/t_{on})$, and/or their pieces at the beginning and ending of the observation interval. The probability for $f(r)$ will thus contain convolutions of such full and partial intervals. N full exponentially distributed on-intervals convolved give the Erlang distribution

$$f_{on}(N,t) = \frac{(1/t_{on})^N t^{N-1}\exp(-t/t_{on})}{(N-1)!}. \qquad (2)$$

A piece "cut" with a uniform probability from an exponential on-interval has the distribution of an incomplete Γ function

$$f_{\text{on-piece}}(t) = \int_0^\infty \frac{(1/t_{on})\ \exp(-t'/t_{on})}{t'}\,dt' = (1/t_{on})\Gamma(0;t/t_{on}). \qquad (3)$$

Convolutions of the Erlang distribution and the incomplete Γ distribution(s) can be calculated numerically. The total cumulative time defined by these convolutions should be $t_{obs}r$. Besides, there should be an analogous convolution for off-intervals to result in a cumulative time of $t_{obs} - t_{obs}r$. The number of full on-intervals within t_{obs} is here arbitrary, so we need to take a sum of all possible numbers. Strictly speaking, it is a sum from 0 to ∞, but, depending on the sizes of $t_{on,off}$ and t_{obs}, it can be reasonably restricted with a few components. As a result, the expression is obtained for $f(r)$ substituting the length of the trajectory for t_{obs}. For a large observation interval it will approach the δ function $\delta(r - t_{on}/(t_{on} + t_{off}))$. As for the distribution $f(r')$, we need to substitute the time slot duration instead of t_{obs}. This distribution will be broad for short time slots.

With the distributions $f(r)$ and $f(r')$, we can calculate the distribution for the deviation $\varepsilon(r,r') = (r - r')/r$ as a function of two independent variables:

$$f(\varepsilon) = \frac{dF(E > \varepsilon)}{d\varepsilon} = \frac{d\left(\int_0^\infty dr \int_{(1-\varepsilon)r}^\infty dr' f(r) f(r')\right)}{d\varepsilon}, \qquad (4)$$

where $r \in [0;+\infty)$ and $r' \in [(1-\varepsilon)r;+\infty)$ is the area where $E > \varepsilon$. Thus, we arrive at the sought-for distribution $f(\varepsilon)$ for the deviation ε between the on-relations.

In conclusion, we demonstrate that correct dynamical parameters and statistical patterns can be obtained from discontinuous observation (with blind times) of single quantum emitter blinking fluorescence. In this case, the deviation of parameters due to the blind times can be estimated, and with great probability it is reasonably small, even in the case of short time slots: time slot duration < blind time < characteristic blinking times. This deviation has been estimated with the help of numerical simulations. Analytical calculations for the expected deviation (errors) of results from the real value are also possible. The result has also been confirmed with the analysis of an experimental intensity trajectory of a single blinking quantum dot CdSe/ZnS on a glass substrate at room temperature. When blind times are introduced into its trajectory, it leads to nothing more than higher statistical uncertainty. The reasoning presented here can also be applied to the case of pulsed laser spectroscopy of single quantum blinking particles.

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[1] R. W. Lawson, Nature (London) **161**, 154 (1948).
[2] W. Hoeffding, J. Am. Stat. Assoc. **58**, 13 (1963).
[3] E. J. Candès and M. B. Wakin, IEEE Signal Process. **25**, 21 (2008).
[4] M. Abo-Zahhad, S. M. Ahmed, and S. N. Abbas, IEEE Signal Process. Lett. **22**, 876 (2015).
[5] A. Daitche and T. Tel, Phys. Rev. E **79**, 016210 (2009).
[6] E. Barkai, A. V. Naumov, Y. G. Vainer, M. Bauer, and L. Kador, Phys. Rev. Lett. **91**, 075502 (2003).
[7] G. Margolin and E. Barkai, Phys. Rev. Lett. **94**, 080601 (2005).
[8] S. V. Orlov, A. V. Naumov, Y. G. Vainer, and L. Kador, J. Chem. Phys. **137**, 194903 (2012).
[9] R. Verberk, A. M. van Oijen, and M. Orrit, Phys. Rev. B **66**, 233202 (2002).
[10] A. Naumov, I. Y. Eremchev, and A. A. Gorshelev, Eur. Phys. J. D **68**, 348 (2014).
[11] A. V. Naumov, Phys. Usp. **56**, 605 (2013).
[12] C. Kurtsiefer, S. Mayer, P. Zarda, and H. Weinfurter, Phys. Rev. Lett. **85**, 290 (2000).
[13] Y. L. A. Rezus, S. G. Walt, R. Lettow, A. Renn, G. Zumofen, S. Gotzinger, and V. Sandoghdar, Phys. Rev. Lett. **108**, 093601 (2012).
[14] M. Tsutsui, S. Rahong, Y. Iizumi, T. Okazaki, M. Taniguchi, and T. Kawai, Sci. Rep. **1**, 46 (2011).
[15] M. Sauer, Angew. Chem., Int. Ed. Engl. **42**, 1790 (2003).
[16] E. A. Viktorov and T. Erneux, Phys. Rev. E **90**, 052914 (2014).
[17] M. Arcari, I. Sollner, A. Javadi, S. Lindskov Hansen, S. Mahmoodian, J. Liu, H. Thyrrestrup, E. H. Lee, J. D. Song, S. Stobbe, and P. Lodahl, Phys. Rev. Lett. **113**, 093603 (2014).
[18] R. Van Noorden, Nature (London) **514**, 286 (2014).
[19] S. Weisenburger and V. Sandoghdar, Contemp. Phys. **56**, 123 (2015).
[20] J. Schuster, F. Cichos, and C. von Borczyskowski, Opt. Spectrosc. **98**, 712 (2005).
[21] C. von Borczyskowski, F. Cichos, J. Martin, J. Schuster, A. Issac, and J. Brabandt, Eur. Phys. J. Spec. Top. **144**, 13 (2007).
[22] H.-C. Ko, C.-T. Yuan, and J. Tang, Nano Rev. **2**, 5895 (2011).
[23] E. A. Riley, C. M. Hess, and P. J. Reid, Int. J. Mol. Sci. **13**, 12487 (2012).
[24] A. P. Beyler, L. F. Marshall, J. Cui, X. Brokmann, and M. G. Bawendi, Phys. Rev. Lett. **111**, 177401 (2013).

[25] F. Cichos, C. von Borczyskowski, and M. Orrit, Curr. Opin. Colloid Interface Sci. **12**, 272 (2007).

[26] R. Schmidt, C. Krasselt, C. Göhler, and C. von Borczyskowski, ACS Nano **8**, 3506 (2014).

[27] J. Houel, Q. T. Doan, T. Cajgfinger, G. Ledoux, D. Amans, A. Aubert, A. Dominjon, S. Ferriol, R. Barbier, M. Nasilowski, E. Lhuillier, B. Dubertret, C. Dujardin, and F. Kulzer, ACS Nano **9**, 886 (2015).

[28] J. Cui, A. P. Beyler, T. C. Bischof, M. W. B. Wilson, and M. G. Bawendi, Chem. Soc. Rev. **43**, 1287 (2014).

[29] P. Spinicelli, S. Buil, X. Quelin, B. Mahler, B. Dubertret, and J. P. Hermier, Phys. Rev. Lett. **102**, 136801 (2009).

[30] N. Amecke, A. Heber, and F. Cichos, J. Chem. Phys. **140**, 114306 (2014).

[31] Y. He and E. Barkai, J. Chem. Phys. **122**, 184703 (2005).

[32] I. S. Osad'ko, Phys. Usp. **49**, 19 (2006).

[33] I. S. Osad'ko, Opt. Commun. **282**, 927 (2009).

[34] I. S. Osad'ko and V. V. Fedyanin, J. Chem. Phys. **130**, 064904 (2009).

[35] I. S. Osad'ko, A. V. Naumov, I. Y. Eremchev, Y. G. Vainer, and L. Kador, Phys. Rev. A **86**, 053802 (2012).

[36] M. Kuno, D. P. Fromm, H. F. Hamann, A. Gallagher, and D. J. Nesbitt, J. Chem. Phys. **112**, 3117 (2000).

[37] T. A. Anikushina and A. V. Naumov, Laser Phys. **24**, 094001 (2014).