Photon Counting Statistics for Blinking CdSe–ZnS Quantum Dots: A Lévy Walk Process†

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We analyze photon statistics of blinking CdSe–ZnS nanocrystals interacting with a continuous wave laser field, showing that the process is described by a ballistic Lévy walk. In particular, we show that Mandel’s $Q$ parameter, describing the fluctuations of the photon counts, is increasing with time even in the limit of long time. This behavior is in agreement with the theory of Silbey and co-workers (Jung et al. Chem. Phys. 2002, 284, 181), and in contrast to all existing examples where $Q$ approaches a constant, independent of time in the long time limit. We then analyze the distribution of the time averaged intensities, showing that they exhibit a nonergodic behavior, namely, the time averages remain random even in the limit of a long measurement time. In particular, the distribution of occupation times in the on-state compares favorably to a theory of weak ergodicity breaking of blinking nanocrystals. We show how our data analysis yields information on the amplitudes of power-law decaying on and off time distributions, information not available using standard data analysis of on and off time histograms. Photon statistics reveals fluctuations in the intensity of the bright state indicating that it is composed of several states. Photon statistics exhibits a Lévy walk behavior also when an ensemble of 100 dots is investigated, indicating that the strange kinetics can be observed already at the level of small ensembles.

I. Introduction

Statistical properties of light emitted from a single emitter, be it a quantum dot, a molecule, or an atom have attracted much interest since they are used to unravel fluctuation phenomena, which cannot be observed when an ensemble of emitters is under illumination.1,3 In optics, a common method to quantify properties of light sources is through their photon statistics.3,4 In particular, let $n$ be the random number of photons counted within a certain time interval $(0, t)$. Important measures of photon statistics are the average number of counts $\langle n \rangle$ and the Mandel $Q$ parameter

$$Q = \frac{\langle n^2 \rangle - \langle n \rangle^2}{\langle n \rangle} - 1 \quad (1)$$

The Mandel parameter yields the deviations from Poissonian photon statistics found when $Q = 0$. When $Q < 0$, the statistics of photons is called sub-Poissonian, as found when emission events are correlated, in particular resonance fluorescence from a two-level atom.5 While $Q > 0$ is called super-Poissonian, as found when emission events are independent of time. For example, consider a collection of atoms in the process of resonance fluorescence interacting with a continuous wave (cw) laser field. We say that the fluorescence process is normal if the average follows $\langle n \rangle \sim t$ when $t \to \infty$, and the fluctuations obey $\langle n^2 \rangle - \langle n \rangle^2 \sim t$, which means that $Q$ approaches a constant in the limit of long measurement times.

A very different abnormal type of behavior was predicted theoretically by Jung et al.,7 for blinking nanocrystals (also called quantum dots). While interacting with a cw laser, the statistics of photons emitted from a nanocrystal was predicted to behave in an anomalous way, where $Q$ increases with time even in the limit of long measurement time (the meaning of a “long” time is defined later). This prediction was based on a simple stochastic theory and is related to previous observations of the power-law distributions of times in on-states and off-states8–10 (see more details below). Lévy statistics,7 aging,11,12 and nonergodicity of the blinking quantum dots.11,13,14 One goal of this paper is to report on the measurement of the photon statistics of blinking dots, showing that the anomalous behavior of the $Q$ parameter can be observed in experiment. We compare data analyses done based on photon counting statistics and other approaches used in the literature, for example, the commonly used method of on and off time histograms. In particular, we show how to extract data on certain amplitude ratios not available so far. Previously, Schlegel et al.15 and Fisher et al.,16 using single photon measurements, showed that photoluminescence of a single dot fluctuates in time, since the nonradiative decay rate is not a time-independent constant. Here, our analysis of photon statistics confirms that the on-state exhibits fluctuations and hence simple models of a single on bright state and a single off-state do not describe the photon statistics with great accuracy.

We then analyze the nonergodic properties of the quantum dots. Previously, Brokmann et al.11 have pointed out the nonergodicity of blinking dots. Following these observations,
we have developed a stochastic theory of nonergodicity for the dots, in particular we obtained the distribution of time averaged observables, for example, the distribution of the time average intensity correlation function. Here, we compare experiments with our theory. The concept of weak ergodicity breaking, which best describes the dynamics, and its relation to power-law waiting times is not limited to single quantum dots, and it is found in general models of glassy dynamics and the anomalous diffusion of a single particle. We start with an overview on Lévy walks and blinking dots.

II. Lévy Walk Approach to Blinking Nanocrystals

Experiments show interesting fluorescence intermittency for single semiconductor nanocrystals such as CdSe illuminated with a cw laser field. In these experiments, a nanocrystal exhibits blinking behavior; at random times, it switches between a bright state in which it emits many photons and a dark state in which it is in an off-state (see Figure 1). The on (off) times are believed to correspond to a neutral (charged) nanocrystal, respectively. Thus, the switching sequence on-off-on-off-off... corresponds to the sequence neutral-charged-neutral-charged...dot. Briefly, the idea is that, once a charge is located within the dot, the nonradiative Auger process of electron hole recombination is faster than the process of spontaneous emission, a charge within the dot quenches the radiation and the dot is in an off-state.

In contrast to expectation, distributions of on times and off times exhibit power-law statistics. The probability density functions (PDFs) of on and off sojourn times exhibit \( \psi_{\text{on}}(t) \propto A_{\text{on}}^{-1+\alpha_{\text{on}}} \) and \( \psi_{\text{off}}(t) \propto A_{\text{off}}^{-1+\alpha_{\text{off}}} \). In many cases, it is found that \( 0 < \alpha_{\text{on}} < 1 \), \( 0 < \alpha_{\text{off}} < 1 \). For example, in ref 11, 215 nanocrystals were measured and the exponents \( \alpha_{\text{on}} = 0.58 \pm 0.17 \) and \( \alpha_{\text{off}} = 0.48 \pm 0.15 \) were found (note that within error of measurement \( \alpha_{\text{on}} = \alpha_{\text{off}} = \alpha = 1/2 \)). In such a case, the average on and off time is infinite since \( \langle t_{\text{on}} \rangle = \langle t_{\text{off}} \rangle = f^{-1} \). Hence, the process has no finite characteristic time scale, and hence, it exhibits a fractal type of behavior. The power-law distributions of the off times are measured over more than five decades in time and seven decades in the PDF \( \psi_{\text{off}}(t_{\text{off}}) \).

This power law does not depend on the temperature of the system and the radius of the nanocrystals; it appears universal in the sense that for a given sample it is the same for all the quantum dots. Some variations of \( \alpha_{\text{off}} \) and \( \alpha_{\text{on}} \) are found, which seem to depend on the dielectric constant of the environment. However, for nearly all cases, \( \alpha < 1 \). Some deviations from power laws are found for very long times where the PDF of sojourn times decays exponentially in particular for the on times. When the laser intensity is weak and temperature is low, this turnover to exponential statistics is found after extremely long times, if at all. In any case, there exists a long time window where power-law sojourn times are observed. Our time traces exhibit power-law behavior from milliseconds to roughly our total measurement time of 1 h, and during the measurement time, the number of transitions between on and off-states is very large.

Several models for the blinking dots have appeared in the literature: fluctuating barrier models, trap models, deep surface state model, and diffusion controlled reaction models. It is not our aim to survey these models here. We only briefly mention that first passage times for a charge carrier ejected from the dot to the medium (corresponding to an off-state), where the ejected charge is following a random walk (diffusion) in the surrounding medium of the dot, follows a power-law decay (under certain conditions). Similar ideas hold also for the on-state. Thus, several simple models can be used to explain the power-law behavior. Indeed, power-law statistics and intermittency are not limited to single quantum dots. It is also found in single organic molecules, in particular for the on and off times. Several recent experiments using Raman spectroscopy exhibit temporal power-law behavior for organic molecules, while ensemble measurements predict a Lévy type of temporal behavior for the dynamics of green fluorescence protein. Also single molecules in low-temperature glasses exhibit Lévy statistics.

Hence, strange strong non-Markovian kinetics and Lévy statistics in single molecule experiments are widespread.

As mentioned, many measurements of the exponents \( \alpha_{\text{on}} \) and \( \alpha_{\text{off}} \) under different physical conditions are reported in the literature (see ref 29 for a mini-review). In contrast, very little is known on the amplitudes \( A_{\text{on}} \) and \( A_{\text{off}} \). the experiments show that for a given sample the exponents are not sensitive to control parameters, for example, the temperature or the size of the dot. The amplitudes on the other hand are expected to be more sensitive to physical and chemical details of the underlying process. For example, if we assume that a simple picture of diffusion is correct, then the theory predicts that the amplitudes of \( A_{\text{on}} \) and \( A_{\text{off}} \) depend on the diffusion constant of an electron hopping in the vicinity of the dot (in the matrix) among deep traps and on the Onsager radius \( r_{\text{on}} = e^2/ke^2T \) and hence on the temperature. In contrast, the exponent \( \alpha_{\text{on}} = \alpha_{\text{off}} = 1/2 \) is predicted which is independent of physical parameters of the system. Note however that deviations from \( \alpha = 1/2 \) can be explained based on adding a tunneling mechanism of the electron from the matrix to the dot which can explain deviations from the simple diffusion picture and \( \alpha = 1/2 \). Here, we show how measurements can yield the amplitude ratio \( A_{\text{on}}/A_{\text{off}} \). Ideally, we would like to have full information of \( \psi_{\text{on}}(t) \) and \( \psi_{\text{off}}(t) \) including the short time dynamics, however our time traces do not yield short time deviations from power-law behavior. Also note that previously Bianco et al. showed that the underlying process is a renewal process, which means that the correlations between on and off times are either very weak or not existing.

Standard methods for data analysis of statistical properties of blinking quantum dots, and more generally single emitters, are the power spectrum analysis, or using time average correlation functions, or renewal theory, or by photon counting statistics as we consider here. The data analysis of blinking behavior should be made with care, since these systems exhibit nonergodicity. The ensemble averages exhibit aging behavior. The time averages remain random even in the long
time limit. And unlike other single molecule experiments, one cannot reconstruct the ensemble average by performing a long time average, since the time averages are irreproducible. However, the situation is not hopeless, one can construct distributions of the time average, and those according to theory are reproducible. Here, we shall investigate the distribution of the occupation time of the on-state, that is, the total time in the on-state, and show that the process is (a) nonergodic, (b) the distribution is in reasonable agreement with theory, and (c) that such measurements can teach us about the amplitude ratio $A_{\text{off}}/A_{\text{on}}$ of on and off statistics (information not available from other measurements so far).

There are several advantages of photon counting experiments discussed in Section III if compared with the standard on and off time statistics. The on and off sojourn time histogram assumes a two-state process and does not give any information on fluctuations within the on-state. Usually, it is assumed that the dots exhibit a two-state behavior of a single on-state and a single off-state, while here we show that the on-state is fluctuating and one needs more than two states to describe the system in detail. In contrast, the data analysis based on photon statistics does not assume an on and off-state to start with. In addition, the anomalous photon statistics is expected to hold also when an ensemble of dots is investigated. When a few independent dots are investigated, clearly, they do not exhibit a simple on/off two-state process and the on and off times distributions are not useful for that case.

Silbey and co-workers noted that photon statistics of quantum dots should in theory exhibit a Lévy walk behavior. The Lévy walk model is a stochastic random walk model, exhibiting an anomalous diffusion process. Its origin is the stochastic description of tracer motion in a turbulent field. In the simplest version of the Lévy walk, a particle in one dimension has a velocity $+1$ or $-1$. The distribution of times in the states $\pm 1$ follow power-law behavior. In particular, the up and down times are mutually independent, identically distributed random variables with a common PDF $\psi(t)$. If the sojourn times have a first moment, but not a second, then the model exhibits superdiffusion $\langle x^2 \rangle \sim t^\alpha$ with $1 < \alpha < 2$, and if the sojourn time has no first moment, then a ballistic phase is found $\langle x^2 \rangle \sim t^2$. Such nonbiased random walks are not described by Gaussian statistics. Instead, Lévy statistics is the correct central limit theorem behind such processes (see also ref 50 for historical references on physical Lévy processes).

From a stochastic point of view, the resemblance between the Lévy walk model and the dynamics of the blinking nanocrystals is striking. In ref 7, the issue of nonstationarity and a line shape theory, which exhibits nontrivial behaviors, as well as the relation between single particle and ensemble of particle measurements were investigated. However, here, we will consider one prediction of the theory and that is that $Q \sim t$ in the limit of long time. More precisely according to ref 7, if the process is a two-state process with intensity $0$ in the off-state and intensity $I_{\text{on}}$ in the on-state and when $0 < \alpha_{\text{on}} = \alpha_{\text{off}} = \alpha < 1$, we have

$$\langle \tilde{n} \rangle \sim p_{\text{on}} I_{\text{on}} t$$

where $I_{\text{on}}$ has units counts per second and $p_{\text{on/off}} = A_{\text{on/off}}/(A_{\text{on}} + A_{\text{off}})$. The overbar $\cdots$ is an average with respect to shot noise, and the averages $\langle \cdots \rangle$ are ensemble averages over the random blinking process. The fluctuations are ballistic in the long time limit

$$\langle \tilde{n}^2 \rangle - \langle \tilde{n} \rangle^2 \sim (1 - \alpha)p_{\text{on}} p_{\text{off}} (I_{\text{off}})^2$$

and hence $Q \sim t$, increasing linearly with time. For $1 < \alpha < 2$, one finds $Q \sim t^{2 - \alpha}$ while when $\alpha > 2$, namely, when the first two moments of the on and off times are finite, $Q \sim t^{\alpha}$ which is the normal behavior. Since $Q \sim t$ when $\alpha < 1$, fluctuations of light emitted from the nanocrystals are very large.

This ballistic behavior can be roughly explained by noting that the case when the average on and off time is infinite corresponds to the case where the dots have one very large on or off time which is of the order of the measurement time, no matter how long this measurement time is. It is noted, however, that in a single time trace many transitions between on and off occur, but for the sake of discussion, we can neglect all the short on and off times and consider only the biggest on or the biggest off time in each time trace (choose the bigger of the two). Then consider ensemble of dots where either the dot is on all the time (say with probability $1/2$) or they are off all the time. Then it is easy to show that $\langle n \rangle = I_{\text{off}}/2$ and $\langle n^2 \rangle = \langle n \rangle^2 + I_{\text{off}}^2/4$, which is ballistic behavior. This simple argument does not give the correct prefactors, but it indicates that the longest on or off times dominate the landscape of the blinking dot and are responsible for the particular statistics observed in experiments. Such a simple argument becomes exact only when $\alpha \to 0$.

### III. Photon Statistics

In this paper, we analyze experimental data and make comparisons with theory. Data were obtained for 100 CdSe–ZnS core–shell nanocrystals at room temperature. A typical fluorescence intensity trace of a single quantum dot is shown in Figure 1, and a histogram of the intensity values of this trace is shown in Figure 2. We first performed data analysis (similar to the standard approach) based on distributions of on and off times and found that $\alpha_{\text{on}} = 0.735 \pm 0.167$ and $\alpha_{\text{off}} = 0.770 \pm 0.106$ for the total duration time $t = T = 3600$ s (bin size 10 ms). We chose the threshold of 0.16 max $I(t)$ for each trajectory to separate between on (above the threshold) and off (below the threshold) states. Within the error of the measurement, $\alpha_{\text{on}} \approx \alpha_{\text{off}} = \alpha \approx 0.75$. The exponent $\alpha \approx 0.5$ found previously is different from ours, due to the different type of environment in which our dots are embedded. In refs 11 and 10, the dots are embedded in PMMA while ours were not. An important issue is whether the exponents vary from one nanocrystal to another. We found that the experimental data is compatible with the assumption that all dots are statistically identical (in our sample) in the sense that fluctuations in $\alpha$ from dot to dot are small in agreement with refs 11 and 23. However, as shown in Figure 2, the intensity histogram of each dot can vary from one dot to the other.

Using eq 1, we calculated the Mandel parameter via three different approaches, soon to be discussed in detail. These results are presented in Figure 3. For the three methods, the data clearly
and $R$ up to 1 h that this ratio lies roughly between 0.5 and 0.8.

Figure 3. Dependence of Mandel’s $Q$ parameter on the duration $t$ of the interval for photon counting. Three different methods are used, as discussed in the text. The thick dashed line illustrates the linear dependence $(Q + 1) \propto t$. For short $t$, all of the methods show such a linear dependence, while there are some deviations as $t$ increases.

shows that $Q \sim t$ which means that the process is a ballistic Lévy walk. The time of the experiment is long in the sense that we observe many transitions between state on and off in our measurement time.

In the first method, we found the number $n$ of photons counted during time interval $[0, t]$ for each dot, where 0 is the time of the start of the experiment for a given dot, giving us 100 values which were averaged for eq 1. Equation 3 is valid for this case only if the process under investigation is a two-state process, namely, when (a) all dots are statistically identical, no fluctuations of intensity of the on-state between members of an ensemble of dots, and (b) the intensity of the on-state is not changing in time (beyond the shot noise). While direct observation of individual dots and an ensemble of dots shows some variations between dots (e.g., distribution of intensities in the on-state is not identical for all dots), still the Lévy scaling $Q \sim t$ holds, as seen in Figure 3.

In the second method, the whole 1 h intensity trace of each dot is split into intervals of length $t$ and $n$ is obtained for each interval. Now $Q$ can be calculated for each dot separately, and in Figure 3, we plot the arithmetic average of $Q$ among all the dots. In this method, the calculation from a single trajectory is essentially the same as that done typically for ergodic signals.

Finally, the third method is similar to the second one, but we start by adding up the number of photons from all the dots together, as if they were simultaneously fluorescing and we were measuring the photons arriving from the ensemble. In this way, we have one intensity trace from all the dots and we calculate $Q$ for it exactly as we calculated $Q$ for each dot.

Assuming a two-state model is valid, and using eqs 2 and 3

$$\frac{\langle n^2 \rangle}{\langle n \rangle^2} - 1 \sim (1 - \alpha) \frac{P_{\text{off}}}{P_{\text{on}}} = (1 - \alpha) \frac{A_{\text{off}}}{A_{\text{on}}}$$

in the limit of long times (i.e., when $\langle n \rangle$ is large). We calculated this ratio using the first method and found for long times $t > 20$ s up to 1 h that this ratio lies roughly between 0.5 and 0.8. And so for large enough $t$ we could estimate, based on eq 4 and $\alpha$ between 0.75 and 0.8, that $A_{\text{off}}/A_{\text{on}} \sim 3 \pm 1$. At shorter times, the ratio decreased gradually from its maximal value of $\approx 1.67$ (at $t = 0.01$ s). However, short times $t < 20$ s are less reliable because only a small number of photons is emitted/counted during them, and it is thus hard to produce a Lévy type statistic. Also, the assumption of a simple two-state process and hence the applicability of eqs 2 and 3 should be kept in mind.

IV. Occupation Times in the On-state

In ref 13, we investigated the distribution of time averaged intensity correlation functions of blinking nanocrystals, using a Lévy walk model. We showed that time averages are not identical to ensemble averages, however distributions of time averaged correlation functions are universal. Here, we analyze our experimental data in particular the distribution of the fraction of time spent in the on-state, namely, $T_{\text{on}}/T$ where $T_{\text{on}}$ is the total time in the on-state and $T$ is the total measurement time. For a two-state process, where the intensity is either $I_{\text{on}}$ or 0, the fraction of time in the on-state is proportional to the time average intensity.

Here, we show that the occupation fraction $T_{\text{on}}/T$ is random even in the limit of long times, indicating ergodicity breaking. The ergodicity breaking is related to the divergence of the mean on and off sojourn times. Ergodicity breaking means that time averages and ensemble averages are not the same even in the limit of long measurement time. For the blinking dots and in the absence of a finite time scale to the process, we can never make time averages long enough, in such a way that time and ensemble averages become identical. More mathematically, one can show that the PDF of the occupation fraction is the Lamperti PDF, which is related to the arcsine law. For stochastic processes with finite on and off times, one finds ordinary Gaussian statistics and ergodicity. Deviations from ergodicity and nontrivial occupation time statistics are the subject of several works, for example, in the context of random walks in random environments, fractional calculus, and the continuous time random walk.

We tested our nonergodic theory and calculated distribution of relative on times $T_{\text{on}}/T$, that is, of the ratios of the total time in the on-state to the total measurement time. We also performed numerical simulations using $\psi_{\text{on}}(T) = \psi_{\text{off}}(T) = \psi(T) = \alpha^{-1} + \alpha^{-1}$ for $\alpha = 0.8$ and binned the signals into the same number of bins as for the experimental trajectories. Experimental and simulated distributions shown in Figure 4 are, overall, in good agreement. Two important conclusions are derived from these distributions of relative on times. First, the data clearly exhibits ergodicity breaking: distribution of relative on times is not delta peaked, instead it is wide in the interval between 0 and 1, for different $T$ values. The second important conclusion is that, for a reasonably chosen threshold (cf. Figure 1), the experimental data is compatible with the assumption

$$\psi_{\text{on}}(T) \approx \psi_{\text{off}}(T)$$

at least for a wide time window relevant to the experiments. In other words, not only $\alpha_{\text{off}} \approx \alpha_{\text{on}}$ (ignoring the cutoffs) but also $A_{\text{on}} \approx A_{\text{off}}$. The observation that $A_{\text{on}} \approx A_{\text{off}}$ cannot be obtained directly from the on and off sojourn time histograms because if only power-law tails are seen these histograms cannot be normalized. To see that in our case $A_{\text{on}} \approx A_{\text{off}}$ note that the distributions of relative on times are roughly symmetric with respect to the median value of $1/2$ (cf. Figure 4), and the ensemble average of relative on times is also close to $1/2$, while in general the ensemble average in our model process is given by $A_{\text{off}}/(A_{\text{on}} + A_{\text{off}})$. In addition, the variance of the experimental
distributions for different $T$ is close to the variance of the Lamperti distribution $(1 - \alpha)/4$ (cf. refs 13 and 14 and eq 3) for $\alpha \approx 0.8$. There are a few comments to make. First, 100 trajectories are insufficient to produce accurate histograms, as can be seen from the right side of Figure 4: ideally, these histograms should be identical for different $T$ and given by the Lamperti distribution (e.g., see refs 14 and 29). Second, there is an effect due to the signal discretization, leading to a flatter and wider histogram at $T = 36$ s. Third, there is a certain slow narrowing of the experimental histogram as $T$ increases and the average relative on time slowly decreases. Both of these trends are probably due to cutoffs in the power-law distributions, especially for the on times.\textsuperscript{10,24,29} These trends slightly depend on the choice of the threshold separating on and off-states. In Appendix A, we address the effect of the binning on measured sojourn times.

In section III, we found $A_{\text{off}}/A_{\text{on}} \sim 3$ while here in section IV we find $A_{\text{off}}/A_{\text{on}} \sim 1$. There is no conflict between these results. In section III, we used the assumption that the process is a simple two-state process. The fact that the two results are not in agreement indicates that the process is not exactly an ideal two-state process, as can be seen in Figure 2. Thus, to model fluctuations of the number of photons, one must consider also fluctuations within the on-state. Or in other words, the on-state is composed of several states (not necessarily discrete states). Even so, the fact that the $Q$ parameter is increasing with time even in the limit of long times indicates that the process is a ballistic Lévy walk, though not a simple two-state ballistic Lévy walk.

Quite surprisingly, we find that $A_{\text{off}}$ and $A_{\text{on}}$ are of the same order of magnitude and are roughly equal. Is this a coincidence? Or perhaps it is somehow the artifact of our data analysis, for example, the selection of the threshold? We made the analysis with different thresholds, and unless the choice was completely unreasonable (very low or very high), the conclusions remained practically unaltered. So one possibility is that it is a coincidence. To check this, more experiments on different types of dots and molecules should be carried out, in particular varying the intensity of the laser and temperature. Note however that if $A_{\text{off}}$ was either much larger or much smaller than $A_{\text{on}}$ we would see either almost no emission or almost no interruption in emission of an individual dot, with high probability. So maybe this

Figure 4. Histograms of occupation fraction of on times $T_{\text{on}}/T$ for 100 experimental (left) and 100 simulated (right) intensity trajectories, for different measurement times $T$. The figure illustrates ergodicity breaking, since the occupation fraction remains random and is not equal to its ensemble average. The simulations indicate that a model without any quenched disorder yields the ergodicity breaking. The ergodicity breaking is due to the temporal power-law dynamics not to variations between different dots. The noise in the figure is due to finite sampling.
V. Summary

We showed that the blinking quantum dots exhibit anomalous photon statistics, and ballistic Lévy scaling, with \( Q \sim t \). As far as we know, this is the first measurement of a ballistic Lévy walk and of a Mandel parameter which is increasing with time. This behavior is found for large times, namely, for the times where we have many transitions between the on-state and the off-state and \( \langle n \rangle \gg 1 \). The anomalous behavior was also found after we averaged over an ensemble of 100 dots. Hence, in principle, one may use photon statistics from not a too large ensemble of dots and detect the strange kinetics indirectly already on the level of an ensemble. This is important since not all emitters can be detected on the single particle level and maybe our methods can be used to unravel strange kinetics in other systems.

Occupation times in the on-states remain random even in the limit of long times, indicating ergodicity breaking. From statistics of occupation times, an interesting symmetry was found \( \psi_{\text{on}}(t) \approx \psi_{\text{off}}(t) \), namely, the amplitude ratio \( A_{\text{on}}/A_{\text{off}} \approx 1 \), at least within our measurement time (for longer times, the on-state PDF exhibits exponential cutoff\(^{10}\)). This finding could be very specific for our sample. It should be checked further by varying control parameters such as the temperature and the laser intensity. However, if confirmed on other systems, it indicates that the on and off-states are controlled by exactly the same process, which is rather surprising. Shimizu et al.\(^{10}\) suggested that the tunneling of an electron from the dot to the matrix and back (i.e., transition from on-state to off-state and vice versa) can happen only when a certain fluctuating energy level reaches a certain value. In this model, we can expect that \( \psi_{\text{off}}(t) \approx \psi_{\text{on}}(t) \), however the model assumes a simple random walk in energy space and the exponent \( \alpha = 1/2 \) while we and others have found deviations from this law.

Our data analysis shows that a simple two-state model of a single bright state (with a fixed intensity) and a single dark state is not sufficient to describe the photon counting statistics with reasonable accuracy. In particular, we showed that assuming a two-state process leads to a mistake of a factor of 3, which we consider a large mistake. The fact that the process is not a simple two-state process can be qualitatively observed directly on the individual quantum dot level as shown in the histograms of the intensity; see Figure 2. Here, our results show that the deviations from a simple two-state picture are actually important for the correct determination of the photon statistics, thus the deviations are important for quantitative statistical analysis.

The fact that photon statistics reveals fluctuations in the on-state indicates that the on-state is composed of several states. Verberk et al.\(^{26}\) suggested that such states may exist and called them gray states.\(^{22}\) Most likely, changes in the vicinity of the dots can be found in several states (e.g., in several traps), and the intensity of the dot in its on-state fluctuates according to the state of these charges. This in turn both controls the single photon experiments,\(^{15,16,60}\) which give the photoluminescence decays on the nanosecond time scale, and controls the photon counting statistic, recorded here on a much longer time scale (e.g., 1 h). Finally, the nonergodicity, and Lévy statistics used for the analysis of the blinking dots, should apply also to other single molecule systems which exhibit power-law kinetics.

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Appendix A. How Does Re-binning Influence the On and Off Times Distributions?

We consider an ideal signal switching between the on-state +1 and the off-state 0, with sojourn times in on and off-states being mutually independent identically distributed random variables. The signal intensity is binned and then using certain threshold is converted again to a two-state signal. When the on and off times are distributed with \( \psi_{\pm} \propto t^{-1-\alpha}, \) \( 0 < \alpha < 1 \) for long \( t \), the total length of all short intervals (shorter than the bin size \( t_b \)) together becomes negligible compared with the signal length \( T \), when \( T \) is large.\(^6\) When the binning procedure is performed, these short intervals become unresolved, but because their total length is negligible, we approximate these intervals as each having zero duration in the example below. For the same reason, we note the average on and off intensity values will remain almost unchanged after the binning, if they are measured in counts per time (i.e., the signal trace stays almost the same, apart from small-scale details).

Example: Let the original signal be generated using

\[
\psi_{\pm}(t) = \begin{cases} 
0 & t < t_0 \\
\alpha t_0^{-\alpha} & t \geq t_0
\end{cases}
\]

where \( t_0 > 0 \) and

\[
\psi_{\pm}(t) = (1 - \gamma)\delta(t - 0) + \gamma \psi_{\pm}(t)
\]

where \( 0 \leq \gamma \leq 1 \), for on and off-states, respectively. In Laplace space, for small \( u (u \to 0) \), \( \hat{\psi}_{\pm}(u) \sim 1 - \frac{A_{\pm}u^\alpha}{\gamma} \) and it is clear that \( A_{-} = \gamma A_{+} \), so that the ensemble averaged intensity will be

\[
\langle I \rangle = \frac{A_{+}}{A_{+} + A_{-}} = \frac{1}{1 + \gamma}
\]

We now bin this original signal with some \( t_b \) values: \( 0 < t_b \ll t_0 \). What then will be the effective on and off interval (sojourn time) distributions?

When we bin the signal, all the zero-size intervals (which occur only in the off-state) are omitted and neighboring on intervals are merged into one. All other off intervals are preserved. Therefore

\[
\psi_{\pm}^{\text{eff}}(t) = \psi_{\pm}(t) \rightarrow A_{\pm}^{\text{eff}} = A_{\pm}
\]

For \( \psi_{+}^{\text{eff}}(t) \), we obtain

\[
\hat{\psi}_{+}^{\text{eff}}(u) = \gamma \hat{\psi}_{+}(u)[1 + (1 - \gamma)\hat{\psi}_{+}(u) + (1 - \gamma)^2\hat{\psi}_{-}^{2}(u) + \cdots] = \frac{\gamma \hat{\psi}_{+}(u)}{1 - (1 - \gamma)\hat{\psi}_{+}(u)}
\]

Using asymptotic expansion for small \( u \) yields

\[
\hat{\psi}_{+}^{\text{eff}}(u) \sim 1 - \frac{A_{+}}{\gamma}u^\alpha \rightarrow A_{+}^{\text{eff}} = \frac{A_{+}}{\gamma}
\]

and also it is clear that \( \psi_{+}^{\text{eff}}(t) \propto t^{-1-\alpha} \) with the same exponent \( \alpha \). The ensemble averaged intensity for the binned signal will therefore be
(22) A slightly more general approach to blinking, also based on a charging mechanism, was suggested for capped dots in ref 26.
(51) See refs 24, 25, and 52 for more on the relation between the emission of a single dot and ensemble of dots.
(53) Core radius 2.7 nm with less than 10% dispersion, 3 monolayers of ZnS, covered by mixture of TOPO, TOP, and TDPA. Quantum dots were spin coated on a flavad fused silica substrate. CW excitation at 488 nm of Ar+ laser was used, excitation intensity in the focus of oil immersion objective (NA = 1.45) was ~600 W/cm².
(54) The standard deviation figure for αopt, here represent the standard deviations of the distributions of the corresponding exponents and not the errors in determination of their mean value. We also note that the on time distributions are less close to the power-law decays than the off times, partly due to the exponential cutoffs and partly due to varying occupations in the on-state (cf. Figure 1).
(60) After our work was completed, a recent study investigated the continuous distribution of emission states from single nanocrystals. Zhang, K.; Chang, H.; Fu, A.; Alivisatos, A. P.; Yang, H. Nano Lett. 2006, 6, 843.
(61) This can be seen as follows: consider only one state with ψ(t) ≈ t⁻¹/α. Then the average length of the interval τa is given by (δa) = ∫ t⁻α+1 dt/∞ (ψ(t))d(t) ∝ t⁻α/α. If b is large enough such that at times t > b and the scaling ψ(t) ≈ t⁻α/α is already present. The average number of jumps (sojourn intervals) during the time T is known to be in Laplace space (u → T) φ(u) = [(1 - ψ(u)/)u]∫ ⋁ T 1 nφ(u) = ψ(u)/a(1 - ψ(u)), and for small u (larger T), we have ψ(u) ~ 1 - Aα leading to (φ(u) ~ 1 - Aα
$1/(\lambda d t^{\lambda+1})$ or in time domain $\langle n \rangle (T) = T^\lambda$. Therefore, the ratio of the total length of all short intervals to the total time $T$ will scale as (most of the intervals are short, because $\int_0^\infty \psi(t) \, dt \sim 1$ for large enough $t_b$) $\langle \langle n \rangle (T) - \langle n \rangle (T_{\text{short}}) \rangle \rangle T \approx (t_b/T)^{\lambda-\eta}$, which goes to zero as $t_b/T$ decreases.

(62) The observed fluctuations in the on-state intensity of a single dot cannot be accounted for by a combination of background noise, shot noise, and the binning. Indeed, the background noise, which is the same for both on and off-states, is relatively small and lies more or less within one bin in the histograms of Figure 2. The shot noise is due to Poisson statistics of photon emission, and its standard deviation is the square root of the emission mean. With the emission intensity mean in the on-state of the order of 100 photons per bin or more (cf. Figure 2), the shot noise is not wide, relative to the mean. Note that in fact not all the emitted photons are counted, and if the detection efficiency is roughly constant, then the effect of the shot noise is even weaker. Finally, if the intensity trace is dominated by the power-law distributed on and off intervals, then there should be only a small minority of bins inside which state switches, which could produce any averaged intensity value for such a bin, occur.