Characterizing Quantum-Dot Blinking Using Noise Power Spectra

Matthew Pelton, David G. Grier, and Philippe Guyot-Sionnest
James Franck Institute, University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637
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Fluctuations in the fluorescence from macroscopic ensembles of colloidal semiconductor quantum dots have the spectral form of 1/f noise. The measured power spectral density reflects the known fluorescence intermittency of individual dots with power-law distributions of “on” and “off” times, and can thus serve as a simple method for characterizing such blinking behavior.

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Semiconductor nanocrystals, or quantum dots (QDs), are valued for their unique optical properties. They can exhibit bright, long-lived fluorescence, with an emission wavelength that is simply tuned by changing the size of the nanocrystal. This property makes them promising, for example, as biological labels, and as the active medium in light-emitting diodes or lasers. However, such applications may be compromised by large-amplitude fluctuations in the intensity of the QD fluorescence. Optical microscopy of immobilized QDs has shown a noisy blinking behavior, with the dots alternating between “on” (fluorescing) and “off” (non-fluorescing) states. Although results from different groups show some differences, many measurements under different conditions have shown similar power-law distributions for on and off periods. For a particular nanocrystal system and a particular experiment, the blinking statistics are robust, and are independent of the particular nanocrystal being observed. While previous studies have focussed on single QDs, this Letter shows that complementary information on the statistics of fluorescence fluctuations is provided by measurements on macroscopic ensembles of QDs, allowing a new perspective on the phenomenon of QD blinking.

In particular, we measured the power spectral density of fluctuations in the fluorescence from QD ensembles. Such noise spectra are commonly used to obtain statistical information about a wide variety of systems. Applying this technique to QDs shows that the QD fluorescence fluctuations have the form of 1/f noise. The ensemble 1/f noise can be understood as the incoherent sum of the noise spectra of individual QDs, all of which exhibit identical 1/f-type noise. The ensemble noise measurements thus provide a simple, rapid technique to obtain information about the blinking statistics of individual QDs. It can be applied to a wide range of environments, including those not previously accessible to experiment.

Our ensemble noise measurements were made on monodisperse CdSe QDs, prepared using established methods, with a fluorescence maximum around a wavelength of 610 nm. We investigated both bare CdSe nanocrystals and nanocrystals capped with ZnS shells; our results were essentially identical for both types. The noise measurements were made by exciting the QDs with a diode-pumped, frequency-doubled Nd:YVO$_4$ laser, which has a stable output at a wavelength of 532 nm. The fluorescence was collected perpendicular to the excitation beam using an optical fiber bundle. The emission was then sent through a dichroic mirror, to eliminate scattered laser light, and was detected with a silicon photodiode. The photodiode output was sent to a low-noise amplifier, whose input incorporates a high-pass filter with a cut-on at 1 Hz; this eliminates the dots’ mean fluorescence, so that only small-signal fluctuations are amplified. The amplified output was sent to a digital signal analyzer, which calculated the associated power spectral density. The digitally sampled time series were analyzed in blocks of 1600 points; 250 blocks were combined using RMS averaging to give the averaged time series $I(t)$. The power spectral density was then calculated as $S(f) = |\mathcal{F}\{i(t)\}|^2$, where $\mathcal{F}$ represents the Fourier transform, and $i(t) = I(t) - \langle I \rangle$ is the instantaneous deviation of the intensity from the mean $\langle I \rangle$.

We recorded power spectra between frequencies of 200 Hz and 3 kHz. At lower frequencies, fluorescence fluctuations are overwhelmed by noise in the excitation laser, while, at higher frequencies, they are overwhelmed by noise in the detection apparatus (photodiode, amplifier, and signal analyzer). By varying the incident laser power, we verified that the measured power spectral density is proportional to the excitation power. This means that fluctuations in the laser power at a particular frequency will result in fluctuations in the fluorescence intensity at the same frequency. In order to remove these effects, which do not reflect the blinking dynamics of the QDs, we divided the power spectrum of the dots by the measured power spectrum of the laser.

For the first measurements, we deposited QDs in a dense layer on a glass slide, providing an environment similar to that experienced by dots in microscopy experiments. The measured noise spectrum is shown in Fig. I and can be seen to have the form of 1/f noise over the experimentally accessible bandwidth. More specifically, it can be fitted using a relationship of the form $S(f) = Af^{\nu - 2} + B$, where $f$ is the frequency, $A$ is an arbitrary proportionality constant, $B$ is an additive offset representing the instrumental noise floor, and $\nu$ is the fitted spectral exponent characterizing the noise-generating
process. In this case, \( \nu = 0.70 \pm 0.02 \).

1/f noise spectra arise in a wide array of systems, including conductance fluctuations of metals and semiconductors, magnetization of spin glasses, financial time series, and biological ion channels. They are qualitatively different from the spectrum obtained for simple molecular systems, as we confirmed by measuring the power spectrum of an ensemble of polystyrene microspheres doped with a green fluorescent dye (Duke Scientific, part number G300). This noise spectrum, shown in Fig. 1, can be fit using a single Lorentzian \( S(f) = A/(f^2 + f_0^2) + B \), with a width \( f_0 = 1.8 \) kHz. The Lorentzian noise spectrum can easily be understood as the result of a fluctuation process with a single, characteristic time scale; in this case, it may reflect shelving in a dark triplet state. The difference between this spectrum and the QD spectrum verifies that the measured 1/f-type power spectrum is characteristic of the QDs.

The ability to characterize the statistics of fluorescence fluctuations in the ensemble means that immobilization of the QDs is not necessary. We therefore made a second measurement, for which we dissolved an ensemble of QDs in chloroform. We illuminated a large volume \( \mathcal{O}(1) \) mm\(^3\), so that the variation in observed particle number due to diffusion was negligible. The measured spectrum is shown in Fig. 1 and can be seen to have the same form as the spectrum of dots on glass, with an equivalent fitted exponent of \( \nu = 0.75 \pm 0.03 \). The observed insensitivity of the blinking statistics to the QD environment is surprising, in the light of currently proposed blinking mechanisms.

Although no unified model of 1/f noise exists, it is often attributed to the collective effect of a broad distribution of independent processes with different characteristic times. 1/f noise in QD fluorescence fluctuations, by contrast, appears to be an intrinsic property of the individual dots. This distinction can be made clear by considering how individual QD spectra contribute to our measurements. By the Wiener-Khinchin theorem, the power spectral density is equal to the Fourier transform of the intensity autocorrelation function. Since the total intensity emitted by an ensemble of dots is the sum of the intensities \( i_n(t) \) emitted by the individual dots, the autocorrelation function of the total emission is

\[
G^{(2)}(\tau) = \sum_n \langle i_n(t) i_n(t+\tau) \rangle + \sum_{m \neq n} \langle i_m(t) i_n(t+\tau) \rangle, \quad (1)
\]

where angle brackets indicate averages over time \( t \). The second term describes cross-correlations of fluctuations from different QDs, and vanishes if they fluctuate independently. In this case, all that remains is the sum of the autocorrelation functions for the individual QDs. These autocorrelations are equal to the Fourier transforms of the individual QD power spectra, so the power spectrum of the total intensity is simply the sum of the single-dot spectra. If all dots fluctuate with the same statistics, then this spectrum also provides insights into the mechanism of single-dot fluorescence intermittency.

This was confirmed by monitoring the fluorescence from single QDs, and combining their emission numerically in order to obtain the corresponding ensemble behavior. A sparse layer of dots with emission maxima around a wavelength of 535 nm was deposited on a glass microscope coverslip. The dots were excited from the opposite side of the coverslip, through an oil-immersion microscope objective, using light with a wavelength of 480 ± 40 nm. Light emitted from the QDs was collected through the same objective, separated from the excitation light using a dichroic mirror, and isolated using a bandpass filter with a center wavelength of 535 nm and a bandwidth of 30 nm. The light was imaged onto a cooled CCD camera, and the intensities from particular QDs were monitored over approximately 13 minutes, with a time resolution of 25 ms.

Time traces for two specific QDs are shown in Fig. 2(a) and (b). Power spectral densities were calculated from these time traces, after subtracting the mean values and multiplying by the Hann window function \( W(t) = \sin^2(\pi t/T) \), where \( T \) is the total duration of the data set. Resulting spectra are shown in Fig. 2(c); they can be seen to have the same 1/f type form as the ensemble power spectra. Fitting the two sample single-dot spectra to an inverse power law over the entire bandwidth of the measurement yields \( \nu = 0.71 \) and \( \nu = 0.83 \), respectively. Comparable results were obtained for all 20 QDs studied.

FIG. 1: Power spectral densities of fluctuations in the fluorescence from macroscopic ensembles of quantum dots, deposited on a glass slide and dissolved in chloroform, and from fluorescently dyed polystyrene beads. The spectra have been offset by arbitrary scale factors for clarity. Thick lines are fits to the power spectra; the dot spectra are fit to power laws, while the dye spectrum is fit to a Lorentzian.
Figure 2: (a), (b): Fluorescence intensity from two individual quantum dots as a function of time. (c): Log-log plot of the power spectral densities calculated from the above time traces (circles), together with power-law fits (solid lines). The two power spectra are offset by arbitrary scale factors for clarity. Also shown is the power spectral density calculated from the sum of 20 single-dot time series (squares). Calculated power spectral densities have been grouped in logarithmic frequency bins.

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with a mean value of $\nu = 0.74 \pm 0.09$. This exponent is indeed the same as that obtained for the QD ensembles.

Further confirmation that the ensemble measurement reflects single-dot statistics is provided by adding together the measured time traces from the individual QDs point by point, and calculating the power spectrum from the time trace of the sum (shown in Fig. 2(c)). The fitted exponent is $\nu = 0.69 \pm 0.03$, in agreement with the average exponent for the individual QD spectra. This is different from the case of electronic $1/f$ noise, for instance, where the ensemble spectrum is an average of individual fluctuators that each display very different dynamics. In our case, the ensemble measurements can provide direct information about the fluctuation statistics of individual QDs.

Ensemble power spectra thus provide a useful tool to complement characterization techniques based on single-dot measurements. In particular, our power spectra are consistent with previously reported distributions of on and off periods for individual QDs. The probability density functions of blinking periods $T_{\text{on/off}}$ have been observed to follow an inverse power law $\Psi(T_{\text{on/off}}) \propto (T_{\text{on/off}})^{-1-\nu}$. Power-law distributions of this type, where $\nu$ lies between zero and one, can be converted into power spectra using the mathematical tools devised to describe Lévy walks. Specifically, we impose lower and upper cutoff durations $T_{\text{min}}$ and $T_{\text{max}}$, respectively, and assume that the probability density falls abruptly to zero outside these limits. Experimentally, $T_{\text{min}}$ can be associated with the measurement time resolution, and $T_{\text{max}}$ with the total duration of the measurement. We ignore any intensity fluctuations within the on and off states, treating the intensity as if it switches discretely between zero and a value $I_o$. If we assume, for simplicity, that the same exponent $\nu$ can be used to describe on and off times, then the time series has a power spectral density $S(f) \propto (1/(\langle T \rangle))^{2-\nu}$, where $\langle T \rangle$ is the mean on/off duration. The cutoff times $T_{\text{min}}$ and $T_{\text{max}}$ enter only through an additional proportionality constant, so the form of the power spectrum is independent of the details of the measurement. The value of $\nu$ that we have obtained from the power spectrum is consistent with the exponents previously obtained by different researchers from probability distributions of bright and dark times. Since previous measurements of blinking-time distributions have covered the bandwidths of both our measurements, we can assume that the power spectra we have measured for QD ensembles reflect the same underlying statistics as the individual QD spectra.

Similar results would be obtained if the on and off durations followed different probability distributions. For example, if they followed power laws with different exponents, the larger value of $\nu$ would dominate the power spectrum; similarly, if one distribution followed an exponential distribution while the other followed a power law, the power spectrum would still be a power law. In other words, power spectral densities cannot separately characterize on and off blinking statistics. On the other hand, they can be measured on ensembles, allowing easy characterization in just a few minutes. Even for measurements on single QDs, unambiguous power spectra can be calculated using well-established methods. By contrast, extracting the distribution of blinking periods from the time series is less straightforward. For example, even while the QD is emitting light, its fluorescence intensity can still vary substantially, making it difficult to establish a clear threshold between the on and off states. As well, blinking events shorter than the time resolution of the measurement will be missed, biasing the probability density function towards longer times; this artifact cannot be corrected without making an assumption about the distribution of blinking periods below the time resolution.

Another complementary method of characterizing QD fluorescence dynamics is to measure the autocorrelation of emitted photons; this allows a wide range of time scales to be covered. Fluorescence correlation spectroscopy (FCS), a particular type of autocorrelation technique, has been used to study the fluorescence of QDs in solution. In these measurements, a microscopic volume of a solution containing QDs is illuminated, and the autocorrelation function of the detected fluorescence is measured as dots diffuse through the illuminated region. The authors of Ref. were able to fit their results with a model...
based only on single-particle diffusion, with no systematic deviation that would need to be explained by blinking. Their results can be reconciled with ours by considering how blinking affects the autocorrelation function. The Lévy-walk model yields $G^{(2)}(\tau) = A - B\tau^{1-\nu} / (T)$, where $A = 1 - (\nu / (1 - \nu))(T_{\text{min}} / (T))$, and $B = T_{\text{min}} / (1 - \nu)$. This expression describes a correlation function that is weakly dependent on delay time $\tau$ for short $\tau$, and abruptly drops to zero as $\tau$ approaches the total measurement time $T_{\text{max}}$. The effects of diffusion in FCS can be approximated by multiplying the above autocorrelation function with one describing diffusion $G^{(2)}$, taking $T_{\text{max}}$ to be the mean diffusion time through the illuminated volume. Since blinking gives a nearly flat correlation function for times shorter than the diffusion time, the combination is nearly indistinguishable from diffusion alone. By contrast, the power spectral density has the advantage of clearly distinguishing blinking from diffusion, and is insensitive to measurement parameters such as the time resolution and the total measurement time. Other ensemble measurement techniques can also provide information on fluorescence fluctuations. For example, the reversible decay in the fluorescence signal from an ensemble of QDs has been shown to have a purely statistical origin.

We have found that it is particularly practical to study the dynamics of QD blinking by measuring the power spectral density of fluorescence fluctuations. The results are free from the ambiguities inherent in measurements based on blinking time distributions and autocorrelation functions. Representative power spectra can be measured on ensembles of dots, contrary to the popular wisdom that blinking studies require isolation of single emitters. This means that blinking can be observed in cases where microscopy is impractical, such as QDs in solution. Using lower-noise components, it should be straightforward to extend the measurement bandwidth beyond that obtained in this first experiment. Since the ensemble power spectrum can be measured very quickly, it will be possible to rapidly characterize the blinking behavior of different samples in different environments, eventually leading to a better understanding of and control over the blinking mechanism. Finally, we have used the same measurement technique to observe the fluorescence dynamics of fluorescent microspheres; indeed, the method we have introduced should be applicable to any fluorophore that exhibits blinking within the observable bandwidth.

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* Electronic address: pelton@uchicago.edu

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