

# Spectral Fluctuations of Single Ag-In-Zn-S Quantum Dots

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## Introduction

Colloidal nanocrystals (NCs) are a promising class of materials when it comes to the search for cheap and efficient light sources. However, in this regard, environmentally safer I-III-VI group ternary quantum dots (QDs), such as AgInS<sub>2</sub> or CuInS<sub>2</sub>, or quaternary alloys like Ag-In-Zn-S, have not been studied as much as toxic Cd- and Pb- chalcogenides. Importantly, the emission mechanism of the former class of materials is still debated in the NC community. In this work, in order to shed light on the photoluminescence (PL) mechanism, we study time-dependent spectral properties of single Ag-In-Zn-S QDs. Our results imply that the light emission in these QDs occurs as a result of a recombination of a delocalized electron and a localized hole (a free-to-bound mechanism), and is not due to the commonly assumed donor-acceptor-pair (DAP) mechanism.

## PL intensity trace

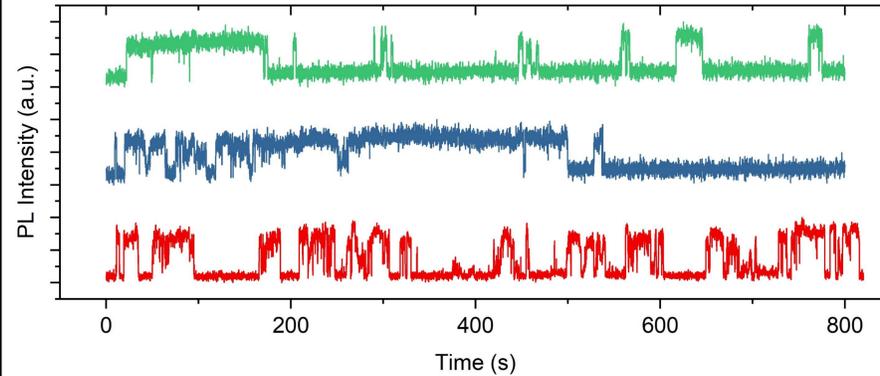


Fig. 1: PL intensity as a function of time for 3 different QDs. Measurements were conducted with a time resolution of 100 ms. In each case, 2 intensity levels can be clearly distinguished, where the lower corresponds to the OFF state and the higher to the ON state.

## Conclusions

- PL broadening: size/shape inhomogeneity and a small contribution from spectral diffusion
- Blinking events are power-law distributed, OFF-state more probable than ON-state.
- Mean ON-state fraction is 15 %.
- Spectral diffusion can be interpreted as originating from a quantum-confined Stark effect.
- Monotonic increase of  $\langle \Delta^2 \rangle$  is incompatible with DAP PL mechanism.
- Strong spectral diffusion indicate recombination via free-to-bound mechanism: between a delocalized electron and localized hole.
- Correlations between spectral parameters can be explained by the effect of an external electric field (from point charges at the QD surface).
- Changes in PL intensity, position and linewidth are attributed to non-zero polarizability of electron wave function.

## PL line broadening

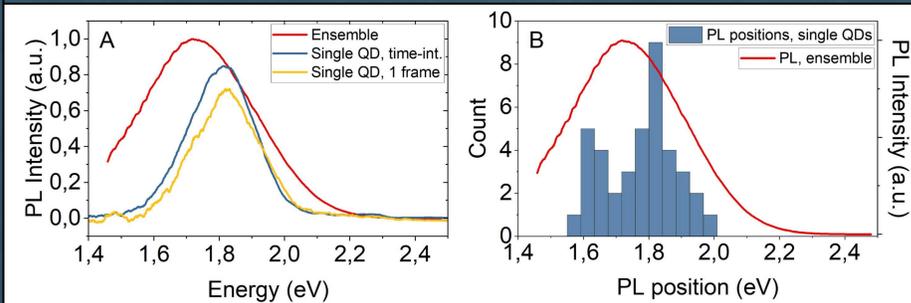


Fig. 2: (A) Colloidal QD solution PL (red curve), a time-integrated single QD PL (blue curve), and from the same dot a PL spectrum from one frame, (300 ms exposure, yellow curve). The FWHMs are 0.43, 0.25 and 0.23 eV, respectively. (B) PL spectrum of the QD colloidal solution (red curve) and the distribution of the positions of the PL maxima of all the dots studied. The results suggest that the inhomogeneity of an ensemble is the main reason for the strong broadening of the PL line. There are QDs of different sizes and shapes in an ensemble, and thus they emit photons of different energies.

## Spectral diffusion

We measured the PL spectra of  $\sim 40$  single QDs. Using exposure time of 300 ms allowed us to reveal the influence of spectral diffusion on a QD spectrum. We observed that the PL position, amplitude, and linewidth fluctuate over time. In order to gain deeper insight into the nature of this effect, we studied correlations between the parameters of Gaussian fits to the recorded spectra (Fig. 6).

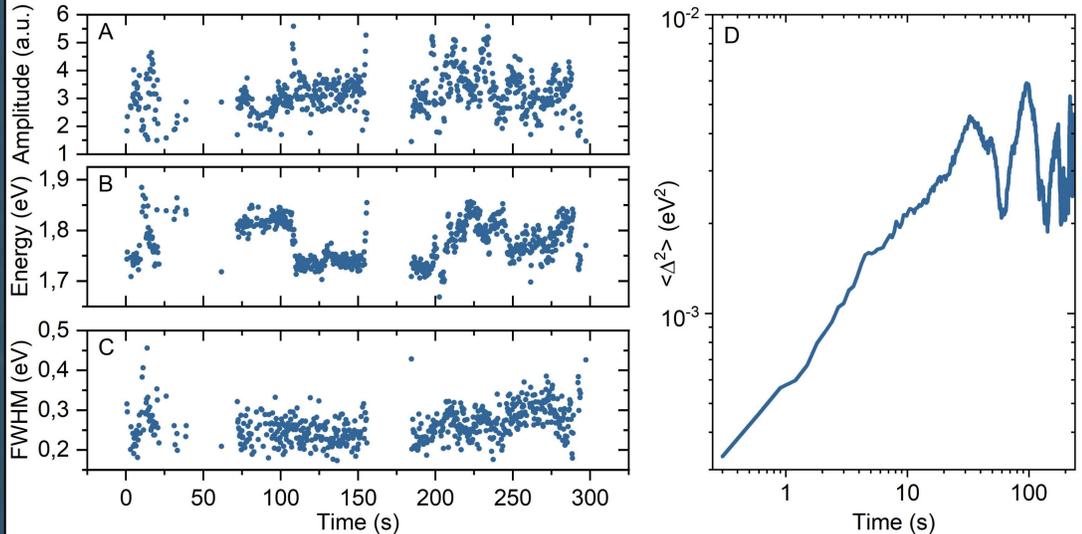


Fig. 5: Changes in (A) Amplitude, (B) PL position, and (C) FWHM of fluctuating spectra of one single QD. There are clear fluctuations of each of these 3 parameters as a function of time. The lack of data for fragments is due to the dot being in the OFF state. (D) Mean square displacement function calculated from the emission position shifts presented in (B).

## Blinking statistics

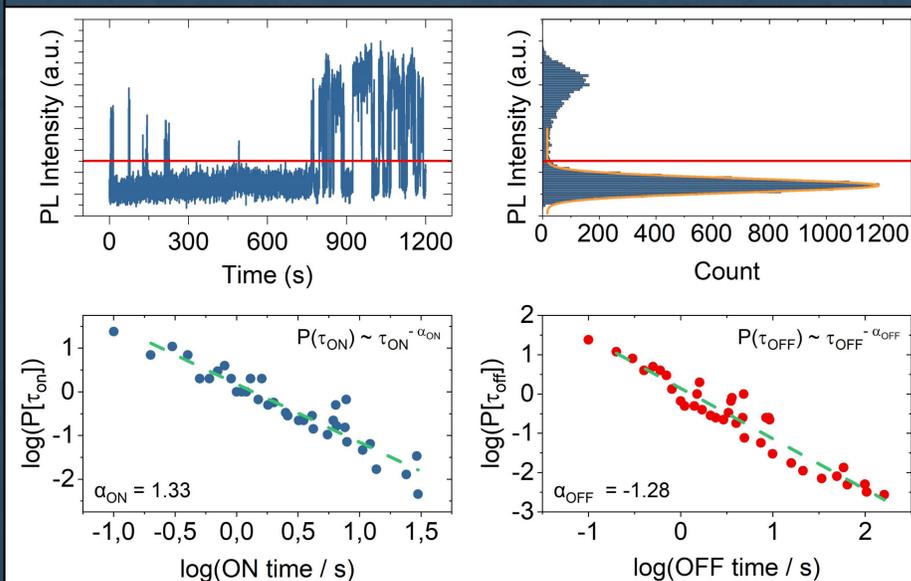


Fig. 3: (A) Example time intensity trace for one QD along with (B) distribution of recorded intensities. The threshold value above which a QD is considered to be in the ON state (red line in both graphics) is determined by fitting a Gaussian function to the background level (orange curve). The threshold value is 3.5 times the standard deviation greater than the maximum number of background counts. (C,D) ON-time and OFF-time probability densities, respectively. The green dashed line corresponds to the linear fit to the points. The slope indicates the power law exponents defining the probability distribution.

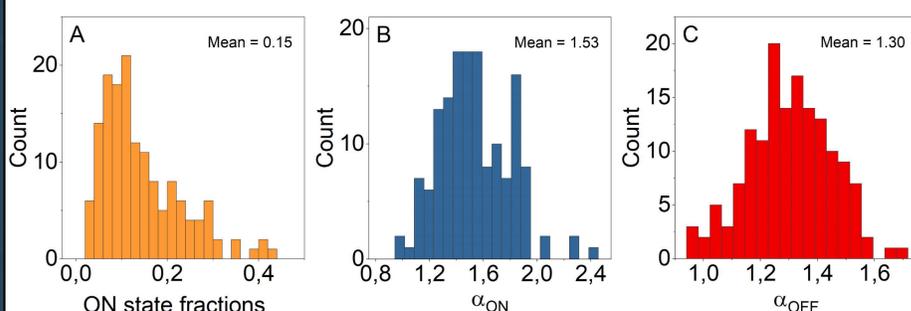


Fig. 4: QDs blinking statistics for  $\sim 150$  QDs. Distributions of: (A) the fraction of time that QDs spend in the ON state; (B) the power law exponents of the ON-time probability density and (C) of the OFF-time probability density. The mean ON-state fraction, 0.15 is comparable to the PL QY in solution, 0.30. The mean value of the power law exponents is 1.53 for ON states which is greater than 1.30 for OFF states.

## Correlations between Gaussian parameters

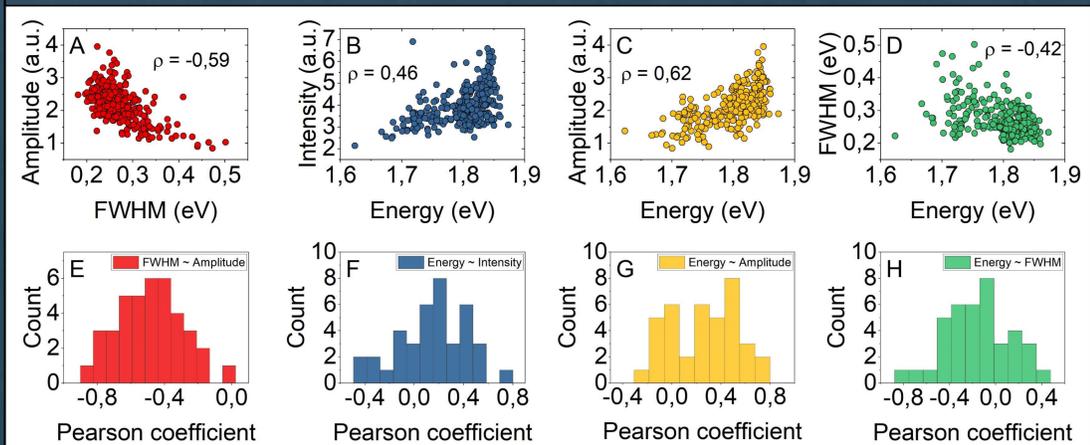


Fig. 6: (A) - (D) Correlations between the Gaussian parameters for one single QD during spectral diffusion measurement. The intensity is calculated as the product of the amplitude and the width of the peak. (E) - (H) The distribution of correlation coefficients ( $\rho$ ) between the parameters of the Gaussian function fit across all the frames for each quantum dot investigated. We found that (E) almost all (95%) QDs show a negative correlation between emission peak amplitude and linewidth with  $\rho$  between -0.25 and -0.85. (F) Almost half of the QDs ( $\sim 45\%$ ) show a positive correlation between PL peak energy and intensity ( $\rho$  between 0.2 and 0.8). (G) In case of 60% of QDs we see a positive correlation between PL peak energy and amplitude and (H) half of the QDs show a negative correlation ( $\rho$  between -0.25 and -0.8) between the PL peak energy and linewidth. These observations are in agreement with predictions for FTB PL mechanism. Changes in spectral parameters are attributed to non-zero polarizability of electron wave function.

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