Rationalizing the Physical Mechanisms behind the Amplified Spontaneous Emission Signatures in $CsPbBr_3$ Nanocrystal Films

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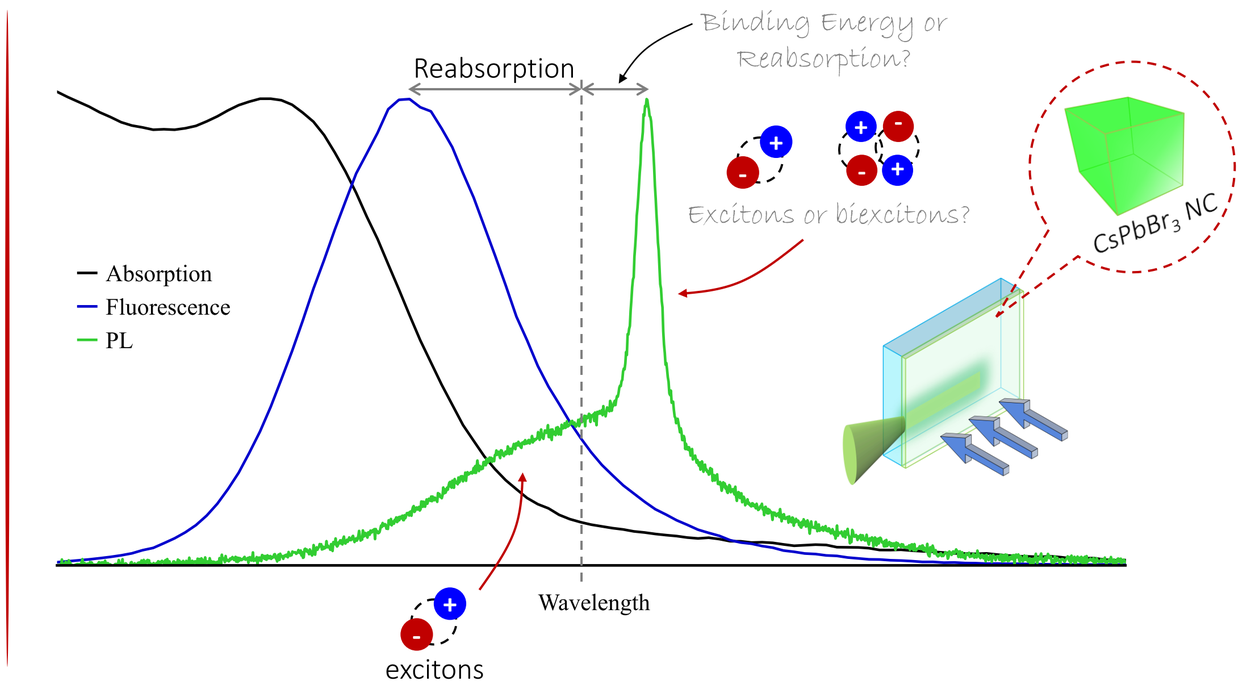
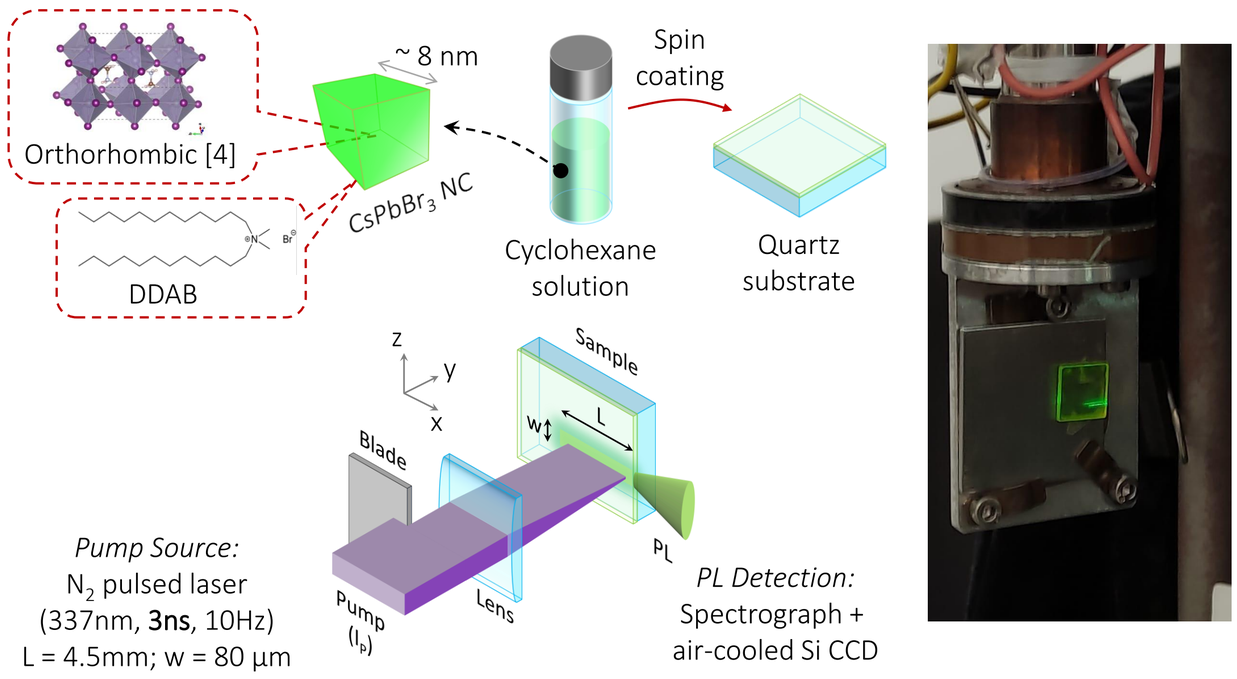
Introduction

Thanks to their optical and electronic properties, lead halide perovskites have become prominent materials in optoelectronics. $CsPbBr_3$ nanocrystals (NCs) stand out as excellent candidates to implement lasers due to their excellent photoluminescence quantum yields, and their facile and low-cost production. Elucidating their stimulated emission mechanisms is fundamental to address their possible limitations and to achieve more efficient perovskite lasers, specially continuous wave or electrically excited ones. Two questions remain open: why the Amplified Spontaneous Emission (ASE) band is shifted from the fluorescence one, and why the former seems to coexist with the latter. These characteristics have led to a debate on which is the mechanism behind the ASE band shift. Some reports claim that the fluorescence comes from single excitons, while the ASE has a biexcitonic origin [1]. Others defend that both fluorescence and ASE are generated by localized single excitons, and the shift owes to reabsorption [2]. In this communication, we address these questions through experimental ASE measurements, combined with numerical simulations, and the use of a novel analytical expression to retrieve the optical gain from these experiments[3]. We show that the ASE behaviour in $CsPbBr_3$ NCs thin films stems from different processes: reabsorption due to a large overlap between the absorption and fluorescence spectra, a strong contribution of excited state absorption at the fluorescence window, and the coexistence of short- and long-lived localized single excitons.

Photoluminescence (PL) signatures in $CsPbBr_3$ NCs films



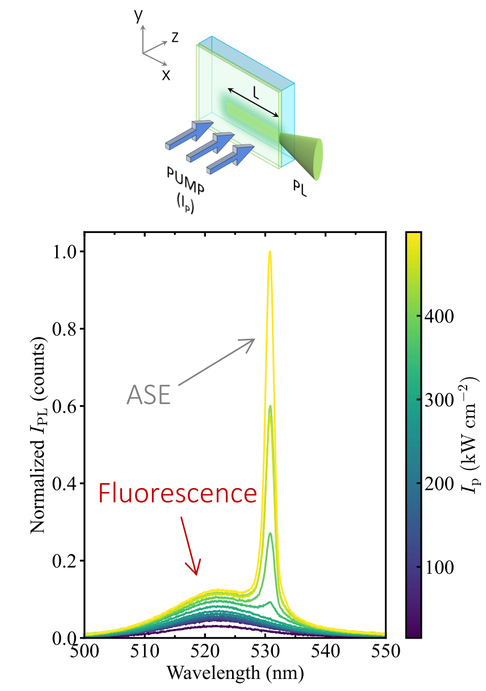
1.1 Methods: *NCs thin film preparation and PL measurement set-up*



Pump Source:
N_2 pulsed laser
(337nm, **3ns**, 10Hz)
L = 4.5mm; w = 80 µm

PL Detection:
Spectrograph +
air-cooled Si CCD

1.2 Methods: *Optical gain g analysis from PL measurements [3, 5]*



$$I_{PL} = \underbrace{\frac{A_1}{g}\left(e^{gL}-1\right)}_{\text{ASE}} + \underbrace{\frac{A_2}{\alpha}\left(1-e^{-\alpha L}\right)}_{\text{Fluorescence}} \quad \text{(1a)}$$

$$g = \gamma\Delta n - \alpha$$

Gain spectrum · Population inversion · Losses spectrum

$$\Delta n(I_p) = \Delta n_0 \frac{I_p/I_{p,1}^s + \left(I_p/I_{p,2}^s\right)^m}{1 + I_p/I_{p,1}^s + \left(I_p/I_{p,2}^s\right)^n} \quad \text{(1b)}$$

To retrieve the gross optical gain (γ), the optical losses (α), and the population inversion (Δn), we fit eqs. 1a and 1b, derived in refs. [3] and [5], to the PL spectra as a function of pump intensity (I_p).

2.2 Results: *Rationalizing the shifted ASE band*

$$g = \gamma\Delta n - \alpha$$

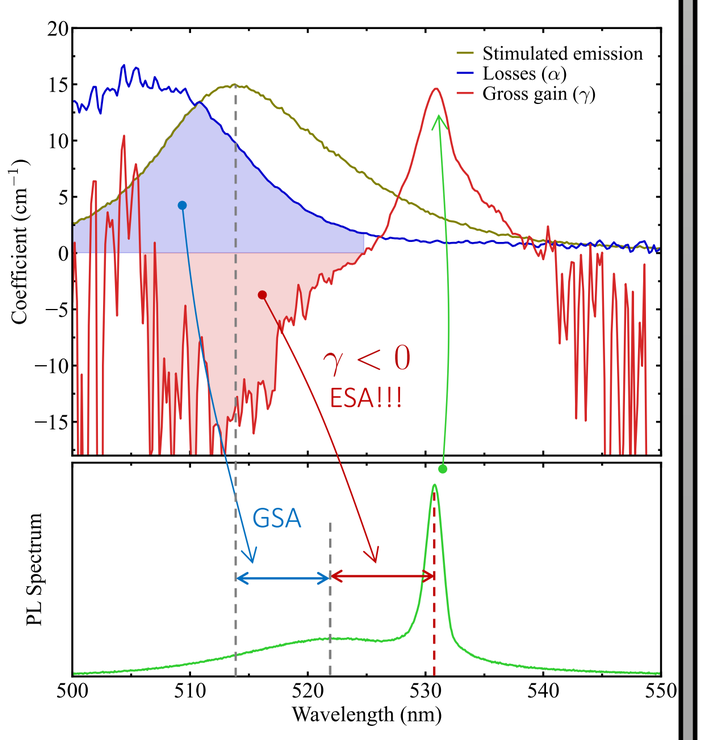
$$\alpha \propto \sigma_{SC} + \sigma_{GSA}$$

scattering · Ground State Absorption

$$\gamma \propto \sigma_{SE} + \sigma_{GSA} - \sigma_{ESA}$$

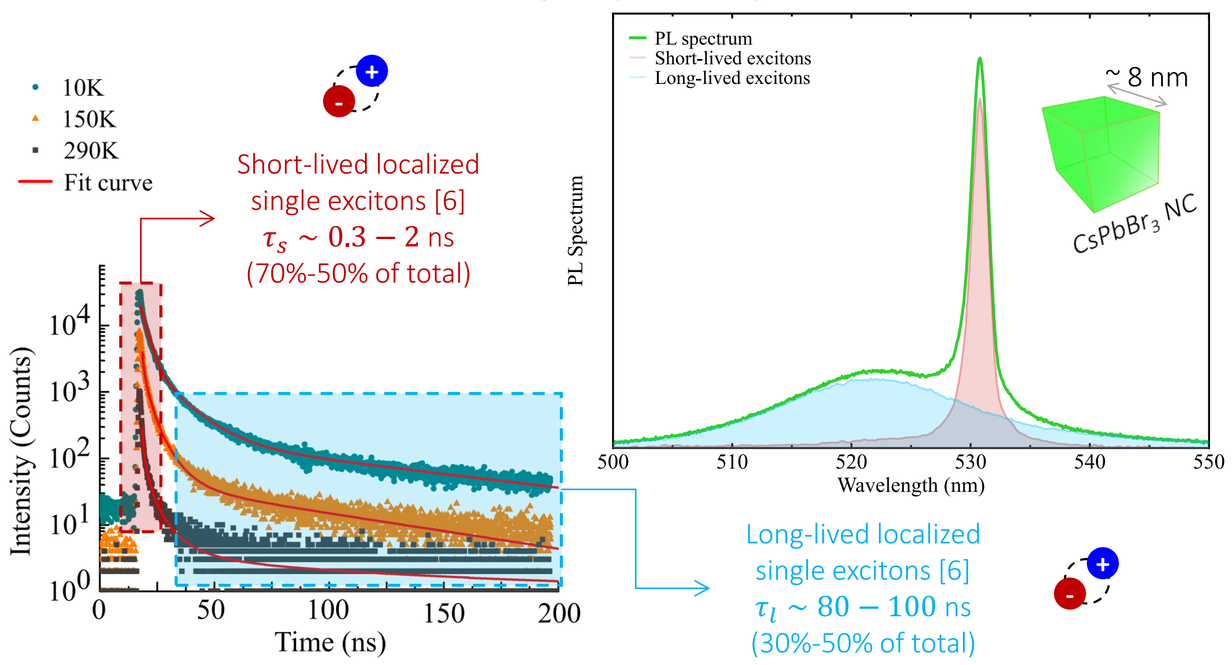
Stimulated emission · Excited State Absorption

ASE band shifted due to *reabsorption* from:
Ground State Absorption (GSA)
Excited State Absorption (ESA)



To large overlap between the gross optical gain (γ) and the optical losses (α) leads to GSA reabsorption, and partially explains the ASE band shift. Nevertheless, it is the presence of a strong ESA band ($\gamma < 0$) overlapping with the emission band what fully explains the remaining ASE band shift.

2.3 Results: *Origin of excess fluorescence*



In reference [6], it was shown that there were two contributions to the fluorescence decay rate in the $CsPbBr_3$ NCs: A short one due to localized single excitons, and a long-lived one due to trapped single excitons. The long-lived excitons have not time to participate in the stimulated emission process (the pump pulse lasts 3 ns), and, hence, we ascribe the background fluorescence to this species. The short-lived excitons are short enough to participate in the amplification process, so we hypothesize that they are responsible for the ASE band.

References

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Acknowledgements

This work was partially funded by MCIN/AEI/10.13039/501100011033 through Grant PID2020-114755GB-C31, and by the Italian Ministry of University (MUR) under Contract P2022B3W29 (PRIN - PNRR 2022 - LOGIFIB); Financed by EU - Next Generation EU, Mission 4, Component 1, CUP: B53D23028440001. L.C. acknowledges support from a Ramón y Cajal Research Fellowship, Grant RYC2022-038362-I, funded by MCIN/AEI/10.13039/501100011033 and by the European Social Fund Plus (ESF+).

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