

# Elucidating the photophysics behind the stimulated emission processes in CsPbBr<sub>3</sub> nanocrystals films

Luis Cerdán<sup>1,\*</sup>, Stefania Milanese<sup>2</sup>, Maria Luisa De Giorgi<sup>2</sup>, Marco Anni<sup>2</sup>, Maryna I. Bodnarchuk<sup>3,4</sup>

<sup>1</sup>Instituto de Química-Física Blas Cabrera (IQF-CSIC), Consejo Superior de Investigaciones Científicas, Spain

<sup>2</sup>Dipartimento di Matematica e Fisica “Ennio De Giorgi”, Università del Salento, Italy

<sup>3</sup>Institute of Inorganic Chemistry, ETH Zürich, Switzerland

<sup>4</sup>Laboratory for Thin Films and Photovoltaics, Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

**Abstract.** Thanks to their excellent photoluminescence quantum yields, their facile and low-cost production, and their processing versatility, CsPbBr<sub>3</sub> perovskite nanocrystals (NCs) stand out as excellent candidates to implement light-emitting devices. Elucidating their stimulated emission mechanisms is fundamental to achieve much more efficient and versatile perovskite lasers. In particular, two questions remain open: why the Amplified Spontaneous Emission (ASE) band is significantly shifted from the fluorescence one, and why the former seems to suddenly emerge from, and coexist with, the latter. These characteristic features have led to a debate, which is not settled yet, on which is the mechanism behind the ASE band shift. In this communication, we try to settle this debate and address these questions through experimental ASE measurements combined with numerical simulations. We show that the ASE behaviour in CsPbBr<sub>3</sub> NCs thin films stems from a combination of reabsorption, excited state absorption, excitation of differently polarized waveguide modes, and the coexistence of short- and long-lived localized single excitons. The results in this work help understanding the stimulated emission mechanisms in perovskites and provide insightful information on research avenues to increase the efficiency of the light-emitting devices based on these materials.

## 1 Introduction

CsPbBr<sub>3</sub> lead halide perovskite nanocrystals (NC) stand out as excellent candidates to implement light-emitting devices thanks to their excellent photoluminescence quantum yields, their facile and low-cost production, and their processing versatility [1, 2]. Elucidating their stimulated emission mechanisms is fundamental to address their possible limitations and to achieve much more efficient perovskite lasers. CsPbBr<sub>3</sub> NCs thin films, and most perovskites for that matter, display very distinctive Amplified Spontaneous Emission (ASE) spectral signatures: the ASE band is usually significantly shifted from the fluorescence one, and, in addition, the former seems to suddenly emerge from, and coexist with, the latter (Fig. 1a). These characteristic features have led to a debate, which is not settled yet, on which is the mechanism behind the ASE band shift. Some reports claim that the fluorescence band is generated by single excitons, while the ASE band has a biexcitonic origin, and is shifted due to the binding energy [1]. Some other reports defend that both the fluorescence and ASE bands are generated by localized single excitons, and the shifts owe to reabsorption effects [3]. Accordingly, the mechanisms behind the photoluminescence spectral signatures in CsPbBr<sub>3</sub> NCs have yet to be fully elucidated. In this communication, we try to settle this debate and

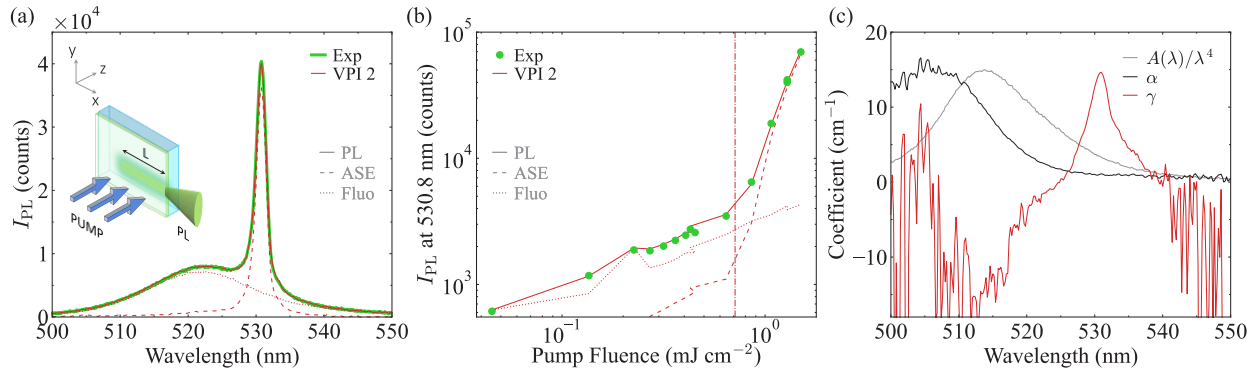
address these questions through experimental ASE measurements, combined with numerical simulations and thorough analysis of the optical gain. Our study shows that the ASE behaviour in CsPbBr<sub>3</sub> NCs thin films stems from four distinctive processes [4]: reabsorption, excited state absorption (ESA), excitation of differently polarized waveguide modes, and the coexistence of short- and long-lived localized single excitons.

## 2 Samples and methodology

The NCs were synthesized by adapting the procedure described in Ref. [5], using didodecyldimethyl ammonium bromide (DDAB) as capping ligand. The films were deposited by spin coating the NCs colloidal solution on fused silica substrates. ASE measurements were performed by exciting the samples with a Nitrogen laser, delivering 3 ns pulses at a wavelength of 337 nm, with a repetition rate of 10 Hz. The pump beam was focused onto the sample surface in a rectangular stripe of 4.5 mm length and 80 μm width (inset of Fig. 1a).

The ASE properties of the films were evaluated by means of Variable Pump Intensity (VPI) measurements, where the photoluminescence (PL) emission is acquired as a function of the pump excitation density. To retrieve the optical gain properties, we used a newly reported

\*E-mail: [l.cerdan@csic.es](mailto:l.cerdan@csic.es)



**Figure 1:** a) Experimental PL spectrum (solid green line) above threshold, and best fit of VPI 2 (solid red line). The dashed and dotted red lines show the contributions of pure ASE and background fluorescence, respectively. Inset: Schematics of a typical experimental configuration to measure ASE in thin films. b) Experimental PL intensity at peak wavelength vs. pump fluence (green points) and best fit of VPI 2. Same colours and line styles code than in a). c) Losses coefficient  $\alpha$  (black line) and gross gain  $\gamma$  spectra (red line) obtained from VPI 2, stimulated emission cross section spectrum  $A_i(\lambda)/\lambda^4$  in arbitrary units (gray line).

analytical method (dubbed VPI 2) that accounts for both ASE (1<sup>st</sup> term in Eq. (1)) and excess fluorescence (2<sup>nd</sup> term in Eq. (1)) [4]:

$$I_{ASE}(\lambda) = \frac{A_1(\lambda)}{\gamma(\lambda)\Delta n - \alpha(\lambda)} (e^{(\gamma(\lambda)\Delta n - \alpha(\lambda))L} - 1) + \frac{A_2(\lambda)}{\alpha(\lambda)} (1 - e^{-\alpha(\lambda)L}) \quad (1)$$

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

where  $\gamma$  and  $\alpha$  are the gross gain and losses, respectively,  $\Delta n$  (Eq. (2)) is the population inversion,  $A_i$  are proportionality factors, and  $I_{p,i}^s$  are saturation intensities that, together with  $m$  and  $n$  ( $m > n$ ), determine when the population inversion grows and saturates.

### 3 Results

VPI 2 allows to obtain a very accurate fit of the emission spectrum above the ASE threshold (Fig. 1a), evidencing that the acquired spectrum is the combination of a strong fluorescence background and a distinctive ASE band. The same holds true for the experimental pump fluence dependence of the emission intensity at the ASE peak wavelength (Fig. 1b). Indeed, below ASE threshold (dashed vertical line) the PL signal is dominated by a background fluorescence contribution that grows linearly with the pump fluence. It is only when approaching threshold that a strong purely ASE signal becomes dominant. This fact rationalizes why the ASE band seems to suddenly emerge from, and coexist with, the fluorescence band. Fig. 1c shows the fitted  $\alpha$  and  $\gamma$  spectra, and the quantity  $A_i(\lambda)/\lambda^4$ , which is proportional to the stimulated emission cross-section. As can be clearly seen, these results point to the presence of reabsorption (due to overlap of  $\alpha$  and  $A_i(\lambda)/\lambda^4$ ), and a very strong ESA band almost overlapping with the fluorescence window, as evidenced by the negative values in  $\gamma$ . These two effects combined explain why the ASE band is shifted with respect to the fluorescence one.

The origin of the background fluorescence signal can be understood attending to the timescales of the pumping

and relaxation processes. CsPbBr<sub>3</sub> NCs display a multiexponential fluorescent decay, with a short lifetime component (sub-nanoseconds) ascribed to a short-range energy migration of localized excitons, and a long lifetime component (tens to hundreds of nanoseconds) due to localized excitons delayed by the activation of a long-range diffusion process. As the pump pulse duration to study ASE in this work (~3 ns) is larger than the lifetime of the short-lived localized excitons, the PL signal generated by these should contribute mostly with ASE. In contrast, the long-lived excitons, with a lifetime much longer than the pulse width, cannot participate in the ASE process, and only provide a fluorescence signal. As this signal accounts for a large percentage of the total emission, the acquired PL spectra displays a huge contribution of excess background fluorescence. Finally, there are other minoritarian processes contributing to the excess fluorescence, like the excitation of two waveguide polarization modes, and time-domain effects related to the pulsed excitation.

In conclusion, the results in this work establish guidelines to analyse the optical gain in perovskite samples, help in understanding the photophysics behind the ASE signatures of CsPbBr<sub>3</sub> NCs, and provide insights to boost their lasing efficiency.

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