All-Optical Coherent Lifting of Spin-Degeneracy in CsPbBr₃ Nanocrystals

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Abstract: We coherently lift the spin-degeneracy in CsPbBr₃ nanocrystals by breaking time-reversal symmetry all-optically without external magnetic field. Huge polarization-selective lifting ~50meV observed, corresponding to Rabi energy >100meV, is highest ever reported in semiconductors at room-temperature. © 2021 The Author(s)

1. Motivation
The peculiar optical properties of lead halide perovskites (LHPs) have led to their impressive growth in optoelectronic applications [1,2]. On the other hand, the presence of intrinsic strong spin-orbit coupling in LHPs enabled efficient spin-manipulation and paved a way for their exploitation in spin-based devices [1]. The conduction band minima (CBM) and valence band maxima (VBM) possess two-fold spin-degenerate states, preserved by time-reversal symmetry. Lifting the spin-degenerate states is of great interest, as it would allow the coherent spin-engineering and holds promising candidature in next-generation applications involving quantum states of matter like quantum information processing and ultrafast switching [3,4]. In general, an external magnetic field can be employed, that breaks the time-reversal symmetry and lift the spin-degeneracy, however, is not viable due to inaccessibility of sufficiently high field strength in the laboratory. Herein, using CsPbBr₃ nanocrystals (NCs) as model LHP system, we accomplish time-reversal symmetry breaking through all-optical, circularly polarized femtosecond pump-probe spectroscopy. We demonstrate room-temperature polarization-selective coherent lifting of spin-degenerate states, also known as optical stark effect (OSE), by as much as 50 meV. The huge shift corresponds to Rabi energy ~100 meV, a measure of strength of light-matter interaction. The Rabi energy obtained, to the best of our knowledge, is highest reported so far at comparable fluences, without any external magnetic field [3].

2. Methods
Using circularly-polarized femtosecond pump-probe spectroscopy we measure the change in absorption (ΔA) of probe in two configurations: (i) CO: pump and probe having same polarization (σσ) and (ii) CX: pump and probe having opposite polarization (σσ⁻). Spin-degeneracy is lifted by breaking time-reversal symmetry using below bandgap pump excitation of 560 nm (2.21 eV), detuning (Δdet) ~ 190 meV. Below bandgap excitation remarkably suppresses the undesired incoherent signal.

3. Results and Discussion
Fig. 1a shows the optical absorption (OA) of monodispersed cubic morphology CsPbBr₃ NCs, synthesis details in [5]. Modelling the OA using Elliott’s equation in [2] reveal the continuum centered at 2.44 ± 0.01 eV and exciton (E₀) positioned at 2.41 ± 0.01 eV.

Fig. 1: (a) OA spectrum of CsPbBr₃ NCs, (b) spectral evolution of ΔA in CO and CX polarization, and (c) corresponding time evolution.
3.1. Polarization selective spin-degeneracy lifting

The spectral evolution of $\Delta A$ in CO and CX polarization, at $\Delta t=0$ ps and pump-fluence 500 $\mu$J/cm$^2$ is shown in Fig. 1b. Under CO polarization, an asymmetric derivative-like feature is observed that consists of a strong bleach at the excitonic position and a photo-induced blue-shifted absorption (BSA) towards the high energy side (blue dashed region). Contrastingly, under CX polarization, only weak bleach is present, and no BSA signature is observed. The presence of BSA in CO and absence in CX manifest the polarization-selectivity. Moreover, the time evolution of the respective features, shown in Fig. 1c, illustrates the existence only for the coherent duration, i.e., they appear only for the pump duration. The polarization-selective coherent BSA is the experimental visualization of OSE i.e., spin-degeneracy lifting. A stark-shift ($\Delta E$) of ~50 meV is obtained by fitting the CO $\Delta A$ using the following equation:

$$\Delta A = A_e e^{\left(\frac{x-E_0-\Delta E}{\omega_e}\right)^2} - A_g e^{\left(\frac{x-E_0}{\omega_g}\right)^2}$$  \hspace{1cm} (1)

Where $A$ and $\sigma$ refers to constant and spectral broadening of exciton. Subscript $e$ and $g$ respectively, refers to excited state and ground state.

![Fig. 2: Absorption of $\sigma^+$ probe in (a) absence of pump, (b) presence of $\sigma^+$ pump, and (c) presence of $\sigma^-$ pump.](image)

To understand the mechanism behind the experimentally observed feature, a two-level photon-dressed model is considered. The law of conservation of angular momentum dictates that $\sigma\pm$ light will enable transition with $\Delta m = \pm 1$. Fig. 2a illustrates the $\sigma^-$ probe absorption in the absence of pump. Now pumping with 560 nm $\sigma^+$, as intuitive will not result in real-exciton population instead it creates a virtual photon-dressed states corresponding to coherent absorption and emission. The formation of photon-dressed states due to intense circularly-polarized light breaks the time-reversal symmetry. The solid green lines in Fig. 2b and 2c represent the virtual states created due to $\sigma$ and $\sigma^-$ pump, respectively, having $m_j$ alike equilibrium Bloch states. As per the quantum mechanical description [3], there exists repulsive interaction between virtual states and equilibrium-Bloch states having the same $m_j$. Therefore, $\sigma^-pumping$ results in uplift and lowering of the CBM ($m_j = \pm \frac{1}{2}$) and VBM ($m_j = \pm \frac{3}{2}$), respectively, known as OSE. Thus, in CO polarization $\sigma^-$ probe detects the stark-shift leading to the observation of derivative-like feature in $\Delta A$. Whereas, in CX no change in absorption of $\sigma^-$ probe occurs. However, the CX $\Delta A$ reveal small coherent bleach signal and might originate either from two photon absorption or many-body interaction. Notably, since the photon-dressed states lie at the origin of time-reversal symmetry breaking, the system regains symmetry as soon as pumping is removed. This explains the coherent duration of observed degeneracy lifting. Moreover, to determine the strength of polarization-selective shift, we evaluate the Rabi energy given by $\Delta E^*2\Delta_{\omega}$ [3]. The Rabi energy $> 100$ meV obtained is one order of magnitude larger than that reported in perovskites so far at comparable fluences.

4. Conclusion

In summary, we demonstrate giant polarization-selective spin-degeneracy lifting ~50meV in CsPbBr$_3$ NCs, by means of all-optical intense circularly polarized field. The corresponding Rabi energy evaluated is $>100$ meV, highest reported so far at room-temperature and at comparable fluences, without aid of external magnetic field. The polarization-controlled coherent manipulation paved a way for potential exploitation of perovskites in next-generation applications like quantum information processing and ultrafast switching.

References


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