Multidimensional coherent spectroscopy reveals triplet state coherences in cesium lead-halide perovskite nanocrystals

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Advances in optoelectronics require materials with novel and engineered characteristics. A class of materials that has garnered tremendous interest is metal-halide perovskites, stimulated by meteoric increases in photovoltaic efficiencies of perovskite solar cells. In addition, recent advances have applied perovskite nanocrystals (NCs) in light-emitting devices. It was found recently that, for cesium lead-halide perovskite NCs, their unusually efficient light emission may be due to a unique excitonic fine structure composed of three bright triplet states that minimally interact with a proximal dark singlet state. To study this fine structure without isolating single NCs, we use multidimensional coherent spectroscopy at cryogenic temperatures to reveal coherences involving triplet states of a CsPbI3 NC ensemble. Picosecond time scale dephasing times are measured for both triplet and inter-triplet coherences, from which we infer a unique exciton fine structure level ordering composed of a dark state energetically positioned within the bright triplet manifold.

**INTRODUCTION**

Cesium lead-halide perovskites were first synthesized over a century ago with a general chemical formula CsPbX3 (where X = Cl, Br, or I). Recently, synthesis of CsPbX3 nanocrystals (NCs) was achieved (1, 2), which combines the advantages of perovskites (e.g., efficient luminescence and long carrier diffusion length) with those of colloidal NC materials (e.g., surface engineering and size-tunable emission). Perovskite NCs exhibit luminescence with quantum yields reaching nearly unity (3), in contrast to the optimized 80% quantum yield achieved by chalcogenide NCs coated with a gradient shell (4). Although all other colloidal materials suffer inhibited emission from lower-energy dark states (5), the unusual brightness of perovskite NCs is now believed to originate from an optically active, nondegenerate triplet state that emits efficiently despite the presence of a dark singlet state (6, 7).

The unique exciton fine structure of perovskite NCs has substantially extended the potential applications of colloidal NCs. In particular, the three nondegenerate bright triplet states and their orthogonally oriented dipole moments (arising from atomic orbital mixing along the lattice symmetry axes) have generated much excitement for potential applications in quantum information processing (8, 9). However, engineering exciton superposition states as information carriers will require an intimate knowledge of their coherent dynamics, which are still not well understood. The exciton fine structure of perovskite NCs has thus far only been studied via single-NC photoluminescence (6, 10, 11) and transient absorption (12, 13) techniques, which have provided information only about their incoherent population dynamics. Furthermore, inhomogeneous spectral broadening due to NC size dispersion limits the utility of linear spectroscopic techniques in studying NC ensembles. More sophisticated methods are thus required (14–17) to extract the desired ensemble-averaged coherent properties of perovskite NCs.

Here, we extract crucial figures of merit for quantum information processing, the ensemble-averaged coherence times, and revealing coherence times of both optical triplet coherences and terahertz inter-triplet coherences for an ensemble of CsPbI3 NCs (see Fig. 1, A and B) at cryogenic temperatures. We also present evidence for a mixed bright-dark level ordering (see Fig. 1C) that renders the triplet state excitation only partially bright. These measurements are enabled by using multidimensional coherent spectroscopy (MDCS) (18) to circumvent the inhomogeneous broadening that obscures spectral signatures of the exciton fine structure and resolve coherent coupling involving different triplet states. The extracted coherence times for CsPbI3 NCs are an order of magnitude longer compared to candidate materials for valleytronics (14, 15, 19), which positions perovskite NCs as a potential material platform for quantum information applications via bottom-up assembly.

**RESULTS**

Multidimensional coherent spectroscopy

To perform MDCS, we use a multidimensional optical nonlinear spectrometer (20), which focuses three laser pulses onto the perovskite NC ensemble sample as a function of three time delays τ, T, and t (schematically shown in Fig. 1, C and D). By Fourier transforming the emitted four-wave mixing (FWM) signal as a function of two or all three time delays, the coherences and populations induced by each pulse are correlated in a multidimensional spectrum. In order, the first pulse (A) generates a coherent superposition between the ground and an optically active excited state, which oscillates at the energy difference hω0. The second pulse (B) then converts this optical coherence into either a population state that decays according to its relaxation rate or a coherence between two neighboring states within a ground or excited state manifold that oscillates at hωT. The last pulse (C) then generates a final optical coherence that oscillates at hωT and radiates an FWM signal. These sequences of light-matter interactions are commonly referred to as quantum pathways [(21)
and the Supplementary Materials]. Fourier transforming along the variables $\tau$ and $t$ returns one-quantum spectra (which correlate the absorption energy $\hbar\omega_A$ with the emission energy $\hbar\omega_B$) and has been applied in recent studies (22–24) to reveal novel electronic properties of various perovskite materials. In this study, we also transform along the variables $T$ and $t$ to obtain zero-quantum spectra [which correlate the intraband mixing energy (25) $\hbar\omega_T$ and the emission energy $\hbar\omega_B$]. Furthermore, the polarization of the second pulse is chosen to align either parallel or orthogonal to the colinear polarizations of the other two pulses to probe different quantum pathways. We denote the two polarization schemes as colinear excitation and cross-linear excitation, respectively, as shown in Fig. 1D.

One-quantum spectra probe optical triplet coherences

One-quantum spectra were acquired at a temperature of 4.6 K with colinear and cross-linear excitation (shown in Fig. 2, A and B). Both spectra reveal numerous peaks elongated in the diagonal direction $|\hbar\omega_A| = |\hbar\omega_B|$, reflecting inhomogeneous spectral broadening (26). Cross-slices taken in the orthogonal direction, which reflect the ensemble-averaged homogeneous response at a certain resonance energy (26), are plotted in Fig. 2 (C and D). In the full slices (inset), asymmetric peaks are observed for $|\Delta E| > 4$ meV, which could arise from either electron-phonon coupling (27) or biexciton transitions (28). Here, we focus on features related to the triplet state fine structure and defer discussion of vibrational features and biexciton transitions [which appear at the biexciton binding energy $\Delta E = -E_{XX}$, which is well over 10 meV (10), and do not influence the low-energy features studied here] to future reports. The main plots of each slice section (highlighted by the yellow boxes inset) show symmetric peaks that, due to their polarization dependence, we attribute to absorption and emission involving different triplet state coherences. As described above, the origin of the observed peaks is interpreted as changes in the system density matrix induced by each pulse that form accessible quantum pathways (21). First, peaks 1 and 3 in Fig. 2C are generated by absorption and emission involving $|g⟩$ and both triplet states $|Ψ_x⟩$ and $|Ψ_y⟩$. We note that our measurements do not inform the ordering of states $|Ψ_{XY}⟩$, so we assume the ordering shown in Fig. 1B for labeling the dephasing rates discussed below. The central peak 2 is likewise generated by quantum pathways involving absorption and emission by coherences of identical resonance energy $|g⟩/⟨Ψ_x|$ and $|Ψ_y⟩/⟨g|$, respectively. In Fig. 2D, peaks 1 and 3 are visible as shoulders on two new peaks 4 and 5, which are generated by absorption and emission of coherences involving $|g⟩$ and triplet states $|Ψ_y⟩$ and $|Ψ_y⟩$.

The polarization dependences of the five observed peaks is not immediately intuitive. To explain the peak structure for both excitation polarization schemes, we theoretically calculate the relative peak strengths for varying dipole matrix elements and vector orientations of each triplet state transition (see the Supplementary Materials). From these calculations, we draw two important conclusions: (i) To observe sidebands
and 5 in the cross-linear slice line shape (Fig. 2D) gives a dephasing rate of \( \gamma_2 = 0.124 \pm 0.008 \) meV (5.32 ps). Fit of peaks 4 and 5 to each be primarily composed of a single peak located at \( \Delta E = \pm \Omega_x \), as suggested by our fitting attempts, the dipole moment of \( |\Psi_y\rangle \) must be substantially stronger than those of \( |\Psi_z\rangle \) and \( |\Psi_z\rangle \). We achieve good agreement with experiment for a 45° angle between the dipole moments of \( |\Psi_y\rangle \) and \( |\Psi_z\rangle \) and a dipole matrix element of \( |\Psi_y\rangle \) that is 1.5 times the magnitude of the dipole matrix elements of \( |\Psi_z\rangle \) and \( |\Psi_z\rangle \) (see the Supplementary Materials).

Fitting the cross-diagonal line shapes also extracts the homogenous linewidths \( \gamma_i \) (25) of triplet state transitions between \( |\Psi_y\rangle \) and \( |\Psi_j\rangle \). In this context, one-quantum spectra are particularly useful when compared to integrated FWM techniques (29), since the cross-diagonal slice position \( |\hbar\omega_x| = |\hbar\omega_y| \approx 1900 \) meV of the (C) colinear and (D) cross-linear excitation one-quantum spectrum. Top plots show theoretically calculated relative peak strengths in the NC reference frame (see the Supplementary Materials). Numbers label peaks arising from electronic interband coherences and populations.

with colinear excitation, the two triplet states involved must have transition dipole moments that are not perpendicular, and (ii) for peaks 4 and 5 to each be primarily composed of a single peak located at \( \Delta E = \pm \Omega_x \), as suggested by our fitting attempts, the dipole moment of \( |\Psi_y\rangle \) must be substantially stronger than those of \( |\Psi_z\rangle \) and \( |\Psi_z\rangle \). We achieve good agreement with experiment for a 45° angle between the dipole moments of \( |\Psi_y\rangle \) and \( |\Psi_z\rangle \) and a dipole matrix element of \( |\Psi_y\rangle \) that is 1.5 times the magnitude of the dipole matrix elements of \( |\Psi_z\rangle \) and \( |\Psi_z\rangle \) (see the Supplementary Materials).

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### Fig. 2. Optical triplet coherences in one-quantum spectra.
(A and B) Magnitude one-quantum spectrum at 4.6 K with (A) colinear and (B) cross-linear excitation. The white/red dashed arrows and solid black lines indicate the cross-slice locations and laser pulse spectra, respectively. (C and D) Bottom plots show normalized cross-slices centered at \( |\hbar\omega_x| = |\hbar\omega_y| = 1900 \) meV of the (C) colinear and (D) cross-linear excitation one-quantum spectrum. Top plots show theoretically calculated relative peak strengths in the NC reference frame (see the Supplementary Materials). Numbers label peaks arising from electronic interband coherences and populations.

### Zero-quantum spectra probe terahertz inter-triplet coherences

Many of the quantum pathways that generate the sidebands in Fig. 2 (A and B) involve inter-triplet coherences, which are quantum coherences between triplet states that are not necessarily dipole-coupled (30). Of both fundamental and practical importance is the inter-triplet coherence time, which defines the time scale during which the superposition states involved may be coherently manipulated. Inter-triplet coherences are those density matrix elements of the form \( \langle \Psi_j | \Psi_i \rangle \) where \( i,j = \{x,y,z\} \) and \( i \neq j \). To directly measure and characterize these coherences, we take zero-quantum spectra at varying temperature and delay \( \tau \). For colinear excitation, no inter-triplet coherences between \( |\Psi_z\rangle \) and \( |\Psi_z\rangle \) are observed (see the Supplementary Materials). It is ambiguous whether their corresponding peaks are weak or are simply obscured by the linewidth of a central \( \hbar\omega_T = 0 \) peak. For cross-linear excitation, we further isolate the inter-triplet
coherence pathways by passing the measured FWM signal through a vertical polarizer. We plot a resultant cross-linear zero-quantum spectrum at 20 K in Fig. 3A. Sidebands are observed at mixing energies identical to the positions of peaks 4 and 5 in Fig. 2D, which we attribute to inter-triplet coherences between $|\Psi_x\rangle$ and $|\Psi_y\rangle$. An inter-triplet coherence between $|\Psi_x\rangle$ and $|\Psi_y\rangle$ is observed in neither the colinear nor cross-linear zero-quantum spectra, which is consistent with a dominant transition dipole of state $|\Psi_y\rangle$ as argued above.

In Fig. 3B, the evolutions of normalized slices (at $h\omega_T = 1890$ meV) as a function of delay $\tau$ and temperature are shown. The FWM signal dephases rapidly with increasing $\tau$ and results in an equally rapid decrease of sideband visibility (see the Supplementary Materials), in contrast to the opposite behavior of vibrational intraband coherences (see (16) and the Supplementary Materials), which confirms its electronic nature. No change in the amplitude ratio between sidebands 6 and 8 is observed as temperature increases, confirming that the state splitting observed indeed belongs to the bright triplet excited state rather than from thermal filling of higher-lying ground states. We note that the triplet state coherences in one-quantum spectra broaden substantially with increasing temperature and are not resolved at temperatures above 15 K. In contrast, minimal broadening of the inter-triplet coherence linewidth is observed up to 40 K (see Fig. 3B), indicating that inter-triplet coherences are robust against thermal dephasing (14).

A slice at $\tau = 0$ fs is plotted in Fig. 3C, from which we can extract the inter-triplet coherence time. However, the quantum pathways that generate peaks 6 and 8 involve identical dipole moments $\mu_y^2, \mu_z^2$, from which we expect equal peak amplitudes contrary to the uneven peaks observed. This difference is due to interference between the three complex Lorentzian line shapes underlying the overall amplitude line shape (see the Supplementary Materials), and the fit to experiment is performed by shifting the phase of each sideband Lorentzian line shape by identical factors of $-\pi/2$ relative to the central $h\omega_T = 0$ peak. These phase factors arise from a $-\pi/4$ phase difference between the complex transition dipole moments $\mu_z, \mu_y$ which may be directly related to structural information about the initial/final states of an optical transition and their associated wave functions (31). From our fit, we extract an energy splitting $\Omega_1 = 1.61$ meV and an inter-triplet coherence time $T_2^{xy} = 1.36$ ps at 20 K.

**DISCUSSION**

It is quite unexpected that the optical dephasing rate $\gamma_T$ is so much faster than those of the other two triplet states $\gamma_x$ and $\gamma_y$. Although this disparity suggests a fundamentally different dephasing mechanism for coherences involving state $|\Psi_z\rangle$, photoluminescence of similar orthorhombic perovskite NCs that exhibit triplet state structure reveals similar emission linewidths for all three states of the manifold (6, 7). We resolve this discrepancy by proposing a unique exciton fine structure composed of a dark singlet state $|\Psi_d\rangle$ that lies above the states $|\Psi_x\rangle$ and $|\Psi_y\rangle$, which form the band edge, while remaining below the third triplet state $|\Psi_z\rangle$ (shown in Fig. 1B). Camargo et al. (24) have similarly applied MDCS to reveal dark states in a perovskite thin film, although the sub-gap defect states they observe are fundamentally different from the dark state discussed here, which arises from the lead-halide atomic orbitals and would exist in a perfect lattice. For our proposed level ordering, rapid relaxation from $|\Psi_d\rangle$ to $|\Psi_y\rangle$ then significantly decreases the population lifetime $T_2^{xy}$ and consequently $T_2^{xy}$ as well (21). Such a fine structure has been theoretically predicted in certain ranges of NC size due to competition between the Rashba effect and electron-hole exchange interaction (32). Although we cannot rule out alternative sources of line broadening, such as the imperfect correlation between the two inhomogeneously broadened transitions between the ground state and $|\Psi_x\rangle, |\Psi_y\rangle$ that would selectively broaden sidebands 4 and 5 in Fig. 2 (see the Supplementary Materials), our hypothesis is further supported by previous photoluminescence studies of CsPbI$_3$ NCs of nearly identical size (10). These incoherent spectra, which are not affected by inhomogeneous broadening correlation, revealed polarized doubles corresponding to $|\Psi_x\rangle$ and $|\Psi_y\rangle$ but did not detect the third triplet
state $|\Psi_3\rangle$ (whose emission would be quenched by nonradiative relaxation to $|\Psi_0\rangle$ according to our hypothesis of a partially bright triplet exciton band edge). In accordance with the predicted size dependence of the relative dark state energy (32), we also observe an abrupt increase in $\tau$ with increasing size position (see the Supplementary Materials), which results from a crossing in energy of $|\Psi_0\rangle$ and $|\Psi_3\rangle$. These results stand in stark contrast to recent studies of CsPbBr$_2$Cl (6) and FAPbBr$_3$ (7) NCs, which have reported the highest- and lowest-lying dark states, respectively. Evidently, a change in even a single constituent atom of the perovskite lattice may drastically alter the exchange and Rashba interaction coefficient ratio that determines the fine structure level ordering (32), which warrants future investigation.

To conclude, we have measured and characterized both optical frequency triplet coherences and terahertz frequency inter-triplet coherences. We have also presented evidence of an exciton band edge whose emission is partially quenched by an intermediate dark state, which contributes important insight into the controversial nature of exciton ground states in different perovskite NC materials (6, 7). As a material still in its infancy, perovskite NCs show promise for applications in optoelectronic devices. In particular, the minimal thermal broadening of inter-triplet coherences observed here motivates study of applications above cryogenic temperatures. For example, in a triple state analog of valleytronics in two-dimensional materials (19), superpositions of triplet states could be initialized and read out with linearly polarized light and coherently manipulated via terahertz radiation as information carriers (33).
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Author contributions: L.A.P. and S.T.C. conceived the concept. Supervised by A.F.N., L.G.B. synthesized the perovskite NC sample. G.N. and L.F.Z. acquired transmission electron microscopy images of the sample and characterized the NC size. A.L. and D.B.A. ran the experiments and acquired the data. A.L. analyzed the results and wrote the manuscript. All authors discussed the results and commented on the manuscript at all stages. 

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