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Phonon-Bottleneck Enhanced Exciton Emission in 2D Perovskites

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Layered halide perovskites exhibit remarkable optoelectronic properties and technological promise, driven by strongly bound excitons. The interplay of spin-orbit and exchange coupling creates a rich excitonic landscape, determining their optical signatures and exciton dynamics. Despite the dark excitonic ground state, surprisingly efficient emission from higher-energy bright states has puzzled the scientific community, sparking debates on relaxation mechanisms. Combining low-temperature magneto-optical measurements with sophisticated many-particle theory, the origin of the bright exciton emission in perovskites is elucidated by tracking the thermalization of dark and bright excitons under a magnetic field. The unexpectedly high emission is clearly attributed to a pronounced phonon-bottleneck effect, considerably slowing down the relaxation toward the energetically lowest dark states. It is demonstrated that this bottleneck can be tuned by manipulating the bright-dark energy splitting and optical phonon energies, offering valuable insights and strategies for controlling exciton emission in layered perovskite materials that is crucial for optoelectronics applications.

1. Introduction

Hybrid metal-halide perovskites represent a unique material system,^[1,2] bridging the electronic properties of epitaxial and organic semiconductors. They emerged as revolutionary materials for photovoltaics,^[3] before a plethora of other possible applications were proposed, from light emission^[4] to quantum optical

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technologies,[5,6] where perovskite nanostructures show particular promise.^[7-9] Both nanocrystals and two-dimensional (2D) layered perovskites are known for their superior emissive properties.^[9-11] Their quantum emission efficiency is one or two orders of magnitude higher than in epitaxial inorganic semiconductors, however the origin of this technologically important characteristic is still the subject of ongoing research and debate.[10-12]

The optical response of perovskites is governed by excitons exhibiting a characteristic fine structure comprising bright triplet and dark singlet states.^[10,11,13,14] Recent studies have shown that the dark state is situated several to tens of meV below the bright states.^[5,10,15,16] Despite this significant splitting, perovskites exhibit surprisingly intense photoluminescence (PL) emission even at cryogenic

temperatures^[9–11,17] making them very attractive for quantum technology. Moreover, in nanocrystals, intense emission is simultaneously observed for all bright states even though they are also separated by several meV.^[10,14] This emissive behavior indicates that the exciton population in perovskites does not follow Boltzmann statistics, however, the origin of this high bright-state occupation has remained elusive. Thus, an in-depth

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quantum mechanical modeling of exciton relaxation dynamics including the interplay of the exciton fine structure and scattering with phonons is required to fully exploit and design perovskites for light emission applications.

Here, we address this problem for an archetypical perovskite, (PEA)₂PbI₄, where PEA stands for phenylethylammonium. This 2D layered perovskite demonstrates significant splitting between the bright and dark states (≈20meV)^[15,16] which is off-resonant with optical phonon modes,^[18-22] indicating a possible bottleneck effect. Using a microscopic and material-specific many-particle theory, we explore the formation, relaxation and decay dynamics of excitons in this structure and show that the energy mismatch between the fine structure of exciton and phonons leads to a pronounced phonon-bottleneck effect. The consequence is an inefficient exciton relaxation to the energetically lowest dark state resulting in an enhanced non-thermal population of bright excitons, explaining the surprisingly high cryogenic PL emission. We find an excellent agreement between theoretical predictions and temperature-dependent magneto-optical spectroscopy measurements offering access to the dark exciton population. Our work provides a comprehensive microscopic picture of the phonon-bottleneck effect between bright and dark exciton states in the family of 2D perovskites, explaining why these materials exhibit strong emission at low temperatures despite their dark ground state.

2. Results

2.1. Exciton Energy Landscape

Strong spin-orbit coupling and exchange interaction in perovskite nanocrystals and 2D perovskites give rise to an exciton fine-structure comprised of a dark singlet and bright triplet states.^[11,13,14,23–25] Recent experimental studies have provided extensive characterization of exciton states, as well as their energy spacing in (PEA)₂PbI₄.^[15,16,26,27] In layered perovskites (see **Figure 1a**) the lowest energy dark state X_D is typically separated by $\approx 15 - 20$ meV from the two in-plane bright states X_+ and X_- and by another ≈ 1 meV from the out-of-plane polarized grey state X_Z . A schematic of the exciton state structure is presented in Figure 1b. We discuss the impact of different crystal phases in the Supporting Information.

We model the electron-hole interaction with the generalised Keldysh potential^[28] (all parameters can be found in Supporting Information). The energy landscape including the material-specific splitting has been determined microscopically by solving the Wannier equation^[29,30] before including the impact of the short- and long-range exchange interaction. Our model accurately recovers qualitatively and quantitatively all characteristic features of the exciton fine structure^[15,16,25,26,31] observed in the exemplary (PEA)₂PbI₄, a reliable basis for studying the excitonic relaxation dynamics.

A quantitative picture of the theoretically predicted (lines) and measured (dots) excitonic landscape can be seen in **Figure 2a**, which shows the spectral shift of the dark, bright and grey states as a function of the applied in-plane magnetic field (Voigt configuration). At zero field, we find a bright-dark splitting, Δ_{BD} , of 21 meV. The magnetic field lifts the degeneracy of the bright inplane states $X_{+/-}$ and changes their polarization from circularly





Figure 1. a) Crystal structure of the 2D perovskite (PEA)₂ PbI₄. b) Schematic of the exciton fine structure including bright (X_+, X_-) , gray (X_2) and dark exciton states (X_D) and their relaxation dynamics. In particular, the phonon-bottleneck is shown to hinder the scattering between bright and dark excitons.



Figure 2. a) Exciton fine-structure of the 2D perovskite (PEA)₂ PbI₄ as a function of in-plane magnetic field, calculated (lines) and measured (dots). The bright-dark splitting, Δ_{BD} , is shown with the arrow. As the magnetic field increases, the polarization of longitudinal (X_L) and dark (X_D), as well as the polarization of gray (X_Z) and transverse polarized (X_T) excitons mix. b,c) Absorption spectra at 30 K for B = 0 T and B = 50 T, respectively. The positions of exciton states are marked with thin vertical lines. Note that without a magnetic field, there are ciruclary polarized states (X_{\pm}) that become linearly polarized ($X_{L,T}$) due to mixing at $B \neq 0$.

to linearly polarized. The new in-plane states are now polarized parallel (longitudinal X_L) and perpendicular (transverse X_T) to the magnetic field. We perform magnetic field and polarization-dependent transmission measurements to experimentally determine the excitonic energy landscape. We find an excellent theory-experiment agreement for the magnetic field dependence of the exciton energy, see Figure 2 a.

The magnetic field mixes the dark X_D and the gray X_Z states with the superposition of the two bright in-plane states,[32] resulting in a partial transfer of the oscillator strength from X_{T} and X_{T} to X_D and X_Z states, respectively. To investigate this, we determine the optical absorption spectra (at 30 K) of (PEA)₂ PbI₄ by numerically evaluating the Elliot formula and second-order Born-Markov equation^[28,29,33] (see Supporting Information for more details). In the absence of a magnetic field (B = 0 T), only absorption related to the bright triplet states can be observed: two degenerate circularly polarized states or a grey state, see Figure 2b. For x-polarized absorption (red line in Figure 2b), signatures from the $X_{+/-}$ excitons are observed, while the gray exciton cannot be seen. On the other hand, for z-polarized light (green line) the gray state is visible, while the bright states are not. The enhanced broadening of the z-polarized emission comes from additional phonon scattering channels to the lower-lying bright excitons (see Figure 1b). The lowest energy spin-dark exciton X_D has a vanishing oscillator strength and cannot be seen, however it can be optically accessed in a magnetic field, see Figure 2c. Here, the dark state becomes visible and L- and T-polarized bright excitons are now clearly distinct. Due to its efficient mixing with the X_{I} state, the dark exciton can be only observed in the L-polarized absorption (orange line), whereas the gray exciton is only visible for T-polarized excitation (blue line) reflecting its mixing with the X_T state.

2.2. Phonon-Bottleneck Effect

Following optical excitation of the bright states, excitons thermalize via scattering within or between excitonic bands. Considering a clean sample in the low-excitation regime, exciton relaxation is driven by phonon-induced scattering. For most semiconductors, fast phonon-mediated scattering leads to a thermalized Boltzmann distribution.^[33,34] However, in systems where phonon-assisted scattering is prohibited due to inherent differences between the initial and final states (mismatch of angular momentum, energy or momentum), a non-thermal distribution can arise. In 2D perovskites, strong spin-orbit coupling in the conduction band mixes different states, facilitating scattering between excitons with opposite spin. Another possible origin for a non-thermal distribution is a mismatch between the energy of the initial and final states and the involved phonon energies. In the case of (PEA)₂PbI₄, it was observed that the excitonic transition is predominantly coupled to the optical phonon with the energy of \approx 35 meV^[18,19,22,29,35] that is significantly larger than the bright-dark splitting $\Delta_{BD} \approx 20$ meV (c.f. Figure 2a).

As a consequence, to scatter from the bright to the dark states, hot excitons need to be formed with considerable excess energy of at least 15 meV to compensate the energy difference between the bright-dark energy splitting $\Delta_{\rm BD}$ and the phonon energy $E_{\rm LO}$. Therefore, optically excited excitons in the light-cone first need to scatter up to higher-momenta states by absorption of acoustic phonons, see Figure 1b. This process is highly unlikely at cryogenic temperatures resulting in a phonon-bottleneck effect, i.e., exciton cannot scatter to the energetically lowest states and thus cannot build a thermal Boltzmann distribution. Note that while Figure 1b shows a typical initial exciton occupation centred at small momenta, the final exciton distribution is independent of the initial excitation conditions, as excitons get trapped when they reach the minimum of the bright exciton band.

To corroborate this explanation, we derive a coupled set of semiconductor Bloch equations describing the temporal evolution of the momentum-resolved exciton occupation $\hat{N}_n^Q(t)$ based on the Heisenberg equation of motion^[33] (see Experimental Section and Supporting Information for details). Here, *n* and *Q* denote the exciton state and its centre-of-mass momentum, respectively. This allows us to track the phonon-mediated relaxation cascade within the excitonic fine structure resolved in time and momentum. We include both acoustic and optical phonons^[29] to capture the relaxation dynamics. In the simulations presented here, we have assumed a pulsed excitation (initial population at time *t* = 0). In the SI, we also show calculations for a continously driven system and observe only small quantitative changes in the calculated exciton temperature.

A thermal equilibrium is obtained when the population of excitonic states becomes time-independent. To quantify the final distribution of excitons across the exchange-split states in 2D perovskites, we define an effective excitonic temperature, $T_{\rm exc}$, as obtained by rearranging the Boltzmann distribution $T_{\rm exc} = \frac{\Delta_{\rm BD}}{k_{\rm g}} \left[\ln \left(\frac{N_D}{N_+} \right) \right]^{-1}$. The excitonic temperature is determined by the ratio of N_D and N_+ corresponding to the exciton density of the dark and the bright exciton X_D and X_+ , respectively. Note that N_+ and N_- are degenerate and thus equally populated at thermal equilibrium without a magnetic field.

By definition, in the case of a Boltzmann distribution, the exciton temperature is equal to the lattice temperature (black line in **Figure 3**a). If excitons are trapped in the higher-energy state, X_{\perp} , then the effective exciton temperature will be larger than the lattice temperature reflecting the excess energy of hot excitons. To determine the excitonic temperature, we assume an initial excitation of the X_{\perp} bright state achieved by applying a circularly polarized laser pulse. We then calculate the time- and momentumresolved population dynamics of the four excitonic states by evaluating the semiconductor Bloch equations until the system is thermalized. In Figure 3a, the effective steady-state temperature of the bright exciton in the (PEA)₂PbI₄ is shown as a function of the lattice temperature *T*. For T > 110K, we find that the effective exciton temperature T_{exc} (orange line) coincides with the lattice temperature as determined by the Boltzmann distribution (black line). At lower temperatures, however, we show that $T_{\rm exc}$ clearly deviates from the lattice temperature, approaching a constant value of around 75 K even as $T \rightarrow 0K$. This signature is a clear indication of a phonon-bottleneck effect, as excitons cannot relax to the energetically lower state and thus exhibit an excess energy that makes them hotter than the lattice temperature. At higher temperatures, this bottleneck effect can be circumvented by the absorption of acoustic phonons lifting bright excitons to higher states and allowing them to scatter down to the dark state, see Figure 1b.





Figure 3. a) Effective steady-state temperature T_{exc} of the bright exciton as a function of the lattice temperature T. The shaded region indicates the phonon-bottleneck effect, i.e., T_{exc} higher than expected from a Boltzman distribution (black line). b) Experimentally obtained exciton temperatures for a pulsed (blue dots) and CW (green dots) excitation. c,d) Theoretical calculations of the temporal evolution of the exciton density at 120 and 20 K, respectively, following a resonant excitation of the bright exciton without a magnetic field. Dashed horizontal line in (c) and (d) shows the expected population of dark exciton assuming a Boltzmann distribution.

We directly compare our theoretical prediction to the experimentally obtained effective exciton temperature in Figure 3b. The latter is obtained by a detailed analysis of the PL response in presence of a magnetic field where dark exciton emission can be directly observed (see Supporting Information for details). The experimental results for pulsed and continuous wave (CW) excitation regime (blue and green points respectively), show a clear deviation from the expected thermal Boltzmann distribution for temperatures lower than 100 K - in excellent agreement with the presented calculation. As the lattice temperature approaches 90 K, we observe that the phonon-bottleneck effect vanishes and the effective exciton temperature goes toward the lattice temperature. This clearly supports the message of a thermally activated phonon-assisted relaxation circumventing the phonon-bottleneck at higher temperatures. Our experimental results show that the phonon-bottleneck is largely independent of the excitation scheme. We compare theoretical calculations of the CW and pulsed excitation regime in the Supporting Information and find a pronounced bottleneck in both cases.

To provide a better understanding of the origin of the phononbottleneck, we resolve the simulated population dynamics of different exciton species in Figure 3c,d at 120 and 20 K, respectively. The initial population of the optically excited X_+ exciton (blue line) begins to decay populating the dark (X_D) and gray (X_Z) states. We assume a weak excitation, such that the contribution of exciton–exciton scattering processes is small and can be neglected. There is no direct coupling between the bright states, as this transition would require the conduction and valence band spin to flip simultaneously,^[11] which is prohibited due to the absence of spin-orbit coupling in the valence band.^[11,36] Instead, excitons from the X_{\perp} state scatter first into the dark or the grey state, before the *X*_ state can be populated. This explains the delayed onset of the X_{-} population. Since the bright and grey state are almost energetically equivalent, their final populations are very similar. The dark state is much lower in energy and therefore is the most populated at any temperature. At T = 120 K, (Figure 3c), the relative steady-state population follows Boltzmann statistics, as seen from the intersection between the dashed Boltzmann line and the dark exciton population after the equilibrium has been reached. In Figure 3d., the 15 meV required to enable interband scattering between bright and dark states cannot easily be satisfied at 20 K, where the thermal energy $k_{\rm B}T \approx 6.5$ meV is too low. Therefore, the relaxation process slows down significantly and the quasi-thermal equilibrium is only reached after tens of ps. Note that exciton lifetimes in layered perovskites ($\approx 40 \text{ ps}^{[37]}$) are longer than the typical thermalization time even at 20 K. At such a low temperature, the entire excitonic population would effectively reside within the dark exciton band under Boltzmann statistics, as indicated by the dashed line in Figure 3d. However, in our dynamics simulations, we find the dark exciton population to be significantly lower and hence the population of optically active excitonic states is orders of magnitude larger than expected from a Boltzmann distribution.

To further strengthen the proposed picture of the pronounced phonon-bottleneck effect in (PEA), PbI, we show the experimental PL spectrum as a function of a magnetic field at 20 K - in direct comparison to our theoretical prediction after a stationary distribution has been reached. The magnetic field shifts the excitonic energy levels, but the quantitative effect is relatively small (≈ 1 -2 meV), and hence has little effect on the relaxation. Therefore, we do not observe a significant effect of the magnetic field on the phonon-bottleneck. We distinguish in theory two cases: taking into account the full exciton dynamics (Figure 4b) and assuming a Boltzmann distribution (Figure 4c). We fix the bright-dark splitting to about 9 meV as extracted from the PL spectra. The reduced splitting compared to the value found in the absorption spectra^[15] (Figure 2c) is likely to be due to disorder, which is characteristic for perovskites^[38,39] and polaronic effects.^[16,40] The presence of disorder gives rise to a red-shift of the bright exciton and can lead to a crystal distortion changing the crystal bond lengths and altering the exchange coupling that is responsible for the brightdark energy splitting. Importantly the observed discrepancy in this splitting does not contradict our theoretical predictions and experimental observations of the non-Boltzmann distribution of excitons. As long as the effective phonon energy is larger than the bright-dark exciton splitting, our theory predicts an enhanced temperature of the exciton population, cf. Figure 5. Our magnetooptical investigations also clearly point to a non-Boltzman distribution despite the reduced bright-dark splitting in PL.

In the experiment, we observe a transition of the dominant PL signal from the bright to the dark state at about B = 15 T. Note that a non-zero oscillator strength of the dark state is observed in the experimental PL at B = 0 T (Figure 4a; Figure S3, Supporting Information), which is attributed to crystal distortion and higher-order optical processes.^[13,15,25,42] As such the dark state is always slightly visible in experiments. Therefore, we add a non-zero optical matrix element for the dark state also in our simulations.



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Figure 4. a) Normalized experimental PL spectra as a function of magnetic field at T=40 K. Theoretically predicted steady-state PL considering the full exciton dynamics (b) and assuming a Boltzmann distribution (c). Dominant exciton resonances at zero magnetic field are indicated with dashed vertical lines.

As the magnetic field is increased, the mixing between the bright and dark states becomes more efficient, such that previously dark exciton gains a progressively larger bright exciton component even dominating the PL spectrum above a certain critical value of the magnetic field. In theory, this occurs at larger values considering the full dynamics (Figure 4b), whereas the dark state dominates already at zero field when assuming a Boltzmann distribution (Figure 4c). This is caused by the much larger



Figure 5. Demonstration of a raised effective exciton temperature as a function of the offset between the optical phonon energy (E_{LO}) and the dark-bright energy splitting (Δ_{BD}). For a vanishing offset, the exciton temperature matches the lattice temperature (dashed line). Examples of offsets measured in other materials are marked with vertical lines including CsPbI₃ nanocrystal (NC),^[5,41] FAPbBr₃ NC,^[10] (PEA)SnI₄,^[15] and (PEA)PbI₄ (this work).

population of the energetically lowest dark exciton provided that there is no phonon-bottleneck. The situation is different when considering the full dynamics, where excitons are trapped in the bright state and cannot scatter further down to the dark exciton, see Figure 3. The interplay between the relative population of bright and dark excitons and the brightening of the dark exciton in the presence of a magnetic field determines which exciton dominates the PL. The theoretical prediction of a transition from the bright to the dark-exciton-dominated PL agrees well with the experiment and is yet further evidence of a phonon-bottleneck effect. Considering a fully thermalized Boltzmann distribution, there is no such transition, as shown in Figure 4c. The quantitative discrepancy between experiment and theory for the critical magnetic field value can be in part attributed to the higher effective exciton temperature predicted by the theory. The latter slightly overestimates the bright exciton population possibly due to small, temperature-dependent changes in the phonon dispersion or excitonic structure not accounted for in our model.

For a given perovskite, the difference between the bright-dark energy splitting Δ_{BD} and the optical phonon energy determines whether and at which temperature the bottleneck occurs. If there exists a phonon mode which couples to these excitons with an energy smaller than or resonant to Δ_{BD} , the bottleneck will not occur. In Figure 5, we show the effective exciton temperature as a function of the energy difference between the dominant longitudinal optical mode (E_{10}) and the dark-bright exciton splitting Δ_{BD} for 100 K (green line) and 20 K (blue line). We find that for $(E_{\rm LO} - \Delta_{\rm BD}) \rightarrow 0$ the exciton temperature converges to the lattice temperature, as expected from a Boltzmann distribution. In contrast, as this energy difference increases, the effective exciton temperature grows larger demonstrating the existence of a phonon-bottleneck. We find the onset of this bottleneck to shift to lower Δ_{BD} the smaller the temperature is, as it becomes more difficult to overcome the energy offset with the thermal energy.

3. Discussion

We have explored exciton optics and dynamics in 2D perovskites, combining a sophisticated microscopic theory with cryogenic magneto-optical spectroscopy measurements. We determined the exciton fine-structure and the brightening of dark excitons in magneto-PL measurements. Contrary to previous studies focused on the relaxation of carriers and excitons from high energy bands to the minimum of bright exciton band^[43,44] here we track the relaxation dynamics between the lowest energy dark and bright states having the dominant impact on the exerimentally accessible time-averaged emission. The exciton dynamics revealed from our simulations corroborate, both qualitatively and quantitatively, the experimentally observed time-averaged PL response, showing how a mismatch between the phonon energy and the splitting between bright and dark states gives rise to a pronounced phonon-bottleneck effect. This explains the observed unexpectedly strong emission of layered perovskites at low temperatures despite the dark ground state. The phonon-mode dictating the phonon-bottleneck originates is related to organic spacers.^[45,46] Therefore, we predict that the chemical engineering of the organic spacer^[47] can close or open the bottleneck. Overall, our joint theory-experiment study sheds new light on the population dynamics and optical response of layered perovskites,

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crucial for optimizing the performance of perovskite-based devices.

4. Experimental Section

Exciton Fine-Structure: To model the optics and dynamics of excitons in layered perovskites, the Wannier equation^[28] was first evaluated to derive the exciton binding energies and wavefunctions, taking into account screening from the lead-halide layer itself and from the organic spacer layers. More details could be found in the Supporting Information, including the form and parametrization^[29,48] of this interaction. The study was restricted to 1s excitons, since the 1s-2s separation was very large (\approx 180 meV) compared to the exciton fine-structure including dark, bright and gray states. The 1s binding energy was determined to be 230 meV,[18,48] which was in good agreement with previous studies. While a monolayer perovskite is assumed, stacking additional layers had little effect on the band structure, owing to the separation introduced by the organic spacer layer.^[49] The reduction in the excitonic binding energy from monolayer to bulk stems from the increased screening and was on the order of 10-20%,^[35] which was much smaller than the monolayer-bulk comparison in other layered semiconductors, such as TMDs^[50] exhibiting a reduction of up to 90%. The results were therefore valid for a larger number of perovskite layers, with increased screening reducing the exchange interaction, further enhancing the mismatch with the optical phonon energy and enhancing the bottleneck.

The exciton fine-structure was determined by both the spin-orbit coupling and the exchange interaction. In layered perovskites, the spin orbit coupling lead to a mixing of the orbital composition of the lowest conduction band,^[11] which became a linear combination of *p*-orbitals. In contrast, there was no mixing of the valence band s orbitals. An expression for the exchange interaction in the excitonic basis was derived, taking into account the spin-orbit coupling in the conduction band. Details and the derivation can be found in the Supporting Information.

Exciton Optics: The absorption spectra of the perovskite monolayer could be calculated using the Elliot formula^[28] where the absorption was described by a series of Lorentzian peaks centred at the exciton resonances which took into account both the radiative and non-radiative broadening. The absorption was calculated for σ -polarized light. The magnitude of the absorption signal was primarily determined by the optical matrix element. By taking into account the exchange interaction, the optical matrix elements and hence optical polarization of the excitonic states could be determined. The time-resolved photoluminescence could also be described using an Elliot formula, only now it was also proportional to the time-resolved occupation of the excitonic states, as detailed further in the Supporting Information.

Phonon-Driven Exciton Dynamics: A series of semiconductor Bloch equations was derived to capture the time evolution of the excitonic populations,^[28,33] following optical excitation of the bright state X_+ . The Heisenberg equation of motion, $i\hbar\partial_t N_{\mathbf{Q}}^n = \left\langle [N_{\mathbf{Q}}^n, \hat{\mathbf{H}}_X] \right\rangle$ was employed to derive these equations. The second-order Born-Markov approximation^[28] was applied to truncate the equations to the most important terms, taking into account the exciton-phonon interaction. Both the emission and absorption of optical and acoustic phonons was considered, allowing excitons to thermalize both in momentum and between excitonic bands. The optical phonons were particularly crucial in driving the exciton relaxation, owing to the strict momentum and energy conservation for the scattering processes. A detailed description was provided in the Supporting Information. Due to the strong spin-orbit coupling in these materials, the conduction band spin could be flipped in an exciton-phonon scattering event. For 2D perovskites, this process was necessary to enable phonon-scattering between the bright and dark/gray excitons.

Optical Spectroscopy: The photoluminescence was excited with a continuous wave laser emitting at 407 nm or second harmonic of pulsed fs-Ti: sapphire laser (450 nm, ~150fs pulse duration). The sample was mounted inside a helium cryostat placed in a nitrogen-cooled pulsed magnet, providing a maximum field of 68 T with a pulse duration of 500 ms. The measurements were performed in the Voigt configuration, with the **c**-axis of the sample perpendicular to the magnetic field and parallel to the ${\bf k}$ vector of the exciting laser. Linear polarization was resolved in situ using a broadband polarizer.

Sample Fabrication: Glass substrates were ultrasonically cleaned sequentially using detergent solution, deionized water, acetone, and isopropanol. Subsequently, the substrates were dried in an oven $T = 140 \degree C$ for ≥ 10 min before treatment with ultraviolet ozone for 20 min. Immediately after cleaning, the substrates were placed in a nitrogen-filled glove box for film deposition. A stoichiometric precursor solution was used, prepared by dissolving PEA (Phenethylammonium iodide, 98.0% TCI) and PbI2 at a molar ratio of 2:1 in a mixed solvent of N,N'- dimethylformamide and dimethyl sulfoxide (4:1 volume ratio, 0.5 M concentration). To homogenize the solutions, they were stirred for at least 3 h at room temperature before deposition. A spin-coating process with antisolvent treatment was used to deposit the precursor solution onto the cleaned substrates. A rotation speed of 2000 rpm was used for the first 10 s of the spin-coating process. The speed was then accelerated to 8000 rpm for the remaining 30 s. Five seconds before the end of the spin-coating cycle, the antisolvent (chlorobenzene) was added to the substrate. The films were immediately annealed at 100 °C in a nitrogen atmosphere for 10 min.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

exciton dynamics, excitons, layered perovskite, phonons

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Supporting Information

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Phonon-Bottleneck Enhanced Exciton Emission in 2D Perovskites

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Supporting Information: Phonon-bottleneck enhanced exciton emission in 2D perovskites

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I. ORHTORHOMBIC VS TRICLINIC STRUCTURE

In perovskites, crystal distortion can lead to the material adopting a triclinic rather than orthorhombic phase, leading to a symmetry breaking. The latter is due to small differences in the perovskite crystal lattice in the x and y direction [1–3]. As a result, the exchange interaction along x and y is slightly modified, leading to a distinct optical response, cf. Fig. S1. We find an energy splitting between the x- and y-polarised absorption peaks in the bluetriclinic phase (Fig. S1b) corresponding to distinct excitonic states. This splitting has little effect on the exciton dynamics and optics in perovskite monolayers, as the bright-dark splitting is an order of magnitude larger [4], and more pronounced effects can be generated with a magnetic field. Therefore in the main text, we neglected the in-plane exciton states splitting seen in some samples [2, 3].



Figure S1: Absorption spectra for an (a) orthorhombic and (b) triclinic perovskite monolayer at 30 K for different polarisations.

II. PULSED VS CONTINUOUS WAVE EXCITATION

In this section, we compare the onset of the phonon-bottleneck for a continuous-wave (CW) and a pulsed excitation (as presented in the main text).

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Figure S2: Effective steady-state temperature T_{exc} of the exciton population as a function of the lattice temperature T. The X_+ exciton is initially driven by (a) pulsed excitation (as in the main manuscript) or (b) CW excitation. The shaded region indicates the phonon-bottleneck effect, i.e. T_{exc} higher than expected from a Boltzman distribution (black line). (c) Experimental results for CW excitation with linear extrapolation at low and higher temperatures, where a measurement was not possible (dashed blue).

In Figure S2, we show the calculated exciton temperature, assuming the X_+ exciton is either driven (a) with a pump pulse before t = 0 (a) or (b) with a CW excitation. The two figures are qualitatively the same, and display only small quantitative differences, namely that we predict a slightly larger exciton temperature in the CW case (81 K compared to 78 K at T=0 K). This leads to a larger bottleneck region, starting at a lattice temperature of 135 K in the CW case compared to 120 K in the pulsed case. This is because the excitation continuously repopulates the X_+ band in the CW case leading to a perceived larger exciton temperature. In general, we find that the CW exciton temperature is between 1 and 3 K higher in the bottleneck region owing to this continuous driving.

III. EXPERIMENTAL ANALYSIS

To experimentally determine the effective temperature of the exciton population, we compare the PL emission intensity of the dark exciton state (brightened with a magnetic field) to the one of the bright exciton. To do this we first identify the origin of the individual PL peaks in PL spectra based on their behaviour in a magnetic field as shown in Fig S3. At zero-magnetic-field (violet line) the PL spectrum is composed of two well-defined peaks i.e. BX emission on the high energy side and traps [5, 6] or polaronic-like emission [3, 7] on the lower energy side.

With the increasing magnetic field two additional signals emerge, i.e. the DX and (probably)



Figure S3: PL spectra of $(PEA)_2PbI_4$ measured in the external magnetic field in Voigt geometry with CW excitation

its phonon replica labeled DX'. Importantly at 0 T the intensity of BX PL emission can be reliably determined whereas at 60 T the DX dominates the spectra. This allows for precise determination of DX occupation as we show further.

To support the common origin of both X_D and X_B emission lines in Fig. S4 we present the temperature evolution of dark exciton (X_D , measured at B = 60 T, Fig. S4a) and bright exciton (X_B , measured at B = 0 T, Fig. S4b). Both these emissions blueshift with increasing temperature.



Figure S4: The photoluminescence of (a) dark exciton and (b) bright exciton measured for different sample temperatures. The spectra in panel (a) measured at B = 60 T. In panel (c) the peak energy of both emissions is presented.

The temperature-induced blueshift is similar for both emissions as presented in Fig. S4c.

To determine the PL intensity of the dark (X_D) and the bright (X_B) exciton, the PL spectra are fitted with a Gaussian-profiled lineshape. In Fig. S5 and Fig. S6 the result of such a fitting procedure is presented with the data measured at T=20 K and 2 K under CW and pulsed excitation conditions, respectively, and several magnetic field strengths. The black points represent the experimental data, whereas the fitting components are plotted with lines. We begin the intensity analysis by fitting the zero-magnetic-field spectrum presented in Fig. S5. The spectrum is composed of two well-defined peaks i.e. BX emission (blue) and trapping-states/polaronic-like emission (short-dot gray), according to the current literature [3, 5-7]. To account for a broadband background observed in CW excitation we accommodate a third flat and broad peak (dashed gray in Fig. S5), whose intensity and energy are kept constant throughout the whole magnetic field range. With the increasing magnetic field (5 - 60 T panels in Fig. S5) two additional signals are included, i.e. the DX (black solid) and its replica (gray dash-dot). The validity of our fits is supported by the energy dependence of bright and dark exciton states as shown in Fig. S7. We obtain a very good agreement with absorption measurements [4] despite the lower bright-dark splitting, which we ascribe to disorder in the investigated material and the tendency of the PL to probe the tail in the density of state.

The effective temperature of exciton population was determined based on the ratio of the dark to bright exciton population (as described in the manuscript) N_D/N_+ :

$$T_{exc} = \frac{\Delta_{BD}}{k_B} \left(\ln \left(\frac{N_D}{N_+} \right) \right) \tag{1}$$

The ratio of the two populations was extracted by the comparison of the PL intensity of the bright state at 0 T to the PL intensity of the dark state at 60 T, taking into account the difference in the oscillator strength. According to previous work [4], the dark state gains around 10% of the bright state oscillator strength at 60 T. The intensity of the PL related to a given excitonic transition is a product of the state occupation N and the oscillator strength f, i.e. $I_{PL} = fN$. As a result, the occupation ratio reads:

$$\frac{N_D}{N_+} = 10 \frac{I_D^{PL}(60T)}{I_+^{PL}(0T)}$$
(2)

We use the dark exciton emission from the maximum magnetic field since it is the most intense and the determination of its intensity is most robust.



Figure S5: Photoluminescence (PL) spectra (data points) measured at different magnetic fields, under the CW excitation (T=20 K). To reproduce the PL spectra in the whole range of magnetic fields five Gaussian-profiled components were used. Blue and dark solid lines represent X_B and

 X_D emissions, respectively. The dotted gray line describes the localized/polaronic emission[3, 5–7]. Dash-dotted gray contribution behaves similarly to X_D in the magnetic field and thus is understood as a phonon replica. An additional component (dashed gray) mitigates the

broad background. Inset shows the non-zero X_D contribution at 0 T



Figure S6: Photoluminescence (PL) spectra (data points) measured at different magnetic fields (T=2 K) under the pulsed excitation. To reproduce the PL spectra in the whole range of magnetic fields four Gaussian-profiled components were used. Blue and dark solid lines represent X_B and

 X_D emissions, respectively. The dotted gray line describes the localized/polaronic emission [3, 5–7]. Dash-dotted gray contribution behaves similarly to X_D in the magnetic field and thus is understood as a phonon replica.



Figure S7: Magnetic field dependence of bright (BX) and dark (DX) exciton states extracted from pulsed-excited PL spectra and theoretical curves (solid lines) predicting the magnetic-field dependence of BX and DX [4].

IV. THEORETICAL MODEL

A. Wannier Equation

To have a microscopic access to excitonic binding energies, ϵ_{η}^{b} and wavefunctions, φ_{k}^{η} , we evaluate the Wannier equation [8, 9]

$$\left(\frac{\hbar^2 k^2}{2\mu_r} + E_{\text{Gap}}\right) \varphi_k^{\eta} + \sum_{k'} V_{\text{Kel}}^{kk'} \varphi_{k'}^{\eta} = \epsilon_{\eta}^{\mathsf{b}} \varphi_k^{\eta}$$
(3)

where E_{Gap} is the electronic band gap, \boldsymbol{k} the relative momentum, $V_{\text{Kel}}^{\boldsymbol{k}\boldsymbol{k}'}$ the Fourier transform of the 2D Keldysh potential [10], the reduced mass $\mu_r = \left(\frac{1}{m_e} + \frac{1}{m_h}\right)^{-1}$, and the centre-of-mass mass $M = m_e + m_h$ with $m_e = 0.19m_0$ and $m_h = 0.25m_0$ as the electron and hole effective mass, respectively (with input parameters obtained from a previous joint DFT/experiment study [11]). Finally, the 2D Keldysh potential is defined as $V_{\text{Kel}}^{\boldsymbol{k}\boldsymbol{k}+\boldsymbol{q}} = e_0^2 \left(2\varepsilon_0\varepsilon_s L^2|\boldsymbol{q}| \left(1 + \frac{d_P\varepsilon_P}{2\varepsilon_s}|\boldsymbol{q}|\right)\right)^{-1}$ with $\varepsilon_s = 3.3$ and $\varepsilon_P = 6.1$ as the dielectric constant of the organic spacer layer and perovskite slab, respectively [9, 12], while $d_P = 0.636$ is the thickness of the perovskite layer.

B. Exchange matrix element

The exchange Hamiltonian can be written in second quantisation as

$$\hat{H}_{ex} = \sum_{\substack{k_1k_2k_3k_4\\s_1,s_2,s_3,s_4}} I_{k_1k_2k_3k_4}^{s_1s_2s_3s_4} \hat{c}_{k_1s_1}^{\dagger} \hat{v}_{k_2s_2}^{\dagger} \hat{c}_{k_3s_3} \hat{v}_{k_4s_4}$$
(4)

where $\hat{a}^{(\dagger)}$ are annihilation (creation) operators in the conduction ($\hat{a} = \hat{c}$) and valence ($\hat{a} = \hat{v}$) bands. The interaction strength $I^{s_1s_2s_3s_4}_{k_1k_2k_3k_4} = \int dr dr' \psi^{\dagger c}_{k_1s_1}(r) \psi^{\dagger v}_{k_2s_2}(r') V(r-r') \psi^{v}_{k_4s_4}(r) \psi^{c}_{k_3s_3}(r')$ we be expressed in terms of Bloch functions in the 2D case

$$I_{k_{1}k_{2}k_{3}k_{4}}^{s_{1}s_{2}s_{3}s_{4}} = \int dr dr' e^{-ik_{1}r} u_{k_{1}s_{1}}^{c*}(r) e^{-ik_{2}r'} u_{k_{2}s_{2}}^{v*}(r') V(r-r') e^{ik_{4}r} u_{k_{4}s_{4}}^{v*}(r) e^{ik_{3}r'} u_{k_{3}s_{3}}^{c*}(r').$$
(5)

From here we perform Fourier transform of the Coulomb potential for a slab of a thickness d and find

$$I_{k_{1}k_{2}k_{3}k_{4}}^{s_{1}s_{2}s_{3}s_{4}} = \int dr dr' \int_{-d/2}^{d/2} dz dz' \sum_{\boldsymbol{q}_{||}} V_{2\mathrm{D}}(\boldsymbol{q}_{||}) e^{i\boldsymbol{q}_{||}(\boldsymbol{r}-\boldsymbol{r'})} e^{-|\boldsymbol{q}_{||}||\boldsymbol{z}-\boldsymbol{z'}|}$$
(6)

$$e^{-i\mathbf{k_1}\mathbf{r}}u^{c*}_{\mathbf{k_1}s_1}(\mathbf{r})e^{-i\mathbf{k_2}\mathbf{r'}}u^{v*}_{\mathbf{k_2}s_2}(\mathbf{r'})e^{i\mathbf{k_4}\mathbf{r}}u^{v*}_{\mathbf{k_4}s_4}(\mathbf{r})e^{i\mathbf{k_3}\mathbf{r'}}u^{c*}_{\mathbf{k_3}s_3}(\mathbf{r'}).$$
(7)

The orbital wavefunctions can be be decomposed into their individual contributions, determined by the spin-orbit coupling. The latter leads to a mixing of the orbital composition of the lowest conduction band [13] with momentum k, spin s and orbital P_i

$$|s, c, k\rangle = a_z \sigma_s |P_z, s, k\rangle + a_x |P_x, \overline{s}, k\rangle + i a_y \sigma_s |P_y, \overline{s}, k\rangle,$$
(8)

where $\sigma = \pm 1$ denotes the up/down spin, respectively. Here a_i determines the contribution of the orbital P_i to the valence band. Equal weighting of the P_x , P_y and P_z orbitals corresponds to a perovskite with cubic symmetry ($a_x = a_y = a_z = \frac{1}{\sqrt{3}}$). In the orthorhombic phase the weightings differ [14], however the contributing orbitals remain the same. In particular, $a_x = a_y = \cos \theta$ and $a_z = \sin \theta$ where θ is a material specific parameter. There is no mixing of the valence band S orbitals in any phase. As a result we arrive at the following integral

$$\begin{split} I_{\mathbf{k}_{3}\mathbf{k}_{4}}^{s_{1}s_{2}s_{3}s_{4}} &= \sum_{\mathbf{q}} V_{2\mathrm{D}}(\mathbf{q}) \sum_{\mathbf{G}} \delta_{\mathbf{k}_{4}-\mathbf{k}_{1}+\mathbf{q},G} \delta_{\mathbf{k}_{3}-\mathbf{k}_{2}-\mathbf{q},-G} \int_{-d/2}^{d/2} dz dz' e^{-|\mathbf{q}||z-z'|} \\ &\times \int_{\mathrm{UC}} dr \left[a_{z}\sigma_{s_{1}} \left\langle P_{z},s_{1},\mathbf{k}_{4}+\mathbf{q}-\mathbf{G}\right| - a_{x} \left\langle P_{x},\overline{s}_{1},\mathbf{k}_{4}+\mathbf{q}-\mathbf{G}\right| + ia_{y}\sigma_{s_{1}} \left\langle P_{y},\overline{s}_{1},\mathbf{k}_{4}+\mathbf{q}-\mathbf{G}\right| \right] \\ &\times e^{i\mathbf{G}\mathbf{r}} \left| S,s_{4},\mathbf{k}_{4} \right\rangle \\ &\times \int_{\mathrm{UC}} dr' \left\langle S,s_{2},\mathbf{k}_{3}-\mathbf{q}+\mathbf{G}\right| e^{-i\mathbf{G}\mathbf{r}'} \\ &\times \left[a_{z}\sigma_{s_{3}} \left| P_{z},s_{3},\mathbf{k}_{3} \right\rangle - a_{x} \left| P_{x},\overline{s}_{3},\mathbf{k}_{3} \right\rangle - ia_{y}\sigma_{s_{3}} \left| P_{y},\overline{s}_{3},\mathbf{k}_{3} \right\rangle \right]. \end{split}$$

There are two types of interactions that need to be calculated: the long-range interaction with G = 0 and the short-range interaction with $G \neq 0$. Furthermore, since only the wavefunction overlap of same-spin states is non-zero, we can split the above integral into two further parts: those that couple along z, and those that couple in the perovskite plane (x and y). In the electronic picture we arrive at the following expression

$$\begin{aligned} H_{\text{ex-el}} &= \sum_{\substack{\boldsymbol{k_3}\boldsymbol{k_4}\boldsymbol{q}\\s_1,s_2,s_3,s_4}} \left[\sum_{\boldsymbol{G}\neq\boldsymbol{0}} V_{2\text{D}}(\boldsymbol{G}) (\delta_{\overline{s_1},s_4} \delta_{\overline{s_3},s_2} \Gamma_{s_1,s_3}^{\text{SR}}(\boldsymbol{G}) + \sigma_{s_1} \sigma_{s_3} \delta_{s_1,s_4} \delta_{s_3,s_2} \Lambda_{a,d,\text{SR}}^{k_3,k_4}(\boldsymbol{G})) \right. \\ &+ V_{2\text{D}}(\boldsymbol{q}) (\delta_{\overline{s_1},s_4} \delta_{\overline{s_3},s_2} \Gamma_{s_1,s_3}^{\text{LR}}(\boldsymbol{q}) + \sigma_{s_1} \sigma_{s_3} \delta_{s_1,s_4} \delta_{s_3,s_2} \Lambda_{\text{LR}}^{k_3,k_4}(\boldsymbol{q})) \right] \\ &\times \hat{c}_{\boldsymbol{k_4}+\boldsymbol{q}s_1}^{\dagger} \hat{v}_{\boldsymbol{k_3}-\boldsymbol{q}s_2}^{\dagger} \hat{c}_{\boldsymbol{k_3}s_3} \hat{v}_{\boldsymbol{k_4}s_4} + h.c. \end{aligned}$$

Here, the first line corresponds to the short-range interaction (reciprocal lattice vector $G \neq 0$) parametrised by the coupling of the same-spin conduction-band P_z -orbitals with valence-band sorbitals $\Lambda_{SR}^{k_3,k_4}(\boldsymbol{G})$ and the coupling of opposite-spin conduction-band $P_{x/y}$ -orbitals with valenceband S-orbitals $\Gamma_{SR}^{k_3,k_4}(\boldsymbol{G})$. The second line corresponds to the long-range interaction, corresponding to small momentum transfer within the first Brillouin zone, and parameterised in the same way by $\Lambda_{LR}^{k_3,k_4}(\boldsymbol{q})$ and $\Gamma_{LR}^{k_3,k_4}(\boldsymbol{q})$. The spin conservation is described with the Kronecker deltas δ_{s_a,s_b} . The weightings a_z and $a_{x,y}$ have been absorbed into Λ and Γ , respectively.

Using the solution to the Wannier equation, we transform this Hamiltonian into the excitonic basis, with exciton annihilation (creation) operators $\hat{X}_{q}^{\nu,s_{a},s_{b}(\dagger)}$

$$\begin{split} H_{\text{ex-X}} &= \sum_{\substack{\boldsymbol{k}_{3}\boldsymbol{k}_{4}\boldsymbol{q}\\s_{1},s_{2},s_{3},s_{4}}} \left[\sum_{\boldsymbol{G}\neq\boldsymbol{0}} V_{2\text{D}}(\boldsymbol{G}) (\delta_{\overline{s_{1}},s_{4}} \delta_{\overline{s_{3}},s_{2}} \Gamma_{s_{1},s_{3}}^{\text{SR}}(\boldsymbol{G}) + \sigma_{s_{1}} \sigma_{s_{3}} \delta_{s_{1},s_{4}} \delta_{s_{3},s_{2}} \Lambda_{\text{SR}}^{k_{3},k_{4}}(\boldsymbol{G})) \\ &+ V_{2\text{D}}(\boldsymbol{q}) (\delta_{\overline{s_{1}},s_{4}} \delta_{\overline{s_{3}},s_{2}} \Gamma_{s_{1},s_{3}}^{\text{LR}}(\boldsymbol{q}) + \sigma_{s_{1}} \sigma_{s_{3}} \delta_{s_{1},s_{4}} \delta_{s_{3},s_{2}} \Lambda_{\text{LR}}^{k_{3},k_{4}}(\boldsymbol{G})) \right] \\ &\times \sum_{\mu\nu} \varphi_{\boldsymbol{k}_{4}+\beta\boldsymbol{q}}^{\nu} \varphi_{\boldsymbol{k}_{3}-\alpha\boldsymbol{q}}^{\mu*} \hat{\boldsymbol{X}}_{\boldsymbol{q}}^{\nu,s_{1},s_{4}\dagger} \hat{\boldsymbol{X}}_{\boldsymbol{q}}^{\mu,s_{3},s_{2}}. \end{split}$$

In order to derive the exciton fine-structure, we note that we transform the Hamiltonian into a new spin-hybridised basis. Assuming only the lowest energy excitons are relevant $\mu = \nu = 1s$ we write

$$\hat{X}_{q}^{s_{1},s_{4}} = \sum_{n} D_{q}^{s_{1},s_{4},n,*} \hat{Y}_{q}^{n},$$
(9)

such that we only have to solve the eigenvalue equation

$$|\varphi(\boldsymbol{r}=0)|^{2} \begin{pmatrix} I_{Z} & 0 & 0 & -I_{Z} \\ 0 & I_{r}^{s_{1}=\uparrow,s_{3}=\uparrow} & I_{r}^{s_{1}=\downarrow,s_{3}=\uparrow} & 0 \\ 0 & I_{r}^{s_{1}=\uparrow,s_{3}=\downarrow} & I_{r}^{s_{1}=\downarrow,s_{3}=\downarrow} & 0 \\ -I_{Z} & 0 & 0 & I_{Z} \end{pmatrix} \begin{pmatrix} D_{\boldsymbol{q}}^{\uparrow,\uparrow,n} \\ D_{\boldsymbol{q}}^{\uparrow,\downarrow,n} \\ D_{\boldsymbol{q}}^{\downarrow,\uparrow,n} \\ D_{\boldsymbol{q}}^{\downarrow,\downarrow,n} \end{pmatrix} = E_{\boldsymbol{q}}^{n} \begin{pmatrix} D_{\boldsymbol{q}}^{\uparrow,\uparrow,n} \\ D_{\boldsymbol{q}}^{\uparrow,\downarrow,n} \\ D_{\boldsymbol{q}}^{\downarrow,\uparrow,n} \\ D_{\boldsymbol{q}}^{\downarrow,\downarrow,n} \end{pmatrix}$$
(10)

where we define the entries as

$$\begin{split} I_{Z}(\boldsymbol{q}) &= V_{2\mathrm{D}}(\boldsymbol{q})\Lambda_{\mathrm{LR}}(\boldsymbol{q}) + \sum_{\boldsymbol{G}\neq 0} V_{2\mathrm{D}}(\boldsymbol{G})\Lambda_{\mathrm{SR}}(\boldsymbol{G}))\\ I_{r}^{ss'}(\boldsymbol{q}) &= V_{2\mathrm{D}}(\boldsymbol{q})\Gamma_{s,s'}^{\mathrm{LR}}(\boldsymbol{q}) + \sum_{\boldsymbol{G}\neq 0} V_{2\mathrm{D}}(\boldsymbol{G})\Gamma_{s,s'}^{\mathrm{SR}}(\boldsymbol{G}). \end{split}$$

In the orthorhombic phase, with D_{4h} symmetry $I_r^{s_1=\uparrow,s_3=\uparrow} = I_r^{s_1=\downarrow,s_3=\downarrow}$ and off digaonal terms $I_r^{s_1=\downarrow,s_3=\uparrow}$ and $I_r^{s_1=\uparrow,s_3=\downarrow}$ vanish. Important to note is the the first terms in these equations, corresponding to the long-range interaction, vanish at q = 0, which is consistent with previous calculations. The q-dependence, however, shifts the excitonic dispersion from a parabolic towards a more

linear branch. However, due to screening at large q, the effect is only visible at small q [15, 16], and has little effect on the exciton dynamics. The resulting excitonic energy levels are then

$$\begin{split} E_{\boldsymbol{q}}^{n=0} &= \frac{\hbar^2 \boldsymbol{q}^2}{2M} + \epsilon_{1s}^{\rm b}, \\ E_{\boldsymbol{q}}^{n=1} &= 2|\varphi(\boldsymbol{r}=0)|^2 I_Z(\boldsymbol{q}) + \frac{\hbar^2 \boldsymbol{q}^2}{2M} + \epsilon_{1s}^{\rm b}, \\ E_{\boldsymbol{q}}^{n=2} &= |\varphi(\boldsymbol{r}=0)|^2 I_r^{\uparrow\uparrow}(\boldsymbol{q}) + \frac{\hbar^2 \boldsymbol{q}^2}{2M} + \epsilon_{1s}^{\rm b}, \\ E_{\boldsymbol{q}}^{n=3} &= |\varphi(\boldsymbol{r}=0)|^2 I_r^{\uparrow\uparrow}(\boldsymbol{q}) + \frac{\hbar^2 \boldsymbol{q}^2}{2M} + \epsilon_{1s}^{\rm b}. \end{split}$$

In the case of a triclinic crystal, the off-diagonal terms $I_r^{s_1=\uparrow,s_3=\downarrow}$ and $I_r^{s_1=\downarrow,s_3=\uparrow}$ are also non-zero. However, in real systems the asymmetry is small (< 1%) [1] and hence only leads to a small splitting between the resulting eigenstates and does not profoundly change the emergence of a phonon-bottleneck. The splitting is typically of the order of 1-2 meV [3]. The parameterisation of this Hamiltonian is challenging since the short-range terms include an infinite summation, however it is possible to use either DFT [15] or experimental comparison [17] to estimate these parameters. The weightings a_i and the different screening in the in-plane vs out-of-plane directions will dictate the different magnitude of these summations. We fit these to experimental results on the orthorhombic phase and hence obtain an energy-splitting between the bright and gray states.

We include the in-plane magnetic field, B, focusing only on the 1s state

$$H_{X-\text{Mag}} = \sum_{q} \sum_{s_1, s_2, s_3, s_4} \left(g_{\text{mag}}^c \delta_{\overline{s_1}, s_3} \delta_{s_2, s_4} - g_{\text{mag}}^v \delta_{s_1, s_3} \delta_{\overline{s_2}, s_4} \right) X_q^{s_1 s_4 \dagger} X_q^{s_3 s_2}$$
(11)

such that $g_{\text{mag}}^{c/v}(B) = g^{c/v} \frac{\mu_B B}{2}$, where $g^{c/v}$ are the g-factors in the excitonic basis. The exchange eigenproblem in this case becomes modified, with extra terms coupling single-spin flips

$$\begin{pmatrix} I_Z & -g_{\text{mag}}^v(B) & g_{\text{mag}}^c(B) & -I_Z \\ -g_{\text{mag}}^v(B) & I_r^{s_1=\uparrow,s_3=\uparrow} & I_r^{s_1=\downarrow,s_3=\uparrow} & g_{\text{mag}}^c(B) \\ g_{\text{mag}}^c(B) & I_r^{s_1=\uparrow,s_3=\downarrow} & I_r^{s_1=\uparrow,s_3=\uparrow} & -g_{\text{mag}}^v(B) \\ -I_Z & g_{\text{mag}}^c(B) & -g_{\text{mag}}^v(B) & I_Z \end{pmatrix} \begin{pmatrix} D_q^{\uparrow,\uparrow,n}(B) \\ D_q^{\downarrow,\downarrow,n}(B) \\ D_q^{\downarrow,\downarrow,n}(B) \end{pmatrix} = E_q^n(B) \begin{pmatrix} D_q^{\uparrow,\uparrow,n}(B) \\ D_q^{\uparrow,\downarrow,n}(B) \\ D_q^{\downarrow,\downarrow,n}(B) \\ D_q^{\downarrow,\downarrow,n}(B) \end{pmatrix},$$
(12)

absorbing the factor $|\varphi({m r}=0)|^2$ into I_r and I_Z

The characterisation of these excitonic states is determined by their optical behaviour (bright, dark, gray). To this end, we examine the optical matrix element

$$|M_{\sigma}^{n}(B)|^{2} \propto |\psi^{1s}(\boldsymbol{r}=0)|^{2} |\boldsymbol{e}_{\sigma} \cdot \sum_{ss'} d_{cv}^{ss'} D_{0}^{ss'n}(B)|^{2}$$
(13)

where $|\psi^{1s}(\mathbf{r}=0)|^2 = |\sum_k \varphi_k^{1s}|^2$ describes the probability of the constituent electron and hole being located at the same point, \mathbf{e}_{σ} is the polarisation Jones vector of the incoming light, and $d_{cv}^{ss'}$ are the transition dipoles between spin-bands with s and s'.

C. Exciton-phonon scattering

To calculate the phonon-mediated dynamics, we start with the exciton-phonon Hamiltonian as previous calculated [18]

$$\hat{\boldsymbol{H}}_{\text{X-Ph}} = \sum_{\mu\nu\boldsymbol{Q}\boldsymbol{q}\alpha} \Omega_{\alpha\boldsymbol{q}}^{s_1 s_4 s_2 s_3} X_{\boldsymbol{Q}+\boldsymbol{q}}^{s_1 s_4 \dagger} X_{\boldsymbol{Q}}^{s_2 s_3} \hat{\boldsymbol{b}}_{\boldsymbol{q}}^{\alpha} + h.c$$
(14)

We then perform a transformation into the exchange basis

$$\hat{\boldsymbol{H}}_{X-Ph} = \sum_{\mu\nu\boldsymbol{Q}\boldsymbol{q}\alpha} \sum_{n,n'} \Omega^{n'n}_{\alpha\boldsymbol{q}} Y^{n\dagger}_{\boldsymbol{Q}+\boldsymbol{q}} Y^{n'}_{\boldsymbol{Q}} \hat{\boldsymbol{b}}^{\alpha}_{\boldsymbol{q}} + h.c, \qquad (15)$$

where $\Omega_{\alpha q}^{n'n} = \sum_{s,s',s''} \left(G^{\text{elec},\alpha,q*} D_{q}^{ss''n} D_{q}^{s's''n'*} - \delta_{s,s'} G^{\text{hole},\alpha,q} D_{q}^{s''sn} D_{q}^{s''sn'*} \right)$. The strengths of the exciton-phonon scattering, G^{elec} and hole, G^{hole} , are determined as follows

$$G^{\text{elec},\alpha,\boldsymbol{q}*} = g_{\text{ph}}^{c,\alpha,\boldsymbol{q}} \mathcal{F}(\beta \boldsymbol{q}), \quad G^{\text{hole},\alpha,\boldsymbol{q}*} = g_{\text{ph}}^{v,\alpha,\boldsymbol{q}} \mathcal{F}(-\varrho \boldsymbol{q})$$
(16)

with the form factors $\mathcal{F}(q) = \sum_{k} \varphi_{k}^{*} \varphi_{k+q}$. The constants $g_{ph}^{c(v),\alpha,q}$ describe the electron-phonon coupling in the conduction (valence) bands, which we obtain using a deformation potential model [9]. The electron-phonon coupling relates to the deformation potential by $g_{ph}^{c(v),\alpha,q} = D_{q}^{\alpha} (\hbar^{2}/2\rho\hbar\Omega_{q}^{\alpha})^{1/2}$, where ρ is the mass density. For optical phonons, the deformation potential is constant, i.e. $D_{q}^{\text{opt}} \sim D_{0}^{\text{opt}}$ while for acoustic phonons they have a linear dependence on the momentum $D_{q}^{\text{ac}} \sim D_{0}^{\alpha} |q|$. Table I states the phonon parameters used in our calculations.

The exciton dynamics can be calculated by solving a series of semiconductor Bloch equations [18, 19]. We use Heisenberg's equation of motion, $\partial_t N_Q^n = -i\hbar \langle [N_Q^n, \hat{H}_X] \rangle$ to derive these equations, using the Markov and cluster expansion approximation [19] to truncate these equations to the most important terms. Finally, we find for the exciton occupation

$$\partial_t N_{\boldsymbol{Q}}^n = \sum_{n' \boldsymbol{Q'}} \left(W_{\boldsymbol{Q'Q}}^{n'n} N_{\boldsymbol{Q'}}^{n'} - W_{\boldsymbol{QQ'}}^{nn'} N_{\boldsymbol{Q}}^n \right), \tag{17}$$

where the scattering strength from exciton energy level n and momentum Q to level n' and momentum Q' is defined by $W_{QQ'}^{nn'}$. This has the form

$$W_{\boldsymbol{Q}\boldsymbol{Q}'}^{nn'} = \frac{2\pi}{\hbar} \sum_{\alpha \pm} |\Omega_{\alpha \boldsymbol{Q}'-\boldsymbol{Q}}^{nn'}|^2 \left(\frac{1}{2} \pm \frac{1}{2} + n_{\alpha \boldsymbol{Q}'-\boldsymbol{Q}}\right) \delta\left(E_{\boldsymbol{Q}'}^{n'} - E_{\boldsymbol{Q}}^{n} + \hbar\Omega_{\boldsymbol{Q}'-\boldsymbol{Q}}^{\alpha}\right)$$
(18)

Phonon Parameters				
	$\hbar\Omega_{m{q}}$	Energy Parameter	$D^{lpha}_{m{q}}$	Coupling parameter
Acoustic	$\sim \hbar c oldsymbol{q}$	<i>c</i> = 2100 m/s	$\sim D_0^{ m ac} oldsymbol{q} $	$D_0^{\rm ac} = 1.9 \; {\rm eV}$
Optical	$\sim \hbar \omega$	$\hbar\omega=35~{\rm meV}$	$\sim D_0^{\mathrm{opt}}$	$D_0^{\text{opt}} = 158 \text{ eV/nm}$

Table I: Phonon energies and coupling parameters for acoustic and optical phonons. Parameters obtained from [9], where it is assumed that the deformation potential of the electronic and valence states are the same.

where the sum over \pm corresponds to absorption/emission of phonons and where $n_{\alpha q}$ denotes the population of phonons in the mode α and momentum q. The corresponding phonon energy is $\hbar \Omega_q^{\alpha}$. The delta function ensures energy conservation in the process. We include both acoustic and optical modes [9], with the latter being especially crucial for scattering between bright and dark states. Importantly, the mixing of conduction band spins due to spin-orbit coupling relaxes the strict spin conservation. This process is known as the Elliott-Yafet mechanism, a common source of spin-depolarisation in systems with a strong spin-orbit coupling. In this system, this process is necessary to enable phonon-scattering between the bright and dark/gray excitons.

D. Exction optics and linewidth

The exciton absorption can be described using the Elliot formula, which depends on the magnetic field and temperature is

$$I_{Abs}^{\sigma}(B,T) \propto \Im\left(\sum_{n} \frac{|M_{\sigma}^{n}(B)|^{2}}{\hbar\omega - E_{q=0}^{n}(B) + i\gamma(B,T)}\right)$$
(19)

with the linewidth γ and optical energy and polarisation defined as $\hbar\omega$ and σ , respectively. The time-resolved PL can be calculated with

$$I_{\mathsf{PL}}^{\sigma}(B,T,t) \propto \Im\left(\sum_{n} \frac{N_{\boldsymbol{Q}=0}^{n}(B,T,t)|M_{\sigma}^{n}(B)|^{2}}{\hbar\omega - E_{\boldsymbol{q}=0}^{n}(B) + i\gamma(B,T)}\right)$$
(20)

which differs from the absorption due to the temporally evolving exciton population, $N_{Q=0}^n(B,T,t)$. The linewidth of exciton resonances can be be calculated microscopically. We consider radiative broadening as well and phonon-induced non-radiative broadening. The radia-

tive coupling can be described as

$$\gamma_{\rm rad}^n(B) = \frac{\hbar e^2}{2m_0^2 \epsilon_0 c_0 n E_{q=0}^n(B)} |M_{\sigma}^n(B)|^2$$
(21)

with the refractive index n = 1.82. The radiative coupling depends on the excitonic wavefunctions and the exciton energy and is independent of temperature. The non-radiative decay is determined by

$$\gamma_{\text{non-rad}}^{n}(B,T) = \pi \sum_{\boldsymbol{q}\alpha\pm} |\Omega_{\alpha\boldsymbol{q}}^{nn'}|^2 \left(\frac{1}{2} \pm \frac{1}{2} + n_{\alpha\boldsymbol{q}}\right) \delta\left(E_{\boldsymbol{q}}^{n'} - E_{0}^{n} \pm \hbar\Omega_{\boldsymbol{q}}^{\alpha}\right),\tag{22}$$

depending on the phonon population $n_{\alpha q}$ in the mode α and momentum q. We take into account both phonon absorption and emission processes (±). The non-radiative broadening is therefore temperature dependent.

V. INTERBAND SCATTERING



Figure S8: Optical (a) and acoustic (b) phonon-mediated exciton-phonon scattering strength, $|\Omega_{\alpha Q}^{nn'}|^2$, between the dark (n = 0) and bright X_+ (n' = 1) as a function of phonon momentum Q.

The interband exciton relaxation can be mediated by either acoustic or optical phonons. In Figure S8 we present the phonon-mediated exciton-phonon scattering strength, $|\Omega_{\alpha Q}^{nn'}|^2$, between the dark (n = 0) and bright X_+ (n' = 1) as a function of phonon momentum Q. In particular we compare the role of optical Figure S8 (a) and acoustic Figure S8 (b) phonons. We see that the acoustic phonon coupling strength is 3 orders of magnitude smaller than that of the optical phonon for such interband transitions. Furthermore the relatively low energy of the acoustic phonons is such that a similar probability of reverse scattering processes, leads to a very negligible contribution to the exciton dynamics.

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