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2020

Do, T. T. H., Granados Del Águila, A., Xing, J., Liu, S., & Xiong, Q. (2020). Direct and indirect exciton transitions in two-dimensional lead halide perovskite semiconductors. *Journal of Chemical Physics*, 153(6), 064705-. doi:10.1063/5.0012307

<https://hdl.handle.net/10356/146389>

<https://doi.org/10.1063/5.0012307>

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Cite as: J. Chem. Phys. 153, 064705 (2020); doi: 10.1063/5.0012307

Submitted: 19 May 2020 • Accepted: 27 July 2020 •

Published Online: 11 August 2020

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Note: This paper is part of the JCP Special Topic on 2D Materials.

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ABSTRACT

Atomically thin layers of two-dimensional lead halide perovskite semiconductors exhibit prominent light emission due to the inherently strong quantum and dielectric confinement. Electronic band structures and coupled electron-hole pairs (excitons), which govern the optical properties, are not well understood in these emergent two-dimensional materials. Here, we have performed both the steady-state and time-resolved photoluminescence spectroscopies with varying temperature to study the optical responses of a high-quality (PEA)₂PbI₄ single crystal. We observe a multitude of exciton transitions with different responses to temperature that suggests their different origins. Furthermore, our results suggest that the photoluminescence of layered perovskites is dominated by direct exciton transitions at low temperatures, while by an indirect exciton at high temperatures that can be explained by our proposed exciton band structure incorporating the interplay of Coulomb and Rashba effects. Our study sheds light on the intrinsic optical properties of two-dimensional perovskites that may be beneficial for the novel applications of perovskite-based devices.

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I. INTRODUCTION

A plethora of recent ground-breaking research, with the inaugural success on graphene,¹ has motivated the exponentially growing interests on two-dimensional (2D) materials. Their elemental layers bound together via a weak van der Waals force allow for the control of sample thickness down to atomic precision. Besides the semimetallic graphene, high-quality planar monolayers have been obtained for a wide variety of semiconductors such as black phosphorus,² transition metal dichalcogenides (TMDs),³ and hybrid organic-inorganic lead-halide materials.⁴ The crystal

structure plays a decisive role in the electrical, optical, and vibrational (phonon) properties.

Two-dimensional lead halide perovskite semiconductors have recently emerged as a great alternative for the three-dimensional (3D) counterpart in many applications such as solar cells,^{5,6} light-emitting devices,^{7,8} and photodetectors.⁹ The layer structure with alternatively stacked inorganic-organic layers significantly improves the chemical and thermal stability, which is one of the major drawbacks of 3D perovskites. Furthermore, the strong quantum and dielectric confinement on photogenerated carriers on 2D perovskites gives rise to tightly bound excitons with large exciton

binding energies of few hundreds of meV,^{10–13} which are advantageous for studying the exciton–photon coupling (polariton).^{14,15} In contrast to the major focus on applications, the understanding of intrinsic exciton band structures of 2D perovskites is still at its early stage. Origins of different observations on the temperature-dependent energy shift of the bandgap remain unclear.^{16–20} Furthermore, the dark (optically forbidden) or bright (optically allowed) nature of the exciton bands, which dominates the optical properties, is also under debate.

In this work, by performing a combination of steady-state and time-resolved photoluminescence (PL) measurements on high-quality 2D perovskite (PEA)₂PbI₄ (PEA stands for phenylethylammonium) single crystals, we resolve a multitude of optical transitions, which originate from the recombination of 2D excitons with non-zero oscillator strengths. The different excitonic response to the temperature variation reveals their distinct origins. Our results suggest that the optical emission at low temperatures is governed by bright direct excitons, while at high temperatures, an indirect exciton is the dominant factor. We propose an exciton band structure incorporating the interplay of Coulomb and Rashba effects to explain the temperature-dependent emission process. Our work may stimulate theoretical and experimental studies to uncover the microscopic origins of the excitons and may be beneficial for the future applications of these emergent two-dimensional perovskite nanostructures.

II. EXPERIMENTAL

A. Synthesis of 2D perovskites

The 2D perovskite crystals were synthesized by the supersaturation precipitation method²¹ with slight modification. Lead (II) iodide (1 mmol) and phenylethylammonium iodide (2 mmol) were mixed into 1 ml of γ -butyrolactone. The solution was left for several days until the solvent had evaporated and some crystals had grown on the solution surface.

B. Micro-photoluminescence measurement

The exfoliated samples were mounted on a cryostat fed by a continuous flow of liquid helium to control the temperature from 6 K to 300 K. The samples were excited by a broadband light source for absorption experiments and by a 400-nm laser for photoluminescence experiments. The laser excitation was focused onto the sample surface using a microscope objective with a numerical aperture of ~ 0.45 that results in a laser spot diameter of $\sim 4\ \mu\text{m}$. The optical signals were collected through the same objective, dispersed using a single grating of 1200-grooves/mm and a spectrometer with a focal length of 320 mm for steady-state measurements, and recorded by using a nitrogen-cooled silicon CCD detector.

Time-resolved photoluminescence measurement was performed with the excitation wavelength of 400 nm, which was generated by an 800-nm femtosecond pulse laser passing through a non-linear barium borate (BBO) crystal. The energy-resolved decay signal was collected using an avalanche photodiode (APD) placed after the spectrometer and connected to a time-correlated single photon counting (TCSPC). The temporal resolution is ~ 20 ps. The wavelength resolution is 0.03 nm, corresponding to an energy

resolution of ~ 0.2 meV that allows for extracting the PL decay at a specific energy.

III. RESULT AND DISCUSSION

Figure 1(a) illustrates the layer structure of 2D perovskites cut along the crystal axis (c axis). The alternatively stacked inorganic [PbI₄]^{4–} framework and the organic layers formed by long-chain molecules give rise to a multiple quantum-well structure. The barrier potential of above ~ 1 eV²² and the distance of ~ 1.6 nm between the inorganic layers (d -spacing)²³ effectively confine excitons within the inorganic layers. The adjacent organic layers interact via weak van der Waals forces that enable mechanical exfoliation using a scotch tape method. The produced flakes have lateral dimensions of tens of micrometers and a typical thickness ranging from few tens to hundreds of nanometers [see Fig. 1(b), left panel]. Noticeably, unlike transition metal dichalcogenides, layered perovskites exhibit strong optical responses regardless of the number of layers. The fluorescence image [see Fig. 1(b), right panel] indicates the homogeneously prominent emission of the exfoliated crystals. Under the high vacuum condition during our experiments, the samples were very stable. No optical degradation was observed. High-quality single crystals obtained by our synthesis allow for the observation of multiple narrow optical features, which are normally obscured by the broad spectral linewidths in the orders of tens of meV.^{13,24–26}

The 2D perovskite single crystals were intensively studied by absorption, steady-state, and time-resolved photoluminescence spectroscopies as a function of temperature. Figure 1(c) shows the absorption (black curve) and PL (red curve) spectra within the energy range of interest, which were taken at $T = 6$ K. In the absorption spectrum, exciton resonances are clearly resolved at ~ 2.308 eV (X_1), ~ 2.338 eV (X_2), and ~ 2.349 eV (X_3) with non-negligible oscillator strengths. The peculiarly broad feature covering from ~ 2.349 eV to ~ 2.389 eV suggests the existence of other states lying at the higher-energy side of X_3 . The continuum band arises from ~ 2.560 eV, suggesting a large exciton binding energy in the order of ~ 200 meV. The tightly bound excitons are strongly emissive as manifested in the pronounced features observed in the PL spectrum. Four emission channels are resolved at ~ 2.302 eV, ~ 2.328 eV, ~ 2.338 eV, and ~ 2.342 eV. Comparing the absorption and PL spectra, we assign the lowest-energy emission to the exciton X_1 and the features at ~ 2.338 eV and ~ 2.342 eV to the excitons X_2 and X_3 , respectively. The exciton nature of X_1 , X_2 , and X_3 is further confirmed by the linear power dependence of their individual PL intensity (see Fig. S1), which is distinguished from trap states with sublinear dependence (see Fig. S2), or exciton complexes such as trions and biexcitons, which have superlinear relationship. The emission at ~ 2.328 eV, labeled P , is absent in the absorption spectrum. Therefore, P is not associated with a real state. The energy difference between X_2 and P is ~ 10 meV, which matches with a phonon energy of the (PEA)₂PbI₄ crystal lattice (see Fig. S3). Therefore, we attribute P to the phonon replica of X_2 . The emission from the higher-lying states is not observed due to their low exciton population. Noticeably, the PL spectrum at ~ 6 K is dominated by X_2 and X_3 but not by the lowest-energy exciton state X_1 . Such PL intensity distribution in 2D perovskites is in contrast to that in conventional semiconductors that will be discussed later.

FIG. 1. (a) Crystal structure of the two-dimensional perovskite along the crystal axis (c axis). The alternatively stacked inorganic $[\text{PbI}_6]^{4-}$ and organic layers formed by long-chain ligands give rise to a multiple quantum-well structure. (b) Optical (left) and fluorescence (right) images of representative exfoliated samples, showing the homogeneously prominent emission from micrometer-sized nanostructures with typical thicknesses of ~ 100 nm. (c) Absorption (black curve) spectrum showing multiple exciton resonances at ~ 2.308 eV, ~ 2.338 eV, and ~ 2.349 eV labeled X_1 , X_2 , and X_3 , respectively. The broadband absorption covering from ~ 2.349 eV to ~ 2.389 eV suggests the existence of other higher-energy states. The emission features at ~ 2.302 eV (X_1), ~ 2.328 eV (P), ~ 2.338 eV (X_2), and ~ 2.342 eV are resolved in the PL spectrum (red curve), where P is assigned to phonon replica emission of X_2 . (d) Schematic energy diagram of the exciton energies X_i (orange, light-blue, and blue solid lines) and high-lying states (violet solid line). The excitons can either return to ground state $|G\rangle$ via radiative recombination (straight arrows) or relax to lower-energy states (wavy arrows). The energy at P (green dashed line) originates from the electron–phonon coupling, and P is not a real electronic state.

The exciton energies in 2D perovskites are illustrated in a schematic energy diagram shown in Fig. 1(d), where the photogenerated electron–hole pairs at each energy state can either return to the ground state $|G\rangle$ via radiative recombination (straight arrows) or relax among the levels by scattering with phonons (wavy arrows). If the electron–phonon coupling is sufficiently strong as in the case of 2D perovskites,^{21,27} excitons can interact with suitable phonon modes followed by radiative recombination that gives rise to phonon replica feature P . Since P is not a real electronic state, it is represented by a green dashed line.

The exciton transitions are investigated by monitoring the PL spectrum while varying the temperature from ~ 6 K to ~ 300 K [see Fig. 2(a)]. The PL spectra are normalized and shifted vertically for clarity. Overall, as temperature increases, all the peaks shift to a high-energy side (blue-shift), and their linewidths get broader. At below ~ 80 K, all four emission features X_1 , P , X_2 , and X_3 are clearly resolved. Beyond ~ 80 K, due to the thermally broadened line shape, X_2 and X_3 merge together into a single peak, while X_1 and P remain distinguishable. Interestingly, the spectral contribution of X_1 and P to the total PL emission increases with increasing temperature that is opposite to the dropping emission intensity of X_2 and X_3 . At $T \sim 200$ K, the peak P fully obscures the contribution from X_2 and X_3 . On the low-energy side, X_1 keeps growing. At room temperature

($T \sim 300$ K), the emission from X_1 dominates the PL spectrum, while P only contributes $\sim 30\%$ to the total PL. The existence of multiple emission features and their different temperature responses leads to the dramatic changes in the PL line shape.

The PL spectrum at each temperature is fitted by four [see Fig. 2(b)], three, or two Lorentzians accordingly (see Fig. S4). The extracted energies of X_1 , P , X_2 , and X_3 are plotted as a function of temperature [see Fig. 2(c)]. All the peaks show blue-shifts with increasing temperature, which is in contrast to the conventional red-shift of exciton peaks in semiconductors, including III–V quantum wells^{28–30} and other 2D materials.^{31,32} The blue-shifted optical spectra are a common property of lead-based compounds³³ and, particularly, lead halide perovskites.^{34–36} We note that the PL emission is dominated by the high-energy peaks (X_2 and X_3) until ~ 80 K, while the low-energy peaks P and X_1 exhibit the highest intensity at elevated temperatures. Therefore, while individual peaks are blue-shifted, the whole PL spectral weight is, otherwise, red-shifted with increasing temperature, as observed in Ref. 21. The improved optical quality of our PL spectra allows for this systematic temperature-dependent study of individual optical properties, which was not the focus of Ref. 21.

The full-width at half-maximum (FWHM) of each exciton resonances is plotted as a function of temperature in Fig. 2(d).

FIG. 2. (a) Temperature-dependent photoluminescence spectra of 2D perovskite crystals from $T \sim 6$ K (bottom) to ~ 300 K (top). The colored dashed lines indicate the energy shift of the features while varying the temperature. (b) Representative fitting to PL spectra (black line) using four Lorentzians (green lines), resulting in a cumulative fitting curve (red line) in excellent agreement with experimental data. (c) Extracted energies of X_1 (orange squares), P (green circles), X_2 (light-blue up-triangles), and X_3 (blue down-triangles) vs temperature. (d) FWHM of X_1 (orange squares), X_2 (light-blue up-triangles), and X_3 (blue down-triangles) as a function of temperature. The linewidth broadening with temperature is fitted with Eq. (1) considering exciton–phonon interaction (colored solid lines). (e) Spectral weight of X_1 (orange squares), P (green circles), and $X_2 + X_3$ (blue up-triangles) with respect to the total PL intensity as a function of temperature.

Different temperature responses of FWHMs are seen between X_1 (orange squares), X_2 (light-blue up-triangles), and X_3 (blue down-triangles). While the PL linewidth of X_1 increases linearly with temperature, the FWHMs of X_2 and X_3 are thermally insensitive at below 100 K before getting broader at higher temperatures. In semiconductors, the PL linewidth can be modeled by inhomogeneous broadening, which arises from the sample imperfection, and homogeneous broadening, which is associated with the exciton–phonon scattering mechanism,³⁷

$$\Gamma(T) = \Gamma_0 + \gamma_A T + \gamma_O \frac{1}{\exp(E_O/k_B T) - 1}, \quad (1)$$

where Γ_0 is the temperature-independent inhomogeneous term and γ_A and γ_O are coupling strengths between excitons and acoustic and optical phonons, respectively. A good agreement between Eq. (1) and our data is achieved by using different parameter sets for X_1 and $X_{2,3}$. Specifically, the FWHM of X_1 can be well modeled with only the linear acoustic phonon term by a coupling parameter $\gamma_A = (80 \pm 5) \mu\text{eV/K}$. On the other hand, the temperature-invariant FWHMs of $X_{2,3}$ at low temperatures strongly suggest the negligible contribution from acoustic phonons and the need of optical phonons. The thermal broadening of the $X_{2,3}$ PL linewidth is best fitted by using $E_O = (35 \pm 5) \text{ meV}$ and $\gamma_O = (137 \pm 20) \text{ meV}$.

The contribution of each feature to the PL spectrum is quantified by its spectral weight with respect to the total PL intensity [see Fig. 2(e)]. Here, X_2 and X_3 are summed up since their behaviors are

similar. With an increase in T , the weight of I_1 (orange squares) and I_P (green circles) increases, while that of $I_2 + I_3$ (blue up-triangles) decreases. Since the excitons in 2D perovskites are tightly bound with the binding energy of $\sim 200 \text{ meV}$, the thermal dissociation of excitons at room temperature is not expected to explain the weakening of X_2 and X_3 . Instead, the enhancement of the loss channels such as relaxation and non-radiative recombination is more likely to occur. The increase in the phonon replica I_P resulted from the faster exciton–phonon scattering rate at higher temperature due to the larger phonon population. On the other hand, the overall intensification of X_1 with increasing temperature reveals a different nature of the exciton X_1 , which is associated with a phonon-assisted transition, from excitons X_2 and X_3 .

The normalized energy-resolved PL decay traces of the emission features X_1 , P , X_2 , and X_3 taken at $T \sim 6 \text{ K}$ are individually shown in Fig. 3. Overall, most of the PL intensity decays rapidly in the first 2 ns after the pulse excitation, while a weak component decays in the next 10 ns. Importantly, the excitons X_2 (green curve) and X_3 (blue curve) exhibit the same decay traces, suggesting that the emission X_2 and X_3 originates from two identical exciton bands. The phonon replica P (pink curve) follows the dynamics of X_2 and X_3 . On the other hand, X_1 has a different dynamic with a longer fast component and a shorter slow component that arises from the distinct properties of X_1 from X_2 and X_3 . The dynamics of all the emission lines are studied in detail as a function of temperature, while X_1 and X_3 will be shown, here, as representatives.

FIG. 3. Low-temperature ($T = 6$ K) normalized energy-resolved PL decay curves of X_1 (orange curve), P (pink curve), X_2 (light-blue curve), and X_3 (blue curve) in a semi-logarithmic scale. The excitons X_2 and X_3 and the phonon replica P have identical decay traces, while X_1 exhibits a longer fast decay channel and a shorter slow decay channel.

Figure 4(a) shows the normalized time-resolved PL spectrum extracted at the energy of X_1 at selected temperatures. When the temperature increases from $T \sim 6$ K (blue curve) to ~ 40 K (dark-green curve), the PL decays more slowly. At $T \sim 120$ K (orange curve), one decay channel is quenched leaving a single exponential decay. The time-resolved PL curves are modeled with bi-exponential functions (red curves),

$$I_{PL} = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}, \quad (2)$$

where τ_1 and τ_2 are time constants and A_1 and A_2 are the corresponding amplitudes. The average PL decay time, quantified as $\langle \tau \rangle = (A_1 \tau_1 + A_2 \tau_2) / (A_1 + A_2)$, is plotted for X_1 in Fig. 4(b) as a function of temperature. At a low-temperature regime (below ~ 120 K), $\langle \tau_{X_1} \rangle$ increases with an increase in temperature, then remains constant until ~ 200 K, and finally drops when entering the non-radiative regime.

The individual decay channels of X_1 are extracted from the bi-exponential fitting by Eq. (2). The amplitudes of two components are plotted in Fig. 4(c), and the corresponding time constants are shown in Fig. 4(d). The first component, characterized by A_{1,X_1} and τ_{1,X_1} (dark-cyan diamonds), which contributes $\sim 90\%$ to the total PL at ~ 6 K, decays very fast with a time constant of ~ 0.3 ns. With an increase in temperature, the amplitude A_{1,X_1} decreases rapidly, and the time constant τ_{1,X_1} increases slightly to ~ 0.5 ns. At above ~ 100 K, A_{1,X_1} is negligible. On the other hand, the second component, labeled by A_{2,X_1} and τ_{2,X_1} (pink squares), responds to the temperature variation in an opposite manner. Particularly, the amplitude A_{2,X_1} is thermally enhanced that is consistent with the increasing PL intensity of X_1 shown in Fig. 2(e). Furthermore, τ_{2,X_1} is ~ 4 ns at ~ 20 K and is shortened to ~ 2.5 ns at ~ 200 K. We ascribe τ_{1,X_1} to the scattering time of excitons to the light cone and ascribe τ_{2,X_1} to the

FIG. 4. (a) Normalized PL decay curves of X_1 at selected temperatures (colored solid lines), which are fitted by bi-exponential functions (red solid lines). The instrument response function is shown by the gray-shaded region. (b) Characteristic PL decay time $\langle \tau_{X_1} \rangle$ of X_1 vs temperature in radiative (below ~ 200 K) and non-radiative (above ~ 200 K) regimes. (c) Extracted PL amplitudes for the first decay channel A_{1,X_1} (dark-cyan diamonds) and the second decay channel A_{2,X_1} (pink squares). (d) Time constants for two decay channels τ_{1,X_1} (dark-cyan diamonds) and τ_{2,X_1} (pink squares).

radiative recombination time of X_1 within the light cone (around the Γ -point).

The PL dynamic of X_3 is depicted in Fig. 5(a) at selected temperatures. At ~ 6 K, the PL decay consists of two channels, while most of the emission decays within the first 1 ns. When temperature increases to ~ 40 K, the PL lifetime becomes longer and, then, gets shortened again when the temperature goes beyond ~ 40 K. In addition, at above 40 K, the rise time arises in the first 0.25 ns that could be related to the population built up at the exciton band X_3 due to the enhanced relaxation from higher-energy states at high temperatures. The temperature-dependent PL lifetime, represented by $\langle \tau_{X_3} \rangle$, is plotted in Fig. 5(b), where the characteristic time decay is only ~ 0.3 ns at ~ 6 K, increases to ~ 4.5 ns at ~ 40 K, and, then, drops to ~ 2.3 ns at ~ 160 K.

Two decay channels, extracted from the bi-exponential fitting shown in Fig. 5(a), are characterized by the amplitudes A_{1,X_3} and A_{2,X_3} [see Fig. 5(c)] and the corresponding time constants τ_{1,X_3} and τ_{2,X_3} [see Fig. 5(d)]. First, we detect a sharp drop of A_{1,X_3} with increasing temperature [green down-triangles, Fig. 5(c)] that matches with the weakening of the PL emission observed in Fig. 2(a). Therefore, we assign the first channel (τ_{1,X_3}) to the radiative recombination of the exciton X_3 . At ~ 6 K, the coupled electron-hole pairs at the X_3 level radiatively recombine rapidly with a time constant τ_{1,X_3} of ~ 0.2 ns, which is temperature-independent until ~ 20 K. The fast radiative lifetime of X_3 is comparable to the bright exciton transitions in 2D transition metal dichalcogenides,³² II–VI nanoplatelets,³⁸ and III–V quantum wells³⁹ that

FIG. 5. (a) Normalized PL decay curves of X_3 at selected temperature (colored solid lines), which are fitted by bi-exponential functions (red solid lines). The instrument response function is shown by the gray-shaded region. (b) Characteristic PL decay time (τ_{X_3}) vs temperature. (c) Extracted PL amplitudes for the first decay channel A_{1,X_3} (green down-triangles) and the second decay channel A_{2,X_3} (red circles). (d) Time constants for two decay channels τ_{1,X_3} (green down-triangles) and τ_{2,X_3} (red circles).

reveals X_3 (similarly to X_2) is a direct transition with large oscillator strength.

In contrast, A_{2,X_3} increases slightly and τ_{2,X_3} is shortened with temperature [red circles, Figs. 5(c) and 5(d)], suggesting the role of phonons on the second decay channel. We attribute the depopulation of exciton X_3 with the rate of $(\tau_{2,X_3})^{-1}$ to the relaxation from X_3 to lower-energy states X_2 and X_1 . Interestingly, the behavior of τ_{2,X_3} ($\approx \tau_{2,X_2}$) is similar to the radiative recombination $\tau_{2,P}$ of phonon replica P (see Fig. S5). The excitons at the X_2 state either radiatively recombine at the rate of $(\tau_{1,X_3})^{-1} \approx (\tau_{1,X_2})^{-1}$ or release one-phonon energy to emit photons with the energy of P at the rate of $(\tau_{2,P})^{-1} \sim (\tau_{2,X_2})^{-1} \approx (\tau_{2,X_3})^{-1}$. At elevated temperatures, besides the large phonon population, the exciton populations at X_2 and X_3 states get thermally mixed that facilitates the relaxation among the levels leading to a shorter relaxation time τ_{2,X_3} .

Gathering our results from steady-state and time-resolved measurements, we discuss a potential picture for the exciton band structure and the dynamical processes in 2D perovskites at low and high temperatures, as shown in Fig. 6. First, the most intense PL peaks at low temperatures originate from the direct and bright exciton states X_2 and X_3 that is proved by their strong oscillator strengths and fast radiative lifetimes ($\tau_{1,X_2/X_3} \sim 0.2$ ns). At low temperatures, the inefficient relaxation from X_2 and X_3 to X_1 state $\tau_{2,X_2/X_3}$ as compared to the radiative recombination $\tau_{1,X_2/X_3}$ gives rise to their strong optical emission, even though X_2 and X_3 are not the lowest-energy bands.

The direct excitons X_2 or X_3 are coupling states of electrons and holes located at the same k -points in the first Brillouin zone.

Furthermore, X_2 and X_3 are both doubly degenerate states that can be further split into orthogonally oriented dipoles due to the large electron-hole exchange interaction in 2D perovskites.²³ With similar optical properties, temperature responses, and transition symmetries, X_2 and X_3 are not likely to split from a single multiplet by crystal fields or exchange interaction. While crystal fields in perovskite materials cause a typical splitting of few hundreds of meV between substates with different magnetic angular momenta,⁴⁰ electron-hole exchange interaction leads to either dark-bright splitting or bright exciton splitting into orthogonal dipoles that cannot explain the similar properties of X_2 and X_3 . Instead, the energy difference between X_2 and X_3 could be resulted from their different binding energies due to the local lattice deformation, which, consequently, affects the Coulomb screening for electron-hole pairs in $X_{2,3}$. Another possibility could be the internal electric field generated by out-of-plane dipoles that introduces an energy difference between the excitons lying in two adjacent inorganic layers and results in two exciton transitions X_2 and X_3 .

On the other hand, the temperature-induced enhancement of the PL emission of X_1 reveals the participation of phonons in X_1 transition. From the observation of an absorption resonance at X_1 energy and the linear power dependence, we exclude the possibility of trap and bound exciton states. Recently, polarons, which are coupled states of carriers and phonons, have been employed to explain the equally spaced exciton resonances observed in the optical spectra of 2D perovskites. Particularly in Ref. 41, the temperature dependence of optical resonances was presented, showing the weakening of the polaron states with increasing temperature as compared with the free-exciton resonances. This observation agrees with a theoretical calculation predicting the decrease in polaron mass with an increase in temperature that suggests the reduced polaron effects and, consequently, the dissociation of polarons into a free electron/hole and unrenormalized phonons at high temperatures.⁴² These behaviors contrast with the thermally enhanced emission from X_1 in the investigated temperature range. Hence, based on our temperature-dependent experiments, although we do not completely exclude polaron effects in 2D perovskites, it is unlikely that X_1 originates from a polaron state.

We propose that the electron and hole forming X_1 have different momenta ($k_e \neq k_h$). In the exciton representation (see Fig. 6), the energy minimum does not occur at the Γ -point but is shifted by Δk_R . At low temperatures, most of the generated excitons occupy the bottom-band states. For optical transitions to occur, excitons need to return to the Γ -point via scattering with phonons having a momentum of Δk_R during τ_{1,X_1} and, then, radiatively recombine within the light cone during τ_{2,X_1} . With a rise in temperature [see Fig. 6(b)], excitons populate higher-energy states lying closer to the light cone (Γ -point) that follows Boltzmann distribution. Furthermore, the carrier-phonon scattering rate is also enhanced due to a larger phonon population. As a result, the PL intensity increases and the radiative recombination at the Γ -point becomes more efficient (i.e., shorter τ_{2,X_1}) at high temperatures that are opposite to the behaviors of direct excitons X_2 and X_3 .

The indirect character of X_1 may be related to Rashba effects. A degenerate band is evenly split along the momentum space to produce two spin-polarized bands. In lead halide perovskites, momentum-splitting in conduction and valence bands is

FIG. 6. Proposed exciton band structures of 2D perovskites around the Brillouin zone center (Γ -point), showing dynamical processes of X_1 and X_3 as representatives at (a) low temperature and (b) high temperature. Direct and bright exciton bands X_2 and X_3 are represented by a single parabola. Indirect exciton X_1 is momentum-split due to Rashba effects. Straight arrows depict radiative recombination within the light cone (yellow-shaded area). Curved arrows represent the relaxation processes via exciton-phonon scattering with the curve-thickness indicating the efficiency of each process at the respective temperature regime.

not exactly identical, causing a slight momentum mismatch at the band extrema that reduces the overlap between electron- and hole-wavefunctions.⁴³ On the other hand, such a reduction in the wavefunction overlap could be compensated by the strong Coulomb interaction given by quantum and dielectric confinement in atomically thin perovskite layers that, in turn, provides a non-zero oscillator strength for the transition. In $(\text{PEA})_2\text{PbI}_4$, a Rashba splitting of ~ 35 meV to 40 meV is determined at the electronic band extrema^{44,45} that is in line with the energy difference of ~ 40 meV between X_1 and the direct transition X_2/X_3 observed in our work. Our experimental observations suggest that while Rashba may dominate the optical responses of X_1 , the Coulomb interaction may have stronger influence on excitons X_2 and X_3 . Future successful experiments, especially angle-resolved photoemission spectroscopy (ARPES), would provide the direct evidence for our proposed exciton band structure. A complete theoretical calculation considering exciton, Rashba, and polaron effects will be also needed to fully understand the origin of the multiple exciton transitions in 2D perovskites.

IV. CONCLUSION

In conclusion, supported by a combination of steady-state and time-resolved photoluminescence techniques, we have provided a new understanding for the optical properties and exciton dynamics of two-dimensional lead halide perovskite semiconductors. Different classes of excitons behave differently to temperature that reveals their distinct nature. Our results suggest that the optical emission at low temperatures is governed by bright direct excitons, while at high temperatures, an indirect exciton band is the dominant factor. Our findings may stimulate future experiments and theoretical calculations to uncover the microscopic origins of all the exciton transitions and may be beneficial for the future development of novel perovskite-based functional devices.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for additional details on power-dependence PL intensity, Raman spectrum, PL line shape analysis, and PL decay of the phonon replica feature.

AUTHORS' CONTRIBUTIONS

T.T.H.D. and A.G.d.A. contributed equally to this work.

ACKNOWLEDGMENTS

Q.X. acknowledges the support from the Singapore National Research Foundation through the NRF Investigatorship Award (Grant No. NRF-NRFI2015-03) and the Singapore Ministry of Education via the AcRF Tier 3 Programme "Geometrical Quantum Materials" (Grant No. MOE2018-T3-1-002), Tier 2 (Grant No. MOE2018-T2-2-068), and Tier 1 (Grant Nos. RG103/15 and RG113/16). A.G.d.A. gratefully acknowledges the financial support from the Presidential Postdoctoral Fellowship program of Nanyang Technological University.

DATA AVAILABILITY

The data that support the findings of this study are available within the article, and its [supplementary material](#), or from the corresponding author upon reasonable request.

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