Manipulation of hot carrier cooling dynamics in two-dimensional Dion–Jacobson hybrid perovskites via Rashba band splitting

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Hot-carrier cooling processes of perovskite materials are typically described by a single parabolic band model that includes the effects of carrier-phonon scattering, hot phonon bottleneck, and Auger heating. However, little is known (if anything) about the cooling processes in which the spin-degenerate parabolic band splits into two spin-polarized bands, i.e., the Rashba band splitting effect. Here, we investigated the hot-carrier cooling processes for two slightly different compositions of two-dimensional Dion–Jacobson hybrid perovskites, namely, (3AMP)PbI4 and (4AMP)PbI4 (3AMP = 3-(aminomethyl)piperidinium; 4AMP = 4-(aminomethyl)piperidinium), using a combination of ultrafast transient absorption spectroscopy and first-principles calculations. In (4AMP)PbI4, upon Rashba band splitting, the spin-dependent scattering of hot electrons is responsible for accelerating hot-carrier cooling at longer delays. Importantly, the hot-carrier cooling of (4AMP)PbI4 can be extended by manipulating the spin state of the hot carriers. Our findings suggest a new approach for prolonging hot-carrier cooling in hybrid perovskites, which is conducive to further improving the performance of hot-carrier-based optoelectronic and spintronic devices.
Two-dimensional (2D) hybrid perovskites are promising optoelectronic semiconductors because they offer greater structural diversity and stability compared to their three-dimensional (3D) counterparts. In addition, the structural arrangement in 2D hybrid perovskites is akin to quantum wells (i.e., inorganic layers electronically isolated by insulating organic layers), giving rise to intriguing physical phenomena, such as quantum and dielectric confinement effects, the optical Stark effect, and coherent phonon interactions. In addition, similar to 3D hybrid perovskites, the presence of heavy atoms (e.g., lead) can induce Rashba band splitting because of inversion symmetry breaking, making such materials promising candidates for manipulating the spin states in spintronic devices. On the other hand, the spontaneous polarization properties of ferroelectric 2D perovskites can enhance free charge carrier generation and break the Shockley-Queisser limit for the bulk photovoltaic effect. However, the hot-carrier cooling time can be extended up to tens of picoseconds via the combined effects of hot-phonon bottleneck, enhanced Auger heating, and formation of large polarons.

There is also a growing interest in exploring applications involving hot-carrier-based optoelectronic and spintronic devices, especially hot-carrier solar cells (HCSCs), using 2D hybrid perovskites due to the deceleration of their hot-carrier cooling rate, which is mainly governed by quantum and dielectric confinement effects. In this case, the hot-carrier cooling time can be extended up to tens of picoseconds via the combined effects of hot-phonon bottleneck, enhanced Auger heating, and formation of large polarons.

For typical single-layered (001)-oriented 2D hybrid perovskites (n = 1) with the general formula A₂MX₄ or AMX₄ (A = organic cation; M = Pb or Sn; X = Cl⁻, Br⁻, or I⁻), the structural, electronic, and photophysical properties are strongly dependent on the nature of the organic spacers (e.g., size, shape, and electron affinity), as well as the configuration of the inorganic layers. Compared to the extensively studied 2D Ruddlesden–Popper (RP) perovskites with monovalent cations, the 2D Dion–Jacobson (DJ) perovskites show shorter interlayer distances and better stability because diammonium cations (+2) can strongly interact with the inorganic layers via both hydrogen bonding and interlayer van der Waals I···I interactions. Herein, we explored and deciphered the hot-carrier cooling processes in two slightly different compositions of 2D DJ perovskites, namely, (3AMP)PbI₄ and (4AMP)PbI₄ (3AMP = 3-(aminomethyl)piperidinium; 4AMP = 4-(aminomethyl)piperidinium), by combining ultrafast time-resolved spectroscopy and first-principles calculations. In particular, we seek to understand the effect of Rashba band splitting on the cooling processes. We first confirmed the Rashba band splitting in (4AMP)PbI₄ by a combination of electronic properties

![Fig. 1 Crystal structure, electronic bands, and PL spectra of 2D Dion-Jacobson perovskites. a, b Crystal structures of 2D Dion-Jacobson perovskites, (3AMP)PbI₄ and (4AMP)PbI₄, together with the chemical structures of the organic cations. c, d Electronic bands and total and projected density of states (PDOS) of (3AMP)PbI₄ and (4AMP)PbI₄ calculated at the DFT HSE06 level with spin-orbit coupling (SOC). Enlarged electronic bands near the valence band maximum and conduction band minimum are shown in the insets. e, f Temperature-dependent PL spectra of the (3AMP)PbI₄ and (4AMP)PbI₄ films, together with the time-resolved PL decays for the emission from the (3AMP)PbI₄ film at 565 nm and the emission from the (4AMP)PbI₄ film measured at 560 nm and room temperature. The solid lines represent fits to a biexponential decay function. Note that the observed spikes in (e) could be due to the presence of film irregularities that lead to small reflections inside the film.](image-url)
band structure calculations and temperature-dependent photoluminescence (PL) and time-resolved PL experiments. In both (3AMP)PbI4 and (4AMP)PbI4, the carrier-hot phonon interactions combined with the hot-phonon effect are responsible for the fast relaxation of hot carriers at early times (less than 1 ps). The nonadiabatic molecular dynamics (NAMD) simulations reveal that the fast intraband relaxations to the band edges are governed by hybrid vibrations and nonadiabatic couplings between the initial and lower states. Moreover, we attribute the fast hot-carrier cooling at longer time delays (up to hundreds of picoseconds) to spin-flip/precession and spin-phonon scattering of hot electrons. In addition, by controlling the spin state of the hot carriers generated upon circular copolarized excitation, we observe slower hot-carrier cooling in (4AMP)PbI4 that displays Rashba band splitting. This is also supported by NAMD calculations considering the spin-orbit coupling and decoherence effects.

Results and Discussion

Structural, electronic bands, and optical properties of 2D DJ perovskites. The 2D Dion–Jacobson perovskite (3AMP)PbI4 and (4AMP)PbI4 films were prepared from their single crystals using a previously reported method with some modifications (see Materials and Methods for details). The X-ray diffraction (XRD) patterns validate the formation of the 2D phase and the compositional purity (Supplementary Fig. 1a). It also confirms that the perovskite layers are stacked perpendicular to the substrate plane. Atomic force microscopy (AFM) images show a smooth topography of microcrystalline domains that are merged to form compact films (Supplementary Fig. 2). For comparison purposes, 2D Ruddlesden-Popper hybrid perovskites, (PMA)2PbI4 and (PEA)2PbI4, were also investigated here. From the crystal structures of (3AMP)PbI4 and (4AMP)PbI4 (Fig. 1a, b), we find the following: (i) 2D DJ perovskites contain one sheet of divalent +2 cations between the inorganic layers, in which the cations have a balanced positive charge density for both CsNH1.5+ and NH3+ (see the electrostatic potential surfaces in Supplementary Fig. 3). (ii) The Pb–I–Pb angles in 2D DJ perovskites are much more distorted as they are directly exposed to the organic cations. (iii) The strong hydrogen bonding between the organic cations and the inorganic layers can prevent rotational motion, resulting in more restricted cations or fewer degrees of freedom and short interlayer distances of 10.6 Å and 10.9 Å for (3AMP)PbI4 and (4AMP)PbI4, respectively. In contrast, the 2D RP perovskites, (PMA)2PbI4 and (PEA)2PbI4 contain two sheets of interdigitating monovalent +1 cations with a positive charge density for NH3+, leading to more flexible layer stacking and larger distances between the inorganic layers: 15.1 Å for (PMA)2PbI4 and 16.5 Å for (PEA)2PbI4 (the crystal structures are shown in Supplementary Fig. 4).

The optical band gaps of the (3AMP)PbI4 and (4AMP)PbI4 films were deduced from the onsets of the absorption spectra to be 2.16 eV and 2.32 eV, respectively (Supplementary Fig. 1b); these values are consistent with the direct band gaps calculated for (3AMP)PbI4 at the Γ-point (GGA/PBE: 2.08 eV; HSE + SOC: 1.93 eV) and (4AMP)PbI4 at the B-point (GGA/PBE: 2.22 eV; HSE + SOC: 2.16 eV), as shown in Fig. 1c, d. The complete electronic band structures calculated at the GGA/PBE with and without SOC are shown in Supplementary Figs. 5 and 6. Compared to (3AMP)PbI4, the better stacking of inorganic layers in (4AMP)PbI4 allows stronger interlayer electronic couplings via van der Waals I–I interactions, leading to reduced band gaps via enhanced antibonding interactions and destabilization of the valence bands. The corresponding projected densities of states (PDOSs) suggest that hybridization of Pb-6s and I-5p orbitals mainly contributes to the valence bands, while the Pb-6p orbital has a dominant contribution to the conduction bands.

The (4AMP)PbI4 crystal belongs to the P6 space group and the inorganic layers match perfectly with an averaged equatorial Pb–I–Pb angle of 155°. Such polar octahedral distortions can break the inversion symmetry, leading to Rashba band splitting around the conduction band edge (Fig. 1d). The Rashba splitting coefficient αR (defined as 2Eg/k0, where k0 is the momentum offset and Eg is the energy splitting) for (4AMP)PbI4 is 1.46 eVÅ, which is on the same order of magnitude as that obtained from recent experiments (αR = 2.6 eVÅ)21. On the other hand, (3AMP)PbI4 belongs to the centrosymmetric P21/c space group; here, the inorganic layers stack on top of one another with a larger averaged equatorial Pb–I–Pb angle of 165°, and no band splitting is observed for either the conduction band or valence band edge. Such structural and electronic differences between (3AMP)PbI4 and (4AMP)PbI4 can be attributed to the stronger hydrogen bonding interactions between H atoms from NH3+ and I atoms in (4AMP)PbI4 (see the comparison of overlap population for hydrogen bonding in Supplementary Table 1). It should be noted that band splitting is also absent in the 2D RP perovskites (PMA)2PbI4 and (PEA)2PbI4 due to the absence of tilting of the Pb–I–Pb angles.

To confirm the Rashba band splitting in (4AMP)PbI4, we first carried out temperature-dependent PL measurements ranging from 5 K to 300 K. As shown in Fig. 1c, (3AMP)PbI4 shows a single emission peak (564.8 nm) at room temperature and exhibits a spectral red-shift for decreasing temperature. In contrast, the emission peak for (4AMP)PbI4 starts to split into two for temperatures lower than 150 K (Fig. 1f); and two emission peaks located at 558.7 nm and 564.9 nm are observed at 5 K, which can be attributed to the two split bands (see the inset of Fig. 1f). This also agrees well with recent observations of robust ferroelectricity and Rashba band splitting in (4AMP)PbI4 via circularly polarized PL measurements21. We further performed time-resolved PL (TRPL) measurements to confirm the band splitting in (4AMP)PbI4. For excitation close to the band edge, (3AMP)PbI4 shows an average PL lifetime of 0.17 ns, which is slightly shorter than that obtained with high-energy excitation (τave = 0.27 ns). Similar PL decays are observed in 2D RP perovskites (Supplementary Fig. 7), showing an average PL lifetime of 0.25 ns and 0.34 ns for (PMA)2PbI4 and (PEA)2PbI4, respectively. In contrast, (4AMP)PbI4 shows a much longer PL lifetime, especially with high-energy excitation (τave = 7.69 ns). Such slower radiative recombination in (4AMP)PbI4 can be attributed to the indirect bandgap nature induced by spin-polarized Rashba band splitting1022.

Hot carrier cooling processes in 2D DJ perovskites. To assess the hot-carrier cooling properties in 2D DJ perovskite films following excitation at excess energy, we performed femtosecond transient absorption (fs-TA) spectroscopy at different excitation fluences. Figure 2a–d show the normalized TA spectra of 2D DJ perovskite films at high-energy excitation, i.e., 330 nm (3.76 eV) for (3AMP)PbI4 and 316 nm (3.92 eV) for (4AMP)PbI4, with pump fluences of 2.0 μJ/cm2 and 4.0 μJ/cm2 to minimize Auger recombination (see Supplementary Note 1). TA spectra at a lower pump fluence of 0.8 μJ/cm2 were also obtained and are shown in Supplementary Fig. 8. Note that the carrier densities (n0) corresponding to pump fluences of 2.0 μJ/cm2 and 4.0 μJ/cm2 are 8.25 × 1017 and 1.65 × 1018 cm−3 for (3AMP)PbI4 and 8.80 × 1017 and 1.76 × 1018 cm−3 for (4AMP)PbI4 (see Supplementary Note 2). Upon photoexcitation, the TA spectra of both the (3AMP)PbI4 and the (4AMP)PbI4 films show photobleaching (PB) peak (ΔΔ > 0) with high-energy tails near the bandgap due to band filling effects,
The hot-carrier temperature ($T_c$) can be extracted by fitting the high-energy tails of the TA spectra using the Maxwell-Boltzmann function $\exp[(E_f - E)/k_BT_c]$, where $k_B$ is the Boltzmann constant and $E_f$ is the quasi-Fermi energy (see Supplementary Note 3). Figure 2e, f show the $T_c$ evolution following high-energy excitation at different pump fluences. At a low pump fluence of 2.0 $\mu$J/cm$^2$, the initial $T_c$ in the (3AMP)PbI$_4$ film is 524 K, and it cools fast with a time constant of 1.25 ps (obtained from the biexponential fittings of initial $T_c$ decays, see Supplementary Table 3) and an energy loss rate of 1.22 eV/ps (i.e., the initial excess energy divided by the cooling time) until $T_c$ approaches room temperature. At a higher pump fluence of 4.0 $\mu$J/cm$^2$, the initial $T_c$ of the (3AMP)PbI$_4$ film reaches 726 K, and the hot electrons require a longer time to relax to the conduction band edge, giving a time constant of 2.46 ps and an energy loss rate of 0.62 eV/ps. Note that the 2D RP perovskite (PEA)$_2$PbI$_4$ film shows similar evolutions for the high-energy tails in the TA spectra (Supplementary Fig. 9) but exhibits much lower initial $T_c$ experiences a fast decay with $T_c$ time constant of 0.38 ps. It is worth mentioning that the (PMA)$_2$PbI$_4$ film is not stable and may undergo a phase change under a higher pump fluence of 4.0 $\mu$J/cm$^2$, as a new photobleaching signal appears at a wavelength of 408 nm (Supplementary Fig. 10). From these results, it can be concluded that the initial hot-carrier cooling in 2D hybrid perovskites is dominated within the subpicosecond time scale (<1 ps) by the emission of optical phonons, while an additional slow cooling process is observed on a timescale of up to hundreds of picoseconds, especially at a high pump fluence, which can be attributed to the hot-phonon bottleneck effect.

The (4AMP)PbI$_4$ film also exhibits a high initial $T_c$ (523 and 723 K) and rapid initial cooling behavior during thermal equilibrium between the LO-phonon population and hot carriers (<1 ps). The $T_c$ time constant of (4AMP)PbI$_4$ is 1.50 ps at a low pump fluence (energy loss rate of 1.01 eV/ps), and it becomes longer (2.37 ps) at a high pump fluence. The initial fast cooling in (4AMP)PbI$_4$ is comparable to that of (3AMP)PbI$_4$ and 2D RP perovskites, suggesting similar carrier-phonon interactions in $n=1$ 2D perovskites. Furthermore, compared to (3AMP)PbI$_4$, the lower density of states in the conduction bands for (4AMP)PbI$_4$ (Fig. 1c, d) will lead to a reduced energy loss rate of hot carriers due to the presence of fewer available relaxation pathways. However, on a timescale of tens to hundreds of picoseconds, the high-energy tails of the photobleaching signals become fast evolving, indicating that an additional channel is involved in accelerating hot carrier cooling. This faster cooling of the hot carriers closer to the band edges, especially at high pump fluence, can be influenced by spin randomizations and flips of hot electrons from the split bands. Thus, we attribute the further fast $T_c$ decays taking place on the timescale of tens to hundreds of picoseconds to the Rashba band splitting effect, which will be discussed in the following sections.

**Intraband relaxations in 2D DJ perovskites.** Figure 3a, b show the normalized TA kinetics of the (3AMP)PbI$_4$ and (4AMP)PbI$_4$ films probed at the photobleaching peaks with different pump fluences. The buildup of band-edge bleach has been previously used to elucidate hot-carrier cooling processes. However,
both perovskite films show an instantaneous rise in the photo-
bleaching signals that occur at subpicosecond timescales, i.e.,
≤ 120 fs for (4AMP)PbI$_4$ and 120 – 200 fs for (3AMP)PbI$_4$ at pump
fluences from 0.8 μJ/cm$^2$ to 4.0 μJ/cm$^2$. This suggests that (i) the
excess energy gained by the electrons in 2D DJ perovskites can
simultaneously promote the generation of nonequilibrium LO-
phonons and (ii) the Auger heating effect is almost negligible at
these pump fluences. The fitting parameters for the TA kinetics
for (3AMP)PbI$_4$ and (4AMP)PbI$_4$ at different pump fluences are
given in Supplementary Tables 4 and 5; they show a longer initial
decay at high-energy excitations (i.e., $\tau_1 = 0.45$ – 3.50 ps for
(3AMP)PbI$_4$ and $\tau_1 = 0.55$ – 1.86 ps for (4AMP)PbI$_4$) compared
to that obtained with low-energy excitations.

To understand the similar rise and initial decays in the TA
kinetics as well as the intraband relaxations governed by
nonadiabatic coupling among high-energy levels, we performed
nonadiabatic molecular dynamics (NAMD) calculations for
(3AMP)PbI$_4$ and (4AMP)PbI$_4$ with consideration of electronic
coherence effects. Based on the Kohn–Sham energies for the
electronic levels obtained at the GGA/PBE + SOC level (Fig. 3c, d),
the NAMD calculations only involved high-energy conduction
bands (i.e., electron cooling process) as the effective masses for the
electrons are much smaller than those for the holes (i.e., 0.18 vs.
0.34 $m_0$ for (3AMP)PbI$_4$; 0.32 vs. 0.81 $m_0$ for (4AMP)PbI$_4$). To
quantify the intraband relaxations of hot electrons, the population
decay curves were fitted using the equation
\[ f(t) = a \cdot \exp\left(-t/\tau_1\right) + (1-a) \cdot \exp\left(-t/\tau_2\right)^2 \]
and the relaxation times were calculated according to
\[ \tau_{\text{intraband}} = a \cdot \tau_1 + (1-a) \cdot \tau_2. \]

As shown in Fig. 3c, d, the electrons in (3AMP)PbI$_4$ undergo a fast
relaxation from the initial CBM$_7$ (1.52 eV above the
conduction band maximum, CBM) to the band edge, and
the population of electrons in the initial state rapidly decays to the
CBM with a \(\tau_{\text{intraband}}\) of 54 fs. For the case of (4AMP)PbI$_4$, the
population of hot electrons cools down from the initial CBM$_4$ to
the CBM with a relaxation time of \(\tau_{\text{intraband}}\) = 57 fs. The
comparable intraband relaxation times agree well with the rise
times of the photobleaching signals of (3AMP)PbI$_4$ and (4AMP)
PbI$_4$. The fast intraband relaxation times can be attributed to the
direct population transfer from the initial state to the lower states,
i.e., to nonvanishing nonadiabatic couplings (NAC; the NAC
mappings are shown in Supplementary Fig. 11) among these
states, which emerge once spin-orbit coupling is included in the
NAMD calculations: NAC\[<\text{CBM}_7|\text{CBM}_m>\] \((m = 0 – 6)\) = 16 – 28 meV for (3AMP)PbI$_4$; NAC\[<\text{CBM}_4|\text{CBM}_m>\]
m> | (m = 0 − 3) = 15 − 27 meV for (4AMP)PbI4. These couplings allow the acceleration of hot-carrier cooling via multiple intraband relaxation channels31.

Analysis of the experimental Raman spectra, calculated Raman modes, and spectral densities between two conduction bands (i.e., pair states), as shown in Supplementary Fig. 12, confirms that low-frequency Raman modes (at ~40 cm−1 for (3AMP)PbI4 and ~50 cm−1 for (4AMP)PbI4) are responsible for the hot-carrier cooling. In a way similar to the vibrational features found in 3D perovskite structures16,27, the major low-frequency modes can be assigned to the horizontal Pb−I stretching modes and vertical I−Pb−I rocking modes of the inorganic layer (see the vibrational vectors for the major modes in Fig. 3e, f). Since the organic spacers in 2D perovskites are predominantly coupled to the stretching/rocking vibrations of the inorganic layers, these low-frequency “hybrid phonon” modes can accelerate the hot-carrier cooling processes31. Moreover, the hot-carrier cooling in lead halide perovskites is also controlled by electron-phonon coupling (i.e., the interactions between the LO-phonons and electrons)15,32, which can be described by the Fröhlich parameter (α, see Supplementary Note 4). As given in Supplementary Table 6, 2D DJ perovskites have smaller calculated α values (2.53 for (3AMP)PbI4 and 2.29 for (4AMP)PbI4) than the 2D RP perovskites (3.36 for (PMA)2PbI4 and 4.29 for (PEA)2PbI4), indicating that the electronic transitions among the conduction bands in 2D DJ perovskites are less coupled to the vibrations of the inorganic cages. Moreover, (3AMP)PbI4 and (4AMP)PbI4 have similar screened Coulomb interactions among excited charge carriers, as the dielectric constants for the organic cations are almost the same. Although the lifetimes of the intraband relaxations are slightly longer in 2D RP perovskites because of weaker nonadiabatic couplings (Supplementary Fig. 13), the Coulomb interactions are less screened due to the small dielectric constant of the cations (see Supplementary Note 5), leading to a more significant scattering of the hot carriers with optical phonons.

Spin-selective hot carrier cooling processes in 2D DJ perovskites. One way to retard hot-carrier cooling at longer delays in (4AMP)PbI4 is to manipulate the hot carriers via band splitting. To confirm and further understand the role of band splitting in the hot-carrier cooling processes, we performed circular polarized transient absorption (CTA) measurements for (3AMP)PbI4 and (4AMP)PbI4 films. In the CTA measurements, the high-energy excitations were set to be polarized either right-handed circular (σ+) or left-handed circular (σ−), and a copolarized (counter-polarized) probe pulse was used to probe the hot carrier relaxation from spin-up and spin-down states (see the scheme for the experimental setup in Supplementary Fig. 14). As illustrated in Fig. 4a, spin states with total angular momentum (|+1> or |−1>) and high-energy levels (|+n> or |−n>) are generated using the polarized pump pulse. The normalized cocircular and counter circular pump-probe TA spectra of the (3AMP)PbI4 and (4AMP) PbI4 films are shown in Supplementary Figs. 15 and 16, and the corresponding fitting parameters for the kinetics probed at the photobleaching peaks are given in Supplementary Table 7.

Figure 4b, c show the Tex evolution of (3AMP)PbI4 and (4AMP) PbI4 following high-energy excitation with a pump fluence of 4.0 μJ/cm2. For the case of (3AMP)PbI4, the Tex decays are quite similar to those observed in the TA measurements and are not sensitive to the type of circular polarization for the pump and probe. However, (4AMP)PbI4 shows a fast initial decay of Tex and a slower decay of tens of picoseconds when Tex approaches 400 K, especially with the copolarized σ−σ+ pump and probe. The extracted Tex lifetimes and the initial decays (τ1) for (4AMP)PbI4 film are 4–6 ps and 2–3.5 ps, respectively, both of which are much higher than those obtained by the TA measurements with the same pump fluence. Therefore, the Rashba band splitting in (4AMP)PbI4 can induce an additional barrier to spin flipping because |+n> and |−n> are present in different momentum valleys, as well as reduced spin-phonon scattering of hot electrons from two different spin states. We further performed NAMD calculations by treating the hot electrons from two split conduction bands with consideration of electronic decoherence effects as the high-energy levels of (4AMP)PbI4 are well separated33. As shown in Fig. 4d, the lifetimes of hot electrons in (4AMP)PbI4 with spin-up and spin-down states are ~228 fs, which is much longer than that obtained with consideration of coherence effects and agrees well with the rise time (τrise = ~190–210 fs) obtained from the CTA kinetics. However, (3AMP) PbI4 retains a similar rise time (τrise = ~180–200 fs) as compared to that obtained from TA kinetics following the same pump fluence (4 μJ/cm2).

The schematic illustration in Fig. 4e depicts the hot-carrier cooling processes in 2D DJ and RP perovskites. In all cases, the initial cooling processes are mainly governed by the nonequilibrium LO-phonon population (i.e., the scattering of hot electrons with LO-phonons). Then, the hot phonon emission contributes to slow hot-carrier cooling up to tens of picoseconds, especially at a high pump fluence. Moreover, the hot-carrier cooling process can be retarded by Coulomb screening effects, as the macroscopic electric field induced by the out-of-phase displacements of the atoms is weakened by Coulomb screening. For (4AMP)PbI4, the Rashba band splitting means that the hot-carrier cooling is not only dependent on the interactions between hot electrons and LO-phonons but also affected by spin-dependent scattering of hot electrons34. The D’yakonov–Perel’ (DP) mechanism dominates in (4AMP)PbI4 in which there is no inversion symmetry, and the Rashba effect induces spin precession randomized by scattering due to the SOC-induced internal effective magnetic field35. In addition, strong spin-phonon scattering can decrease the hot-carrier lifetime, as it gives rise to faster spin randomization and flip. To minimize spin-dependent scattering, hot carriers with spin-up or spin-down states can be manipulated through circular copolarized light excitation; in that instance, the hot-carrier temperature approaches 400 K and has a longer lifetime.

In summary, we have demonstrated the significant influence of Rashba band splitting on the hot-carrier cooling dynamics in 2D Dion–Jacobson hybrid perovskites. Electronic band structure calculations and measurements of the temperature-dependent PL spectra and PL decay were used to verify the presence of Rashba band splitting in (4AMP)PbI4, which originates from the symmetry breaking by in-plane equatorial distortions. The scattering between hot electrons and LO-phonons governs the initial fast cooling in both (3AMP)PbI4 and (4AMP)PbI4. The spin-dependent scattering of hot electrons generated by the Rashba effect can accelerate hot-carrier cooling in (4AMP)PbI4. Importantly, the cooling process can be slowed down by controlling the spin states of the hot carriers with circular copolarized excitation. Our findings highlight the importance of Rashba band splitting in two-dimensional perovskites as a powerful tool to control hot-carrier cooling dynamics, which can be exploited to design and synthesize 2D materials with promising optoelectronic and spintronic applications.

Methods

Materials. Lead(II) oxide (PbO > 99%), lead(II) iodide (PbI2 > 99%), 3-(aminomethyl)piperidine (3AMP), 4-(aminomethyl)piperidine (4AMP), benzylamine, hypophosphorous acid (H3PO2), N,N’-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and diethyl ether (DEE) were purchased from Sigma Aldrich and...
used without further purification. Phenylethylammonium iodide (PEAI) was purchased from GreatCell Solar, and hydroiodic acid (HI, 55–58%) was obtained from Alfa Aesar.

**Fabrication of 2D perovskite thin films.** The solutions of single crystals were prepared in 1 mL of mixed solvent (DMF:DMSO = 80:20) to reach a concentration of 100 mg/mL. To fabricate the thin films, 100 µL of single crystal solution was pipetted onto the glass substrate and spin-coated at 2000 RPM for 60 sec. After 40 sec, 700 µL of DEE was added as an antisolvent. Then, the (3AMP)PbI4 and (4AMP)PbI4 films were annealed at 140 °C for 5 min and the (PMA)2PbI4 and (PEA)2PbI4 films were annealed at 80 °C for 3 min. The thicknesses of 2D DJ perovskite films were ~300 nm as measured via the thickness profiler; the root mean square roughness (RMS) was 2.6 nm for (3AMP)PbI4 and 8.7 nm for (4AMP)PbI4 (see Supplementary Fig. 2).

**X-ray diffraction measurements.** X-ray diffraction patterns of the (3AMP)PbI4 and (4AMP)PbI4 films were recorded using a Bruker D8 Advance (40 kV, 40 mA) with CuKα radiation (λ = 1.5406 Å) operating at a step size of 0.02° and a speed of 0.4 sec/step at room temperature.

**Steady-state absorption measurements.** Absorption spectra of the (3AMP)PbI4, (4AMP)PbI4, (PMA)2PbI4 and (PEA)2PbI4 films were recorded in absorbance mode using a LAMBDA 1050 (Perkin Elmer).

**Femtosecond transient absorption measurements.** Femtosecond transient absorption measurements were performed for the 2D perovskite films by using a multipass amplified Ti:sapphire laser (800 nm laser pulses with 7 mJ/pulse, pulse width of ~100 fs with a repetition rate of 1 kHz, Astrella from Coherent) in conjunction with Helios spectrometers. Different excitation pump pulses (see the...
Density functional theory (DFT) calculations. DFT calculations were carried out for 2D perovskites, (PMA)$_2$PbI$_4$, (PEA)$_2$PbI$_4$, (3AMP)$_2$PbI$_4$, and (4AMP)$_2$PbI$_4$, using the projector-augmented wave (PAW) method as implemented in the VASP code.$^{37,38}$ The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional was used. A uniform k-mesh grid of 4 × 4 × 2 was used for (PMA)$_2$PbI$_4$, (PEA)$_2$PbI$_4$, and (4AMP)$_2$PbI$_4$, and 4 × 2 × 2 was used for (3AMP)$_2$PbI$_4$. The plane-wave base set cutoffs for the wavefunctions were set at 450 eV. Starting from the experimental lattice parameters (CCDC 1831521 for (3AMP)$_2$PbI$_4$ and CCDC 1831525 for (4AMP)$_2$PbI$_4$)$^{42}$, the atomic positions for all 2D perovskites were fully relaxed by relaxing both the cell parameters and the atomic positions until the supercells had forces of less than 0.01 eV/Å on each atom. The Heyd–Scuseria–Ernzerhof hybrid functional (HSE06), with spin-orbit coupling, was used to calculate the electronic band structures (Fig. 1c, d).

The Raman and far-infrared vibrational mode positions and intensities of the 2D perovskites were calculated by using the Phonon code as implemented in the Quantum Espresso (QE) package.$^{39,40}$ The local density approximation (LDA) exchange-correlation functional with norm conserving pseudopotentials was used, and the plane-wave base set cutoffs for the wavefunctions were set at 90 Ry with a self-consistency threshold of 10$^{-11}$ Ry. The SOC was not included in the Raman calculations, as it plays a less significant role than the geometry in the description of the vibrational properties of heavy metal-based perovskite systems.

Nonadiabatic molecular dynamics (NAMD) calculations. The crystal structures of the 2D perovskites were further optimized at the GGA/PBE level using the PWSCF code as implemented in the QE package.$^{39,40}$ Ultrasoft pseudopotentials were used considering spin-orbit coupling. Uniform Brillouin zone grids of 4 × 4 × 2 k-mesh for (PMA)$_2$PbI$_4$, (PEA)$_2$PbI$_4$, and (4AMP)$_2$PbI$_4$, and 4 × 2 × 2 was used for (3AMP)$_2$PbI$_4$. The plane-wave base set cutoffs for the wavefunctions were set at 450 eV. Starting from the time-dependent Schrödinger equation

\[ i\hbar \frac{\partial \Psi_n(t)}{\partial t} = H \Psi_n(t) \]

where $H$ is the Hamiltonian, and $\Psi_n(t)$ is the electronic wavefunction, the hot carrier relaxations were investigated by calculating the average energy and population of charge carriers from several excited states. The probability of transition between adiabatic states $i$ and $j$ can be calculated using the wavefunction expansion coefficients and coupling, defined as $d_{ij} = \langle \Phi_i | \Phi_j \rangle$. Detailed descriptions for the NAMD theory can be found in Refs. $^{33,41}$. A total of 1500 geometries were randomly selected from the adiabatic trajectories and used as initial conditions in the NAMD calculations.

Data availability

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

Code availability

Vienna ab initio simulation package (VASP) for the periodic DFT calculations is available at https://www.vasp.at/. Quantum Espresso code for the phonon calculations is freely available at https://www.quantum-espresso.org/. PYXAID code for the nonadiabatic molecular dynamics calculations is available at https://github.com/quantum-dynamics-hub/pyxaid2.

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Author contributions

J.Y. conceived the idea and designed the theoretical work. J.Y., O.M.B. and O.F.M. crafted the experimental plan and directed the research. J.Y. performed all the theoretical calculations. J.Y., J.L.B., and O.F.M. analyzed the theoretical results. R.N. prepared the film samples and measured the PL and absorption spectra. P.M. performed the transient absorption spectra measurements. L.G.A. performed the time-resolved PL measurements. D.A. and I.S.R. performed the temperature-dependent PL measurements. J.Y., J.L.B., and O.F.M. wrote the manuscript. All authors discussed and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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