Distinguishing between dynamical and static Rashba effects in hybrid perovskite nanocrystals using transient absorption spectroscopy

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The dynamical and static Rashba effects in hybrid methylammonium (MA) lead halide perovskites have recently been theoretically predicted. However, only the static effect was experimentally confirmed so far. Here we report on the dynamical Rashba effect observed using snapshot transient absorption spectral imaging with 400 nm pumping for a fully encapsulated film of ~20-nm-sized 3D MAPbBr\textsubscript{3} nanocrystals. The effect causes a ~240 meV splitting of the lowest-energy absorption bleaching band, initially appearing over sub-ps timescale and progressively stabilizing to ~60 meV during ~500 ps. The integrated intensities of the split subbands demonstrate a photon-helicity-dependent asymmetry, thus proving the Rashba-type splitting and providing direct experimental evidence for the Rashba spin-split edge states in lead halide perovskite materials. The ultrafast dynamics is governed by the relaxation of two-photon-excited electrons in the Rashba spin-split system caused by a “built-in” electric field originating from dynamical charge separation in the entire MAPbBr\textsubscript{3} nanocrystal.

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Methylammonium (MA) lead halide perovskites appear most promising photovoltaic semiconductors for solar cell applications. Although numerous technological issues to commercialize this hybrid system yet to be resolved, its unique properties, such as long-lived photoexcited carriers and extremely long carrier diffusion lengths, have a special fundamental interest. To explain these properties of hybrid organic-inorganic perovskites (HOIPs), two models were proposed being mainly related to the Rashba spin-split effect and to the large polaron concept. In both cases, the recombination of carriers is expected to be forbidden, thus prolonging the lifetime and diffusion length of carrier in the edge states, as a consequence of the spin/momentum selection rules and screening from other carriers and defects, respectively. However, the joint effect of these two phenomena on the efficiency of HOIP-based solar cells is still under intense debate and need to be addressed more specifically.

On the other hand, the full manipulation of electron spins in semiconductor heterostructures remains one of the most challenging problems for next-generation electronics, called spintronics. 2D and 3D HOIPs [(CH₃NH₃)ₓPbI₃, CH₃NH₃PbBr₃, and CH₃NH₃PbI₃Br], where x = Cl, Br, I] seem again very promising for these purposes since containing heavy elements (Pb and X) possessing strong spin-orbit coupling (SOC). The resulting splitting of spin-states in these systems is expected to occur rather due to the lack of structural inversion symmetry (the Rashba effect) and hence does not require any magnetic field to be applied. This key circumstance governing the zero-magnetic-field Rashba effect can be achieved in a variety of different ways by applying an external or internal electric field, for example. Because inorganic sublattice of HOIPs governs their electronic structure near the conduction band (CB) and valence band (VB) extrema, the Rashba spin-split edge states seem basic for spintronics applications as well.

Such a dual importance of the Rashba effect makes it to be central in developing prospective materials for modern and future electronic/spintronic, optoelectronic/optospintronic, and photovoltaic technologies. The Rashba effect can be either static or dynamical depending on how stable is the source of electric field applied since being linearly dependent on the electric field strength. Specifically, the enormously large (giant) static Rashba effect was observed in 3D and 2D HOIPs as a consequence of the mesoscopic surface depletion field and an external quasi-steady electric field, respectively.

The dynamical Rashba effect is expected to exclusively be observed using time-resolved techniques on sub-ps timescale, since being predicted to reflect the ultrafast MA cation electrostatic dynamics locally breaking structural inversion symmetry. However, similar situation may also occur upon mesoscopic structural perturbations, such as those induced by an internal (“built-in”)/interfacial) electric field, for example, resulting from dynamical charge separation in the entire HOIP nanocrystal (NC) or at the interfaces between HOIP thin films and the corresponding substrates. A giant Rashba splitting in 2D and 3D HOIPs exceeds those observed in the majority of heterostructures and layered systems, such as 2D electron gas at semiconductor heterointerfaces, layered bimetallic materials (Mn₂Au), 2D van der Waals heterostructures, Au(111) surface state, graphene-Au interface, and the Pb monolayer covered semiconductors. However, it is slightly smaller than those appeared in the most efficient systems, such as Bi on Ag surface alloy and the bulk polar semiconductors BiTeF₅. The common techniques for studying the Rashba effect are Shubnikov-de Haas oscillations, angle-resolved photoemission spectroscopy (ARPES) and electro-absorption modulation spectroscopy (EAMS). Although the latter and time-resolved ARPES are potentially capable of monitoring the dynamical Rashba effect, all recent experiments were performed to monitor exclusively a static Rashba effect. Because the steady-state large polaron and Rashba effects in HOIPs can be of comparable magnitude, they remain undistinguishable, being a source of numerous confusions.

Here using transient absorption (TA) spectroscopy employing 400 nm pumping (−3.1 eV photon energy), we studied ultrafast dynamics of the zero-magnetic-field Rashba spin-split energy (ΔE) in thin films (~20 nm thick) of 2D and 3D MAPbBr₃ NCs synthesized by the ligand-assisted reprecipitation technique. The Rashba effect appears as a splitting of the absorption bleaching bands for two CBs (CB1 and CB2). However, it is dynamical for the CB1, while being static for the CB2. The dynamical effect includes ultrafast and slow (quasi-static) components, both appearing on the mesoscopic scale as a consequence of the “built-in” electric field originating from dynamical charge separation in the entire MAPbBr₃ NC. The ultrafast component is caused by the relaxation of two-photon-excited electrons and includes a sub-ps rise to ΔE ~240 meV and a gradual stabilization to ΔE ~60 meV during ~500 ps. The stabilized component originates from the slow (µs timescale) relaxation of one-photon-excited carriers. The static Rashba effect for the CB2 of ΔE ~200 meV is caused by a local electric field affecting the Pb sites due to MA cation reorientation. The integrated intensities of the split subbands for the CB1 demonstrate a photon-helicity-dependent asymmetry, thus confirming Rashba-type splitting and providing direct experimental evidence for the Rashba spin-split edge states in 3D HOIP NCs. We also found that charge separation at the MAPbBr₃/ZnO heterointerface weakens the “built-in” electric field in MAPbBr₃ NCs, thus suggesting a way to control the dynamical Rashba effect.

Results

Sample characterization. Figure 1a shows the transmission electron microscope (TEM) image of the as-grown colloidal cubic-shaped MAPbBr₃ NCs (see also Methods). The corresponding histogram shows the NC size range of ~21.3 ± 1.7 nm. High-resolution TEM image (Fig. 1b) confirms the high crystallinity of the individual MAPbBr₃ NCs with the typical characteristic lattice fringes spaced by ~0.41 nm. X-ray diffraction (XRD) proves a well-defined 3D structure of MAPbBr₃ NCs (Fig. 1f). Figure 1b also shows schematically the synthesis method allowing for fully encapsulating MAPbBr₃ NCs between the two sapphire plates. Specifically, MAPbBr₃ NCs were spin-coated to either the clean sapphire (Sa) plate or to that initially ALD(atomic layer deposition)-coated with a ~40 nm thick ZnO layer, being covered afterwards by another sapphire plate and leaving the air gap above the NC film of ~1 µm (MAPbBr₃/Sa and MAPbBr₃/ZnO samples, respectively). The fully encapsulated MAPbBr₃ NCs demonstrate stable optical properties, such as high transparency and uniform PL (Fig. 1c). The thickness of the MAPbBr₃ layer viewed by scanning electron
microscopy (SEM) just slightly exceeds the NC size (Fig. 1d and e), suggesting that not more than two layers of the closely packed MAPbBr$_3$ NCs were deposited.

Figure 1g and h shows the room-temperature conventional absorption and photoluminescence (PL) spectra of MAPbBr$_3$/Sa and MAPbBr$_3$/ZnO. The absorption spectrum of MAPbBr$_3$/Sa reveals two contributions associated with electronic transitions from the VB to the CB1 and to the CB2. The ZnO layer additionally contributes to the absorption spectrum in the UV range for MAPbBr$_3$/ZnO (Fig. 1g). The Stokes shift was estimated as:\[ \hbar \Delta \omega_{\text{stokes}} = \lambda_e + \lambda_h = -60 \text{ meV}, \]
where $\hbar$ is the reduced Planck constant, $\Delta \omega_{\text{stokes}}$ is the frequency difference between the 1s free exciton peak in absorption spectra and PL-peak, and $\lambda_e$ and $\lambda_h$ are the corresponding polaronic reorganization energies for electrons and holes, respectively. The latter quantities can also be estimated in the frame of the Fröhlich large polaron model as $\lambda_e = -32.6 \text{ meV}$ and $\lambda_h = -39.2 \text{ meV}$ for the longitudinal-optical (LO)-phonons contribution (Supplementary Note 1). The intensity of the 1s free exciton peak decreases in MAPbBr$_3$/ZnO due to the interfacial-field-induced exciton dissociation, the process which balances the relative densities of free carriers and excitons. The latter process is accompanied by a blue-shift of PL-peak ($\sim$10 meV) (Fig. 1h). These facts together with good coincidence between polaronic reorganization energies and the Stokes shift all prove the free exciton (polaronic exciton) nature of the band-edge light emission at room temperature. The latter statement is also well consistent with the large free polaronic exciton binding energy in MAPbBr$_3$ ($\sim 35 \text{ meV}$), much exceeding the room temperature $\kappa_B T = 25.7 \text{ meV}$, where $\kappa_B$ is the Boltzmann constant and $T$ is the temperature. Nevertheless, as will be seen further below, this picture in not complete and should be
Fig. 2 TA spectra of MAPbBr\textsubscript{3}/Sa and MAPbBr\textsubscript{3}/ZnO. a Conventional absorption and PL spectra of MAPbBr\textsubscript{3}/Sa and MAPbBr\textsubscript{3}/ZnO (the same as those shown in Fig. 1g and h). b and c TA spectra of MAPbBr\textsubscript{3}/Sa and MAPbBr\textsubscript{3}/ZnO, respectively, measured using the cross-linearly-polarized geometry at delay-times and pump powers, as indicated. The inhomogeneously broadened Rashba spin-split low-energy (CB1L, CB2L) and high-energy (CB1H, CB2H) subbands are highlighted for the CB1 and the CB2 by different color Gaussian profiles. The red curves are the fits to the spectra when only broad negative subbands were taken into account. The splitting energy is labeled as $\Delta E$. The white-color Lorentzian profiles (shown in b) provide an example of the homogeneously broadened components of ~10 meV FWHM. d and e The energy band diagrams of MAPbBr\textsubscript{3}/Sa and MAPbBr\textsubscript{3}/ZnO are shown together with the pump regimes and the relaxation pathways. The “built-in” ($E_{\text{b-in}}$) and interfacial ($E_{\text{in}}$) electric fields are marked by arrows.

modified by adding the spin-split states resulting from the Rashba effect. However, because Rashba energies in the steady state are comparable to (or even less than) the corresponding reorganization energies of polaronic quasiparticles, the large polaron and Rashba effects in HOIPs are indistinguishable one from the other, however, they can be recognized more specifically in the time-resolved mode.

**TA spectra: the peak assignments and the excitation regimes.** Figure 2 compares the conventional absorption and TA spectra of MAPbBr\textsubscript{3}/Sa and MAPbBr\textsubscript{3}/ZnO. The TA spectra were measured at room temperature with 400 nm pumping of ~1.0 mW average power using cross-linearly-polarized pump-probe geometry (pump vertical and probe horizontal) and sub-ps delay-times (Supplementary Note 2). The broad negative contributions demonstrating a distinct splitting trend are due to the absorption bleaching (Pauli blocking), the process which extends the material band gap $E_g$ (VB-CB1 ~2.4 eV) and is known as the Burstein-Moss (BM) shift\textsuperscript{41,42} (Supplementary Note 3). The positive contributions originate from the many-body effects\textsuperscript{41-44}, such as a correlated motion of carriers and their scattering with ionized impurities or optical phonons. The resulting band gap renormalization (BGR) leads to the $E_g$ narrowing and induces unoccupied states responsible for photo-induced absorption\textsuperscript{45}. The corresponding positive spectral features energetically situate below and above the negative BM contributions of TA spectra (Supplementary Note 3). The BGR phenomenon is hence a mesoscopic effect influencing the entire CB, being similar to its local counterpart associated with the large polaron formation. However, the lowest-energy BGR states are initially unoccupied, alternatively to the polaronic quasiparticle states resulting from carrier self-trapping. Further occupation of BGR states by polarons causes the polaronic subband to be formed, which
Fig. 3 The light polarization effect. a and b TA spectra (CB1 BM contributions), which were measured with ~0.7 ps delay-time. The linearly and circularly polarized light was applied for the pump and probe beams, as indicated. Photon polarization was varied by rotating the λ/4 waveplate.

The pump and probe average powers were ~0.5 and ~0.4 mW, respectively. The Rashba spin-split subbands were fitted using Gaussian profiles of the integrated intensities $I_{CB1L}$ and $I_{CB1H}$. c The ratio of the spin-split component integrated intensities reveal a pump photon-helicity-dependent behavior (numbers accompanying each of the dots represent the actual ratios) and closely follows the sin^2 $\alpha$ law, where $\alpha$ is the λ/4 waveplate rotation angle. Broad horizontal lines present the theoretically predicted ratios when ignoring the pump photon polarization effect.

d Optical transitions linked to the corresponding spin levels (see text for all notations).

completely governs the light emission from the sample. This behavior is proven by matching the BGR TA and PL peaks (Fig. 2a and b). Consequently, the energetic difference of ~40 meV between the 1s exciton peak in the conventional absorption spectrum and the lowest-energy absorption bleaching peaks in the TA spectrum corresponds to the polaronic exciton binding energy\textsuperscript{39,40}. Other processes which can potentially contribute to TA spectra are expected to be negligible (Supplementary Note 4).

The broad BM bands of MAPbBr\textsubscript{3}/Sa are split out into two subbands spaced $\Delta E \sim 220$ meV apart for the CB1 and $\Delta E \sim 200$ meV for the CB2 (they are referred further below to as the lower-energy (CB1L, CB2L) and higher-energy (CB1H, CB2H) subbands, respectively) (Fig. 2b). The former value increases from $\Delta E \sim 160$ to ~240 meV with increasing pump power from ~0.3 to ~2.0 mW, whereas the latter one remains nearly constant with pump power (Supplementary Note 3). The $\Delta E$ range closely matches that previously observed using ARPES and EAMS and assigned to the giant Rashba effect in 2D/3D HOIP materials\textsuperscript{5,6}. The effect drops down to $\Delta E \sim 130$ meV for the CB1 of MAPbBr\textsubscript{3}/ZnO (Fig. 2c). Consequently, the pump power dependence becomes sharper since involving a broader splitting range extending from $\Delta E \sim 60$ to ~240 meV (Supplementary Note 3). Furthermore, the splitting of the CB2 for this sample is masked by the BM contribution of the ZnO CB.

The fact that ~3.1 eV pump photons induce broad TA contributions appearing at higher photon energies suggests two-photon pumping to occur in both MAPbBr\textsubscript{3} and ZnO, giving rise to the CB absorption bleaching (Fig. 2d and e). Additionally, there is a narrow negative feature peaked at ~3.1 eV, thus suggesting that one-photon pumping is also involved. Because the latter feature is delay-time independent and appears at energy much exceeding $E_g$, it points to the VB absorption bleaching (see
also Methods). Specifically, one-photon-excited holes rapidly relax towards the VB edge ($\leq 0.16$ ps) (Supplementary Note 5) and block out the one-photon pumping transitions. Because the lifetime of holes may approach to the inverse repetition rate of the laser used (~1.0 ms), the ~3.1 eV feature is presented in TA spectra constantly as long as the sample is optically pumped. This quasi-steady dynamics occurs hence because one-photon-excited carriers do not relax completely between the two sequential pump pulses$^{46}$.

We also note that the CB1H subband is spectrally noisier than the CB1L one (Fig. 2b). Because this tendency weakens with a gradual filling of the CB1H subband (as demonstrated further below in Fig. 4a), we associate this behavior with a partial removal of the inhomogeneous broadening when electron population over the subband is still not high enough. The inhomogeneous broadening is believed to arise from the structural fluctuations at the interfaces$^{47}$ appearing through the internal (“built-in”) electric field ($E_{\text{int}}$) with a standard deviation of the Gaussian distribution, rather than from the quantum confinement induced variations$^{48}$ remaining ineffective since the size of NCs significantly exceeds the exciton Bohr radius (a few nm)$^{49}$. Consequently, the homogeneously broadened features can be recognized (Fig. 2b) and fitted using a Lorentzian profile to estimate the spin decoherence time $T_2 = h/\gamma = 130$ fs, where $\gamma$ denotes the dephasing rate [Lorentzian full width at half maximum (FWHM) = 2$\gamma$]. The origin of the spin dephasing seems appropriate to the inelastic collisions of spin-polarized electrons with the NC boundaries. Consequently, the electron Fermi velocity obtained as $v_F = 20$ nm/130 fs = 1.5$\times$10$^7$ m/s matches those known for the majority of semiconductors$^{49}$. In general, the spin relaxation dynamics in HOIP NCs seems to combine the D’yakonov-Perel’ and Elliot-Yafet mechanisms, additionally including multiple spin-flip and spin-filtering processes$^{44}$, because dealing with the relaxation of extremely hot (non-equilibrium) electrons relaxing through the Rashba spin-split subbands of the CB2 and the CB1.

**The light polarization effect: the spin-dependent splitting dynamics.** The ratio between integrated intensities of TA peaks associated with the spin-split subbands reveals a photon-helicity dependence (Fig. 3a and b), which closely follows the sin$2\alpha$ law when the $\lambda/4$ waveplate controlling the pump beam polarization is rotated by an angle $\alpha$ (Fig. 3c). This finding suggests the spin-dependent optical pumping$^{50,51}$ and the Rashba-type spin splitting for both the CB1L and the VB (Fig. 3d), despite two-photon pumping energetically exceeding the CB2 edge is applied. The latter behavior implies that the Rashba spin-split subbands of the CB2 preserve the initial spin polarization of two-photon-excited electrons since flipping their spins twice.

Additionally, we found that the integrated intensity of the CB1L subband dominates over the CB1H one ($I_{\text{CB1L}} / I_{\text{CB1H}} > 1$) when left-handed ($\sigma^-$) probe light is applied and vice versa for $\sigma^+$ light ($I_{\text{CB1L}} / I_{\text{CB1H}} < 1$) (Fig. 3a and b). This observation points to the different transition probabilities, which can be obtained explicitly in assumption that $E_g$ (VB-CB1L) is located at the R point of the Brillouin zone and the VB is mainly formed by the Pb(6s)Br(5p) orbitals while the CB1 originates mainly from Pb(6p) orbitals$^{52}$. Consequently, SOC split out the CB1 into the lower twofold ($J = 1/2$) and upper fourfold ($J = 3/2$) states, where $J = L + S$ represents the total angular momentum with $L = 1$ being the orbital angular momentum and $S = 1/2$ being the electron’s spin. Alternatively, the VB remains unchanged ($L = 0$). The lowest-energy subband of the CB1 and the VB are doubly degenerate ($m_j = \pm 1/2$, where $m_j$ is a projection of $J$-momentum onto the positive $z$ axis). The degeneracy is lifted due to the Rashba effect. Specifically, using Clebsch-Gordan coefficients, the resulting $J$-states can be presented as a linear superposition of spin-up ($m_j = +1/2$) and spin-down ($m_j = -1/2$) states$^{52}$. Consequently, the modulus squared Clebsch-Gordan coefficients represent the probability of spin-up and spin-down states to be filled up with spin-up and spin-down electrons photoexcited with probing light. The Rashba spin-split states for the CB1 (CB1L and CB1H subbands) and the VB can subsequently be characterized by two quantities, $|m_j, m_J|$ (Fig. 3d). Because the $\sigma^-$ and $\sigma^+$ probing light changes the angular momentum by $+\hbar$ and $-\hbar$ ($\Delta m_j = 1$ and $\Delta m_j = -1$), the resulting occupation ratios of the CB1L and CB1H subbands with $m_j = +1/2$ and $m_j = -1/2$ intended to be occupied with spin-up and spin-down electrons are $2/3$ to $1/3$ and $1/3$ to $2/3$, respectively. The resulting ratios $I_{\text{CB1L}} / I_{\text{CB1H}} \approx 2$ and $I_{\text{CB1L}} / I_{\text{CB1H}} = 0.5$ are hence in good agreement with those experimentally observed (Fig. 3c).

**The static and dynamical Rashba effects.** Figure 4a and b shows a snapshot TA spectral imaging of MAPbBr$_3$/Sa and MAPbBr$_3$/ZnO (Supplementary Note 2), demonstrating that two-photon-excited electrons progressively relax down towards the CB edges of MAPbBr$_3$ and ZnO. However, there exists a ~0.4 ps offset of the TA signal for MAPbBr$_3$/Sa, as discussed further below. The relaxation process is caused by the electron-LO-phonon inelastic scattering$^{53-58}$, allowing for gradually filling up all the lower energy CB2 and CB1 states. These relaxation trends appearing in TA spectra of HOIPs were intensively studied$^{45,54,58}$, but exclusively for energies below the one-photon pump energy.

The spectacular relaxation dynamics observed here involving simultaneous one-photon and two-photon pumping suggests the different origins of the Rashba effect for the CB1 and the CB2. Specifically, despite $\Delta E$ remains nearly constant when the intensity of the CB2H subband gradually redistributes with delay-time towards the CB2L one, the similar redistribution between the CB1H and CB1L subbands is accompanied by a decrease of $\Delta E$. This behavior distinguishes between the static and dynamical Rashba effects occurring in the CB2 and the CB1, respectively. The former of $\Delta E \approx 200$ meV is caused by a local electric field due to MA cation reorientation$^{2,47}$. This ligand-type electric field is less sensitive to the charge separation in the entire NC, since affecting more energetic and well screened inner Pb orbitals forming the CB2 edge.

The dynamical effect includes the ultrafast and slow components which are associated with two-photon- and one-photon-excited carriers, respectively. Because one-photon absorption is more efficient compared to the two-photon one (Supplementary Note 6) and because one-photon-excited carriers are less energetic than the two-photon-excited ones (Supplementary Note 5), the former are expected to be self-trapped at the interfaces preferably through the polaron mechanism since they reach quasi-equilibrium with lattice polar phonons much faster (<0.2 ps) than the two-photon excited carriers (~1.0 ps) (Supplementary Note 5). The resulting charge...
Fig. 4 Snapshot TA spectral imaging and the ultrafast Rashba splitting dynamics. a and b TA spectra of MAPbBr$_3$/Sa and MAPbBr$_3$/ZnO, respectively, which were measured in a cross-linearly-polarized geometry with the pump power of ~2 mW and different delay-times indicated. The Rashba spin splitting energy ($\Delta E$) is indicated for each pair of the TA peaks highlighted by the different-color Gaussian profiles. The white-color Lorentzian profiles (shown in a for 0.7 ps delay-time) present the homogeneously broadened components (Fig. 2). c A schematic presentation of the Rashba effect for the CB and the corresponding Rashba energy ($E_R$), Rashba spin-split energy ($\Delta E$), and momentum ($k_0$). d and e The evolution of the Rashba energy and Rashba parameter, respectively, in the CB1 and CB2 of MAPbBr$_3$/Sa and in the CB1 of MAPbBr$_3$/ZnO measured with different pump powers, as indicated by the corresponding colors.

separation in the entire NC arises from different relative diffusivities of one-photon-excited electrons and holes (the photo-Dember effect)\textsuperscript{59}. The latter process supposedly enhances the surface fields associated with the downward and upward band bending at the MAPbBr$_3$/Sa and the MAPbBr$_3$/Air interfaces\textsuperscript{60,61}, respectively (Fig. 2d). The resulting $E_{b-in}$ is normal to the film plane and hence induces the Rashba effect. The slow dynamics of $\mu$s timescale is expected to be due to the $E_{b-in}$-induced dipolar MA cation reorientation dynamically changing the PbBr$_6$ octahedra equilibrium coordinates or due to the extremely low recombination rates of spatially separated and self-trapped carriers, or both.

Alternatively, the ultrafast Rashba effect is caused by two-photon-excited carriers, which initially enhance $E_{b-in}$ and hence the Rashba effect above the level maintained by one-photon-excited self-trapped carriers and then weaken it upon relaxation during ~500 ps. This dynamics occurs as a consequence of a finite number of self-trapping states at the interfaces being already occupied with one-photon-excited carriers. Because two-photon-excited electrons should lose their energy first to be spectrally detectable by our experimental setup limited to ~3.7 eV, a ~0.4 ps offset of the TA signal occurs. This offset disappears in MAPbBr$_3$/ZnO (Fig. 4b) because two-photon-excited electrons in ZnO populate the CB1 edge of MAPbBr$_3$ much faster than two-photon excited electrons in MAPbBr$_3$ (Fig. 2e). Consequently, two-photon-excited carriers retain mobile and are involved into subsequent diffusion and higher-rate recombination extending over a few ns timescale.

TA traces measured in cross-linearly-polarized geometry for all peaks appeared in TA spectra of MAPbBr$_3$/Sa show a multi-exponential decay behavior (Fig. 5). The longest decay-times (a few ns) for the CB1L, CB2L, and CB2H subbands are found to
be similar to those previously observed\textsuperscript{5,16} whereas the CB1H and BGR-related features decay much faster (a few or a few tens ps). In addition, TA traces associated with the CB1H and CB1L subbands both reveal the shortest decay-time components of \textasciitilde0.1 ps (Fig. 5a), which might be associated with direct or phonon-mediated CB1H-CB1L and CB1L-BGR spin-flip relaxation\textsuperscript{2,63}. Both processes are strongly affected by LO-phonon bottleneck and therefore subsequently elongate the dynamics up to \textasciitilde7 ps\textsuperscript{55-58}. The BGR spin states are expected to form dark and bright polaronic excitons\textsuperscript{62}, the population of which is mainly controlled by the CB1L and CB1H population. Consequently, the dark excitons annihilate non-radiatively much faster whereas the bright polaronic excitons exclusively contribute to PL (Fig 2a and b). The relaxation dynamics associated with CB2 also includes the relaxation of two-photon excited carriers through the CB2 BGR states. However, the nature of the long decay-time constants of CB2L and CB2H subbands are poorly understood and call for further investigations. The rise-time for the majority of the TA traces is \textasciitilde0.1 ps, despite it slightly increases for some of them as a consequence of the gradual filling of the subbands within the complex relaxation dynamics. The longest rise-times correspond to the lowest energy BGR states, thus suggesting the lowest rate of their filling. The relaxation dynamics associated with the CB1 in MAPbBr\textsubscript{3}/ZnO is quite similar to that occurring in MAPbBr\textsubscript{3}/Sa. The ZnO contribution reveals typical relaxation dynamics for this material\textsuperscript{38}.

In contrast, the spin relaxation time \textasciitilde35 ps is comparable to that observed for MAPbI\textsubscript{3} thin films\textsuperscript{52}, being much shorter than carrier relaxation time and that the stabilization of Rashba splitting takes (Fig. 6). As circularly polarized pump is applied to MAPbBr\textsubscript{3}/Sa, the linearly polarized probing shows quite similar relaxation dynamics to that observed with linearly polarized pumping and associated with direct or phonon-mediated spin-flip relaxation and LO-phonon bottleneck (Fig. 5a and Fig. 6a and c). The latter fact points to the low sensitivity of probing light to spin-polarized dynamics in this case. Alternately, applying
circularly polarized probing, one can recognize that direct CB1H-CB1L spin-flip relaxation occurs during ~0.1 ps whereas the phonon-mediated CB1H-CB1L spin-flip relaxation takes ~1.5 ps, independently of light helicity (aligned/opposite) of the pump-probe beams (Fig. 6c and f). Despite direct spin-flip relaxation from the CB1L subband to the BGR spin states remains to be of the same timescale (~0.1 ps), the phonon-mediated spin relaxation in the CB1L subband takes ~7 and ~35 ps for the aligned helicity of the pump and probe beams and for the opposite one, respectively (Fig. 6b and e). The similarity of this dynamics for both \( \sigma^{+} \) and \( \sigma^{-} \) light pumping suggests that the final spin alignment in the CB1L and CB1H subbands is governed by filtering of spins within their relaxation process through the Rashba spin-split system of the CB2 rather than due to the initial light helicity of two-photon pumping. The observed spin relaxation times are reasonably ~20-fold shorter compared to that obtained at low temperatures (10 K)\(^{37}\).

To treat the Rashba effect, we use the effective Hamiltonian for a 2D electron gas subjected to SOC\(^{13}\). Consequently, the kinetic energy term \( \frac{\hbar^2 k^2}{2m_e} \) with \( k \) and \( m_e^* \) being the wave vector, and the electron effective mass, respectively, is extended by a Rashba term \( \mathcal{H}_R(k) = \alpha_R(k_x \sigma_y - k_y \sigma_x) \), where \( \alpha_R \) is the Rashba parameter and \( \sigma_i (i = x, y, z) \) denotes the Pauli matrices. The parallel and perpendicular directions with respect to the plane of the NC film are hence \( k_{||} = (k_x, k_y) \) and \( k_{\perp} = k_z \), respectively. Once \( E_{b-in} \) is applied, the lack of inversion symmetry leads to the Rashba spin splitting appearing in the \( k_{||} \) space. The corresponding energy eigenvalues can be presented as two parabolas shifted in the \( k_{||} \) space, \( E^{\pm} = \frac{\hbar^2 k_{||}^2}{2m_e} \pm \alpha_R |k_{||}| \) (Fig. 6).
Fig. 7 The Rashba effect versus the large polaron effect and potential fluctuation at the interfaces of MAPbBr$_3$ NCs. a and b The CB1L subband shift in TA spectra with delay-time measured with different pump powers, as indicated by the corresponding colors. The Rashba effect and the large polaron effect is weakened (a blue-shift) and strengthened (a red-shift) on sub-ps timescale, respectively, giving rise to a plateau-type trend followed by an overall red-shift for longer delay-times. c and d FWHM variations of the CB1H and CB1L subbands with delay-time and their $\Delta E$ dependences, respectively. All the parameters were extracted from the TA spectra measured with different pump powers, as indicated by the corresponding colors. The linear fit (red straight lines) and the corresponding slopes are shown.

The observed $\Delta E = -240 \text{ meV}$ in MAPbBr$_3$/Sa suggests that $E_R = -60 \text{ meV}$, $k_0 = -0.0452 \text{ Å}^{-1}$, and $\alpha_R = -2.655 \text{ eV} \cdot \text{Å}$. These quantities well match those recently reported for 2D/3D HOIPs$^{5,6}$. It is important that $E_R$ significantly exceeds the aforementioned polaronic reorganization energy $\lambda_o = -32.6 \text{ meV}$. This behavior implies that the Rashba effect dominates over the large polaron effect in sub-ps timescale. The temporal dynamics demonstrates a decrease and stabilization of $E_R$ and $\alpha_R$ for CB1 during $-500 \text{ ps}$ (Fig. 4d and e). The resulting value of $E_R = -18 \text{ meV}$ is now much less than the polaronic reorganization energies, indicating that the Rashba effect should be masked by the large polaron effect. The crossover between the two occurs mainly on sub-ps timescale, when $E_R$ decreases to $-35 \text{ meV}$ (a blue-shift of CB1L subband) whereas $\lambda_o$ increases to $-32.6 \text{ meV}$ upon reaching equilibrium with polar phonons (a red-shift of CB1L subband). The resulting dynamics appears as a plateau-type trend followed by an overall red-shift of the CB1L subband with delay-time (Fig. 7a and b).

Alternatively, $E_R$, $k_0$, and $\alpha_R$ remain nearly unchanged for the CB2, demonstrating the static Rashba effect. Additionally to $\Delta E$ and $E_R$, the Gaussian bandwidths (FWHM) of the CB1H and CB1L subbands also decrease with delay-time (Fig. 7c). Plotting FWHM versus $\Delta E$ (Fig. 7d), one can recognize the linear dependence, which is in good agreement with the recent simulations$^{17}$ proving that the potential fluctuations at the interfaces affect $E_{\text{bun}}$ (appears through $\Delta E$) and is mainly caused by the dipolar MA cation reorientations (appears through FWHM).
The initial $\Delta E = \sim -240$ meV in MAPbBr$_3$/ZnO decreases more rapidly. We associate this behavior with the ultrafast charge separation at the MAPbBr$_3$/ZnO heterointerface (Fig. 2e), the process which forces electrons and holes to reside preferably in ZnO and MAPbBr$_3$, respectively. Consequently, $E_{b-in}$ in MAPbBr$_3$ NCs decreases, significantly weakening the dynamical Rashba effect (Fig. 4d and e). This considerable suppression of the dynamical Rashba effect in MAPbBr$_3$/ZnO suggests being controlled by the $E_{b-in}$ strength. However, the effect tends to weaken with increasing pump power, signifying that the charge separation at the MAPbBr$_3$/ZnO heterointerface becomes less efficient with increasing photoexcited carrier density.

**Discussion**

This paper provides direct experimental evidence for the Rashba spin-split edge states induced by the “built-in” electric field in thin films of 3D MAPbBr$_3$ NCs. The main advantage of our experimental approach allowing us to directly observe the Rashba splitting effect is that we used a specific procedure encapsulating preferably not more than two layers of the closely packed ~20 nm sized NCs, thus reducing the effect of structural perturbations associated with the interfaces and the NCs aggregation. Furthermore, our findings are expected to differ significantly from those obtained for colloidal solutions of MAPbBr$_3$ NCs due to incomparable rates of carrier cooling and charge separation. Additionally, we used a thoroughly tested over sub-ps timescale TA setup and a much wider spectral range for measuring TA spectra, which includes pump photon energy and the range exceeding it. This approach is in stark contrast to those previously applied$^{35,54-58}$, where TA spectra were measured exclusively at energies below the one-photon pump energy. Consequently, we found that TA spectra mainly present the relaxation dynamics of two-photon-excited carriers instead of one-photon-excited ones, as initially thought. Additionally, our findings prove that the variations of TA spectra initially assigned to the hot carrier cooling should include the Rashba spin-split effect for the most reasonable explanation of these experiments. Furthermore, we demonstrated that one-photon-excited carriers play a major role in the slow charge separation dynamics providing a quasi-steady Rashba spin-split system to exist as long as the sample is optically pumped. Specifically, the Rashba energy much exceeds the polaronic reorganization energy on sub-ps timescale whereas they are getting comparable at ~1 ps timescale, followed by a dominant contribution of the polaronic reorganization energy over longer delay-times. Consequently, these two effects become undistinguishable in steady-state conditions despite both governing the transport and light-emitting properties of HOIP NCs.

Our findings offer a new direction for researchers to characterize ultrafast spin/carrier dynamics in Rashba spin-split systems with high precision. We also showed that the charge separation at the MAPbBr$_3$/ZnO heterointerface considerably weakens the “built-in” electric field in MAPbBr$_3$ NCs over sub-ps timescale, thus demonstrating a way for controlling the dynamical Rashba effect.

**Methods**

**Sample fabrication.** The CH$_3$NH$_3$PbBr$_3$ NCs were synthesized by the ligand-assisted reprecipitation (LARP) technique$^1$. Specifically, 0.0112 g methylammonium bromine (CH$_3$NH$_3$Br, powder, 99%; Xi’an p-OLED) and 0.0367 g lead (II) bromide (PbBr$_2$, powder, 98%; Sigma Aldrich) were dissolved in 1 mL anhydrous N,N-dimethylformamide (DMF, 99.8%; J&K Scientific) forming a mixture with a concentration of 0.1 mM and then 200 μL oleic acid (~70%; Aladdin) and 20 μL oleylamine (80~90%; Aladdin) were added into this mixture. Afterwards, 100 μL mixture of various precursors was injected into 3 mL chloroform. Then, a yellow-greenish colloidal solution was acquired. For purification, 1.5 mL toluene/acetone mixture with a volume ratio of 1:1 was added into the solution for a centrifugation at 9000 rpm for 2 min, and afterwards the acquired sediment was dispersed in 300 μL hexane for another centrifugation at 4000 rpm for 2 min. Finally, the supernatant was collected for further use.

To prepare the fully encapsulated thin films of 3D CH$_3$NH$_3$PbBr$_3$ NCs (CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbBr$_3$/ZnO samples), the sapphire plates (10x10x0.3 mm; Jiangsu Hanchen New Materials) were cleaned by successively soaking them in an ultrasonic bath with deionized water, acetone, and isopropanol for 10 min each and dried with nitrogen. The sapphire substrates were transferred afterwards into the atomic layer deposition (ALD) system (PICOSUN™ R-200) to grow a ZnO film. Diethyl zinc (DEZn, Zn(C$_2$H$_5$)$_2$) and H$_2$O were used as precursors. High purity nitrogen with dew point below -40 °C was used as a purging and carrier gas. The reactor chamber pressure was set as 1000 Pa during the growth. When the growth temperature of 200 °C was reached, DEZn was introduced to the reactor chamber with a flow rate of 150 sccm followed by purging with nitrogen to remove the residues and byproducts. The precursor of H$_2$O with a flow rate of 200 sccm was introduced afterwards into the reactor chamber to start with the ZnO layer growth. The number of ALD growth cycles was selected to grow a ZnO layer with thicknesses of ~40 nm. Closely packed and uniformly distributed CH$_3$NH$_3$PbBr$_3$ NCs were spin-coated to the clean sapphire plate or to that initially ALD-coated with a ZnO layer by optimizing the spin speed to 1500 rpm. The resulting structure was covered afterwards by another sapphire plate, leaving the air gap above the NC film of ~1μm and gluing sapphire plates on sides by UV adhesive.

**Experimental set-up.** Transient absorption spectra were measured using the Transient Absorption Spectrometer (Newport), which was equipped with a Spectra-Physics Solstsic Ace regenerative amplifier (~100 fs pulses with 1.0 KHz repetition rate) for the probe beam and a Topas light converter for the pump beam. Specifically, we exploited an optical pump at $h\nu_{pump} = 400$ nm ($h\nu_{pump} = 3.1$ eV) with a bandwidth of ~26 meV and the white light supercontinuum probe within the entire visible range ($h\nu_{probe} = 1.65 - 3.8$ eV) generated in a sapphire plate. All measurements were performed in air at room temperature using either a cross-polarized geometry (probe horizontal, pump vertical) or a circularly polarized geometry (pump and probe could be either left-handed or right-handed circularly polarized). The probe beam was at normal incidence, whereas the pump beam was at an incident angle of ~30°. The narrow negative feature that appears in TA spectra at 3.1 eV has nothing to do with a pump scattering light since disappears with the probe light block. Therefore it is associated with the VB absorption bleaching induced by one-photon pumping. The spot size for pump and probe beams were ~400 and ~150 μm, respectively. The pump beam average power was in the range of ~0.3 - 2.0 mW (~2.4 - 16 GWcm$^{-2}$). The corresponding photoexcited carrier density was calculated to range from ~2.38×10$^{19}$ to 1.62×10$^{20}$ cm$^{-3}$ [see Supplementary information, Note 3]. The probe beam power was ~0.4 mW, which provides the power within the range comparable to the pump bandwidth of ~4.0 μW, thus being extremely weak to affect the discussed carrier dynamics.

**Data availability.** The data that support the findings discussed in this article are available from the corresponding author on request.
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Author contributions
Y.D.G.: designed the optical experiments and created the optical setup. Y.D.G. and R.Cai: performed all the optical measurements and treated the optical experiment data. R.Cai: prepared all the samples and performed their characterization using SEM, TEM, XRD. The optical measurements were performed in the laboratory hosted by T.He. All authors contributed to discussions. Y.D.G: performed theoretical treatment and wrote the paper. X.W.S.: guided the research and supervised the project.
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Supplementary Materials

Distinguishing between dynamical and static Rashba effects in hybrid perovskite nanocrystals using transient absorption spectroscopy

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Supplementary Notes

Note 1. The ground-state Fröhlich polaron energies (the polaronic reorganization energies).

The ground-state Fröhlich polaron energy for electrons and holes is \( \lambda_{e,h} = -\langle \hbar \omega_{\text{TO/LO}} \rangle \langle \alpha_{e,h} \rangle \), where \( \langle \alpha_{e,h} \rangle = \frac{e^2}{\hbar} \frac{1}{4\pi\varepsilon_0} \left( \frac{m_{e,h}^*}{2\langle \hbar \omega_{\text{TO/LO}} \rangle} \right) \left( \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_s} \right) \) is the polaron coupling coefficient which is a measure of electron(hole)-phonon coupling strength\textsuperscript{2-4}, where \( m_{e,h}^* = 0.13m_0 \) and \( m_{e,h}^* = 0.19m_0 \) are the effective masses for electrons and holes, respectively, with \( m_0 \) being the free-electron mass, \( e \) is the electron charge, \( \varepsilon_s = 21.36 \) is the static dielectric constant, \( \varepsilon_\infty = 4.4 \) is the high-frequency dielectric constants, respectively, \( \varepsilon_0 \) is the permittivity of free space, and \( \langle \hbar \omega_{\text{TO/LO}} \rangle \) are the effective energies of TO/LO-phonons (\( \langle \hbar \omega_{\text{TO}} \rangle = 5 \text{ meV} \) and \( \langle \hbar \omega_{\text{LO}} \rangle = 18.6 \text{ meV} \))\textsuperscript{5-8}. One can obtain the following Fröhlich polaron coupling coefficients \( \langle \alpha_e \rangle = 3.37, \langle \alpha_h \rangle = 4.07 \) and \( \langle \alpha_e \rangle = 1.75, \langle \alpha_h \rangle = 2.11 \) for TO and LO phonons, respectively, which are well consistent with those calculated using the Feynman-Osaka model\textsuperscript{3}. The resulting reorganization energies can be calculated as \( \lambda_e = \sim 16.9 \text{ meV} \) and \( \lambda_h = \sim 20.35 \text{ meV} \) for TO-phonons and \( \lambda_e = \sim 32.6 \text{ meV} \) and \( \lambda_h = \sim 39.2 \text{ meV} \) for LO-phonons. These estimates imply that LO-phonons mainly govern the room-temperature ~60 meV Stokes shift (\( \lambda_e + \lambda_h \)) discussed in the main text.

Note 2. TA spectra measured at different pump powers using a cross-linearly-polarized geometry.

In this note we present the whole set of the transient absorption (TA) spectra of MAPbBr\textsubscript{3}/Sa and MAPbBr\textsubscript{3}/ZnO (Figs. 1S - 4S), which were measured at room temperature with 400 nm pumping (3.1 eV photon energy) of different powers and delay-times, as indicated for each of the Figures. A part of this data has been used in Figures 2 and 4 of the main text.

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Fig. 1S The snapshot spectral imaging of the MAPbBr$_3$/Sa and MAPbBr$_3$/ZnO samples. The TA spectra were measured for MAPbBr$_3$/Sa (a and b) and MAPbBr$_3$/ZnO (c and d) samples with 100 fs delay steps in the range of 0 – 1.0 ps and at delay times in the range of 1.5 – 1000 ps, as indicated for each of the spectra. The spectra were shifted along the ΔOD axis for better observation. The pump power was ~0.3 mW.
Fig. 2S  The snapshot spectral imaging of the MAPbBr$_3$/Sa and MAPbBr$_3$/ZnO samples. The TA spectra were measured for MAPbBr$_3$/Sa (a and b) and MAPbBr$_3$/ZnO (c and d) samples with 100 fs delay steps in the range of 0 – 1.0 ps and at delay times in the range of 1.5 – 1000 ps, as indicated for each of the spectra. The spectra were shifted along the ΔOD axis for better observation. The pump power was ~0.6 mW. The different color filled Gaussian profiles show an example of absorption bleaching components associated with the Rashba spin-splitting in the CB1 (CB1L and CB1H, the low-energy and high-energy components, respectively) and in the CB2 (CB2L and CB2H). The absorption bleaching component associated with the ZnO CB is also marked in c.
Fig. 3S The snapshot spectral imaging of the MAPbBr$_3$/Sa and MAPbBr$_3$/ZnO samples. The TA spectra were measured for MAPbBr$_3$/Sa (a and b) and MAPbBr$_3$/ZnO (c and d) samples with 100 fs delay steps in the range of 0 – 1.0 ps and at delay times in the range of 1.5 – 1000 ps, as indicated for each of the spectra. The spectra were shifted along the ΔOD axis for better observation. The pump power was ~1.0 mW.
Fig. 4S The snapshot spectral imaging of the MAPbBr$_3$/Sa and MAPbBr$_3$/ZnO samples. The TA spectra were measured for MAPbBr$_3$/Sa (a and b) and MAPbBr$_3$/ZnO (c and d) samples with 100 fs delay steps in the range of 0 – 1.0 ps and at delay times in the range of 1.5 – 1000 ps, as indicated for each of the spectra. The spectra were shifted along the ΔOD axis for better observation. The pump power was ~2.0 mW.
Note 3. TA spectra and the peak assignment. The snapshot TA spectral imaging of MAPbBr$_3$/Sa and MAPbBr$_3$/ZnO shown in Fig. 4a and b of the main text and in Supplementary Note 2 (Figs. 1S-4S) clearly demonstrates that TA spectra consist of the negative and positive contributions, the intensity of which scales as the optical density change ($\Delta$OD) because according to Beer’s law the absorption coefficient $\alpha$ relates to OD $\equiv \ln[I_0/(1 - R)/I_T]$ as $\alpha = (1/d) \times \text{OD}$, where $I_0$ and $I_T$ are the incident and transmitted light intensities, respectively, $R$ is the reflectance, and $d$ is the film thickness. All the negative and positive contributions reveal a splitting behavior, which, nevertheless, manifests itself more distinctly for negative contribution and disappears for delay times longer than a few 100’s ps. The splitting range of ~60 - 240 meV closely matches that previously assigned to a giant Rashba spin splitting effect in 2D/3D hybrid organic-inorganic perovskites.$^{10,11}$

One of the typical processes contributing to TA spectra is absorption bleaching (AB) which is due to the Pauli blocking.$^{12-16}$ Specifically, the absorption coefficient modified due to the photoexcited electron population can be expressed as $\alpha = \alpha_0 (1 - f_e)$, where $f_e = \exp[[\hbar \omega_{\text{probe}} - E_g - E_F]/k_B T] + 1$ is the Fermi–Dirac occupancy factor for electrons with $E_g + E_F$ being the Fermi energy measured from the top of the VB, where $E_g$ is the band gap energy, $\hbar \omega_{\text{probe}}$ is the probe photon energy with $\hbar$ and $\omega_{\text{probe}}$ being the reduced Planck constant and the probe light frequency, respectively, $k_B$ is the Boltzmann constant, $T_L$ is the lattice temperature, and $\alpha_0 = A(\hbar \omega_{\text{probe}} - E_g)^{3/2}/\hbar \omega_{\text{probe}}$ is the absorption coefficient with no pump applied, where $A$ is a constant. The TA signal in this case is known as the Burstein–Moss (BM) shift$^{12-14}$ and can be defined as $\Delta$OD$^{BM} = d \Delta \alpha = - d \alpha_0 f_e$, thus being negative once the pump-excited free electrons fill up the CB states in accordance with their occupancy factors (CB-AB). This behavior dynamically extends $E_g$ by the value of $E_F = \frac{\hbar^2}{2m^*_e} (3\pi^2 n_e)^{2/3}$, where $m^*_e = 0.13 m_0$ is the electron effective mass and $n_e$ is the photoexcited electron density. Consequently, the amplitude of the corresponding signal in TA spectra should approximately vary with $n_e$ as $\Delta$OD$^{BM} \propto n_e^{1/6}$. The situation is inverted for the VB, thus leading to the similar Fermi–Dirac occupancy factor for holes ($f_h$) and to the negative feature appearing in TA spectra and being associated with VB-AB.

Owing to many-body effects, such as the correlated motion of carriers and their scattering with ionized impurities or polar phonons, the photoexcited electrons can also induce the gap shrinkage [band gap renormalization (BGR)]$^{12-16}$, which leads to the band gap narrowing being proportional to $n_e^{1/3}$. Upon reaching equilibrium, the BM and BGR effects are supposed to act simultaneously, thus giving rise to the optical gap that can be expressed as $E_g^{opt} = E_g + \Delta$E$^{BM} - \Delta$E$^{BGR}$. In particular, BGR reduces minimum energies of the Rashba spin-split components of the CB1 and the CB2 by $\Delta$E$^{BGR}$, thus inducing the corresponding unoccupied states. The resulting unoccupied states are responsible for the photo-induced absorption (PIA) which appears in TA spectra as positive contributions energetically occurring just below and above the negative AB (BM) contributions associated with the CB1 and the CB2. The corresponding magnitude of the $\Delta$OD$^{BGR}$ signal in TA spectra is expected to vary with $n_e$ as $\Delta$OD$^{BGR} = d \Delta \alpha = d (\alpha_{BGR} - \alpha_0) = \frac{Ad}{h \omega_{\text{probe}}} \left[ (\hbar \omega_{\text{probe}} - E_g + \Delta$E$^{BGR})^{1/2} - (\hbar \omega_{\text{probe}} - E_g)^{1/2} \right] \approx \frac{Ad \Delta$E$^{BGR}}{2h \omega_{\text{probe}}(h \omega_{\text{probe}} - E_g)^{1/2}} \propto n_e^{1/3}$.

Consequently, owing to scattering with LO-phonons, the two-photon-excited carriers relax first into the Rashba spin-split components of the CB2, giving rise to the corresponding Fermi–Dirac distribution. The latter causes the BM upward shift of the CB2 and induces the corresponding BGR unoccupied states. Subsequent LO-phonon-assisted relaxation of carriers from the CB2 to the CB1 populates the Rashba spin-split components of the CB1 and establishes the corresponding Fermi level, thus causing the BM upward shift of the CB1 and inducing the corresponding BGR unoccupied states.

Figure 5Sa-c shows the corresponding modeling of TA spectra of thin films of 3D MAPbBr$_3$ nanocrystals using the BM and BGR contributions. It should be noted that despite we ignored in this modeling the exciton and Rashba splitting effects and used a simple square root function for continuum states, the modeled TA
The spectrum describes quite well all the main peculiarities of the measured TA spectra. One can clearly see that all TA peaks tend to be doublets, thus indicating that the Rashba splitting affects both the AB and PIA bands (BM and BGR contributions, respectively). Furthermore, Rashba splitting progressively increases from the initial value of ~60-130 meV to ~200-240 meV with increasing pump power (photoexcited carrier density), as shown in Fig. 5Sd and f. However, the rate of this increase in MAPbBr₃/ZnO is much higher compared to MAPbBr₃/Sa. This behavior implies that the Rashba splitting effect in MAPbBr₃/ZnO is significantly suppressed due to charge separation at the MAPbBr₃/ZnO heterointerface (Fig. 2d and e in the main text) and only at higher carrier densities it becomes comparable to that occurring in MAPbBr₃/Sa.

Measuring power dependences of TA spectra (Fig. 5Sd-h) and plotting the magnitudes of their peaks as a function of the pump power (photoexcited carrier density) [Fig. 5Si-I], we confirm the validity of the BM and BGR effects to be used for treating TA spectra. Specifically, the magnitude of the positive peaks associated
with the PIA effect (BGR) in MAPbBr$_3$/Sa scales as $\sim n_e^{1/3}$ for both the non-equilibrium (delay-time $\sim 0.8$ ps) and quasi-equilibrium (delay-time $\sim 1.5$ ps) dynamics, being saturated for higher pump powers. In contrast, the magnitude of the negative peaks associated with the AB effect (BM shift) scales as $\sim n_e^{1/6}$. The pump power effect on the non-equilibrium and quasi-equilibrium carrier relaxation dynamics in MAPbBr$_3$/ZnO slightly differs since it is overlapped with the charge separation dynamics and hence the corresponding pump power dependences might show more notable deviation from the theoretical predictions.

It should also be noted that another carrier-density-related process which potentially can appear in TA spectra as a positive contribution is the free-carrier absorption, which might include the Drude absorption$^{19}$ and the inverse bremsstrahlung absorption$^{20,21}$. However, the absorption efficiency of these processes is expected to be negligible (Supplementary Note 4). Moreover, the latter processes are expected to reveal a linear dependence of absorption coefficient on $n_e$, that is, it completely disagrees with experimental observations presented here.

**Note 4. Free carrier absorption (FCA).**

The plasma frequency of the maximal free carrier density photoexcited in HOIP MAPbBr$_3$ NCs within one-photon excitation regime ($n_e = 1.5 \times 10^{20}$ cm$^{-3}$) and screened by the high-frequency dielectric constant $\varepsilon_\infty = 4.4$ can be estimated as $\nu_p = (1/2\pi)\sqrt{n_e e^2/\varepsilon_0 m^*_e \varepsilon_\infty} = 145.1$ THz, where $e$ is the electron charge, $\varepsilon_0$ is the permittivity of free space, $m^*_e = 0.13 m_0$ is the electron effective mass with $m_0$ being the rest mass of electron$^{19}$. This frequency corresponds to $\sim 2.1$ $\mu$m wavelength and to $\sim 0.59$ eV photon energy. The Drude absorption in the free-carrier population occurs at frequency $\nu < \nu_p$ and the corresponding absorption coefficient can be taken in a traditional form as $\alpha_D(\nu < \nu_p) = \varepsilon_\infty \nu_p^2 \gamma_c / n_e (\nu^2 + \gamma_c^2)$, where $c$ is speed of light, the electron-electron scattering rate is $(1/\gamma_c) \sim 50$ fs, i.e. $\gamma_c \sim 20$ THz, and $n_e$ is the real part of refractive index, which is approximately independent of $\nu$. For the high-frequency limit$^{19}$, the Drude absorption coefficient can be modified to $\alpha_D(\nu < \nu_p) = \varepsilon_\infty \nu_p^2 \gamma_c / n_e \nu^2 = \frac{n_e e^2 \gamma_c \lambda^2}{4\pi^2 \varepsilon_0 m^*_e n_e c^3}$, and hence $\alpha_D(\nu < \nu_p) \propto n_e \propto I_{pump}$ and $\alpha_D(\nu < \nu_p) \propto \lambda^2_{probe}$, where $\lambda_{probe} = c/\nu$ is the probe light wavelength.

The Drude absorption coefficient for $\nu > \nu_p$ approaches to zero and hence the photoexcited electron-hole plasma become transparent because free electrons and holes are not able to absorb light in this case due to the energy-momentum conservation restrictions$^{19}$. However, if the plasma becomes dense enough ($n_e \sim 10^{18}$ cm$^{-3}$), the absorption of light due to collisions between free carriers and photoionized ions becomes possible, the process which allows energy and momentum to be conserved simultaneously. This kind of FCA is known as the inverse bremsstrahlung absorption$^{20}$ which can be characterized by the corresponding absorption coefficient $\alpha_{IB}(\nu > \nu_p) \approx \frac{1}{12\pi^2 \varepsilon_\infty^4 (m_e)^5} \frac{n_e n_{ion} e^4 (Ze)^2}{v^2 v_{th}} (\ln \frac{2Te}{h \nu})^{21}$, where $n_{ion}$ and Ze are the density of ions and their charge, respectively, $v_{th}$ and $T_e$ are the thermal velocity of carriers and their temperature, respectively, and $h$ is the Planck constant. Consequently, $\alpha_{IB}(\nu > \nu_p) \propto n_e \propto I_{pump}$ and $\alpha_{IB}(\nu > \nu_p) \propto \lambda^2_{probe}$.

The corresponding $\Delta OD^{FCA}$ might provide a positive contribution in this case, because $\Delta OD^{FCA} = d(\alpha_D - \alpha_0)$ for $\nu < \nu_p$ and $\Delta OD^{FCA} = d(\alpha_{IB} - \alpha_0)$ for $\nu > \nu_p$. It is worth noting that despite the different absorption mechanisms can be taken into consideration for FCA in HOIP MAPbX$_3$ NCs, $\Delta OD^{FCA}$ show identical trends with variations of $I_{pump}$ and $\lambda_{probe}$. This comparison implies that $\Delta OD^{FCA}$ should vary with $n_e$ (with $I_{pump}$) linearly. However, the experimentally observed power dependences show much weaker dependences as $n_e^{1/6}$ and $n_e^{1/3}$, indicating that the FCA effect is negligible and suggesting that the BM and BGR effects completely govern the TA spectra of HOIP MAPbBr$_3$ NCs in the visible light spectrum range.
Note 5. The carrier-LO-phonon relaxation time in MAPbBr₃ and ZnO.

The photoexcited carrier relaxation time associated with the LO-phonon scattering cascade in MAPbBr₃ nanocrystals can be estimated for the one-photon excitation regime from the excess electron energy \([\left(\hbar\omega_{\text{pump}} - E_g\right)/2]\) \(\sim 0.35\) eV [the corresponding electronic temperature \(T_e = \frac{2}{3} \left(\frac{\hbar\omega_{\text{pump}} - E_g}{2k_B}\right)\sim 1,350\) K]²² and the rate of LO-phonon emission by hot carriers, \(\frac{1}{\tau_{e-ph}} = \frac{e^2}{\hbar} \frac{1}{4\pi\varepsilon_0} \sqrt{\frac{2m^*_e}{\hbar^2}} \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_s}\right)^{23,24}\), where \(e\) is the electron charge, \(m^*_e = 0.13m_0\) (\(m^*_h = 0.19m_0\)) is the electron (hole) effective mass with \(m_0\) being the rest mass of electron, \(\varepsilon_0\) is the permittivity of free space, \(\langle\hbar\omega_{\text{LO}}\rangle = 18.6\) meV is the average LO-phonon energy, and \(\varepsilon_\infty = 4.4\) and \(\varepsilon_s = 21.36\) are the high-frequency and static dielectric constants, respectively²⁵,²⁶. The excess electron energy implies that \(\sim 18.8\) LO-phonon scattering events are required for one-photon-excited carriers to reach the MAPbBr₃ CB/VB edges. The time required for emitting a single LO-phonon by a hot electron (hole) can be estimated as \(\tau_{e-ph} \sim 10.1\) fs (\(\tau_{e-ph} \sim 8.3\) fs), and the resulting electron (hole) relaxation time is \(\sim 0.19\) ps (\(\sim 0.16\) ps), which is comparable to the laser pulse duration of 0.1 ps.

As the two-photon excitation regime is applied, the excess electron energy is \([\left(2\hbar\omega_{\text{pump}} - E_g\right)/2]\) \(\sim 1.9\) eV [the corresponding electronic temperature \(T_e = \frac{2}{3} \left(\frac{2\hbar\omega_{\text{pump}} - E_g}{2k_B}\right)\sim 14,700\) K] and \(\sim 100\) LO-phonon scattering events are required for two-photon-excited electrons (holes) to reach the MAPbBr₃ CB/VB edges. The resulting electron (hole) relaxation time is \(\sim 1.0\) ps (0.8 ps), which sets a temporal limit between the non-equilibrium and quasi-equilibrium carrier dynamics and implies that the quasi-Fermi level is formed at delay-times longer than \(\sim 1.0\) ps.

The relaxation time of two-photon-excited electrons in ZnO through the LO-phonon cascade can be estimated in a similar manner using the corresponding excess electron/hole energy \([\left(2\hbar\omega_{\text{pump}} - E_g\right)/2]\) \(\sim 1.415\) eV (\(T_{e,h} \sim 10,950\) K) and taking into account the following ZnO parameters: \(m^*_e = 0.24m_0\), \(\langle\hbar\omega_{\text{LO}}\rangle = 73\) meV, \(\varepsilon_\infty = 3.7\), and \(\varepsilon_s = 8.0^{27,28}\). Consequently, \(\sim 20\) LO-phonon scattering events are required for two-photon-excited electrons to reach the ZnO CB edge. The time required for emitting a single LO-phonon by a hot electron can be estimated as \(\tau_{e-ph} \sim 4.6\) fs, and the resulting carrier relaxation time is \(\sim 0.1\) ps, thus being of the same order as the laser pulse duration of \(\sim 0.1\) ps.

Note 6. The carrier densities photoexcited by the pump in MAPbBr₃ nanocrystals.

The spot sizes of the pump and probe beams were \(\sim 400\) and \(\sim 150\) µm, respectively. The pump beam average power ranged \(I_{\text{pump}} \sim 2 - 2\) mW (the pump pulse power density was \(I_{\text{pump}} \sim 2.4 - 16\) GWcm⁻²). The probe beam power was \(I_{\text{probe}} \sim 0.4\) mW, which for the similar to the pump beam bandwidth (\(\sim 26\) meV) provides the probe pulse power density of \(\sim 0.15\) GWcm⁻². The latter power density is much weaker compared to the pump pulse power density and hence its effect on the carrier excitation is expected to be negligible.

We estimate first the photoexcited carrier density in the linear optical regime. The attenuation of light of intensity \(I\) propagating a distance \(z\) through a absorbing medium is \(\frac{dl}{dz} = -\alpha l\),¹⁹ where \(\alpha\) is the linear (one-photon) absorption coefficient (\(\alpha \sim 10^5\) cm⁻¹). Consequently, \(I = I_0(1 - R)e^{-\alpha d}\), where \(I_0\) is the peak intensity of pump light [we use 1 mW pump power (\(I_0 = 8.0\) GW cm⁻²) for estimates presented further below] entering the sample of the thickness \(d\) (\(\sim 40\) nm) and \(R\) is the sample reflectance (\(\sim 0.38\)). The resulting power density absorbed in a media is \(P = -\nabla I\). The corresponding carrier density then is \(n_e = \frac{P \tau_L}{\hbar\omega_{\text{pump}}} = \sim 8.0\times10^{19}\) cm⁻³, where \(\tau_L\) is the laser pulse duration (\(\sim 10^{-13}\) s) and \(\hbar\omega_{\text{pump}}\) is the pump photon energy (\(\sim 3.1\) eV).
To estimate the photoexcited carrier density in the two-photon regime, we used \[ \frac{dt}{dz} = -\beta I^2 \] where \( \beta \) is the two-photon absorption coefficient, which is unidentified for 400 nm light since it has never been studied experimentally for the blue spectral range. Nevertheless, it is well known to be \( \beta \approx 8.5 \text{ cmGW}^{-1} \) for 800 and 1064 nm light\(^{29,30} \). Assuming the same range of \( \beta \) for 400 nm light as well, the propagating light intensity is \[ I = \frac{I_0(1-R)}{1+I_0(1-R)\beta d} \] and the power density absorbed in a media can be estimated as \( P = -\nabla_z I = \beta \left( \frac{I_0(1-R)}{1+I_0(1-R)\beta d} \right)^2 \) = \( 2.1 \times 10^{11} \text{ W cm}^{-2} \). Consequently, \( n_e = \frac{P_{TL}}{2\hbar\omega_{pump}} = 2.0 \times 10^{16} \text{ cm}^{-3} \). The carrier density photoexcited in the two-photon regime is hence much less than that photoexcited in the one-photon regime. We note that the latter conclusion remains totally valid for increasing \( \beta \) within 1-2 orders of magnitude.

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