

Large Polaron Self-Trapped States in Three-Dimensional Metal-Halide Perovskites

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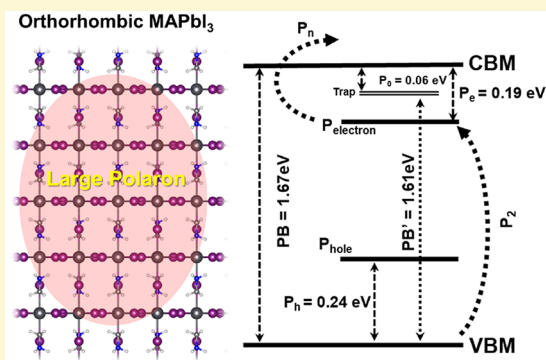
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Supporting Information

ABSTRACT: In recent years, metal halide perovskites have generated tremendous interest for optoelectronic applications and their underlying fundamental properties. Because of the large electron-phonon coupling characteristic of soft lattices, self-trapping phenomena are expected to dominate hybrid perovskite photoexcitation dynamics. Yet, while the photogeneration of small polarons was proven in low-dimensional perovskites, the nature of polaron excitations in technologically relevant 3D perovskites, and their influence on charge carrier transport, remain elusive. In this study, we used a combination of first principle calculations and advanced spectroscopy techniques spanning the entire optical frequency range to pin down polaron features in three-dimensional metal halide perovskites. Mid-infrared photoinduced absorption shows the photogeneration of states associated with low energy intragap electronic transitions with lifetime up to the millisecond time scale, and vibrational mode renormalization in both frequency and amplitude. Density functional theory supports the assignment of the spectroscopic features to large polarons leading to new intragap transitions, hardening of phonon mode frequency, and renormalization of the oscillator strength. Theory provides quantitative estimation for the charge carrier masses and mobilities increase upon polaron formation, confirming experimental results. Overall, this work contributes to complete the scenario of elementary photoexcitations in metal halide perovskites and highlights the importance of polaronic transport in perovskite-based optoelectronic devices.



Metal halide perovskites (MHPs) are attracting enormous interest as solution-processed^{1,2} active materials in a variety of device applications.^{3–15} The prototype compound is methylammonium lead iodide (MAPbI₃), which is a three-dimensional (3D) hybrid perovskite known for its remarkable transport properties, such as long charge carrier lifetime¹⁶ and diffusion length,^{17–19} small nonradiative bimolecular recombination coefficient (γ) of the order of 10^{-10} cm³ s⁻¹, comparable to those of crystalline semiconductors such as GaAs,^{20,21} and apparent insensitivity to defects.^{22–25} However, the nature of the charge carriers responsible for such remarkable performance is still under

debate. Reported charge carrier mobilities in perovskite films between 10^{-4} and 10 cm² V⁻¹ s⁻¹, depending on measurement technique,^{16,17,20,26–30} are indeed in net contrast with the prediction of the Langevin model for free charge carrier recombination in semiconductors, where $\gamma/\mu = e/(\epsilon_0\epsilon_r)$.²⁷ The origin of such apparent inconsistency is still debated³¹ and points toward the role of polaronic protection of charge carriers in the perovskite lattice.^{32,33}

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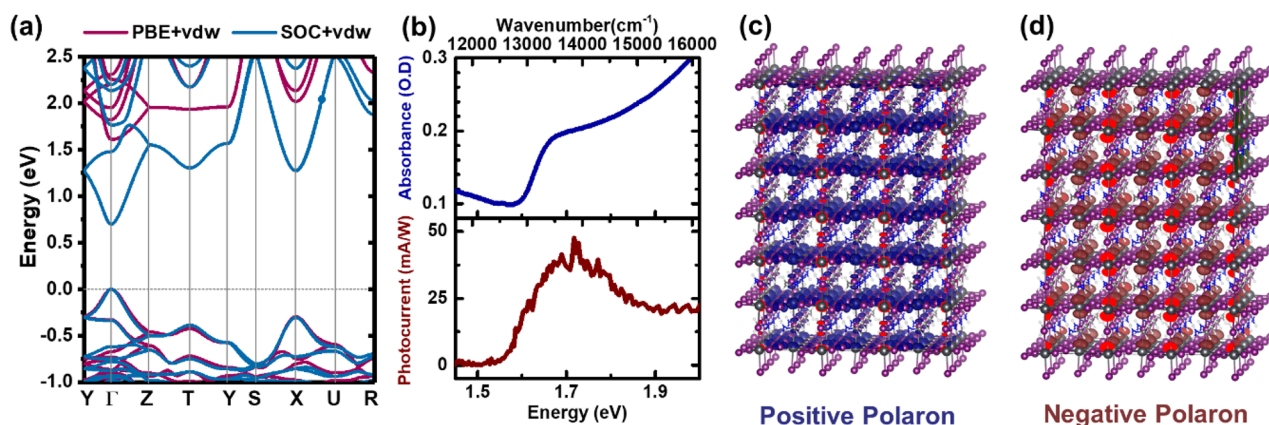


Figure 1. Electronic structure, absorption spectra, and photocurrent spectra of orthorhombic MAPbI₃. (a) Calculated band structures at GGA/PBE + vdw level without and with SOC effects; (b) linear absorption (top) and normalized steady-state photocurrent spectra obtained with illumination intensity of $\sim 20 \mu\text{W}/\text{cm}^2$ under applied field of $9 \text{ kV}/\text{cm}$ (bottom); (c, d) electronic charge densities of positive polaronic states (panel (c)) and negative polaronic states (panel (d)) for a $3 \times 3 \times 3$ supercell calculated at the GGA/PBE level.

Table 1. Calculated Effective Mass (m^* , $\times m_0$) and Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, Average of Different Crystallographic Directions) of Free Charges and Polarons in Tetragonal- and Orthorhombic-Phase MAPbI₃ (Including Spin-Orbit Coupling Effects)

type	Tetragonal (300 K)			Orthorhombic (77 K)		
	Effective Mass		mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Effective Mass		mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
	M(Y) \rightarrow Γ	$\Gamma \rightarrow$ Z		M(Y) \rightarrow Γ	$\Gamma \rightarrow$ Z	
free hole	0.240	0.180	332.2	0.166	0.253	1491.6
positive polaron	1.411	1.058	215.4	0.976	1.487	497.9
free electron	0.220	0.107	630.5	0.121	0.204	5122.0
negative polaron	1.293	0.629	225.9	0.711	1.199	550.7

Because of the highly deformable and polar nature of the metal halide framework, MHPs are prone to lattice relaxation, which is expected to cause self-trapping of the elementary excitations into phonon-dressed localized states.^{34–36} In low-dimensional perovskites (e.g., two-dimensional (2D) and one-dimensional (1D) structures), where Coulomb interactions are enhanced by reduced dielectric screening and quantum confinement effects, the formation of self-trapped excitons (*small polarons*) manifests itself in apparent radiative recombination effects, such as white-light emission in compounds such as (EDBE)PbBr₄.^{35,37–39} Here, ab initio calculations have indicated that the excess charge is spatially confined to one crystal unit cell or less, inducing local distortions of the lead-halide framework. Photoexcitation in 2D perovskites gives rise to photoinduced lattice deformations^{34,35,40} associated with polaron exciton states, with a characteristic fine structure in the absorption lineshapes.⁴¹ On the other hand, for charge carriers in 3D perovskites,⁴² because of the long-range electron phonon interaction typical of ionic crystals, polarons may extend over several lattice sites (*large polarons*). Large polarons can display bandlike coherent transport with a mobility of $>1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, which decreases as the temperature increases.^{33,43} In addition, the electrostatic screening brought about by the ionic (polar) lattice deformation could hinder Coulomb-mediated processes such as Auger cooling and Langevin recombination.⁴⁴

Several recent works have postulated the existence of large polaron states in 3D MHPs. Among these are the electrical conductivity exhibiting characteristic power-law temperature dependence,⁴⁵ the steady-state photoinduced absorption (PIA) in the visible⁴⁶ and far-infrared (FIR) spectral range,⁴⁷ terahertz spectroscopic investigations,^{48,49} and time-resolved

optical Kerr effect spectroscopy (TR-OKE)³² and optical absorption spectroscopy (TR-OAS).⁵⁰ Formation of long-lived energetic carriers with $\sim 10^2$ ps lifetime in MAPbBr₃ and FAPbBr₃ points toward the screening of charge carriers in the form of large polarons through liquidlike collective reorientation of the molecular dipoles.⁵¹ Impulsive Raman scattering performed on MAPbBr₃⁵² revealed the presence of coherent phonon modes generated via displacive excitation that is indicative of strong electron-phonon coupling, instrumental to polaron formation but not a proof of their existence. Similarly, a polaron state has been invoked to explain the octahedral distortion of $[\text{PbI}_6]^{4-}$ sustained by coherent vibrations of the Pb–I normal modes in MAPbI₃.⁵³ Nonetheless, the impact of carrier-induced lattice distortion on polaron formation and charge transport in optoelectronic devices has remained elusive.¹⁶

In this work, we identify the geometrical pattern associated with large self-trapped polaron states in MAPbI₃ by combining an advanced theoretical investigation of charge-induced lattice relaxation with the experimental study of specific vibrational modes. We assign the unique spectroscopic signatures in the infrared (IR) spectral region to the polaron-induced lattice relaxation and those in the near-infrared (NIR) to visible range to the polaron-induced electronic transitions. Based on this assignment, we further study polaron generation and long decay dynamics with femtosecond temporal resolution and present the first “real time” fast photocurrent transients, which directly measure charge carrier relaxation at the picosecond time scale and beyond. The correspondence between transient absorption and photocurrent decay kinetics supports the conjecture that polarons are primary charge carriers in 3D perovskites.

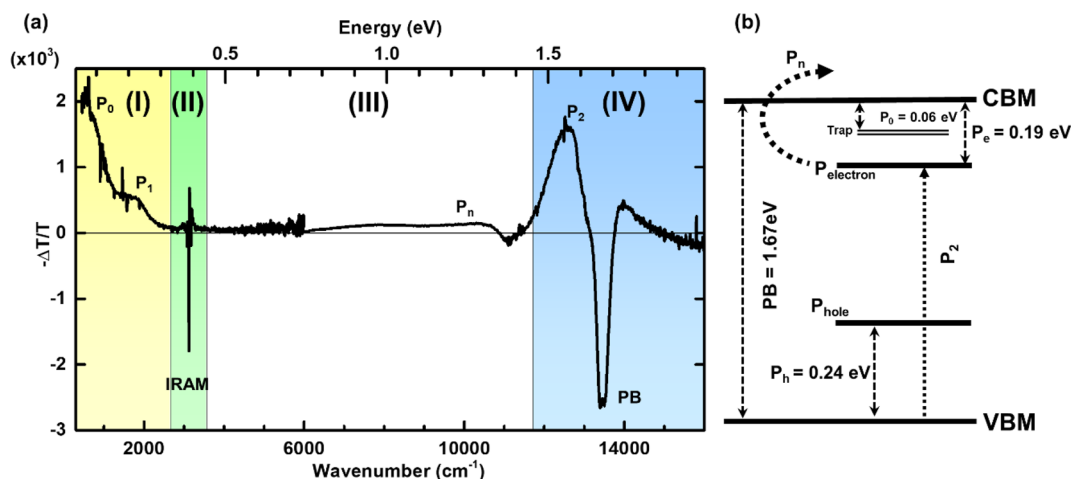


Figure 2. (a) cw-PIA spectrum of MAPbI₃. Region I (500–2600 cm⁻¹) shows the intragap polaron electronic transition $P_1 = 0.20$ eV and the trap state absorption $P_0 = 0.06$ eV, convoluted with infrared-active vibrational (IRAV) modes. Region II (2600–3500 cm⁻¹) shows infrared-active modulation (IRAM) of the C–H and N–H vibrational mode frequencies. Region III (3500–11700 cm⁻¹) indicates the presence of PIA transitions to higher lying states. Region IV (11700–16000 cm⁻¹) contains high-energy intragap polaron transitions and photobleaching (PB) of ground-state absorption. (b) Proposed electronic energy diagram and associated transitions, based on the calculated polaron state energies. P_1 is assigned to the convolution of positive polaron $P_h = 0.24$ eV and negative polaron $P_e = 0.187$ eV transitions above the valence band maximum (VBM) and below the conduction band minimum (CBM), respectively.

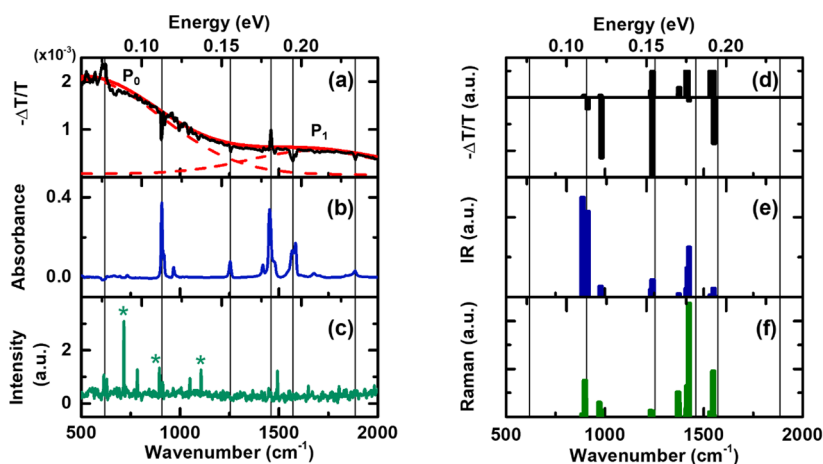


Figure 3. Experimental and simulated infrared active vibrational (IRAV) and Raman modes. (a) PIA spectrum ($T = 78$ K) fitted to two Gaussian peaks centered at ~ 1650 cm⁻¹ and 516 cm⁻¹ (red dashed lines), (b) FTIR spectrum ($T = 78$ K), and (c) Raman spectrum ($\lambda_{\text{exc}} = 1024$ nm, $T = 300$ K), where green asterisks denote peaks from the CaF₂ substrate. (d) Simulated photoinduced absorption modes obtained as $-\Delta T/T = -(\text{IR}_{\text{neut}} - \text{IR}_{\text{exc}})/\text{IR}_{\text{neut}}$ where IR_{exc} and IR_{neut} are the IR mode intensities of excited and ground states, respectively. (e, f) Calculated IR and Raman mode intensity spectra of orthorhombic MAPbI₃. The main vibrational modes are indicated by black vertical lines, showing the correspondence between IRAV modes and Raman modes, which become IR-active under photoexcitation.

The band structure of orthorhombic-phase MAPbI₃ was calculated at GGA/PBE + vdW level without and with spin-orbit coupling (SOC) effects (Figure 1a). The resulting bandgap (1.61 eV, without SOC) is in good agreement with the experimental value deduced from the steady-state absorption spectra and the onset of steady-state photocurrent (Figure 1b). Inclusion of SOC in the band structure calculations considerably reduces the bandgap to 0.70 eV due to band splitting. As shown in Table 1, the extracted values of free carriers effective masses (m^*) along the $M \rightarrow \Gamma/\Gamma \rightarrow Z$ directions are 0.166/0.253 (hole) and 0.121/0.204 (electron) for the low-temperature orthorhombic-phase MAPbI₃. The similar values obtained for hole and electron effective masses confirm the ambipolar nature of charge transport in MAPbI₃, while the different values for different crystallographic directions reflects the intrinsic anisotropy of the 3D perovskite

lattice. Similar results are obtained for the high-temperature tetragonal phase, except for the inverted transport anisotropy.

Adding a positive/negative charge to the neutral lattice induces spontaneous structural relaxation of the supercell to a new equilibrium geometry, leading to the formation of positive and negative polarons (Figures 1c and 1d). The new half-filled energy level associated to the negative polaron lies 0.187 eV below the conduction band minimum (CBM), while that associated to the positive polaron lies 0.235 eV above the valence band maximum (VBM). The resulting charge density distributions suggest that the self-trapped polaron states are localized in spatially distinct regions within ~ 2 –3 inorganic atomic layers. Charge localization with comparable spatial extent was also observed in 3D and 2D perovskites when varying the Pb–I distances³⁵ or increasing the tilting of Pb–I–Pb angles.³² Accordingly, the calculated polaronic effective

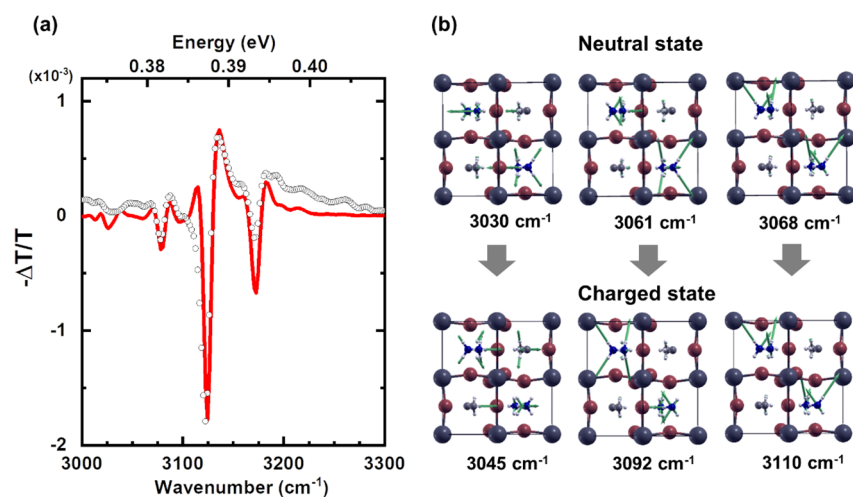


Figure 4. Infrared active modulation (IRAM) of C–H and N–H vibrational modes. (a) Experimental data fitted to a linear combination of first and second derivative of the IR absorption spectrum $f(\bar{\nu})$, $f_{\text{der}}(\bar{\nu}) = -0.0075f'(\bar{\nu}) + 0.1f''(\bar{\nu})$. The first derivative indicates a spectral shift of the absorption peak, while the second derivative indicates its spectral broadening; in this case, C–H and N–H mode hardening upon photoexcitation induces a blue shift of the vibrational modes. (b) Representative IR vibrational frequencies and displacement vectors obtained from phonon calculations, and corresponding blue-shift of IR-active-mode frequencies in the charged state.

masses in MAPbI₃ system are ~ 5 times larger than those of free carriers and calculated polaron mobilities are 1.5–8 times smaller than free charge carrier mobilities.

The electronic and vibrational structure of semiconductors are strongly affected by polaron formation: (i) half-filled electronic states appear within the gap, giving rise to new optical transitions; (ii) vibrational mode frequencies are renormalized by the change in bond geometry, including modes of the inorganic lattice and of the organic moiety that “feel” a deformed environment (*spectator modes*),^{51,53,54} but are not directly coupled to the carrier; and (iii) geometric distortion induces local symmetry breaking that relaxes vibrational selection rules and eventually activates vibrational modes that are silent for bare states. To test all these specific predictions, we measured the IR-photoinduced absorption of MAPbI₃ over a broad spectral range (Figure 2a).

Low-temperature ($T \approx 80$ K) steady-state continuous wave photoinduced absorption (cw-PIA) measurements of the MAPbI₃ film (see the “Experimental Methods” section in the Supporting Information for details) show clear evidence for the generation of long-lived photoexcited states (with typical lifetimes of the order of milliseconds). Four regions of interest are identified in the cw-PIA spectrum in Figure 2: a photoinduced absorption region between 500–2500 cm⁻¹ containing two absorption peaks (region I), a vibrational mode region at 3000–3300 cm⁻¹ (region II), a second photoinduced absorption region containing a broad (P_n) transition at ~ 6000 – $11\,500$ cm⁻¹ (region III), and a high-energy modulation region just below the band gap, featuring photoinduced absorption (PA) and photobleaching (PB) (region IV). The concomitant disappearance of P_1 , P_2 , and P_n at room temperature indicates their common origin (see Figure S3 in the Supporting Information).

Figure 3a show details of the PIA spectrum in region I, featuring two photoinduced absorption bands centered at ~ 516 cm⁻¹ (P_0) and 1650 cm⁻¹ (P_1), as determined by Gaussian fitting curves shown in red, and a series of small features at 620, 908, 1254, 1460, and 1570 cm⁻¹ (solid black lines running across Figures 3a–c and 3d–f) that correspond to the amplitude modulation of the main IR active vibrational

(IRAV) modes.⁵⁵ An exception is the photoinduced mode at 600 cm⁻¹ (within the range of C–N vibrational modes of the organic moiety), which corresponds to an IR inactive Raman mode; this suggests breaking of the inversion symmetry that governs mutually exclusive Raman and IR mode selection rules due to the local distortion of the lattice in the presence of the self-trapped charge.⁵⁵

Density functional theory (DFT) calculations accurately account for the experimental observations in region I of the spectrum. The broad PA band P_1 at 1650 cm⁻¹ (0.204 eV) corresponds to a convolution of electronic transitions from negative and positive polaron states at $P_e = 0.187$ eV below the CBM and $P_h = 0.235$ eV above the VBM, respectively. Conversely, the P_0 peak centered at 516 cm⁻¹ (0.06 eV), that does not emerge from the calculations, is likely due to a trap state.²⁵ Figures 3e and 3f show the calculated IR and Raman spectra, which correspond to the experimental modes assigned to the organic moiety. The photoinduced modulation of the IRAV modes from 750 cm⁻¹ to 2000 cm⁻¹ is reproduced reasonably well by the calculations. Figure 3d shows the spectrum obtained by computing the difference between the spectra calculated in the undistorted (Figure 3e) and distorted perovskite lattices. The modulation sign is in agreement with the experiment for each mode, accounting for amplitude increase or decrease of the vibrational transitions upon polaron formation. Notably, this suggests that negative PA dips are due to a decrease of the vibrational transition oscillator strength, rather than to Fano resonances due to quantum interference of electronic and vibrational transitions.⁵⁶

The orthorhombic-phase MAPbI₃ shows several IR peaks in the spectral region of 3000–3300 cm⁻¹, which can be assigned to both C–H and N–H stretching modes of the organic cations. The photoinduced modulation of these modes in region II is particularly interesting (Figure 4). We fitted the experimental PA data in this region to its first and second derivative (Figure 4a). The first derivative component of the absorption spectrum gives an indication of the spectral blue shift of the peak, while the second derivative component is related to the peak broadening.⁵⁷ Both effects can be attributed to the modulation of C–H and N–H bonds induced by the

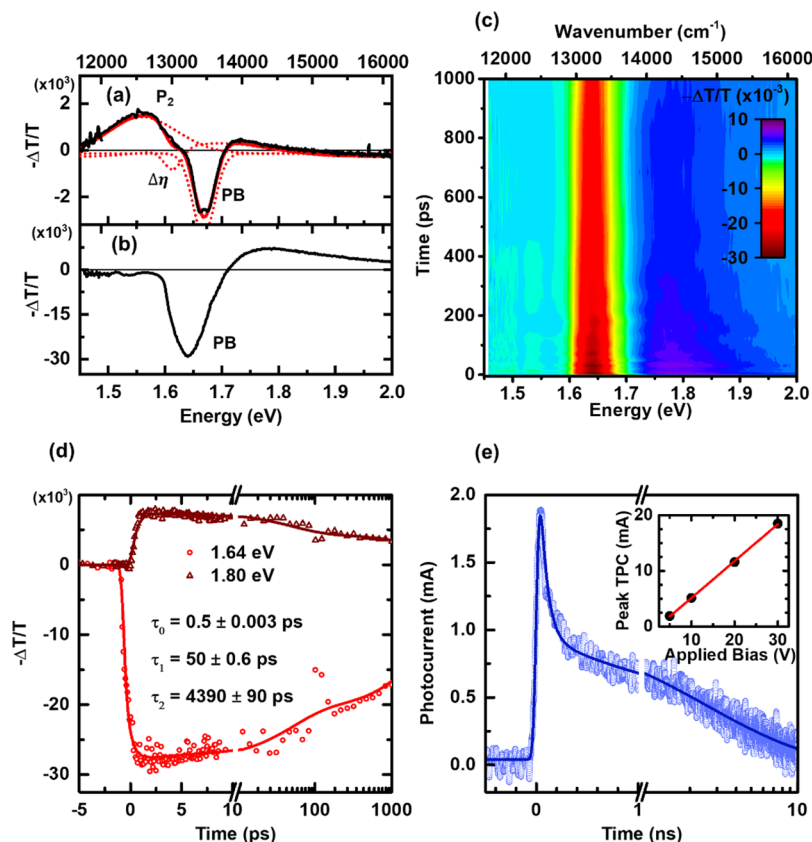


Figure 5. Ultrafast polaron formation and decay dynamics. (a) Comparison between steady-state (top panel) and $t = 1.5$ ps transient (bottom panel) photoinduced absorption spectra of MAPbI₃. The steady-state spectrum (also shown in Figure 2) was fitted with four Gaussian curves: P_2 centered around 1.55 eV, PB centered around 1.67 eV and the effect of change in refractive index modeled by the sum of two Gaussians centered around 1.61 and 1.69 eV. (b) Two-dimensional (2D) map of transient absorption; global fitting yielded three distinctive lifetimes $\tau_0 = 0.500 \pm 0.003$ ps, $\tau_1 = 50.0 \pm 0.6$ ps, and $\tau_2 = 4390 \pm 90$ ps. (c) Temporal slices of transient absorption at 1.64 and 1.80 eV, displaying similar decay dynamics. (d) Fast transient photocurrent decay obtained with an applied voltage of 5 V; fitting to a biexponential decay yielded distinctive lifetimes of $\tau_1 = 101 \pm 1$ ps and $\tau_2 = 4220 \pm 20$ ps. The inset shows the linear dependence of the transient photocurrent peak on applied bias. In panels (c) and (d), note the shift in time scale from linear to logarithmic, in correspondence to the scale break.

polaron which, by locally distorting the perovskite lattice, indirectly affect their vibrational potential through the hydrogen bonds between hydrogen atoms of $-\text{NH}_3$ and I atoms in charged MAPbI₃ (*spectator modes*). Note that thermal modulation cannot account for this effect as it determines an opposite red shift of the mode frequency (mode softening), see the Supporting Information. Despite the slight mismatch of calculated and experimental IR mode frequencies in both neutral and excited states (Figure 4b), the blue shift induced by the lattice distortion on the vibrational modes is correctly reproduced by the calculations. Thus, the observed long-lived vibrational frequency renormalization upon photoexcitation is a clear fingerprint of the generation of a geometrically relaxed state.

The concomitant photoinduced electronic spectrum, with intragap transitions, corroborate the assignment to photo-generated polarons. Details of the cw-PIA spectrum in region IV are shown in the top panel of Figure 5a. The spectrum can be fitted to four Gaussian curves, labelled P_2 (centered at ~ 1.55 eV), PB (centered at ~ 1.67 eV), and a sum of two Gaussians centered at ~ 1.61 eV and ~ 1.69 eV to model the effect of the change in refractive index, as reported by Price et al.⁵⁸ P_2 corresponds well to the energetics determined for ground state to polaron transitions, while the PB peak is

assigned to the valence to conduction band (refer to the energy diagram in Figure 2b).

All steady-state spectroscopy results seem to point to large polarons being the primary photoexcitations in 3D MAPbI₃. To determine their generation and relaxation dynamics, we performed ultrafast (fs) transient absorption and fast (ps) transient photocurrent measurements (see Figure 5). The time evolution of the transient photoinduced absorption (TPA) spectrum upon pulsed laser excitation ($t \approx 100$ fs, $\lambda = 400$ nm, $I = 5$ nJ/pulse) is shown in the 2D contour plot in Figure 5b. There are two key features in the TPA spectrum, consisting of a broad absorption peak from 1.7 eV to 2.0 eV ($13\,700\text{--}16\,100$ cm⁻¹) and a sharp peak centered at 1.64 eV ($13\,200$ cm⁻¹), which corresponds to the ground-state bleaching of MAPbI₃. Comparison of the cw-PIA and TPA spectra of MAPbI₃ (Figures 5a, top and bottom panels) shows good qualitative agreement, with coexistence of PIA and PB components at different relative positions. The red-shift of the photobleaching peak in cw-PIA, relative to the transient data, is likely due to the change in bandgap from 1.67 eV to 1.64 eV, from the high-temperature tetragonal phase to the low-temperature orthorhombic phase,⁵⁹ since cw-PIA was collected at ~ 80 K, whereas TPA was obtained at room

temperature. Moreover, the TA spectrum contains contributions from both neutral excitons and charged polarons.

The correspondence between early-time TPA and cw-PIA spectra indicates that the long-lived polaronic species are generated at an ultrafast time scale ($t < 100$ fs). From the global fitting of the spectral decays (see representative dynamics in Figure 5c), we determined three distinctive time constants of $\tau_0 = 0.500 \pm 0.003$ ps, $\tau_1 = 50.0 \pm 0.6$ ps, and $\tau_2 = 4390 \pm 90$ ps for sequential exponential decays. We attribute the ultrafast relaxation process of 0.500 ps to lattice thermalization, and we attribute the longer time constants to polaron population decay. The recombination process is far from being completed within our experimental temporal range, suggesting a long-lived polaron population that is consistent with the observation up to the millisecond (ms) time domain. Note that transient features between 1.7 eV and 2.0 eV have been previously observed in MAPbI₃ films^{17,18,60,61} and assigned to band filling effects by Manser et al.,⁶⁰ while Zhai et al. ascribed them to the photogeneration of free carriers.⁶¹ The long-lived decay was also determined in an earlier study, but not attributed to specific features.¹⁷

The picosecond transient photocurrent (TPC) induced by a femtosecond laser pulse in a photoconductive switch was measured by using a new-generation high-speed oscilloscope equipped with a 65 GHz real-time sampling channel (Figure 5d). Unlike all-optical photoinduced absorption measurements that may include signatures of neutral (e.g. excitonic) photogenerated species, fast TPC waveforms provide a direct and selective measurement of charge carrier generation and decay dynamics that immediately correlate with transport characteristics of photovoltaic devices. The fast rise time of the TPC signal (limited by the instrument response function) is consistent with the sub-picosecond polaron generation inferred from TPA measurements. The characteristic photocurrent decay times obtained by a biexponential fit with $\tau_1 = 101 \pm 1$ ps and $\tau_2 = 4220 \pm 20$ ps also compare well against the long-lived polaron lifetimes observed in transient absorption ($\tau_1 = 50.0 \pm 0.6$ ps and $\tau_2 = 4390 \pm 90$ ps). Note that the initial dynamics of TPA is likely to include exciton decay, which accounts for its faster early time constant. The inset of Figure 5c shows the linear relation between peak transient photocurrent and applied voltage, which enables the extraction of charge carrier mobility in the linear regime (see the "Experimental Methods" section in the Supporting Information). The resulting early-time polaron mobility is of the order of $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. In comparison, the mobility obtained from steady-state photocurrent measurements of the same sample is on the order of $\mu_{\text{ss}} = 0.2\text{--}2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, assuming a long polaron lifetime extending to the 1–10 ms time scale. Early-time (pre-trapping) mobility values are indeed expected to be larger than steady-state mobility values, which are dominated by thermally activated trapping and detrapping,⁶² and closer to bandlike mobility estimated by first-principles calculations.³

Theory for single-crystal MAPI₃ yields the mobility values summarized in Table 1 for both positive and negative polarons in the relevant crystallographic directions. The important outcomes are described as follows:

- (i) Polaron mobilities are systematically lower than free carrier mobilities, as expected from the enlarged effective masses associated to the phonon clouds. In the low-temperature phase, polaron mobilities are 3–8 times smaller than free carrier effective masses, whereas in the

high-temperature phase, polaron mobilities are 1.3–3 times smaller.

- (ii) Mobility anisotropy of polarons is smaller than their effective mass anisotropy.
- (iii) Theory compares reasonably well with data in the literature reporting mobilities of perovskite single crystals from $2.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $600 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^{49,63–66}

Our experimental data were obtained in polycrystalline films and cannot be compared directly to single-crystal data nor theoretical values. In addition, measurements at different time scales provide different effective mobility values. Just on single crystals,⁶⁷ reported mobilities vary from almost 1000 to $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ going from THz (ps time scale) through microwave reflectivity (μs time scale) to space-charge limited current (ms time scale) experimental techniques. In films, mobilities span 2 orders of magnitude, from $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $80 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Our results are obtained with complementary techniques not yet reported, and they compare reasonably well with the existing literature data.

In conclusion, we have provided a clear indication that the same type of lattice relaxation known to lead to the photogeneration of small polarons in low-dimensional perovskites also occurs in the 3D metal halide perovskite MAPbI₃. However, in the 3D case, topological constraints limit the extent of lattice deformation, because of the balance between the electronic energy and the lattice elastic energy. In this situation, the phonon dressed self-trapped states give rise to large polarons with radius extending over a few lattice sites. Such large polarons are generated at ultrafast time scale and are long-lived, with a fraction of the initial population surviving up to the millisecond (ms) time domain, as we see in cw-PIA spectra that clearly indicate vibrational mode frequency renormalization. Large polarons bring about an increase of the effective carrier mass and a concomitant reduction in mobility, overall preserving a large $\mu\tau$ product. Theory accounts for the geometrical relaxation and the vibrational mode renormalization associated to the polaron state, predicts transport anisotropy, and reproduces the low-energy polaron electronic spectrum seen in cw-PIA. It also predicts a small charge symmetry breaking, yielding ambipolar transport, even in the polaron regime. Carrier recombination is affected by their polaronic nature, for the phonon cloud around the carrier in 3D ionic crystals increases charge screening and reduces Coulomb-mediated interactions. This picture validates the idea that large polarons are responsible for the anomalous transport characteristics of metal halide perovskites, including lowering of carrier mobility via rescaling of the effective mass, protection against carrier scattering, and suppression of bimolecular (Langevin) recombination channels.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialslett.9b00276>.

Materials and methods; computational details; supporting figures and table (PDF)

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Notes

The authors declare no competing financial interest.

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