A-site cation influence on the conduction band of lead bromide perovskites

Gabriel J. Man1,8, Chinnathambi Kamal2,3,4, Aleksandr Kalinko5, Dibya Phuyal6, Joydev Acharya7, Soham Mukherjee1, Pabitra K. Nayak7, Håkan Rensmo1, Michael Odelius2 & Sergei M. Butorin1

Hot carrier solar cells hold promise for exceeding the Shockley-Queisser limit. Slow hot carrier cooling is one of the most intriguing properties of lead halide perovskites and distinguishes this class of materials from competing materials used in solar cells. Here we use the element selectivity of high-resolution X-ray spectroscopy and density functional theory to uncover a previously hidden feature in the conduction band states, the \( \sigma-\pi \) energy splitting, and find that it is strongly influenced by the strength of electronic coupling between the A-cation and bromide-lead sublattice. Our finding provides an alternative mechanism to the commonly discussed polaronic screening and hot phonon bottleneck carrier cooling mechanisms. Our work emphasizes the optoelectronic role of the A-cation, provides a comprehensive view of A-cation effects in the crystal and electronic structures, and outlines a broadly applicable spectroscopic approach for assessing the impact of chemical alterations of the A-cation on perovskite electronic structure.
lead halide perovskites (HaP) of the form APbX₃ have attracted renewed research interest for over a decade, motivated by initially dramatic gains in HaP solar cell efficiencies and now other optoelectronic applications¹⁻⁵. The prototypical A-site cations (A-cations) are organic (methylammonium or MA⁺, formamidinium or FA⁺) or inorganic (Cs⁺), the B-site cation is lead(II) and the X-site anion is iodide/bromide/chloride. At present, in spite of the substantial growth of many new subclasses of HaP-related materials and their applications, many fundamental questions related to the prototypical HaPs remain unanswered, despite a history of basic research dating back to as early as the late 1970’s⁶⁻⁷. One such question concerns the optoelectronic function of the A-cation⁸. Studies based on a range of complementary approaches: time-resolved photoluminescence (PL), combined electron spectroscopy and partial density of states (PDOS) calculations, mechanical nanoindentation and solar cell characterization have yielded evidence for and against the existence of A-cation optoelectronic functionality⁹⁻¹³.

To unravel this conundrum, we utilize element- and orbital-selective core level spectroscopy which includes X-ray absorption spectroscopy (XAS) for probing conduction band states and resonant X-ray emission spectroscopy (RXES) for probing valence band states¹⁴. The energy resolution of conventional XAS is intrinsically limited by core-hole lifetime broadening, which may obscure conduction band features probed in the spectra¹⁵. We circumvent this limitation by using High Energy Resolution Fluorescence Detected XAS (HERFD-XAS) which yields reduced broadenings of 2.2 eV (vs. 2.5 eV) and 2.5 eV (vs. 6.1 eV) for the bromine K-edge (1s → p transition) and lead L₂-edge (2p₃/₂ → s,d transition) absorption spectra, respectively¹⁵,¹⁶. Only two reports of HERFD-XAS, applied to the study of HaP thin films, exist, with just one report examining the prototypical compounds methylammonium lead tri-iodide/bromide (MAPI/B)¹⁷,¹⁸.

In this work, we report a joint experimental and computational investigation of three prototypical lead bromide perovskites (APB): MAPB, formamidinium lead tribromide (FAPB), cesium lead tribromide (CsPB), facilitated by single crystals which are durable under X-ray irradiation. Density functional theory (DFT) was employed for ab initio molecular dynamics simulations (AIMD) combined with ground-state PDOS and bromine K-edge XAS calculations. The use of HERFD-XAS enables us to differentiate, in terms of electronic structure, between compounds with the same lead/bromide formal oxidation states and ultimately attribute measured differences to A-cation type. We find the strength of electronic coupling between the A-cation and bromide-lead sublattices increases in this order: Cs⁺ → MA⁺ → FA +, and influences the energetic width of the conduction band via the σ–π splitting. We discuss the connection between σ–π splitting and slow cooling of hot electrons, which is relevant for potential HaP-based hot carrier solar cells which could surpass the Shockley–Queisser thermodynamic limit. We observe that higher coupling strength correlates with higher Br-Pb bond ionicity and a decreased energy offset between a given energy level and Br Js, and link this finding to energy level matching at optoelectronic device interfaces.

Results
We first focus on the unoccupied conduction band states as the occupied states of HaPs have been investigated more frequently, possibly due to the higher availability of commercial photoelectron spectroscopy (PES) instrumentation. We experimentally profile the unoccupied states in an element- and orbital-resolved manner via HERFD-XAS spectra derived from RXES maps. The maps are generated with a synchrotron beamline and a crystal-based X-ray spectrometer¹⁹,²⁰. A representative Br K RXES map, recorded from single crystal MAPB, is displayed in Fig. 1a and features resonant and off-resonant X-ray emission from three p → s transitions: Kp₁,₂,₃ (2p₃/₂/2p₁/₂ → 1s) and Kp₂,₃ (4p → 1s). An energy level schematic is shown in Fig. 1b and depicts the one-electron transitions related to X-ray absorption into conduction band states and emission from valence band and shallow core level states. The final state of valence photo-emission is shown for reference. A representative Pb L₃ RXES map is displayed in Supplementary Fig. 1 and the analysis is described in Supplementary Note 1. Vertical dashed lines in all RXES maps represent constant-emission-energy map cuts through the maximum of the RXES intensity that yield the HERFD-XAS spectra. For material systems with relatively delocalized states, such a RXES map cut has been shown to be a good high-resolution approximation to the conventional XAS spectrum²¹. The conduction band states of interest are profiled in the near-edge features, which we enclose with a box marked region of interest (ROI).

The Br K ROIs for PbBr₂, FAPB, CsPB and MAPB are displayed in Fig. 1c–f. The A-cation has an observable effect on the near-edge features. The ROI for PbBr₂ shows the first HERFD-XAS feature from ~13466 to ~13471 eV in incident energy. The ROIs for the APB compounds show HERFD-XAS features in the same energetic region as PbBr₂ and up to ~13475 eV, suggesting the higher energy part of the HERFD-XAS feature is affected by bromide interaction with the A-cation. We observe a difference in the energetic width of the HERFD-XAS feature between FAPB and CsPB, where the width of the CsPB feature is ~80% of the width of the FAPB feature. Despite the influence of the Br 1s core hole present in the final state of the spectroscopic process, the Br K spectrum can be conceptually viewed as a reflection of the unoccupied Br p-state distribution. Hence we deduce that the A-cation influences the width of the conduction band and contributes states to the higher energy part of the conduction band in APB compounds. The HERFD-XAS feature at lowest photon energy is related to the part of the unoccupied states close to the conduction band minimum (CBM), relevant for optoelectronic device operation.

We plot Br K HERFD-XAS cuts of PbBr₂, FAPB, MAPB and CsPB as one-dimensional spectra in Fig. 2a for quantitative analysis. Conventional XAS spectra recorded in Total Fluorescence Yield (TFY) mode are shown for comparison. The resolution improvement of Br K HERFD-XAS (2.2 eV) versus TFY-XAS (2.5 eV) is small but is still important for resolving spectral differences between APB compounds in the energy region between ~13466 to ~13475 eV. For example, the notch in the spectrum of FAPB (~13470.3 eV, Fig. 2b), resolved with HERFD-XAS but not with TFY-XAS, indicates that the main absorption feature (main-edge) is formed in two main components. All four Br K HERFD-XAS spectra show a feature at ~13469 eV. Additionally, the spectra for the APB compounds show features around 13471.5 eV which are affected by A-cation replacement, as noted above. We further confirm this deduction using calculations. The Pb L₃ ROIs and HERFD-XAS spectra are shown in Supplementary Fig. 1 and the analysis is described in Supplementary Note 1. We use Pb L₃ as a direct spectroscopic probe of changes in the electronic structure caused by A-cation-induced crystal structure changes and the resolution enhancement yielded by HERFD-XAS (2.5 vs. 6.1 eV) is crucial.

We sigmoid-fit the Br K HERFD-XAS spectra of FAPB, MAPB and CsPB to extract numerical parameters (Fig. 2b). Given the signal-to-noise level of our measurements and nearly identical absorption onsets for MAPB and CsPB, we find the sigmoid fit better suited for differentiating the main-edge positions as compared to the first derivative (Supplementary Fig. 2). We find an
absorption onset trend, based on edge positions associated with a 0.5 step height, which increases in this order: FAPB (13466.6 eV), MAPB (13467.1 eV), CsPB (13467.2 eV). The sigmoid fit uncertainty is 20 meV. The A-cation influences the absorption onsets, suggesting the A-cation affects device-relevant conduction band energy level positions referenced to Br 1s in the ground-state. The Br K spectra show a post-edge region at ~13476 eV and higher, at a sigmoid step height of 0.75. Using this step height to systematically compare main-edge widths, we estimate widths of ~7.2 eV (FAPB), ~6.9 eV (MAPB) and ~6.0 eV (CsPB).

To understand the origin of the spectral differences and link the crystal and electronic structures, we carry out periodic DFT calculations and AIMD simulations and sample calculated Br K XAS spectra using the transition potential DFT method with the half-core hole approximation. To capture the structural dynamics of the A-cation accurately, we use three or four configurations, each involving between 81 and 96 bromine atoms, with 10 ps time differences in the AIMD trajectory. The longest time constant of the AIMD trajectory is ~2 ps.

From the XAS component spectra, we observe that the rising part of the main-edge can be assigned to Br 4p states with \( \sigma \)-symmetry while features in the higher energy region of the main-edge are contributed by Br 4p states with \( \pi \)-symmetry, in all cases. We also notice that due to the spatial extent of the states of \( \pi \)-symmetry, they are more strongly influenced by A-cation interactions. The lower energy position of the \( \sigma \)-symmetry states suggests the states in the vicinity of the CBM in the ground-state are primarily of Br-Pb \( \sigma \)-anti-bonding character. Additional details on the comparison between experimental and calculated XAS are presented in Supplementary Note 2.

We observe a trend in the energetic separation (\( \sigma-\pi \) splitting) between the maxima of the \( \sigma \) and \( \pi \)-symmetry distributions in the main-edge: ~3.5 eV (CsPB) \( \rightarrow \) ~4.0 eV (MAPB) \( \rightarrow \) ~4.2 eV (FAPB). We compare relative energy separation from calculation versus relative main-edge width from experiment. The CsPB: FAPB ratios are ~0.83 (calculation) and ~0.83 (experiment) and the MAPB: FAPB ratios are ~0.95 (calculation) and ~0.96 (experiment). We find a positive and potentially linear correlation between the relative measures of main-edge width and conclude that the A-cation influences the Br K main-edge width of the APB compounds via the \( \sigma-\pi \) splitting. The use of HERFD-XAS has revealed A-cation-induced differences in APB electronic structure, and the close agreement between experimental and calculated XAS trends offers an opportunity to computationally elucidate the \( \sigma-\pi \) splitting mechanism.

We study the Br-(A-cation) interaction using calculated Br PDOS from ground-state Kohn-Sham orbitals. For FAPB and MAPB, we choose two geometries around Br atoms, representing strong (H-Br bond distances of ~2.37 Å (FAPB), 2.47 Å (MAPB)) and weak (H-Br bond distance >3.0 Å) hydrogen bonds.
We calculate the approximate σ- and π-symmetry contributions to the Br PDOS along Pb-Br-Pb in the crystal frame (remembering there is a bend in Pb-Br-Pb) and connect them with XAS σ- and π-symmetry contributions. The Br 4s,p PDOS for strong hydrogen bonds is presented in Fig. 3a, b; the PDOS for weak bonds is presented in Supplementary Fig. 3. The Br 4p PDOS comprises the bulk of the valence band states, as shown in Supplementary Fig. 4, which displays the Br 4p PDOS and the total DOS (contributions from all elements). We observe that the occupied Br 4p π from −4 to 0.7 eV and Br 4s from −15 to −11.5 eV for CsPB, and MAPB/FAPB with short/long H-Br bonds are similar. The 4p σ from −4.5 to 0.5 eV shows some dependence on the A-cation type. On the other hand, the unoccupied Br 4p PDOS exhibits striking differences. The bands of π-symmetry are shifted and change shapes for FAPB or MAPB with respect to CsPB (between ~4 and ~16 eV); this clearly shows the influence of hydrogen bonding. We observe that the difference for FAPB versus CsPB is larger than for MAPB versus CsPB, in agreement with the increased hydrogen bond strength (H-Br bond distance is shorter for FAPB). We quantify the ground-state σ–π splitting with peak and center-of-gravity fits (Supplementary Table 1) and find, irrespective of the H-Br bond distance, that the σ–π splitting increases going from CsPB → MAPB → FAPB. This is in qualitative agreement with the σ–π splitting trend in the XAS spectra.

To investigate the physicochemical interactions underlying the σ–π splitting trend, MA+/FA+ were artificially substituted with Cs+ in the geometries of MAPB/FAPB while maintaining the Br–Pb sublattice structure. Remarkably, when the organic A-cations are substituted by Cs+, the sharpness and energetic positions of both the π and σ contributions in the unoccupied states become CsPB-like, even though the structural models have not been relaxed. The σ–π splitting for CsPB is of comparable magnitude to the splittings for Cs-substituted MAPB/FAPB, and no systematic trend is observed for short/long H-Br bond distances (Supplementary Table 1). Hence, these artificial investigations provide computational evidence that hydrogen bonding in MAPB/FAPB has a strong influence on the conduction band and an electronic coupling exists between the A-cations and the Br-Pb sublattice. This is consistent with reported electronic coupling in the unoccupied states of MAP24. Furthermore, the
influence on the σ and π symmetry contributions of the Br PDOS indicates that the magnitude of the σ–π splitting in the XAS spectra is influenced by the strength of H-bonding interaction. We find a positive correlation between the average strength of N–H ... Br hydrogen bonding and the average magnitude of the σ–π splitting and deduce that the rotation/oscillation of the organic A-cations likely do not have a causal relationship with the magnitude of the splitting. Further details can be found in Supplementary Discussion 1, where we also argue that the σ–π splitting is a time-averaged feature in the conduction band states and expect it to influence all electron dynamics irrespective of timescale. In Supplementary Note 3, we briefly discuss potential limitations to DFT calculations of the conduction band electronic structure, and deduce that the σ–π splitting trend is unaffected due to its magnitude of several eV.

To evaluate the possible influence of spin-orbit coupling (SOC) on the conclusions of our analysis, we performed total electronic density of states (TDOS) calculations for all three lead bromide perovskites using DFT with/without SOC effects. Further details are found in the Methods. The results of the calculations, shown in Supplementary Fig. 5, suggest that given our convolution scheme the influence of SOC on the peak positions (variations of less than 0.05 eV) at higher energy with respect to the CBM as well as the orbital characters of the states in the conduction band region is negligible. Hence, the influence of SOC on the analysis of the Br K-edge XAS data is negligible also. Furthermore, we note that the SOC effect on the lead and bromine PDOS of the three perovskites should be similar, given the same PbBr6 octahedra, and in this work we focus on relative, A-cation-induced changes in the σ–π energy separation between the three perovskites. The influence of SOC is very small for the valence band region up to ~10 eV, except for the Cs 5p feature in CsPB (~6 to ~10 eV). The computed TDOS shows the Pb 5d splitting around ~12 to ~20 eV, which is consistent with the shallow core photoelectron spectra of Pb 5d (Supplementary Fig. 6) and confirms the inclusion of SOC in the TDOS calculations.

We turn our attention to possible manifestation(s) of A-cation influence in the occupied states and in the crystal structure. Our calculations suggest the occupied Br 4p PDOS near the valence band maximum (VBM) is weakly affected by A-cation type (Fig. 3a). To investigate further, we analyze the Br K valence-to-core (VtC) XES spectra (Fig. 4 right inset) since the Br Kβ2,3 transition, shown in the RXES map (Fig. 1a) and measured simultaneously with the Kβ1 transition which yields the HERFD-XAS spectrum, carries information on the distribution of Br 4p states in the valence band. We fit a Voigt peak to the main VtC line and observe that the ~13462 to ~13472 eV region is similar for all compounds, in agreement with calculation. This finding, combined with our earlier finding of mostly Br-Pb σ-states near the CBM (Fig. 2c–e), could explain why band-edge carrier dynamics in APB crystals are independent of the A-cation type25. Additionally, we observe that the relative VtC intensity of FAPB is higher than MAPB/CsPB (Fig. 4 center inset), given the same number of bromide X-ray emitters (normalized to Kβ1,3). This shows the number of electrons in Br 4p is higher for FAPB and suggests the Br-Pb bond for FAPB is more ionic. We confirm this observation by examining the chemical shift, finding an increasing Br–Pb ionicity trend (CsPB → MAPB → FAPB) which matches the σ–π splitting trend. Technical details are found in Supplementary Note 4. In principle, bond ionicity originates from the electronegativity difference between lead and bromine, hence the trend is unanticipated and reveals the A-cation influence on carrier mobility, which has previously been exponentially correlated with halide-lead bond ionicity26. Additionally, the Kβ1 trend matches the XAS onset trend of FAPB → MAPB → CsPB, thus we see that there is a correlation between the strength of A-cation coupling and Br-Pb bond ionicity, which determines relative shifts in all energy levels referenced to Br Is and has implications for energy level matching at device interfaces.

We utilize hard X-ray PES (HAXPES) measurements for a complementary investigation of the VBM DOS, where differences in spectral profiles could be assigned to differences in lead contributions as we have shown the Br 4p PDOS of FAPB, MAPB and CsPB are similar. We observe that the A-cation influences the DOS near the VBM (Supplementary Fig. 6) and deduce that the A-cation type modifies the degree of Pb 6s/6p hybridization with
the Br 4p states, which may be relevant for visible light absorption/emission and Rashba band-splitting effects. Further analysis and discussion are found in Supplementary Note 5.

Through a combined analysis of Pb L₃ RXES, AIMD-derived bond angles/distances (Supplementary Fig. 7) and Goldschmidt tolerance factor (GTF), we examine A-cation effects in the crystal structure27. Our X-ray diffraction measurements confirm the crystal structures are as expected (Supplementary Table 2) and Pb L₃ RXES confirms the unit cell symmetry increases with increasing GTF. We find that cooperative PbBr₆ octahedral tilting shows the largest geometrical variation between the APB compounds, but were unable to relate that mechanistically to the σ–π trend which instead is related directly to hydrogen bonding. We derive relative GTF ratios for MAPB: FAPB (0.98) and CsPB: FAPB (0.79) and find they nearly match the relative main-edge width MAPB: FAPB ratios of 0.96 (measured) and 0.95 (calculated) and CsPB: FAPB ratios of 0.83 (measured) and 0.83 (calculated). This is a positive and potentially linear correlation between relative GTF and relative conduction band width which applies to the APB compounds and possibly all HaP compounds. Consequently, we deduce that the GTF can be regarded as both a measure of H-bonding strength in MA and Cs⁺ as well as an approximate measure of octahedral tilting. Technical details can be found in Supplementary Note 6. A-cation influence on the crystal structure and optoelectronic functionality has previously been investigated28,29. Our XRD, Br K and Pb L₃ HERFD-XAS, and Br Kβ₁ measurements show that symmetry lowering of the Br–Pb framework increases Br–Pb covalency and shifts the CBM up in potential energy, which is consistent with the findings of a pure computational study28. Hence, we find A-cation effects on the crystal and electronic structures that are generally consistent with previous findings. Additionally, we provide direct measurements of the relative Br-Pb bond ionicity/covalency with XES and Br K-edge HERFD-XAS measurements of the bromine-projected conduction band states. We summarize the numerical quantities obtained through our experimental and computational work and aforementioned correlations in Fig. 5.

**Discussion**

Using Fig. 5, we briefly discuss the implications of our findings for energy level matching at device interfaces and slow hot electron cooling. We note that direct and inverse PES measurements of device-relevant energy level positions show a trend which systematically matches our Br K XES and HERFD-XAS trends31. The interface energetics are sensitive to A-cation coupling strength; even a ~100 meV (~4k_b T at room temperature) shift in the energy levels will substantially affect interfacial carrier transport mechanisms where current density depends exponentially on the magnitude of the energy barrier/offset (i.e. thermionic emission). State-of-the-art HaP solar cells and light-emitting diodes typically feature a mixture of MA⁺, FA⁺ and Cs⁺ A-cations and depth-profiled with HAXPES has revealed spatial variations of A-cations near the surface30,31. Our study reveals that the A-cation(s) present, intended or not, in the few perovskite layers adjacent to the interface are expected to influence the interface energetics and hence device performance. As for the σ–π splitting, we expect it to influence slow hot carrier cooling in HaPs, which is of interest due to the technological potential of hot-carrier solar cells32.

Single-junction solar cells, irrespective of device architecture and solar absorber material, are thermodynamically limited in power conversion efficiency (PCE) to slightly above 30%33. This limit assumes all excess energy from above-bandgap light absorption is unavailable to do work. Current certified PCE for thin-film crystal GaAs, single-crystal Si, and halide perovskite solar cells are 29.1%, 26.7% and 25.7%, respectively1. While the use of terrestrial-based, non-concentrator triple-junction solar cells (39.5% PCE) is possible, and silicon/perovskite tandem solar cells (29.8% PCE) are being commercialized, single-junction cells with PCE surpassing the Shockley-Queisser limit are highly attractive for techno-economic reasons. If the energy from above-bandgap photoexcitation is available to do work, the thermodynamic limit could be substantially higher34. Actual hot carrier solar cells have yet to be demonstrated, though the concept was proposed forty years ago35.

The development of a hot carrier solar cell hinges on several prerequisites, such as the existence of slow cooling of hot carriers in the light absorber and efficient extraction of hot carriers at device interfaces32. At comparable electron temperatures of ~1000 K, hot carrier cooling time constants are considerably longer for HaPs (100’s of ps) versus state-of-the-art GaAs (~10 ps)12,36. This suggests HaP-based solar cell technology has the potential to become the leading single-junction photovoltaic technology. Slow hot carrier cooling in HaPs has been experimentally observed, and phenomenologically explained

![Figure 4](https://example.com/figure4.png)

**Fig. 4** X-ray emission spectra of FAPB, MAPB and CsPB. The Kβ₁ and Kβ₂/VIC peaks are fitted with Voigt peaks; the fitted values and uncertainties are displayed in the insets. The Voigt peak fit of the main VIC emission line is intended to extract the energy position of the peak maximum. The center inset shows VIC intensities associated with normalized Kβ₁ intensities.
with the polaronic screening and hot phonon bottleneck mechanisms\textsuperscript{12,37,38}. Our finding, of the $\sigma-\pi$ splitting in the conduction band, provides an alternative mechanism for electron cooling, thus advancing the general understanding of electron dynamics in HaPs and spurring technological development of HaP-based hot carrier solar cells. Simultaneously, our study highlights the mostly-overlooked optoelectronic role of the A-cation, shedding light on a well-debated issue and providing guidance to HaP application developers who are tailoring HaP properties for various optoelectronic applications.

Practical HaP-based hot carrier solar cells may operate with hot electrons and/or holes, and we discuss the potential for utilizing both starting with hot holes. Slow hot hole cooling in CsPI, with the polaronic screening and hot phonon bottleneck mechanisms\textsuperscript{12,37,38}. Our finding, of the $\sigma-\pi$ splitting in the conduction band, provides an alternative mechanism for electron cooling, thus advancing the general understanding of electron dynamics in HaPs and spurring technological development of HaP-based hot carrier solar cells. Simultaneously, our study highlights the mostly-overlooked optoelectronic role of the A-cation, shedding light on a well-debated issue and providing guidance to HaP application developers who are tailoring HaP properties for various optoelectronic applications.

Practical HaP-based hot carrier solar cells may operate with hot electrons and/or holes, and we discuss the potential for utilizing both starting with hot holes. Slow hot hole cooling in CsPI, with the polaronic screening and hot phonon bottleneck mechanisms\textsuperscript{12,37,38}. Our finding, of the $\sigma-\pi$ splitting in the conduction band, provides an alternative mechanism for electron cooling, thus advancing the general understanding of electron dynamics in HaPs and spurring technological development of HaP-based hot carrier solar cells. Simultaneously, our study highlights the mostly-overlooked optoelectronic role of the A-cation, shedding light on a well-debated issue and providing guidance to HaP application developers who are tailoring HaP properties for various optoelectronic applications.

Practical HaP-based hot carrier solar cells may operate with hot electrons and/or holes, and we discuss the potential for utilizing both starting with hot holes. Slow hot hole cooling in CsPI, with the polaronic screening and hot phonon bottleneck mechanisms\textsuperscript{12,37,38}. Our finding, of the $\sigma-\pi$ splitting in the conduction band, provides an alternative mechanism for electron cooling, thus advancing the general understanding of electron dynamics in HaPs and spurring technological development of HaP-based hot carrier solar cells. Simultaneously, our study highlights the mostly-overlooked optoelectronic role of the A-cation, shedding light on a well-debated issue and providing guidance to HaP application developers who are tailoring HaP properties for various optoelectronic applications.

Practical HaP-based hot carrier solar cells may operate with hot electrons and/or holes, and we discuss the potential for utilizing both starting with hot holes. Slow hot hole cooling in CsPI, with the polaronic screening and hot phonon bottleneck mechanisms\textsuperscript{12,37,38}. Our finding, of the $\sigma-\pi$ splitting in the conduction band, provides an alternative mechanism for electron cooling, thus advancing the general understanding of electron dynamics in HaPs and spurring technological development of HaP-based hot carrier solar cells. Simultaneously, our study highlights the mostly-overlooked optoelectronic role of the A-cation, shedding light on a well-debated issue and providing guidance to HaP application developers who are tailoring HaP properties for various optoelectronic applications.

Practical HaP-based hot carrier solar cells may operate with hot electrons and/or holes, and we discuss the potential for utilizing both starting with hot holes. Slow hot hole cooling in CsPI, with the polaronic screening and hot phonon bottleneck mechanisms\textsuperscript{12,37,38}. Our finding, of the $\sigma-\pi$ splitting in the conduction band, provides an alternative mechanism for electron cooling, thus advancing the general understanding of electron dynamics in HaPs and spurring technological development of HaP-based hot carrier solar cells. Simultaneously, our study highlights the mostly-overlooked optoelectronic role of the A-cation, shedding light on a well-debated issue and providing guidance to HaP application developers who are tailoring HaP properties for various optoelectronic applications.

Practical HaP-based hot carrier solar cells may operate with hot electrons and/or holes, and we discuss the potential for utilizing both starting with hot holes. Slow hot hole cooling in CsPI, with the polaronic screening and hot phonon bottleneck mechanisms\textsuperscript{12,37,38}. Our finding, of the $\sigma-\pi$ splitting in the conduction band, provides an alternative mechanism for electron cooling, thus advancing the general understanding of electron dynamics in HaPs and spurring technological development of HaP-based hot carrier solar cells. Simultaneously, our study highlights the mostly-overlooked optoelectronic role of the A-cation, shedding light on a well-debated issue and providing guidance to HaP application developers who are tailoring HaP properties for various optoelectronic applications.

Practical HaP-based hot carrier solar cells may operate with hot electrons and/or holes, and we discuss the potential for utilizing both starting with hot holes. Slow hot hole cooling in CsPI, with the polaronic screening and hot phonon bottleneck mechanisms\textsuperscript{12,37,38}. Our finding, of the $\sigma-\pi$ splitting in the conduction band, provides an alternative mechanism for electron cooling, thus advancing the general understanding of electron dynamics in HaPs and spurring technological development of HaP-based hot carrier solar cells. Simultaneously, our study highlights the mostly-overlooked optoelectronic role of the A-cation, shedding light on a well-debated issue and providing guidance to HaP application developers who are tailoring HaP properties for various optoelectronic applications.

Practical HaP-based hot carrier solar cells may operate with hot electrons and/or holes, and we discuss the potential for utilizing both starting with hot holes. Slow hot hole cooling in CsPI, with the polaronic screening and hot phonon bottleneck mechanisms\textsuperscript{12,37,38}. Our finding, of the $\sigma-\pi$ splitting in the conduction band, provides an alternative mechanism for electron cooling, thus advancing the general understanding of electron dynamics in HaPs and spurring technological development of HaP-based hot carrier solar cells. Simultaneously, our study highlights the mostly-overlooked optoelectronic role of the A-cation, shedding light on a well-debated issue and providing guidance to HaP application developers who are tailoring HaP properties for various optoelectronic applications.

Practical HaP-based hot carrier solar cells may operate with hot electrons and/or holes, and we discuss the potential for utilizing both starting with hot holes. Slow hot hole cooling in CsPI, with the polaronic screening and hot phonon bottleneck mechanisms\textsuperscript{12,37,38}. Our finding, of the $\sigma-\pi$ splitting in the conduction band, provides an alternative mechanism for electron cooling, thus advancing the general understanding of electron dynamics in HaPs and spurring technological development of HaP-based hot carrier solar cells. Simultaneously, our study highlights the mostly-overlooked optoelectronic role of the A-cation, shedding light on a well-debated issue and providing guidance to HaP application developers who are tailoring HaP properties for various optoelectronic applications.

Practical HaP-based hot carrier solar cells may operate with hot electrons and/or holes, and we discuss the potential for utilizing both starting with hot holes. Slow hot hole cooling in CsPI, with the polaronic screening and hot phonon bottleneck mechanisms\textsuperscript{12,37,38}. Our finding, of the $\sigma-\pi$ splitting in the conduction band, provides an alternative mechanism for electron cooling, thus advancing the general understanding of electron dynamics in HaPs and spurring technological development of HaP-based hot carrier solar cells. Simultaneously, our study highlights the mostly-overlooked optoelectronic role of the A-cation, shedding light on a well-debated issue and providing guidance to HaP application developers who are tailoring HaP properties for various optoelectronic applications.
increase from ~30 fs to ~30 ps as the optically-injected-carrier concentration is increased from ~10^{17} to ~10^{18} cm^{-3}. The cause was attributed to the hot-phonon bottleneck mechanism, where hot phonons are not cooled quickly enough and re-heat the hot carriers. An alternative and possibly complementary explanation is that the average cooling time constant increases when a fraction of σ states are occupied upon photoexcitation, impeding fast thermalization of electrons occupying the π states. Fourth, Zhu et al. have reported hot fluorescence cooling time constants, measured using picosecond time-resolved photoluminescence, for the same compounds investigated here in the same single crystal form. When photoexcited with ~3.1 eV (~0.8 eV higher than the bandgap value), Zhu et al. measure decay constants of 190 ± 20 ps (FAPB), 160 ± 10 ps (MAPB) and no measurable hot fluorescence from CsPb. We observe a positive correlation between hot fluorescence cooling time constant and σ–π splitting: ~4.2 (FAPB), ~4.0 (MAPB) and ~3.5 (CsPb) eV. Dynamical screening via solvation or large polaron formation was used to explain the long time constants. While these effects may be present during hot carrier thermalization, we suggest that a larger σ–π splitting energetically shifts the π states further away from the CBM (towards the vacuum level or ionization threshold) and thus reduces the average carrier thermalization rate. Our finding of the σ–π splitting can explain many experimental optical spectroscopy observations reported in the literature. Taken together, our findings combined with more recent experimental evidence from the literature indicate that slow hot electron cooling dominates the overall rate of slow hot carrier cooling in HaPs, and the σ–π splitting influences slow hot electron cooling in HaPs.

Although current evidence suggests that hot holes cool much faster than hot electrons, it may still be possible to design a hot carrier HaP solar cell to extract both hot holes and electrons. Visible optical absorption depths are shorter, for shorter optical wavelengths, and the hot holes, having shorter lifetimes and hence diffusion lengths, should be photogenerated close to the sun-facing contact. A potential planar device architecture for a HaP hot carrier solar cell features the HaP-absorber/hole-selective-contact–hot-workfunction electrode on the sun-facing side. This is essentially the “inverted” or “p-i-n” HaP solar cell architecture with specially designed hot carrier selective contacts. Hot-electrons, having much longer lifetimes and hence diffusion lengths, could diffuse to the electron-selective contact on the backside. Properties of the carrier-selective contacts, such as energy level alignment and effective density-of-states matching, would need to be designed to pass through hot carriers and perhaps some colder carriers, to balance electron/hole extraction, photovoltage versus photocurrent, etc. At present, the “conventional” or “n-i-p” architecture, with the electron-selective-contact on the sun-facing side, has shown higher PCE (25.6%) compared to the p-i-n architecture (23.7%). Aside from historical differences in development time and suboptimal cell design and/or fabrication, suboptimal selection/implementation of selective contacts, etc. in the p-i-n architecture, we cannot think of any other (intrinsic) reasons for the disparity in performance.

Aside from its influence on electron thermalization, we expect the σ–π splitting to affect electron transport. The potential connection between the σ–π character of the conduction band and polaron-like carrier transport is discussed in Supplementary Discussion 2.

In conclusion, through a joint experimental-computational investigation, we show that the energetic width of the conduction band depends on the strength of electronic coupling between the A-cation and the lead-bromide sublattice. Our finding of the σ–π splitting in the conduction band provides an additional mechanism to consider, in the search for the origins of slow hot carrier cooling and polaronic transport. In both the occupied and unoccupied states, we find a correlation between higher coupling strength and higher bromide-lead bond ionicity and a decreased energy offset between a given energy level and Br 1s, and discuss the implications for energy level matching at perovskite device interfaces. We foresee the spectroscopic approach we have employed in this work being utilized to study A-cation effects in other halide perovskites and potentially non-halide perovskites as well, thus unraveling unexplored structure-property relationships in these materials and furthering the development of optoelectronic devices.

**Methods**

**APB crystal growth.** The MAPb and FAPb single crystals were solution-grown using methods reported by Dr. Papira Nayak previously. The CsPb single crystals were solution-grown using a method reported by others. All single crystals were grown in an ambient air environment, then transferred into vials of chlorobenzene for storage and preservation.

**X-ray diffraction.** X-ray diffraction measurements were performed on FAPB and CsPb single crystals at room temperature using a Rigaku diffractometer with graphite-monochromated molybdenum Kα radiation (h = 0.7073 Å). Data processing was performed with the CrysAlisPro software. Empirical absorption correction was applied to the collected reflections with SCALE3 ABSPACK and integrated with CrysAlisPro. The structures of the single crystals were solved by direct methods using the SHELXTL program, and refined with the full-matrix least-squares method based on F^2 by using the SHELXL program through the Olex interface. The crystallographic parameters for MAPb are taken from reference, since a similar growth procedure was used by the same preparer.

**Hard X-ray absorption and emission spectroscopy.** The measurements were performed (on APB crystals from the same batch characterized with XRD) at beamline P64 of the synchrotron facility PETRA III. Incident photon energy calibration at the Pb L_3 edge was performed with metallic lead foil. The photon flux was determined using a Si(220) crystal reference with the detector placed 0.71073 Å away from the sample. The X-ray beam was monochromatized using a Si(111) crystal placed 1.5 eV above the HERFD XES edge energy. The energy resolution of the spectrometers was determined at the Pb L_3 edge by energy-calibrating using several elastic and inelastic XES maps recorded using a monochromatic hard X-ray spectrometer mounted in a Bragg scattering configuration. The spectrometer measured 8 crystal analyzers; the third-order refraction of the Si(220) crystal analyzers was used for Pb L_2 and the fourth-order refraction was used for Pb K_α, measurements. Energy calibration of the two-dimensional detector images was performed with custom Python-based software written by Dr. Aleksandr Kalinko. The Br K maps were energy-calibrated using several elastic inelastic XES maps recorded for the energy window ±5 eV around the Br K edge. The energy resolution of the spectrometer was determined using the Pb L_3-edge energy resolution as a standard and the Pb L_2-edge energy resolution as a reference. The Pb L_3-edge energy resolution was 10551 and 10449 eV, respectively. Bromine K (~13.47 keV) and lead L_2 (~13.04 keV) HERFD-XES spectra were generated as averaged intensities of the slice cut from RXES maps. The energetic width of the slice on the emitted energy axis (HERFD linewidth) was 300 eV, while the RXES slice cut through the RXES maximum. The HERFD linewidth was selected based on a balance between energy resolution and signal-to-noise (Supplementary Fig. 8). The off-resonant, higher incident energy half of the RXES map was used to generate the X-ray emission spectrum. The energy resolution of the HERFD-XES spectra was determined by the ~0.3 eV photon bandwidth of the Si(311) monochromator and the ~1.5 eV FWHM Gaussian broadening of the spectrometer. Single crystals were prepared for measurements by first extracting them from chlorobenzene, blowdowning with compressed air/nitrogen in an ambient air environment, then mounting them into a Linkam T95 heating/cooling stage (~ 5 min total). All measurements on the APB single crystals were performed (on APB crystals from the same batch characterized with XRD) at the HIKE endstation attached to the beamline P64 of the synchrotron facility BESSY II. With an excitation energy of 11.5 keV (~13.04 keV HERFD-XES X-ray energy), the HERFD-XES measurements were performed on APB single crystals and degraded MAPb (long beam exposure, iteration 13).
from the FWHM of Gaussian-broadened Au 4f$_2$ photoelectron lines, is 0.3 eV and is governed primarily by the photon bandwidth of the Si(311) monochromator. Binding energy calibration was performed by recording Au 4f from a reference gold foil and setting the binding energy of E$_{\text{Au}4f_7/2}$ to 84.0 eV. Multiple iterations of core level spectra were recorded, to distinguish the onset of beam damage. See Supplementary Note 7 and Supplementary Fig. 10 and 11 for further details.

Calculations. We performed periodic DFT calculations using the Quickstep code in the CP2K package$^{22-24}$. We used the Perdew–Burke–Ernzerhof (PBE) general-ized gradient approximation as the exchange-correlation (XC) functional$^{35}$. In addition, we have included a Van der Waals correction using Grimme’s D3 method$^{26}$. The geometry optimizations were performed using the Gaussian plane-wave (GPW) method with Goedecker–Teter–Hutter (GTH) pseudopotentials as well as TZVP-MOLOPT-GTH (for carbon, nitrogen, hydrogen) and DZVP-MOLOPT-GTH (for lead and bromine) basis sets$^{27-39}$. An energy cut-off of 600 Ry was used along with a multi-grid consisting of five grids. The starting geometries for MAPb, FAPb and CsPb are (cubic, 3 × 3 × 3), (cubic, 3 × 3 × 3) and (orthorhombic, 2 × 2 × 2), respectively, taken from the literature$^{40-42}$. All electronic structure calculations were performed at the gamma point of the supercells. Ab initio molecular dynamics simulations were carried out with the same computational parameters within an NPT ensemble at 300 K and 0 atm. The MD simulations were performed for a minimum of 30 ps using a 0.5 fs time step. The drift in the conserved energy is observed to be below 10$^{-6}$ a.u. ps$^{-1}$ atom$^{-1}$. To assess the potential influence of spin-orbit coupling on the calculated electronic structures, total density of states calculations including SOC have been performed using DFT at the GGA level with the Quantum Espresso (QE) package for all three lead bromide perovskites$^{43}$. These calculations employed fully relativistic Rappe–Rabe–Koutselinis–Joannopoulos ultrafast pseudopotentials, including nonlinear core corrections, for all constituent atoms available in the QE pseudopotential library$^{44,45}$. Similar to the CP2K calculations, the PBE exchange-correlation functional and the gamma point of the supercells have been used$^{46}$. We chose plane-wave energy cutoffs of 45 and 455 Ry for the electronic wave function and charge density, respectively.

X-ray absorption spectra were calculated using the Gaussian augmented plane-wave (GAPW) implementation of core-level spectroscopy in CP2K, which allows for a mixed pseudopotential and all-electron description$^{22,25}$. The bromine, hydrogen, carbon and nitrogen atoms were treated at an all-electron level and described by 6-311G** basis sets while the GTH pseudopotential with TZVP basis sets were used for the lead and cesium atoms. To simulate core-hole relaxation effects, we use the transition potential method with a half-core hole (TPHH) at the Br 3s state. Separate spectral simulations were carried out for each bromine atom in the supercell, where the supercells are obtained from geometry optimization as well as AIMD snapshots (three or four configurations are selected for FAPb, MAPb or CsPb with 10 ps time differences in the AIMD trajectory and close to 100 Br atoms for each configuration). Individual spectra are then averaged together to generate aggregate spectra. The calculated, discrete XAS spectra are convoluted with a Gaussian function with a broadening parameter or $\sigma$ of 1.0 eV (corresponding to FWHM of 2.355 eV) to simulate experimental spectra. Absorption energies obtained from simulation are underestimated in comparison to experimental data; this is a known limitation of the TPHH approximation. Consequently, an ad-hoc rigid shift of +194.3 eV (+1.5%) was added to all calculated Br K XAS spectra for direct comparison to the experiment.

Data availability
The processed data presented in this work are available from the corresponding authors on reasonable request. The unprocessed experimental data is associated with the beamtime proposal identifiers listed in the Acknowledgements, and is available from the corresponding authors on reasonable request.

Received: 16 September 2021; Accepted: 14 June 2022; Published online: 04 July 2022

References
1. National Renewable Energy Laboratory. Best Research-Cell Efficiency Chart (National Renewable Energy Laboratory, 2021).
2. Kojima, A., Teshima, K., Shirai, Y. & Miyasaka, T. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. J. Am. Chem. Soc. 131, 6043-6045 (2009).
3. Yang, W. S. et al. Iodide management in formamidinium-lead-halide-based perovskite layers for efficient solar cells. Science 356, 1376-1379 (2017).
4. Nayak, P. K., Mahesh, S., Snait, H. J. & Cahen, D. Photovoltaic solar cell technologies: analysing the state of the art. Nat. Rev. Mater. 4, 269-285 (2019).
5. Moseley, O. D. I., Doherty, T. A. S., Parmee, R., Anaya, M. & Stranks, S. D. Halide perovskites scintillators: unique promise and current limitations. J. Mater. Chem. C 9, 11588-11604 (2021).
6. Akkerman, Q. A. & Manna, L. What de...
34. Ross, R. T. & Nozik, A. J. Efficiency of hot-carrier solar energy converters. J. Appl. Phys. 38, 3813–3818 (1967).
35. Ferry, D. K., Goodnick, S. M., Whiteside, V. R. & Sellers, I. R. Challenges, myths, and opportunities in hot carrier solar cells. J. Appl. Phys. 120, 220903 (2020).
36. Rosenwaks, Y. et al. Hot-carrier cooling in GaAs: quantum wells versus bulk. Phys. Rev. B 48, 14675–14678 (1993).
37. Yang, Y. et al. Long-range balanced electron- and hole-transport lengths in organic-inorganic CH3NH3PbI3. Science 342, 344–347 (2013).
38. Yang, Y. et al. Observation of a hot-phonon bottleneck in methylammonium lead triiodide perovskite crystals. Nat. Photonics 10, 53–59 (2016).
39. Shen, Q. et al. Slow hot carrier cooling in cesium lead iodide perovskites. Appl. Phys. Lett. 111, 153903 (2017).
40. Kawai, H., Giannozzi, P., Marini, A. & Yamashita, K. The mechanism of slow hot-hole cooling in lead-iodide perovskite: first-principles calculations on lifetime from electron–phonon interaction. Nano Lett. 15, 3103–3108 (2015).
41. Verkamp, M. et al. Carrier-specific hot phonon bottleneck in CH3NH3PbI3 revealed by femtosecond XUV absorption. J. Am. Chem Soc. 143, 20176–20182 (2021).
42. Man, G. J. Metal Oxide/semiconductor Heterojunctions as Carrier-selective Contacts for Photovoltaic Applications (Princeton University, 2017).
43. Jeong, J. et al. Pseudo-halide anion engineering for formamidinium lead bromide. Inorg. Chem. 56, 10433–10441 (2017).
44. Ayabe, K. et al. Quantum Hall liquid and recoverable memory using perovskite quantum dots. Nat. Mater. 19, 915–920 (2020).
45. Poglitsch, A. & Weber, D. Dynamic disorder in exciton diffusion and phase separation dynamics of hybrid perovskites. J. Chem. Phys. 150, 121105 (2019).
46. Yang, Y. et al. Observation of a hot-phonon bottleneck in methylammonium lead triiodide perovskite crystals. Nat. Commun. 7, 13303 (2016).
47. Kabakova, I. V. et al. The effect of ionic composition on acoustic phonon speeds in hybrid perovskites from Brillouin spectroscopy and density functional theory. J. Mater. Chem. C 6, 3861–3868 (2018).
48. Ding, D. N., Chen, X., Shyryakarenko, Y. & Kovalenko, M. V. Solution-grown CsPbBr3 perovskite single crystals for photon detection. Chem. Mater. 28, 8470–8474 (2016).
49. Caliebe, W. A., Murzin, V., Kalinin, A. & Göröltz, M. High-flux XAFS-beamline P64 at PETRA III. in: AIP Conf. Proc. 2054, 060301 (2019).
50. Steierer, K. X. et al. Defect tolerance in methylammonium lead triiodide perovskite: First-principles calculations of defect energetics, formation energies, and bandgap narrowing. ACS Energy Lett. 1, 360–366 (2016).
51. Klein-Kedem, N., Cahn, D. & Hodes, G. Effects of light and electron beam irradiation on halide perovskites and their solar cells. Acc. Chem. Res. 49, 347–354 (2016).
52. Schäfers, F. The crystal monochromator beamline KMCI-1 at BESSY II. J. Large-scale Res. Facil. JSLRF 2, A36 (2016).
53. Hohenberg, P. & Kohn, W. Inhomogeneous electron gas. Phys. Rev. 136, B864–B871 (1964).
54. Kohn, W. & Sham, L. J. Efficient implementation of the density functional for a many-fermion system. Phys. Rev. 113, A1133–A1135 (1965).
55. Hutter, J., Iannuzzi, M., Schiffmann, F. & VandeVondele, J. CP2K: an atomistic simulation program for condensed matter systems. Wiley Interdiscip. Rev. Comput. Mol. Sci. 4, 15–25 (2014).
56. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).
57. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for a wide range of chemical systems. J. Chem. Theory Comput. 3, 366–376 (2007).
58. Lippert, G., Hutter, J. & Parrinello, M. A hybrid Gaussian and plane wave density functional scheme. Mol. Phys. 92, 477–488 (1997).
59. Goedecker, S., Teter, M. & Hutter, J. Separable dual-space Gaussian pseudopotentials. Phys. Rev. B 54, 1703–1710 (1996).
60. VandeVondele, J. & Hutter, J. Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. J. Chem. Phys. 127, 114105 (2007).
61. Poddighe, A. & Weber, D. Dynamic disorder in methylammoniumtrihalogenoplumbates (II) observed by millimeter-wave spectroscopy. J. Chem. Phys. 87, 6373–6378 (1987).
62. Schüller, E. C. et al. Crystal structure evolution and notable thermal expansion in hybrid perovskites formamidinium tin iodide and formamidinium lead bromide. Inorg. Chem. 57, 695–701 (2018).
63. Stoumpos, C. C. et al. Crystal growth of the perovskite semiconductor CsPbBr3: a new material for high-energy radiation detection. Cryst. Growth Des. 13, 2722–2727 (2013).
64. Giannuzzi, P. et al. Advanced capabilities for materials modelling with Quantum ESPRESSO. J. Phys. Condens. Matter 29, 465901 (2017).
65. Rappé, A. M., Rabe, K. M., Kaxiras, E. & Joannopoulos, J. D. Optimized pseudopotentials. Phys. Rev. B 41, 1227–1230 (1990).
66. Krack, M. & Parrinello, M. All-electron ab-initio molecular dynamics. Phys. Chem. Chem. Phys. 2, 2105–2112 (2000).

Acknowledgements
The XAS measurements were carried out at beamline P64 of the synchrotron facility PETRA III at DESY, a member of the Helmholtz Association (HGF). The van Hove-type hard X-ray spectrometer was realized by the group of Prof. Matthias Bauer (University of Paderborn) in the frame of projects FKZ 05KJ1UK1 and FKZ 05K14PF1, supported by Bundesministerium für Bildung und Forschung. We thank DESY for the provision of beamtime (Proposal No. 201801082 EC, I-20190356 EC). User (G.J.M., S.M.B., D.P.) experiments at PETRA III have been supported by the project CALIPPSplus under the Grant Agreement 730872 from the EU Framework Programme for Research and Innovation HORIZON 2020. The HAXPES measurements were performed at the HIKE endstation attached to the beamline KMC-1 of the synchrotron facility BESSY II. We thank HZB for the provision of beamtime (Proposal No. 192-08827). S.M.B. and G.J.M. thank the Swedish Research Council (contract 2018-05525) for financial support. H.R., G.J.M., D.P., and S.M. acknowledge the Swedish Research Council (grant # 2018-06465 and # 2018-04330) and the Swedish Energy Agency (P50636) for funding. P.K.N. acknowledges support from the Department of Atomic Energy, Government of India, under Project Identification no. RTI 4007, Science and Engineering Research Board India core research grant (CRG/ 2020/003677) and Swarma Jayanti Fellowship, DST, India. M.O. acknowledges support from the European Unions Horizon 2020 Research and Innovation programme under the Marie Skłodowska-Curie grant agreement No 860553, and the Swedish Energy Agency (contract 2017-06367). The calculations were enabled by resources provided by the Swedish National Infrastructure for Computing (SNIC) at the Swedish National Supercomputer Center (NSC), the High Performance Computer Center North (HPCCN), and Chalmers Centre for Computational Science and Engineering (C3SE) partially funded by the Swedish Research Council through grant agreement no. 2018-05973. We thank Sigurd Wagner (Princeton) for discussions related to the mechanism of hot carrier cooling in HaP.

Author contributions
G.J.M. and S.M.B. conceived and designed the experimental study. P.K.N. grew the single crystals. G.J.M., S.M.B., and A.K. performed the XES measurements and analyzed the data. D.P., S.M., and G.J.M. performed the HAXPES measurements; D.P. and G.J.M. analyzed the data. I.A. performed the XRD characterization and analysis, under the supervision of P.K.N. C.K. performed AIMD simulations, PDOS and XAS calculations for the snapshots and analyzed all computational results. G.J.M., S.M.B., C.K., and M.O. analyzed the XAS. G.J.M. proposed the links between the findings and questions of technological relevance. G.J.M. and S.M.B. wrote the first draft of the manuscript. All authors contributed to revisions of the manuscript. G.J.M., H.R., M.O., and S.M.B. supervised the project.

Funding
Open access funding provided by Uppsala University.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-022-03146-y.

Correspondence and requests for materials should be addressed to Gabriel J. Man or Sergei M. Butorin.

Peer review information Nature Communications thanks the anonymous reviewers for their contribution to the peer review of this work. Peer reviewer reports are available.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.