Tailoring Energies and Band Gaps of Ruddlesden-Popper Halide Perovskites with Octahedral Tilting

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Abstract. Ruddlesden-Popper halide perovskites are highly versatile quasi-twodimensional energy materials with a wide range of tunable optoelectronic properties. Here we use the all-inorganic Cs_{n+1}Pb_nX_{3n+1} Ruddlesden-Popper perovskites with X=I, Br, and Cl to systematically model the effect of octahedral tilting distortions on the energy landscape, band gaps, macroscopic polarization, and the emergence of Rashba-/Dresselhaus splitting in these materials. We construct all unique n = 1 and n = 2 structures following from octahedral tilts and use first-principles density functional theory to calculate total energies, polarizations and band structures, backed up by band gap calculations using the GW approach. Our results demonstrate that the energies and band structure properties of this class of materials are governed by a complex interplay of the amplitude, direction, and character of the distortion modes that contribute to each octahedral tilt pattern. Our results provide design rules for tailoring structural distortions, band gaps and the Rashba-/Dresselhaus effect by inducing octahedral tilts, for example via deliberate choice of organic spacer molecules or by epitaxial strain.
1. Introduction

Ruddlesden-Popper (RP) halide perovskites are heterogeneous, layered materials with exceptional photophysical properties due to their quasi-two-dimensional (2D) structures [1, 2, 3, 4, 5, 6, 7, 8, 9]. This family of materials with chemical formula $A_{n-1}A'B_nX_{3n+1}$ can be thought of as derived from the 3D $ABX_3$ perovskites, where $A$ and $A'$ are monovalent cations, $B$ is a divalent metal cation (e.g. Pb), $X$ is a halogen anion, and $n$ refers to the number of perovskite layers. Even more so than their 3D congeners, RP perovskites feature an enormous structural versatility and can be synthesized in bulk form [1, 2, 6, 10, 11, 12, 13], exfoliated as a monolayer [14], and assembled in interfaces or heterostructures with other layered materials [15, 16]. They owe this flexibility and their robust stability under ambient conditions in a large part to the wide range of organic $A$ and $A'$ site cations which have been shown to significantly affect the photophysical and thermal properties of this class of materials due to structural and dielectric effects [17, 18, 19, 20, 21, 22, 23, 24].

A particularly intriguing feature of RP perovskites is that their quasi-2D structure, in which the corner-sharing connectivity of the $BX_6$ octahedra is severed in the stacking direction, can lead to a rich landscape of octahedral tilting distortions [25]. In 3D metal-halide perovskites, octahedral tilting is the primary energy-lowering structural distortion. It is well-understood that octahedral tilting in 3D metal-halide perovskites leads to a blueshift of the band gap due to the antibonding nature of the valence band maximum (VBM) and conduction band minimum (CBM) [26]. However, octahedral tilting in 3D perovskites cannot lead to non-centrosymmetric structures; these distortions preserve a global centrosymmetric space group. 3D perovskites with polar space groups that could exhibit properties like a macroscopic polarization, ferroelectricity, or Rashba-/Dresselhaus splitting are therefore rare [27]. This is different in RP perovskites. In RP oxides, octahedral tilting distortions have been explored in depths and led to the development of the concept of hybrid improper ferroelectricity [28] followed by a multitude of predictions of ferroelectric oxides [29, 30]. In RP halide perovskites, the energy landscape of octahedral distortions and their effects on the electronic structure properties has not been systematically studied yet.

Halide perovskites have garnered attention due to their potential for spin-dependent physics that arises as a consequence of strong spin-orbit coupling due to the presence of heavy B site metals like Pb [31, 32]. In combination with noncentrosymmetric structures, spin-orbit coupling leads to the Rashba-/Dresselhaus effect, a lifting of the degeneracy of the energy bands in reciprocal space [33, 34]. This effect can be used for spin-orbitronics, spin-dependent exciton physics, and circular dichroism [35, 36, 37, 21] and is tunable through chemical substitution, electric fields and epitaxial strain [38]. It has also been speculated to contribute to the long carrier recombination times observed in 3D halide perovskites [39], although the experimental evidence for a Rashba-/Dresselhaus effect in 3D halide perovskites is debated due to the lack of a global noncentrosymmetric structure of these materials [40, 41, 42].
A recent study by Jana et al., combining first-principles calculations and experimental structural characterization unraveled design rules for Rashba-/Dresselhaus splitting in hybrid organic-inorganic 2D halide perovskite monolayer resembling \( n = 1 \) RP perovskites [43]. These authors showed that some organic-inorganic monolayer perovskites do not exhibit Rashba-/Dresselhaus splitting, despite their globally noncentrosymmetric space groups. Instead, Jana et al. correlated the magnitude of the splitting in reciprocal space to an asymmetry in the interoctahedral tilting angles. A similar observation was made in a paper by Maurer et al. who studied all-inorganic RP perovskites \( \text{Cs}_{n+1}\text{Pb}_n\text{I}_{3n+1} \) with \( n = 1, 2, 3, \infty \) and showed that only certain types of polar distortions lead to significant Rashba-/Dresselhaus splitting in the CBM [44]. While this systematic study clarified that Rashba-/Dresselhaus splitting is non-negligible in RP perovskites with polar distortions that correspond to diagonal Pb displacements towards the in-plane edges of the \( \text{PbI}_6 \) octahedron, the effect of the energetically more favorable octahedral tilting distortions on Rashba-/Dresselhaus splitting in RP perovskites was not studied.

Here we use first-principles density functional theory (DFT) to systematically study octahedral tilting distortions in all-inorganic Pb-based RP perovskites. We construct all possible octahedral tilting distortions in \( \text{Cs}_{n+1}\text{Pb}_n\text{X}_{3n+1} \) (\( \text{X}=\text{I}, \text{Br}, \text{Cl} \)) with \( n = 1 \) and \( n = 2 \) layers and determine their effect on the complex energy landscape of these materials, elucidating energetically favorable distortion modes. We then determine how octahedral tilting can be used to change the band gap of these systems, considering both the size of the gap as well as the emergence of Rashba-/Dresselhaus splitting. Our results, which we corroborate using Green’s function-based many-body perturbation theory, show which distortion modes have the most significant effects on the band gap. Unlike in \( \text{ABX}_3 \) halide perovskites, not all types of octahedral tilts and rotations open the band gap; the contribution of Pb and X site distortions to the total distortion amplitude is shown to be decisive for predicting the effect of specific distortion modes on the band gap. Furthermore, we show that out of a total of 24 polar structures with \( n = 1 \) and \( n = 2 \) for \( \text{Cs}_2\text{PbI}_4 \) only five exhibit a pronounced Rashba-/Dresselhaus splitting, confirming previous results. In fact, the ground state of \( n = 2 \) is polar, but has negligible Rashba-/Dresselhaus splitting because the dominant polar distortion modes corresponds to an alternating displacement of the Cs ions which do not contribute electronically to the band edges. Finally, to isolate the effect of interlayer stacking in RP halide perovskites, we briefly discuss results for model 2D systems consisting of free-standing halide perovskite mono- and bilayers, respectively. We find that the energy landscape and available band gap ranges are similar to the RP perovskites. However, the lack of interlayer stacking leads to a much smaller number of possible space groups and a lack of polar space groups for the monolayer.

We start our discussion with a description of our methods and nomenclature for all RP halide perovskite structures with \( n = 1 \) and \( n = 2 \) in Section 2. In Sections 3 and 4 we discuss the energy landscape and range of band gaps accessible via octahedral tilting distortions. For clarity we focus on materials with \( \text{X}=\text{I} \) and provide complete
results for X=Br and X=Cl in the Appendices. We then focus on RP halide perovskites with non-centrosymmetric space groups and their macroscopic electronic polarization and Rashba-/Dresselhaus splitting in Section 5. The final Section 6 is dedicated to a discussion of 2D mono- and bilayer halide perovskites and the energy landscape and electronic structure of these model systems.

2. Methods

2.1. Computational Methods

First-principles DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) [45, 46] with projector augmented wave (PAW) pseudo-potentials [47] with the following electronic configurations: Cs (5s25p66s1), Pb (6s25d106s2), I (5s25p5), Br (4s24p5), and Cl (3s23p5). We used a cutoff energy of 500 eV for the expansion of Kohn-Sham orbitals in the plane wave basis. The exchange-correlation functional of Perdew, Burke, and Ernzerhofer (PBE) [48] was used for all calculations, and spin-orbit-coupling (SOC) was included in the band structure calculations of Section 5. PBE is known to overestimate lattice volumes by ∼4% and underestimate band gaps in halide perovskites. Since these are systematic errors and we are primarily interested in the trends of how octahedral tilting distortions affect the energy landscape of RP halide perovskites, we performed all total energy calculations with the PBE exchange-correlation functional and symmetry adapted k-point grids using a 6 × 6 × 6 mesh for cubic CsPbI3 as reference. All structural relaxations were performed until forces were smaller than 0.001 eV/Å. Phonon dispersions were obtained within the harmonic approximation using the Phonopy code [49] using 224 and 192 atoms supercells for n = 1 and n = 2, respectively. Additionally, we performed band gap calculations for selected RP perovskites using Green’s function-based many-body perturbation theory in the ”one-shot” G0W0 approximation to corroborate the trends we found using the DFT-PBE and with SOC included self-consistently. For these calculations we constructed the zeroth-order one-particle Green’s function G0 and the screened Coulomb interaction W0 from PBE eigenfunctions and eigenvalues calculated using the QUANTUM ESPRESSO [50, 51] software package. In QUANTUM ESPRESSO, we used a cutoff energy for the plane-waves of 60 Ry and norm-conserving fully relativistic pseudopotentials from the PseudoDojo [52] repository with the following atomic configurations: Cs (5s25p66p1), Pb (6s25d106p2), I (5s25p5). The GW calculations were performed in the BERKELEYGW [53] software package using a polarizability cutoff of 8 Ry, 1200 bands and a half-shifted k-point grid consisting of 4 × 4 × 4 and 4 × 4 × 2 points for structures with Cmce and I4/mmm symmetry, respectively.

2.2. Structures

The all-inorganic RP structure with formula An+1BnX3n+1, shown in Figure 1(a) can be described as a series of alternating ABX3 perovskite and AX rock-salt layers. The
rock-salt layer breaks the connectivity of the BX$_6$ octahedra in c-direction (defined as the out-of-plane direction [001]), creating two quasi-2D perovskite slabs A and B, which are shifted by ($a/2$, $a/2$, 0) in the ab-plane against each other ($a$ is the in-plane lattice parameter). The number of layers per slab is denoted by $n$. We constructed the undistorted reference structures with $n = 1$ and $n = 2$ and space group $I4/mmm$ shown in Figure 1(a) starting from the fully relaxed cubic structure of CsPbX$_3$. Starting from

![Figure 1.](image)

Figure 1. (a) Structure of $n = 1$ Cs$_2$PbI$_4$ (left) and $n = 2$ Cs$_3$Pb$_2$I$_7$ (right) RP perovskites. Both structures consist of two perovskites slabs A and B. (b) Left: $n = 1$ structure with tilt pattern $a^+a^-a^0$ in A and $a^0a^0a^-$ in B. Full tilt pattern: $(a^+a^+a^0/a^0a^0a^-,111)$. Right: $n = 2$ structure with in- and out-of-phase rotation in c-direction in A and B. Full tilt pattern: $(a^0a^0a^+/a^0a^0a^-,111)$.

the reference structure, we constructed $n = 1$ and $n = 2$ structures with unique space groups arising from all possible octahedral tilt patterns.

To classify the octahedral tilt pattern of this perovskite family, we adapted the Glazer notation to account for the additional degrees of freedom that arise due to the broken octahedral connectivity in c-direction as shown in Figure 1(b). Our notation consists of two tilt patterns, e.g. $a^-a^0a^0/a^0a^+a^+$, corresponding to the tilt patterns of slab A and slab B, respectively. Note that for $n = 1$ RP perovskites, one cannot distinguish between in- and out-of-phase rotation along the c-direction, as each slab consists of only one perovskite layer. In this case, we use the ”+” sign to indicate the presence of a rotation along $c$. Finally, due to the separation of the slabs, there is no unique definition for the direction of rotation of adjacent octahedra of different slabs [54]. We therefore used an additional value of ±1, denoting the relative rotation of slabs A and B.
Applying all different combinations of tilt patterns and the different relative rotations of slab A and B to the untilted $I4/mmm$ structure leads to 38 unique space groups for $n = 1$, of which 9 structures are polar. For $n = 2$ we found 55 unique space groups, 15 of which are polar. Additionally, for both $n = 1$ and $n = 2$ we created two structures each via simple lead displacement: the $Immm$ structure, in which all Pb ions are displaced along the $a$-direction, and the $I4mm$ structure with Pb ions displaced in $c$-direction. The lists of all space groups for $n = 1$ and $n = 2$ are provided in Tables 1 and 2, respectively. Note that the tilt patterns reported in these Tables correspond to the octahedral rotations of the unrelaxed structures we used as starting points. After geometry optimization using the methods described above, the tilt patterns may change. Tables 1 and 2 list the space groups of all structures. Corresponding tables for the $n = 1$ and $n = 2$ bromides and chlorides are shown in Appendix A. The relaxed Br-structures were created starting from the relaxed I-structures, and the relaxed Cl-structures starting from the relaxed Br-structures. The space group only rarely changed throughout relaxation. For the iodides, this only happened for a Cs$_2$PbI$_4$ structure with initial space group $Pm$ which turned into $Pmc2_1$. For the bromides and chlorides, symmetry changes during relaxation were observed in several cases, owing to the smaller spread in total energies as compared to the iodides (see Section 3).

### 3. Energy Landscape of RP Halide Perovskites

We start by investigating the energy landscape of all possible Cs$_2$PbI$_4$ and Cs$_3$Pb$_2$I$_7$ structures. The energy gain with respect to the $I4/mmm$ parent structure is listed in Tables 1 and 2, respectively. We first note that similar to 3D ABX$_3$ perovskites, displacive distortions resulting in space groups $I4mm$ and $Immm$ are energetically unfavorable, whereas octahedral rotations and tilts lead to a lowering of the energy. For $n = 1$ RP perovskites, the overall energy landscape is similar for all three halogen anions. The ground state of Cs$_2$PbI$_4$ has $Cmme$ symmetry with an energy gain of -69.3 meV. For Cs$_2$PbBr$_4$ and Cs$_2$PbCl$_4$ the ground state has $P4_2/ncm$ symmetry with energy gains of -56.6 meV and -51.2 meV, respectively. All three structures have a tilt pattern of $a^-a^0a^0/a^0a^-a^0$, but differ in their relative rotation. Furthermore, in all cases there are several other structures that are energetically very close to the ground state with energy differences smaller than $\sim$10 meV, i.e., within the range of numerical accuracy of our calculations. Four of these structures have polar space groups. For Cs$_2$PbI$_4$, the lowest-energy polar structure has space group $Pmc2_1$ and is only 2 meV higher in energy than the ground state. For Cs$_2$PbBr$_4$ and Cs$_2$PbCl$_4$, the polar space groups $Cc$ ($X=Br$) and $Pmc2_1$ ($X=Cl$) are within $\sim$1 meV of the ground state. Contrasting this finding to the 3D perovskites CsPbI$_3$, CsPbBr$_3$, and CsPbCl$_3$, for which the lowest-energy polar structure with $R3c$ symmetry is found 43 meV, 29 meV, and 21 meV above the non-polar ground state, suggests that polar space groups should be more easily accessible in RP perovskites than in their 3D congeners, e.g., through uniaxial or biaxial strain [38].

For $n = 2$, the ground state is the polar $Cmc2_1$ structure with energy gains
### Table 1. Initial tilt pattern, energy gain $\Delta E$, size and position of the band gap for Cs$_2$PbI$_4$. All values were calculated using PBE and no SOC. Polar space groups are marked in green.

| space group | tilt pattern | k-point | $\Delta E$ (meV) | band gap (eV) |
|-------------|--------------|---------|------------------|--------------|
| 1 P1        | a’ a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -61.76          | 2.00         |
| 2 P2        | a’b’ b’/a’b’ b’           | 111 $\Gamma$ | -62.64          | 2.00         |
| 4 P2        | a’ a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -60.62          | 2.00         |
| 5 C2        | a’ a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -46.32          | 2.02         |
| 6 Pn        | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -67.41          | 2.02         |
| 7 Pc        | a’b’ b’/a’b’ b’           | 111 $\Gamma$ | -31.92          | 2.00         |
| 9 Cc        | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -66.46          | 2.03         |
| 10 P2/m     | a’ a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -68.04          | 2.02         |
| 11 P2/m     | a’ a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -68.24          | 2.02         |
| 12 P2/m     | a’ a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -58.48          | 2.02         |
| 13 Pn        | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -62.99          | 1.99         |
| 14 Pn        | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -60.34          | 2.16         |
| 15 Pn        | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -41.73          | 2.13         |
| 16 Pn        | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -64.62          | 2.04         |
| 26 Pm       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -67.08          | 2.02         |
| 31 Pm       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -25.82          | 2.05         |
| 41 Pa       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -23.35          | 2.02         |
| 51 Pn       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -68.08          | 2.02         |
| 53 Pn       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -59.77          | 2.02         |
| 55 Pn       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -1.28           | 2.12         |
| 56 Pn       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -44.54          | 2.10         |
| 57 Pn       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -45.71          | 1.99         |
| 59 Pn       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | 1.92            | 1.90         |
| 61 Pn       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -63.67          | 2.13         |
| 62 Pn       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -24.94          | 2.05         |
| 64 Pn       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -1.30           | 2.18         |
| 66 Pn       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -41.24          | 1.97         |
| 67 Pn       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -69.30          | 2.01         |
| 85 Pm       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | 1.42            | 1.99         |
| 86 Pm       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -69.26          | 2.02         |
| 94 Pm       | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -45.48          | 2.03         |
| 114 Pm      | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -66.39          | 2.04         |
| 127 Pn      | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | 2.92            | 1.91         |
| 129 Pn      | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | 1.32            | 1.91         |
| 134 Pm      | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -46.82          | 1.99         |
| 137 Pm      | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -2.60           | 1.97         |
| 138 Pm      | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -69.23          | 2.02         |
| 139 Pm      | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | 0.00            | 1.90         |
| 107 Pm      | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | 0.20            | 1.90         |
| 44 Pm      | a’ a’ a’ / a’ a’ a’ | 111 $\Gamma$ | -0.18           | 1.93         |

of -136.6 meV (Cs$_3$Pb$_2$I$_7$), -102.2 meV (Cs$_3$Pb$_2$Br$_7$), and -90.4 meV (Cs$_3$Pb$_2$Cl$_7$) with respect to the reference structure I4/mmm. In contrast to $n = 1$, the ground state is distinct and ~5 meV lower in energy than all other structures. Note that the tilt pattern of Cmc$_2$$_1$ ($a^-a^-a^0/a^-a^-a^+$), corresponds to the tilt pattern of the low-energy Pnma phase of the 3D ABX$_3$ perovskites, which is, however, not polar. This finding is in line with the observation that Cmc$_2$$_1$ is also the ground state in oxide [54, 55] and other RP perovskites [56, 57]. For the all-inorganic RP halide perovskite Cs$_3$Sn$_2$X$_7$ (X= I, Br), the ground state was found to be a structure with P4$_2$/mmm symmetry. However, a transition to Cmc$_2$$_1$ was observed due to the appearance of an in-phase rotation under compressive stress [54]. Since Sn has a smaller ionic radius than Pb, the tolerance factor of Cs$_3$Pb$_2$I$_7$ is smaller than that of Cs$_3$Sn$_2$I$_7$, and the rotation required for the polar phase is stable even without strain [58]. Finally, we note that all 15 polar structures of $n = 2$...
that arise due to octahedral tilting are within 46 meV (Cs$_3$Pb$_2$I$_7$), 34 meV (Cs$_3$Pb$_2$Br$_7$), and 30 meV (Cs$_3$Pb$_2$Cl$_7$) of the energy of the ground state structure, whereas the $I4mm$
Table 3. Selected modes representing different tilt patterns and distortions in Cs$_2$PbI$_4$ ($n = 1$) and Cs$_3$Pb$_2$I$_7$ ($n = 2$) RP perovskites.

| $n = 1$ | $n = 2$ |
|---------|---------|
| mode | distortion pattern | mode | distortion pattern |
| $X_2^+$ | $a^0a^0a^+$ | $X_2^+$ | $a^0a^0a^+$ |
| $X_1^-$ | $a^0a^0a^-$ | $X_2^+$ | $a^0a^0a^+$ |
| $X_3^+$ | $a^-a^-a^0$ | $X_4^-$ | $a^-a^-a^0$ |
| $X_4^+$ | $a^-a^-a^0$ | $X_1^-$ | $a^+a^0a^0$ |
| $\Sigma_3$ | $a^+a^0a^0$ | $\Sigma_1$ | $a^+a^0a^0$ |
| $\Gamma_3^-$ | displacement along c | $\Gamma_3^-$ | displacement along c |
| $\Gamma_5^-$ | displacement along $a$, $b$ | $\Gamma_5^-$ | displacement along $a$, $b$ |

and $Imm2$ structures are energetically highly unfavorable.

To gain a better understanding of how octahedral rotations lower the energy of RP halide perovskites, we proceeded by decomposing every structure into distortion modes (using ISODISTORT [59]). An overview of selected modes and the distortions they correspond to is shown in Table 3. For example, $\Sigma_1$ and $\Sigma_3$ modes in $n = 1$ and $n = 2$, respectively, correspond to in-phase rotations along the in-plane $a$- and $b$-directions, whereas $X_2^+$ and $X_1^-$ describe the in- and out-of-plane rotation along the out-of-plane $c$-axis. Both $X_3^\pm$ and $X_4^\pm$ correspond to the same tilt pattern based on the relative rotation between slabs A and B. Depending on which ions are affected by the mode, the tilt pattern occurs only in one or in both slabs. More complex tilt patterns like $a^-b^+b^+$ are a combination of these modes. Finally, the $\Gamma_3^-$ and $\Gamma_5^-$ modes describe polar displacements along the in-plane $a$ and $b$ or out-of-plane $c$-direction, respectively, like in the $Imm2$ and $I4mm$ structures. Phonon dispersions (shown in Figure A1) for $n = 1$ reveal symmetry breaking instabilities along several symmetry lines in the Brillouin zone, dominated by octahedral tilts comprising I atom displacements. Similar results are expected for $n = 2$, where the additional inorganic layer increases the degree of cooperativity of octahedral tilts along the out-of-plane $c$-direction.

In Figures 2(a) and (b), we show the mode decomposition of every Cs$_2$PbI$_4$ and Cs$_3$Pb$_2$I$_7$ structure as a function of the energy gain with respect to the $I4/mmm$ parent compound. Each structure is composed of several distortion modes which we sorted such that the dominant mode with the largest amplitude is at the bottom of each bar. We normalize these amplitudes with respect to the $I4/mmm$ parent cell so that amplitudes of different space groups of the same layer number $n$ are comparable. For $n = 1$ in Figure 2(a), we observe a clear clustering of structures with the same dominant distortion mode. All of the lowest energy structures are dominated by an $X_3^+$ mode, followed by a group of structures dominated by an $X_4^+$ mode, and a group of structures with dominant $\Sigma_3$ mode. Within each cluster, structures can further be sorted based on their second-largest mode, in particular in the $X_3^+$-dominated group, where structures
Figure 2. Mode decomposition for all polar structures within (a) \( n = 1 \) \( \text{Cs}_2\text{PbI}_4 \) and (b) \( n = 2 \) \( \text{Cs}_3\text{Pb}_2\text{I}_7 \) RP structures, showing the amplitude of each distortion mode within the distorted structure as a function of energy gain with respect to the \( I4/mmm \) parent structure. Each bar represents one structure and shows the total mode amplitude and its individual contributions. The modes are sorted by amplitude with the dominant one at the bottom. For clarity, we only included modes accounting for 90% of the total amplitude. Color code is included at the bottom of the figure.

with secondary \( \Sigma_3 \) distortion are lower in energy than those with \( X_4^+ \) as the second largest mode.

For \( n = 2 \) in Figure 2(b), most of the dominant modes (specifically \( X_3^- , X_4^- , \Sigma_1 , X_2^+ , X_1^- \)) correspond to octahedral rotations. The large \( \Gamma_5^- \) mode in the ground state structure with \( Cmc2_1 \) symmetry and the \( Aem2 \) structure at \( \sim 120 \) meV originates from an alternating shift of the Cs-ions that breaks the centrosymmetry of these structures [25, 57]. In comparison to \( n = 1 \), the grouping of structures with similar dominant
distortion modes is less distinct. Furthermore, unlike for \( n = 1 \) where in particular the low-energy structures are dominated by two to three distortion modes, for \( n = 2 \) multiple modes with similar amplitudes contribute to the overall distortion.

Overall, we find that for both \( \text{Cs}_2\text{PbI}_4 \) and \( \text{Cs}_3\text{Pb}_2\text{I}_7 \), structures with a dominant mode corresponding to out-of-phase tilts in \( a/b \)-direction (\( X_3^\pm, X_4^\pm \)) are energetically most favorable, followed by in-phase tilts in \( a/b \)-direction (\( \Sigma_3, \Sigma_4 \)). Rotation around the \( c \)-axis (\( X_2^+, X_1^- \)) is mainly found in energetically higher structures.

4. Tuning of Band Gaps through Octahedral Rotations

Octahedral tilts are well-known to strongly affect the band gaps of 3D ABX\(_3\) perovskites [60, 61]. In these materials, octahedral tilts open the band gap because they lead to a stabilization of both the anti-bonding VBM and CBM with a larger energy reduction of the VBM due to the bond-length sensitivity of the Pb-6s lone pair that contributes to the VBM [26]. Here, we will explore to which extent different octahedral tilt patterns affect the band gap of RP halide perovskites. Unless otherwise noted, our band gap calculations are based on Kohn-Sham DFT calculations with the PBE exchange-correlation functional [48] and without including the effects of SOC. This leads to an error cancellation in the magnitude of the band gap, since the spin-orbit splitting of the CBM’s Pb \( p \) states lowers the band gap of Pb-based halide perovskite by \( \sim 1 \text{eV} \), whereas the inherent band gap underestimation of Kohn-Sham DFT with a semilocal functional such as PBE leads to an underestimation of the band gap of similar size. We believe that this approach is justified since we are only interested in trends and not in accurate band gap predictions. Furthermore, we have confirmed the accuracy of our reported band gap ranges by performing additional calculations based on the \( G_0W_0@PBE \) approach including SOC, which gives reliable band gaps for a wide range of halide perovskites [62, 63, 64, 65].

The band gaps of all structures calculated using PBE can be found in Tables 1 and 2 for \( \text{Cs}_2\text{PbI}_4 \) and \( \text{Cs}_3\text{Pb}_2\text{I}_7 \), respectively. Results for the bromides and chlorides are listed in the Appendix A and Appendix B and follow similar trends. The Tables also report the k-point at which the band gap of these semiconductors is located. In most cases, the band gap is direct at the \( \Gamma \) point, or an equivalent high-symmetry point for non primitive unit cells after band unfolding. The band gaps of the structures with the lowest and highest band gap, and of the ground state structure are reported in Table 4.

In both \( n = 1 \) and \( n = 2 \), the band gap difference between the lowest- and the highest band gap structure is \( \sim 0.3 \text{eV} \), for all three halides. Our \( G_0W_0 \) calculations confirm previous observations of an error cancellation between neglecting SOC and neglecting quasiparticle corrections [63], resulting in band gaps very close to the ones calculated with DFT-PBE. The ground state structure features a band gap right in between the range of accessible band gaps in all cases. Furthermore, the structure with the lowest band gap is the undistorted parent structure \( I4/mmm \) only in the case of \( \text{Cs}_2\text{PbI}_4 \), raising the question how exactly octahedral rotations affect the band gap of
Table 4. DFT-PBE band gaps for the Cs$_2$PbI$_4$ ($n = 1$) and Cs$_3$Pb$_2$I$_7$ ($n = 2$) structures with the lowest and the highest band gap, and of the ground state structure. $G_0W_0$@PBE+SOC band gaps of Cs$_2$PbI$_4$ with $I4/mmm$ and $Cmce$ symmetry are reported in brackets.

| X site | $n = 1$ | $n = 2$ |
|--------|---------|---------|
|        | space group | $E_{\text{gap}}$ (eV) | space group | $E_{\text{gap}}$ (eV) |
| I      | $I4/mmm$   | 1.90 (1.87) | $P4/mbm$   | 1.77 |
|        | $Cmce$    | 2.18 (2.12) | $Ccce$    | 2.09 |
|        | $Cmme$    | 2.01       | $Cmc2_1$  | 2.01 |
| Br     | $Pmmm$    | 2.27       | $P4/mbm$  | 2.10 |
|        | $Cmce$    | 2.55       | $Ccce$    | 2.40 |
|        | $P4_2/ncm$| 2.38       | $Cmc2_1$  | 2.35 |
| Cl     | $Cccm$    | 2.68       | $P4/mbm$  | 2.52 |
|        | $Cmce$    | 2.99       | $Ccce$    | 2.81 |
|        | $P4_2/ncm$| 2.84       | $Cmc2_1$  | 2.78 |

To characterize the connection between tilt pattern and band gap, we first determined the octahedral rotation angle - defined as the angle of rotation around the out-of-plane axis, and the octahedral tilt angle - calculated as $(180° - \theta)/2$, where $\theta$ is the bond angle of Pb-X-Pb. We found no correlation between the average tilt or rotation angle for any of the systems that we studied here. In fact, these average angles remain constant over a wide range of structures with band gaps differences of up to $\sim0.2$ eV. We then used the average of the sum of the tilt and rotation angle as a measure for the overall distortion of the structure. For $n = 1$, we find that the band gap increases with this total distortion, however, for $n = 2$ we do not observe a similar trend. The overall distortion is nearly constant for a wide range of structures for which the band gap widens by more than $\sim0.2$ eV. Evidently, and contrary to their 3D congeners, band gap changes in these materials cannot be understood based on the magnitude of octahedral tilts and rotations alone.

We therefore proceeded by analysing the band gap variation in terms of dominant distortion modes, distinguishing three classes of structures. In Figure 3, we illustrate the most important trends for three representative cases:

(i) First case: Structures for which the band gap increases with the amplitude of the dominant distortion mode (determined in the same way as in Section 3) and depicted in Figure 3(a) for the case of Cs$_2$PbI$_4$ structures with dominant $X_2^+$ mode.

(ii) Second case: Structures with a large band gap variation that does not depend on the amplitude of the dominant mode, shown in Figure 3(c) for the case of Cs$_2$PbI$_4$ structures in which the dominant distortion mode is $X_3^+$. 
(iii) Third case: Structures with no correlation between the amplitude of the dominant distortion mode and the size of the band gap, shown in Figure 3(e) for the case of Cs$_3$Pb$_2$I$_7$ with dominant $\Gamma_5^-$ mode.

The full mode decomposition for these case studies are shown in Figures 3(b), (d), and (f), respectively. It is important to note that considering all possible $n = 1$ and $n = 2$ structures, the correlation between band gap size and the amplitude of the dominant mode is weak. This is not surprising since the band gap is a macroscopic property of the material which is determined by an interplay of all modes. However, the picture barely changes when the second-largest mode is taken into account. These findings can
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be explained by analysing the amplitude of the dominant distortion mode in terms of its contributions from Pb- and I-displacements, since the band edges and hence the size of the band gap of these materials are derived from Pb $s$ and I $p$ (VBM) and Pb $p$ (CBM) orbitals, respectively. We calculate the percentage of the total amplitude, $a_{\text{total}}$, corresponding to displacements of Pb and I, $a_{\text{PbI}} = a_{\text{Pb}} + a_{\text{I}}$, as $\sqrt{\sum a_{\text{PbI}}^2 / a_{\text{total}} \cdot a_{\text{PbI}}}$. This percentage contribution is shown in color in Figures 3(a), (c), and (e), respectively.

Our analysis shows that the influence of the mode on the band gap depends on the Pb-I contribution of the mode. For modes where the amplitude of the dominant mode leads to large band gap changes, as exemplified by our first case in Figure 3(a), the contribution is almost constant at 100%. For our second case (Figure 3(c)), the dominant mode amplitude is $\sim 1 \text{ Å}$ for a wide range of different structures with varying degrees of secondary and tertiary mode contributions. However, structures with dominant $X_3^-$ contribution primarily coming from Pb-I distortions have larger band gaps than those structures in which the distortion also contains significant Cs contributions. In the third case (Figure 3(e)), the lowest band gap structure with $Imm2$ symmetry is derived entirely from a $\Gamma_5^-$ mode with 100% PbI character (an off-center displacement of Pb), but the amplitude of the mode is very small. The $\Gamma_5^-$ mode of the other structures has a significantly lower PbI contribution, indicating that their large band gap originates from their secondary $X_3^-$ or $X_4^-$ modes which have amplitudes between 1.1 and 1.5 Å.

5. Magnitude of Rashba-/Dresselhaus Splitting in Polar Structures

We now focus on the band structure of only those Cs$_2$PbI$_4$ and Cs$_3$Pb$_2$I$_7$ perovskites featuring a polar space group. Polar, i.e., non-centrosymmetric materials, with strong SOC in their electronic structure can exhibit Rashba- [33], Dresselhaus- [34], or mixed Rashba-/Dresselhaus-splitting. In all three cases, the defining characteristic is a splitting of the energy bands in $k$-space, that can be quantified by the parameter $\alpha = E_R/2k_R$, with $E_R$ and $k_R$ as defined in Figure 4. In the following, we will not distinguish between pure and mixed Rashba and/or Dresselhaus cases and refer to the effect as Rashba-/Dresselhaus splitting. An in-depth exploration of these spin-textures can be found in Ref. [44].

We start by calculating the macroscopic electronic polarization of all polar Cs$_2$PbI$_4$ and Cs$_3$Pb$_2$I$_7$ structures using the Berry phase approach within the modern theory of polarization as well as with the Born effective charge approximation. These values are given in Table 5 and are in very good agreement with each other. For Cs$_2$PbI$_4$ only the structures with $Pc$ and $Aea2$ symmetry display a significant polarization of 3.4 and 2.7 μC/cm$^2$, respectively. All other structures have polarizations well below 1 μC/cm$^2$. For Cs$_3$Pb$_2$I$_7$, several polar structures have a polarization above 1 μC/cm$^2$. In particular the ground state structure with $Cmc2_1$ symmetry has a polarization of 1.9 μC/cm$^2$. The two other phases with significant polarization are $Aem2$ with 1.8 μC/cm$^2$ and $Pm$ with 1.6 μC/cm$^2$, respectively. Note that these values are of the same order of magnitude as what was calculated for all-inorganics ABX$_3$ perovskites [38], but well below the
polarization of typical oxide ferroelectrics.

Table 5. Macroscopic polarization in $\mu C/cm^2$. Reported values are computed according to the modern theory of polarization ($p_{Berry}$) and the Born effective charge approximation ($p_{BEC}$). $\alpha$ is the Rashba parameter calculated as described in the main text in eVÅ.

| space group | $p_{Berry}$ | $p_{BEC}$ | $\alpha$ | space group | $p_{Berry}$ | $p_{BEC}$ | $\alpha$ |
|-------------|-------------|-----------|----------|-------------|-------------|-----------|----------|
| Pmc2$_1$    | 0.03        | 0.03      | 0.0      | Cmc2$_1$    | 1.91        | 1.93      | 0.0      |
| Cc          | 0.02        | 0.02      | 0.0      | Cm          | 0.04        | 0.03      | 0.0      |
| P1          | 0.01        | 0.01      | 0.0      | Pmm2$_1$    | 0.08        | 0.09      | 0.0      |
| P2$_1$      | 0.00        | 0.01      | 0.0      | Pmm2        | 0.01        | 0.01      | 0.0      |
| C2          | 0.04        | 0.04      | 0.0      | P2          | 0.02        | 0.01      | 0.0      |
| Pc          | 3.44        | 3.20      | 0.9      | Aem2        | 1.75        | 1.78      | 0.0      |
| Pmm2$_1$    | 0.35        | 0.41      | 0.9      | P2$_1$      | 0.04        | 0.07      | 0.0      |
| Aea2        | 2.66        | 2.66      | 0.7      | P1          | 0.85        | 0.86      | 0.0      |
| Imm2        | 0.80        | 0.80      | 0.0      | Pma2        | 0.01        | 0.01      | 0.0      |
| I4mm        | 0.12        | 0.12      | 0.0      | Pc          | 0.78        | 0.77      | 0.0      |
|             |             |           |          | Ama2        | 0.14        | 0.12      | 0.0      |
|             |             |           |          | Amm2        | 0.11        | 0.09      | 0.0      |
|             |             |           |          | C2          | 0.25        | 0.24      | 0.3      |
|             |             |           |          | Pm          | 1.57        | 1.37      | 0.5      |
|             |             |           |          | Pmc2$_1$    | 0.85        | 0.84      | 0.0      |
|             |             |           |          | Imm2        | 0.01        | 0.12      | 0.0      |

For evaluating the magnitude of the Rashba-/Dresselhaus effect, we calculated the band structure of all polar structures listed in Table 5 across the entire Brillouin zone including SOC self-consistently. The Rashba parameter $\alpha$ was calculated by fitting a fourth-degree polynomial to the conduction band. For Aea2 we additionally evaluated the Rashba parameter using a regular three-dimensional grid around the $\Gamma$ point to ensure that we are measuring the Rashba splitting in the reciprocal space direction where it is largest. The value reported in Table 5 refers to this calculation. Note that due to numerical accuracy, a Rashba-/Dresselhaus effect smaller than $\sim0.1$ eVÅ will not be resolved in our calculations.

Our main finding is that even though a total of 27 structures have polar space groups in our study, a clear Rashba-/Dresselhaus effect at the CBM, i.e., around the $\Gamma$ point is only visible in five structures: $Pmm2_1$, $Aea2$, and $Pc$ for $Cs_3PbI_4$ and $Pm$ and $Cm$ for $Cs_3Pb_2I_7$. For many of the analyzed structures this finding can simply be explained by the vanishing polarization of the structures. However, for some structures with significant polarization, for example the polar ground state of $Cs_3Pb_2I_7$ and the
In the $Aem2$ structure, we also do not observe Rashba-/Dresselhaus splitting of the CBM or in the lowest-energy conduction band at other $k$-points across the Brillouin zone. This finding can be explained by the direction of the polar distortion mode and its Pb-I contribution.

In Cs$_2$PbI$_4$, all three structures with significant Rashba-/Dresselhaus splitting are dominated by a $\Sigma_3$ mode. In these structures, the combination of $\Sigma_3$, $X_2^+$ and other secondary modes results in an asymmetry in the octahedral tilt angles that enhances the Rashba effect, as described in Ref. [43]. In addition, note that both $I4mm$ and $Imm2$, which are generated by a single $\Gamma_5^-$ mode, do not display Rashba-/Dresselhaus splitting, in agreement with Ref. [44], which studied Rashba-/Dresselhaus splitting for Pb off-center displacements and observed significant splitting only for in-plane out-of-bond Pb displacements towards octahedron edges. Similarly, for Cs$_3$Pb$_2$I$_7$, we find that both structures with significant splitting are dominated by a $\Sigma_1$ mode, equivalent to $\Sigma_3$ in $n = 1$. In these structures, similar to the $n = 1$ case, the combination of $\Sigma_1$, $X_2^+$ and other secondary modes leads to a symmetry breaking octahedral tilt with a relatively larger Rashba effect. In structures like $Cmc2_1$ and $Aem2$, Rashba-/Dresselhaus splitting is not observed because the polar $\Gamma_5^-$ mode primarily comprises Cs ion displacements which do not contribute electronically to the band edges. Note, that in the hybrid organic-inorganic RP perovskites studied by Jana et al., octahedral tilt angle asymmetries arise out of an interplay of octahedral rotations inherent to the inorganic layers and structural symmetry breaking constraints at the organic-inorganic interfaces. In summary, we predict that significant Rashba-/Dresselhaus splitting in RP halide perovskites can be engineered by inducing out-of-bond Pb displacements through $\Sigma$-mode in-phase octahedral tilts, for example by deliberate chemical substitution of organic molecules or by inducing strain.
6. Energy Landscape and Polarization of Free-Standing 2D Halide Perovskite Layers

Pb-based all-inorganic RP perovskites have at this point and to the best of our knowledge not been synthesized. However, a multitude of hybrid quasi-2D perovskites exist [6]. Additionally, these materials can be prepared as single crystal monolayers by mechanical exfoliation [14], prompting us to ask the question whether our findings for RP halide perovskites can be translated to mono- and bilayer halide perovskites. For this purpose we constructed mono- and bilayer slices from fully relaxed CsPbI$_3$ and separated periodic repeat units by 20 Å of vacuum to avoid spurious interlayer interactions. The undistorted structure of this material class has $P4/mmm$ symmetry. Inducing all possible tilt patterns to the reference structure as before results in 13 and 16 unique space groups for the mono- and bilayer case, respectively. Importantly, and in contrast to the RP perovskites, octahedral rotations cannot break inversion symmetry in the monolayer case. For the bilayer, we find four polar space groups. A list of space groups, their energies relative to the reference structure, and their PBE band gaps can be found in Appendix C.

The ground state structures for the mono- and bilayer have $P1$ and $Cmmm$ symmetry and energy gains of -105 meV and -163 meV with respect to the reference structure, respectively. Similar to before, we find a clear energetic grouping of structures based on their dominant distortion mode. For the monolayer, structures with a dominant $M^+_5$ distortion, corresponding to an $a^−a^0a^0$ tilt pattern, i.e., out-of-phase rotation along the $a$- and $b$-directions, have the lowest energy, similar to the RP halide perovskites. This is followed by two structures with dominant $M^+_3$ mode ($a^0a^0a^+$) and another cluster with dominant $X^+_3$ ($a^+a^0a^0$) mode. This is different from the RP perovskites for which the in-phase rotation around the $c$-direction was the energetically least favorable. For the bilayer, the energetic ordering in terms of dominant distortion modes is the same as for the $n = 2$ RP perovskites. In particular, the polar $Pmc2_1$ structure which is dominated by a large $\Gamma_5^−$ mode is originating from an alternating shift of Cs ions which is responsible for a significant polarization of this structure.

In line with our results of Section 5, none of the polar bilayer structures exhibits Rashba-/Dresselhaus splitting, since in all cases structures with a significant polarization are dominated by either an in-bond $\Gamma_5^−$ mode or by a $\Gamma_5^−$ mode associated primarily with Cs displacements.

7. Summary and Outlook

In summary, we have systematically studied the complex energetic and electronic structure landscape of all-inorganic RP halide perovskites. Octahedral tilts allow for a significant tunability of the band gaps of these materials. The range of accessible band gaps is comparable to the change in band gap due to halide substitution. We find a multitude of polar structures for both $n = 1$ and $n = 2$ RP halide perovskites; contrary
to 3D ABX$_3$ perovskites polar space groups are accessible via octahedral tilts in RP perovskites. However, many of these polar structures have only very small polarization and only 5 display a significant Rashba-/Dresselhaus splitting in the CBM due to the direction and Pb-I contribution of their dominant polar distortion mode. This situation is even more pronounced in mono- and bilayers of these materials, since the lack of a "stacked" or layered structure as present in the RP perovskites reduces the amount of possibilities for generating polar structures via octahedral tilts.

Since Cs$_2$PbI$_4$ and Cs$_3$Pb$_2$I$_7$ have not been synthesized yet, it is important to connect our findings to the much more common hybrid organic-inorganic RP halide perovskites. The energy landscape and structural distortions in these hybrid systems are clearly determined by steric effects and interactions at the organic-inorganic interface, allowing for a wider range of distortions and other structural parameters such as the interlayer distance and stacking. Nonetheless, since band gaps and the Rashba-/Dresselhaus effect are determined by the inorganic sublattice of these materials, we expect our findings for the effect of octahedral tilts on the band structure and the emergence of Rashba-/Dresselhaus splitting to be of relevance for these hybrid systems too.

Rashba-/Dresselhaus splitting and related phenomena such as the effect of chiral space groups on the bandstructure lead to spin-dependent optoelectronic properties [17]. At the same time, the optical response of RP halide perovskites is known to be dominated by excitonic effects due to quantum and dielectric confinement in these systems [7, 66, 24]. Our work provides a stepping stone for further first-principles studies of the effects of tailored octahedral distortions on linear and circular optical properties of this class of materials.
Appendix A. Data for Other Halides with \( n=1 \)

This Appendix provides a Table with tilt patterns, energies, and band gaps of the \( n = 1 \) bromide and chloride RP perovskites not reported in the main text, as well as the phonon band structure of \( \text{Cs}_2\text{PbI}_4 \) computed as described in Section 2.

\[ \text{Figure A1.} \quad \text{Phonon band structure of the} \ I4/mmm \ \text{structure of} \ \text{Cs}_2\text{PbI}_4. \ \text{The colors of the bands indicate the contributions of} \ \text{Cs (red), Pb (green) and I (blue)} \ \text{displacements to each phonon mode.} \]
**Table A1.** Initial tilt pattern, energy gain $\Delta E$, size and position of the band gap for Cs$_2$PbBr$_4$ and Cs$_2$PbCl$_4$. The tilt pattern and position of the band gap are the same for both materials. All values were calculated using PBE and no SOC. Polar space groups are marked in green.

| space group | tilt pattern | $\mathbf{k}$-point | Cs$_2$PbBr$_4$ $\Delta E$ (meV) | Cs$_2$PbCl$_4$ $\Delta E$ (meV) |
|-------------|--------------|---------------------|-------------------------------|-------------------------------|
| 1 P1        | a"a/a/a"    | Γ                   | -48.64                        | -43.11                        | 2.784                        |
| 2 P1        | a"b/b/a"    | Z                   | -49.81                        | -44.14                        | 2.767                        |
| 4 P2/m      | a"a/a/a"    | Γ                   | -49.25                        | -43.84                        | 2.765                        |
| 5 C2        | a"a/a/a"    | Γ                   | -31.89                        | -25.69                        | 2.768                        |
| 6 Pm        | a"a/a"      | Γ                   | -55.70                        | -50.65                        | 2.85                        |
| 7 Pmc       | a"b/b/a"    | Γ                   | -16.42                        | -11.46                        | 2.865                        |
| 9 Cc        | a"a/a/a"    | Γ                   | -55.77                        | -50.63                        | 2.838                        |
| 10 P2/m     | a"a/a"      | Γ                   | -55.89                        | -50.79                        | 2.836                        |
| 11 P2/m     | a"a/a"      | Γ                   | -55.96                        | -50.90                        | 2.836                        |
| 12 C2/m     | a"a/a/a"    | Γ                   | -47.94                        | -42.97                        | 2.726                        |
| 13 P2/c     | a"b/c/a"    | Γ                   | -49.59                        | -43.23                        | 2.787                        |
| 14 P2/c     | a"b/a/a"    | Y                   | -47.03                        | -41.98                        | 2.85                         |
| 15 C2/c     | a"a/c/a"    | Γ                   | -27.61                        | -21.61                        | 2.865                        |
| 16 P2/c     | a"a/a/a"    | Γ                   | -53.38                        | -50.11                        | 2.837                        |
| 26 Pmc/2    | a"a/a"      | Γ                   | -54.31                        | -50.65                        | 2.835                        |
| 31 Pmc/2    | a"a/a"      | Γ                   | -13.06                        | -9.49                         | 2.827                        |
| 41 Aea2     | a"a/a/a"    | Γ                   | -5.22                         | -4.44                         | 2.789                        |
| 51 Pmmn     | a"a/a/a"    | Γ                   | -55.94                        | -50.74                        | 2.837                        |
| 53 Pmma     | a"a/a/a"    | Γ                   | -48.75                        | -43.44                        | 2.718                        |
| 55 Pbmn     | a"a/a/a"    | Γ                   | 1.89                          | -0.04                         | 2.948                        |
| 56 Pccn     | a"a/a/a"    | Γ                   | -29.97                        | -24.08                        | 2.881                        |
| 57 Pccn     | a"a/a/a"    | Γ                   | -31.84                        | -25.86                        | 2.802                        |
| 59 Pmma     | a"a/a/a"    | Γ                   | 0.79                          | -0.25                         | 2.708                        |
| 61 Pheca    | a"a/a/a"    | Γ                   | -50.01                        | -44.42                        | 2.897                        |
| 62 Pmma     | a"a/a/a"    | Γ                   | -12.28                        | -8.48                         | 2.836                        |
| 64 Cmce     | a"a/a/a"    | Γ                   | 3.12                          | 0.95                          | 2.990                        |
| 66 Omcn     | a"a/a/a"    | Γ                   | -29.40                        | -23.33                        | 2.680                        |
| 67 Cmme     | a"a/a/a"    | Γ                   | -56.11                        | -51.18                        | 2.836                        |
| 85 P4/1b    | a"a/a/a"    | Γ                   | 1.38                          | -0.02                         | 2.796                        |
| 86 P4/1b    | a"a/a/a"    | Γ                   | -56.61                        | -51.08                        | 2.837                        |
| 94 P4/2b    | a"a/a/a"    | Γ                   | -31.28                        | -26.02                        | 2.801                        |
| 114 P4/2b   | a"a/a/a"    | Γ                   | -55.81                        | -50.65                        | 2.836                        |
| 127 P4/mnm  | a"a/a/a"    | Γ                   | 1.41                          | 0.43                          | 2.710                        |
| 129 P4/mnm  | a"a/a/a"    | Γ                   | 1.21                          | 0.21                          | 2.711                        |
| 134 P4/mnm  | a"a/a/a"    | Γ                   | -33.18                        | -27.03                        | 2.801                        |
| 137 P4/mnm  | a"a/a/a"    | Γ                   | -0.71                         | -1.20                         | 2.776                        |
| 138 P4/mnm  | a"a/a/a"    | Γ                   | -56.58                        | -51.09                        | 2.836                        |
| 139 Cmcm     | a"a/a/a"    | Γ                   | 0.60                          | 0.00                          | 2.712                        |
| 147 P4/mnm  | a"a/a/a"    | Γ                   | 2.368                         | 2.85                          |
| 144 Eamma   | a"a/a/a"    | Γ                   | 2.268                         | 2.00                          |

The tilt pattern and position of the band gap are the same for both materials. All values were calculated using PBE and no SOC. Polar space groups are marked in green.
Appendix B. Data for Other Halides with n=2

The following Table contains tilt patterns, energies, and band gaps for the bromide and chloride n = 2 RP perovskites not reported in the main text.

**Table B1.** Initial tilt pattern, energy gain ΔE, size and position of the band gap for Cs$_3$Pb$_2$Br$_7$ and Cs$_3$Pb$_2$Cl$_7$. The tilt pattern and position of the band gap are the same for both materials. All values were calculated using PBE and no SOC. Polar space groups are marked in green.

| space group | tilt pattern | k-point | Cs$_3$Pb$_2$Br$_7$ band gap (eV) | Cs$_3$Pb$_2$Cl$_7$ band gap (eV) |
|-------------|--------------|---------|-------------------------------|-------------------------------|
| Pm | a' b' c' / a' b' c' | 111 Γ | -25.56 2.400 -27.54 2.815 | 81 Pmma a' b' c' / a' b' c' 111 Γ -25.05 2.281 -24.43 2.693 |
| Pmc2 | a' a' a' / a' a' a' | 111 Γ | -61.46 2.295 -55.20 2.695 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -96.58 2.209 -80.03 2.643 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -80.26 2.295 -74.40 2.693 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -24.84 2.198 -23.46 2.636 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -70.85 2.293 -62.36 2.726 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -96.74 2.209 -86.04 2.646 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -96.75 2.210 -86.22 2.645 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -95.04 2.205 -85.15 2.639 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -96.67 2.209 -86.13 2.644 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -61.46 2.295 -55.20 2.695 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -67.23 2.257 -60.07 2.660 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -74.56 2.240 -65.70 2.668 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -96.31 2.242 -87.85 2.679 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -102.22 2.353 -90.41 2.775 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -77.87 2.233 -72.76 2.622 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -82.91 2.336 -71.13 2.755 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -72.35 2.249 -63.57 2.675 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -95.48 2.236 -87.32 2.676 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -25.06 2.193 -25.91 2.636 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -25.82 2.390 -27.68 2.805 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -79.52 2.229 -74.22 2.624 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -64.59 2.277 -57.77 2.680 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -24.65 2.366 -26.04 2.781 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -78.79 2.329 -67.55 2.763 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -45.74 2.228 -39.10 2.655 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -83.82 2.310 -77.37 2.698 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -97.29 2.343 -86.24 2.773 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -79.34 2.234 -73.97 2.625 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -24.33 2.376 -25.85 2.792 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -96.34 2.240 -87.38 2.679 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -71.02 2.258 -62.54 2.676 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -60.24 2.215 -53.62 2.601 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -25.56 2.400 -27.54 2.815 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -25.05 2.281 -24.43 2.693 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -21.80 2.337 -23.08 2.672 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -96.16 2.243 -87.38 2.682 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -23.40 2.243 -23.57 2.667 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -10.31 2.105 -11.31 2.523 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -25.12 2.180 -26.76 2.796 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -10.35 2.103 -11.36 2.524 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -3.94 2.100 -6.82 2.521 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -3.48 2.100 -6.25 2.520 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -29.81 2.203 -28.47 2.629 |
| Pm | a' b' c' / a' b' c' | 111 Γ | -74.44 2.241 -65.55 2.667 |
| Pm | a' a' a' / a' a' a' | 111 Γ | -96.28 2.244 -87.73 2.680 |
| Pm | a' b' c' / a' b' c' | 111 Γ | 0.00 2.104 0.00 2.524 |
| Pm | a' a' a' / a' a' a' | 111 Γ | 0.11 2.104 0.07 2.524 |
Appendix C. Data for Free-Standing Mono- and Bilayer Perovskites

The following Table contains tilt patterns, energies, and band gaps of the mono- and bilayer perovskites of Section 6.

**Table C1.** Initial tilt pattern, energy gain ΔE, size and position of the band gap for 2D mono- and bilayer structures. Polar groups are marked in green.

| n = 1 Cs$_3$PbI$_4$ | space group | tilt pattern | k-point | ∆E (meV) | band gap (eV) |
|---------------------|-------------|--------------|---------|----------|--------------|
| PT                  | a−b−a+      | Z            | -104.57 | 2.16     |
| P2$_1$/m            | a−a+ a+     | Γ            | -96.99  | 1.98     |
| C2/m                | a−a^0 a+    | Γ            | -99.90  | 1.94     |
| P2/c                | a−b−a^0     | Γ            | -96.57  | 1.95     |
| P2$_1$/c            | a−a− a−     | Γ            | -97.62  | 2.13     |
| Pmma                | a^0 a^0     | X            | -10.59  | 1.90     |
| Pnna                | a−a− a^0    | Z            | -91.32  | 1.94     |
| Pbcm                | a−a− a^0    | Γ            | -97.12  | 1.98     |
| Pnmm                | a^0 a^+ a^0 | Γ            | -33.76  | 2.23     |
| Cmma                | a−a^0 a^0   | Γ            | -100.15 | 1.94     |
| P4/mmm              | a^0 a^0 a^0 | M            | 0.00    | 1.84     |
| P4/nbbm             | a^0 a^0 a^+ | Γ            | -34.53  | 2.24     |
| P4/nmmm             | a^0 a^0 a^0 | Γ            | -6.15   | 1.97     |

| n = 2 Cs$_8$Pb$_2$I$_4$ | space group | tilt pattern | k-point | ∆E (meV) | band gap (eV) |
|-------------------------|-------------|--------------|---------|----------|--------------|
| PT                      | a−b−a−      | Γ            | -162.45 | 1.86     |
| Pm                    | a−b−a^0      | Γ            | -132.38 | 1.92     |
| P2/m                   | a−b− a^0     | Γ            | -162.37 | 1.86     |
| P2$_1$/m               | a−a+ a−      | Γ            | -155.06 | 2.05     |
| C2/m                   | a−a^0 a−     | Γ            | -162.38 | 1.86     |
| P2/c                   | a−a− a−      | B            | -124.77 | 1.98     |
| Pm2                    | a−a+ a+      | Γ            | -160.55 | 1.87     |
| Pmc$_2$$_1$            | a−a+ a+      | Γ            | -157.30 | 2.03     |
| Anm2                   | a−a^0 a^+    | Γ            | -162.24 | 1.86     |
| Pnmmm                  | a^0 a^+ a^0  | U            | -57.54  | 1.82     |
| Pnma                  | a−a− a^0     | Γ            | -117.77 | 1.92     |
| Cmmm                   | a−a^0 a^0    | Γ            | -162.81 | 1.86     |
| Fmmm                   | a^0 a^+ a^0  | Γ            | -43.66  | 1.96     |
| P4/mmmm                | a^0 a^0 a^0  | M            | 0.00    | 1.76     |
| P4/nbbm                | a^0 a^0 a−   | Γ            | -37.89  | 2.07     |
| P4/nmmm                | a^0 a^0 a^+  | Γ            | -36.63  | 2.07     |

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