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► **To cite this version:**

Amanda J Neukirch, Iwnetim I Abate, Liujiang Zhou, Wanyi Nie, Hsinshan Tsai, et al.. Geometry Distortion and Small Polaron Binding Energy Changes with Ionic Substitution in Halide Perovskites. *Journal of Physical Chemistry Letters*, 2018, 9 (24), pp.7130-7136. 10.1021/acs.jpcllett.8b03343 . hal-01948488

HAL Id: hal-01948488

<https://hal.science/hal-01948488>

Submitted on 3 Jul 2024

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Geometry Distortion and Small Polaron Binding Energy Changes with Ionic Substitution in Halide Perovskites

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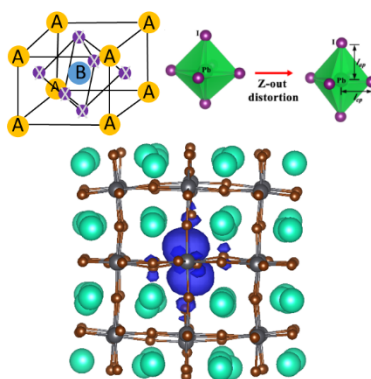
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ABSTRACT

Halide perovskites have demonstrated remarkable performance in optoelectronic applications. Despite extraordinary progress, questions remain about device stability. We report an in-depth computational study of small polaron formation, electronic structure, charge density, and reorganization energies of several experimentally relevant halide perovskites using isolated clusters. Local lattice symmetry, electronic structure, and electron-phonon coupling are interrelated in polaron formation in these materials. To illustrate this, first principles calculations are performed on (MA/Cs/FA)Pb(I/Br)₃ and MASnI₃. Across the materials studied, electron small polaron formation is manifested by Jahn-Teller like distortions in the central octahedron, with apical PbI bonds expanding significantly more than the equatorial bonds. In contrast, hole polarons cause the central octahedron to uniformly contract. This difference in manifestation of electron and hole polaron formation can be a tool to determine what is taking place in individual systems to systematically control performance. Other trends as the anion and cations are changed, are established for optimization in specific optoelectronic applications.

TOC GRAPHIC



Solution-processed halide perovskites (HPs) are promising candidates for a diverse range of applications including photovoltaics, light-emitting diodes,^{1,2} hydrogen generation,³ X-ray and gamma-ray detection,^{4,5} spintronic,⁶ and sensor applications.⁷ They combine low solution-processing costs with composition of earth abundant materials. Further development of perovskite materials requires a fundamental understanding of structure-property relationships in order to control emergent optoelectronic properties through materials design.

We recently demonstrated the reduction of photocurrent in crystalline large grain perovskite solar cells of MAPbI₃ under constant solar illumination.⁸ The efficiency recovers to its original value after less than 1 minute in the dark. Our previous studies attributed the photo-degradation to light-activated metastable trap states of atomistic origin.^{8,9} Our experimental and theoretical characterizations in those previous studies suggested that localized charged states strongly couple to local structural lattice distortions and methyl ammonium (MA) quasi-static configurations. The presence of a charge initiates lattice distortions that then stabilize the charge in a spatially confined area. These seed the formation of macroscopic charged domains preventing efficient charge extraction.

Since this initial prediction of small polaron formation in HPs, several groups using spectroscopic techniques and ab initio calculations have found evidence of polaron formation in MAPbI₃,^{10–12} MAPbBr₃ (bulk¹³ and nanoparticle¹⁴), MAPb(I_xBr_{1-x})₃,¹⁵ CsPbBr₃,¹⁶ 2D APbCl₄ and MAPbBr₄,^{17,18} and wide-bandgap defect HPs A₃M₂I₉ (A=Cs, Rb; M= Bi, Sb).^{19,20} Polaronic species are reported to be either holes^{11,16} or electrons,¹⁴ while some studies suggest that the polaron formation is facilitated by defects, or interface disorder.^{10,11} A recent experimental-theoretical work quantified lattice displacements when photoexcited excitons evolve into a polaronic state.¹² There is experimental evidence that hole polaron formation is the initial stage of

iodide vacancy.²¹ Polaron formation could be responsible for halide phase separation, specifically localized strain induced by photoexcited charge interacts with the soft ionic lattices to promote halide phase separation.¹⁵ In addition, photoinduced strain in MAPbBr₃ is said to cause large blue shifts to its Raman spectra that indicate significant structural deformations, this photostriction is stable for 30 days.¹³ A recent manuscript found that the formation of small polarons required the co-presence of MA, Sn, and Br.²² Thus, further understanding of small polaron formation in various metal halide perovskites is highly necessary to provide the foundations of engineering applied to optoelectronic devices

In this manuscript, we perform Density Functional Theory (DFT) simulations of small polaron binding energy as a function of chemical composition in a variety of halide perovskites. We show first that replacing MA with FA lowers the polaron binding energy below that of MAPbI₃. Indeed, the formation of small polarons in MAPbI₃ was initially traced to MA rotation AND volumetric lattice strain.⁹ This interpretation was consistent with lower polaron binding energies in CsPbI₃ for both electrons and holes, and led to the hypothesis that FAPbI₃ would be the best pure material to alleviate the photodegradation.¹¹ Further systematic studies are performed by substituting Pb with Sn in MAPbI₃, and I with Br in MAPbI₃, CsPbI₃, and FAPbI₃. Finally, conclusions are drawn on the influence of lattice symmetry, electronic structure, and electron phonon coupling on the formation of small polarons in HPs. It is found that for electrons the polaron binding energy gets smaller as the A-site cation is changed from MA to Cs to FA. Less intuitive is that Br substitution tends to create a larger electron polaron binding energy and a smaller hole polaron binding energy. MASnI₃ has smaller polaron binding energies for electrons and holes compared to MAPbI₃. Structurally, formation of electron polarons are universally concomitant to the central Pb-halide bonds expansion by about 25% in one direction forming a Jahn-Teller distortion. It should be noted

that local central symmetry breaking such as this should lead to larger Rashba-like splitting in hybrid perovskites.²³ Hole polarons see the central Pb-halide bonds contract uniformly in all directions. Observed difference in structural changes of the lattice between hole and electron polarons can be used to identify which species are dominant in a given experimental system.

We briefly want to point out that due to the size of the systems, use of hybrid functional, and intentional use of local basis functions, spin orbit coupling (SOC) could not be taken into account for these calculations. This does add a few caveats to our results. The electron reorganization and polaron binding energies will be overestimated because of the lack of inclusion of SOC. Previously, we have also observed that because our calculations do not have SOC to correctly break the degeneracy at the bottom of the conduction band, the Jahn-Teller distortions and displacements we calculate, are larger than those observed in experiment.¹² In spite of these caveats, general trends across the materials series are predicted correctly, particularly for the Pb perovskites. Comparisons between Sn and Pb systems are a little bit trickier as the SOC contribution in Sn materials is smaller and so those results should be less overestimated.²⁴ Another way to reduce the computational complexity in perovskite systems enough to include SOC is to replace hybrid functionals with DFT+U²⁵ or to use the Tran-Blaha modified Becke Johnson exchange potential approximation.²⁶ The rest of the computational details are presented at the end and in the SI. Below we briefly highlight some important facts about each material studied, as well as the reference bulk geometry used.

MAPbI₃: Most ubiquitous perovskite material. This material had rapid success in the solar cell community and is still in use in perovskite alloys with currently 23.3% efficiency.²⁷ However, it has been shown that the pure material is unstable to continuous exposure to light,⁸ and small polaron formation was proposed as one of the possible mechanisms in addition to iodide vacancy

migration.⁹ We started from space group $Pm\bar{3}m$ with cubic lattice parameters calculated from the low temperature tetragonal supercell derived from variable temperature powder X-ray diffraction experiments.²⁸

CsPbI₃: Simplified version of MAPbI₃, important for state of the art quantum dot-based solar cells.²⁷ Our reference bulk structure was a cubic perovskite structure with space group $Pm\bar{3}m$ and a lattice parameter derived from variable temperature powder X-ray diffraction.²⁹

FAPbI₃: FAPbI₃ is the main component of state of the art alloys for solar cell applications and of interest because it is the most likely pure material to reduce polaron formation. Our reference bulk structure was from the $Imm2$ space group determined from X-ray diffraction experiments.³⁰

MAPbBr₃: The polaron concept has been used to explain the I/Br phase separation^{31–34} in MAPbBr₃ (bulk¹³ and nanoparticle¹⁴), MAPb(I_xBr_{1-x})₃,¹⁵ and MAPbBr₄,^{17,18} Here we start from the refined neutron powder diffraction $Pnma$ structure.^{35,36}

FAPbBr₃: Our reference bulk structure was from the $Imm2$ space group, similar to FAPbI₃, but using lattice parameters that take into account Br instead of I.

CsPbBr₃: Our reference bulk structure was a cubic perovskite structure with space group $Pm\bar{3}m$ and using a lattice parameter that was derived to give the same volume per unit cell as the orthorhombic $Pnma$ CsPbBr₃.³⁷

MASnI₃: One goal of the perovskite community is to remove Pb from the formula, replacing Pb with non-toxic Sn is the simplest way to achieve that goal. Our reference bulk structure was the experimentally determined tetragonal structure with space group $P4mm$.³⁸

One important aspect of carrier self-trapping is symmetry breaking, that may show itself in the activation of normally forbidden infrared modes.^{39,40} Electron coupling with acoustic or polar optical phonons leads to different polaronic species in semiconductor lattices with well-defined

point group symmetries.⁹ Empirical Hamiltonians, like Holstein's,⁴⁰ are built to introduce a non-linearity into Schrodinger's equation and provoke a bifurcation. A purely small polaron scenario related to totally symmetric local strain was presented in our previous manuscript.⁹ The importance of electron polarons for both MAPbI₃ and CsPbI₃ through Jahn-Teller (JT) distortions^{41,42} is yet undiscussed (Figure 1). A distortion is typically observed among octahedral complexes where the two apical bonds are longer than the equatorial bonds. The JT distortion is intimately linked to electronic degrees of freedom, since, traditionally, it manifests to remove an electronic degeneracy, opening a band gap and favoring a particular electronic state, all of which are quite common in perovskite materials.^{43,44}

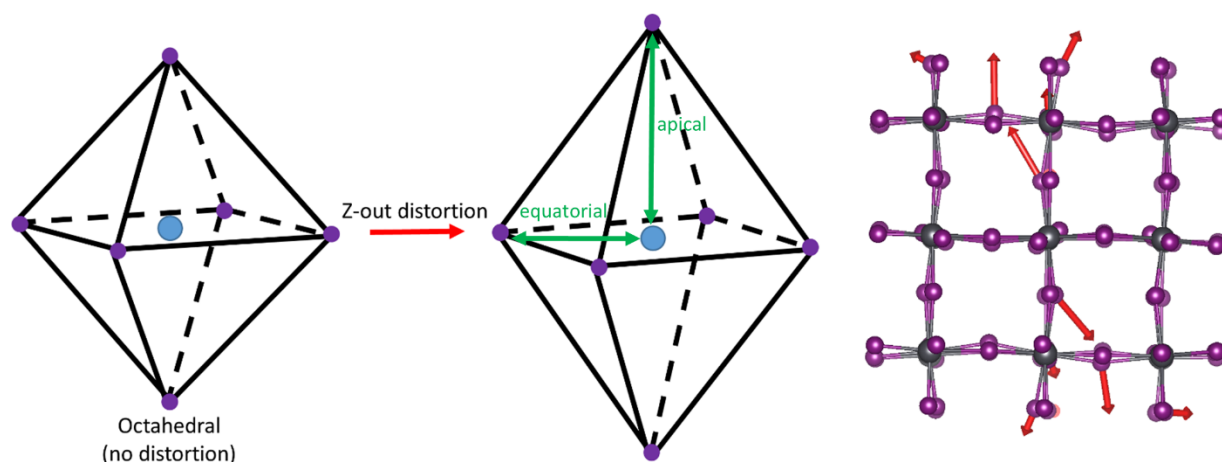


Figure 1 (a) Schematic of Jahn-Teller distortion. (b) The optimized neutral PbI₃ framework of the CsPbI₃ cluster with arrows on the atoms that move the most, and pointed in the direction of the same atoms within the optimized charged cluster (atomic displacements are scaled by a factor of 3 for clarity).

In Ge or Cl based HPs, these polar and anisotropic distortions are commonly spread over the entire lattice,²⁴ but in this work we show that it plays an important role at the local scale for polaronic states in all the HPs. To do this we compare bond lengths, tilt angles, and energies of clusters that are optimized when neutral to clusters that are optimized when charged. The hole polaron bond lengths (in the central octahedron) universally shrink by 5% in all the directions (Table 1). The fact that all systems exhibit a negative and isotropic effect for holes and positive

and anisotropic effects for electrons, suggests that while bond length variations are important for polaron formation, the two types of carrier must be discussed separately. Indeed, for the electron polaron in all materials studied here, the bond lengths of the 4 equatorial Metal/Halide bonds in the central octahedral remain almost unchanged compared to the neutrally optimized system, and the 2 apical bond lengths undergo a sizeable increase, by about 25% (Table 1). Again the contribution of the phonon mode associated with Jahn-Teller distortions using this method appears to be overestimated when comparing to experiment.¹² This is likely due to the exclusion of SOC in the present study. Therefore, there is a spurious true degeneracy that is broken with the addition of the charge, while in real systems SOC already lifts this conduction band degeneracy thus observed anisotropic effect should not be as strong. However, the observed variations of local octahedra geometries for electrons and holes is a general and genuine trend, Figure 1b.

Table 1 The change in PbI equatorial and apical bond lengths (Figure 1) of the central octahedron

Change in Pb-I bond length (%)			
	Electron		Hole
	Equatorial	Apical	Equatorial and Apical
MAPbI₃	2	25	-5
CsPbI₃	2	32	-5
FAPbI₃	-2	23	-6
MAPbBr₃	2	21	-5
CsPbBr₃	2	37	-6
FAPbBr₃	2	27	-6
MASnI₃	2	27	-5

The in-plane octahedral tilting of the central octahedron between the neutral and charged systems (Figure 2a), depends strongly on the constituent ions. Besides bond length variations, it is an efficient way to locally relax the lattice strain.⁴⁵ Such angular variations have been linked to the evolution of the electronic band gap with respect to structural deformation of the perovskite.^{46–49}

Across all systems studied, MA-based compounds exhibit the largest changes in in-plane tilt angles (Table 2). Moreover, electron localization is more likely to induce a large in-plane tilt angle than hole localization.

Table 2 The average change of in-plane tilt angle between the optimized neutral system and the optimized charged system.

Change in in-plane tilt angle(°)		
	Electron	Hole
MAPbI₃	5.3	0.3
CsPbI₃	0.5	2.1
FAPbI₃	0.3	1.0
MAPbBr₃	5.7	-0.1
CsPbBr₃	2.7	1.1
FAPbBr₃	1.1	1.3
MASnI₃	6.5	0.3

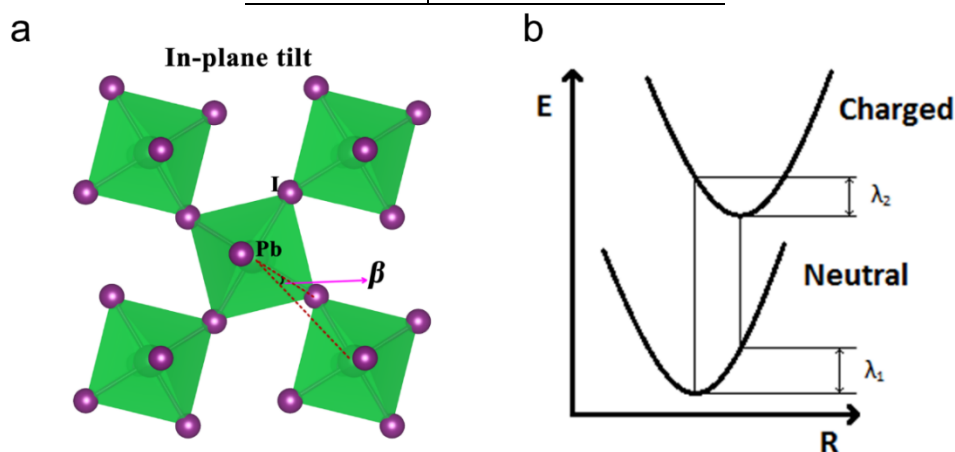


Figure 2: Definition of the (a) in-plane tilt angle β and (b) internal reorganization energies of the small polaron: polaron binding energy λ_2 and change in energies of the neutral species λ_1 .

To further explore the polaronic picture, we switch from the characterization of the local lattice distortions by both bond elongations and tilt angles, to the modifications of the electronic properties. In order to quantify the polaron binding energy, we calculate the two relaxation energies, the sum of which is the reorganization energy, further described in the SI, in a standard Marcus theory describing electron transfer, Figure 2b.⁵⁰ The internal reorganization energy

essentially quantifies variation of electronic energy due to the geometry changes when an electron is added or removed from the cluster.⁵¹

It is found that for electrons in iodide compounds, the polaron binding energy, λ_2 , gets smaller as the A-site cation is changed from MA to Cs to FA. Going from I to Br typically reduces the binding energy for holes. MAPbBr₃ has a substantially lower polaron binding energy for electrons compared to MAPbI₃, but going from I to Br with Cs or FA as the cation causes the polaron binding energy to get larger. Bromide compounds have a larger λ_1 than corresponding iodide compounds. This is consistent with the experimental observation of the enhanced softness of the latter compounds.⁵² Interestingly, it has been shown that Br based perovskites have stronger electron phonon coupling compared to I perovskites.⁵³ We find that MASnI₃ has smaller polaron binding energies for electrons and holes compared to MAPbI₃, however, it is expected to be less overestimated for electrons because Sn has smaller contributions from SOC.²⁴

Table 3 Reorganization energies, in meV, for charged clusters

CAM-B3LYP	Electron			Hole		
	λ_1	λ_2	λ	λ_1	λ_2	λ
MAPbI ₃	510	1377	1887	528	578	1106
CsPbI ₃	724	918	1642	365	274	639
FAPbI ₃	536	723	1259	310	533	816
MAPbBr ₃	1230	816	2046	566	275	841
CsPbBr ₃	857	1270	2127	486	342	828
FAPbBr ₃	719	1064	1783	379	433	812
MASnI ₃	519	1059	1578	268	460	730

Changes in polaron binding strength, λ_2 , correspond to changes in polaron size. Figure 3 (top row) shows the spin density of the electron polaron created in the CsPbI₃ system ($\lambda_2=918$ meV), is more localized than that of the FAPbI₃ system ($\lambda_2=723$ meV) for the same isosurface value. The same trend holds when comparing CsPbBr₃ ($\lambda_2=1270$ meV) to FAPbBr₃ ($\lambda_2=1064$ meV), Figure

S1. Figure 3 (bottom row) displays that the hole polaron for the MAPbI₃ system ($\lambda_2=578$ meV) is more localized than the hole polaron for MAPbBr₃ ($\lambda_2=275$ meV).

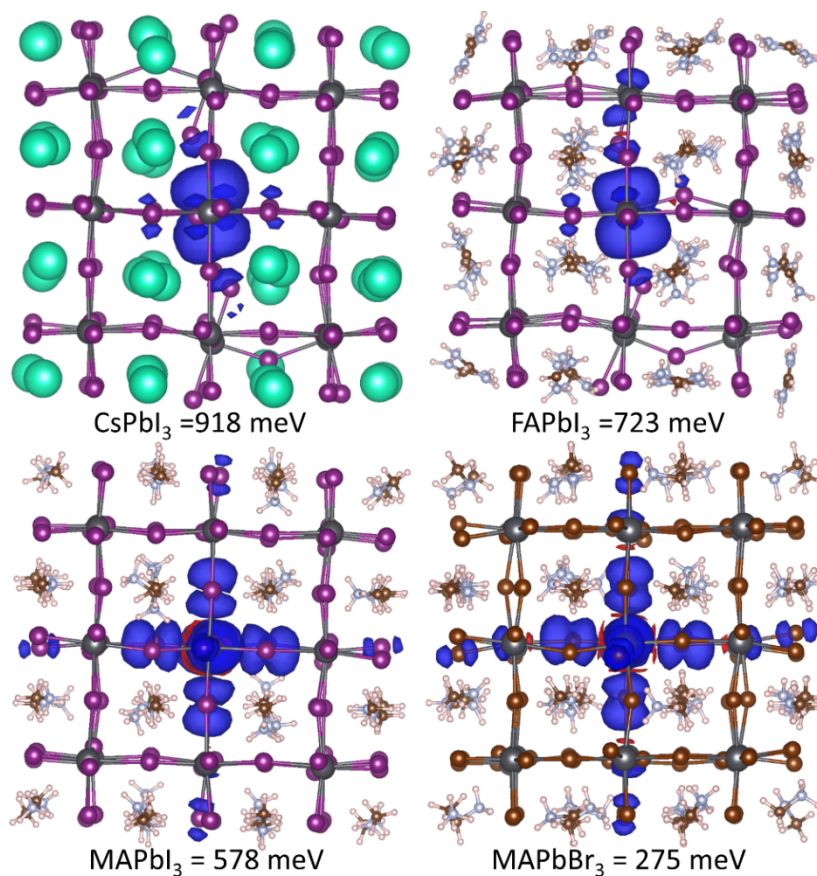


Figure 3: Top row: Spin density comparing the electron polaron in the CsPbI₃ system (left) and FAPbI₃ system (right). Bottom row: Spin density comparing the hole polaron in the MAPbI₃ system (left) and MAPbBr₃ system (right). (Isosurface of 0.0002 a_0^{-3})

A general trend in electron and hole small polaron formation is that the induced local volume variations are opposite. This trend might be useful for experimental detection of polaron type. With a wide variety of experimental evidence pointing from everything from large polarons,⁵⁴ or only electron polarons,¹⁴ or only hole polarons,^{11,16} there is the possibility that what minority carriers populate a given system/device depends on a number of factors including the crystal quality, surfaces, contacts, and interfaces.^{10,22} Thus, a particular system may be more prone to electron or hole small polaron formation, and as we see from the computed data (Table 3), the materials that

minimize polaron binding energy are different for electrons and holes. We believe the results presented in this manuscript demonstrate that polaronic effects in iodide compounds will decrease when going from MA to Cs to FA. However, there are a couple of areas that require more consideration and discussion when putting the results presented in this manuscript into context, namely, material elasticity, and dimensionality.^{45,52}

This study only provides a glimpse of the depth of the potential energy surfaces. Our simulations give no information about the stiffness of the local potentials or the time scale for formation of lattice distortions. It is likely that while a system has the potential to form a very deep polaron, the time scale to do so is so slow that the carriers are extracted before polaron formation. It is important to note that charge carriers moving in hybrid perovskite compounds experience an extremely perturbed electrostatic landscape, due to stochastic structural fluctuations of the organic and inorganic components and other sources of lattice softness.⁵⁵ Furthermore, elasticity characterizes the ability of a lattice to undergo long-range strain. It has been established that Br-based systems have indeed a higher bulk modulus than I-based perovskites, and are therefore stiffer and less prone to long range distortions.^{52,56} It should be noted that the present study probes only local distortions, the bond lengths and tilting within the central octahedron of Br-based system involves more atomic displacement compared to the I-based system. It is thus likely that our simulation is capturing only the short-range distortions produced by the small polarons but not properly capturing long-range distortions owing to the small size of the computed clusters. The missing long-range part of the lattice distortions around the small polarons may reduce the predicted energetic differences between Br and I materials. When comparing the displacements of all Pb and halide atoms in MAPbI₃ and MAPbBr₃, the average is greater for the Br system, however, the standard deviation is greater for I.

Polaronic contributions are significant in nano systems.^{14,57} Strong polaronic activity is also linked to defects and surfaces^{10,11} which commonly occur in nano-scale systems. While present systems were designed to be large enough to approximate bulk, they are in fact perhaps closer to nano-systems with a large surface to volume ratio and probably overestimate the polaronic contributions in terms of absolute numbers.

In summary, our DFT modeling of polaronic features compared structural distortions and energetics across several experimentally relevant halide perovskite materials. The most consistent trend identified is that electron polarons and hole polarons exhibit very different structural deformations. Across the materials studied, electron polaron formation is manifested by Jahn-Teller like distortions in the central octahedron, with apical PbI bonds expanding about 25% and equatorial PbI bonds expanding about 2%. In contrast, hole polarons cause the central octahedron to uniformly contract by about 5%. This different structural footprint for formation of electron and hole polarons can be a tool to determine what is taking place in individual systems and devices, so that electron-phonon phenomena and dynamics can be optimized accordingly. We observe that for electrons, the polaron binding energy in I-based compounds gets smaller as the A-site cation is changed from MA to Cs to FA. The local softness of the lattice in iodide compounds leads to smaller neutral reorganization energy than in bromide compounds. MASnI₃ has smaller polaron binding energies for electrons and holes compared to MAPbI₃. Finally, it is also found that the amount of change in in-plane tilt between the optimized neutral and charged structures is a good proxy for polaron binding energy.

Computational Details

The computational details follow reference [9], DFT calculations of HOP isolated clusters were performed using the CAM-B3LYP functional combined with the LANL2dz (for Pb, Sn, Br, Cs,

and I) and 6-31G* (for N, C, and H) basis sets using Gaussian 09 software package⁵⁸. Due to the size of the system, use of hybrid functional, and intentional use of a local basis functions, spin orbit coupling (SOC) could not be taken into account for these calculations.

Acknowledgements

The work at Los Alamos National Laboratory (LANL) was supported by the LANL LDRD program (A.J.N., I.A., L.Z., W.N, H.T., J.J.C., and S.T.). This work was done in part at Center for Nonlinear Studies (CNLS) and the Center for Integrated Nanotechnologies CINT), a U.S. Department of Energy and Office of Basic Energy Sciences user facility, at LANL. This research used resources provided by the LANL Institutional Computing Program. LANL is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. The work in France was supported by Agence Nationale pour la Recherche (TRANSHYPERO project). J.E. acknowledges financial support from the Institute Universitaire de France. A.D.M acknowledges the DOE-EERE 0001647-1544 grant for this work. AJN would like to thank Mikael Kepenekian for useful insight and discussion on the set up of the calculations.

Supporting Information Available

Further discussion of computational details. Explanation of reorganization energy definitions
Spin density comparing the electron polaron in CsPbBr₃ and FAPbBr₃

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Supporting Information

Geometry Distortion and Small Polaron Binding Energy Changes with Ionic Substitution in Halide Perovskites

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Discussion of Computational Details

The hybrid exchange-correlation CAM-B3LYP functional (where exact exchange varies from 20% to 65%)¹ was chosen because it correctly reproduces the polaronic effects in organic semiconductors in a polarizable solvent.² However, it will overestimate the reorganization energy

and polaron binding energy for both holes and electrons. Additionally, we include a polar solvent ($\epsilon = 78$), in the range of the static dielectric constant at room temperature for these materials,^{3,4} via the conductor-like polarizable continuum model.⁵

Several aspects were considered when designing the isolated HOP structures. The starting structure for each system is described below.⁶ In order to minimize dangling bonds, the clusters were all terminated on all sides with the large organic cation (MA or FA) or the inorganic Cs⁺ cation and halide (I or Br). More, charge balance was also ensured through Eqs. 1 and 2 to keep More, charge balance was also ensured through Eqs. 1 and 2 to keep the overall system neutral:

$$6n_{Pb} = 2n_{X_2} + n_{X_1}, \quad (1)$$

$$2n_{Pb} + n_{MA} = n_{X_1} + n_{X_2}. \quad (2)$$

Here n_{Pb} , n_{MA} , and n_l are the number of Pb/Sn, MA/FA/Cs, and I/Br atoms, respectively. X_1 corresponds to an I/Br atom on the surface that is only bonded to one Pb/Sn atom, while X_2 corresponds to an I/Br atom that is bonded to two Pb/Sn atoms. The cluster must be large enough to include at least 8 MA/FA/Cs cations surrounding the central Pb atom. To fulfill all conditions, we end up with a cluster having the following stoichiometry: $A_{54}B_{27}X_{108}$ ($X_1=X_2=54$). A cube fully terminated by MA (FA/Cs) would require 64 MA molecules. In order to achieve charge balance between the ions and to maximize symmetry, the 8 corner MA's (FA/Cs) were removed as were two opposite MA (FA/Cs) molecules on opposite edges.

All perovskites studied exist in multiple phases and undergo phase transitions at different temperatures with different inherent stabilities. Specifically, MAPbI₃, MAPbBr₃, and FAPbI₃ have been reported to undergo a structural phase transition between 130 and 160 K.⁷⁻⁹ A further phase transition to the cubic phase follows at higher temperatures for the MA perovskites (at ~330K for MAPbI₃ and 240K for MAPbBr₃), whereas a transition to trigonal phase occurs at around 200 K

for FAPbI₃. Meanwhile, all geometrical optimizations are necessarily performed without accounting for these temperature effects. The varying phases and stabilities of each material at different temperatures do add a layer of complication that is not fully possible to take into account.

Reorganization energy

The intramolecular reorganization energy is the sum of two components (λ_1 and λ_2) defined as

$$\lambda_{reorg} = \lambda_1 + \lambda_2 = (E^* - E) + (E_c^* - E_c) \quad (3)$$

Where λ_1 represents the change in energy between the neutral species in the optimized geometry of charged state (E^*) and the relaxed neutral species (E). The respective energy difference for the charged system at the neutral species geometry (E_c^*) and at the relaxed charge geometry (E_c), is represented by λ_2 , which corresponds to the polaron binding energy.

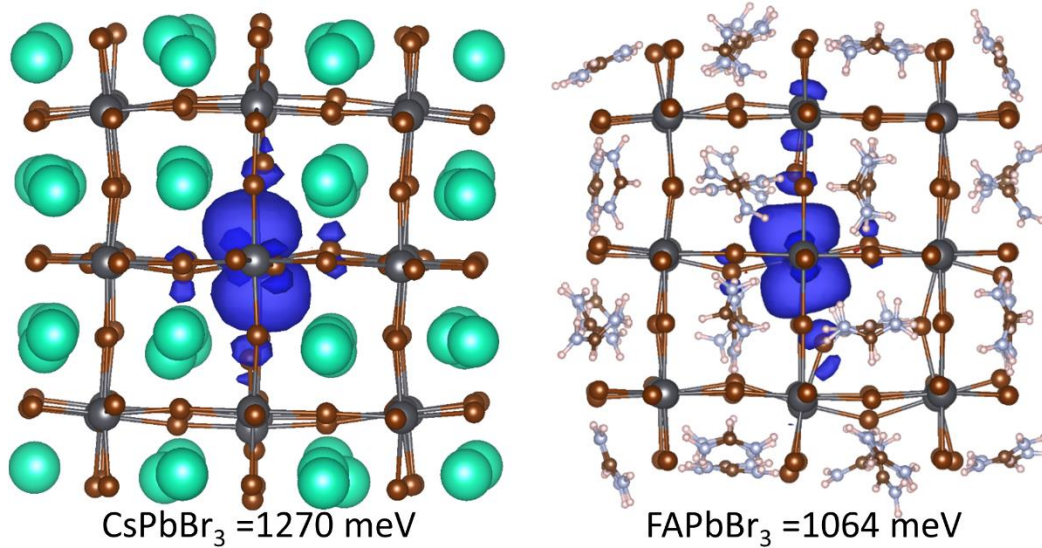


Figure S1: Spin density comparing the electron polaron in CsPbBr₃ (left) and FAPbBr₃ (right).

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