

Supplementary Information for:

Ab initio study of the role of iodine in the degradation of

CH₃NH₃PbI₃

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Section SI1: The effects of the size of the slab model

To justify the choice of the size of the slab model in this work, we performed the I₂ adsorption calculations using a larger supercell with the vacuum gap increased from 12 Å to 16 Å, and with a thicker slab of 3 layers. The adsorption sites shown in Figures 2a and 3a were studied for the different simulation models. As shown in Table SI1, the adsorption energies from the calculations with the different supercell sizes are in close agreement.

Table SI1: The I₂ adsorption energies on the perovskite surface (Figures 2a and 3a).

MAI-terminated surface (Figure 2a)			PbI ₂ -terminated surface (Figure 3a)		
Slab layers	Vacuum length (Å)	<i>E</i> _{ads} (kcal/mol)	Slab layers	Vacuum length (Å)	<i>E</i> _{ads} (kcal/mol)
2.5	12	-29.7	2.5	12	-29.0
2.5	16	-29.8	2.5	16	-28.9
3	12	-29.1	3	12	-28.5

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Section SI2: Wannier Centers (WCs) of selected iodines for the structure in Figure 2e

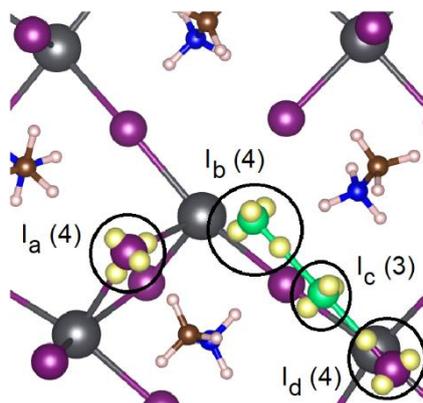


Figure SI1 WCs (shown as yellow spheres) of selected iodines for the structure in Figure 2e. Each WC represents two electrons for the spin-unpolarized calculation. The parentheses show the sum of WCs for the selected iodines. The charge state of the iodine I_a is -1. The overall charge of the triiodide (I_b - I_c - I_d) is -1. The color codes for different atoms follow those in Figure 1. To distinguish different types of iodine ions, the iodine in I_2 molecules are green while the iodide ions in the pristine surfaces are purple.

Section SI3: Wannier Centers of selected iodines for the structure in Figure 3e

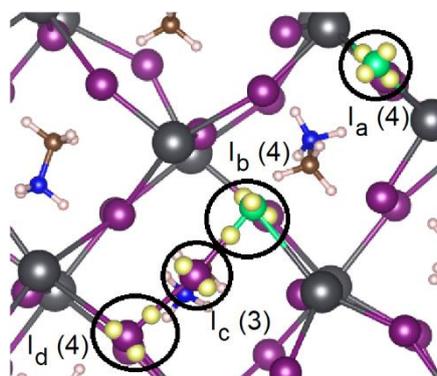


Figure SI2 WCs (shown as yellow spheres) of selected iodines for the structure in Figure 3e. Each WC represents two electrons for the spin-unpolarized calculation. The parentheses show the sum of WCs for the selected iodine ions. The charge state of the I_a iodine is -1. The overall charge of the triiodide (I_b - I_c - I_d) is -1. The color codes for

different atoms follow those in Figure 1. To distinguish different types of iodine ions, the iodine in I_2 molecules are green while the iodide ions in the pristine surfaces are purple.

Section SI4: Wannier Centers of selected iodines for the structure in Figure 4c

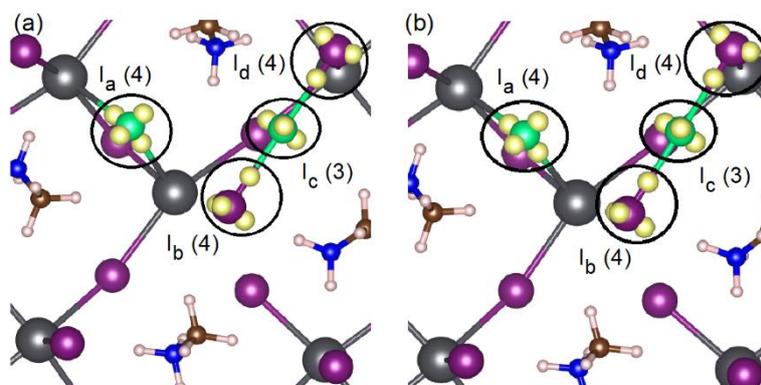


Table SI3 WCs (shown as yellow spheres) of selected iodines for the structure in Figure 4c for (a) spin up and (b) spin down electrons. Each WC represents one electron for the spin-polarized calculation. The parentheses show the sum of WCs for the selected iodine ions. The charge state of the I_a iodine is -1. The overall charge of the triiodide (I_b - I_c - I_d) is -1. The color codes for different atoms follow those in Figure 1. To distinguish different types of iodine ions, the iodine in I_2 molecules are green while the iodide ions in the pristine surfaces are purple.

Section SI5: Wannier Centers of selected iodines for the structure in Figure 5c

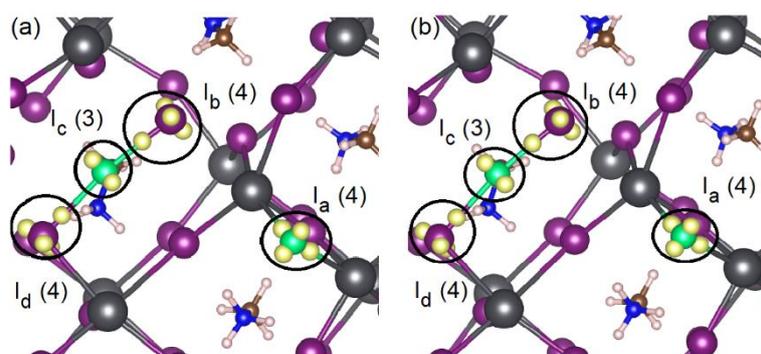


Table SI4 WCs (shown as yellow spheres) of selected iodines for the structure in Figure

5c for (a) spin up and (b) spin down electrons. Each WC represents one electron for the spin-polarized calculation. The parentheses show the sum of WCs for the selected iodine ions. The charge state of the I_a iodine is -1. The overall charge of the triiodide ($I_b-I_c-I_d$) is -1. The color codes for different atoms follow those in Figure 1. To distinguish different types of iodines, the added I^\bullet radicals are green while the iodide ions in the pristine perovskite surfaces are purple.