Supplementary Information for:

Charge localization and trapping at surfaces in lead-iodide perovskites: The role of polarons and defects

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S1. Binding energy of polaron vs slab thickness

In order to test the robustness of the polaron binding energy reported in the main text against the thickness of the employed slab, we perform extra calculations with thicker slabs. We consider slabs with six and seven PbI₂ layers with both PbI₂ and MAI terminations. The simulation cell is equivalent to that reported in the main text for the 5-layers slabs, with the exception of the *c* axis which is increased by 5 (10) Å for the 6 (7)-layers slab, in order to preserve the length of the vacuum layer separating the replicas of the slab. For the considered systems, we calculate $E_b(h^+)$ using the same procedure employed for the 5-layer slabs (cf. main text). From Table S1, we observe that the values of $E_b(h^+)$ are essentially stable with respect to the thickness of the slab for both PbI₂ and MAI surfaces, thus ensuring that the results presented in the main text are converged with respect to the

numbers of layers. Furthermore, analysis of the hole wave-function indicates that also polaron localization is unaffected by the thickness of the slab (e.g. for the PbI₂ surface in Fig. S1).

Table S1. Calculated values of $E_{\rm b}(h^+)$ (cf. main text) for PbI₂ and MAI slabs of the (001) MAPbI₃ surface with different number of layers. All values are given in meV.

PbI ₂	MAI
120	80
110	74
110	77
	PbI2 120 110 110



Figure S1. Isodensity representations of an extra hole (purple) for a PbI_2 slab with (a) 6 and (b) 7 PbI_2 layers. Lead in brown, iodine in pink, nitrogen in blue, carbon in cyan, and hydrogen in white. The *c* axis lies vertically.

S2. Comparison between bulk and surface V^0_{Pb}

We here describe the local structures of bulk and surface V_{Pb}^0 on the PbI₂ slab. Both the bulk and the surface defect feature the formation of a triiodide moiety (I_3^-). In Fig. S2, we present the most stable structural configurations achieved for bulk and surface V_{Pb}^0 . For both, we observe that the trimer bridges two different PbI₂ planes. On this regard, we note that the configuration in which the I_3^- occupies a single PbI₂ layer is 0.32 (0.10) eV less stable than the bridging I_3^- for the bulk (surface) defect. The I-I bond lengths for the bulk and surface I_3^- are equivalent, but there is a noticeable difference in the $I_t \hat{I}_c I_t$ angle, where I_t and I_c are the terminal and central iodine atoms of the triiodide, respectively. In fact, for the bulk defect $I_t \hat{I}_c I_t = 176.0^\circ$, a value 4° lower than that of the linear triiodide anion. In contrast, we observe $I_t \hat{I}_c I_t = 178.5^\circ$ for the surface I_3^- , which is therefore significantly less distorted. Furthermore, we notice that the formation of the I_3^- moiety in the bulk implies also a deformation of the Pb-I_t bonds (cf. Fig. S2), which is instead reduced for surface atoms, than can more easily displace to accommodate the triiodide moiety.



Figure S2. Structural configurations of (a) bulk and (b) surface V_{Pb}^0 . In panel (a), the c axis lies horizontally. In panel (b), MA molecules are not shown for clarity and the c axis lies vertically.