

Supplementary Information for:

**Ab initio study of the role of oxygen and excess electrons in the
degradation of CH₃NH₃PbI₃**

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Section SII: The effects of the supercell size

To justify the choice of the supercell size in this work, we performed calculations using a larger supercell with the vacuum gap increased to 16 Å from 12 Å used in this work. We first studied superoxide adsorption on the perovskite surface at the adsorption sites shown in Figures 2a and 2b. Table SII shows the structural and energetics results from the calculations with the two supercell sizes. As shown in the table, the O-O bond length ($d_{(O-O)} = 1.33$ Å) of the superoxide remains unchanged. Moreover, the adsorption configuration in Figure 2b was also found to be more stable than the configuration in Figure 2a. The energy difference is 8.7 kcal/mol with the larger supercell, which is very close to the value of 9.1 kcal/mol from the calculations with a vacuum gap of 12 Å. We also calculated the adsorption energy of an O₂ on the charged degraded surface shown in Figure 5. The adsorption energies from the calculations with the two supercell sizes are also in very close agreement (-10.7 kcal/mol for vacuum = 16 Å versus -10.6 kcal/mol for vacuum = 12 Å). Meanwhile, the O-O bond length ($d_{(O-O)} = 1.26$ Å) of the O₂ on the charged degraded surface remains unchanged.

Table SII Selected bond lengths (Å) of the superoxide adsorption on the perovskite surface (Figure 2a and 2b) and their energy difference [$(E_{2a} - E_{2b})$, kcal/mol]. The

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adsorption energy of an O₂ (E_{ads} , kcal/mol) on the charged degraded surface and the O-O distance (Å) in Figure 5 (The labels of the ions are the same as in Figure 3a or Table 2).

	Figure 2a	Figure 2b				Figure 5	
	O _b -O _c	O _b -O _c	Pb _a -O _b	Pb _a -O _c	$E_{2a} - E_{2b}$	E_{ads}	O-O
12 Å	1.33	1.33	2.21	2.43	9.1	-10.6	1.26
16 Å	1.33	1.33	2.21	2.44	8.7	-10.7	1.26

Section SI2: Introduction of an excess electron to the less stable adsorption configuration in Figure 2a

The optimized structure after the introduction of an excess electron to the less stable adsorption configuration is shown in Figure SI1 (marked as *ISI*). The resulting system has zero net magnetization suggesting that the added electron was abstracted by the OOH species. Concertedly, a proton in the NH₃ groups of MA cation was found to transfer to the OOH. This forms a hydrogen peroxide via an overall proton-coupled electron transfer process. The O-O distance ($d_{(\text{O}-\text{O})}$) is 1.46 Å which is close to that of an isolated hydrogen peroxide molecule ($d_{(\text{O}-\text{O})} = 1.45$ Å) in our PBE calculation further confirming that it is a hydrogen peroxide. It turns out that this hydrogen peroxide can reach a more stable configuration when it diffuses close to a nearby MA cation (marked as *FSI* in Figure SI1). This is a more stable configuration because of the formation of more hydrogen bonds between the hydrogen peroxide and the MA cation. We performed CI-NEB calculations to evaluate the activation energy of the hydrogen peroxide diffusion. The energy profile is shown in Figure SI1. The transition-state image is marked as *TSI* which has an activation energy of +7.7 kcal/mol.

To evaluate the activation energy of the O-O bond dissociation, we performed constrained optimization by gradually lengthened the O-O bond from the *FSI* structure. The transition-state structure is shown in Figure SI2a. The next image after the transition state is shown in Figure SI2b. In this structure, upon the cleavage of the O-O

bond, one resulting OH abstracts a hydrogen from a nearby MA cation to form a H₂O (highlighted by the black oval in Figure SI2b). Another OH forms a covalent bond with an iodide ion. Interestingly, the last image (Figure SI2c) shows that the proton of the H₂O formed in Figure SI2b transfers back to the CH₃NH₂ molecule and the resulting OH⁻ ion forms a covalent bond with a surface Pb (the OH⁻ is highlighted by the green oval in the Figure SI2c). As shown in Figure SI2d, the activation energy is +22 kcal/mol which is considerably larger than the value obtained in Figure 3d (i.e., +11.7 kcal/mol) suggesting that this reaction pathway is kinetically unfavorable.

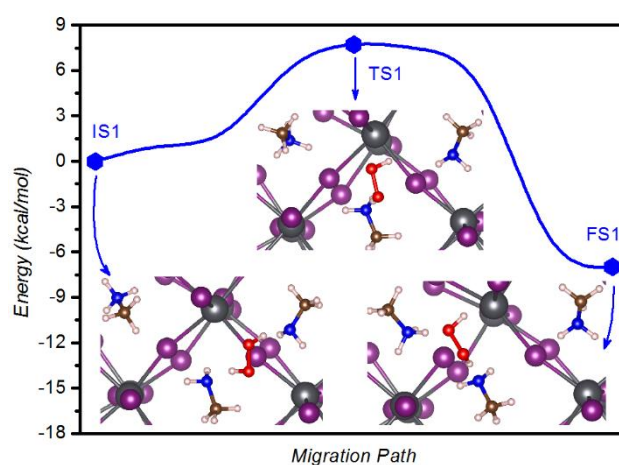


Figure SI1 The energy profile along the migration of the hydrogen peroxide. The insets are the optimized structure of the hydrogen peroxide adsorbed on the MAPbI₃ surface (marked as *ISI*), the transition state of the hydrogen peroxide migration on the MAPbI₃ surface (marked as *TSI*), and the optimized structure after the migration of the hydrogen peroxide (marked as *FSI*).

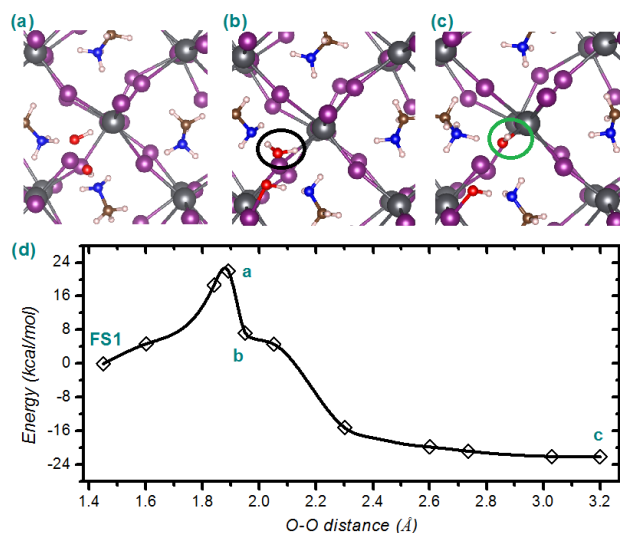


Figure SI2 (a) The transition state of the dissociation of the O-O bond in the HOOH radical. (b) The structure of an intermediate image (the subsequent image after the transition state). (c) The optimized structure after the O-O bond dissociation. (d) Energy profile along the dissociation of O-O bond in the HOOH radical. *FS1* is the final structure in Figure SI1 which becomes the initial structure here before the O-O bond dissociation.

Section SI3: The pathway towards the formation of the local PbO structure and the Maximally-localized Wannier function analysis

The pathway towards the formation of the local PbO structure are summarized in five steps (Step 1 ~ Step 5). The charge states of different atoms were determined by counting the number of Wannier centers (WCs) assigned to them.

Step 1: A superoxide (O_2^-) is absorbed on the perovskite surface by forming a covalent bond with a top-layer Pb

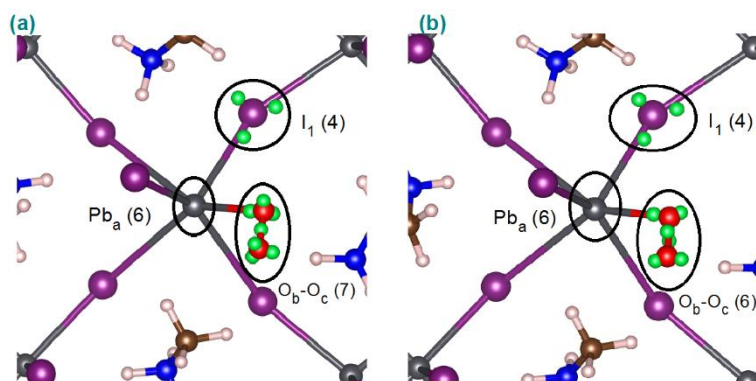


Figure SI3 WCs (shown in green balls) of the selected species in the structure in Figure 2b for (a) spin up and (b) spin down electrons. The numbers of WCs for the selected species are shown in the parentheses. The view of some WCs are blocked by the atoms. There is one unpaired electron in the O_b-O_c and the net charge of the dioxygen is -1, which indicates that it is a superoxide. The color code for different atoms is the same as in Figure 1.

Step 2: Introduction of an excess electron to the superoxide-adsorbed MAPbI₃ surface

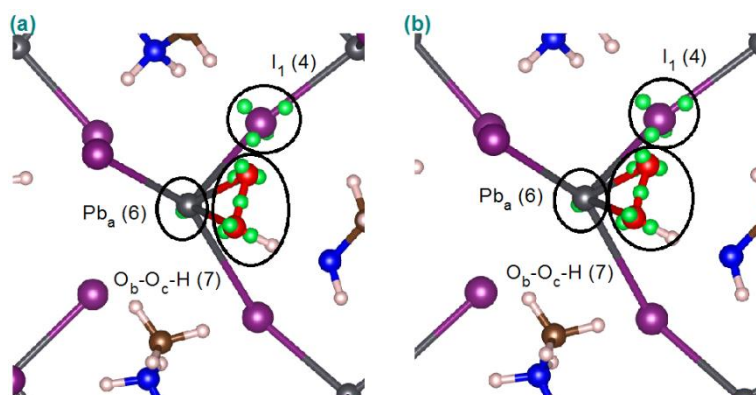


Figure SI4 WCs (shown in green balls) of the selected species in the structure in Figure 3a for (a) spin up and (b) spin down electrons. The numbers of WCs for the selected species are shown in the parentheses. The view of some WCs are blocked by the atoms. The added electron is abstracted by the superoxide and a proton spontaneously transfer from the NH_3 group of the MA cation, converting the superoxide into an OOH^- via a proton-coupled electron transfer process. The color code for different atoms is the same as in Figure 1.

Step 3: Dissociation of the O_b - O_c bond in the OOH^- species

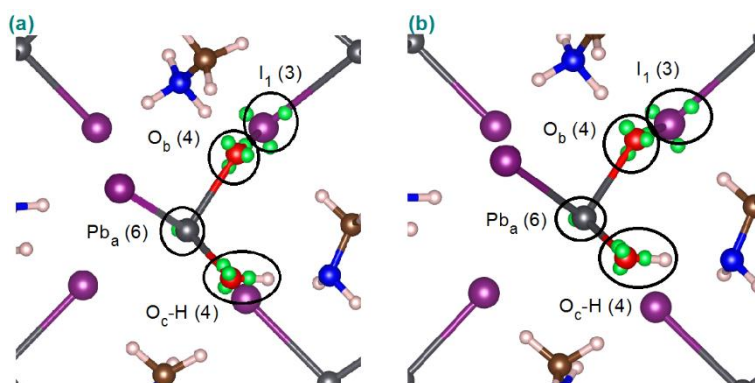


Figure SI5 WCs (shown in green balls) of the selected species in the structure in Figure 3c for (a) spin up and (b) spin down electrons. The numbers of WCs for the selected species are shown in the parentheses. O_b forms a covalent bond with a surface iodide (I_1) upon the dissociation of the O-O bond. Two electrons are transferred from the iodide ion to the oxygens, forming the I^+ , O^{2-} and OH^- ions. The color code for different atoms is the same as in Figure 1.

Step 4: Introduction of an additional O_2 to the degraded surface

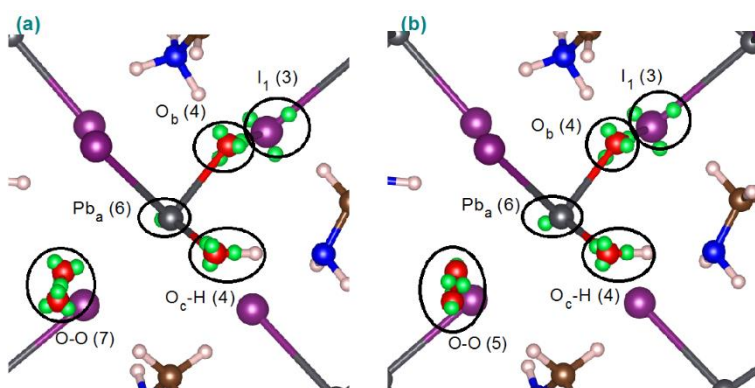


Figure SI6 WCs (shown in green balls) of the selected species in the structure in Figure 5a for (a) spin up and (b) spin down electrons. The view of some WCs are blocked by the atoms. The numbers of WCs for the selected species are shown in the parentheses. The overall charge of the additional dioxygen is neutral and there are two unpaired electrons on it. This confirms that the additional O_2 molecule remains to be a neutral molecule. The color code for different atoms is the same as in Figure 1.

Step 5: Introduction of another excess electron to the above O₂-adsorbed MAPbI₃ surface

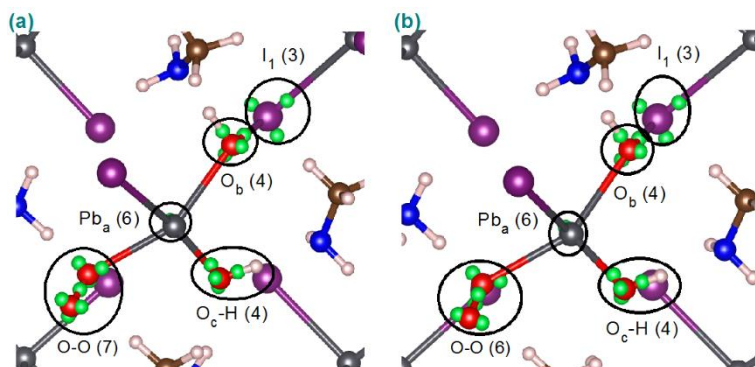


Figure SI7 WCs (shown in green balls) of the selected species in the structure in Figure 6c for (a) spin up and (b) spin down electrons. The view of some WCs are blocked by the atoms. The numbers of WCs for the selected species are shown in the parentheses. The oxygen molecule abstracted the additional electron to form a superoxide which in turn forms a covalent bond with the surface Pb. The color code for different atoms is the same as in Figure 1.