Supporting Information for:

Why Oxygen Increases Carrier Lifetimes but Accelerates Degradation of CH$_3$NH$_3$PbI$_3$ Under Light Irradiation: Time-Domain Ab Initio Analysis

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We estimated the radiative lifetimes for the pristine MAPbI$_3$, O$_2$, O$_2^{-1}$ and O$_2^{-2}$ systems by calculating the Einstein coefficient of spontaneous emission, $A_{21}$, between VBM and CBM

$$A_{21} = \frac{8\pi^2\nu_2^2\epsilon^2}{\epsilon_0 m_e c^3} g_2 f_{12}$$

Here, $\epsilon_0$, $m_e$, $\epsilon$, and $c$ are the fundamental constants, $\nu$ is the transition frequency, $g_l$ is degeneracy of state $l$, and $f_{12}$ is the oscillator strength between states 1 and 2.

The radiative lifetime is inverse of the Einstein coefficient:

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$$\tau_{21} = [A_{21}]^{-1} = \frac{\varepsilon_0 m e^3 g_2}{8\pi^2 v^2_{21} e^2 g_1 f_{12}} = \frac{\varepsilon_0 m e^3}{8\pi^2 v^2_{21} e^2 f_{12}}$$

We assume that, \( g_1 = g_2 = 1 \) because thermal atomic fluctuations destroy the system symmetries.

**Table S1.** Spin-up Caniocularly Averaged Bandgap, Absolute Value of NA Coupling, Pure-Dephasing Time, Nonradiative Electron–Hole Recombination Time and Radiative Lifetime for the VBM-CBM Transition in the Pristine MAPbI₃, O₂, O₂⁻¹ and O₂⁻² systems.

<table>
<thead>
<tr>
<th></th>
<th>Bandgap (eV)</th>
<th>NA coupling (meV)</th>
<th>Dephasing (fs)</th>
<th>Recombination (ns)</th>
<th>Radiative lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI₃</td>
<td>1.65</td>
<td>0.70</td>
<td>11.04</td>
<td>2.12</td>
<td>7.02</td>
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<tr>
<td>O₂</td>
<td>1.66</td>
<td>1.23</td>
<td>14.59</td>
<td>1.22</td>
<td>3.29</td>
</tr>
<tr>
<td>O₂⁻¹</td>
<td>1.61</td>
<td>1.34</td>
<td>2.25</td>
<td>0.66</td>
<td>2.61</td>
</tr>
<tr>
<td>O₂⁻²</td>
<td>1.65</td>
<td>0.55</td>
<td>9.88</td>
<td>4.70</td>
<td>8.57</td>
</tr>
</tbody>
</table>
Figure S1. Spin-up projected densities of states (PDOS) and charge densities of the VBM and CBM in the pristine MAPbI$_3$, O$_2$, O$_{2^{-1}}$ and O$_{2^{-2}}$ systems. The presence of various oxygen species does not create deep trap states within the fundamental bandgap in the spin-up channel. The increased VBM-CBM overlap in the neutral oxygen (b) and superoxide (c) systems leads to stronger NA coupling and faster electron-hole recombination. In contrast, the decreased VBM-CBM overlap in the peroxide system (d) reduces the NA coupling and slows charge recombination.
Figure S2. Spin-polarized projected densities of states (PDOS) of the pristine MAPbI₃, O₂, O₂⁻¹ and O₂⁻² systems, including simultaneously spin-up and spin-down projections.
Figure S3. Projected densities of states (PDOS), top, and charge densities, bottom, of key states involved in charge trapping and recombination in the $O_2$, $O_2^-$, and $O_2^{-2}$ systems, obtained using GW+SOC with a 48-atom MAPbI$_3$ supercell.
Figure S4. Electron–hole recombination dynamics for the spin-up channel in the pristine MAPbI$_3$, O$_2$, O$_2^{-1}$ and O$_2^{-2}$ systems. Similarly to the spin-down channel, neutral oxygen molecule and superoxide accelerate charge recombination, while peroxide slows it down.