Supporting Information for:

Unravelling the Effects of Oxidation State of Interstitial Iodine and Oxygen Inhibits Charge Trapping and Recombination in CH$_3$NH$_3$PbI$_3$ Perovskite: A Time-Domain Ab Initio Study

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S1 Coupled Kinetic Equations

Here, we consider the following processes that characterize the charge carrier relaxation pathways in pristine MAPbI$_3$, I$_i$, I$_i^-$, I$_i^{+1}$ and IO$_3^{−1}$ systems. The schematics of related charge processes are depicted in Figure S1-S4. The obtained charge trapping and recombination dynamics between two states are shown in Figure S5-S13. Here, the transition rate between the conduction band minimum (CBM) and valence band maximum (VBM), CBM and electron trap, electron trap and VBM, VBM and hole trap is denoted by $k_{\text{(cbm→vbm)}}$, $k_{\text{(cbm→trap)}}$, $k_{\text{(trap→vbm)}}$, $k_{\text{(vbm→trap)}}$, respectively. The rate constants shown in Figure S5-S13 are obtained by fitting the key state population to an function $f(t) = t/A$. Constant A is depending on the system.

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(a) pristine MAPbI₃: electron-hole recombination across CBM and VBM. Figure S1
gives the basis set. The time-dependent populations of excited state (CBM) and
ground state (VBM) are described by equations 1-2 and their solutions are given by
equations 3-4. Figure S5 gives the ground state population growing and rate
contant.

coupled kinetic equations:

\[
\frac{d[ES]}{dt} = -k_{(cbm\rightarrow vbm)}[ES] \tag{1}
\]
\[
\frac{d[GS]}{dt} = k_{(cbm\rightarrow vbm)}[ES] \tag{2}
\]

the solutions for this set of equations are:

\[
[ES] = e^{-k_{(cbm\rightarrow vbm)} t} \tag{3}
\]
\[
[GS] = 1 - e^{-k_{(cbm\rightarrow vbm)} t} \tag{4}
\]

![Diagram](image)

Figure S1. The schematic of electron-hole recombination pathway in pristine MAPbI₃.
(b) I: electron-hole recombination mediated by trap states. Figure S2 and S3 give the basis set of electron trap- and hole trap-assisted electron-hole recombination. The electron-trap assisted charge recombination is described by equations 5-7 and whose solutions are presented in equations 8-10. The hole-trap mediated electron-hole recombination is described by equations 11-13 and the corresponding solutions are shown in equations 14-16. The dynamics processes and transition constants of \( k_{(cbm\rightarrow vbm)} \), \( k_{(vbm\rightarrow trap)} \), \( k_{(cbm\rightarrow trap)} \) are shown in Figure S6-S8.

**Coupled kinetic equations for electron-hole recombination containing electron trapping:**

\[
\frac{d[ES]}{dt} = -(k_{(cbm\rightarrow vbm)} + k_{(cbm\rightarrow trap)})[ES] \tag{5}
\]

\[
\frac{d[\text{trap}]}{dt} = k_{(cbm\rightarrow trap)}[ES] - k_{(\text{trap}\rightarrow vbm)}[\text{trap}] \tag{6}
\]

\[
\frac{d[GS]}{dt} = k_{(cbm\rightarrow vbm)}[ES] + k_{(\text{trap}\rightarrow vbm)}[\text{trap}] \tag{7}
\]

The solutions for this set of equations are:

\[
[ES] = e^{-(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)})t} \tag{8}
\]

\[
[\text{trap}] = \frac{k_{(cbm\rightarrow trap)}}{(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)}-k_{(\text{trap}\rightarrow vbm)})} \left(e^{-k_{(\text{trap}\rightarrow vbm)}t} - e^{-(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)})t}\right) \tag{9}
\]

\[
[GS] = 1 - \frac{1}{(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)}-k_{(\text{trap}\rightarrow vbm)})} \left\{k_{(cbm\rightarrow trap)} e^{-k_{(\text{trap}\rightarrow vbm)}t} - \right.
\]

\[
\left. (k_{(cbm\rightarrow vbm)} - k_{(\text{trap}\rightarrow vbm)}) e^{-(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)})t}\right\} \tag{10}
\]
**Figure S2.** The schematic of electron-hole recombination containing electron trapping pathways in I.

**coupled kinetic equations for electron-hole recombination containing hole trapping:**

\[
\frac{d[ES]}{dt} = -(k_{(cbm\rightarrow vbm)} + k_{(vbm\rightarrow trap)})[ES]
\]  \hspace{1cm} (11)

\[
\frac{d[trap]}{dt} = k_{(vbm\rightarrow trap)}[ES] - k_{(cbm\rightarrow trap)}[trap]
\]  \hspace{1cm} (12)

\[
\frac{d[GS]}{dt} = k_{(cbm\rightarrow vbm)}[ES] + k_{(cbm\rightarrow trap)}[trap]
\]  \hspace{1cm} (13)

**the solutions for this set of equations are:**

\[
[ES] = e^{-(k_{(cbm\rightarrow vbm)}+k_{(vbm\rightarrow trap)})t}
\]  \hspace{1cm} (14)

\[
[trap] = \frac{k_{(vbm\rightarrow trap)}}{(k_{(cbm\rightarrow vbm)}-k_{(cbm\rightarrow trap)}+k_{(vmb\rightarrow trap)})} \left( e^{-(k_{(cbm\rightarrow trap)})t} - e^{-(k_{(cbm\rightarrow vbm)}+k_{(vbm\rightarrow trap)})t} \right)
\]  \hspace{1cm} (15)

\[
[GS] = 1 - \frac{k_{(vbm\rightarrow trap)}}{(k_{(cbm\rightarrow vbm)}-k_{(cbm\rightarrow trap)}+k_{(vbm\rightarrow trap)})} \left( e^{-(k_{(cbm\rightarrow trap)})t} - \frac{(k_{(cbm\rightarrow vbm)}-k_{(cbm\rightarrow trap)}+k_{(vbm\rightarrow trap)})}{(k_{(cbm\rightarrow vbm)}-k_{(cbm\rightarrow trap)}+k_{(vbm\rightarrow trap)})} e^{-(k_{(cbm\rightarrow vbm)}+k_{(vbm\rightarrow trap)})t} \right)
\]  \hspace{1cm} (16)
Figure S3. The schematic of electron-hole recombination containing hole trapping pathways in I.
(c) $I_{i-1}$: electron-hole recombination across CBM and VBM of the system. The transition rate $k_{(cbm\rightarrow vbm)}$ is obtained by fitting the ground state (VBM) population (Figure S9). The kinetic processes and basis set are same to the pristine MAPbI$_3$, see equations 1-4 and Figure S1.

(d) $I_{i+1}$: electron-trap assisted electron-hole recombination. The time-dependent populations of the excited state (CBM), trap state, and ground state (VBM) are described by equations 17-19 and whose solutions are presented in equations 20-22. The basis set is shown in Figure S4. The transition rates $k_{(cbm\rightarrow vbm)}$, $k_{(trap\rightarrow vbm)}$, $k_{(cbm\rightarrow trap)}$ are obtained by fitting the key state population shown in Figure S10-S12.

**coupled kinetic equations:**

$$\frac{d[ES]}{dt} = -(k_{(cbm\rightarrow vbm)} + k_{(cbm\rightarrow trap)})[ES] \quad (17)$$

$$\frac{d[trap]}{dt} = k_{(cbm\rightarrow trap)}[ES] - k_{(trap\rightarrow vbm)}[trap] \quad (18)$$

$$\frac{d[GS]}{dt} = k_{(cbm\rightarrow vbm)}[ES] + k_{(trap\rightarrow vbm)}[trap] \quad (19)$$

**the solutions for this set of equations are:**

$$[ES] = e^{-(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)})t} \quad (20)$$

$$[trap] = \frac{k_{(cbm\rightarrow trap)}}{(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)}-k_{(trap\rightarrow vbm)})} \left( e^{-k_{(trap\rightarrow vbm)}t} - e^{-(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)})t} \right) \quad (21)$$

$$[GS] = 1 - \frac{1}{(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)}-k_{(trap\rightarrow vbm)})} \left( k_{(cbm\rightarrow trap)} \cdot e^{-k_{(trap\rightarrow vbm)}t} - (k_{(cbm\rightarrow vbm)} - k_{(trap\rightarrow vbm)}) \cdot e^{-(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)})t} \right) \quad (22)$$
Figure S4. The schematic of electron-hole recombination and electron trapping pathways in $I_{1}^{+1}$.

(e) $IO_{3}^{-1}$: electron-hole recombination across CBM and VBM of the system. The transition rate $k_{(cbm\rightarrow vbm)}$ is obtained by fitting the ground state (VBM) population (Figure S13). The kinetic equations, solutions and basis set is same to the pristine MAPbI$_3$, see equations 1-4 and Figure S1.
S2 Additional Figures

**Figure S5.** Time evolution of the ground state’s population due to recombination of the valence band hole with conduction band electron in pristine MAPbI₃. The fitting function is $f(t) = t/(1.554 \times 10^6)$.

**Figure S6.** Time evolution of the ground state’s population due to recombination of the valence band hole with conduction band electron in Iᵢ. The fitting function is $f(t) = t/(0.540 \times 10^6)$.
Figure S7. Time evolution of the trap state’s population due to hole trapping from valence band maximum (VBM) to trap state in \( I_i \). The fitting function is \( f(t) = \frac{t}{(0.030 \times 10^6)} \).

Figure S8. Time evolution of the ground state’s population due to recombination of the trapped hole with conduction band electron in \( I_i \). The fitting function is \( f(t) = \frac{t}{(1.00 \times 10^6)} \).
Figure S9. Time evolution of the ground state’s population due to recombination of the valence band hole with conduction band electron in $I_i^{-1}$. The fitting function is $f(t) = t/(2.045 \times 10^6)$.

Figure S10. Time evolution of the ground state’s population due to recombination of the valence band hole with conduction band electron in $I_i^{+1}$. The fitting function is $f(t) = t/(1.088 \times 10^6)$. 
Figure S11. Time evolution of the ground state’s population due to recombination of the trapped electron with valence band hole in I$_i^{+1}$. The fitting function is $f(t) = t/(2.271 \times 10^6)$.

Figure S12. Time evolution of the ground state’s population due to electron trapping form conduction band minimum (CBM) to trap state in I$_i^{+1}$. The fitting function is $f(t) = t/(0.042 \times 10^6)$. 
Figure S13. Time evolution of the ground state’s population due to recombination of the valence band hole with conduction band electron in \( \text{IO}_3^{-1} \). The fitting function is \( f(t) = t/(4.221 \times 10^6) \).
Figure S14. Evolution of populations of the key states for electron trapping in I.
Electronic configurations of product (final) and reactant (initial) states.

(1) The electronic configuration of product (final) and reactant (initial) states in the pristine MAPbI$_3$, I$_{i}^{-1}$ and IO$_{3}^{-1}$ systems during electron-hole recombination between VBM and CBM:

<table>
<thead>
<tr>
<th>Final State</th>
<th>Initial State</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBM</td>
<td></td>
</tr>
<tr>
<td>VBM</td>
<td></td>
</tr>
<tr>
<td>Basis Set</td>
<td>[1,-1]</td>
</tr>
</tbody>
</table>

(2) The electronic configuration of product (final) and reactant (initial) states in the I$_{i}$ system for electron-hole recombinaiton between CBM and VBM bypassing the trap state:

<table>
<thead>
<tr>
<th>Final State</th>
<th>Initial State</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBM</td>
<td></td>
</tr>
<tr>
<td>Trap</td>
<td></td>
</tr>
<tr>
<td>VBM</td>
<td></td>
</tr>
<tr>
<td>Basis Set</td>
<td>[1,-1,2]</td>
</tr>
</tbody>
</table>
(3) The electronic configuration of (final) and reactant (initial) states in the $I_i$ system for recombinations between VBM and the trap state:

![Diagram of electronic configuration](image1)

(4) The electronic configuration of (final) and reactant (initial) states in the $I_i$ system for electron trapping between CBM and the trap state:

![Diagram of electronic configuration](image2)

(5) The electronic configuration of (final) and reactant (initial) states in the $I_i$ system for hole trapping assisted recombination between CBM and trap state:

![Diagram of electronic configuration](image3)
(6) The electronic configuration of (final) and reactant (initial) states in the $I_i$ system for hole trapping between VBM and trap state:

<table>
<thead>
<tr>
<th></th>
<th>Final State</th>
<th>Initial State</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trap</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VBM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basis Set</td>
<td>[1,-1,3]</td>
<td>[-1,2,3]</td>
</tr>
</tbody>
</table>

(7) The electronic configuration of (final) and reactant (initial) states in the $I_i^{+1}$ for electron-hole recombinaiton between CBM and VBM bypassing the electron trap state:

<table>
<thead>
<tr>
<th></th>
<th>Final State</th>
<th>Initial State</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trap</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VBM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basis Set</td>
<td>[1,-1]</td>
<td>[-1,3]</td>
</tr>
</tbody>
</table>

(8) The electronic configuration of (final) and reactant (initial) states in the $I_i^{+1}$ for recombination between VBM and electron trap state:
(9) The electronic configuration of (final) and reactant (initial) states in the $I_{i}^{+1}$ for electron between CBM and the electron trap state: