Ab initio study of the role of iodine in the degradation of CH$_3$NH$_3$PbI$_3$

Linghai Zhang$^a$ and Patrick H.-L. Sit $^{a,1}$

$^a$School of Energy and Environment, City University of Hong Kong, Kowloon, Hong Kong S.A.R., China;

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 I$_2$ 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 I$_2$ adsorption energies on the perovskite surface (Figures 2a and 3a).

<table>
<thead>
<tr>
<th>Slab layers</th>
<th>Vacuum length (Å)</th>
<th>$E_{ads}$ (kcal/mol)</th>
<th>Slab layers</th>
<th>Vacuum length (Å)</th>
<th>$E_{ads}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>12</td>
<td>-29.7</td>
<td>2.5</td>
<td>12</td>
<td>-29.0</td>
</tr>
<tr>
<td>2.5</td>
<td>16</td>
<td>-29.8</td>
<td>2.5</td>
<td>16</td>
<td>-28.9</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>-29.1</td>
<td>3</td>
<td>12</td>
<td>-28.5</td>
</tr>
</tbody>
</table>

$^1$Corresponding Author, E-mail: patrick.h.sit@cityu.edu.hk, Phone: (852)34426709.
**Section SI2: Wannier Centers (WCs) of selected iodines for the structure in Figure 2e**

![Figure SI1](image1)

**Figure SI1** WC (shown as yellow spheres) for the structure in Figure 2e. Each WC represents two electrons for the spin-unpolarized calculation. The parentheses show the sum of WC for the selected iodines. The charge state of the iodine Iₐ is -1. The overall charge of the triiodide (Iₐ-Iₐ-Iₐ) is -1. The color codes for different atoms follow those in Figure 1. To distinguish different types of iodine ions, the iodine in I₂ 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](image2)

**Figure SI2** WC (shown as yellow spheres) for the structure in Figure 3e. Each WC represents two electrons for the spin-unpolarized calculation. The parentheses show the sum of WC for the selected iodine ions. The charge state of the Iₐ iodine is -1. The overall charge of the triiodide (Iₐ-Iₐ-Iₐ) is -1. The color codes for
different atoms follow those in Figure 1. To distinguish different types of iodine ions, the iodine in I₂ 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 Iₐ iodine is -1. The overall charge of the triiodide (Iₐ-Iₖ-Iₙ) is -1. The color codes for different atoms follow those in Figure 1. To distinguish different types of iodine ions, the iodine in I₂ 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 Iₐ iodine is -1. The overall charge of the triiodide (Iₐ-Iₐ-Iₐ) is -1. The color codes for different atoms follow those in Figure 1. To distinguish different types of iodines, the added I• radicals are green while the iodide ions in the pristine perovskite surfaces are purple.