Unveiling Roles of Halogen Ions in Surface Passivation of CsPbI$_3$ Perovskite Solar Cells

Shichuang Han, Li Guan*, Tao Yin, Jianen Zhang, Jianxin Guo, Xiaobo Chen§*, Xu Li*

† Key Laboratory of High-precision Computation and Application of Quantum Field Theory of Hebei Province, College of Physics Science and Technology, Hebei University, Baoding 071002, PR China
§ Department of Chemistry, University of Missouri – Kansas City, MO 64110, USA

Data availability. All data generated or analyzed during this study are included in this published article (and its Supplementary Information files). All relevant data are available from the authors.
Figure S1. (a). Comparison of absorption spectra for PbI₂ and CsI terminations of perovskites CsPbI₃ (001) surface. (b). The absorption spectra of perovskite film (PbI₂ terminations) with various slab thicknesses.

To maintain a stable CsPbI₃ structure, the chemical potentials of Cs, Pb, and I need
satisfy the thermodynamic equilibrium condition:

$$
\Delta \mu_{Cs} + \Delta \mu_{Pb} + 3\Delta \mu_{I} = \Delta H (CsPbI_3) 
$$  \hspace{1cm} (1)

$$
\Delta \mu_{Cs} + \Delta \mu_{I} < \Delta H (CsI) 
$$  \hspace{1cm} (2)

$$
\Delta \mu_{Pb} + 2\Delta \mu_{I} < \Delta H (PbI_2) 
$$  \hspace{1cm} (3)

where $\Delta H (CsPbI_3), \Delta H (CsI), \Delta H (PbI_2)$ are the formation enthalpy of CsPbI$_3$ CsI and PbI$_2$, respectively. $\mu_i$ represents the chemical potential of atom $i$ (i=Cs, Pb, I). Here $\mu_i = \mu_i^{\text{bulk}} + \Delta \mu_i$, where $\mu_i^{\text{bulk}}$ is the total energy of corresponding metal or molecule.

According to Eqs. (1)-(3), the chemical potential for stabilizing CsPbI$_3$ is determined in yellow area shown as Fig S2. There are three thermodynamic equilibrium conditions (Pb Pb-rich labeled as A, I-rich labeled as B and Moderate labeled as C) for calculating surface energy and formation energy. The used chemical potentials of Cs, Pb, I are shown in Table S2.

**Figure S2.** Chemical potential range for stable CsPbI$_3$. 

S3
Figure S3. Enlarged DOSs of defect-free (a) and defective (b) CsPbI$_3$ films.
Figure S4. Enlarged DOSs of defective CsPbI$_3$ films passivated by halogen ions F$^-$ (a), Cl$^-$ (b), and Br$^-$ (c).
Figure S5. Electronic band structures of uncoordinated Pb$^{2+}$ passivated by F$^-$. 
Figure S6. Difference charge density of perfect, defective and passivated systems. Isosurface level is 0.00385 e/bohr$^3$. 
Table S1. The Value of Chemical Potential in Different Conditions.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$\mu_{\text{Cs}}$ (eV)</th>
<th>$\mu_{\text{Pb}}$ (eV)</th>
<th>$\mu_{\text{I}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Pb-rich)</td>
<td>-3.14</td>
<td>-3.91</td>
<td>-2.60</td>
</tr>
<tr>
<td>B (I-rich)</td>
<td>-4.05</td>
<td>-5.79</td>
<td>-1.67</td>
</tr>
<tr>
<td>C (Moderate)</td>
<td>-3.26</td>
<td>-4.18</td>
<td>-2.47</td>
</tr>
</tbody>
</table>
### Table S2. Comparison between Experimental Data and the Calculated Effective Masses of Electrons and Holes, Reduced Mass, Static Dielectric Constant and Exciton Binding Energy of bulk CsPbI$_3$.

<table>
<thead>
<tr>
<th></th>
<th>PBE+SOC</th>
<th>Exp.$^{2,3}$</th>
<th>Theory$^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>GGA</td>
</tr>
<tr>
<td>$m_e^*(m_0)$</td>
<td>0.144</td>
<td></td>
<td>0.219</td>
</tr>
<tr>
<td>$m_h^*(m_0)$</td>
<td>0.186</td>
<td></td>
<td>0.190</td>
</tr>
<tr>
<td>$\mu(m_0)$</td>
<td>0.081</td>
<td></td>
<td>0.014-0.214</td>
</tr>
<tr>
<td>$\varepsilon_{\text{eff}}$</td>
<td>9.820</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>$E_b$(meV)</td>
<td>11.440</td>
<td></td>
<td>14-16, 21.2</td>
</tr>
</tbody>
</table>

### REFERENCES