Ab Initio Thermodynamic Study of PbI$_2$ and CH$_3$NH$_3$PbI$_3$ Surfaces in Reaction with CH$_3$NH$_2$ Gas for Perovskite Solar Cells

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Abstract

Hybrid organic-inorganic halide perovskites for photovoltaics have attracted research interest due to their unique material properties, but suffered from poor material stability. In this work, we investigated the surface phase diagrams of PbI$_2$ and cubic CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) for a better understanding of precursor effect on perovskite synthesis via solid-gas reaction, by density functional theory calculations combined with thermodynamics. Using the devised slab models of PbI$_2$(001) and MAPbI$_3$(100), (110) and (111) surfaces with perfect and various vacant defect terminations, we calculated their formation energies and adsorption energies of CH$_3$NH$_2$ molecule on the PbI$_2$(001) surfaces under different synthesis conditions of temperature, pressure and pH via chemical potentials of species. Our calculations revealed that the adsorption can be facilitated by including HI or NH$_3$I molecule by dissociation of this additive and formation of CH$_3$NH$_2^+$ cation or NH$_3$CH$_2$NH$_3^+$ complex, which is beneficial for conversion of PbI$_2$ to MAPbI$_3$ via solid-gas reaction. Furthermore, we found that among different perovskite MAPbI$_3$ surfaces, the MA-terminated (110) and MAI-terminated (100) surfaces are placed on the thermodynamically stable region of chemical potentials at pH values of 1 and 6, being agreed well with the experimental findings. We believe this work gives a fundamental understanding of solid-gas reaction for high-crystallinity perovskite synthesis towards perovskite solar cells with improved stability.

**Key words:** Methylammonium lead triiodide, Lead iodide, Methylamine, Surface, Phase diagram, Ab initio thermodynamics

1. Introduction

In the past decade, perovskite solar cells (PSCs) utilizing halide perovskites as photovoltaic materials have attracted significant attention in photovoltaic community [1, 2]. Compared with other solar cells, the power conversion efficiency of PSCs has been rapidly growing, so that the latest conversion efficiency has been already certified to be 25.5% [5], being over the record of single crystalline Si solar cells. Moreover, the fabrication cost is quite low due to the abundance of raw materials and facile synthesis method, highlighting their industrial potentiality and practicality [6, 7]. However, the long-term stability of PSCs was found to be poor [9, 10, 11, 12, 13], representing one of the challenges hindering their commercial utilization [14, 15]. This is originated from constituent materials such as perovskite photoabsorbers and electron-hole transporting materials (EHTMs) as well as device architecture. To address this challenging issue, there have been developed numerous technologies including materials composition engineering [16, 17, 18] and interface engineering [19, 20, 21, 22].

Advancing fabrication methods for halide perovskites is one of the key ways for enhancing stability of PSCs. In this line, Long et al. [23] developed a two-step nonstoichiometric acid-base reaction route to increase moisture resistivity, which includes a conversion from the precursor HPbI$_3$ to the perovskite CH$_3$NH$_3$PbI$_3$ (methylammonium lead tri-iodide; MAPbI$_3$) using excess methylamine (CH$_3$NH$_3$; MA$^+$) gas. Liu et al. [24] introduced a simple method to fabricate perovskite films with over 1μm thickness via a fast solid-gas reaction of chlorine-incorporated hydrogen lead triiodide HPbI$_3$(Cl) and MA$^+$ gas. Pang et al. [25] also reported the MA$^+$ gas-based fabrication method to induce the transformative evolution of ultrasmooth and full-coverage perovskite thin films from rough and partial-coverage HPbI$_3$ thin films. Therefore, the MA$^+$ gas treatment is regarded as an effectual process to produce a high-quality perovskite layer and improve its material stability.

In the meantime, as another approach to solve the long-term stability issue of PSCs, HTM-free carbon electrode-based PSCs have been envisioned, based on the consideration that the organic HTM, e.g., Spiro-OMeTAD, is one of main causes for chemical degradation of PSCs [26, 27, 28, 29, 30]. In these HTM-free PSCs, perovskite layer serves as hole transport layer as well as the photoabsorber, and thus the quality of perovskite layer is crucial to the performance. In addition to high-quality perovskite layer, MA$^+$ gas treating also improves the surface smoothness of perovskite layer on the thick TiO$_2$ mesoporous scaffold, which is directly associated with a better contact between the perovskite and carbon electrode layers in the carbon-based PSCs [31]. Wei et al. [27] introduced the MA$^+$ gas treatment process as the second step for converting precursor materials to the perovskite MAPbI$_3$ layer for printable carbon-based PSCs, demonstrating that among different precursors PbI$_2$+HI and HPbI$_3$+PbI$_2$+NH$_3$I yield a fast and perfect perovskite con-
soft pseudopotentials of constituent atoms were constructed using scalar relativistic version 6.2) package [32]. With additional consideration of diatomic molecules, MA \textsubscript{3} \textsubscript{I} \textsubscript{2}, including (100), (110) and (111) surfaces with different terminations, to investigate the effect of growth conditions, in particular, the partial pressure of MA \textsubscript{3} \textsubscript{I} \textsubscript{2} gas. This work gives a comprehensive understanding of solid-gas reaction process for organic-inorganic hybrid perovskites and thus paves the way for fabricating high-performance PSCs.

### 2. Methods

All calculations within density functional theory (DFT) framework were performed by using the pseudopotential plane-wave method as implemented in the Quantum ESPRESSO (QE, version 6.2) package [32]. With additional consideration of scalar relativistic effect for heavy I and Pb atoms, the ultra-soft pseudopotentials of constituent atoms were constructed using the LD1 code and input files from the PSlab library (version 1.0.0), where the electron configurations are Pb-5d\textsuperscript{10}6s\textsuperscript{2}6p\textsuperscript{2}, 1s\textsuperscript{2}2s\textsuperscript{2}2p\textsuperscript{6}, 2s\textsuperscript{2}2p\textsuperscript{6}. To account for the effect of van der Waals (vdW) interactions between the molecular moieties, we adopted the rev-vdW-DF2 exchange-correlation functional [33, 34, 35]. We set kinetic cutoff energies as 70 and 700 Ry for the wave function and electron density, and special k-point meshes as 6 × 6 × 6 and 2 × 2 × 1 for bulk and surface calculations, respectively. With these parameters, the total energy of bulk and formation energy of surface converged within 5 meV per atom and 5 mJ/m\textsuperscript{2}, respectively. All atoms were relaxed until the atomic forces converged within 5 meV per atom and 5 mJ/m\textsuperscript{2} for these slab models. For the defective surfaces and 15 Å-thick vacuum layer. When increasing the atomic layers from top layer in both sides were allowed to relax, while the middle three layers were fixed at their bulk positions. Then the surface free energy is calculated as follows:

\[
\gamma = \frac{1}{2A} \left[ E_{\text{slab}}[(\text{MAPbI}_3)_0\text{PbI}_2\text{MA}_3\text{I}_2] - \alpha \mu_{\text{PbI}} - \beta \mu_\text{Pb} - \delta \mu_\text{I} \right] \]

\[
\mu_{\text{PbI}} = E_{\text{PbI}} + \Delta \mu_{\text{PbI}},
\]

\[
\mu_\text{Pb} = E_{\text{Pb}} + \Delta \mu_\text{Pb}, \quad \mu_\text{I} = E_\text{I} + \Delta \mu_\text{I}.
\]

where \( \Delta \) is the surface area, \( E_{\text{slab}} \) is the total energy of “compound” in “phase”, and \( \mu_\text{spec} \) is the chemical potential of “species”. We consider thermodynamic constraints for the chemical potentials of Pb, I and PbI \textsubscript{2} based on the fact that the bulk PbI \textsubscript{2} material is in equilibrium state, as follows,

\[
\Delta \mu_\text{PbI} = 0, \quad \Delta \mu_\text{Pb} + 2\Delta \mu_\text{I} = \Delta H_{\text{PbI}},
\]

where \( \Delta H_{\text{PbI}} = E_{\text{PbI}} - E_{\text{Pb}} - 2E_\text{I} \) is the formation enthalpy of PbI \textsubscript{2} bulk in rhombohedral phase. Here, Pb bulk is in face-centered cubic (fcc) phase with space group \textit{Fm\textsubscript{3}m}, and I bulk in orthorhombic (orth) phase with space group \textit{Cmca}.

Given the relaxed clean surface models, we studied adsorption of MA \textsubscript{3} molecule on the surfaces in the presence of HI or NH \textsubscript{4}I molecule. After rough prediction of adsorption configuration, atomic relaxations were again performed and the adsorption energies were calculated using the total energies of supercells for the molecule-adsorbed surface, clean surface, and isolated molecule, respectively. The molecule was simulated using the cubic supercell with a cell length of 15 Å.

To investigate the effect of growth condition on the formation of MAPbI \textsubscript{3}, we also considered its surface with only low-indexes such as (100), (110) and (111) with different terminations using the slab models with \( 1 \times 1 \) surface unit cells, nine atomic layers and 15 Å thick vacuum layer. The surface formation energy per area is calculated as follows,

\[
\gamma = \frac{1}{2A} \left[ E_{\text{slab}}[(\text{MAPbI}_3)_0\text{PbI}_2\text{MA}_3\text{I}_2] - \alpha \mu_{\text{MAPbI}_3} - \beta \mu_\text{Pb} - \delta \mu_\text{I} - \eta \mu_{\text{MA}_3\text{I}_2} - \xi \mu_\text{H}_2 \right],
\]

\[
\mu_{\text{MAPbI}_3} = E_{\text{MAPbI}_3} + \Delta \mu_{\text{MAPbI}_3},
\]

\[
\mu_{\text{MA}_3\text{I}_2} = E_{\text{MA}_3\text{I}_2} + \Delta \mu_{\text{MA}_3\text{I}_2}, \quad \mu_\text{H}_2 = \frac{1}{2} E_{\text{H}_2} + \Delta \mu_\text{H}_2.
\]

Assuming that \( \Delta \mu_{\text{MAPbI}_3} = 0 \) and the compounds are under equilibrium, the thermodynamically stable condition for MAPbI \textsubscript{3} is expressed as,

\[
\Delta \mu_\text{Pb} + 3\Delta \mu_\text{I} + \Delta \mu_{\text{MA}_3\text{I}_2} + \Delta \mu_\text{H}_2 = \Delta H_{\text{MAPbI}_3},
\]

where \( \Delta H_{\text{MAPbI}_3} = E_{\text{MAPbI}_3} - E_{\text{Pb}} - 3E_\text{I} - E_{\text{MA}_3\text{I}_2} - \frac{1}{2} E_{\text{H}_2} \) is the formation enthalpy of MAPbI \textsubscript{3} bulk in cubic phase. Here, \( \Delta \mu < 0 \) must be satisfied to prevent the formation of simple substance in the conversion. Also, the competing binary or ternary compounds should not be formed, giving the constraints,

\[
\Delta \mu_\text{Pb} + 2\Delta \mu_\text{I} \leq \Delta H_{\text{PbI}},
\]

\[
\Delta \mu_{\text{MA}_3\text{I}_2} + \Delta \mu_\text{H}_2 \leq \Delta H_{\text{MA}_3\text{I}_2}.
\]
where $\Delta H_{\text{MAI}} = E_{\text{MAI}}^{\text{gas}} - E_{\text{MAI}}^{\text{sol}} - E_{\text{I}}^{\text{sol}}$ is the formation enthalpy of MAI bulk in cubic phase with space group $Pm$. To prevent the dissociation of MAPbI$_3$ into its constituents of PbI$_2$ and MAI, the following constraint must be satisfied,

$$\Delta H_{\text{MAPbI}_3} - \Delta H_{\text{MAI}} \leq 2 \Delta H_{\text{PbI}_2} \leq \Delta H_{\text{MAI}}.$$  (9)

The calculated total energies and formation enthalpies of all the compounds under study, with their phases, are given in Table S1 in the Supporting Information.

The chemical potential of MA$^0$ varies according to the partial pressure $P$ and temperature $T$ as follows,

$$\Delta \mu_{\text{MA}}(T, P) = \Delta \mu_{\text{MA}}(T, P^0) + k_B T \ln \frac{P}{P^0},$$  (10)

where $P^0$ is the atmospheric pressure and $k_B$ is the Boltzmann constant. We extracted the value of $\Delta \mu_{\text{MA}}(T, P^0)$ from the experimental data [36] as follows,

$$\Delta \mu_{\text{MA}}(T, P^0) \approx [H^0(T) - H^0(T_0)] + [H^0(T) - H^0(0)] - T S^0(T),$$  (11)

where $T_0$ = 298.15 K is the reference temperature, and $H^0$ and $S^0$ are the enthalpy and entropy measured at $P^0$ [37].

The presence of HI solution allows us to consider pH condition as the chemical potential of hydrogen $\Delta \mu_H$, as it is an inverse linear function of the pH value [38]. When $\Delta \mu_H$ reaches its maximum ($\Delta \mu_{\text{max}}^{\text{H}} = -E_{\text{H}}^{\text{gas}}$) or minimum ($\Delta \mu_{\text{min}}^{\text{H}} = E_{\text{OH}}^{\text{gas}} - E_{\text{H}}^{\text{gas}}$) according to $\mu_{\text{H},0} = \mu_{\text{H},+} + \mu_{\text{OH}},$ where $\mu_{\text{H},+} = \mu_{\text{H}}$ for simplification, the pH value will be 0 (acidic) or 14 (basic). Then, the pH value can be estimated by linear interpolation as pH = $14(\Delta \mu_H - \Delta \mu_{\text{max}}^{\text{H}})/(\Delta \mu_{\text{min}}^{\text{H}} - \Delta \mu_{\text{max}}^{\text{H}})$ [38].

3. Results and Discussion

3.1. Surface phase diagram of PbI$_2$ surface

We first calculated the lattice constants of bulk unit cells of PbI$_2$ and MAPbI$_3$ by optimization. The obtained lattice constants were $a = b = 4.572$ Å, $c = 7.018$ Å for PbI$_2$ and 6.337 Å for MAPbI$_3$, which agree well with their experimental values of $a = b = 4.558$ Å, $c = 6.986$ Å [39] and $a = 6.329$ Å [40], respectively (Figure 1). We also performed atomic relaxations of the isolated CH$_3$NH$_3$ molecule, for which the bond lengths are 1.101, 1.020 and 1.475 Å for C–H, N–H and C–N bonds in good agreement with the previous theoretical and experimental values of 1.093, 1.011 and 1.474 Å [41] (Figure S1). These indicate that the calculations undertaken here could provide reasonable description for the systems under study.

We then performed surface relaxations of PbI$_2$(001) surface slabs with 2×2 supercell and different terminations. We considered the two different terminations, i.e., I- and Pb-terminations, for which perfect and defective surfaces were constructed. The stoichiometric (perfect) I-terminated PbI$_2$(001) surface is characterized by type-2 according to the Tasker’s classification scheme [42], indicating that there is no net dipole moment perpendicular to the surface and therefore it can be easily formed from bulk as a stable surface without any reconstruction under vacuum condition. On the contrary, Pb-termination invokes the surface dipole moment, thereby making it difficult to create the surface. When the surface formation occurs under ambient condition in contact with its reservoirs such as iodine and lead crystal, various surface reconstructions

\[ \text{Figure 1: Polyhedral view of optimized bulk unit cells of rhombohedral PbI}_2 \text{ (left) and cubic CH}_3\text{NH}_3\text{PbI}_3 \text{ (right). Black, purple, brown, blue and white spheres denote Pb, I, C, N and H atoms, respectively.} \]
should be considered due to the interaction with them. Therefore, it is natural that the defective PbI$_2$(001) surfaces are expected to be formed at a certain condition given by the chemical potential of iodine. We considered one, two, and three I vacancies for I-terminated perfect surface, and the same number of Pb vacancies for Pb-terminated surface. In total, eight different models for the PbI$_2$(001) surface in contact with iodine crystal using 2×2 surface supercells were constructed in this work (see Figures S2 and S3 in the Supporting Information).

We computed the formation energies of these eight surfaces by applying Eqs. 1 and 2 (Figure 2a) presents the calculated phase diagram of the PbI$_2$(001) surface as a function of the iodine chemical potential. As expected above, the I-terminated perfect surface was found to have the lowest formation energy of 0.09 J/m$^2$ among the eight surfaces. At lower limit of iodine chemical potential under the I-poor/Pb-rich condition, which is ∼0.98 eV estimated from the bulk PbI$_2$ formation energy of −1.95 eV, the I-terminated V$_1$ defective surface has the second lowest formation energy of −0.45 J/m$^2$. In fact, creating I vacancies on the perfect I-terminated surface induces surface dipole moment and remarkable surface relaxation, which get more pronounced as increasing the number of I vacancies (see Figure S2), resulting in the increase of formation energy. On the other hand, under the I-rich/Pb-poor condition, the Pb-terminated 2V$_{Pb}$ defective surface was shown to be favorable for the formation, which is related with the fact that removing two Pb atoms recovers PbI$_2$ stoichiometry on the surface, thereby net-zero dipole moment. Figure 2b presents polyhedral view of these three relaxed surfaces, which will be used in further calculations for molecule adsorption.

3.2. CH$_3$NH$_2$ adsorption on PbI$_2$(001) surface

To simulate the initial process of MAPbI$_3$ perovskite formation via solid-gas reaction between PbI$_2$ solid and CH$_3$NH$_2$ gas [24, 25, 27], we investigated adsorption of CH$_3$NH$_2$ (MA$^0$) molecule on the PbI$_2$(001) surface. As aforementioned, the three types of surfaces with the lowest formation energies, i.e., I-terminated perfect, I-terminated V$_1$ defect, and Pb-terminated 2V$_{Pb}$ defective surfaces were used as substrates. We also appended a HI or NH$_3$ molecule as an additional adsorbate, since HI or NH$_3$ gas could be added to facilitate the reaction in experiment [27]. Two different surface cells of 1×1 and 2×2 were used for I-terminated perfect surface to consider different concentrations of adsorbate coverage.

For calculation of adsorption energy, we considered the enthalpy and entropy terms for MA$^0$ gas at finite temperature, while for solids only the DFT total energies were used because the both terms are in general 3~4 order smaller than the internal energy difference. For the MA$^0$ molecule adsorption, the adsorption energy can be calculated as follows,

$$E_{ads} = E_{surf-MA^0} - (E_{surf} + G_{MA^0})$$ (12)

where $E_{surf-MA^0}$ and $E_{surf}$ are the total energies of supercells for the MA$^0$-adsorbed surface and clean surface, respectively. The Gibbs free energy of MA$^0$ molecule in gas phase, $G_{MA^0}$, was obtained by applying Eqs. 10 and 11 using the DFT total energy as the internal energy and the experimental data for enthalpy and entropy terms from experimental data [26]. In the presence of HI or NH$_3$I, the adsorption energy was evaluated as,

$$E_{ads} = E_{surf-HI/NH_3I-MA^0} - (E_{surf} + E_{HI/NH_3I} + G_{MA^0})$$ (13)

where $E_{HI/NH_3I}$ is the total energy of the isolated HI or NH$_3$I molecule in supercell, simulating the aqueous solution. Table I presents the calculated adsorption energies of MA$^0$ molecule on the different types of PbI$_2$(001) surfaces without or with the presence of HI or NH$_3$I molecule at different temperatures of 0, 300 and 400 K.

Table 1: The calculated adsorption energies of CH$_3$NH$_2$ molecule on different types of PbI$_2$(001) surfaces without or with the presence of HI or NH$_3$I at different temperatures.

| Surface type | Additive | 0 K  | 300 K | 400 K |
|--------------|----------|-----|-------|-------|
| 1×1 I-term. perf. | HI       | −0.37 | 0.29 | 0.55 |
| 2×2 I-term. perf. | HI       | −1.08 | −0.42 | −0.16 |
| 2×2 I-term. V$_1$ | HI       | −1.00 | −0.34 | −0.08 |
| 2×2 Pb-term. 2V$_{Pb}$ | HI       | −1.45 | −0.78 | −0.52 |

The adsorption energy on the I-terminated perfect surface with 1×1 cell, i.e., with a coverage of 1ML, was calculated to be −0.37 eV at 0 K, indicating that the adsorption is exothermic. As temperature increases, the adsorption energy changed from being negative to positive (0.29, 0.55 eV at 300, 400 K), implying that the adsorption became endothermic over room temperature. The adsorption looks like being molecular through the weak hydrogen bond between H atom of amino group of MA$^0$ molecule and I atom of substrate surface (Figure S4), for which some amount of electrons are shown to be transferred from the molecule to the surface (Figure S4). When adding a HI molecule, the adsorption could occur more easily by seeing that the adsorption energy became lower as −0.42 eV at 0 K and negative even at higher temperatures (−0.42, −0.16 eV at 300, 400 K). For comparison, we also calculated the adsorption energy of only HI molecule on the same surface, which was 0.16 eV. During the adsorption, two-step chemical reactions were found to occur, i.e., dissociation of HI molecule and binding HI$^+$ to CH$_3$NH$_2$ molecule, forming CH$_3$NH$_3$I$^+$ cation (Figure S4), which can be a cause of lowering adsorption energy by adding HI molecule. This is consistent with the experimental finding that the conversion is significantly enhanced in the presence of H$^+$/I$^−$ or H−I group [27].

Then, we considered the adsorption of MA$^0$ molecule on the three types of PbI$_2$(001) surfaces with 2×2 surface cells (0.25 ML coverage), selected from the surface formation energy evaluation. The effect of HI and NH$_3$I inclusion was also considered. Figure 3 shows the relaxed geometries of MA$^0$ molecule.
without and with the presence of HI or NH₄I molecule adsorbed on the PbI₂(001) I-terminated perfect, I-terminated V₁ and Pb-terminated 2VPb defective surfaces. For the cases of only MA³⁺ molecule adsorptions, the adsorption energies were determined to be −0.03, −0.63 and −0.65 eV for the three types of surfaces in the same order to above text, indicating that the defective surfaces are more favorable to MA³⁺ adsorption than the perfect surface. As shown in Figure 3(a), the adsorptions occur through chemical bonding between N atom and surface Pb atom with N–Pb bond lengths of 2.66 and 2.73 Å for I-terminated perfect and defect surfaces, which is confirmed by electron transfer from adsorbate to the Pb atom upon adsorption. For the Pb-terminated defective surface, no explicit binding was observed. As increasing temperature, the adsorption energies became positive like 0.64, 0.03, 0.02 eV at 300 K, and 0.90, 0.29, 0.25 eV at 400 K for the three types of surfaces, respectively.

When adding a HI or NH₄I molecule, the adsorption energies were found to be lower for all the cases, indicating easier conversion by this additive. For the I-terminated surfaces, the HI addition has slightly enhanced effect than NH₄I due to lower adsorption energies in the former cases (−1.00, −1.67 eV) than those in the latter cases (−0.84, −1.45 eV). Meanwhile, NH₄I addition (−3.36 eV) is more favorable to MA³⁺ adsorption than HI one (−3.25 eV) for the Pb-terminated defective surface.

Moreover, it was found that the defective surfaces are preferable to the perfect surface, and the Pb-terminated 2VPb defective surface is the most desirable for adsorption. To understand the underlying mechanism, we provide the analysis of optimized geometries with electronic charge redistribution. As shown in Figure 3(b), the dissociation of HI in the case of MA³⁺ + HI adsorption, HI was dissociated into H⁺ and I⁻ ions, of which the H⁺ cation was bonded with N atom to form CH₃NH⁺⁺ cation and I⁻ anion was combined with the PbI₅ polyhedron. For the I-terminated V₁ surface, the dissociated I⁻ anion occupied the I-vacant site of the PbI₅ polyhedron to recover the PbI₆ octahedron, while for the perfect surface the abnormal PbI₇ polyhedron was formed (Figure S5), thereby implying that the defective surface is preferable. For the Pb-terminated 2VPb surface, the additional I⁻ anion leads to forming a pair of face-sharing PbI₅ square pyramids (Figure S5), which are connected each other via corner-sharing and thus are relatively stable. The newly formed MA⁺⁺ cation was strongly bound to the surface through hydrogen bonds with H–I bond lengths ranging from 2.48 to 2.67 Å.

Similar findings were obtained for the NH₄I addition. That is, the NH₄⁺ I was dissociated into NH⁴⁺ and I⁻ ions, which were bound with MA³⁺ through the weak hydrogen bond (bond length spans from 1.57 to 1.72 Å) and PbI₅, respectively. Since the dissociation of NH₄I is likely to occur more hardly than that of HI...
and the binding of NH$_4$-CH$_3$NH$_2$ is relatively weak, the effect of NH$_4$I is slightly weaker than HI. For the case of I-terminated V$_1$ surface, the I$^-$ ion is not recovering PbI$_2$ octahedron due to the strong interaction from NH$_4^+$ (Figure 3(a) and Figure S6), resulting in slightly higher adsorption energy (Table 1). Meanwhile, similar configuration of substrate surface was found for the Pb-terminated defective surface, while enhanced interaction between adsorbate and substrate was observed, resulting in lowering the adsorption energy compared with that by HI addition. These findings indicate that both HI and NH$_4$I play a positive role in synthesizing MAPbI$_3$ from PbI$_2$ precursor by combining with the surface Pb atom with I$^-$ and helping MA$^0$ gas adsorption on that with either H$^+$ or NH$_4^+$ cation. It is now confirmed that the higher crystallinity and superior morphology of MAPbI$_3$ layer synthesized from NH$_4$I-PbI$_2$ precursor, reported in Ref. [27], is attributed to the slow conversion process including the release of NH$_3$ gas.

3.3. Surface phase diagram of MAPbI$_3$ surface

As the next stage of calculation, we investigated the phase diagram of MAPbI$_3$ surface under consideration of the different synthesis conditions, which helps understanding of PbI$_2$ conversion to MAPbI$_3$. To do this, we evaluated the surface formation energies of the low-index MAPbI$_3$ surfaces with various terminations by using Eq. 4 as varying the chemical potentials of MA$^0$ ($\Delta \mu_{MA^0}$) and H ($\Delta \mu_H$) species. The range of $\Delta \mu_{MA^0}$ was confined by Eq. 9, giving the relative temperature and pressure conditions by Eq. 10 while $\Delta \mu_H$ was controlled to give the pH value between 0 and 14. For the representative values of pH, we took the two points of pH $= 1$ and 6, correspondingly $\Delta \mu_H = -0.26$ and $-1.57$ eV (Table S3), reflecting that the hydroiodic (HI) solution used in the synthesis experiment is strongly acidic. With these two values of $\Delta \mu_H$ and the calculated formation enthalpies of the relevant compounds, we determined the lower limits of $\Delta \mu_{MA^0}$ as $-3.84$ and $-2.53$ eV at pH $= 1$ and 6, respectively. In the same way, the lower limits of iodine chemical potential $\Delta \mu_I$ were determined to be $-1.28$ and $-0.84$ eV at these pH values.

With the calculated formation enthalpies of MAPbI$_3$, PbI$_2$ and MAI ($-4.10$, $-1.96$, $-1.92$ eV in Table S1), the chemical potentials of MA$^0$ and I for stable MAPbI$_3$ satisfying Eqs. 7-9 were determined, as shown with the yellow-colored regions in Figure 3(a) and 3(b) for pH $= 1$ and 6, respectively. The left red- and right blue-colored oblique lines indicate the borders for bulk PbI$_2$ and MAI formations, respectively. The bottom axes show the partial pressure of MA$^0$ gas converted from its chemical potential at temperatures of 300 and 400 K by using Eqs. 10 and 11 (Table S2). The narrow shape of the stable region is consistent with the previous calculations regarding the formation of MAPbI$_3$ from the reaction of MAI and PbI$_2$. [33] [43]. It was found that the chemical potential range for equilibrium growth condition of MAPbI$_3$ bulk is more confined in the case of pH $= 6$ than that of pH $= 1$, indicating that lower pH condition is more favorable for synthesis of MAPbI$_3$. In addition, we found that for the stable region of chemical potentials the partial pressure of MA$^0$ gas ($P_{MA^0}$) should be lower than 1 atm at pH $= 1$ while should be higher at pH $= 6$.

The morphology of perovskite surface and interface is modified according to the growth condition, which plays a decisive role in photovoltaic performance of PCs. In this sense, we drew the surface phase diagram of cubic MAPbI$_3$ by calculating formation energies of low-index (100), (110) and (111) surfaces with different terminations under aforementioned growth conditions. We applied two different terminations for the (100)
surface, i.e., (100)-PbI$_2$ and (100)-MAI, both of which are type 1 surfaces with equal anions and cations on each plane according to the Tasker’s classification [42]. For the (110) surface, the charged planes stacking alternately produce a dipole moment perpendicular to the surface (type 3), and thus we consider not only two types of typical terminations, (110)-MAPbI and (110)-PbI, but also substantially reconstructed surfaces for stabilization, (110)-I$_2$ and (110)-MA. The (111) surface also shows a type 3 stacking sequence, and in the same way, ideal surfaces of (111)-MAI$_3$ and (111)-Pb along with the modified (111)-I surface were treated in this work. Figure 5 depicts the different terminations of these low-index surfaces. To avoid a probable failure in supercell calculations by net dipole moment, we used symmetric slab supercells with the top and bottom surfaces with the same terminations (Figure S7).

Figure 6(a) and 6(b) present the three-dimensional graphs showing the surface formation energies of the nine surfaces calculated at the chemical potential ranges of MA$^0$ and I species under pH = 1 and 6 conditions, respectively. When projecting them onto the $\Delta \mu_{\text{MA}^0}$-$\Delta \mu_{\text{I}}$ plane shown in Figure 4, two terminated surfaces appeared as stable ones on the plane for each index surface (Figure S8). In the case of (100) surface, the MAI-terminated surface is stable at the MA$^0$-rich condition, while PbI$_2$-terminates one is stable at the MA$^0$-poor condition. The thermodynamically stable chemical potential range for the equilibrium growth of MAPbI$_3$ (the yellow region in Figure 4) is occupied by the MAI-terminated surface, indicating that this type of surface is a dominant one [Figure S8(a)]. The same result was observed at both pH values, but at pH = 6 condition the PbI$_2$-terminated surface appeared further away from the thermodynamically stable region compared with the case of pH = 1. Among the four terminations of the (110) plane, the MA- and PbI-terminated surfaces are the ground states in the whole chemical potential range. At both pH values, i.e., for the entire acidic condition range, the MA-terminated surface occupies fully the stable region. At pH = 1, the (110)-PbI surface is closer to the stable region, indicating that this type of surface might be more probable at low pH conditions than high pH conditions. Meanwhile, the MAPbI- and I$_2$-terminated (110) surfaces have higher formation energies, indicating that these types of surfaces are not likely to appear in synthesized samples, which is consistent with the expectation that these surfaces would be unstable due to being polar. Similarly, for the (111) surfaces, the polar Pb-terminated surface does not appear on the triangle, but I- and MAI$_3$-terminated surfaces appear. At pH = 1, the reconstructed I-terminated surface is mostly placed on the stable region, whereas at pH = 6 MAI$_3$-terminated surface occupies the most part of the stable region.

By combining these, we drew the phase diagram of MAPbI$_3$ surfaces projected onto $\Delta \mu_{\text{MA}^0}$-$\Delta \mu_{\text{I}}$ triangle, as shown in Figure 6(c) and 6(d) at pH = 1 and 6, respectively. The chemical potential triangles were found to be occupied by (110)-PbI,
Table 2: The calculated surface formation energies for all types of surfaces considered in this work under MA\(^{0}\)-poor/I-rich (point A and C) and MA\(^{0}\)-rich/I-poor (point B and D) conditions at pH = 1 (A, B) and 6 (C, D).

| Type           | Surface formation energy \(\gamma\) (J/m\(^2\)) |
|----------------|-----------------------------------------------|
| (100)-PbI\(_2\) | 0.26 0.31 0.29 0.29 |
| (100)-MAI       | 0.16 0.12 0.13 0.13 |
| (110)-MAPbI     | 0.77 0.46 0.77 0.65 |
| (110)-I\(_2\)   | 0.30 0.61 0.30 0.42 |
| (110)-MA        | 0.16 0.10 0.12 0.12 |
| (110)-PbI       | 0.33 0.39 0.37 0.37 |
| (111)-Pb        | 0.79 0.56 0.81 0.71 |
| (111)-MAI       | 0.36 0.59 0.34 0.44 |
| (111)-I         | 0.39 0.42 0.41 0.41 |

We finally analyzed the electronic states of the (110)-MA, (100)-MAI, (110)-PbI, (100)-PbI\(_2\), (110)-MAI, and (110)-MA surfaces in the order of \(\Delta G_{MAI}\) increasing. The thermodynamically stable regions for equilibrium growth of cubic MAPbI\(_3\) crystal, with a shape of narrow trapezoid bordered by red and blue oblique lines, were occupied by (100)-MAI and (110)-MA surfaces for pH = 1, while occupied by only (110)-MA surface for pH = 6. As shown in Figure 5(c), the (110)-MA and (100)-MAI surfaces coexist on the thermodynamically stable region under pH = 1 condition, indicating the predominance of these surfaces in MAPbI\(_3\) perovskite fabricated from MA\(^{0}\) gas-PbI\(_2\) solid reaction. On the contrary, at pH = 6, only the (110)-MA surface was found on the whole range of stable region, which is consistent with X-ray diffraction patterns of MAPbI\(_3\) films synthesized from MA\(^{0}\)-based reaction route [23]. It should be noted that the (100)-PbI\(_2\) surface is not so far from the thermodynamically stable range and (110)-PbI surface is stable at only MA\(^{0}\)-poor condition being far away from that range. Table 2 summarizes the calculated surface formation energies of the nine MAPbI\(_3\) surfaces at different points shown in Figure 4 including A (\(\Delta G_{MAI} = -1.88\), \(\Delta G_0 = 0\), \(\Delta G_{Pb} = -1.95\) eV), B (\(\Delta G_{MAI} = -0.58\), \(\Delta G_0 = -1.09\), \(\Delta G_{Pb} = 0\) eV), C (\(\Delta G_{MAI} = -0.42\), \(\Delta G_0 = -2.11\) eV) and D (\(\Delta G_{MAI} = 0\), \(\Delta G_0 = -0.42\), \(\Delta G_{Pb} = -1.27\) eV). In accordance with the phase diagram, the (110)-MA and (100)-MAI surfaces have the lowest formation energies of 0.10-0.16 J/m\(^2\) at the four points, then the (100)-PbI\(_2\) surface with 0.26-0.31 J/m\(^2\), and the (110)-PbI surface with 0.33-0.39 J/m\(^2\).

4. Conclusions

In this work, we have systematically investigated PbI\(_2\) and cubic MAPbI\(_3\) surfaces by using combined density functional theory and thermodynamic calculations, aiming at a better understanding of precursor effect on perovskite synthesis via solid-gas reaction. We devised the slab models of PbI\(_2\)(001) and MAPbI\(_3\)(100), (110) and (111) surfaces with perfect and various vacant defect terminations, and calculated their formation energies and adsorption energies of \(\text{CH}_3\text{NH}_3\) molecule on the PbI\(_2\) surfaces under different synthesis conditions of temperature, pressure and pH through chemical potentials of species. We revealed that the adsorption of \(\text{CH}_3\text{NH}_3\) molecule can be facilitated by including HI or \(\text{NH}_4\)I molecule due to lowering adsorption energies and their being negative even at 300 or 400 K through dissociation of this additive and formation of \(\text{CH}_3\text{NH}_3^+\) cation or \(\text{NH}_4^+\) complex, which is advantageous for conversion of PbI\(_2\) to MAPbI\(_3\) via solid-gas reaction. Moreover, it was found that among nine different types of the MAPbI\(_3\) low-index surfaces, the MA-terminated (110) and MAI-terminated (100) surfaces occupy the thermodynamically stable region for equilibrium synthesis of bulk MAPbI\(_3\) at pH = 1 and 6, being agreed well with the experimental findings. This work can provide a fundamental understanding of solid-gas reaction for high-crystallinity perovskite synthesis towards high performance perovskite solar cells.

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