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Electronic Supplementary Information (ESI) for

Fast Self-Diffusion of Ions in $CH_3NH_3PbI_3$: the Interstiticaly Mechanism versus Vacancy-Assisted Mechanism

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1. Calculation Methods for Defect Properties

To determine the defect formation energies and defect transition energy levels, we used the total energy $E(\alpha,q)$ for the supercell in Fig. 1 containing the relaxed defect α in its charge state q and the total energy $E(MAPbI_3)$ for the same supercell in the absence of the defect. The defect formation energy $\Delta H_f\,(\alpha,q)$ as a function of the electron Fermi level E_F and the atomic chemical potentials μ_i is given by:

$$\Delta H_f(\alpha,q) = \Delta E(\alpha,q) + \sum n_i\mu_i + qE_F\ , \quad (1)$$

where $\Delta E(\alpha,q) = E(\alpha,q) - E(MAPbI_3) + n_iE(i) + qE_{VBM}$, E_F is referenced to the valence band maximum (VBM) of perfect MAPbI$_3$, and μ_i is the chemical potential of constituent i referenced to elemental solid or gas with energy $E(i)$. Here, the chemical potential of MA is referenced to a quasi-bcc artificial structure constituent of CH$_3$NH$_3$ similar to bulk Cs, the chemical potential of I is referenced to I$_2$ solid phase with a Cmca symmetry, the chemical potential of Pb is referenced to the fcc Pb solid phase. Their calculated total energies of these bulks are list in Table S1 with spin-polarization and van der waals interactions considered. The $n's$ are the numbers of atoms taken out of the supercell to form the defects, and q is the number of electrons transferred from the supercell to the Fermi reservoirs in forming the defect cell. The defect transition energy level $\varepsilon_\alpha(q/q')$ is the Fermi level E_F in Eq. (2) at which the formation energy $\Delta H_f\,(\alpha,q)$ of defect α at charge q is equal to that of the same defect at another charge state q', i.e.,

$$\varepsilon_\alpha(q/q') = [\Delta E(\alpha,q) - \Delta E(\alpha,q')]/(q' - q). \quad (2)$$

The core level correction, band filling correction, and image charge correction are explicitly taken into consideration.

Under equilibrium growth conditions, the chemical potential μ_i should satisfy the following conditions to avoid the formation of second phases such as MAI, PbI$_2$, and elemental solids:

$$\mu_{MA} + \mu_{Pb} + 3\mu_I = \Delta H_f(MAPbI_3) =- 4.46\ eV\ , \quad (S1)$$

$$\mu_{Pb} + 2\mu_I < \Delta H_f(PbI_2) =- 1.65\ eV, \quad (S2)$$

$$\mu_{MA} + \mu_I < \Delta H_f(MAI) =- 2.92\ eV \quad (S3)$$

$$\mu_{MA} < 0\ eV, \mu_I < 0\ eV, \mu_{Pb} < 0\ eV\ . \quad (S4)$$

Where $\Delta H_f(MAPbI_3)$ is the formation enthalpy of $MAPbI_3$ defined as the total energy difference $\Delta H_f(MAPbI_3) = E(MAPbI_3) - E(MA) - E(Pb) - 3E(I)$, $\Delta H_f(PbI_2)$ the formation enthalpy of PbI_2 defined as the total energy difference $\Delta H_f(PbI_2) = E(PbI_2) - E(Pb) - 2E(I)$, and $\Delta H_f(MAI)$ the formation enthalpy of MAI defined as the total energy difference $\Delta H_f(MAI) = E(MAI) - E(MA) - E(I)$. Here we used cubic NaCl structure for MAI containing 4 formulas. The orientation of organic molecules is carefully considered and its effect on the total energy of MAI is less than 4 meV/formula. For PbI_2, we used a layered hexagonal structure. Note that, the intrinsic stability of $MAPbI_3$ against decomposition into MAI and PbI_2 has nothing to do with the choice of the elemental phases but only depends on the choice of MAI and PbI_2. Our calculated total energies of PbI_2, MAI, and elemental energies are in good agreement with those in Ref. 19 of the main text. However, our calculation suggests that tetragonal $MAPbI_3$ is intrinsically unstable because the decomposition is always energetically favorable, i.e., $E(MAPbI_3) - E(MAI) - E(PbI_2) =$ 0.10 eV, which is in agreement with the conclusion of Ref. 48 in the main text. As a result, non-equilibrium growth conditions have to be considered to get the defect formation energies, as discussed in the main text.

Table S1. Calculated total energies of involved components. Energy is given in unit of eV/atom or eV/formula.

Phase	I	Pb	MA	MAI	PbI2	MAPbI3
Energy	-1.71	-3.57	-37.75	-42.38	-8.66	-50.92

2. V_I^- diffusion

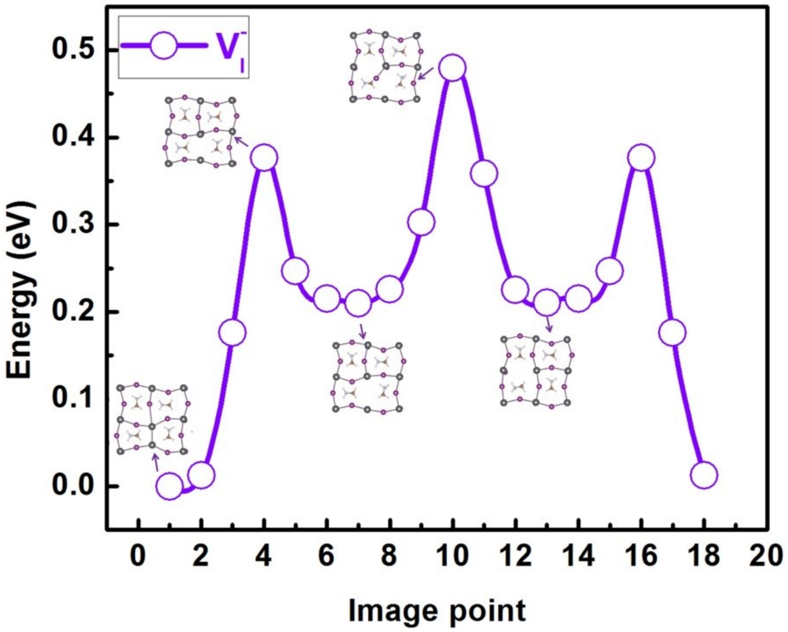

Fig. S1. Calculated diffusion path for V_I^-. Atomic configurations for structures of V_I^- at local energy minimum points and at saddle point are shown in the insets for better understanding the diffusion process.

3. Effect of organic molecule orientation on diffusion barriers

To study the effect of organic molecule orientation on diffusion barriers, we also used Fig. 1(b) structure to calculate the diffusion barriers for V_{MA}^{-}, MA_{i}^{+}, V_{I}^{+}, and I_{i}^{-}. As shown in Fig. S2, the barrier values are 0.57 eV, 0.28 eV, 0.38 eV, and 0.20 eV for the diffusion of V_{MA}^{-}, MA_{i}^{+}, V_{I}^{+}, and I_{i}^{-}, respectively, when organic molecules are antiferroelectrically aligned.

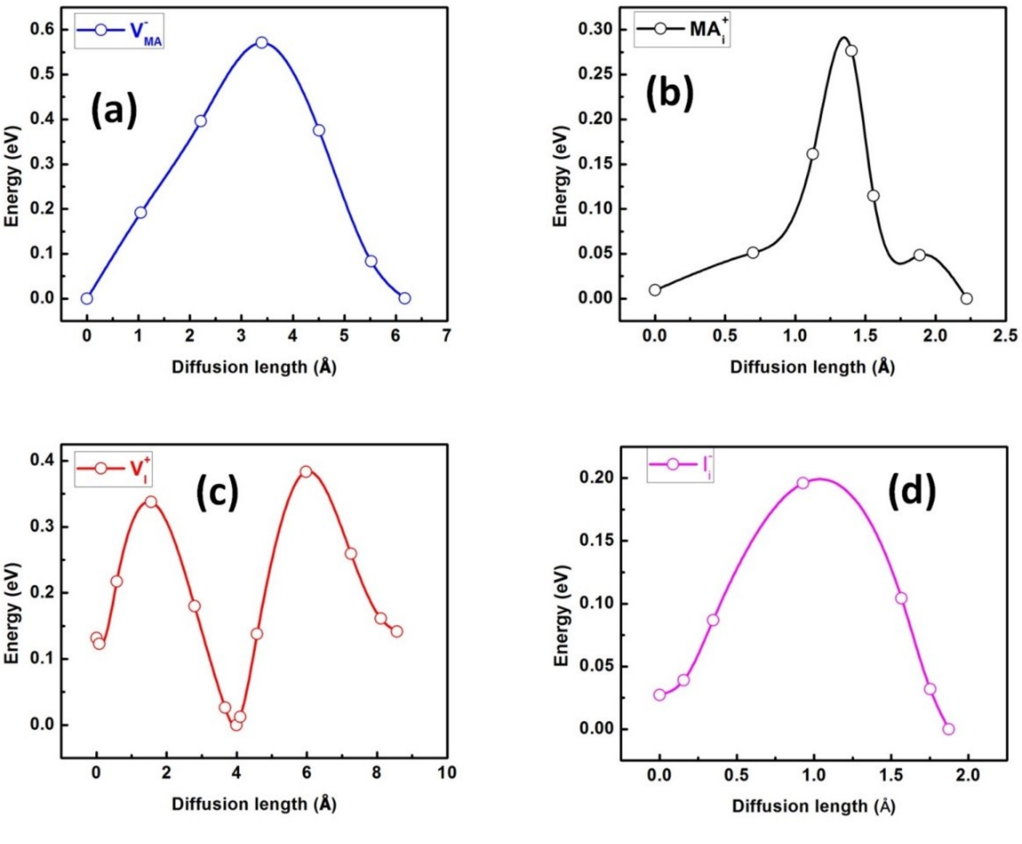

Fig. S2. Calculated diffusion paths for (a) V_{MA}^{-}, (b) MA_{i}^{+}, (c) V_{I}^{+} and (d) I_{i}^{-} when organic molecules are antiferroelectrically aligned.

4. Effect of number of image points on the calculated diffusion barriers

To make sure our calculated energy barriers are well converged using 5 image points, we did a test using 8 image points to check the change of the diffusion barrier of MA interstitials. As shown in Fig. S3, the energy barrier is 0.21 eV, compared to 0.24 eV using five image point in the main text. The results are well converged within 0.05 eV.

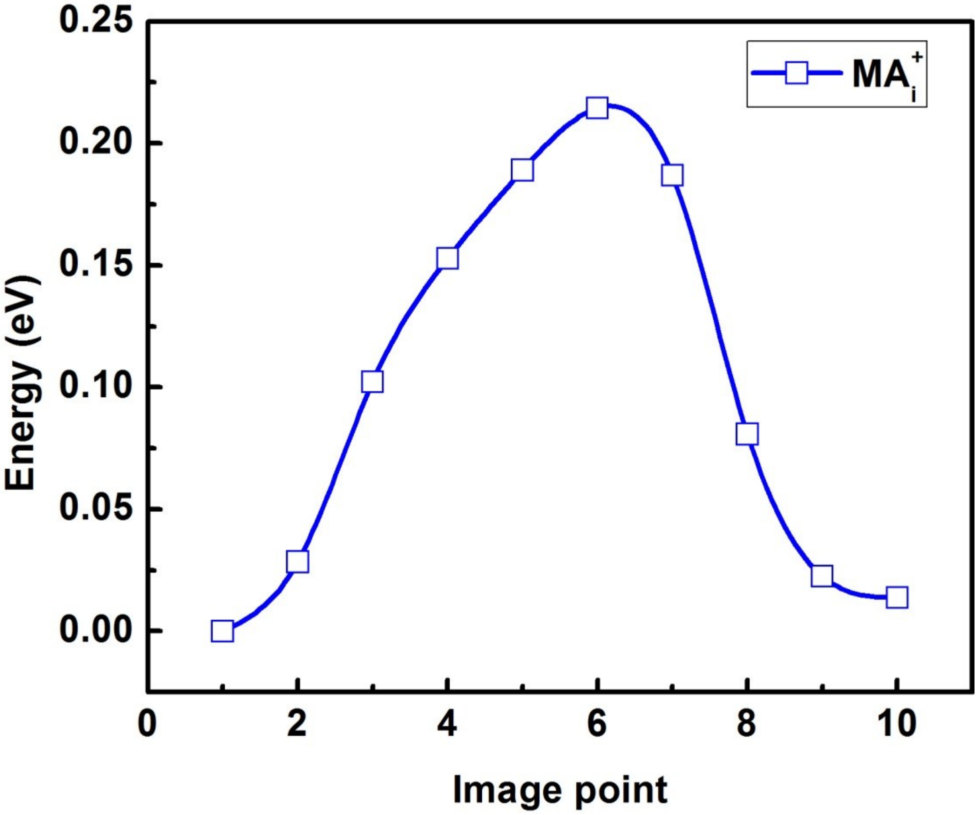

Fig. S3. Calculated diffusion barrier of MA_i^+ using 8 image points.