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Moisture Effect on the Structures and Properties of Lead Halide Perovskites: A First-principles Theoretical Investigation

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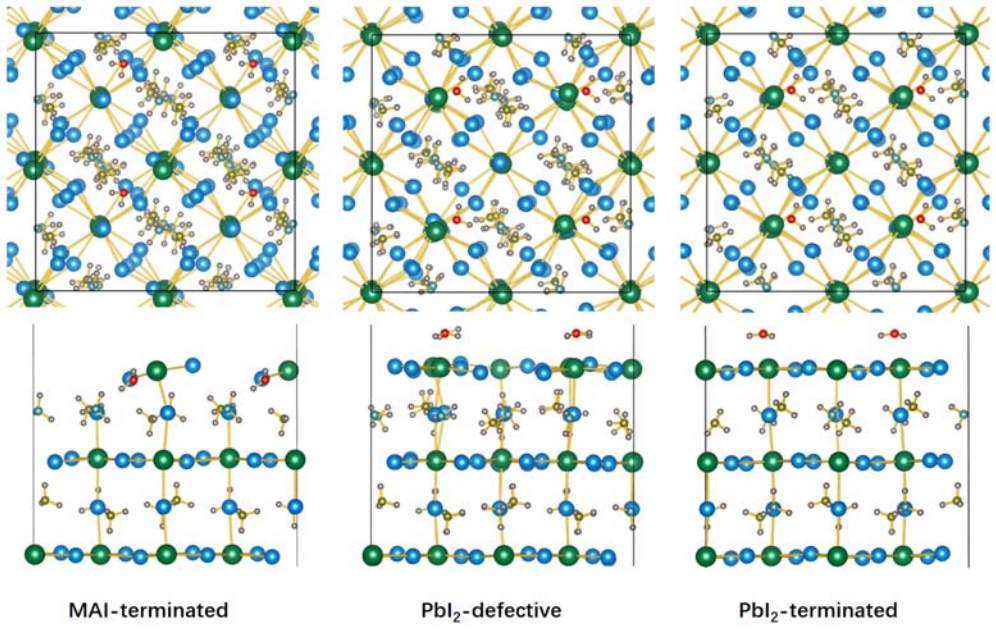

Figure S1. MAI-terminated, PbI_2-defective and PbI_2-terminated surfaces absorbing four water molecules of $MAPbI_3$ perovskite.(top and lateral views) The green, blue and red balls denote the Pb, I and O atoms, respectively.

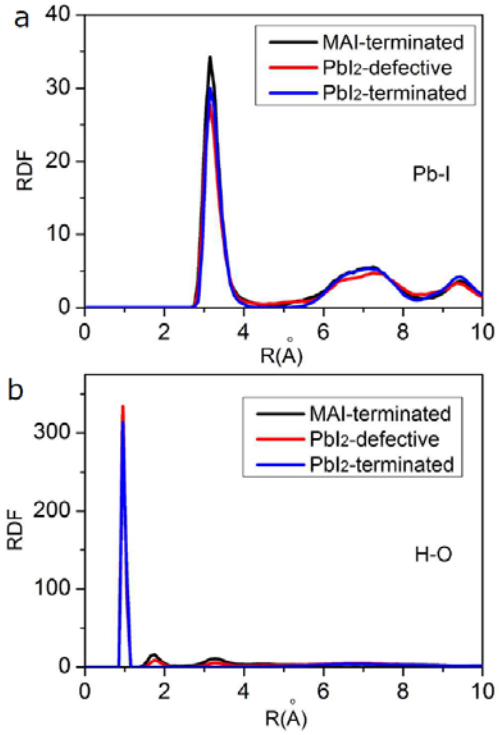

Figure S2. RDFs of Pb-I and H-O pairs of the "sur" components of MAI-terminated, PbI_2-defective and PbI_2-terminated surfaces absorbing water molecules.

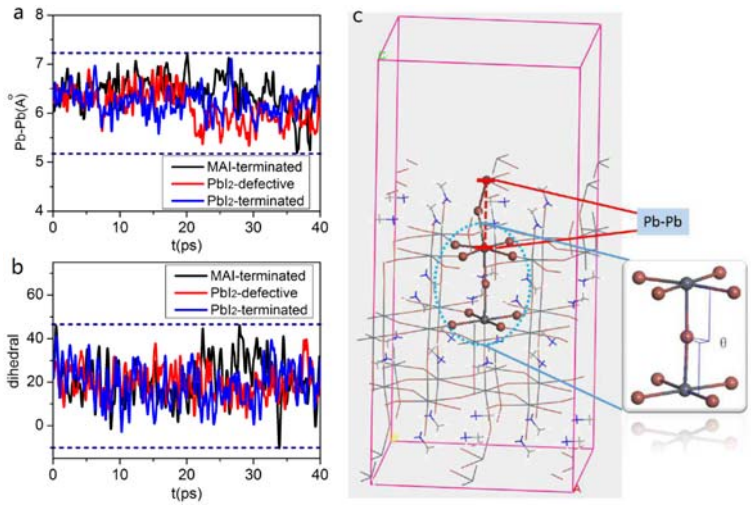

Figure S3. (a)Evolution of Pb-Pb distances for the three surfaces under the interaction of water molecules.(b) Evolution of Pb-Pb dihedral for the three surfaces under the interaction of water molecules. (c) The Pb-Pb distance and dihedral are selected in MAI-terminated slab as an example.

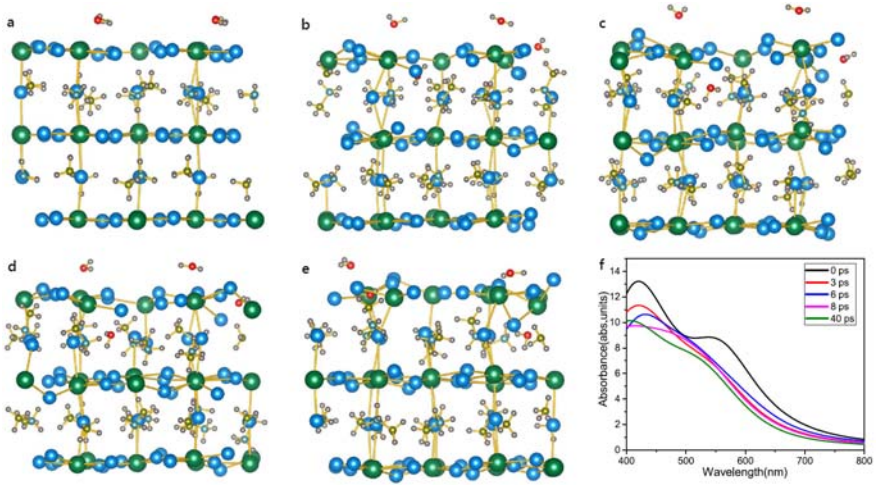

Figure S4. (a∼e) The hydrate slabs with PbI_2-detective surface containing four water molecules at 0, 3, 6, 8, and 40 ps simulated time, respectively. (f) Calculated optical absorption spectra of the corresponding slabs at different simulated times. The green, blue and red balls denote the Pb, I and O atoms, respectively.

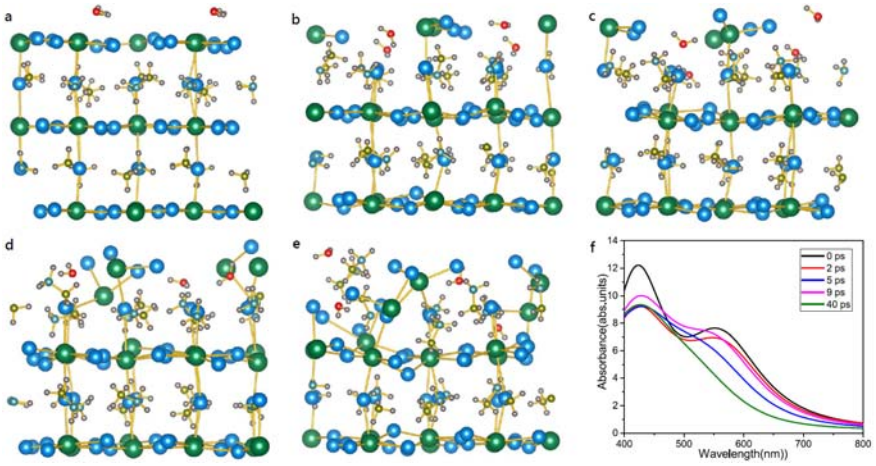

Figure S5. (a∼e) The hydrate slabs with MAI-terminated surface containing four water molecules at 0, 2, 5, 9, and 40 ps simulated time, respectively. (f) Calculated optical absorbance spectra of the corresponding slabs at different simulated times. The green, blue and red balls denote the Pb, I and O atoms, respectively.

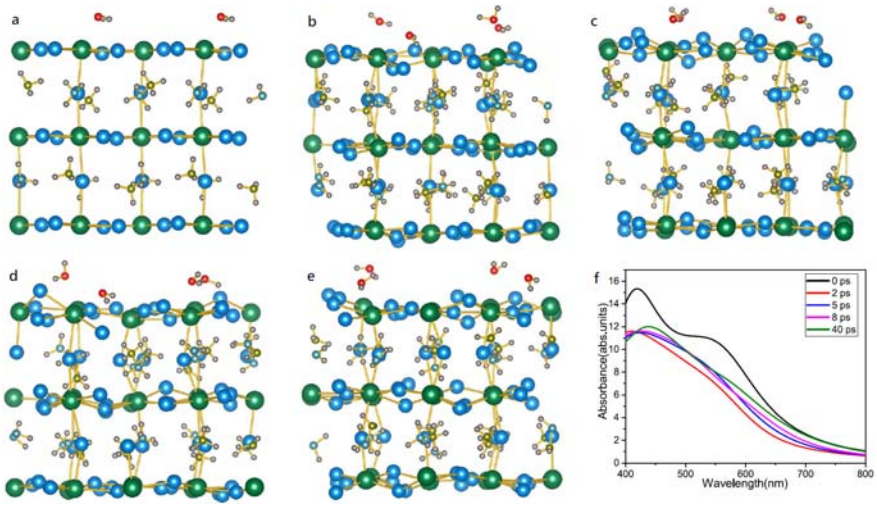

Figure S6. (a∼e) The hydrate slabs with PbI_2-terminated surface containing four water molecules at 0, 2, 5, 8, and 40 ps simulated time, respectively. (f) Calculated optical absorbance spectra of the corresponding slabs at different simulated times. The green, blue and red balls denote the Pb, I and O atoms, respectively.

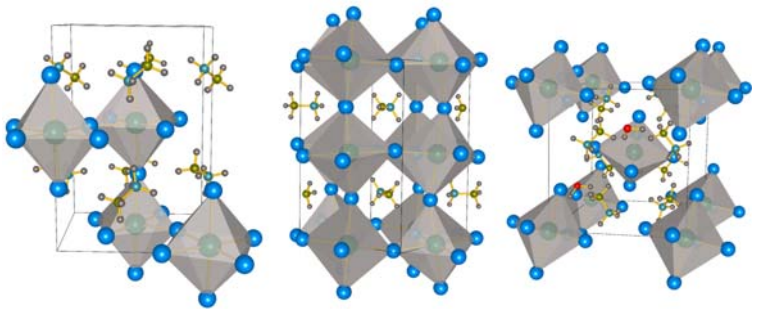

Figure S7. The unit cells of I4cm (left), Pnma (middle) phases and $MA_4PbI_6{\cdot}2H_2O$ (right), respectively. The green, blue and red balls denote the Pb, I and O atoms, respectively.

Table S1. The calculated and experimentally-measured lattice constants of β-phase, γ-phase $MAPbI_3$, and $MA_4PbI_6{\cdot}2H_2O$ crystal.

	Expt.			Calc.		
	β-phase	γ-phase	$MA_4PbI_6{\cdot}2H_2O$	β-phase	γ-phase	$MA_4PbI_6{\cdot}2H_2O$
crystal system	tetragonal	orthorhombic	monoclinic			
space group	I4cm	Pnma	P21/N			
unit cell	a=8.929Å		a=10.421Å	a=8.900Å	a=9.093Å	a=10.421Å
	α=90.00°		α=90.00°	α=90.00°	α=90.00°	α=90.00°
	b=8.929Å		b=11.334Å	b=8.922Å	b=12.807Å	b=11.334Å
	β=90.00°		β=91.73°	β=90.00°	β=90.00°	β=91.73°
	c=12.688Å		c=10.668Å	c=12.962Å	c=8.578Å	c=10.668Å
	γ=90.00°		γ=90.00°	γ=90.00°	γ=90.06°	γ=90.00°
volume	1011.58Å^3		1259.44Å^3	1029.16Å^3	999.01Å^3	1259.44Å^3

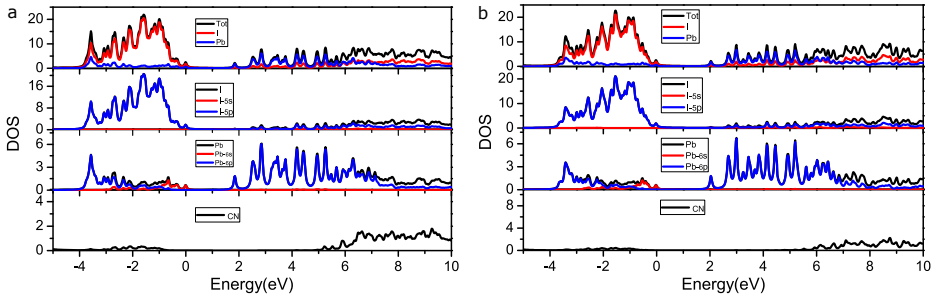

Figure S8. Computed DOS and PDOS for (a) I4cm-, (b) Pnma-phase perovskites, respectively. The Fermi level is set to zero.

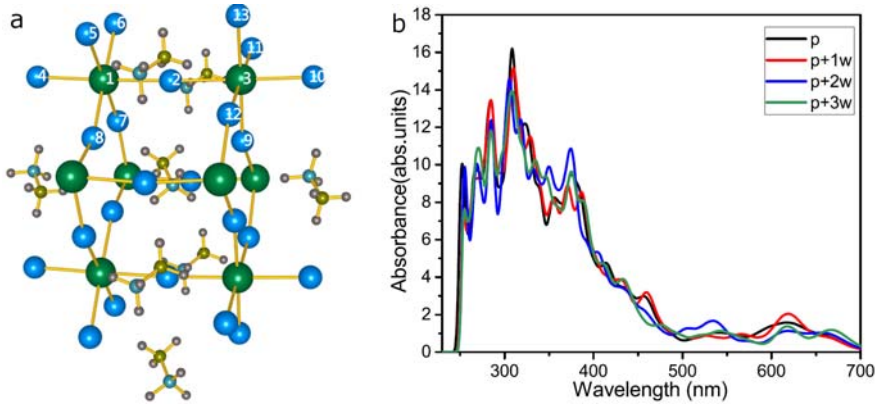

Figure S9. (a) Atomic labels of $(CH_3NH_3PbI_3)_8$ cluster. (b) The absorption spectra for $(CH_3NH_3PbI_3)_8$ and $(CH_3NH_3PbI_3)_8{\cdot}nH_2O$ clusters. The green and blue balls denote the Pb, and I atoms, respectively.

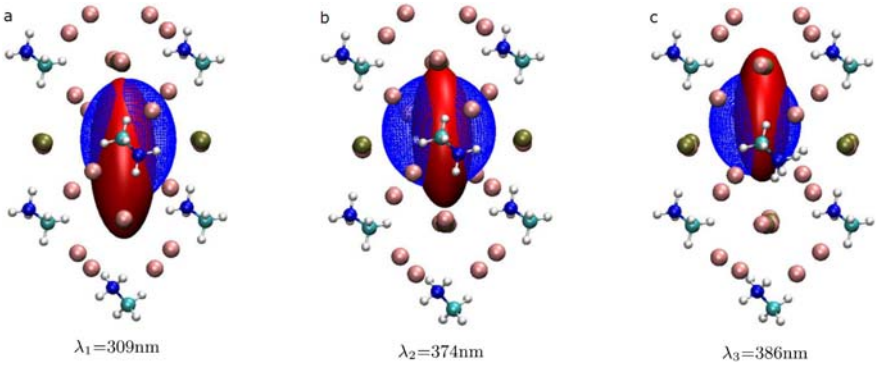

Figure S10. Electron density differences between the excited states and ground state for $(CH_3NH_3PbI_3)_8$ cluster. Red isosurfaces represent electron density decreases while blue ones represent electron density increases.

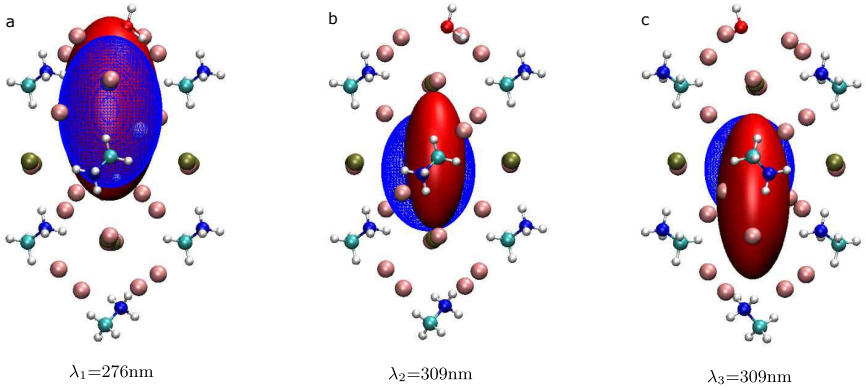

Figure S11. Electron density differences between the excited states and ground state for $(CH_3NH_3PbI_3)_8{\cdot}H_2O$ cluster. Red isosurfaces represent electron density decreases while blue ones represent electron density increases.

Table S2. The calculated Wiberg bond index values of ground state and excited states for $(CH_3NH_3PbI_3)_8{\cdot}2H_2O$ compound.

Bond	GS	ES1 (286 nm)	ES2 (305 nm)	ES3 (373 nm)	ES4 (626 nm)
Pb1-I2	0.29	0.29	0.27	0.29	0.33
Pb1-I4	0.63	0.59	0.58	0.61	0.52
Pb1-I5	0.62	0.58	0.58	0.59	0.60
Pb1-I6	0.72	0.68	0.65	0.70	0.69
Pb1-I7	0.17	0.16	0.17	0.17	0.17
Pb1-I8	0.18	0.17	0.16	0.17	0.20
Pb3-I2	0.28	0.26	0.25	0.27	0.27
Pb3-I9	0.16	0.16	0.16	0.15	0.16
Pb3-I10	0.64	0.63	0.58	0.62	0.63
Pb3-I11	0.69	0.64	0.63	0.67	0.65
Pb3-I12	0.18	0.19	0.18	0.18	0.19
Pb3-I13	0.68	0.66	0.63	0.65	0.68

Table S3. The calculated Wiberg bond index values of ground state and excited states for $(CH_3NH_3PbI_3)_8{\cdot}3H_2O$ compound.

Bond	GS	ES1 λ_1=284nm	ES2 λ_2=302nm	ES3 λ_3=308nm	ES4 λ_3=616nm
Pb1-I2	0.24	0.20	0.20	0.23	0.24
Pb1-I4	0.67	0.55	0.55	0.61	0.66
Pb1-I5	0.62	0.54	0.54	0.52	0.60
Pb1-I6	0.73	0.62	0.62	0.62	0.73
Pb1-I7	0.18	0.19	0.19	0.18	0.19
Pb1-I8	0.16	0.15	0.15	0.15	0.16
Pb3-I2	0.23	0.22	0.22	0.22	0.23
Pb3-I9	0.16	0.16	0.16	0.16	0.16
Pb3-I10	0.67	0.64	0.64	0.64	0.65
Pb3-I11	0.71	0.68	0.68	0.67	0.70
Pb3-I12	0.18	0.17	0.18	0.17	0.18
Pb3-I13	0.73	0.71	0.71	0.69	0.72