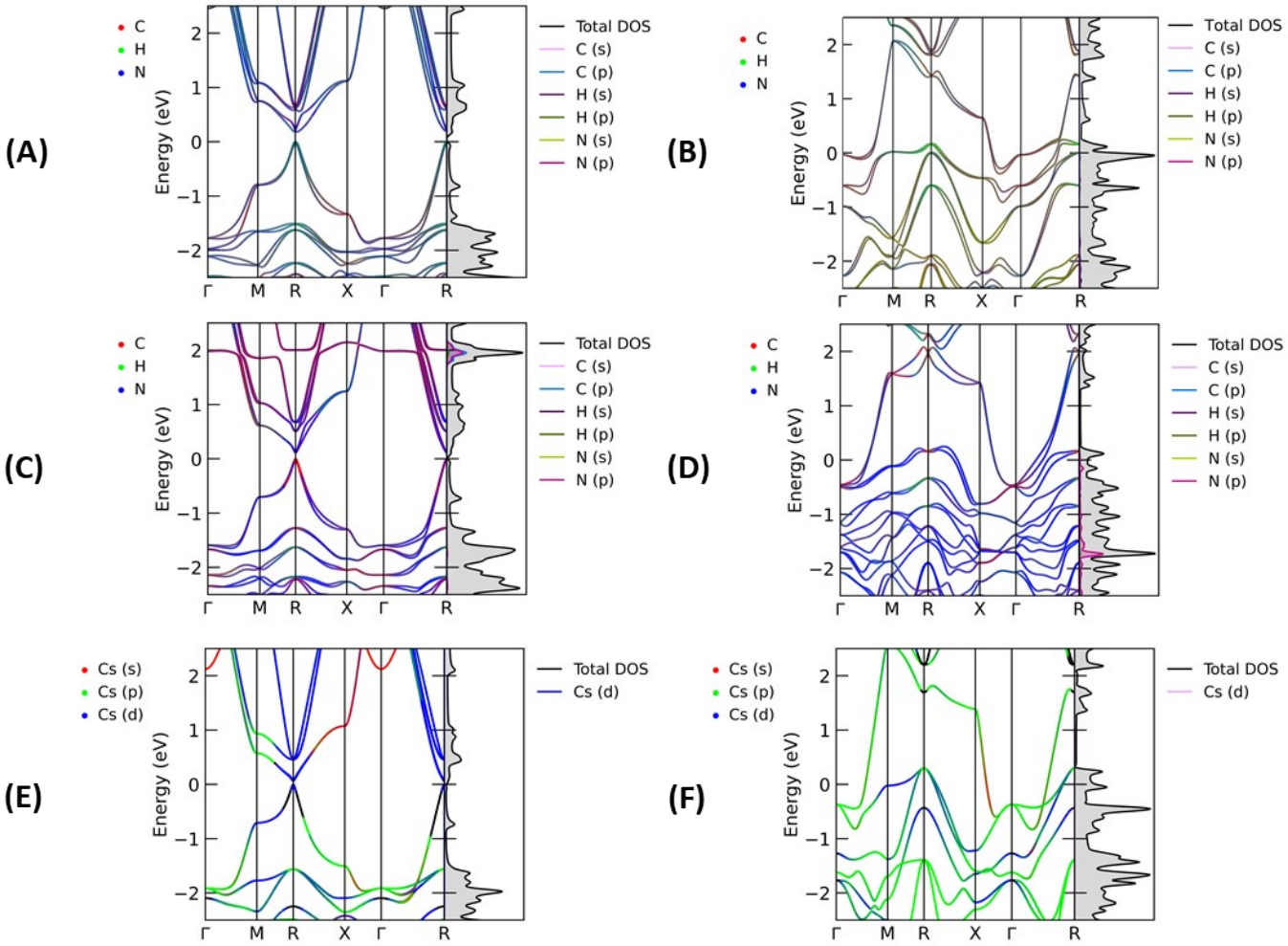

Figure S1. Band structure and density of states plots for (A) $MASnI_3$, (B) $[MASnI_3]^{2+}$, (C) $FASnI_3$, (D) $[FASnI_3]^{2+}$, (E) $CsSnI_3$ and (F) $[CsSnI_3]^{2+}$, orbital projections highlighting C, H and N or Cs s, Cs p and Cs d are shown on the band structure plot according to the key in the top left of each plot, and partial density of states projections for C, N and H or Cs are shown in the key in the top right of each plot. All energies are relative to the Fermi energy (E_F).

Table S1. Comparison of initial valence electrons per element and system.

Atom/Ion	No. of Valence Electrons	Valence Orbitals of Atoms
Sn	14	$5d^{10}\ 6s^2\ 6p^2$
I	7	$5s^2\ 5p^5$
C	4	$2s^2\ 2p^2$
H	1	$1s^1$
N	5	$2s^2\ 2p^3$
Cs	9	$5s^2\ 5p^6\ 6s^1$
$MASnI_3$	50	-
$[MASnI_3]^{2+}$	48	-
$FASnI_3$	54	-
$[FASnI_3]^{2+}$	52	-
$CsSnI_3$	44	-
$[CsSnI_3]^{2+}$	42	-

Table S2. Comparison of bond angles and lengths in relaxed $MASnI_3$ and $[MASnI_3]^{2+}$

Criteria	$MASnI_3$	$[MASnI_3]^{2+}$
I1-Sn-I1 bond angle	171.51 ◦	164.32 ◦
I2-Sn-I2 bond angle	174.11 ◦	159.95 ◦
I3-Sn-I3 bond angle	172.09 ◦	164.36 ◦
Mean Sn-I bond length	3.13 Å	2.65 Å
Mean Sn-I bond length standard deviation	0.09 Å	0.09 Å
Average lattice parameter to Sn-I bond length ratio	1.99	1.98
MA-SnI_6 octahedra bond length	5.24 Å	4.56 Å
C-N bond length	1.49 Å	1.45 Å
Mean C-H bond length	1.09 Å	1.09 Å
Mean C-H bond length standard deviation	<0.01 Å	<0.01 Å
Mean N-H bond length	1.04 Å	1.03
Mean N-H bond length standard deviation	<0.01 Å	<0.01 Å

Table S3. Comparison of bond angles and lengths in relaxed FASnI3 and $[FASnI3]^{2+}$

Criteria	$FASnI_3$	$[FASnI_3]^{2+}$
I1-Sn-I1 bond angle	170.69°	157.78°
I2-Sn-I2 bond angle	175.50°	179.93°
I3-Sn-I3 bond angle	169.12°	164.47°
Mean Sn-I bond length	3.31 Å	2.69 Å
Mean Sn-I bond length standard deviation	0.08 Å	0.04 Å
Average lattice parameter to Sn-I bond length ratio	2.00	1.98
FA-SnI_6 octahedra bond length	5.50 Å	4.75 Å
Mean C-N bond length	1.31 Å	1.29 Å
N-C-N bond angle	124.92°	116.46°
C-H bond length	1.09 Å	1.09 Å
Mean N-H bond length	1.02 Å	1.01
Mean N-H bond length standard deviation	<0.01 Å	<0.01 Å

Table S4. Comparison of bond angles and lengths in relaxed $CsSnI_3$ and $[CsSnI_3]^{2+}$

Criteria	$CsSnI_3$	$[CsSnI_3]^{2+}$
I1-Sn-I1 bond angle	180.00°	180.00°
I2-Sn-I2 bond angle	180.00°	180.00°
I3-Sn-I3 bond angle	180.00°	180.00°
Mean Sn-I bond length	3.10 Å	2.58 Å
Mean Sn-I bond length standard deviation	<0.01 Å	<0.01 Å
Average lattice parameter to Sn-I bond length ratio	2.00	2.00
Cs-SnI_3 octahedra bond length	5.38 Å	4.46 Å

Table S5. Comparison of Bader valence charge for atoms in $MASnI_3$ and $[MASnI_3]^{2+}$, the difference in the Bader charge for the H atoms is due to the hydrogen bonding with Iodine, in this case reduces the Bader charge of H atoms that are bonded with N.

Atom	$MASnI_3$ Bader Charge	$[MASnI_3]^{2+}$ Bader Charge	Difference
Sn_1	13.18	12.84	-0.34
I_1	7.53	6.97	-0.56
I_2	7.52	6.96	-0.56
I_3	7.52	6.98	-0.54
N_1	6.14	6.09	-0.05
C_1	3.88	3.70	-0.18
H_1	0.51	0.56	+0.05
H_2	0.51	0.55	+0.04
H_3	0.89	0.94	+0.05
H_4	0.89	0.94	+0.05
H_5	0.88	0.92	+0.04
H_6	0.53	0.54	+0.01

Table S6. Comparison of Bader valence charge for atoms in $FASnI_3$ and $[FASnI_3]^{2+}$, the difference in the Bader charge for the H atoms is due to the hydrogen bonding with Iodine, in this case reduces the Bader charge of H atoms that are bonded with N.

Atom	$FASnI_3$ Bader Charge	$[FASnI_3]^{2+}$ Bader Charge	Difference
Sn_1	13.15	12.77	-0.38
I_1	7.53	7.00	-0.53
I_2	7.54	6.93	-0.61
I_3	7.53	7.09	-0.44
N_1	6.25	6.22	-0.03
N_2	6.30	6.22	-0.08
C_1	2.81	2.66	-0.15
H_1	0.81	0.84	+0.03
H_2	0.53	0.55	+0.02
H_3	0.53	0.56	+0.03
H_4	0.53	0.56	+0.03
H_5	0.48	0.56	+0.08

Table S7. Comparison of Bader valence charge for atoms in $CsSnI_3$ and $[CsSnI_3]^{2+}$

Atom	$CsSnI_3$ Bader Charge	$[CsSnI_3]^{2+}$ Bader Charge	Difference
Sn_1	13.16	12.80	-0.36
I_1	7.58	7.03	-0.55
I_2	7.58	7.01	-0.57
I_3	7.53	6.99	-0.54
Cs_1	8.14	8.16	+0.02

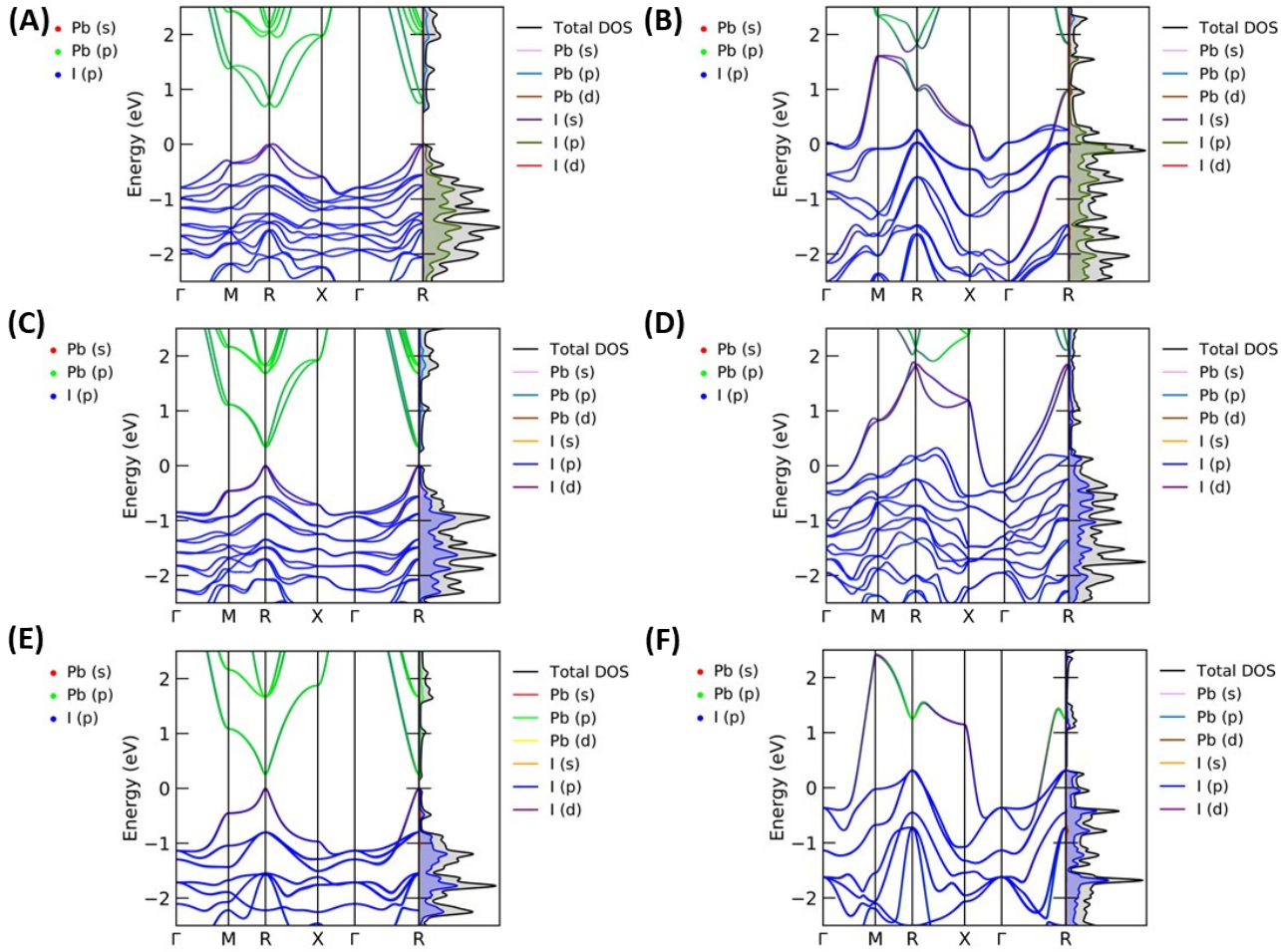

Figure S2. Band structure and density of states plots for (A) $MAPbI_3$, (B) $[MAPbI_3]^{2+}$, (C) $FAPbI_3$, (D) $[FAPbI_3]^{2+}$, (E) $CsPbI_3$ and (F) $[CsPbI_3]^{2+}$, orbital projections highlighting Sn s, Sn p and I p are shown on the band structure plot according to the key in the top left of each plot, and partial density of states projections for Sn and I are shown in the key in the top right of each plot. All energies are relative to the Fermi energy (E_F).

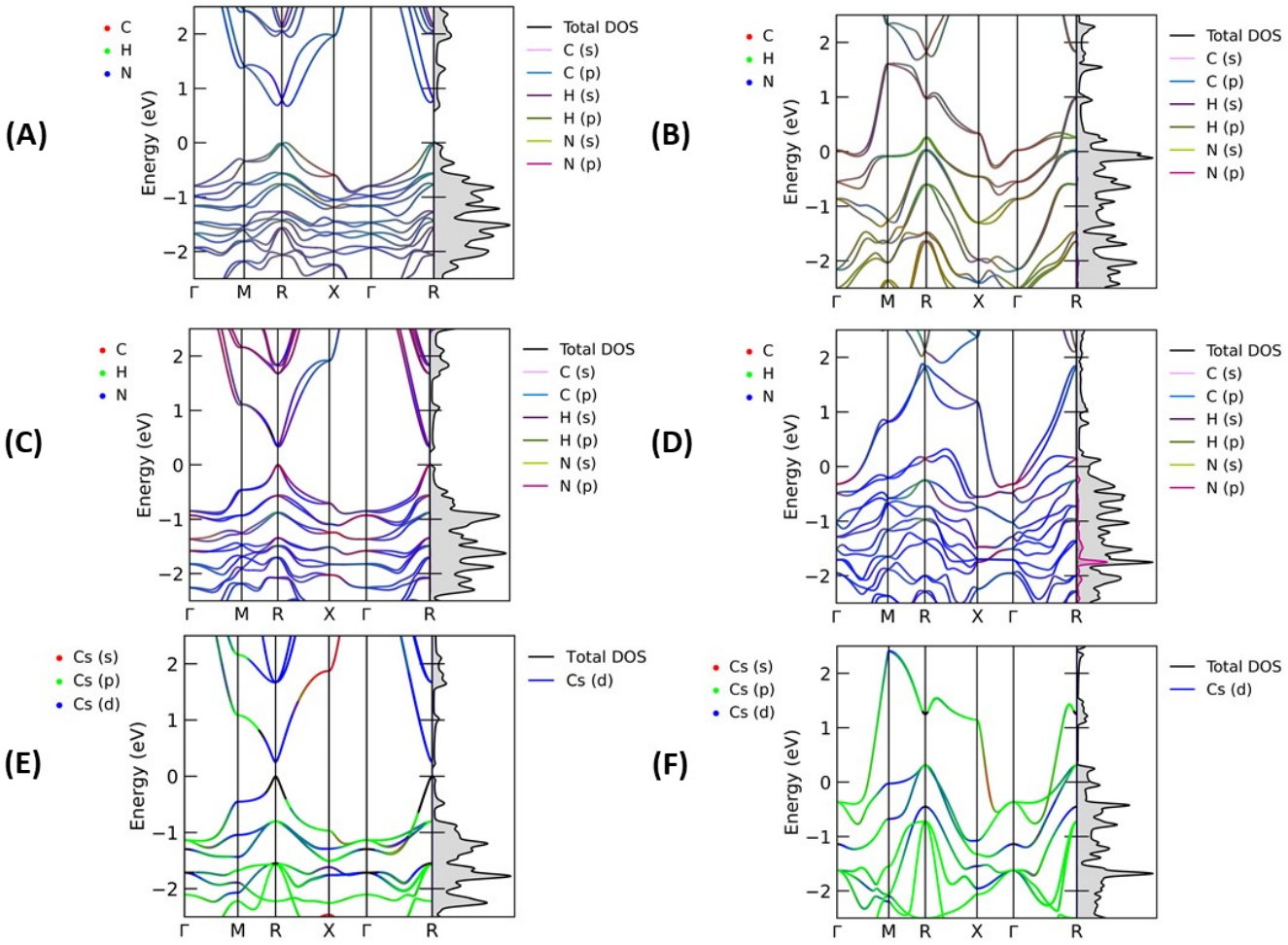

Figure S3. Band structure and density of states plots for (A) $MAPbI_3$, (B) $[MAPbI_3]^{2+}$, (C) $FAPbI_3$, (D) $[FAPbI_3]^{2+}$, (E) $CsPbI_3$ and (F) $[CsPbI_3]^{2+}$, orbital projections highlighting C, H and N or Cs s, Cs p and Cs d are shown on the band structure plot according to the key in the top left of each plot, and partial density of states projections for C, N and H or Cs are shown in the key in the top right of each plot. All energies are relative to the Fermi energy (E_F).

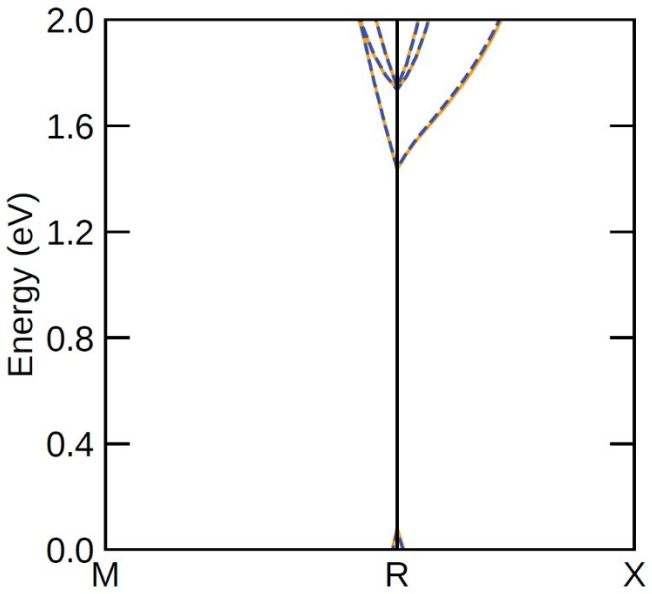

Figure S4. HSE06 Band Structure for $MAPbI_3$ using a k-point mesh of 4x4x4, showing a direct band gap of 1.36 eV at the R specific point.

Table S8. Comparison of lattice parameters and volume for $MAPbI_3$, $[MAPbI_3]^{2+}$, $FAPbI_3$, $[FAPbI_3]^{2+}$, $CsPbI_3$ and $[CsPbI_3]^{2+}$.

Material	a (Å)	b (Å)	c (Å)	α(θ)	β(θ)	γ(θ)	Unit Cell Volume (Å^3)
$MAPbI_3$	6.20	6.31	6.37	84.96°	88.17°	91.70°	247.94
$[MAPbI_3]^{2+}$	5.33	5.34	5.33	82.62°	84.12°	82.05°	148.42
$FAPbI_3$	6.43	6.28	6.32	90.06°	90.00°	90.00°	255.34
$[FAPbI_3]^{2+}$	5.32	5.56	5.34	90.01°	90.00°	90.03°	157.75
$CsPbI_3$	6.31	6.31	6.31	90.00°	90.00°	90.00°	250.99
$[CsPbI_3]^{2+}$	5.24	5.24	5.24	90.00°	90.00°	90.00°	144.29

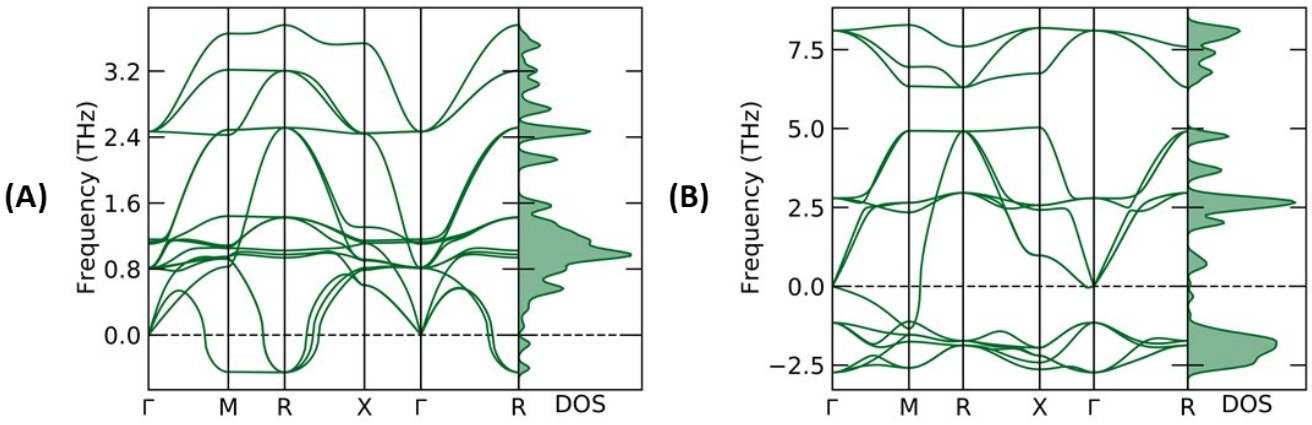

Figure S5. Phonon band structure and density of states for (A) $CsPbI_3$ and (B) $[CsPbI_3]^{2+}$. Negative frequencies are shown in the case of $[CsPbI_3]^{2+}$, indicating instability, whereas $CsPbI_3$ contains only positive frequencies.

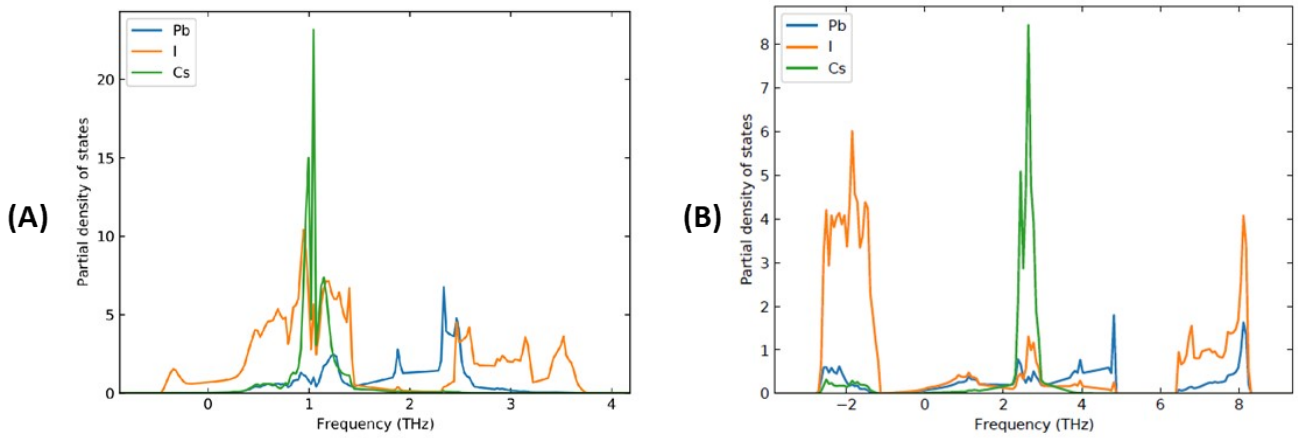

Figure S6. Phonon partial density of states for (A) $CsPbI_3$ and (B) $[CsPbI_3]^{2+}$ where each element is labelled in the top left. Negative frequencies are shown in the case of $[CsPbI_3]^{2+}$, indicating instability, whereas $CsSnI_3$ contains only positive frequencies.

Table S9. Comparison of Bader valence charge for atoms in $MAPbI_3$ and $[MAPbI_3]^{2+}$

Atom	$MAPbI_3$ Bader Charge	$[MAPbI_3]^{2+}$ Bader Charge	Difference
Pb_1	13.16	13.17	+0.01
I_1	7.53	6.89	-0.64
I_2	7.53	6.87	-0.66
I_3	7.54	6.84	-0.70
N_1	6.10	6.05	-0.05
C_1	3.91	3.73	-0.18
H_1	0.55	0.56	+0.01
H_2	0.52	0.55	+0.03
H_3	0.87	0.94	+0.07
H_4	0.88	0.92	+0.04
H_5	0.87	0.92	+0.05
H_6	0.54	0.57	+0.03

Table S10. Comparison of Bader valence charge for atoms in $FAPbI_3$ and $[FAPbI_3]^{2+}$

Atom	$FAPbI_3$ Bader Charge	$[FAPbI_3]^{2+}$ Bader Charge	Difference
Pb_1	13.18	13.07	-0.11
I_1	7.53	6.85	-0.68
I_2	7.51	6.84	-0.67
I_3	7.54	7.02	-0.52
N_1	6.25	6.21	-0.04
N_2	6.25	6.22	-0.03
C_1	2.77	2.72	-0.05
H_1	0.87	0.84	-0.03
H_2	0.52	0.57	+0.05
H_3	0.52	0.55	+0.03
H_4	0.52	0.55	+0.03
H_5	0.52	0.55	+0.03

Table S11. Comparison of Bader valence charge for atoms in $CsPbI_3$ and $[CsPbI_3]^{2+}$

Atom	$CsPbI_3$ Bader Charge	$[CsPbI_3]^{2+}$ Bader Charge	Difference
Pb_1	13.21	13.17	-0.04
I_1	7.54	6.92	-0.62
I_2	7.54	6.88	-0.66
I_3	7.54	6.88	-0.66
Cs_1	8.16	8.15	-0.01

Data S1-12. (separate files)

Collection of relaxed unit cell in VASP (POSCAR/CONTCAR) and .cif format attached.