Supporting Information

Reducing Hot Carrier Cooling Rate in Metal Halide Perovskites

Through Lead Vacancies: Time-domain Ab Initio Analysis

Junguang Hu,[1] Ning Li,[1] Junping Xie,[2] Yong Pei,[2] Oleg V. Prezhdo,[3*] and Wei Li[1*]

[1]School of Chemistry and Materials Science, Hunan Agricultural University, Changsha, PR China

[2]Department of Chemistry, Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, Xiangtan University, Xiangtan 411105, China

[3]Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States

---

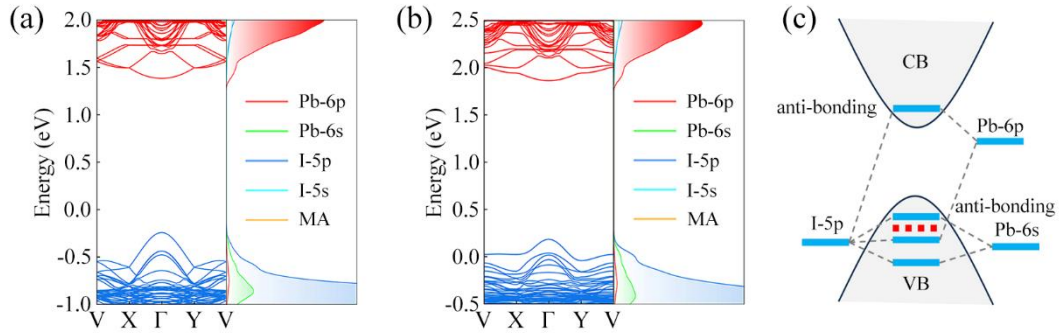[*]Corresponding authors: weili@hunau.edu.cn (W.L.); prezhdo@usc.edu (O.V.P.)

Figure S1. Band structure and projected density of states (PDOS) for pristine MAPbI₃ (**a**) and MAPbI₃ with a Pb vacancy (**b**). Schematic diagram of bonding and antibonding orbitals of MAPbI₃ perovskite (**c**). VBM and CBM are mainly formed from the Pb 6p orbital and antibonding coupling of the Pb 6s and I 5p orbitals, respectively. Pb vacancies do not generate mid-gap states within the bandgap; instead, they introduce intra-band states (dashed line) within the valence band.
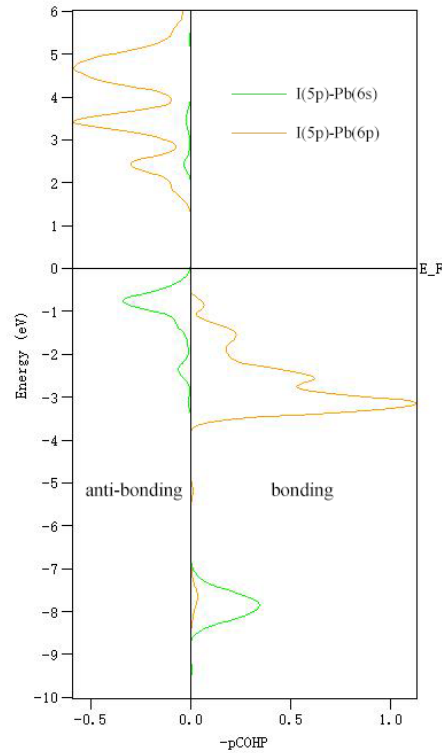

Figure S2. The orbital-resolved crystal orbital Hamiltonian population (-pCOHP) analysis of MAPbI₃ perovskite based on the 0K structure. The negative, zero, and positive values of -pCOHP correspond to the antibonding, nonbonding, and bonding characters, respectively.
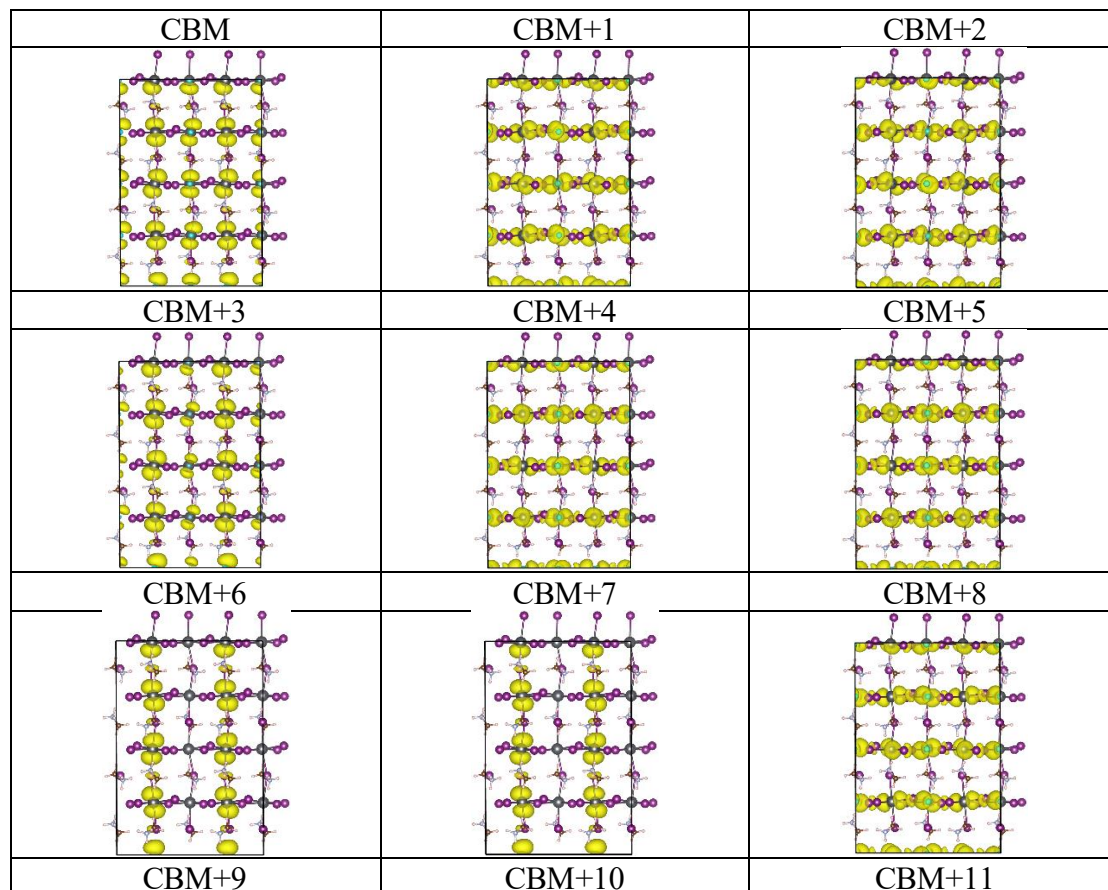
Table S1. The Pb-I bond length (Å) and Pb-I-Pb bond angle (degree) at 0K and averaged from MD trajectories at 300K in pristine and defective systems.

	Pb-I bond length (0K)	Pb-I-Pb angle (0K)	Pb-I bond length (300K)	Pb-I-Pb angle (300K)
Pristine	3.210	155.74	3.186	157.99
Pb_V	3.214	156.25	3.187	158.75

Table S2. The root-mean-square (RMS) displacement (Å) of each atomic species in pristine and defective $MAPbI_3$ obtained by averaging over 3 ps trajectories at 300 K.

	C	N	H	Pb	I
Pristine	0.006902	0.0066	0.01545	0.002205	0.002777
Pb_V	0.006924	0.0069	0.01736	0.002200	0.002682

Table S3. Charge density distribution of CB states with excess energy $\Delta E_e \leq 0.5$ eV in pristine $MAPbI_3$.
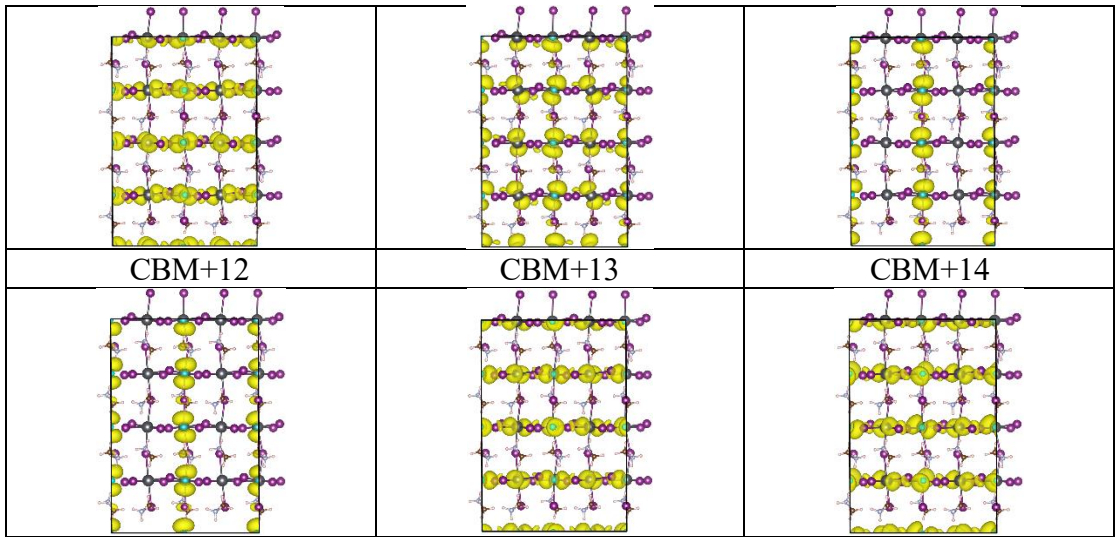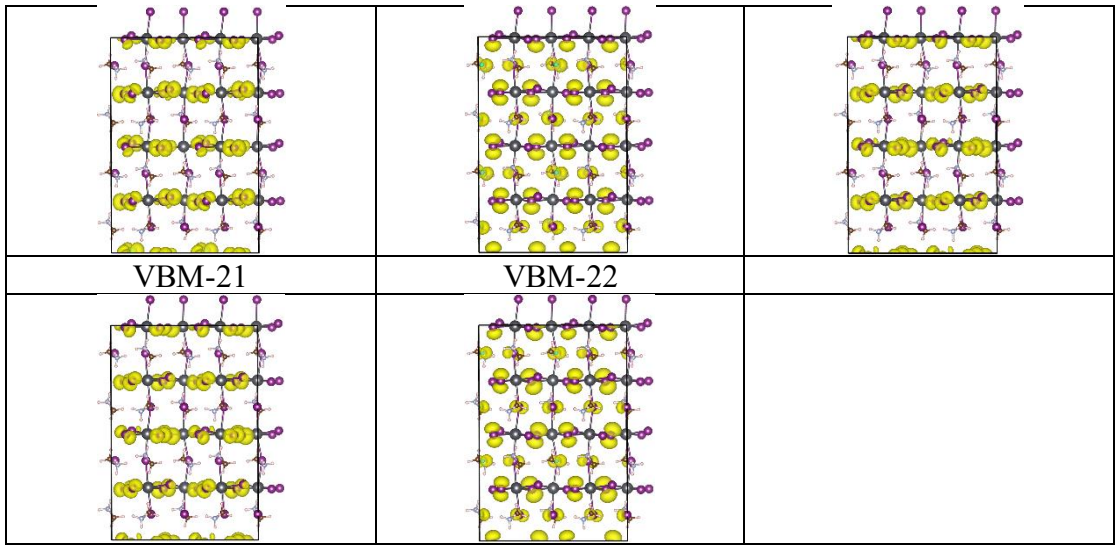
CBM	CBM+1	CBM+2
CBM+3	CBM+4	CBM+5
CBM+6	CBM+7	CBM+8
CBM+9	CBM+10	CBM+11

CBM+12	CBM+13	CBM+14

Table S4. Charge density distribution of VB states with excess energy $\Delta E_h \leq 0.5$ eV in pristine MAPbI$_3$.

VBM	VBM-1	VBM-2
VBM-3	VBM-4	VBM-5
VBM-6	VBM-7	VBM-8
VBM-9	VBM-10	VBM-11
VBM-12	VBM-13	VBM-14
VBM-15	VBM-16	VBM-17
VBM-18	VBM-19	VBM-20

VBM-21	VBM-22	

Table S5. Charge density distribution of CB states with excess energy $\Delta E_e \leq 0.5$ eV in the Pb_V system.
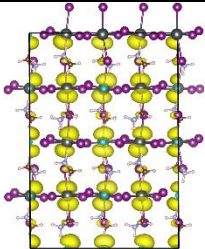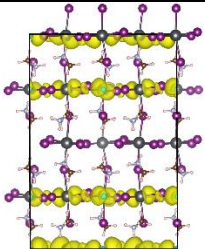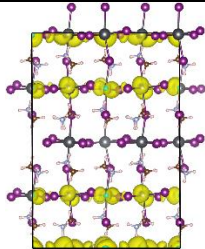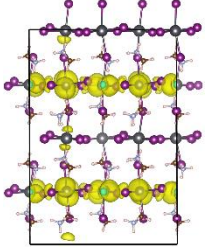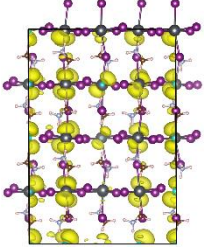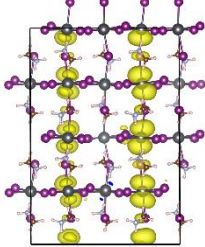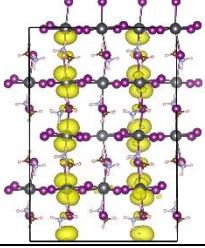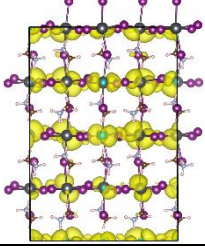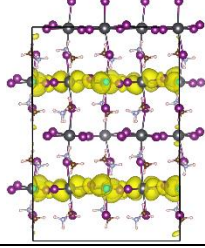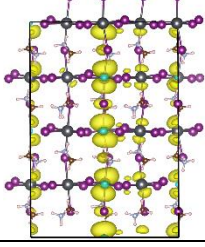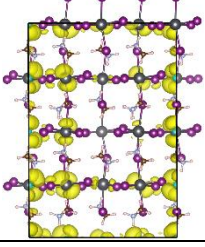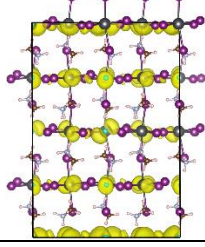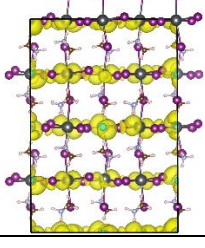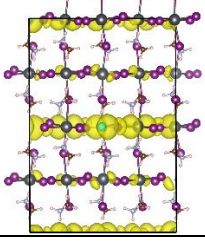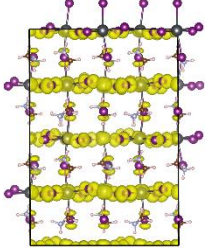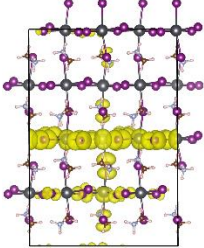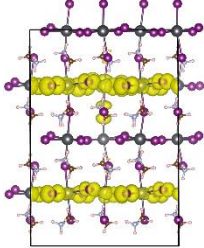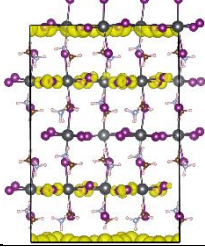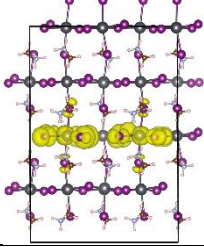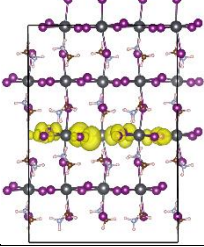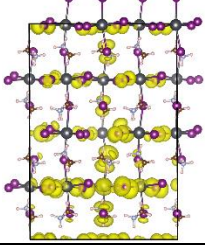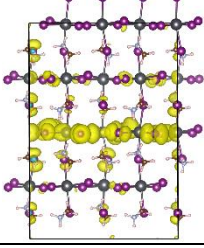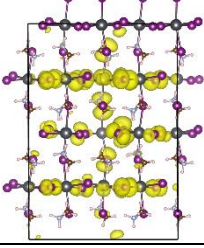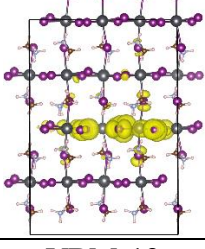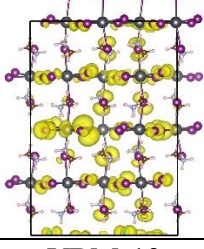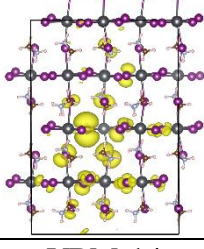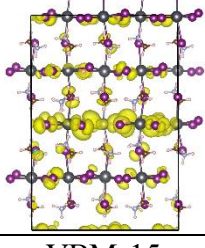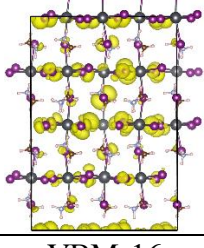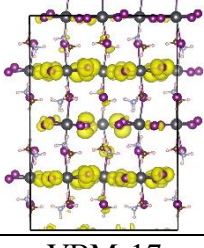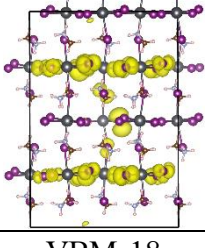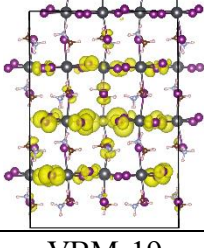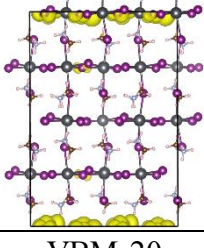
CBM	CBM+1	CBM+2

CBM+3	CBM+4	CBM+5

CBM+6	CBM+7	CBM+8

CBM+9	CBM+10	CBM+11

CBM+12	CBM+13	

Table S6. Charge density distribution of VB states with excess energy $\Delta E_h \leq 0.5$ eV in the Pb_V system.

VBM	VBM-1	VBM-2
VBM-3	VBM-4	VBM-5
VBM-6	VBM-7	VBM-8
VBM-9	VBM-10	VBM-11
VBM-12	VBM-13	VBM-14
VBM-15	VBM-16	VBM-17
VBM-18	VBM-19	VBM-20

VBM-21	VBM-22	VBM-23
VBM-24	VBM-25	VBM-26
VBM-27	VBM-28	VBM-29
VBM-30	VBM-31	VBM-32
VBM-33	VBM-34	

Table S7. Excited state populations of hot electrons with $\Delta E_e \leq 0.5$ eV for pristine MAPbI$_3$.

$\Delta E = 0.127$ eV	$\Delta E = 0.180$ eV	$\Delta E = 0.223$ eV
$\tau = 8.151$ ps	$\tau = 0.966$ ps	$\tau = 0.702$ ps
$\Delta E = 0.252$ eV	$\Delta E = 0.278$ eV	$\Delta E = 0.304$ eV
$\tau = 0.680$ ps	$\tau = 0.685$ ps	$\tau = 0.447$ ps
$\Delta E = 0.326$ eV	$\Delta E = 0.350$ eV	$\Delta E = 0.369$ eV
$\tau = 0.476$ ps	$\tau = 0.391$ ps	$\tau = 0.345$ ps
$\Delta E = 0.392$ eV	$\Delta E = 0.415$ eV	$\Delta E = 0.437$ eV
$\tau = 0.325$ ps	$\tau = 0.350$ ps	$\tau = 0.354$ ps
$\Delta E = 0.465$ eV	$\Delta E = 0.497$ eV	
$\tau = 0.414$ ps	$\tau = 0.572$ ps	
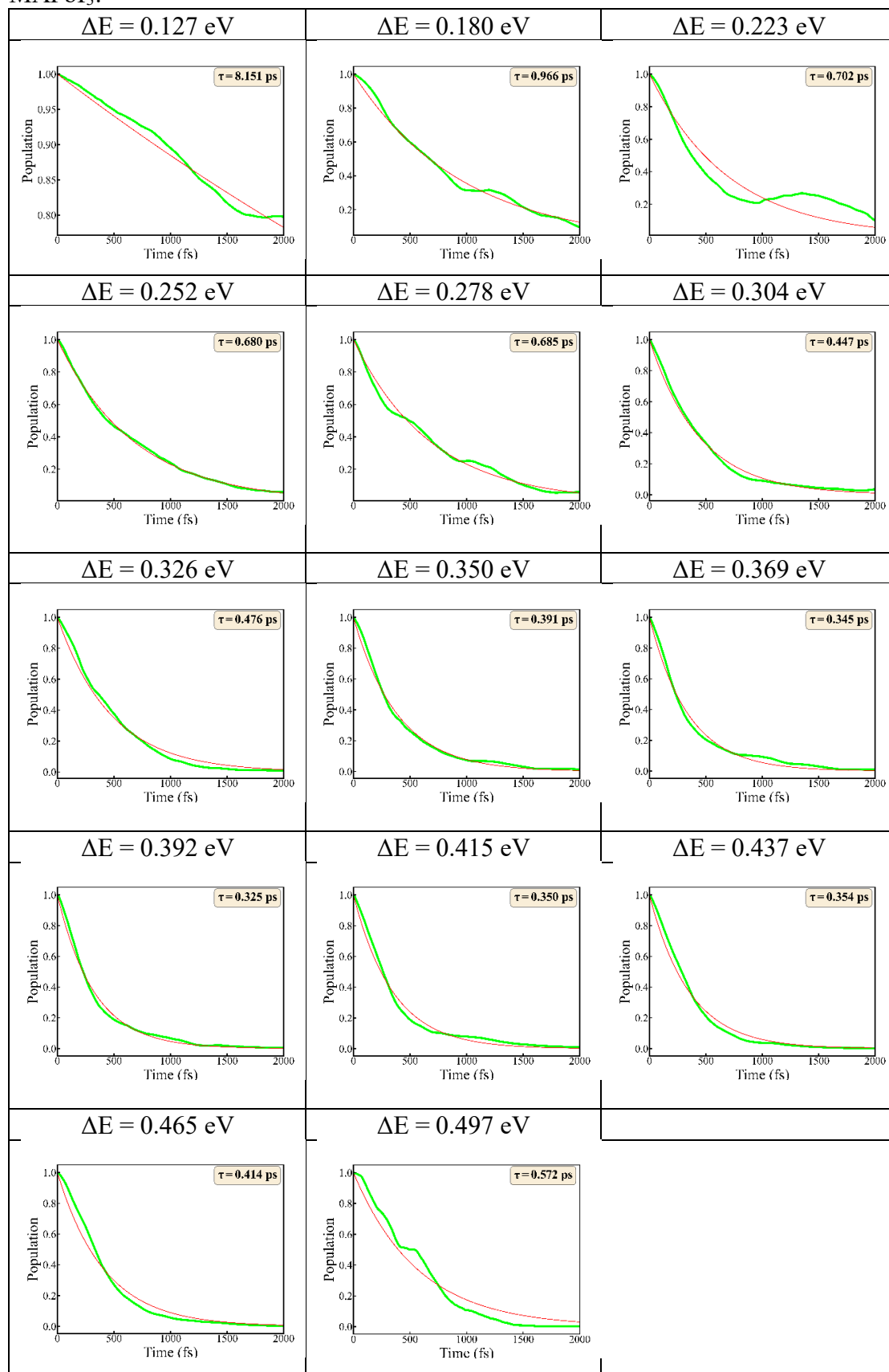
Table S8. Excited state populations of hot holes with $\Delta E_h \leq 0.5$ eV for pristine MAPbI$_3$.

$\Delta E = 0.103$ eV	$\Delta E = 0.152$ eV	$\Delta E = 0.190$ eV
$\tau = 1.101$ ps	$\tau = 0.571$ ps	$\tau = 0.371$ ps

$\Delta E = 0.217$ eV	$\Delta E = 0.240$ eV	$\Delta E = 0.261$ eV
$\tau = 0.285$ ps	$\tau = 0.229$ ps	$\tau = 0.201$ ps

$\Delta E = 0.281$ eV	$\Delta E = 0.299$ eV	$\Delta E = 0.319$ eV
$\tau = 0.190$ ps	$\tau = 0.156$ ps	$\tau = 0.185$ ps

$\Delta E = 0.331$ eV	$\Delta E = 0.375$ eV	$\Delta E = 0.410$ eV
$\tau = 0.189$ ps	$\tau = 0.120$ ps	$\tau = 0.109$ ps

$\Delta E = 0.457$ eV	$\Delta E = 0.494$ eV	
$\tau = 0.095$ ps	$\tau = 0.089$ ps	
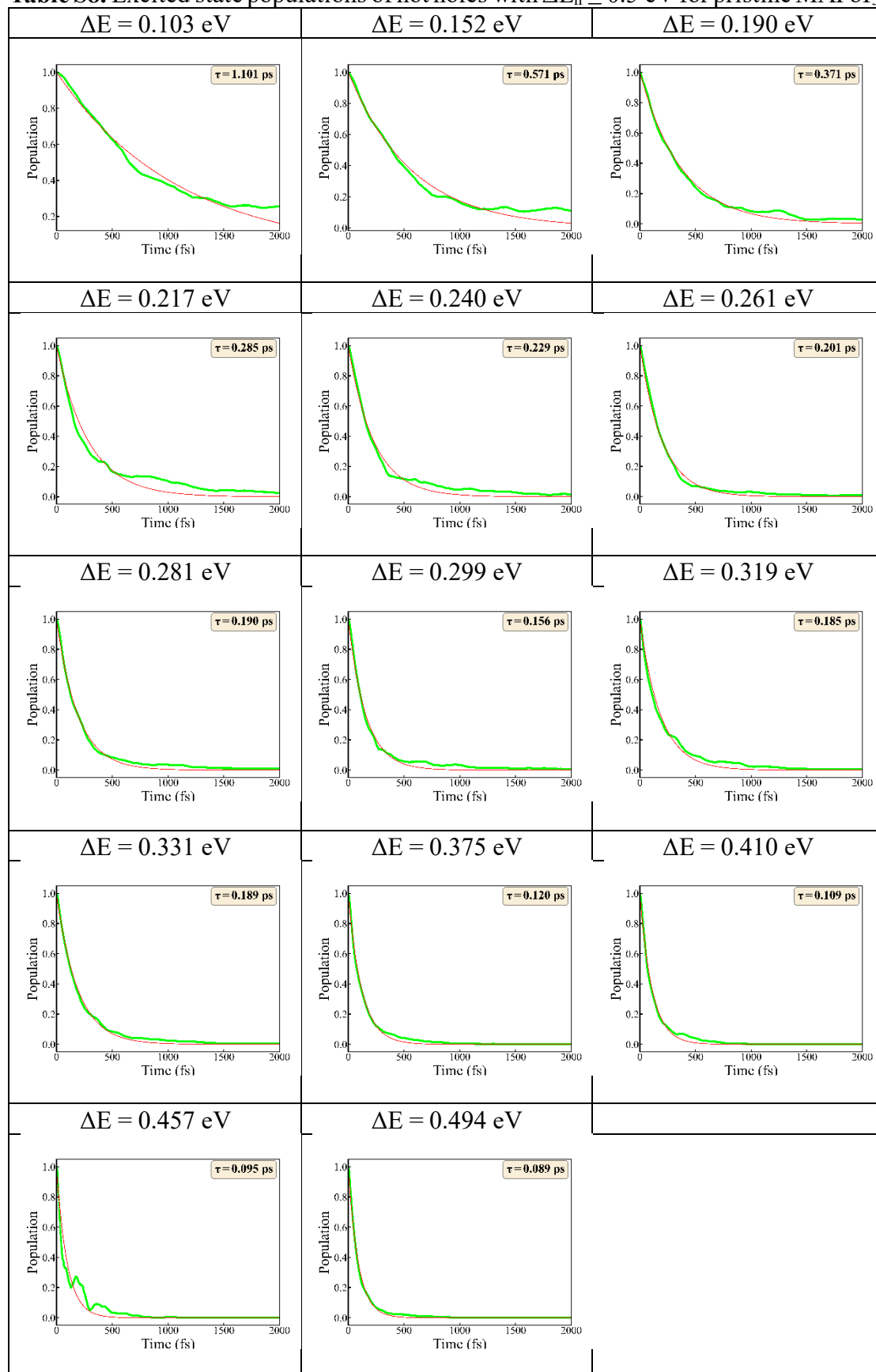
Table S9. Excited state populations of hot electrons with $\Delta E_e \leq 0.5$ eV for MAPbI$_3$ with Pb$_V$.

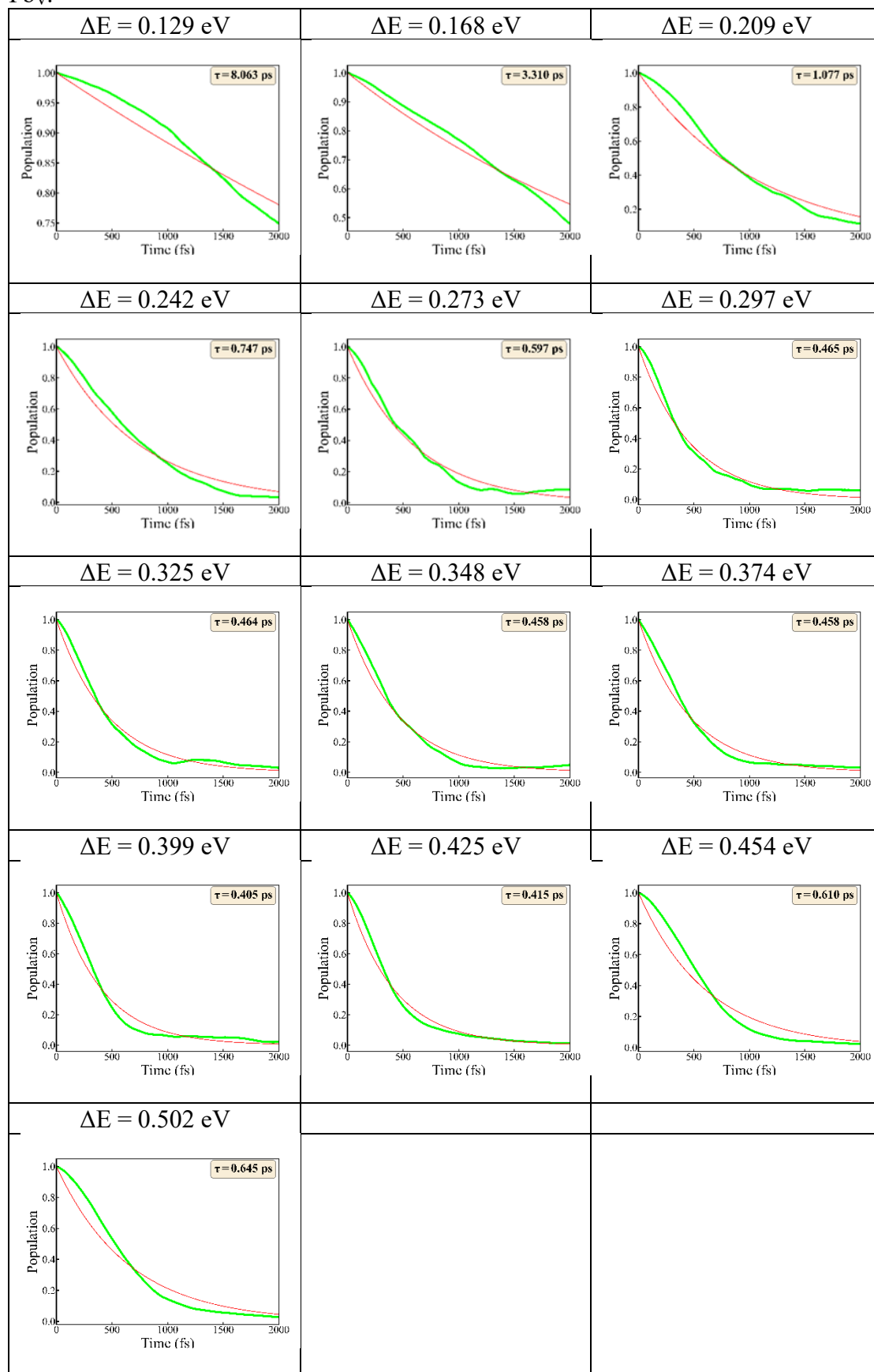| $\Delta E = 0.129$ eV	$\Delta E = 0.168$ eV	$\Delta E = 0.209$ eV
$\tau = 8.063$ ps	$\tau = 3.310$ ps	$\tau = 1.077$ ps
$\Delta E = 0.242$ eV	$\Delta E = 0.273$ eV	$\Delta E = 0.297$ eV
$\tau = 0.747$ ps	$\tau = 0.597$ ps	$\tau = 0.465$ ps
$\Delta E = 0.325$ eV	$\Delta E = 0.348$ eV	$\Delta E = 0.374$ eV
$\tau = 0.464$ ps	$\tau = 0.458$ ps	$\tau = 0.458$ ps
$\Delta E = 0.399$ eV	$\Delta E = 0.425$ eV	$\Delta E = 0.454$ eV
$\tau = 0.405$ ps	$\tau = 0.415$ ps	$\tau = 0.610$ ps
$\Delta E = 0.502$ eV		
$\tau = 0.645$ ps		

Table S10. Excited state populations of hot holes with $\Delta E_h \leq 0.5$ eV for MAPbI$_3$ with Pb$_V$.

$\Delta E = 0.104$ eV	$\Delta E = 0.144$ eV	$\Delta E = 0.175$ eV
$\tau = 0.578$ ps	$\tau = 0.613$ ps	$\tau = 0.607$ ps
$\Delta E = 0.192$ eV	$\Delta E = 0.209$ eV	$\Delta E = 0.227$ eV
$\tau = 0.355$ ps	$\tau = 0.164$ ps	$\tau = 0.247$ ps
$\Delta E = 0.244$ eV	$\Delta E = 0.287$ eV	$\Delta E = 0.319$ eV
$\tau = 0.306$ ps	$\tau = 0.888$ ps	$\tau = 0.799$ ps
$\Delta E = 0.348$ eV	$\Delta E = 0.385$ eV	$\Delta E = 0.412$ eV
$\tau = 0.842$ ps	$\tau = 0.850$ ps	$\tau = 0.815$ ps
$\Delta E = 0.441$ eV	$\Delta E = 0.472$ eV	$\Delta E = 0.500$ eV
$\tau = 0.845$ ps	$\tau = 0.974$ ps	$\tau = 0.820$ ps