

# Cation Effect on Hot Carrier Cooling in Halide Perovskite Materials

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**Supporting Information** 

**ABSTRACT:** Organic–inorganic lead-halide perovskites have received a revival of interest in the past few years as a promising class of materials for photovoltaic applications. Despite recent extensive research, the role of cations in defining the high photovoltaic performance of these materials is not fully understood. Here, we conduct nonadiabatic molecular dynamics simulations to study and compare nonradiative hot carrier relaxation in three lead-halide perovskite materials:  $CH_3NH_3PbI_3$ ,  $HC(NH_2)_2PbI_3$ , and  $CsPbI_3$ . It is found that the relaxation of hot carriers to the band edges occurs on the ultrafast time scale and displays a strong quantitative dependence on the nature of the cations. The obtained results are explained in terms of electron–phonon couplings, which are strongly affected by the atomic displacements in the Pb–I framework triggered by the cation dynamics.



Recently, organometallic lead-halide-based perovskites have attracted a lot of attention as promising solar harvesting materials with the efficiency already exceeding  $22\%^1$  (see refs 2 and 3 for reviews). Such a high performance of perovskite solar cells is related to favorable electronic, optical, and transport properties. These properties can be further refined by chemical engineering, e.g., through mixing of halogen atoms.<sup>4-6</sup> Organic cations also play an important role in determining the photoconversion performance of perovskite-based solar cells.<sup>7-13</sup> Photoexcited state properties of hybrid perovskite materials have also been the subject of recent extensive theoretical and experimental investigations.<sup>14-20</sup> It is known that the hot carrier cooling process depends on both sample properties and external conditions such as excitation energy or photon fluence (i.e., carrier density). Recent experiments show the possibility of increasing the cooling time of hot carriers by almost 1 order of magnitude by increasing the excitation pump fluence.<sup>21-23</sup> Yang et al.<sup>24</sup> reported a further increase of the relaxation time at higher carrier densities which was related to the hot phonon bottleneck effect.

Despite recent progress in hybrid perovskite solar cell development, a little attention has been paid to the effect of the cations on hot carrier relaxation dynamics. On the other hand, fundamental understanding of the excited-state properties and charge carrier dynamics in these materials is essential for improving the photovoltaic performance of solar cell devices. Therefore, in this work, we investigated hot carrier cooling in perovskite materials using nonadiabatic molecular-dynamics (NAMD) simulations in combination with time-dependent density functional theory (DFT). In order to identify the role played by the cations during the cooling process, we considered three different halide perovskites in their cubic crystalline phases: CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (MAPbI<sub>3</sub>), HC(NH<sub>2</sub>)<sub>2</sub>PbI<sub>3</sub> (FAPbI<sub>3</sub>), and CsPbI<sub>3</sub>. We found that for most of the excitation energies, both hot electrons and holes relax slower in CsPbI3 as compared to the other two systems. This is explained in terms of the reduced electron-phonon couplings in the all-inorganic system due to reduced interaction between the Cs cations and the PbI<sub>6</sub> inorganic framework. To stress the effect of cations dynamics on the cooling process, we conducted simulations for MAPbI<sub>3</sub> system by freezing the methylammonium (MA) molecules. Significant enhancement of the relaxation time is obtained in the latter system, which also emphasizes the profound role of cation dynamics in hot carrier dynamics in lead halide perovskites.

Figure 1 depicts a schematic of the hot charge carrier relaxation processes. The relaxation dynamics of hot electrons is investigated by exciting the electrons from the valence band maximum (VBM) to the conduction band states with an excess energy  $\Delta E_{\rm e}$  above the conduction band minimum (CBM) (see Figure 1). In this scenario only hot electrons are formed, and the holes will always be in the lowest energy state. Similarly, the cooling of the hot holes is studied by promoting electrons from the states with an excess energy  $\Delta E_{\rm h}$  below VBM to the CBM.

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Figure 1. Schematic diagram representing hot carrier relaxation dynamics in the system.

Thus, the dynamics of hot electrons and hot holes is studied separately. The cooling processes are driven mainly by the carrier-carrier and carrier-phonon interactions. The last interactions drive the hot carriers to relax by transferring their energy to the lattice. The carrier-carrier interaction was identified to be the dominant process in the first step of the buildup of a thermal Boltzmann distribution (after optical excitation of the perovskite material).<sup>25</sup> Depending on the carrier density, the time for this thermal distribution was reported to be in the range from 8 to 85 fs.<sup>25</sup> Because the electron-hole interaction is neglected in our approach, which is in part justified by the small exciton binding energy in these perovskite materials,<sup>26,27</sup> the cooling of hot carriers occurs because of the interaction between charge carriers of the same type and carrier-phonon interactions. We describe the relaxation process using NAMD in combination with Tully's surface hopping method.<sup>28</sup>

Figure 2 illustrates the computed dynamics of charge carrier relaxation in three materials. To facilitate the comparison, we consider the comparable amounts of the excess energy in all of them. Figure 2a shows the relaxation kinetics of the hot electrons for the excitation energies  $\Delta E_e \approx 0.31$  eV (CBM + 2),  $\Delta E_e \approx 0.31$  eV (CBM + 4), and  $\Delta E_e \approx 0.27$  eV (CBM + 3), respectively, for MAPbI<sub>3</sub>, FAPbI<sub>3</sub>, and CsPbI<sub>3</sub> samples. It is seen from this figure that the fastest relaxation of hot electrons occurs in FAPbI<sub>3</sub> (blue curve), whereas much slower cooling is obtained in CsPbI<sub>3</sub> (black curve). Similar results are obtained for hot hole cooling processes (see Figure 2b): the slowest nonradiative relaxation is obtained for the fully inorganic system, whereas hot holes relax to the lowest energy states much faster in the two hybrid perovskites.

Figure 3a,b shows the population decay of hot electrons (a) and hot holes (b) promoted to different excited states with similar excess energies  $\Delta E$  (see preceding paragraph for the values of  $\Delta E_{\rm e}$  and  $\Delta E_{\rm h}$ ). Hot electrons in FAPbI<sub>3</sub> completely relax to the lower energy states already after 1 ps (blue curve in Figure 3a). This process is 2-fold slower in the MAPbI<sub>3</sub> system (red curve in Figure 3a). The slowest relaxation of hot electrons is obtained for the fully inorganic system: less than 80% of the electronic population is transferred to lower states after 2 ps of time (black curve in Figure 3a). Similar results are obtained for hot hole population decay: hot holes relax to the lowest energy state in hybrid systems almost 4 times faster as compared to the



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**Figure 2.** Time evolution of the Kohn–Sham population-weighted energies of (a) hot electrons (with excess energies  $\Delta E_e \approx 0.31 \text{ eV}$ ,  $\Delta E_e \approx 0.31$ , and  $\Delta E_e \approx 0.27 \text{ eV}$  for MAPbI<sub>3</sub>, FAPbI<sub>3</sub>, and CsPbI<sub>3</sub> samples, respectively) and (b) hot holes (with excess energy  $\Delta E_h \approx 0.28 \text{ eV}$  for all three systems).  $\Delta E$  is calculated with respect to the CBM and VBM for hot electrons and hot holes, respectively.

case of the CsPbI<sub>3</sub> sample (Figure 3b). In order to quantify the cooling time of hot charge carriers, we fitted the population decay curves by the sum of an exponential plus a Gaussian function:<sup>29</sup>

$$f(t) = a e^{(-t/\tau_1)} + (1 - a) e^{(-(t/\tau_2)^2)}$$
(1)

Then, the cooling time for hot charge carriers is calculated as<sup>29</sup>

$$\tau = a\tau_1 + (1 - a)\tau_2 \tag{2}$$

Tables 1 summarizes the values of the fitting parameter *a* and relaxation times for hot electrons and hot holes (see Figures S3–S5 in the Supporting Information for the fitted curves and cooling times of the charge carriers excited to different energy states). For the considered excitation energies, the shortest relaxation time of hot electrons is found for FAPbI<sub>3</sub> system ( $\tau_e = 179.0 \text{ fs}$ ), whereas the CsPbI<sub>3</sub> sample gives almost 1 order of magnitude longer cooling time ( $\tau_e = 1294.5 \text{ fs}$ ). In addition, the electron population relaxation curve in FAPbI<sub>3</sub> is fully exponential (i.e., a = 1), whereas for the CsPbI<sub>3</sub> system, we obtained an exponential plus Gaussian relaxation curve (i.e., a < 1). For the MAPbI<sub>3</sub> system, we also obtained a biexponential curve (a = 0.568) with relaxation time  $\tau_e = 617.4 \text{ fs}$ . The largest hot hole relaxation time was also obtained for the fully inorganic system ( $\tau_h = 762.8 \text{ fs}$ ), as compared to the other



Figure 3. Population dynamics of hot electrons (a) and hot holes (b) excited to different energy states with similar excess energies.

Table 1. Parameters of the Exponential Plus Gaussian Fit to Hot Electron and Hot Hole Population Decays As Shown in Figure 3

	FAPbI <sub>3</sub>	MAPbI <sub>3</sub>	CsPbI <sub>3</sub>
a <sub>e</sub>	1.00	0.568	0.421
$\tau_{\rm e}~({\rm fs})$	179.0	617.4	1294.5
$a_{ m h}$	1.0	0.78	0.67
$ au_{ m h}~({ m fs})$	203.1	146.2	762.8

hybrid systems. However, hole relaxation curves follow an exponential behavior (i.e.,  $a \Rightarrow 1$ ).

To understand the difference in the relaxation process of hot charge carriers in the considered perovskite systems, we computed the carrier-phonon nonadiabatic couplings (NACs) between states in both the valence and conduction bands. Figure 4 shows the NAC absolute value averaged over 3.5 ps molecular dynamics (MD) trajectories, where i = 0means the VBM state and i = 1 is the CBM state. In all cases, the coupling along the subdiagonal lines are strong, indicating that nonradiative transitions are most likely to occur between adjacent states (for more details see Table S2). Small NAC is obtained between the states separated by a large gap. This behavior is expected, knowing the fact that the strength of the NAC is inversely proportional to the difference between the energy levels.<sup>30,31</sup> However, direct population transfer between the initial state and the lower excited states (band edges) is also possible because of the nonvanishing NAC between these two states. This indicates that the mechanism of carrier relaxation



**Figure 4.** Average magnitude of the carrier-phonon nonadiabatic couplings (in units of millielectronvolts) for the three perovskites systems: FAPbI<sub>3</sub> (a), MAPbI<sub>3</sub> (b), and CsPbI<sub>3</sub> (c). Here, i = 0 means the VBM state and i = 1 is the CBM state; other states are assigned indices based on these two reference points.

goes beyond the sequential stepwise fashion and may include several relaxation channels activated in parallel. Clearly, NAC between the states in the valence band (negative Kohn-Sham indices) is significantly larger as compared to the NAC in the conduction band (positive Kohn-Sham indices) (see also Table S2). The reason for such stronger coupling is the larger density of states (DOS) in the valence band as compared to the DOS in the conduction band (see Figure S2). Notice also that the NAC becomes smaller between states close to the VB or CB edges. The largest NACs are found for the FAPbI<sub>3</sub>, which might explain the faster relaxation of hot charge carriers in this material. The analysis of the partial DOS shows a notable fraction of the FA cation states mixing into the CB and VB. Consequently, the motion of the FA cation will cause larger changes of the wave functions leading to larger couplings. The smallest NAC is obtained for the CsPbI<sub>3</sub> system as compared to the other systems, which explains the slowest relaxation of the hot carriers in the former system.

Analysis of the partial DOS (Figure S2) shows that the VB states of all studied perovskite systems consist mainly of the I Sp orbitals that overlap with the Pb 6p and Pb 6s positioned closely to the band edges. The CB states close to the edge are dominated by Pb 6p orbitals. Consequently, for small excess energies, the hot electrons relax mainly via the motion of Pb

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atoms and the hot holes via the motion of both I and Pb atoms. For states close to the CBM, and for an excess energy up to 1 eV, the contribution of the cation to the DOS is not significant and the main contribution to the DOS comes from Pb 6p (see Figure S2). This indicates that only high-energy photons can excite the electronic states localized within the MA, FA, and Cs cations. It is worth noting that the states of the FA cation are well mixed into the CB and VB, whereas for states of the MA and Cs, cations mix only in the VB states. As already mentioned, the orbitals near the conduction band edge mostly consist of contributions from the Pb p orbitals; consequently, the NAC between electronic states should be highly sensitive to the displacements of the Pb atoms. Similarly, the NAC between hole states should be sensitive to the motion of both I and Pb atoms. To quantify the effect of the cationic motion on the dynamics of the P-I framework, we have computed the magnitude of atomic fluctuations using the ensemble-averaged standard deviation  $\sigma_i = \sqrt{\langle r_i^2 \rangle} - \langle r_i \rangle^2$ , following the approach previously applied to black phosphorus.<sup>32</sup> The values obtained for Pb atoms are  $\sigma_{\rm Pb} = 0.098$ , 0.117, and 0.131 Å for CsPbI<sub>3</sub>, MAPbI<sub>3</sub>, and FAPbI<sub>3</sub>, respectively, showing that Pb atoms in the CsPbI<sub>3</sub> are less mobile than in the other two systems. Consequently, the smaller average displacement of the Pb atoms results in weaker NACs.

Figure 5 illustrates the dependence of the electron (a) and hole (b) relaxation times as a function of excess energies  $\Delta E_{\rm e}$ 



Figure 5. Cooling time of hot electrons (a) and hot holes (b) as a function of excess energies in CsPbI<sub>3</sub> (solid circles), FAPbI<sub>3</sub> (blue squares), and MAPbI<sub>3</sub> (red triangles) perovskite systems.



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Figure 6. Relaxation time of hot electrons as a function of excitation energy in MAPbI<sub>3</sub> when MA molecules are free to move (black circles) and when they are frozen (red squares).

and  $\Delta E_{\rm h}$  for all three considered systems. As a general trend, the relaxation time decreases with increasing the excitation energy for both electrons and holes. Also seen from this figure is a clear and strong increase in the carrier cooling time for small excess energies. For the MAPbI<sub>3</sub> and FAPbI<sub>3</sub> systems, a saturation can be observed for the excess energies starting from 0.3 eV. In most of the cases, the relaxation time of electrons is longer than the one of the holes for a given value of the excess energy. As we have mentioned above, much slower cooling dynamics of charge carriers is obtained in the case of allinorganic perovskite CsPbI<sub>3</sub> as compared to the other two organic-inorganic perovskite systems. In fact, the relaxation time of the hot carriers can be more than three times greater in the latter system. This indicates the profound role of the cations on the cooling process of the charge carriers in leadhalide perovskites. Note that in the present study, only carrierphonon interaction contributes to hot carrier relaxation dynamics. Further studies are needed to investigate and identify the effect of carrier-carrier interaction on the nonradiative relaxation dynamics of hot carriers.

Next, we compare our computational findings on the relaxation time of hot carriers with the experimental results. Recently, Piatkowski et al.<sup>33</sup> experimentally estimated the cooling time for hot hole in FAPbI<sub>3</sub> to be 300 fs. Niesner et al.<sup>34</sup> reported that hot electrons in MAPbI<sub>3</sub> with excess energy  $\sim$ 1 eV above the CBM cool initially in about 280 fs, leaving an electron excess energy ~0.25 eV which in turn decays in very slow regime with a time scale of about ~100 ps. Mondal and Samanta<sup>20</sup> studied the charge carrier dynamics in all-inorganic perovskite nanocrystals CsPbI3 and estimated the hot electron cooling time to be in the range of 0.5-1 ps depending on the excitation energy. Our computed values for the cooling time of hot charge carriers are in good agreement with these experimental results. In other recent experiments an efficient slowing of the hot carrier cooling has been reported,<sup>19,21,24,25,35,36</sup> which was attributed to a hot phonon bottleneck effect that results in carrier reheating by reabsorption of the optical phonons. Our results are in good agreement with experimental values for low excitation pump fluences.<sup>21,24,25</sup> Note that our model does not quantitatively capture the cooling time for hot carriers with excess energies less than 0.25 eV for which the formation of large polarons is possible.  $^{34}$  In addition, we use only  $\Gamma$  point Brillouin zone



Figure 7. Carrier–phonon nonadiabatic couplings (in millielectronvolts) for MAPbI<sub>3</sub> when the MA molecules are free to move (a) and when they are frozen (b). The same index notations for the couplings are used as in Figure 4.

sampling during the excited-state dynamics (i.e.,  $\Gamma$  valley cooling), which does not allow us to account for relaxations of charge carriers between different symmetry points in the energy band structure (i.e., transition between *M* and  $\Gamma$  points<sup>35</sup>). This requires further research to identify the effect of valley-specific transitions on the cooling process of hot charge carriers. It is worth mentioning that the hydrogen bonding interactions<sup>37,38</sup> between the organic cations and the inorganic framework may also contribute to the charge carrier dynamics. However, further investigations are needed to identify the effect of hydrogen bonding interactions process.

To emphasize the importance of the cation nature on the relaxation process of hot charge carriers, we artificially constrained the cation motion in the MAPbI<sub>3</sub> system. This resulted in an increase of hot electron cooling time by a factor of 3 for all values of  $\Delta E_e$  (Figure 6). This can be explained in terms of the strongly reduced NACs in the latter systems, as shown in Figure 7. The reduction in the NACs are obtained for both valence and conduction bands and can be related to smaller vibrations of the Pb–I framework. The calculated  $\sigma$ values for Pb(I) atoms is 0.108(0.151) Å and 0.117(0.161) Å for frozen and mobile MA systems, respectively. Thus, the magnitude of the cation motion can impact significantly the hot carrier cooling process. This sheds light on the cation mixing and engineering strategies in order to slow the carrier cooling process and to enable their collection before the excess energy dissipates to the lattice.

In summary, the nonradiative relaxation dynamics of hot carriers in FAPbI<sub>3</sub>, MAPbI<sub>3</sub>, and CsPbI<sub>3</sub> perovskites has been studied using NAMD simulations in combination with timedependent DFT. The ultrafast relaxation of hot carriers to the band edges is obtained, which is in good agreement with recent experiments conducted at low excitation pump fluences. Our study reveals that the cooling of hot carriers is mediated by the strength of the displacements of I and Pb atoms due to the electron-phonon couplings. Interestingly, the cations play a major role in the hot carrier cooling dynamics. For example, the motion of MA and FA organic cations enhances electronphonon couplings compared to inorganic Cs cations, therefore leading to a faster cooling dynamics. Considerable increase in the relaxation time was also obtained when the MA molecules in MAPbI<sub>3</sub> were artificially frozen. Our findings reveal that the cation motion has a strong impact on the hot carrier cooling process. Therefore, cation mixing and engineering could be possible strategies leading to a slowing of the cooling process.

## COMPUTATIONAL METHODS

The carrier relaxation dynamics is studied using NAMD simulations implemented in the PYthon eXtension for Ab Initio Dynamics (PYXAID)<sup>39-41</sup> package. The computational approach is based on a combination of the fewest-switches surface hopping approach<sup>28</sup> and Kohn-Sham single-particle description within the so-called neglect of back-reaction approximation (NBRA). The coordinates of the initial structures were optimized using the Vienna ab initio simulation package (VASP).<sup>42,43</sup> The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)<sup>44</sup> was used to represent the exchange-correlation functional. Electronic structure calculations and adiabatic molecular dynamics are carried out using the Quantum Espresso (QE) code.45 Dispersion correction vdW-DF-obk8<sup>46</sup> implemented in QE was used to account for van der Waals interactions. More details about the simulation and the NAMD methodology can be found in refs 39-41 and in the Supporting Information. Our model systems consist of  $2 \times 2 \times 2$  unit cells of MAPbI<sub>3</sub>, FAPbI<sub>32</sub> and CsPbI<sub>3</sub> cubic phase perovskites for which the band gaps are along the  $\Gamma$  point (see Figure S1). Therefore, the excited-state calculations are performed using  $\Gamma$  point Brillouin zone integration. Ground-state molecular dynamics trajectories are sampled from the NVT ensemble utilizing the velocity Verlet scheme<sup>47</sup> combined with the Andersen thermostat.<sup>4</sup> The 7 ps trajectories are obtained with the integration time step of 1 fs and the Andersen thermostat collision frequency of 0.05 fs<sup>-1</sup>. The initial 1 ps of the trajectory were used for nuclear subsystem thermalization (equilibration). The subsequent 6 ps were used for the NAMD simulations and for the analysis. The hot carrier relaxation processes is studied by choosing a minimal basis of adiabatic excited states represented by excited Slater determinants constructed from the Kohn-Sham orbitals.<sup>49</sup> In order to get reliable statistics, the results are averaged over 1000 stochastic realizations of the surface hopping algorithms and over 20 starting geometries. The hot carrier relaxation dynamics is investigated by computing the average energy and population of several excited charge carrier states.

# ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b01732.

Lattice parameters used in the simulations; averaged values of NACs; electronic band structures; density of states; electronic population dynamics in FAPbI<sub>3</sub>, MAPbI<sub>3</sub>, and CsPbI<sub>3</sub> (PDF)

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#### Notes

The authors declare no competing financial interest.

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