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Supporting Information for:

Hot Carriers in Halide Perovskites: How Hot Truly?

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Methods

Materials:

Lead (II) Iodide (PbI_2 , 99.999%), Lead (II) Bromide (PbBr_2 , 99.999%), Oleylamine (>98%), n-Octylamine (99%), Oleic Acid (90%), Acetonitrile (99.8%), N, N-Dimethylformamide, (anhydrous, 99.8%) and Toluene (anhydrous, 99.7%) were purchased from Sigma-Aldrich. Methylammonium Bromide (MABr) and Methylammonium Iodide (MAI) were purchased from Greatcell Solar. The precursor materials were used without further purification.

Sample Fabrication

MAPbI₃ thin-film:

63.6 mg of MAI and 184.4 mg of PbI_2 were dissolved in 2 mL of N, N-Dimethylformamide and stirred overnight at 70 °C to produce a clear precursor perovskite solution. 30 μL of this precursor solution was spread on a cleaned quartz substrate and spin-coated at 5000 rpm for 12 s. At 3 s, 100 μL of toluene was dropped on the spinning substrate. At the end of spin coating, the substrate was annealed on a hotplate at 100 °C for 30 minutes.

MAPbI₃ Nanocrystals:

MAPbI₃ NCs were synthesized according to a previously reported method by Zhang et al.¹ Briefly, a precursor solution of MAPbI₃ was obtained by dissolving 15.9 mg of MAI and 46.1 mg PbI_2 into 2 mL of acetonitrile. 20 μL of oleylamine and 0.2 mL of oleic acid was subsequently added to this precursor solution. The precursor solution was added dropwise to 10 mL of anhydrous toluene under vigorous stirring to obtain a crude NCs solution. To purify the NCs, the crude solution was centrifuged first at 8000 rpm for 10 min and the supernatant was discarded. Subsequently, the precipitate was redispersed and centrifuged again at 4000

rpm for 10 min. Finally, the precipitate containing large-sized particles was discarded and the supernatant kept in a nitrogen environment prior to further studies.

MAPbBr₃ Nanocrystals:

MAPbBr₃ NCs were synthesized with a similar process. Briefly, 0.16 mmol of MABr and 0.2 mmol PbBr₂ were dissolved into 5 mL of N, N-Dimethylformamide. 50 μ L of oleylamine and 1.5 mL of oleic acid was subsequently added to this precursor solution. 200 μ L of precursor solution was swiftly injected into 5.0 mL of anhydrous toluene under vigorous stirring to obtain a crude NCs solution. To purify the NCs, the crude solution was centrifuged at 12000 rpm for 10 min and the precipitate containing large particles was discarded. The supernatant containing smaller sized particles was kept in a nitrogen environment prior to further studies.

Ultrafast Transient Absorption Spectroscopy

TA spectroscopy was conducted with a HELIOS femtosecond transient absorption spectrometer (Ultrafast Systems, LLC). The 400 nm (3.1 eV) pump pulses were generated by frequency doubling of the 800 nm fundamental output from the regenerative amplifier (Coherent Legend, 1 kHz, 150 fs) with a BBO crystal. The regenerative amplifier was seeded with a Ti-Sapphire mode-locked oscillator (Coherent Vitesse, 100 fs, 80 MHz). The probe pulse used was a visible white light continuum (400 – 850 nm) generated by focusing the 800 nm fundamental output from the regenerative amplifier into a 2 mm sapphire crystal. The probe white light beam was passed through a 750 nm short-pass filter to eliminate any residual 800 nm fundamental components to prevent any strong secondary photoexcitation of the sample. The signals were collected using a CMOS sensor within the spectrometer. Thin-film samples were kept in a nitrogen-filled sample chamber during the conduct of the TA spectroscopy to prevent ambient exposure. Colloidal nanocrystal solutions were filled into 2 mm path length quartz cuvettes in a nitrogen-filled environment and continuously stirred during the conduct of TA spectroscopy to prevent any unwanted artefacts due to photo-charging.

Supplementary Figures

S1. Effect of choice in fitting range on extracted carrier temperatures

Figure S1: Effect of the choice of the fitting region on the extracted carrier temperature from the TA spectra of MAPbI₃. (a – d) Illustration of the fits (red lines) performed using various length L of the fitting range along the energy axis (x-axis) and (e) their corresponding carrier temperatures. (f – i) Illustration of the fits (red lines) performed with different start points H expressed as the fraction of the main PB peak maximum, and (j) their corresponding carrier temperatures.

S2. Calculated derivatives of MAPbI₃ TA Spectra

Figure S2: Numerically calculated derivatives of the TA spectra of MAPbI₃ thin-film at $t = 0.6$ ps, normalized to the region of interest (ROI). The derivatives were computed using the finite difference method of the original spectra, with the central-difference scheme. The shaded region highlights the ROI within the “high energy tail”. The amplitude of this region diminishes with higher-order derivatives, indicating that the region does not conform to equation (2) in the main text.

S3. Normalized derivatives of Maxwell-Boltzmann Distribution

Figure S3: Normalized derivatives of the Maxwell-Boltzmann distribution, f_{MB} . The Fermi energy was set at 0 eV, indicated by the grey vertical lines as a guide. (a) f_{MB} (blue solid line) and its first derivative (orange solid line). The shape of the curve is unaltered and is a mirror image about the x-axis. (b) Higher-order derivatives (up to the 4th) of f_{MB} . The 2nd derivative completely overlaps the initial function, so does the 3rd overlap the 1st and so on.

S4. Convergence of $f_e(E)$ and $f_{MB}(E)$ at different temperatures

Figure S4: (a) The Fermi-Dirac (FD, solid lines) and Maxwell-Boltzmann (MB, dashed lines) distribution functions plotted at 300 K (blue lines) and 1000 K (red lines). E_F is set to 0 for simplification. (b) Values of Δ plotted for both temperatures. The dashed line corresponds to $\Delta = 10^{-3}$ to serve as a guide.

S5. Extracted fitting parameters for Nanocrystals

Figure S5: Extracted parameters (Γ and ΔE_g) for (a) MAPbI₃ and (b) MAPbBr₃ NCs from the fitting procedure discussed in the main text.

S6. Normalized TA surface plots of MAPbBr₃ Nanocrystals

Figure S6: Normalized pseudo-colour TA surface plot of MAPbBr₃ NCs. The NCs were excited with 3.1 eV pulses at a fluence corresponding to an initial photogenerated number of excitons per NC of (a) $\langle N \rangle \sim 0.11$ and (b) $\langle N \rangle \sim 1.50$

S7. Absorption and PL Spectra of MAPbI₃ Thin-film

Figure S7: (a) Normalized linear absorption and PL spectra of MAPbI₃ thin-film. (b) Fitting of absorption spectrum (background subtracted) with Elliott's equation. The fit yields $E_g = 1.65 \pm 0.01$ eV and $E_b = 10 \pm 1$ meV.

S8. Absorption and PL Spectra of MAPbI₃ Nanocrystals

Figure S8: (a) Normalized linear absorption and PL spectra of MAPbI₃ nanocrystals. (b) Fitting of absorption spectrum (background subtracted) with Elliott's equation. The fit yields $E_g = 1.73 \pm 0.01$ eV and $E_b = 20 \pm 2$ meV.

S9. Absorption Spectra of MAPbBr₃ Nanocrystals

Figure S9: (a) Normalized linear absorption and PL spectra of MAPbBr₃ nanocrystals near the band edge. (b) Fitting of absorption spectrum (background subtracted) with Elliott's equation. The fit yields $E_g = 2.50 \pm 0.01$ eV and $E_b = 31 \pm 1$ meV.

S10. TEM Analysis of MAPbI₃ Nanocrystals

S11. TEM Analysis of MAPbBr₃ Nanocrystals

Supplementary Text:

N1. Detailed discussion on approximation

The commonly adopted procedure to determine T_c utilizes the following equation to fit the region of interest (ROI) of the TA spectra:

$$\frac{\Delta T}{T}(E) \propto \exp \frac{E_F - E}{k_b T_c} \quad (1)$$

This equation stems from the approximation of the Fermi-Dirac distribution to the Maxwell-Boltzmann distribution. The Fermi-Dirac distribution function reads as:

$$f_e(E) = \frac{1}{e^{E-E_F/k_b T_c} + 1} \quad (2)$$

When $(E - E_F) \gg k_b T_c$, the term $e^{E-E_F/k_b T_c} \gg 1$, so that:

$$f_e(E) \approx f_{MB}(E) = \frac{1}{e^{E-E_F/k_b T_c}}. \quad (3)$$

The difference, Δ , can be expressed as (Equation (3) of the main text):

$$\Delta = f_{MB}(E) - f_e(E) = \frac{1}{\exp\left(\frac{\bar{E}}{k_b T_c}\right) + \exp\left(\frac{2\bar{E}}{k_b T_c}\right)} \quad (4)$$

For any positive value of Δ , equation (4) can be rearranged as follows:

$$\bar{E} = k_b \log\left(\frac{1}{2}\left(\sqrt{4e^\Delta + 1} - 1\right)\right) \times T_c \quad (5)$$

Equation (5) suggests that $\bar{E}$, the distance on the energy axis away from E_F , increases linearly with T_c . This implies that at high T_c , the region of fitting shifts substantially away from E_F and may overlap with the second PB peak from a deeper valence band to the conduction band

commonly seen in halide perovskites.²⁻³ Furthermore, this reveals an inherent circular problem; to know the region where this approximation holds, we would need to know T_c , which we can only get from the fitting in the first place. Therefore, this shows that an arbitrary choice of a fitting region is usually inaccurate, as the approximation may not necessarily be true in this arbitrary choice of ROI.

N2. A detailed description of the fitting model

A band-filling model based on the parabolic band hypothesis was used to model the TA spectra of perovskites. The model assumes that the parabolic band hypothesis is valid in the fitting window, which is reasonable within ~ 0.2 eV of the bandgap.⁴ Similar models have been used with success in describing the properties of perovskites in previous studies.⁴⁻⁶ The TA signal (change in absorption) can be modelled with equation (7) of the main text, assuming $m_e \approx m_h$ ⁷⁻⁸ so that $f_h \approx f_e$:

$$\Delta A = \left(1 - f_e(E, E_F, T_c)\right)^2 \times A_{ex}(E; E_g - \Delta E_g) - A_0(E; E_g) \quad (6)$$

where ΔA is the change in absorption, f_e is the Fermi-Dirac distribution, E_F is the quasi-Fermi energy, T_c is the carrier temperature, E_g is the bandgap energy, ΔE_g is the shift in the bandgap, A_{ex} is the absorption spectrum after excitation and A_0 is the absorption spectrum before excitation. A can be modelled based on Elliott's theory and includes contributions from both excitons and free carriers as follows:

$$A = A_{cont}\left(E, E_g, \Delta E_g(t), E_F(t), E_b, \Gamma(t)\right) + A_{exc}\left(E_g(t), E_b, \Gamma(t)\right) \quad (7)$$

where E_b is the exciton binding energy and Γ is the spectral linewidth. The continuum contribution, A_{cont} can be described by:

$$A_{continuum} \propto \frac{\sqrt{E_b}}{\hbar\omega} \frac{\Theta(\hbar\omega - E_g)}{1 - \exp^{-2\pi\sqrt{E_b/(\hbar\omega - E_g)}}}$$

where we have also considered the enhancement of the absorption by coulomb effects.

Similarly, the exciton contribution A_{ex} can be described by:

$$A_{exciton} \propto \frac{1}{\hbar\omega} \sum_{i=1}^{\infty} E_b^{3/2} \frac{\delta(\hbar\omega - E_g + E_b/i^2)}{i^3}$$

The fitting window was chosen within ~ 0.2 eV of the bandgap energy, in the range where the parabolic band hypothesis should still hold well.⁴

As the fitting is sensitive to the initial values of the parameters, they were determined by fitting the linear absorption spectra of the samples to Elliott's model (equation 7). ΔE_g , Γ and E_F were time varying while E_g and E_b were shared global parameters. An appropriate range for the time varying parameters was chosen such that their trend is continuous and not erratic with discontinuities. Fitting was performed using the Levenberg-Marquardt least squares method and by globally minimizing the fitting residues across all the spectra at several time delays of interest.

N3. Applicability of model to Nanocrystals

One of the key concepts behind our fitting model is that the electrons and holes obey Fermi-Dirac statistics and form a Fermi-Dirac distribution following thermalization. This may be obvious in bulk semiconductors but not so in the case of nanocrystals (NCs). Our MAPbI₃ and MAPbBr₃ NCs are in the weak confinement regime, where the NCs size is much larger than the Bohr radius (~ 2.0 nm for MAPbBr₃ and ~ 2.2 nm for MAPbI₃⁹). As such, the spacing between discrete energy levels of the individual NCs is expected to be small, such that $\Delta E \ll$

$k_b T_c$. In this limit, the energy levels of the NCs can be treated like a continuum similar to the bulk semiconductor¹⁰.

Moreover, the ensemble of NCs, has an intrinsic size distribution which causes inhomogeneous broadening in absorption transitions. This is evident in the absorption spectra of the NCs vs bulk (Figure S7 & S8, respectively); it can be observed that the width of the exciton contribution in the MAPbI₃ NCs is much broader than the bulk thin-film. This broadening is also evident in the TA spectra of NCs; the main PB peak in the TA spectrum of NCs is much broader than that of the bulk. It should also be noted that the standard fitting method does not take this broadening into account, and the broadening of the PB peak may additionally inflate the extracted carrier temperatures, as previously reported for a similar analysis of TRPL data.¹¹ Our proposed model takes this broadening into account within the linewidth factor Γ .

Hence, the combination of the two factors essentially implies that macroscopically, electronic states in the NCs ensemble resemble that of the bulk semiconductors and thus, the Fermi-Dirac distribution can be used to describe the TA spectrum of the ensemble of NCs.

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