

## Supporting information

### Many-Body Interactions in Photo-Excited Lead Iodide Perovskite

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#### 1) Sample preparation

We followed the method of Liu et al.<sup>1</sup> using dual-source thermal evaporation method to prepare the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite thin film.  $\text{CH}_3\text{NH}_3\text{I}$  powders were synthesized from hydriodic acid (57 wt%, stabilizer free in water, Sigma Aldrich) and methylamine solution (33 wt% in ethanol, Sigma Aldrich).  $\text{PbCl}_2$  were purchased from Sigma Aldrich and used as received. Sapphire crystals (z-cut, 0001 orientation, MTI cooperation) were used as substrates and rinsed with isopropanol prior to use. For the preparation of so-called mixed halide perovskites, we evaporated  $\text{CH}_3\text{NH}_3\text{I}$  and  $\text{PbCl}_2$  from separate crucibles in a high vacuum chamber (base pressure  $<10^{-7}$  mbar) with the ratio of deposition rates of  $\sim 10:1$ , as monitored by a quartz crystal microbalance (QCM) positioned next to the sample substrates. During the vapor-deposition process, the substrates were slowly rotated along the surface normal for homogeneous film formation. The vapor pressure (mainly due to  $\text{CH}_3\text{NH}_3\text{I}$ ) was  $\sim 2 \times 10^{-5}$  torr during deposition. The obtained perovskite films were annealed at 100 °C for 40 mins in a  $\text{N}_2$  filled glovebox to remove the excess organic molecules and to facilitate further crystallization.

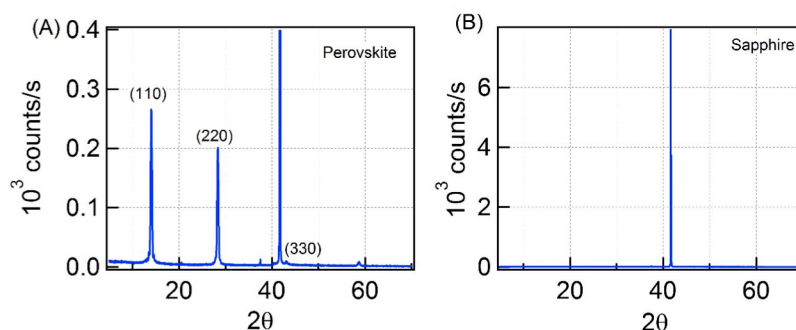


Figure S1. XRD spectra for lead iodide perovskite grown from  $\text{PbCl}_2$  precursor on sapphire (A) and bare sapphire substrate (B).

Figure S1 (A) and (B) show the X-ray diffraction (XRD) spectra of vapor deposited lead iodide perovskites from  $\text{PbCl}_2$  precursor and the sapphire substrate, respectively. The XRD spectra were taken on an X'Pert<sup>3</sup> Powder instrument from PANalytical in  $\omega$  -  $2\theta$  mode with Cu K- $\alpha$  source. The peaks at  $14.12^\circ$ ,  $28.44^\circ$  and  $43.23^\circ$  match well with the (110), (220) and (330) positions from vapor evaporated perovskite.<sup>1</sup> Note that the most intense peak at  $41.63^\circ$  in Fig. 1 (A) comes from the sapphire substrate, Fig. S1 (B).

## 2) Transient Absorption (TA) measurement

We carrier out ultrafast transient absorption measurements using a commercial Ti:sapphire laser (800 nm, 100 fs, 3.5 mJ, 1 kHz). Part of the fundamental laser beam was directed into an optical parametric amplifier (TOPAS, Coherent Inc.) to generate tunable pump laser (UV to near IR). A small portion of the fundamental beam was focused onto a sapphire crystal to produce the white-light super-continuum light (visible: 450 nm – 830 nm, NIR: 850 nm – 1600 nm) as probe. The pump beam was lightly focused into the sample with a spot diameter of  $\sim 1$  to 2 mm depending on the pumping colors. The transmitted probe beam was focused onto a fiber coupled high speed multichannel detector and collected by a high speed spectrometer (HELIOS, Ultrafast Systems). All samples were mounted in a  $\text{N}_2$  filled sample tube for TA measurements at room temperature.

## 3) Hot carrier cooling rate

We obtain hot carrier cooling time constants from single exponential fits to ground state recovery dynamics at different excitation photon energies, Fig. 1F. The carrier cooling time constants (blue dots) are plotted against the excess excitation energy ( $h\nu_1 - E_g$ ) in Fig. S2. A linear fit (red line) gives an energy-loss rate,  $dE/dt$ , of  $5.0 \pm 0.4$  eV/ps.

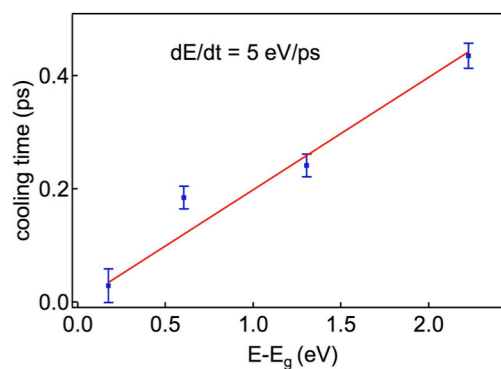


Fig. S2. Dependence of hot carrier cooling time constants (blue dots) on excess excitation photon energy above band gap. The red line is a linear fit.

### 3) Spectra red-shift from global fits

Assuming the absorption at the band-edge is given by a Gaussian distribution, the difference in absorption,  $\Delta A$ , is given by:

$$\Delta A(\varepsilon) = A_t e^{-\left(\frac{\varepsilon - \varepsilon_0 - \Delta\varepsilon}{W}\right)^2} - A_0 e^{-\left(\frac{\varepsilon - \varepsilon_0}{W}\right)^2}$$

where  $A_0$  is absorption amplitude before pumping,  $\varepsilon_0$  and  $\Delta\varepsilon$  are the optical gap energy and spectral shift, respectively.  $W$  is the Gaussian width.  $A_t$  is amplitude at pump-probe delay  $t$ . Taking into account bleaching due to carrier population after pumping, we can describe  $A_t$  as:

$$A_t = A_0 \left[ 1 - b \left( 1 - e^{-\frac{t}{\tau}} \right) \right]$$

where  $\tau$  is the hot carrier cooling time obtained from Fig. 1F in the main text;  $b$  is the fraction of bleaching at  $t \gg \tau$ ,  $0 \leq b \leq 1$ , here the value of 0 or 1 represents total transmission or total bleaching, respectively. All constants are global parameters except  $\Delta\varepsilon$ .

The optical gap,  $\varepsilon_0$ , is determined from 2<sup>nd</sup> derivative of the linear absorption spectrum, as shown figure S3.

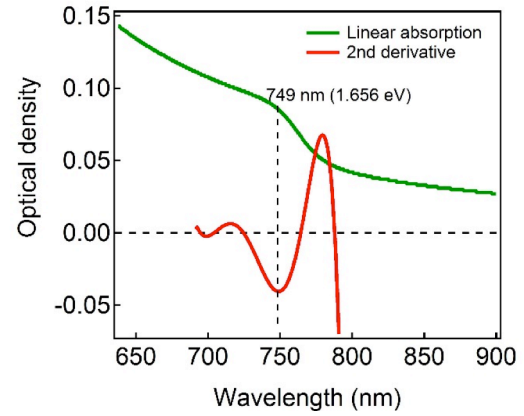


Figure S3. Linear absorption of the lead iodide perovskite and its 2<sup>nd</sup> derivative. The optical gap is determined as a local minimum of the 2<sup>nd</sup> derivative at 749 nm (1.656 eV).

### 4) Auger recombination models: global fits

The solution to the eqn. (2) is given by:

$$N = \frac{Ck_1 e^{-k_1 t}}{1 - Ck_A e^{-k_1 t}} \quad (S1)$$

where  $C = \frac{N_0}{k_1 - k_A N_0}$ .

In fitting to equation (3), we find the trapping channel is negligible, and all data sets can be well-described by setting  $k_I = 0$ . Equation (3) can be solved as:

$$t = C + \frac{1}{k_2 N} + \frac{k_A}{k_2^2} \ln \left( \frac{N}{k + k_A N} \right) \quad (S2)$$

Figure 4 shows the bleaching dynamics at various excitation densities and global fits to eqns. (S1) and (S2).

### 5) Conversion from absorption to excitation density

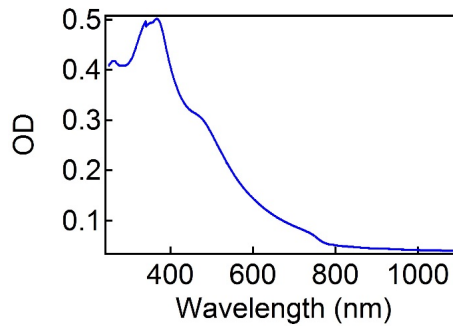
The number of absorbed photon per pulse is given by:

$$N = \frac{\Delta P}{500 * A * E * 1.6 * 10^{-19}}$$

Where A is the area of the pump spot (diameter = 2 mm).  $E = 2.95$  eV is the pump photon energy. 500 is the number of laser pulses in 1 s. The different power before and after the sample is given by:

$$\Delta P = \Delta I = I_0(1 - e^{-OD * \ln(10)})$$

The optical density (OD) at 2.95 eV (420 nm) is 0.355. At 50  $\mu$ W (3.2  $\mu$ J/cm<sup>2</sup>) and the sample thickness of 35 nm, the absorbed photon density is  $1.1 \times 10^{18}$  cm<sup>-3</sup>.



*Figure S4. Optical absorption spectrum of a 35 nm thin film of lead iodide perovskite. The film thickness was determined in atomic force microscopy with part of the film scratched off the sapphire surface.*

## References

1. Liu, M., Johnston, M. B. & Snaith, H. J. Efficient planar heterojunction perovskite solar cells by vapour deposition. *Nature* **501**, 395–8 (2013).
2. Manser, J. S. & Kamat, P. V. Band filling with free charge carriers in organometal halide perovskites. *Nat. Photonics* **8**, 737–743 (2014).
3. Guyot-Sionnest, P. & Hines, M. A. Intraband transitions in semiconductor nanocrystals. *Appl. Phys. Lett.* **72**, 686 (1998).
4. Pankove, J. I. *Optical Processes in Semiconductors*. (Courier Dover Publications, 1971)