

# Hole Cooling Is Much Faster than Electron Cooling in PbSe Quantum Dots

## Supporting Information

*Frank C. M. Spoor,<sup>†</sup> Lucas T. Kunneman,<sup>†</sup> Wiel H. Evers,<sup>†,‡</sup> Nicolas Renaud,<sup>†</sup> Ferdinand C. Grozema,<sup>†</sup> Arjan J. Houtepen<sup>\*†</sup> and Laurens D. A. Siebbeles<sup>\*†</sup>*

Email: A.J.Houtepen@tudelft.nl; L.D.A.Siebbeles@tudelft.nl

<sup>†</sup>Optoelectronic Materials Section, Department of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

<sup>‡</sup>Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands

## Positive background in the high energy TA spectrum

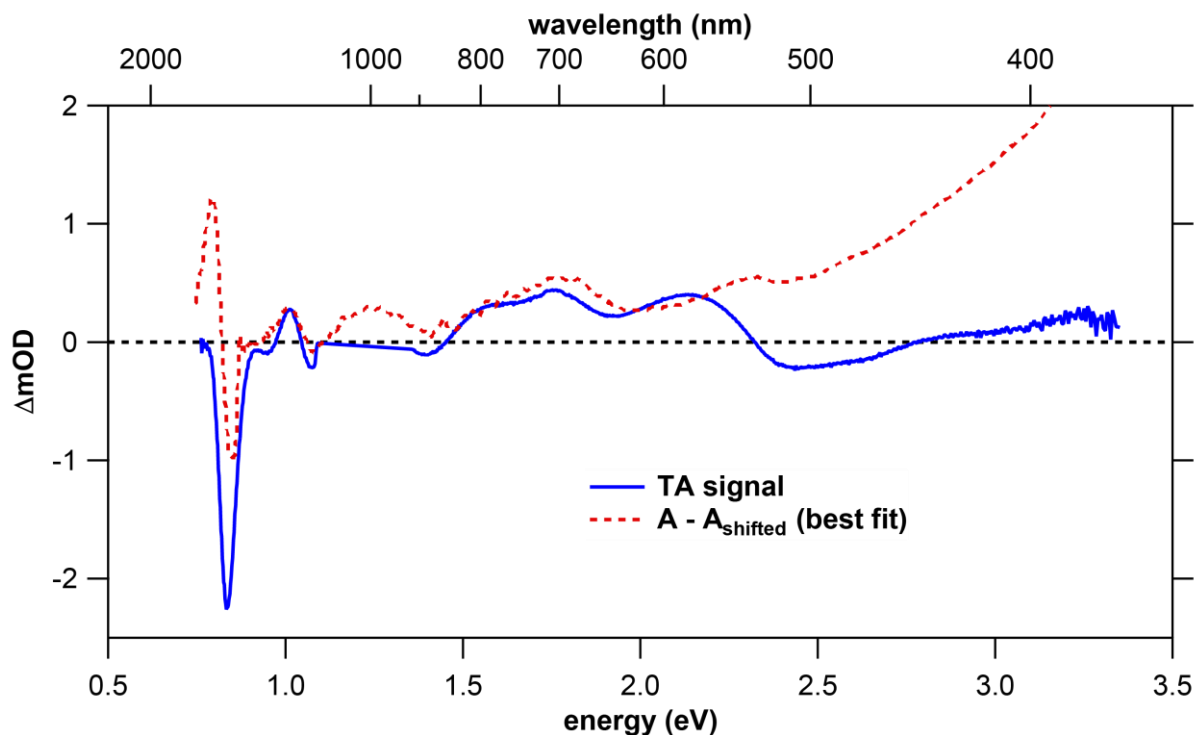
We examine the influence of the positive background on the results of our fit model of the high energy transient absorption (TA) spectrum. Figure S1 shows the TA spectrum for 4.8 nm PbSe quantum dots (QDs) obtained for pump photon energy at the band gap. For comparison we also show the difference between the ground-state absorption spectrum and a red-shifted ground-state absorption spectrum. The magnitude of the red-shift was adjusted to achieve an optimal fit to the TA spectrum. This way the visible part of the TA spectrum is well reproduced. By contrast, the high energy part of the TA spectrum deviates significantly from the fit result. Evidently the TA spectrum cannot be described by a constant red-shift of the ground-state absorption spectrum, but possibly the red-shift is a function of energy and/or intraband absorption also contributes to the signal. The negative part is caused by bleach features X and Y as discussed in the main text on top of this positive background.

To improve the agreement we use a phenomenologically determined function to describe the positive background in the high energy part of the TA spectrum. Figure S2 shows the TA spectrum near the energies of the bleach features X and Y (transitions  $L_{4-6}$  and  $L_{5-7}$ , see main text) and a fit without background (a), with an energy independent background (b) and a background that depends on energy as a first order polynomial (c) or second order polynomial (d). We observe that fits without background or an energy independent background fail to reproduce the low and high energy edges of the TA spectrum. Therefore we do not consider these backgrounds further. The first and second order polynomial backgrounds reproduce the TA spectrum.

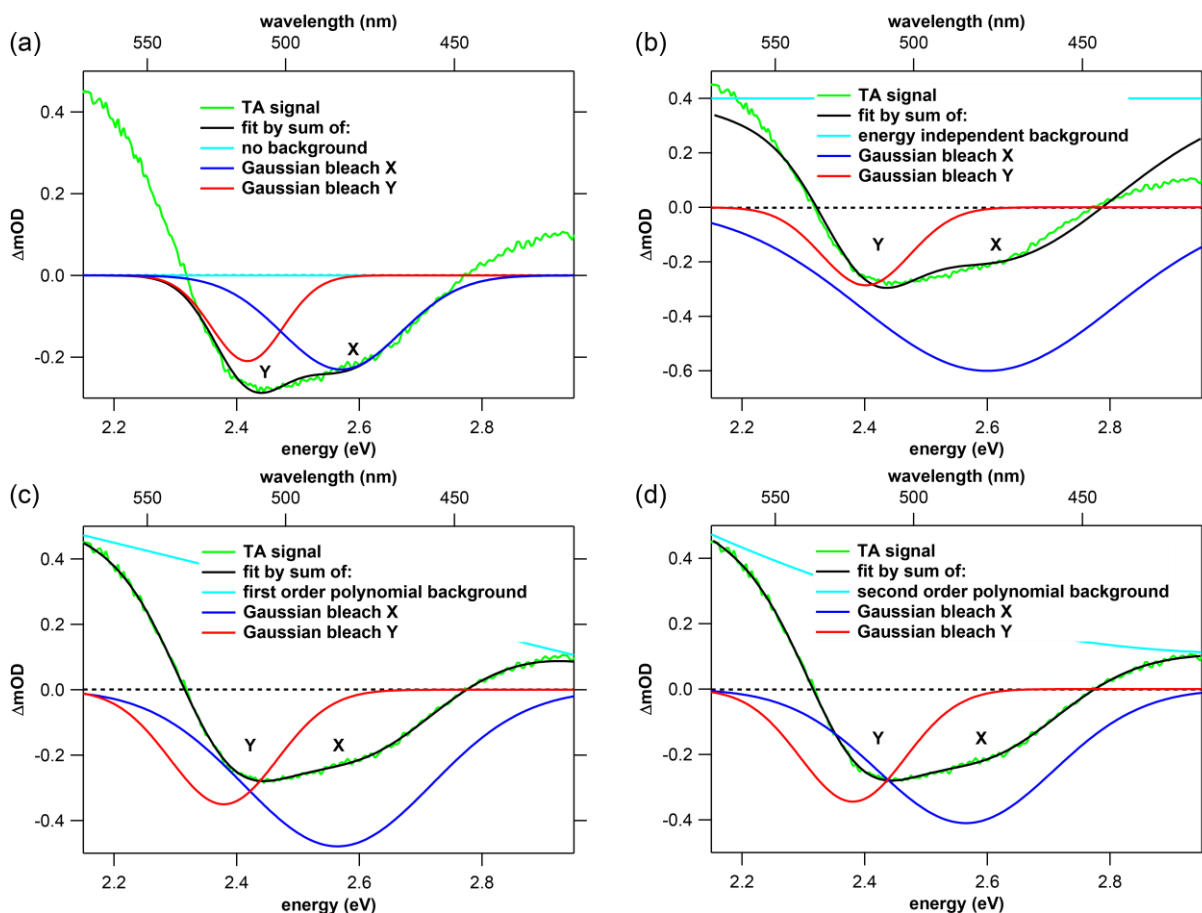
The fits of our model to the TA spectrum for each pump-probe delay yield the time-dependent amplitudes of the Gaussian functions that describe the bleach of the  $L_{4-6}$  and  $L_{5-7}$  transitions. The increase of the amplitudes of the Gaussians during time could be described by single exponential

functions (see main text). We show the time constants of these exponentials as a function of excitation energy in Figure S3 for the  $L_{4-6}$  transition and in Figure S4 for the  $L_{5-7}$  transition for backgrounds with a first or second order polynomial shape. The time constants for the increase of the  $L_{4-6}$  and  $L_{5-7}$  transition bleach with time are similar for the first and second order polynomial background. We choose the first order polynomial background.

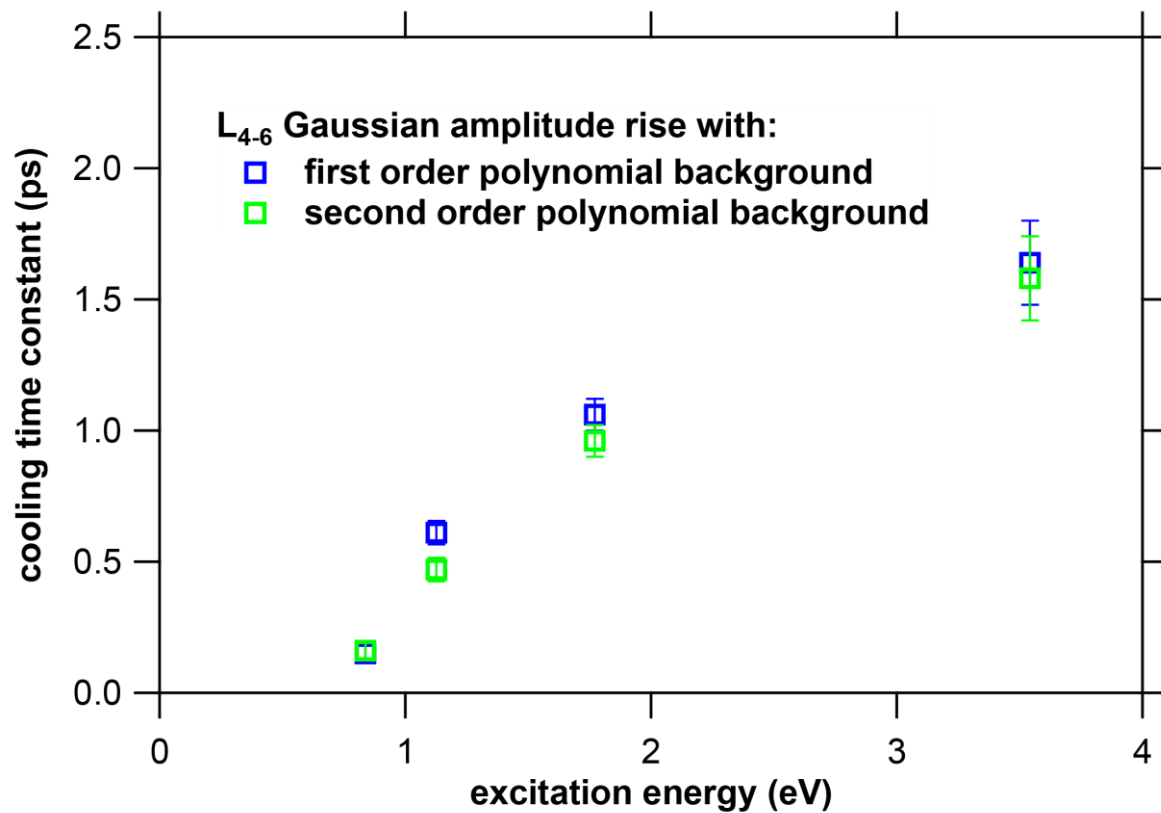
With this modeling we can estimate the absorption strength of the  $L_{4-6}$  and  $L_{5-7}$  transitions compared to the  $L_{5-6}$  (band edge) transition. A single cold exciton will cause a bleach of  $1/4$  of the  $L_{5-6}$  absorption peak due to the 8-fold degeneracy of the 1S level in this band and taking into account stimulated emission. Likewise, the cold exciton will cause a bleach of  $1/8$  of the  $L_{4-6}$  and  $L_{5-7}$  absorption peaks due to the absence of stimulated emission. Therefore  $\left(\frac{\Delta A}{A}\right)_{5-6} = 2 \left(\frac{\Delta A}{A}\right)_{4-6 \text{ or } 5-7}$  and taking the required values from the ground-state absorption and TA spectra we find that  $A_{4-6} = A_{5-7} = 0.12 A_{5-6} = 5.5 \text{ mOD}$ .



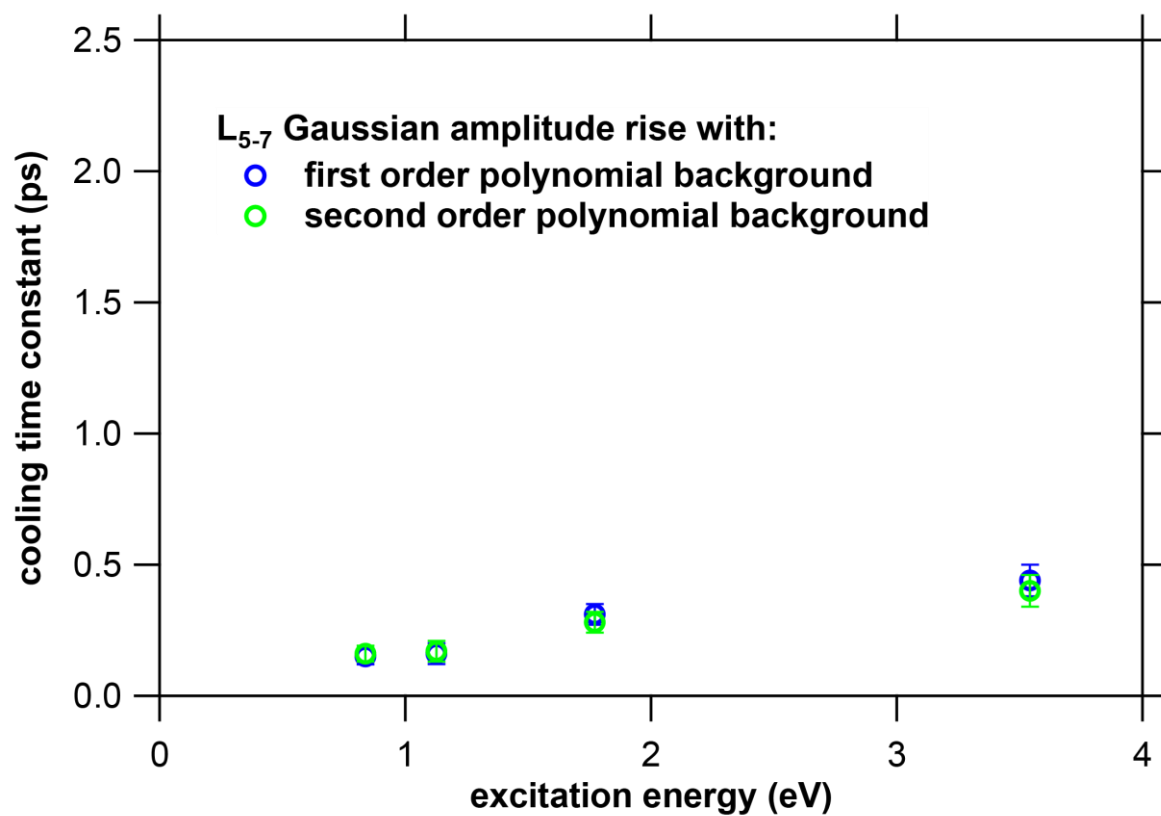
**Figure S1.** TA spectrum for 4.8 nm PbSe quantum dots (QDs) excited by a pump laser pulse with photon energy at the band gap (0.83 eV, 1500 nm) together with the difference between the ground-state absorption spectrum and the red-shifted ground-state absorption spectrum.



**Figure S2.** Different background models and the resulting fits on top of the high energy TA spectrum for 4.8 nm PbSe QDs excited at the band edge. Results are shown without background (a), with an energy independent background (b) and a background that depends on energy as a first order polynomial (c) or second order polynomial (d).



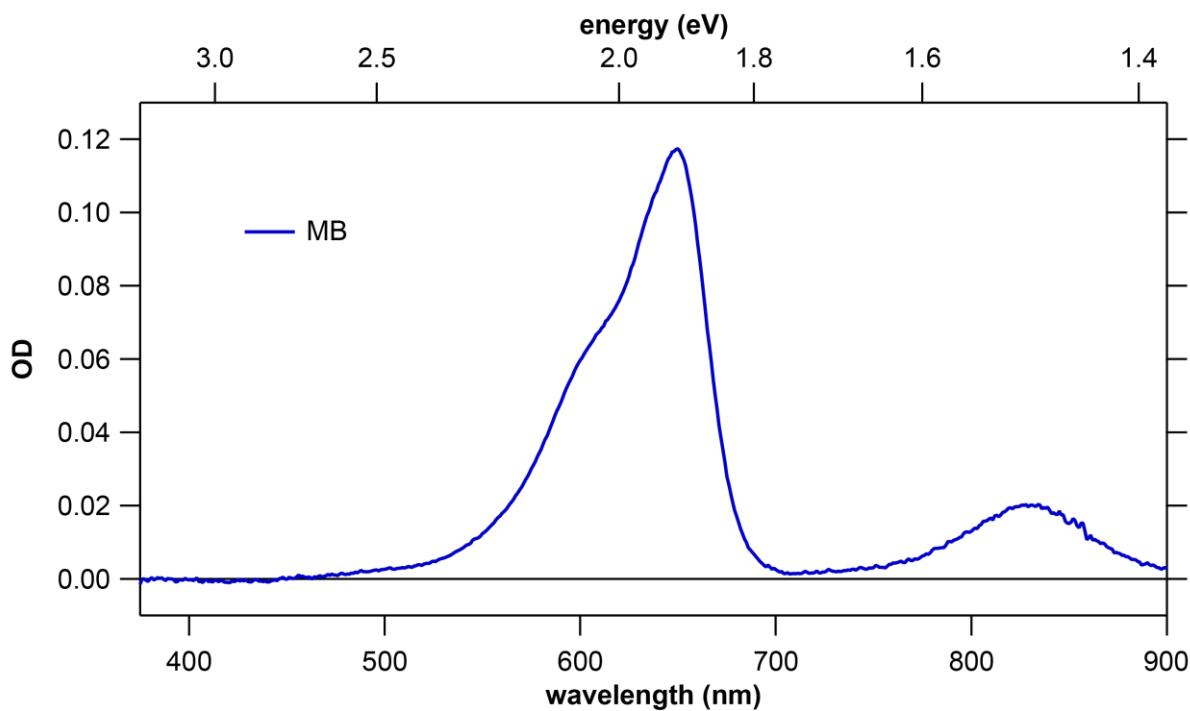
**Figure S3.** Time constants describing the rise of Gaussian amplitude of the L<sub>4-6</sub> transition during time using single exponential fit functions, obtained with a background that depends on excitation energy as a first or second order polynomial.



**Figure S4.** Time constants describing the rise of Gaussian amplitude of the  $L_{5-7}$  transition during time using single exponential fit functions, obtained with a background that depends on excitation energy as a first or second order polynomial.

### Methylene Blue (MB) absorption

We show the ground-state absorption spectrum of MB in Figure S5. We observe that MB has absorption features at 550-700 nm and 800-900 nm. Since the high energy TA signal and especially the bleach features X and Y we consider in the main text are situated at 450-550 nm we can rule out any influence of MB on our analysis. The bleach feature of MB appearing in TA experiments after electron transfer is situated at approximately 650 nm and is therefore unfortunately just outside of the range of 375-600 nm we consider.

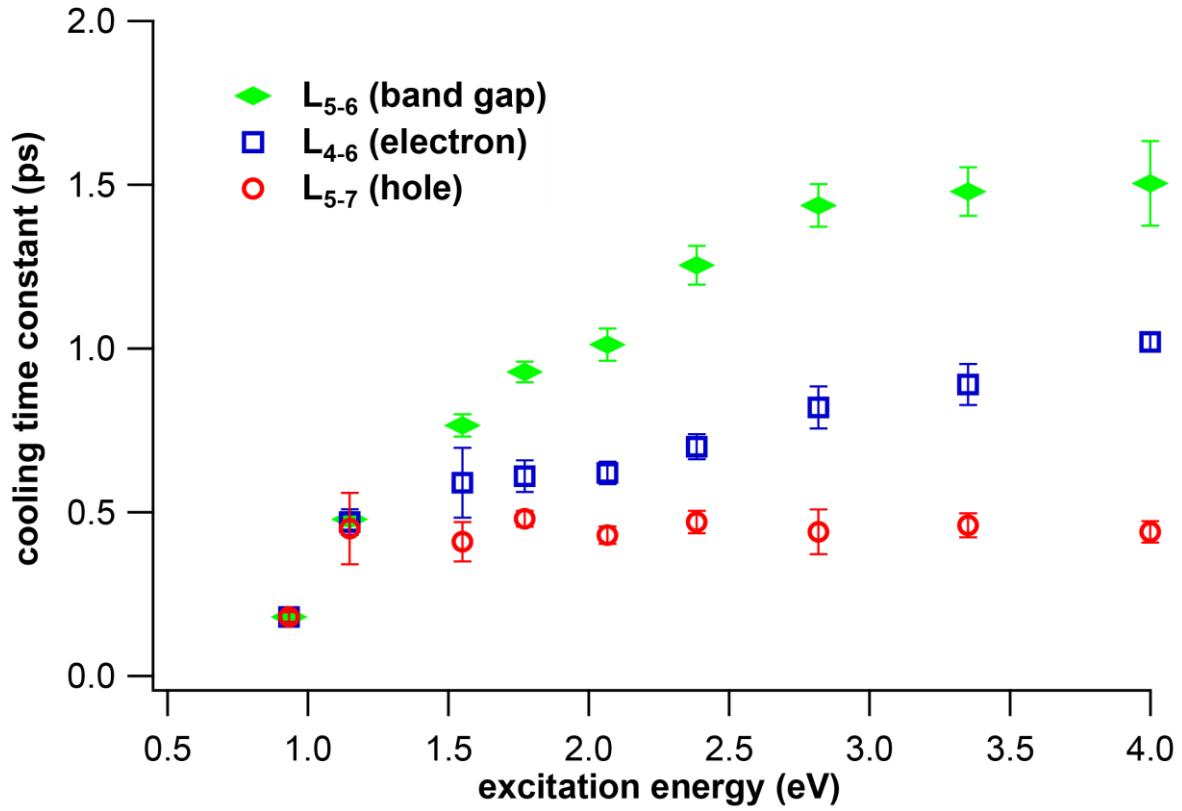


**Figure S5.** Ground-state absorption spectrum of Methylene Blue (MB).



### Cooling time constants for 3.9 nm PbSe QDs

We show cooling time constants in Figure S6 for 3.9 nm PbSe QDs using an identical analysis as for the 4.8 nm PbSe QDs (see main text). We observe that again hole cooling is much faster than electron cooling, although the exact cooling time constants are somewhat different.



**Figure S6.** Time constants describing the rise of the  $L_{5-6}$  bleach and the rise of the Gaussian amplitudes of the  $L_{4-6}$  and  $L_{5-7}$  transitions using single exponential fit functions for 3.9 nm PbSe QDs.

### Effective masses at the L-point

We observed (see main text) that the  $L_{4-6}$  transition energy changes less with QD diameter than the  $L_{5-7}$  transition energy. Table S1 shows the transverse and longitudinal effective masses calculated for bands 4-7 at the L-point, obtained by numerical differentiation of their energies as implemented in BAND. The effective masses of charges in band 7 are lower than in band 4, while the effective masses of charges in band 5 and 6 are comparable. This agrees with the stronger dependence of the  $L_{5-7}$  transition energy on QD diameter than the  $L_{4-6}$  transition.

**Table S1.** PbSe transverse and longitudinal effective masses for bands 4-7 at the L-point obtained from DFT calculations.

Direction	Band 4	Band 5	Band 6	Band 7
Longitudinal	2.884	0.152	0.140	0.424
Transverse	0.195	0.055	0.057	0.149