SUPPORTING INFORMATION

Intraband dynamics of mid-infrared HgTe Quantum dots

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Modelling of band edge dynamics

To include exciton cooling in the band-gap dynamics upon non-resonant excitation, we employ a rate equation model as depicted in figure 1. Excitation by the laser is treated as instantaneous, which creates a highly excited electron hole pair $|e_i,h_i\rangle$. This exciton then relaxes to lowest excitonic state $|e_0,h_0\rangle$ with a cooling time τ_c. The exciton recombination time is denoted as τ_e. Since the exciton cooling times are much shorter than the recombination time (also see figure 2) we neglect direct recombination of the initial state $|e_i,h_i\rangle$. The populations of the initial state, N_i, and ground state, N_0, are then described by the resulting differential equation:

$$\frac{dN_i}{d_t} = -\frac{N_i}{\tau_c} \tag{1}$$

$$\frac{dN_0}{d_t} = -\frac{N_0}{\tau_e} - \frac{dN_i}{d_t} \tag{2}$$

It has the following solution for the band-gap state population upon non-resonant excitation:

$$N_0(t) = \Theta(t) \cdot \frac{N_i(0) \cdot \tau_e}{\tau_c - \tau_e} \cdot \left[\exp\left(-\frac{t}{\tau_c}\right) - \exp\left(-\frac{t}{\tau_e}\right)\right] . \tag{3}$$

This equation still holds for resonant excitation, in the limit of vanishing cooling time. To incorporate bi-exciton dynamics into this model, we mimic the commonly used bi-exponential model[1,2] by using two instances of the above equation, one representing the single exciton decay, the other one the bi-exciton recombination, where the exciton lifetime, τ_e is replaced by the bi-exciton recombination time, τ_b, arriving at:

$$N_{0(t)} = \Theta(t) \cdot \left[\frac{N_{i,e}(0)\tau_e}{\tau_c - \tau_e} \cdot \left(\exp\left(-\frac{t}{\tau_c}\right) - \exp\left(-\frac{t}{\tau_e}\right)\right) + \frac{N_{i,b}(0)\tau_b}{\tau_c - \tau_b} \cdot \left(\exp\left(-\frac{t}{\tau_c}\right) - \exp\left(-\frac{t}{\tau_b}\right)\right)\right]. \tag{4}$$

Here, $N_{i,e}(0)$ and $N_{i,b}(0)$ denote the number of excited electron hole pairs in particles with a single exciton only and particles with two excitons, respectively.

Calculation of the mean excitation number from the band-gap dynamics

We first consider a population conserving rate-equation model for Auger decay of bi-excitons and recombination of excitons:

$$\frac{dN_B(t)}{dt} = -\frac{N_B(t)}{\tau_B} \tag{5}$$

$$\frac{dN_E(t)}{dt} = -\frac{N_E(t)}{\tau_E} - \frac{dN_B(t)}{dt} \,. \tag{6}$$

Here, τ_B and τ_E are the Auger decay time for bi-excitons and the recombination time of excitons, N_B and N_E denote the numbers of excited bi-excitons and excitons, respectively. It was assumed that all bi-excitons decay into excitons via direct recombination, i.e. there is no direct recombination for bi-excitons, which is a reasonable approximation given the more than 20-fold difference in lifetimes. The solution to equations 5+6 is:

$$N_B(t) = N_B \cdot e^{-\frac{t}{\tau_B}} \tag{7}$$

$$N_E(t) = \left(N_E + \frac{\tau_E}{\tau_E - \tau_B} N_B\right) e^{-\frac{t}{\tau_E}} - \frac{\tau_E}{\tau_E - \tau_B} N_B \cdot e^{-\frac{t}{\tau_B}}. \tag{8}$$

From equations 7+8 the bleach signal, $S(t)$, is constructed as:

$$S(t) \propto N_E(t) + 2 \cdot N_B(t) \tag{9}$$

$$\propto \left(N_E + \frac{\tau_E}{\tau_E - \tau_B} N_B\right) e^{-\frac{t}{\tau_E}} + \left(2 - \frac{\tau_E}{\tau_E - \tau_B}\right) N_B \cdot e^{-\frac{t}{\tau_B}}. \tag{10}$$

This retrieves the commonly used bi-exponential model for multi-excitonic decays. The factor of 2 accounts for the fact, that the bi-excitonic state results in approximately twice the bleach signal as a singly excited quantum dot. For low excitations densities, we assume Poissonian statistics for the probability, P(N), to find N excitations in a single particle:

$$P(N) = \frac{\langle N \rangle^N}{N!} \cdot e^{-\langle N \rangle}. \tag{11}$$

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Comparing the probabilities for double and single excitations in equation 11, the mean exciton number per particle, *<N>*, is found as

$$\langle N \rangle = 2 \cdot \frac{P(2)}{P(1)} = 2 \cdot \frac{N_B}{N_E}. \tag{12}$$

The parameters N_B and N_E can be extracted from a bi-exponentail fit of the band-gap dynamics in conjunction with equation 10.

In the limit $\tau_B \ll \tau_E$ the temporal evolution of the bleach signal (equation 10) could also be simplified to

$$S(t) \propto (N_E + N_B) e^{-\frac{t}{\tau_E}} + N_B \cdot e^{-\frac{t}{\tau_B}}. \tag{13}$$

For the exciton and bi-exciton lifetimes presented in this work, this would lead to an overestimation for N_B of approximately 5%. In the regime of a bi-exponential model for the band-gap dynamics,

$$S(t) = A_{fast} \cdot e^{-\frac{t}{\tau_{fast}}} + A_{slow} \cdot e^{-\frac{t}{\tau_{slow}}}, \tag{14}$$

the exciton numbers can be estimated as $N_{biexc} = A_{fast}$ and $N_{exc} = A_{slow} - A_{fast}$, leaving

$$< N > = 2 \cdot \frac{N_B}{N_E} \tag{15}$$

$$= 2 \cdot \frac{A_{fast}}{A_{slow} - A_{fast}}. \tag{16}$$

Extracting the exciton and bi-exciton numbers from a bi-exponential fit is only valid as long, as there are no tri-excitons present, as they are not accounted for in the model. We estimate, that this treatment is valid, as long as there are at least tenfold more bi-excitons than tri-excitons. From equation 11 one can derive:

$$\frac{P(3)}{P(2)} = \frac{\langle N \rangle}{3} \leq 0.1 \tag{17}$$

$$\Rightarrow \langle N \rangle \leq 0.3 \tag{18}$$

An overview of extracted mean exciton numbers for low fluences can be found in the inset of figure S1.

Excitation density dependence of the transient signal

In the MEG range, Poisson statics can no longer be employed. We therefore employ an Einstein coefficient-based approach to be able to compare excitations densities below and above the MEG onset. We neglect carrier relaxation during our 100 fs pump pulse. The carrier dynamics can then be described by excitation by photon absorption and de-excitation by stimulated emission. Using the Einstein-coefficient for absorption, A, the number of excited electron hole pairs, N, can be described as:

$$dN = A \cdot N_{gs} \cdot dP - A \cdot N \cdot dP \tag{19}$$

$$= A \cdot (N_{tot} - 2N) \cdot dP. \tag{20}$$

Here, N_{gs} denotes the number of unexcited electron hole pairs, P is the excitation power. N_{tot} is the number of electron hole pairs in the system that are in resonance with the pump. This inhomogeneous differential equation is solved by:

$$N(P) = 0.5 \cdot N_{tot} \cdot (1 - \mathrm{e}^{-2AP}\ ). \tag{21}$$

This relationship gives a good representation for our data as shown in figure S1. Here, F_0 denotes the fluence, at which 50% of the saturation value is reached. For excitations below the MEG onset

also the mean exciton numbers extracted from the band gap dynamics as described above are shown in the inset. The linear relation between the mean exciton number, $\langle N \rangle$, and the normalized fluence is commensurate with the two-fold degenerate LUMO state in the se particles and further justifies the Einstein coefficient-based approach.

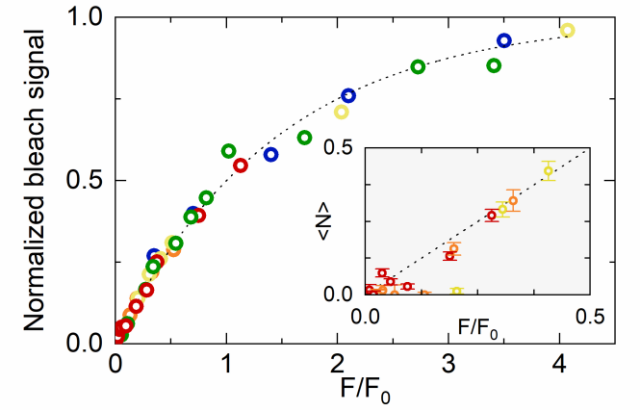

Figure S1: Normalized bleach signal as a function of pump fluence. All data points have been fit to a model based on Einstein coefficients for absorption and stimulated emission (dotted line). The value F_0 denotes the fluence, where 50% of the saturation value is reached, which is also the threshold for a linear relationship between fluence and bleach signal. Different pump wavelengths are color-coded as 2.4 µm (red), 2.0 µm (orange), 1.2 µm (yellow), 800 nm (green) and 400 nm (blue). The inset shows the mean exciton number per quantum dot as retrieved from Poissonian statistics using the same normalized fluence.

References

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2. Melnychuk, C. & Guyot-Sionnest, P. Multicarrier dynamics in quantum dots. *Chem. Rev.* **121**, 2325–2372 (2021).