Investigating charge carrier recombination in perovskite materials

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Thanks to their ideal band-gap and high absorption coefficient, perovskite materials are good candidates for the next generation of solar cells with an impressive certified 25.2% power conversion efficiency[1]. In particular, $CH_3NH_3PbI_3$ (MAPI) solar cells presents a simple solution processing alongside an easy deposition method by spin coating. However, point defects such as iodide vacancies have been shown to be responsible for degradation and performance losses in such devices [2-3]. Time resolved photoluminescence (TRPL) allows to investigate charge carrier recombinations and defects in perovskites. Here the interpretation of such measurement is discussed.

Introduction

- Defect-induced trap states are responsible for degradation and performance losses in perovskites [2-3];
- TRPL is a measure of the probability of a photon to be emitted by the perovskite through a radiative charge carrier recombination after a certain time after a short excitation pulse.
- Radiative recombinations compete with other recombination processes including trap states mediated recombinations.
- Time correlated single photon counting (TCPSC) allows to measure TRPL and thus to investigate trap states in perovskites.

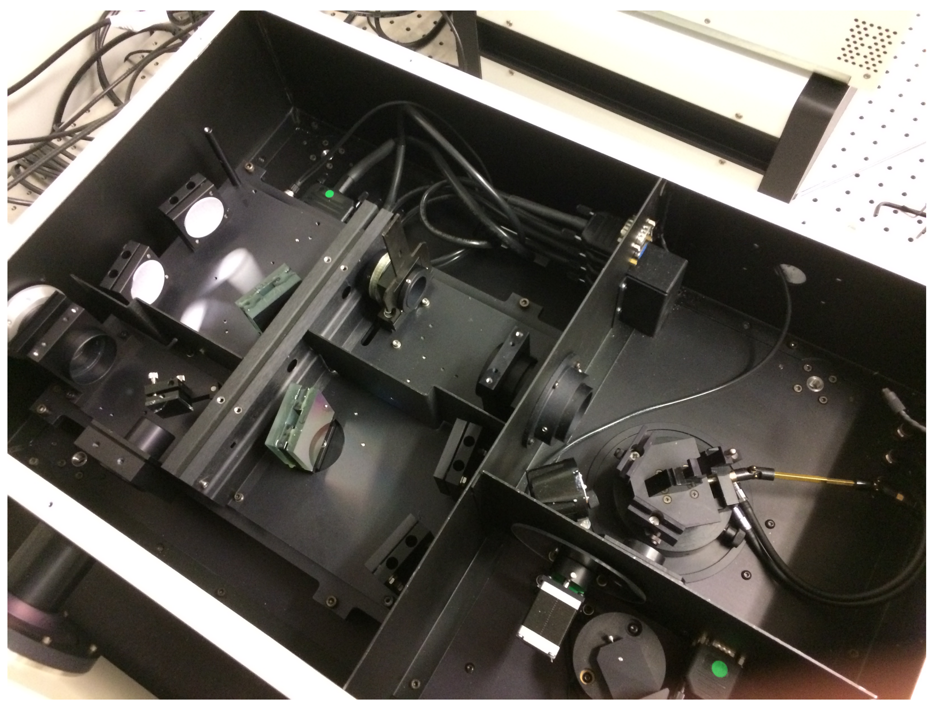


Figure 1: Insides of a TCSPC. A laser repeatedly excite electrons in the sample and after each excitation pulse, 0 or 1 emitted photons are measured.

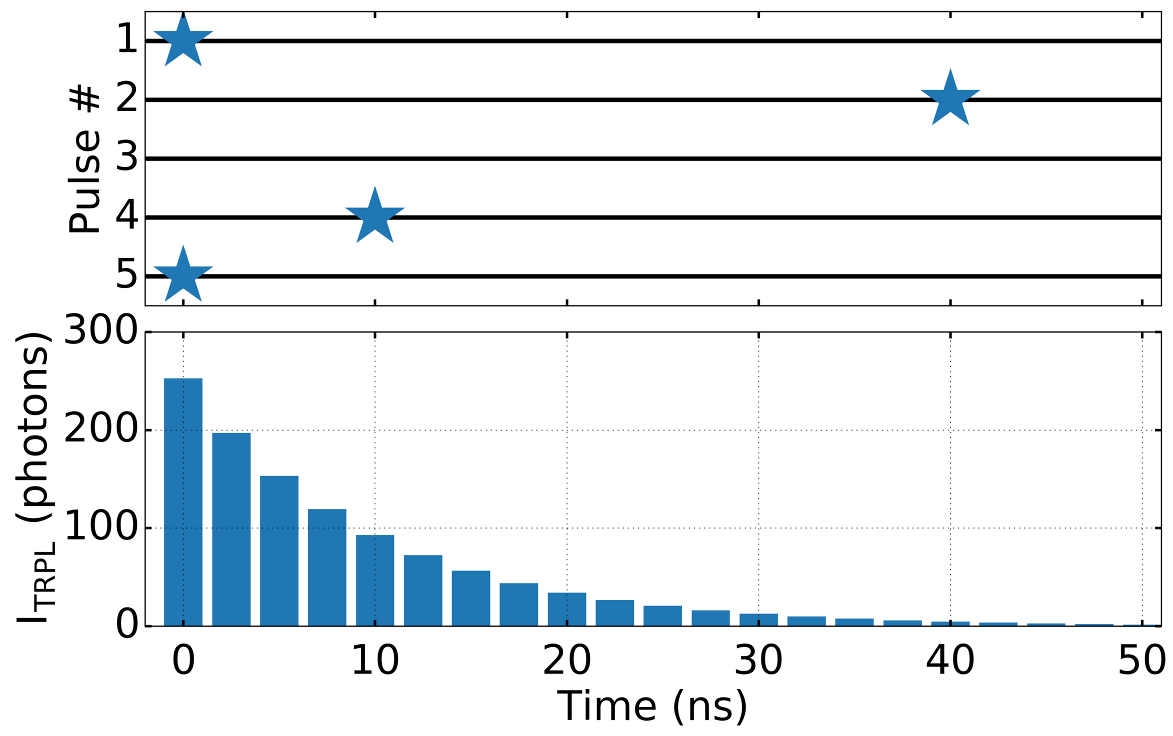
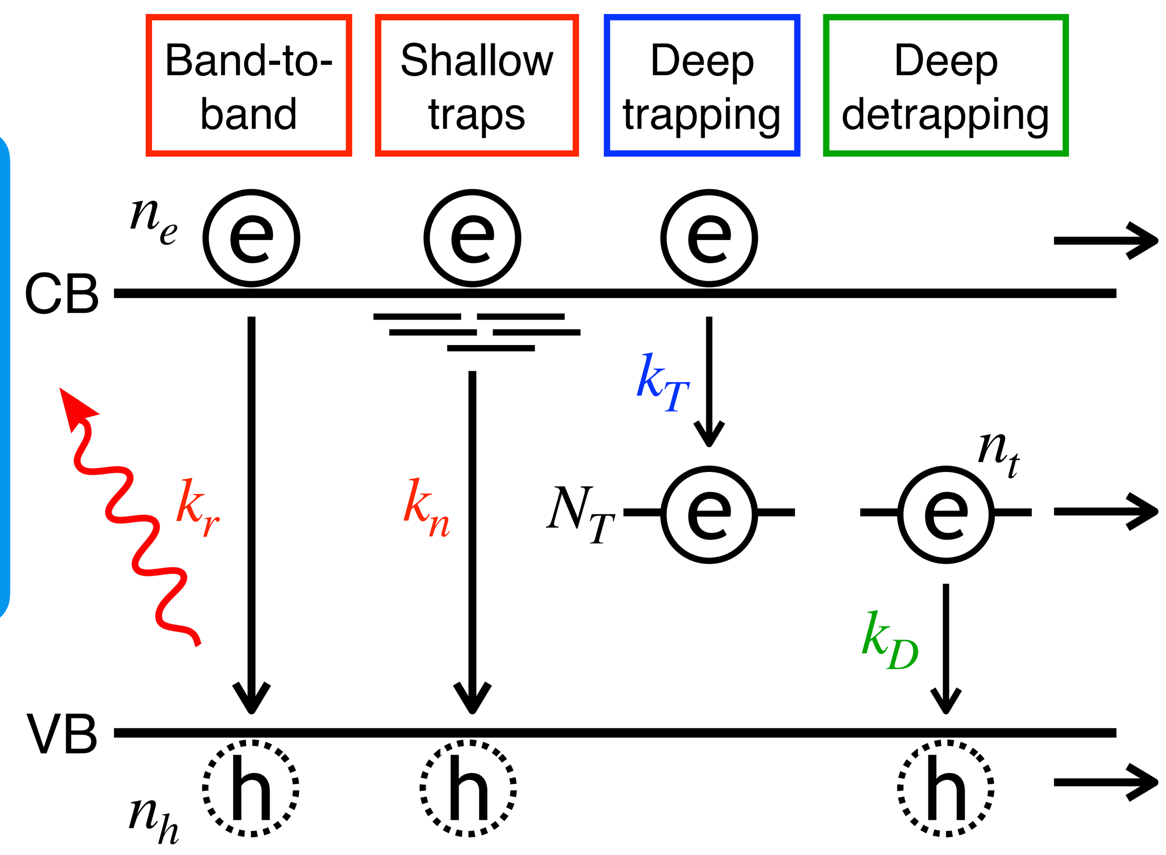


Figure 2: Example of photons measured after 5 consecutive pulses at t=0 (*top*) and TRPL intensity obtained after multiple excitation pulses (*bottom*).

Methodology

n_e: Photoexcited electron concentration
n_h: Photoexcited hole concentration
n_t: Trapped electron concentration
N_T: Deep trap state concentration



$$\frac{dn_e}{dt} = -(\underbrace{k_r + k_n}_{k_b})n_e n_h - k_T n_e (N_T - n_t)$$

$$\frac{dn_t}{dt} = k_T n_e (N_T - n_t) - k_D n_t n_h$$

$$\frac{dn_h}{dt} = -(\overbrace{k_r + k_r}^{k_b})n_e n_h - k_D n_t n_h$$

- The probability of two carriers recombining in a perovskite is equal to the product of their concentration multiplied by the associated recombination rate [4-5]:
- Band-to-band recombination: radiative direct electron n_e - hole n_h recombination (rate k_r);
- Shallow trap states assisted recombination: non-radiative direct electron n_e - hole n_h recombination (rate k_n);
- Deep trap states trapping: non radiative recombination between electrons n_e and unoccupied deep trap states $N_T - n_t$ (rate k_T);
- Deep trap states detrapping: non radiative recombination between trapped electrons n_t and holes n_h (rate k_D);
- The TRPL intensity is proportional to the number of photons emitted *i.e.* $I_{TRPL}(t) \propto k_r n_e(t) n_h(t)$;
- The laser excitation pulse creates the same amount of photoexcited electrons and holes *i.e.* $n_e(t=0) = n_h(t=0) = N_0$. The trap states are assumed empty before the excitation pulse *i.e.* $n_t(t=0) = 0$

Results

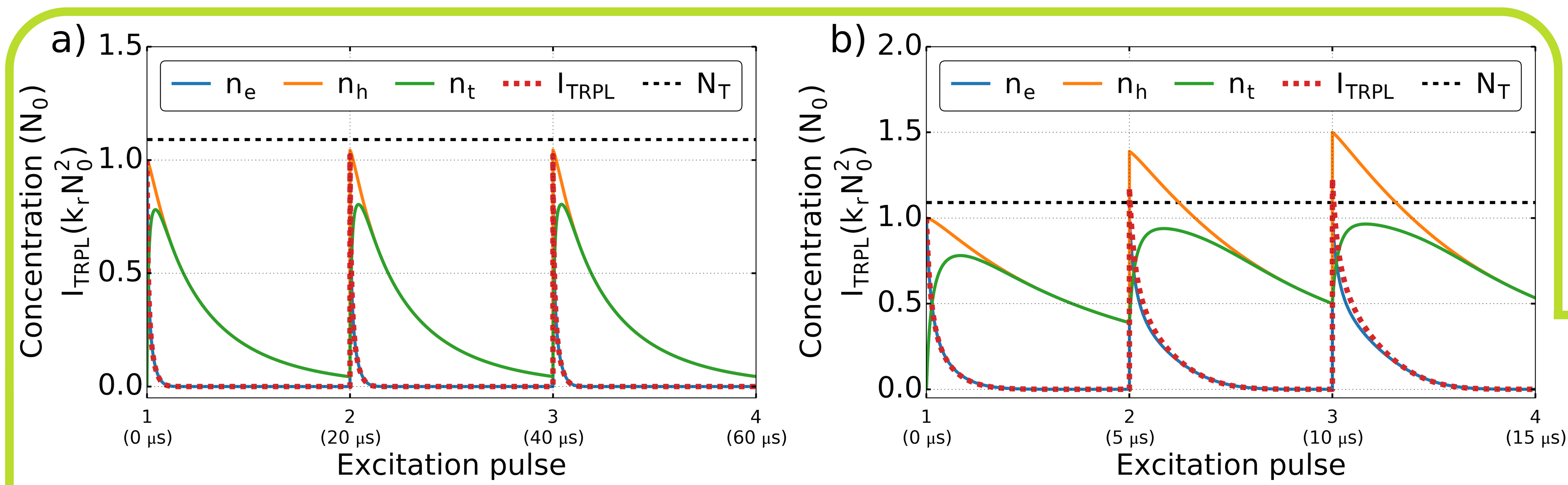


Figure 3: Evolution of the charge carrier concentrations and TRPL intensity after 3 consecutive excitation pulses for excitation pulse repetition rates of **a)** 20 μs and **b)** 5 μs simulated using constants from [5].

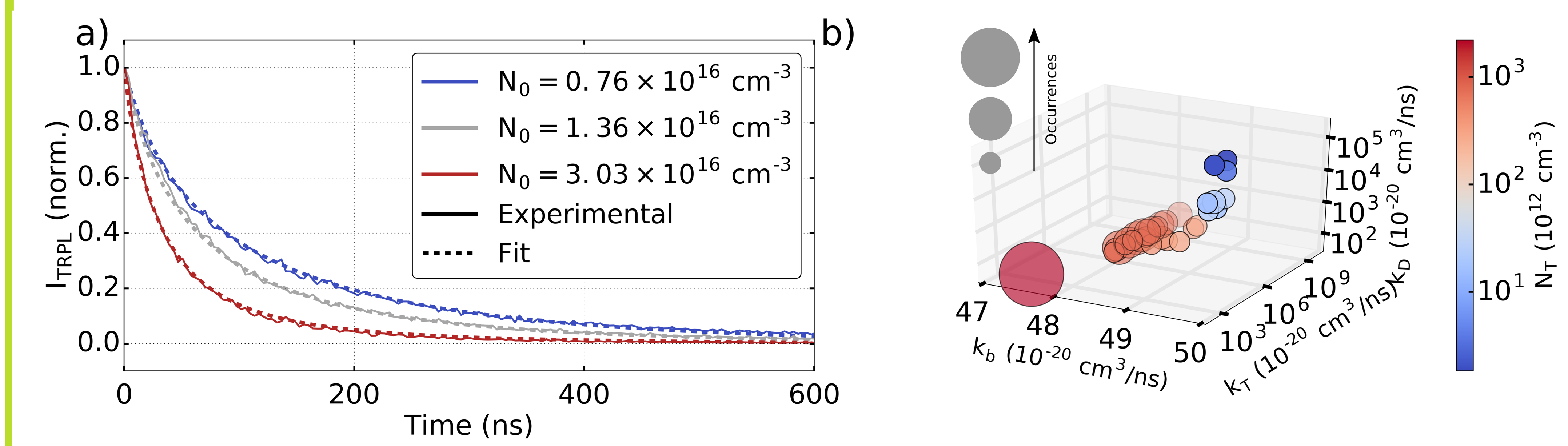


Figure 4: **a)** Fitting of TRPL decays of a MAPI thin film on glass measured at different excitation fluencies and **b)** results of the fitting of the same data using a wide range of guess parameters.

- Most recombinations happen after the TRPL reaches zero and are thus "invisible";
- Fitting of experimental data by simulating a unique excitation pulse requires that the experimental variation of the carrier concentrations after each excitation pulse are identical;
- Fitting of TRPL decays of a MAPI thin film on glass using the recombination model gives a high $R^2 = 0.998$;
- However, the optimised fitting parameters depend on the guess parameters. Multiple values of the k_T, k_D and N_T are found to be acceptable fits to the experimental data while a small range of k_b is found;
- It is likely that the excitation fluencies were high enough to saturate the deep trap states. Deep trapping and detrapping are thus negligible at this fluencies and the information associated (k_T, k_D and N_T) cannot be retrieved from the TRPL decay.

Conclusion

- Charge carrier recombination in perovskites require two carriers to happen and thus depend on the carrier concentrations;
- It is possible to fit experimental TRPL decays by simulating a single excitation pulse;
- However, this requires to ascertain that all experimental pulses lead to the same variation of the carrier concentrations;
- Samples need to be measured with a wide range of excitation fluencies in order to observe all the recombination processes.

References

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Acknowledgments

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