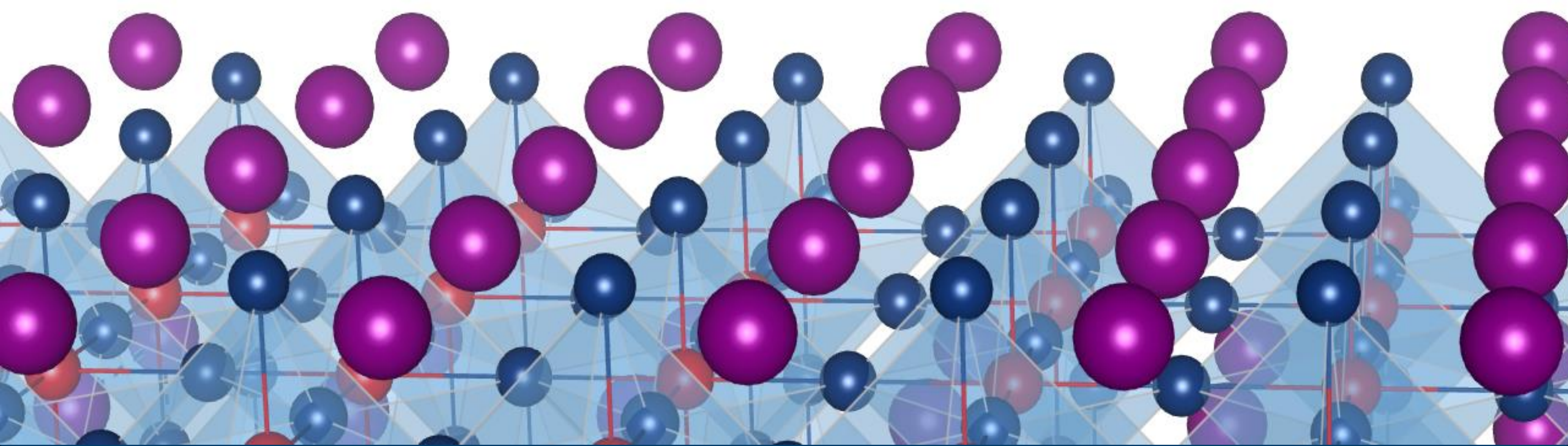


RECOMBINATION AND THE CONCEPT OF CHARGE CARRIER LIFETIMES IN LEAD-HALIDE PEROVSKITES

Thomas Kirchartz[1,2], Lisa Krückemeier[1], Zhifa Liu[1], Uwe Rau[1]

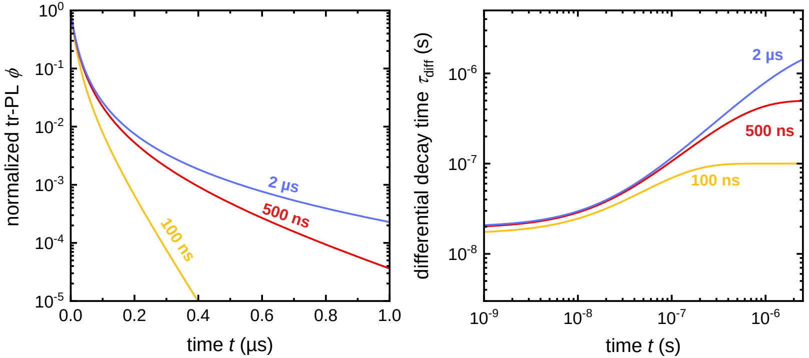
[1]IEK-5 Photovoltaik, Forschungszentrum Jülich,

[2]NST and CENIDE, Universität Duisburg-Essen

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

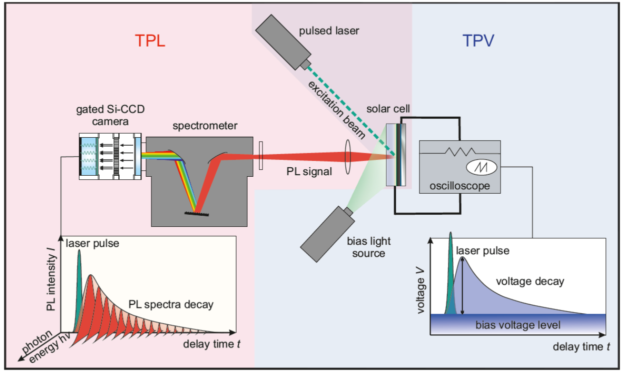
JÜLICH Forschungszentrum

Outline

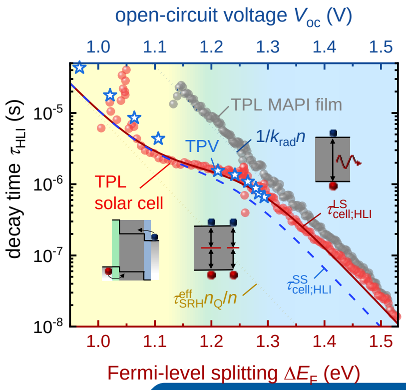


1) What is a charge carrier "lifetime"?
2) Why is it important?

3) How do I measure it on different sample types?



4) How to interpret the data?



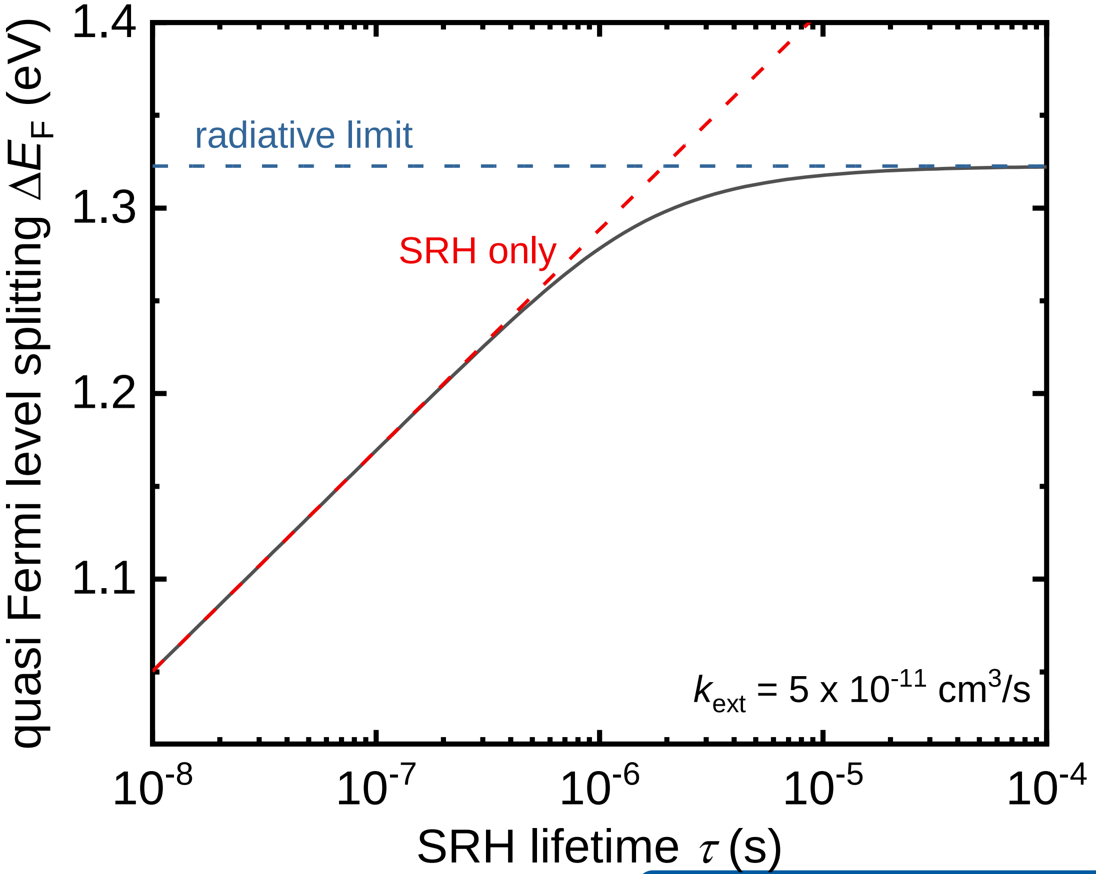
Why are charge carrier lifetimes relevant?

@ open circuit

$$G = kn^2 + \frac{n}{\tau}$$

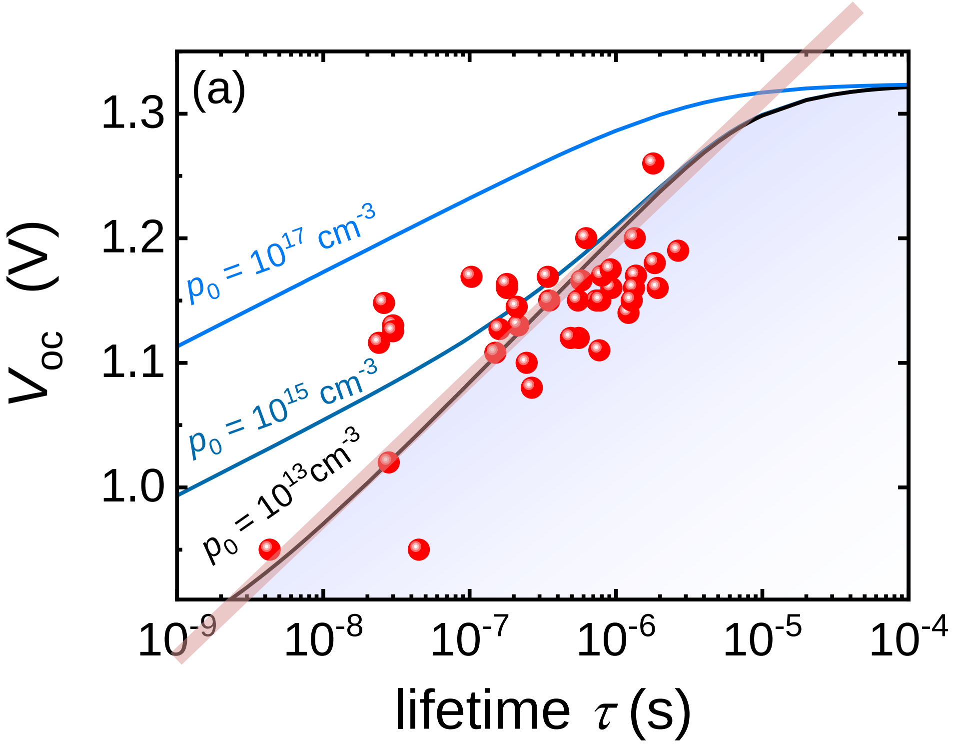
lifetime

$$\Delta E_F = kT \ln\left(\frac{n^2}{n_i^2}\right)$$



Kirchartz et al. Adv. Energy Mater. 2020

Why things are more difficult in reality than in theory?

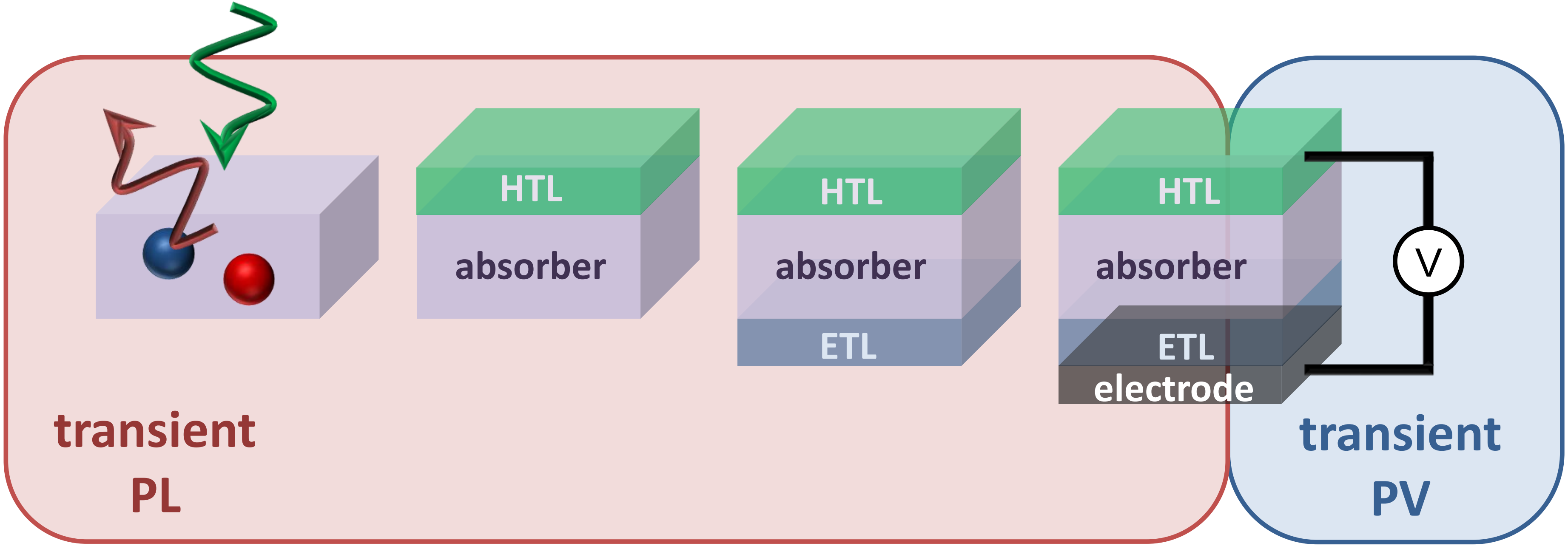


$$\Delta E_F = 2kT \ln\left(\frac{G\tau}{n_i}\right)$$

Kirchartz et al. Adv. Energy Mater. 2020

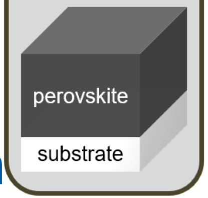
How can transient methods help…

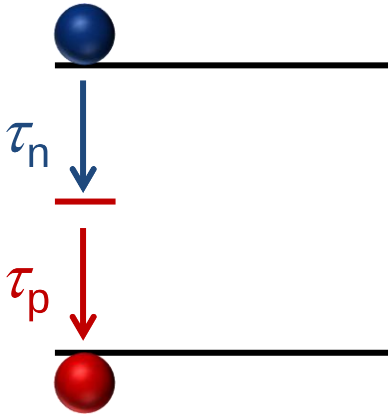
…to study recombination and voltage losses

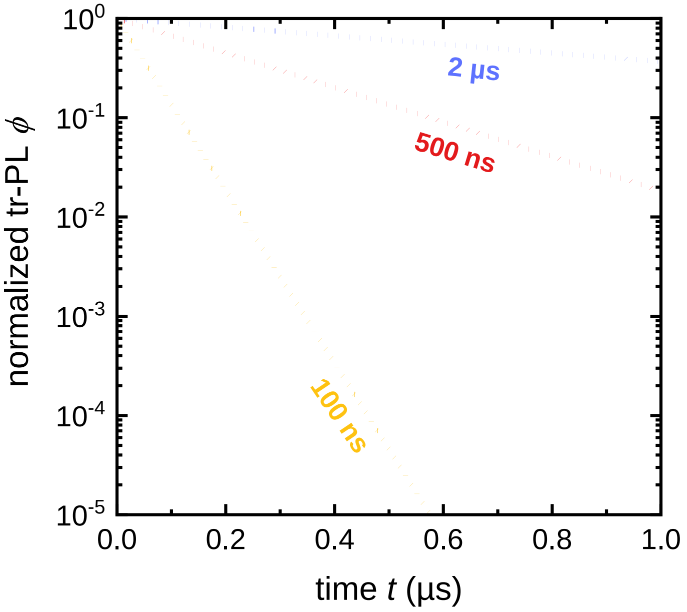


Transient Photoluminescence

Layer on Glass – SRH Recombination







$$n = p$$

$$\frac{dn}{dt} = -\frac{np}{\tau_p n + \tau_n p} = -\frac{n}{\tau_p + \tau_n} = -\frac{n}{\tau_{SRH}}$$

$$n(t) = n(0)\exp\left(-t/\tau_{SRH}\right)$$

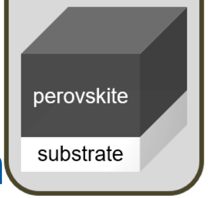
$$PL(t) \propto n^2(t) \propto \exp\left(-2t/\tau_{SRH}\right)$$

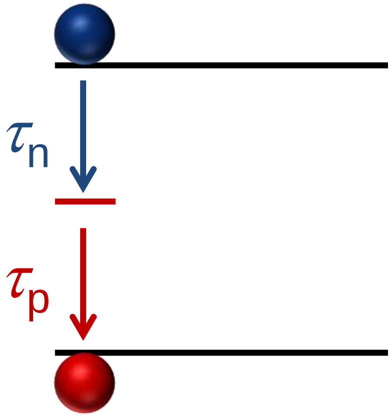
$$\frac{dn}{dt} = -\frac{np}{\tau_p n + \tau_n p}$$

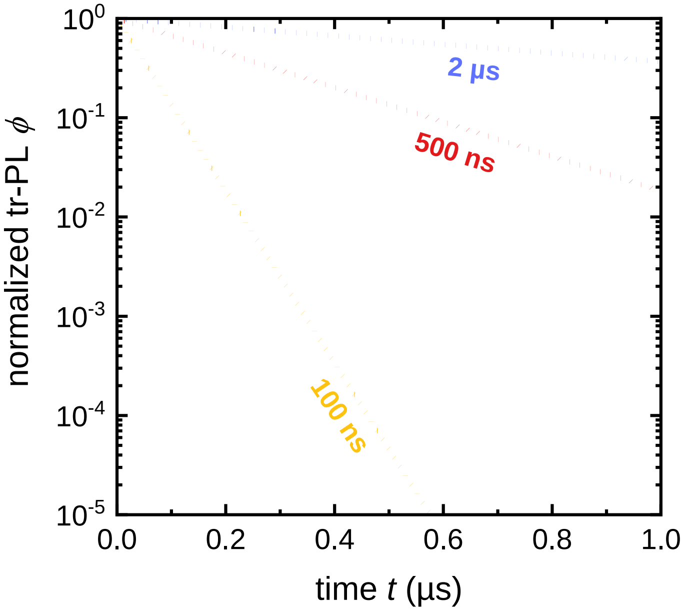
Shockley-Read-Hall (SRH) recombination only

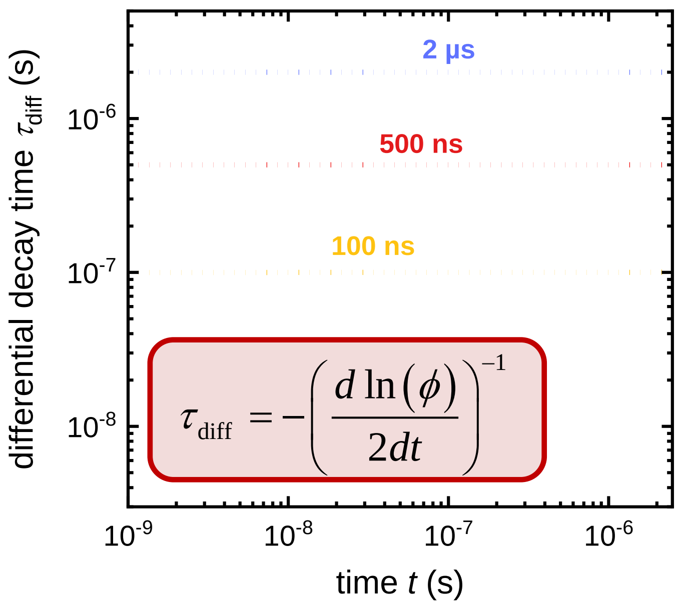
Transient Photoluminescence

Layer on Glass – SRH Recombination







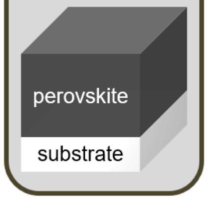


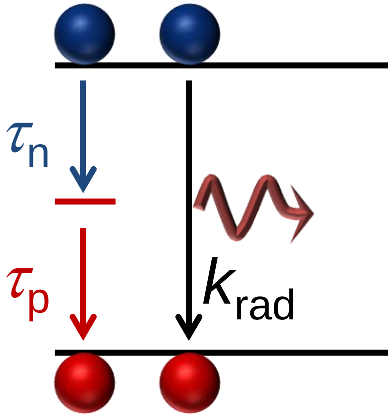
$$\frac{dn}{dt} = -\frac{np}{\tau_p n + \tau_n p}$$

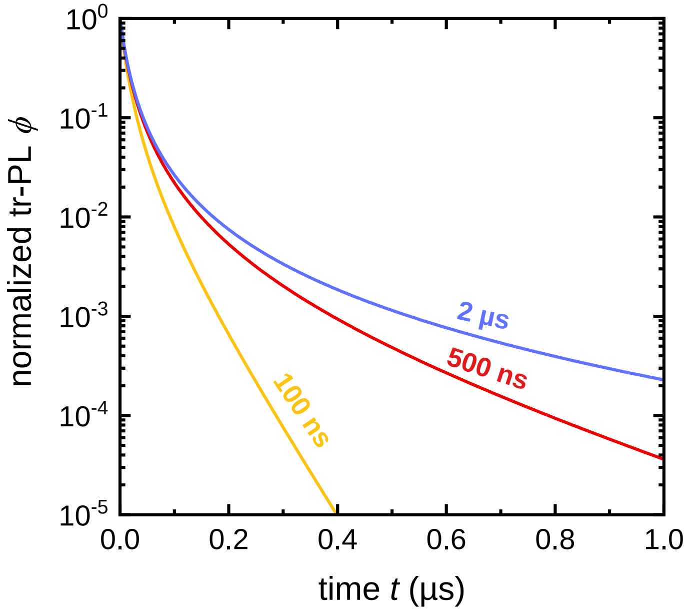
Shockley-Read-Hall (SRH) recombination only

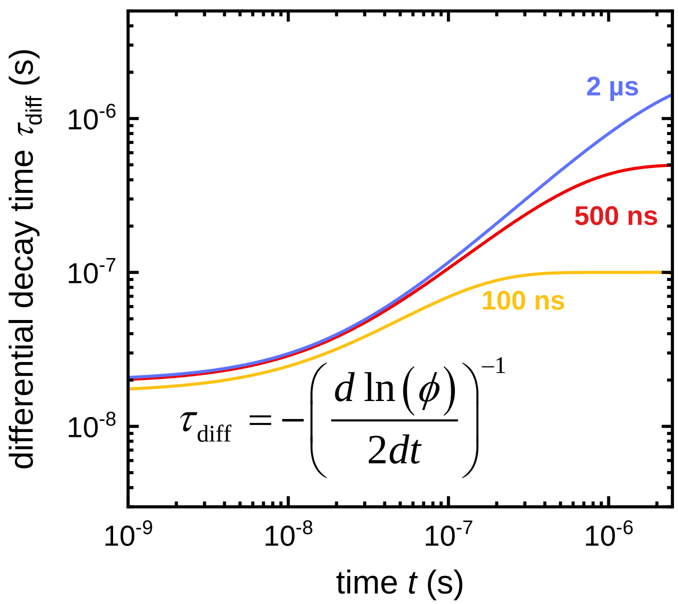
Transient Photoluminescence

Layer on Glass – Bulk Recombination







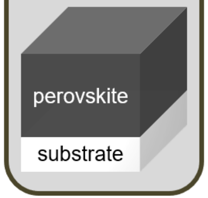


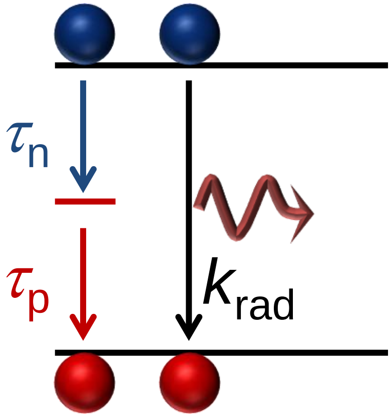
$$\frac{dn}{dt} = -k_{rad}np - \frac{np}{\tau_p n + \tau_n p}$$

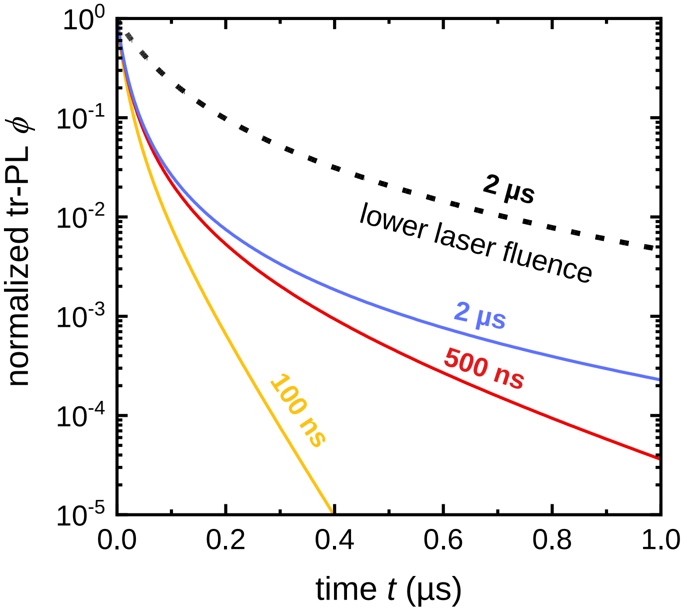
SRH + radiative recombination

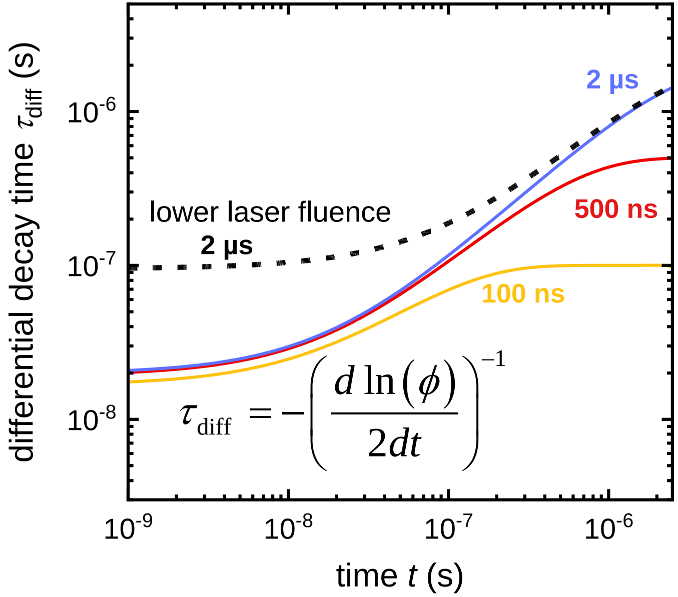
Transient Photoluminescence

Layer on Glass – Bulk Recombination







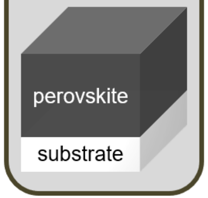


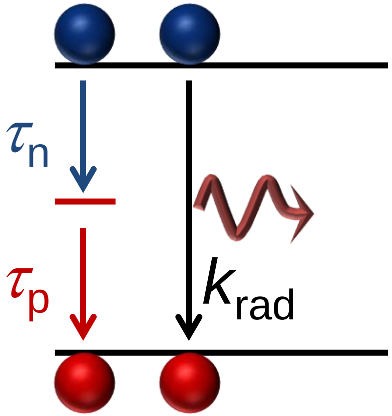
$$\frac{dn}{dt} = -k_{rad}np - \frac{np}{\tau_p n + \tau_n p}$$

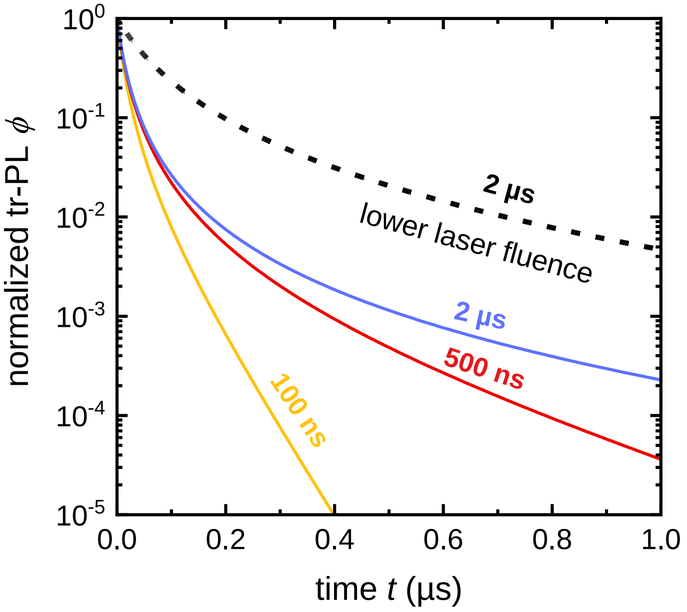
SRH + radiative recombination

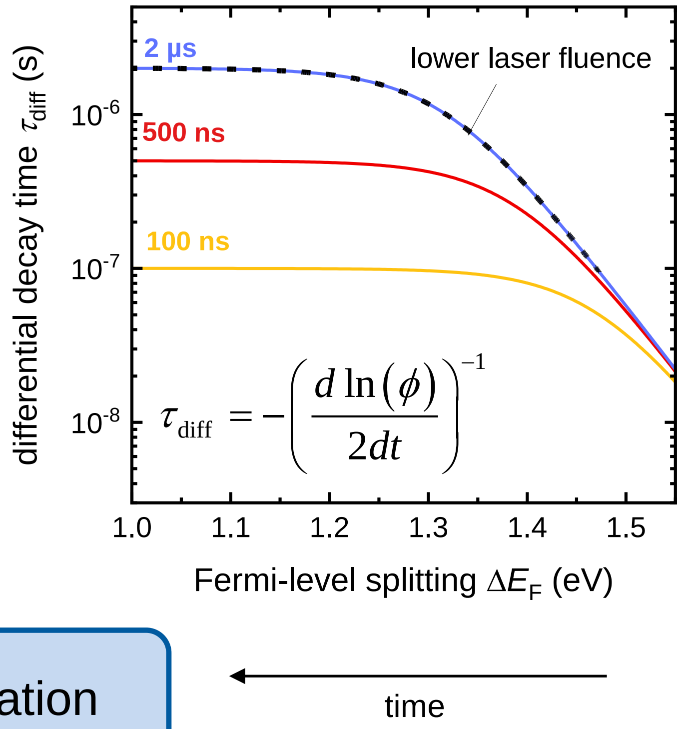
Transient Photoluminescence

Layer on Glass – Bulk Recombination





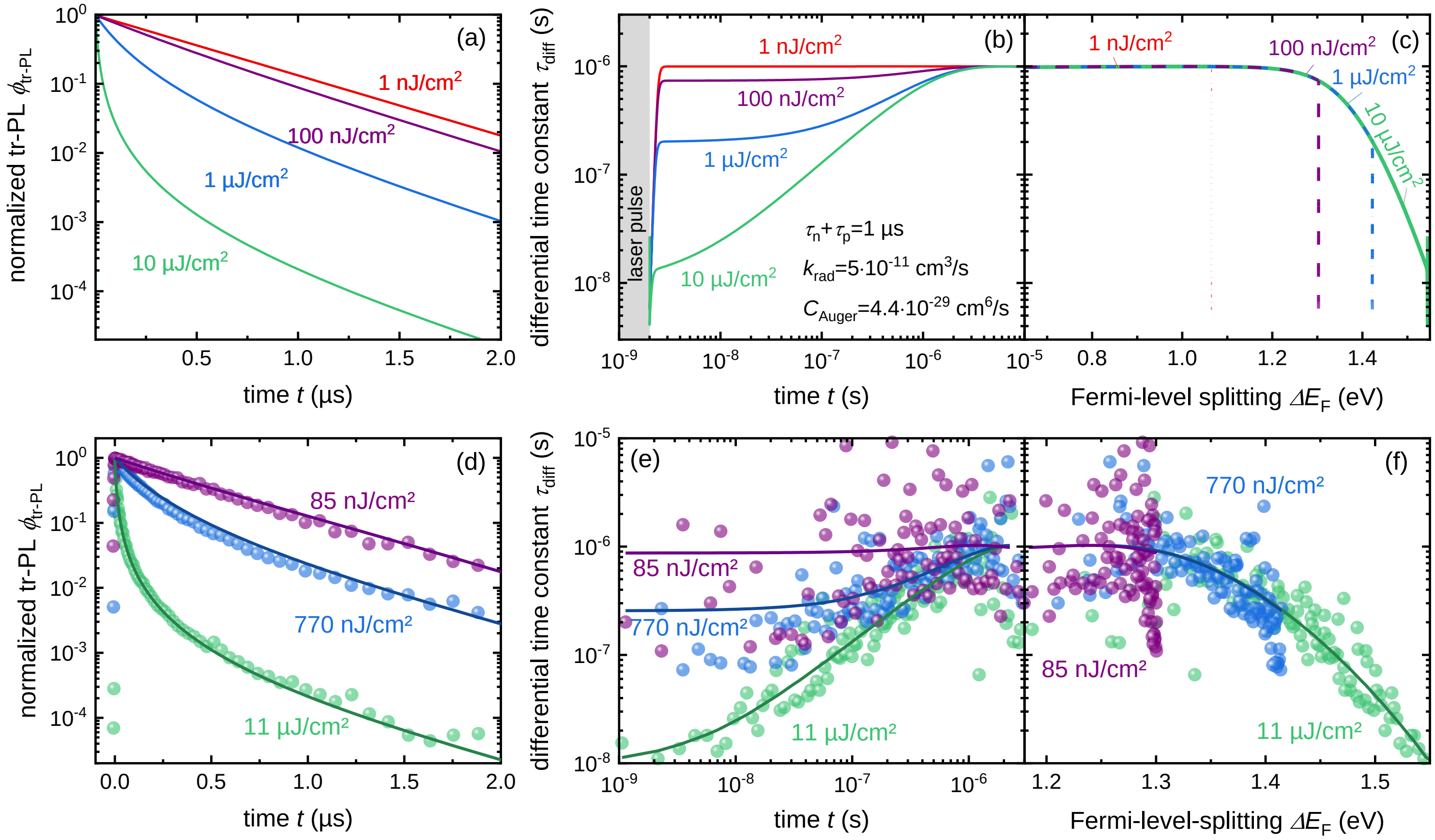




$$\frac{dn}{dt} = -k_{rad}np - \frac{np}{\tau_p n + \tau_n p}$$

SRH + radiative recombination

From time axis to QFLS axis

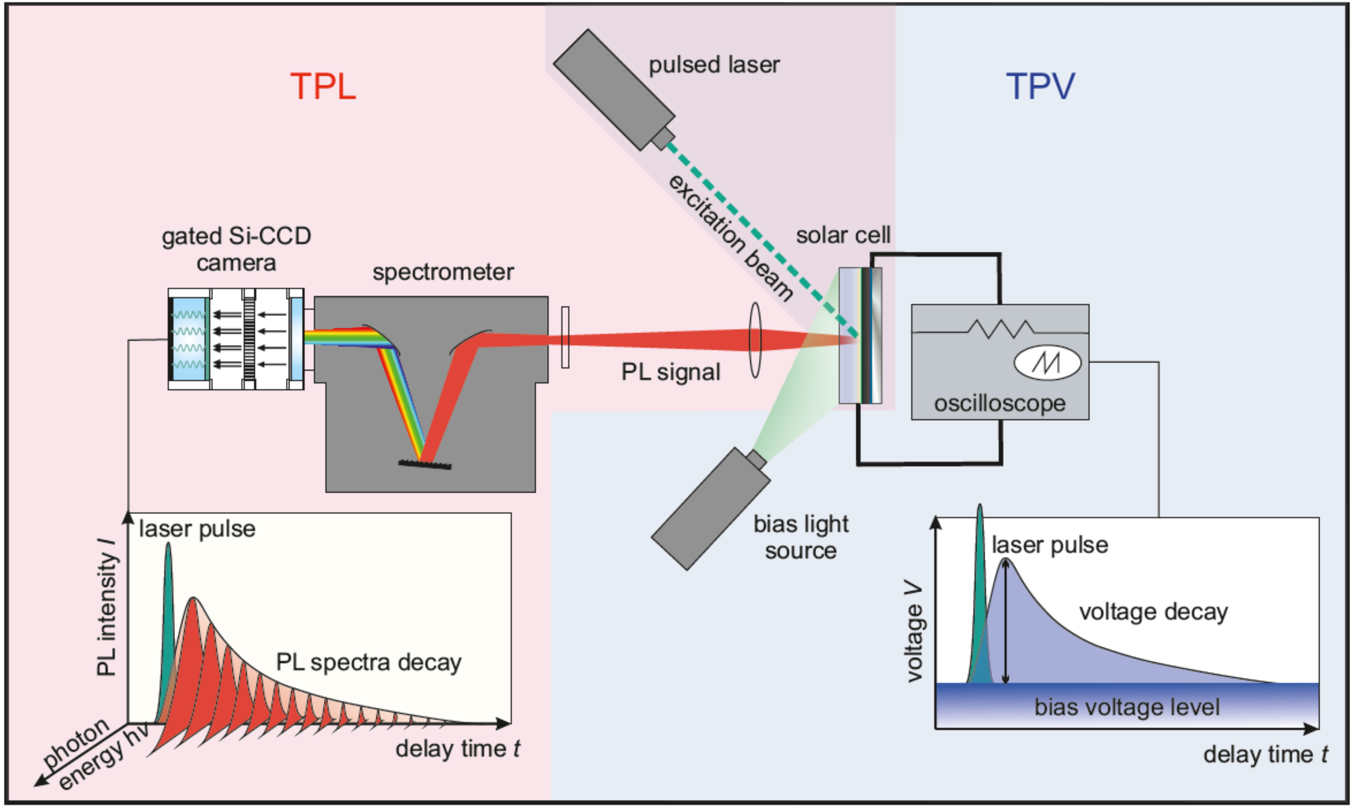


Transient Photoluminescence (TPL)

measures the luminescence decay

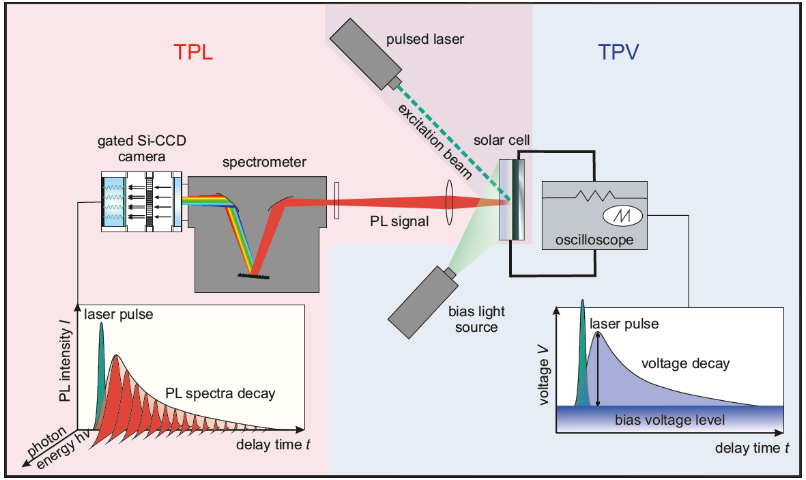
Transient Photovoltage (TPV)

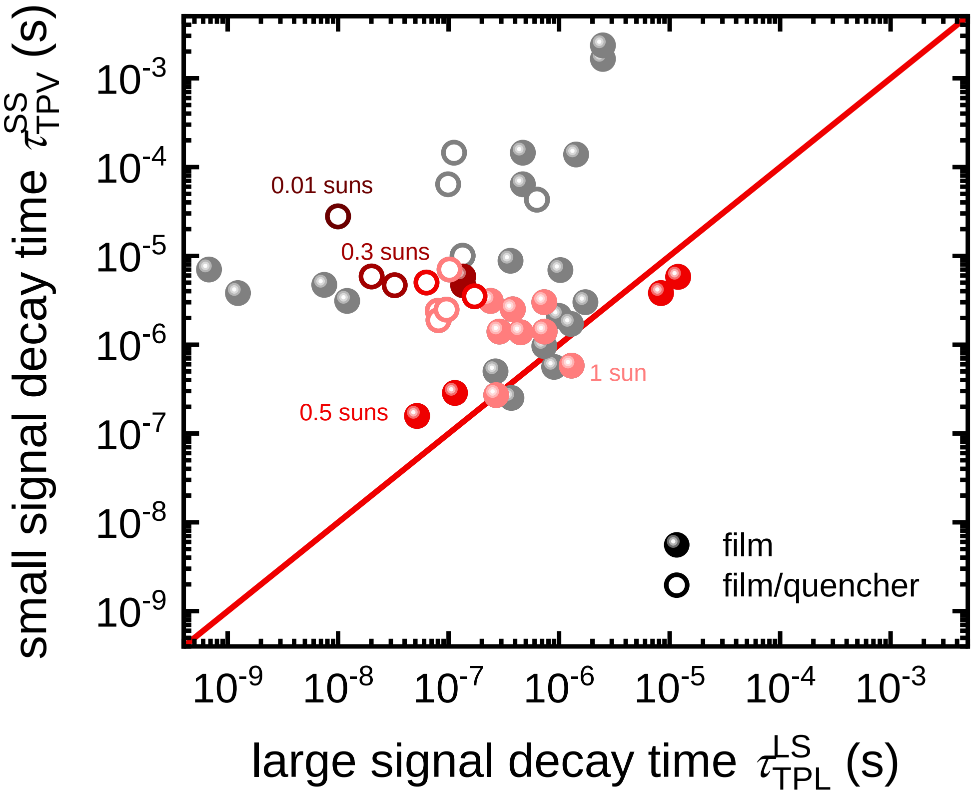
measures the decay of an external voltage



Metaanalysis: TPV vs. TPL

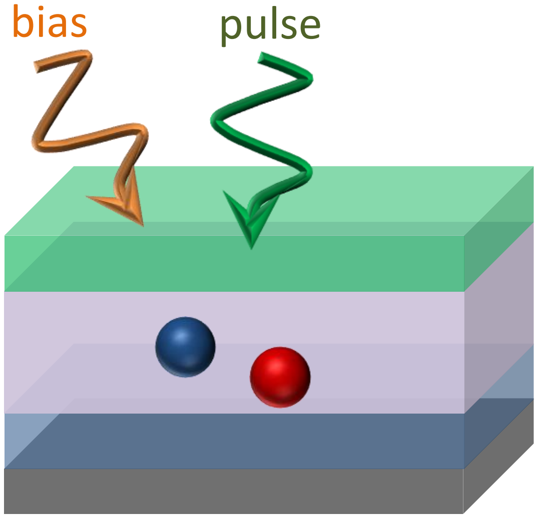
Fairly poor correlation between the two decay times. Why?

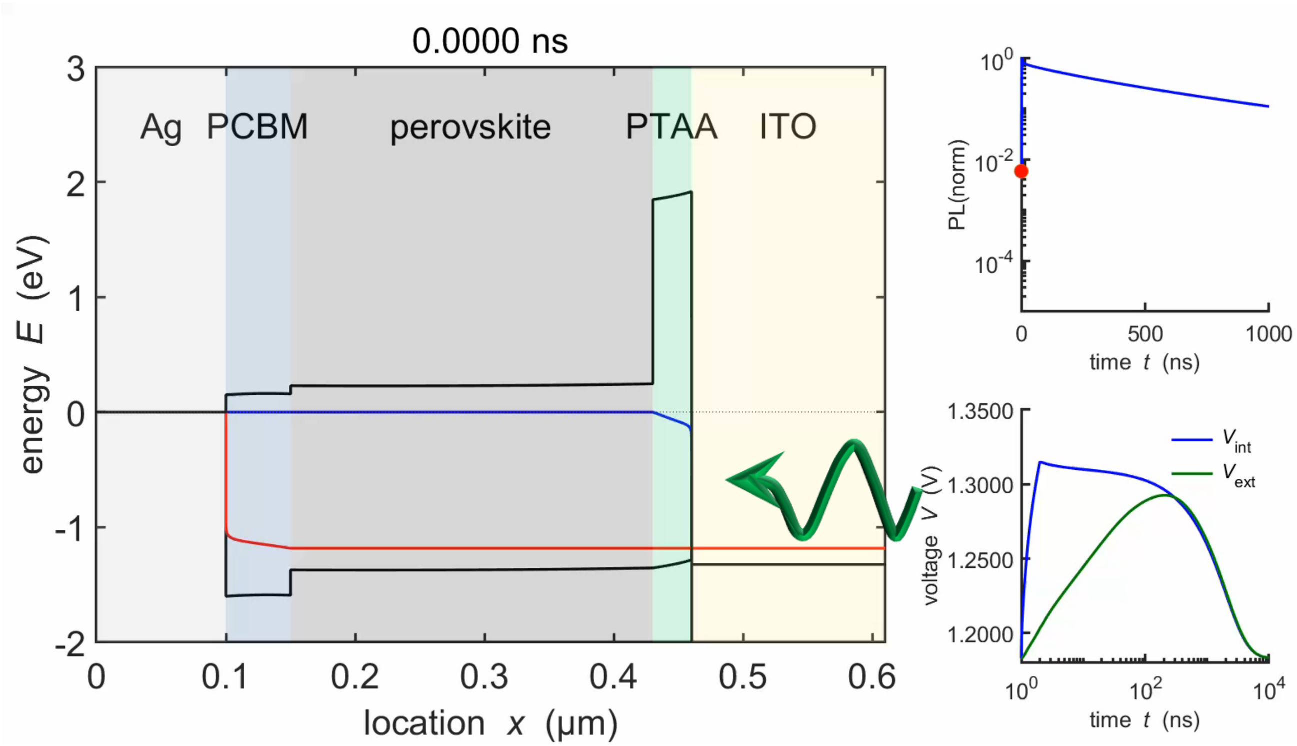




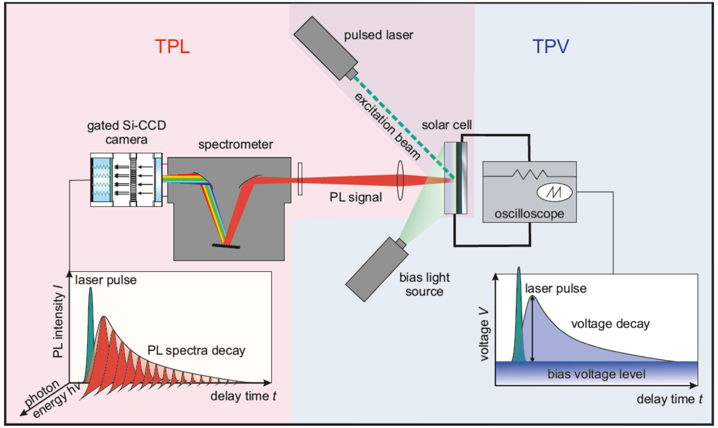
Transients with bias light

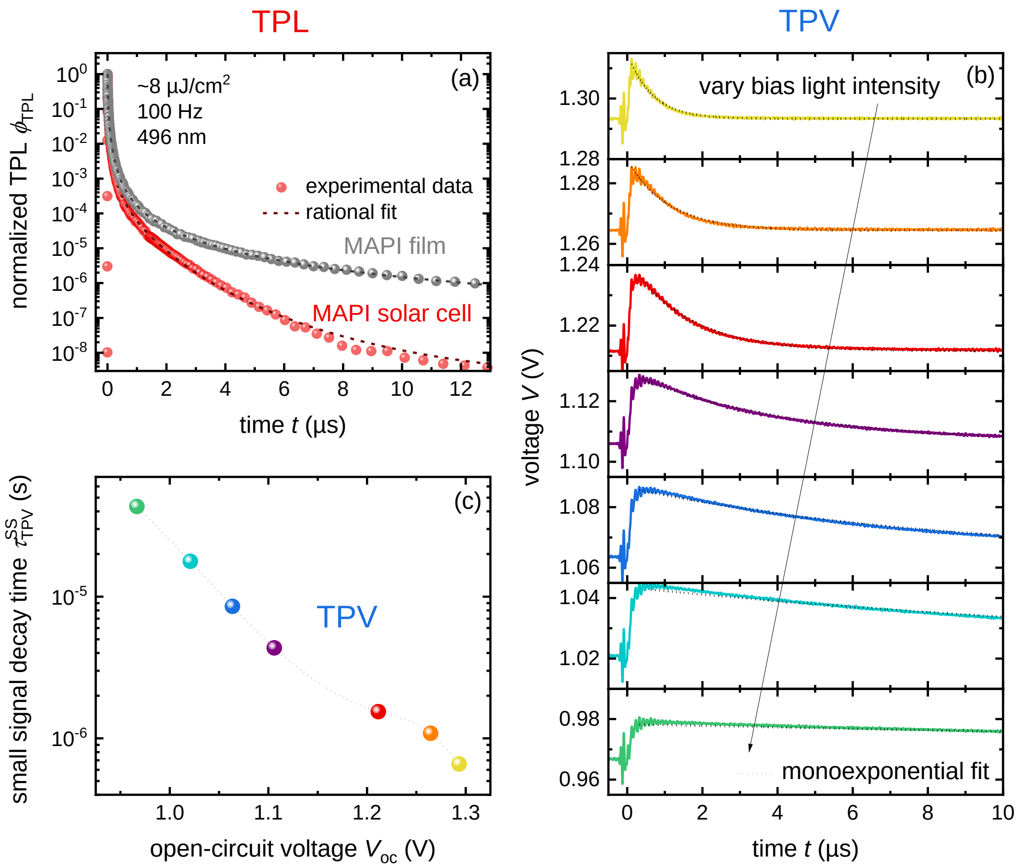
Video TPV vs. TPL



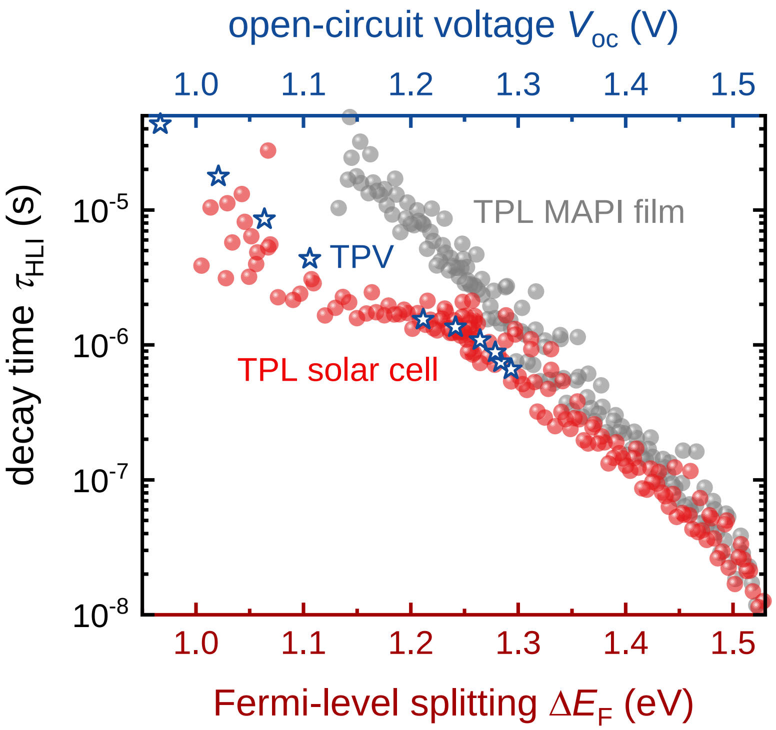


What is typically measured?





How to make sense out of it

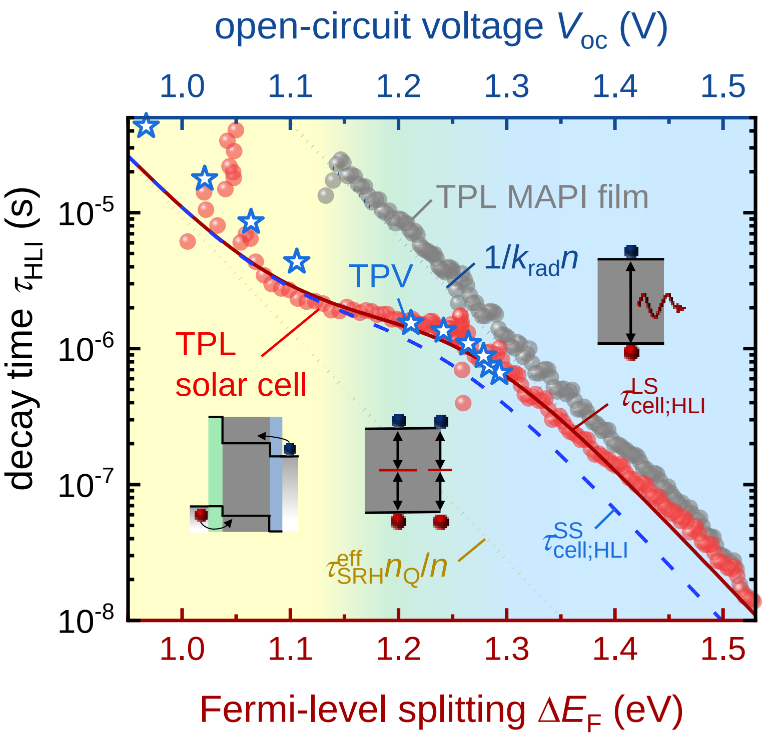


$$\frac{dn(t)}{dt} = -k_{rad} n(t)^2 - \frac{n(t)}{\tau_{SRH}^{bulk}} - \frac{C_{area}}{q d_{pero}} \frac{dV_{ext}(t)}{dt} + G$$

$$\tau_{cell,\,HLI}^{LS} = -\frac{n(t)}{dn(t)/dt} = \frac{n_Q/n(t)+1}{k_{rad} n(t) + 1/\tau_{SRH}^{eff}}$$

$$n_Q = 2C_{area} k_B T / \left(q^2 d_{pero}\right)$$

How to make sense out of it



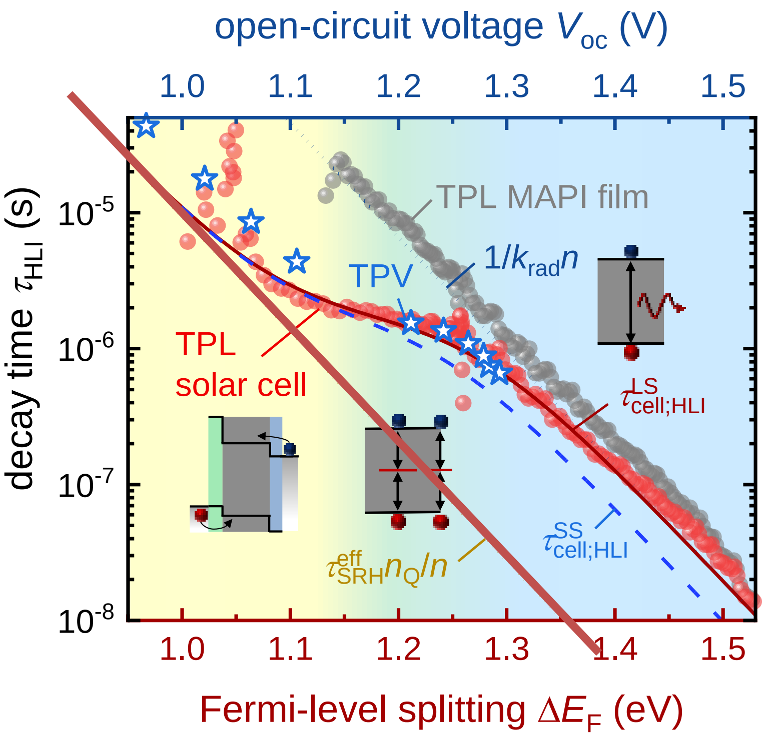
Capacitive charging of the electrodes

$$\frac{dn(t)}{dt} = -k_{rad} n(t)^2 - \frac{n(t)}{\tau^{bulk}_{SRH}} - \frac{C_{area}}{q d_{pero}} \frac{dV_{ext}(t)}{dt} + G$$

$$\tau^{LS}_{cell,\,HLI} = -\frac{n(t)}{dn(t)/dt} = \frac{n_Q/n(t) + 1}{k_{rad} n(t) + 1/\tau^{eff}_{SRH}}$$

$$n_Q = 2 C_{area} k_B T / \left(q^2 d_{pero}\right)$$

How to make sense out of it



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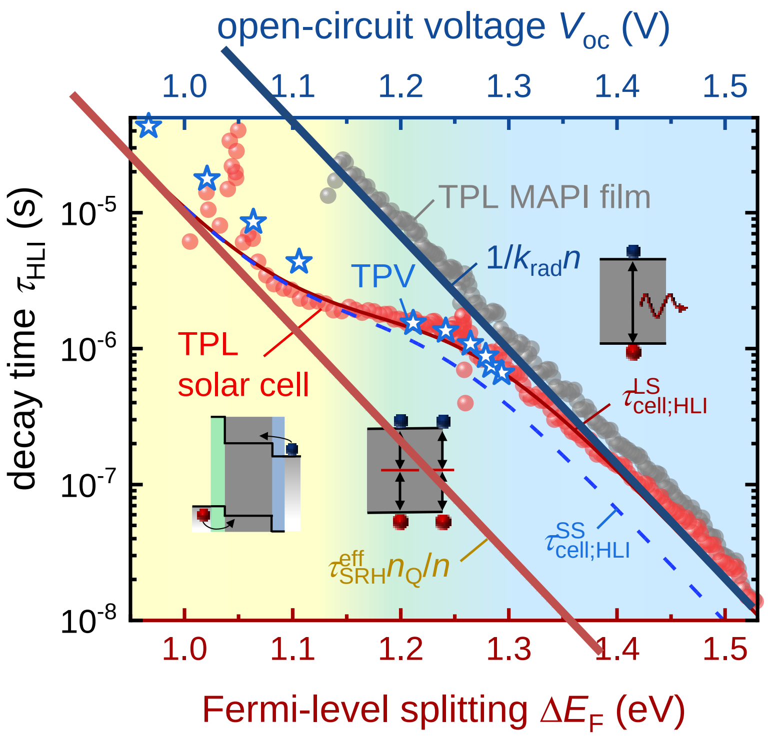
How to make sense out of it



$$\frac{dn(t)}{dt} = -k_{rad}n(t)^2 - \frac{n(t)}{\tau_{SRH}^{bulk}} - \frac{C_{area}}{qd_{pero}}\frac{dV_{ext}(t)}{dt} + G$$

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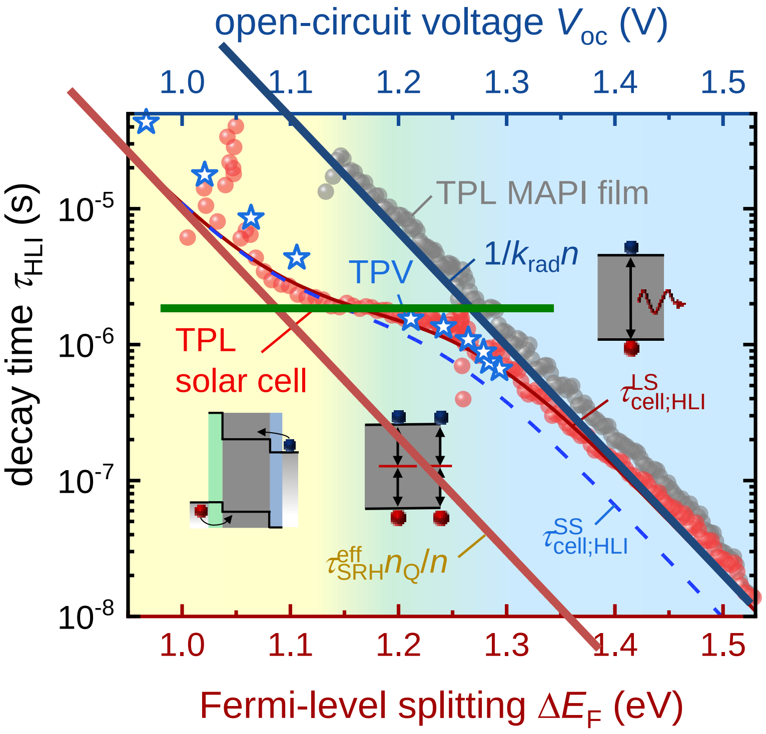
How to make sense out of it



$$\frac{dn(t)}{dt} = -k_{rad}n(t)^2 - \frac{n(t)}{\tau_{SRH}^{bulk}} - \frac{C_{area}}{qd_{pero}}\frac{dV_{ext}(t)}{dt} + G$$

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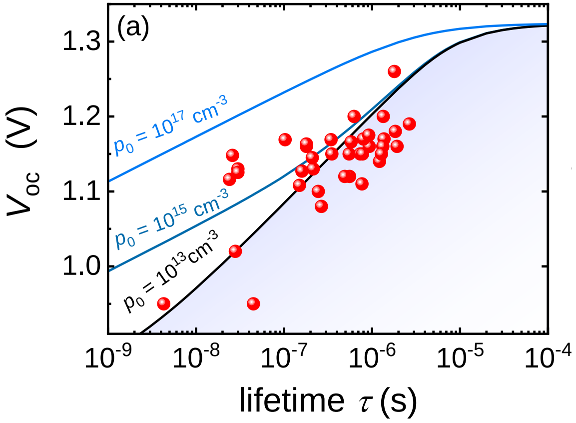
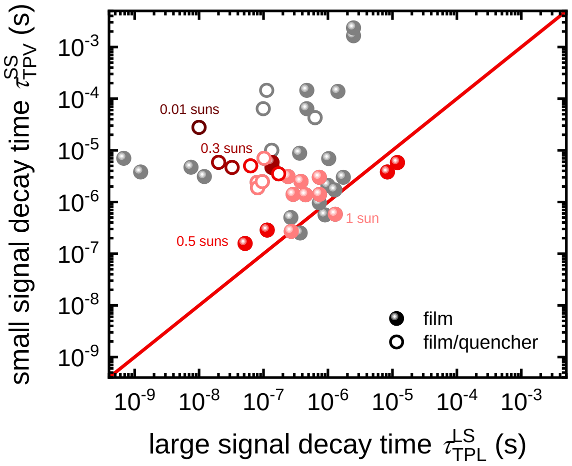
$$n_Q = 2C_{area}k_BT/\left(q^2 d_{pero}\right)$$

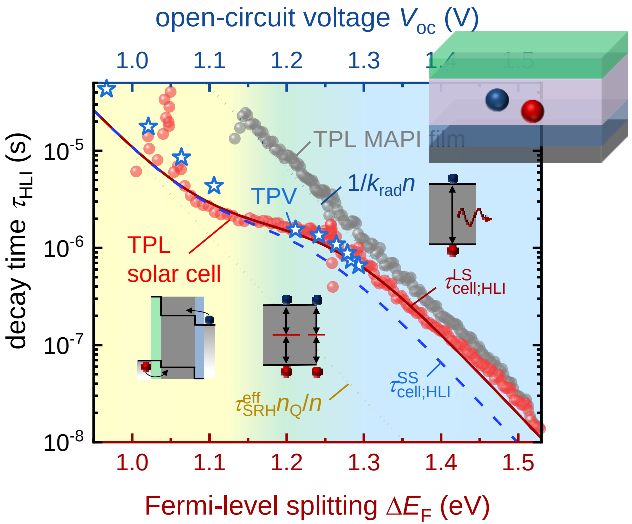
Summary



1) "Lifetimes" correlate with V_{oc} but not in an easy way
2) "Lifetimes" are rarely constants

3) Huge method to method variation in "lifetimes" results from voltage dependence of decay times





Thanks to
Thomas Unold
Jose Marquez
Martin Stolterfoht
Helmholtz Association for Funding

Thank you for your attention

PROGRESS REPORT

ADVANCED ENERGY MATERIALS
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Photoluminescence-Based Characterization of Halide Perovskites for Photovoltaics

Thomas Kirchartz, José A. Márquez, Martin Stolterfoht, and Thomas Unold**

FULL PAPER

ADVANCED ENERGY MATERIALS
www.advenergymat.de

Understanding Transient Photoluminescence in Halide Perovskite Layer Stacks and Solar Cells

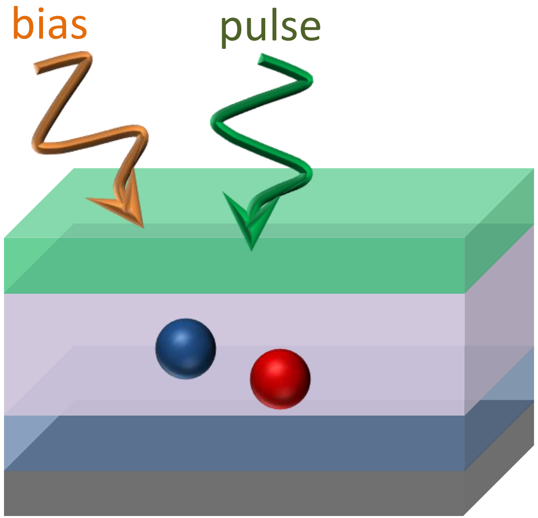
Lisa Krückemeier, Benedikt Krogmeier, Zhifa Liu, Uwe Rau, and Thomas Kirchartz**

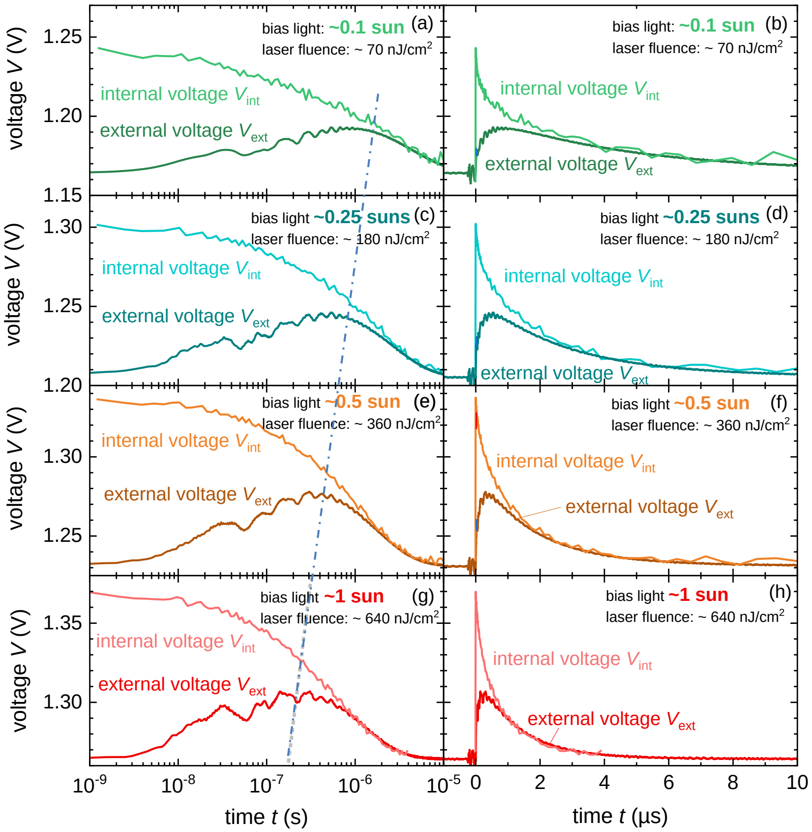
Useful literature on the contents of the talk

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

JÜLICH Forschungszentrum

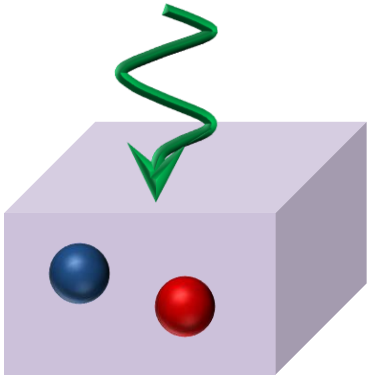
Experimental data – internal vs. external voltage

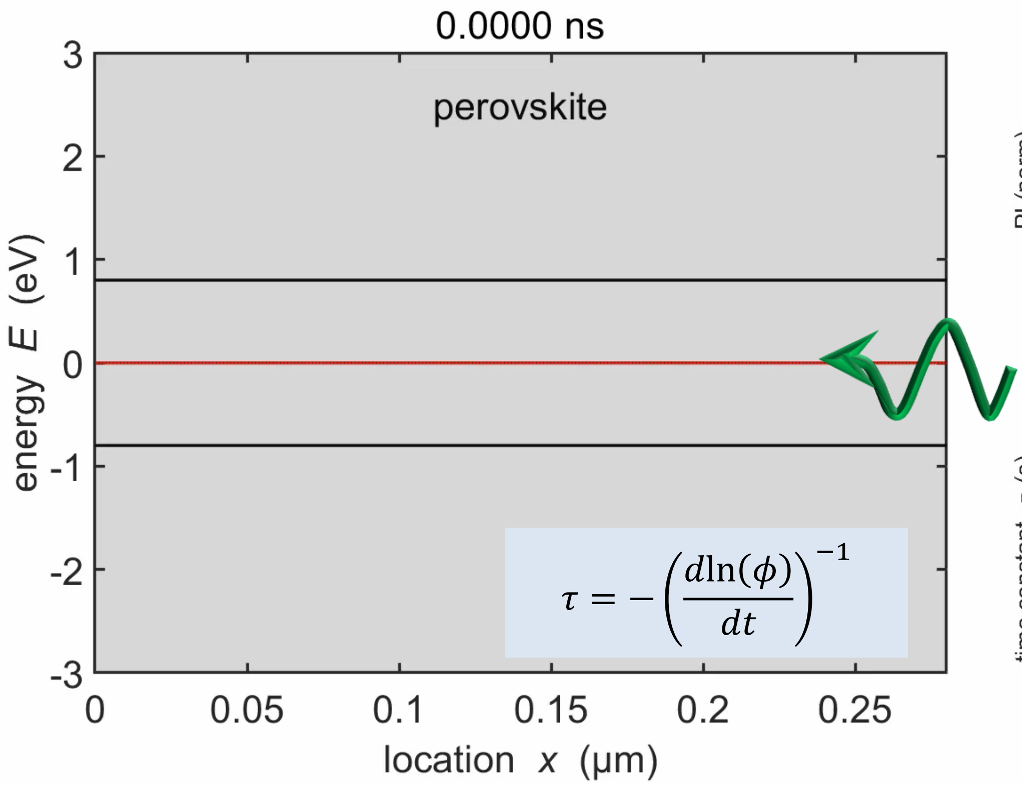




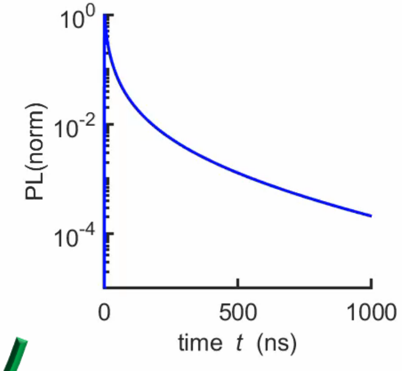
Transient Photoluminescence

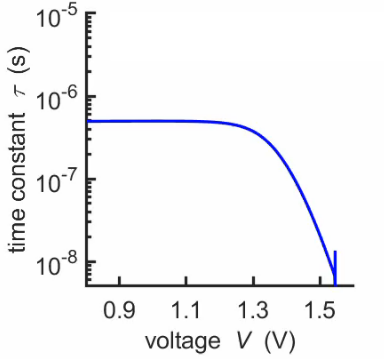
Layer on glass - Video





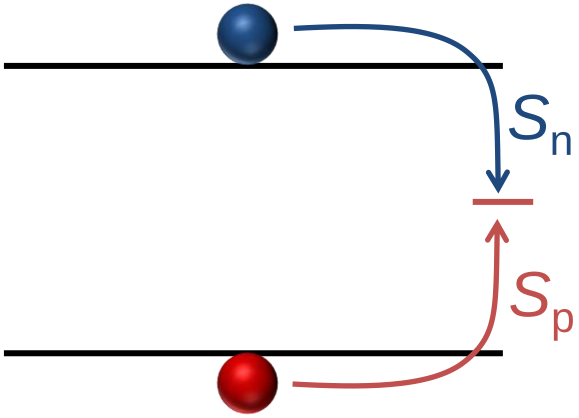
$$\tau = -\left(\frac{d\ln(\phi)}{dt}\right)^{-1}$$

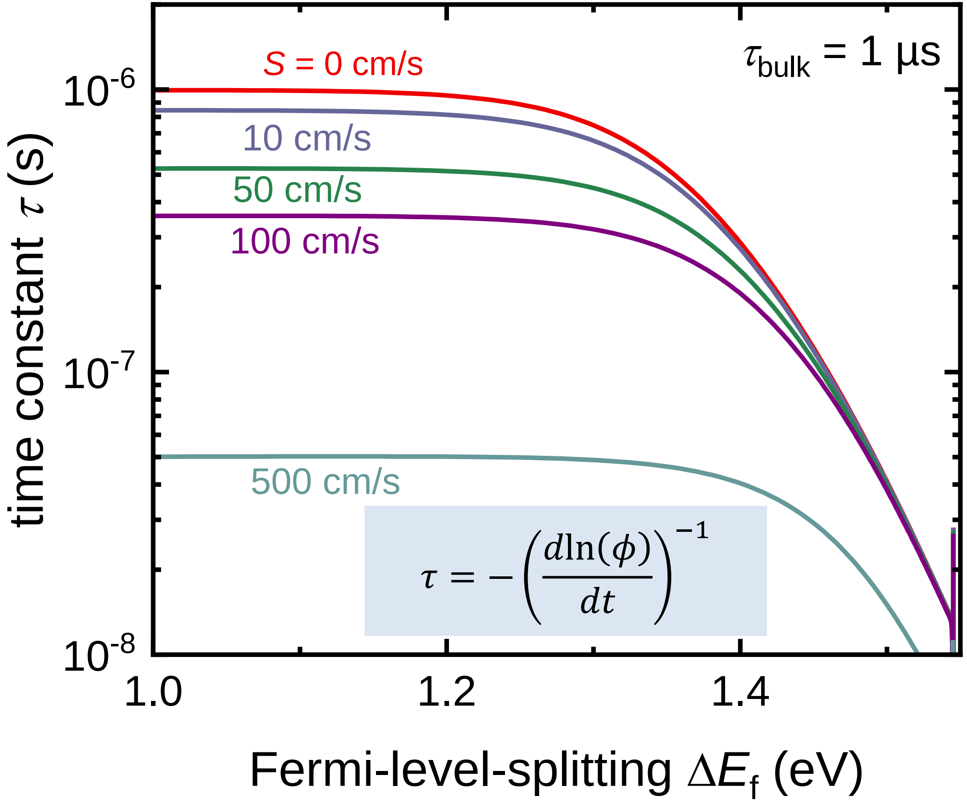




Transient Photoluminescence

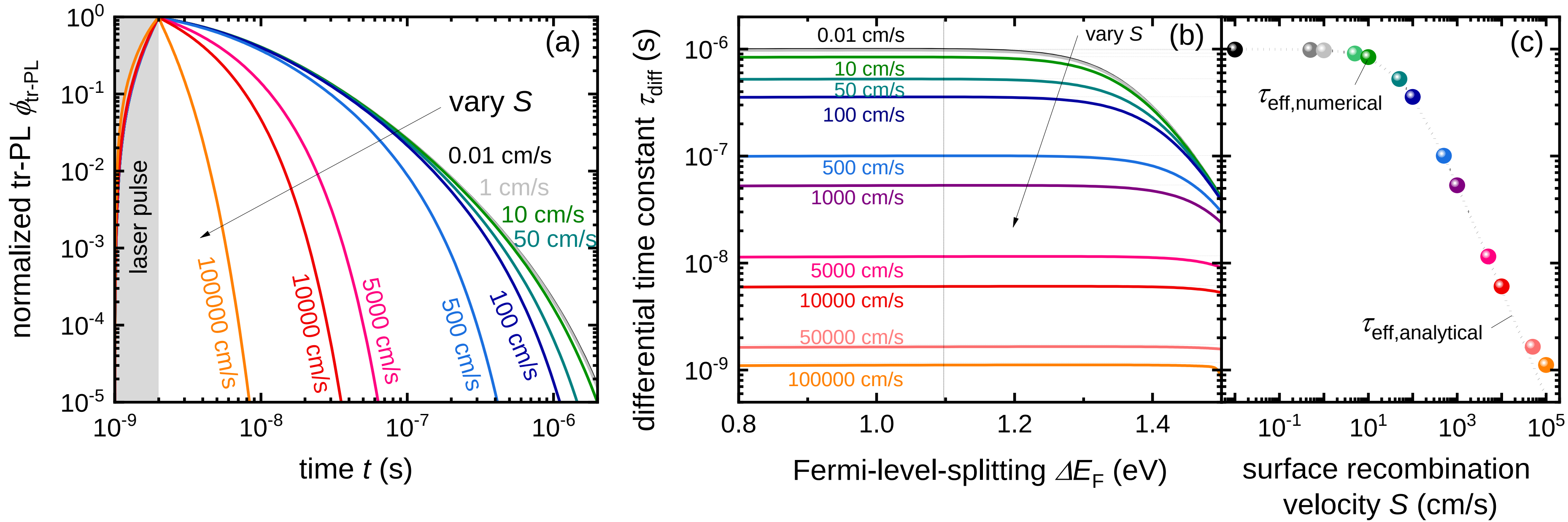
Layer on glass – Surface recombination





Transient Photoluminescence

Layer on glass – Surface recombination



TPV Decay Constants

Experiment vs. Simulation