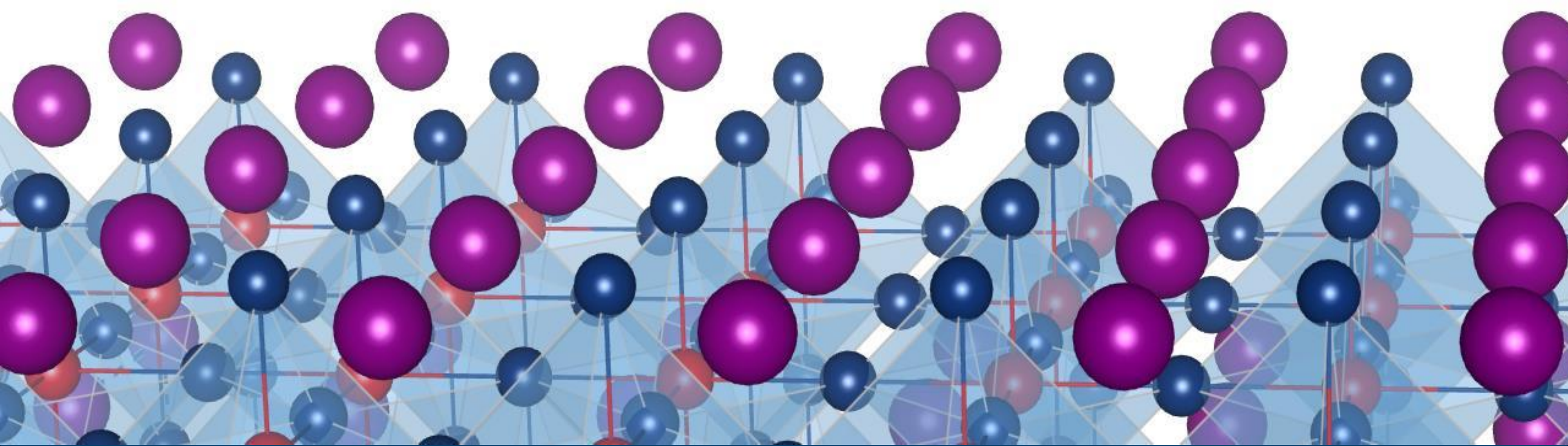


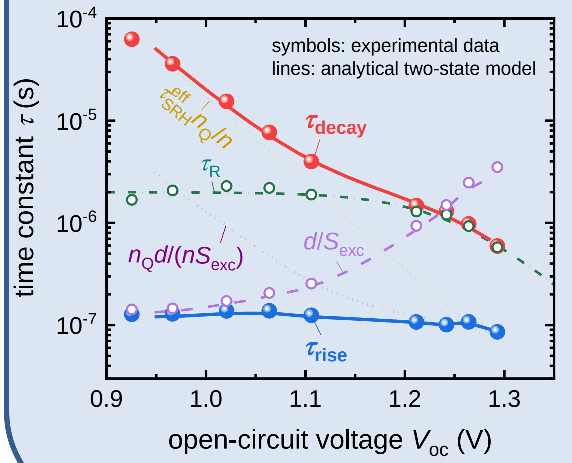
Using Transient Methods to Characterize Recombination and Extraction in Halide Perovskite Solar Cells

Thomas Kirchartz, Genghua Yan, Ye Yuan, Lisa Krückemeier, Uwe Rau

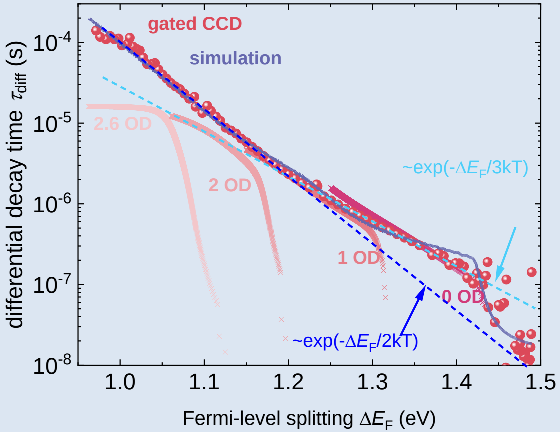
IEK-5 Photovoltaik, Forschungszentrum Jülich

Outline

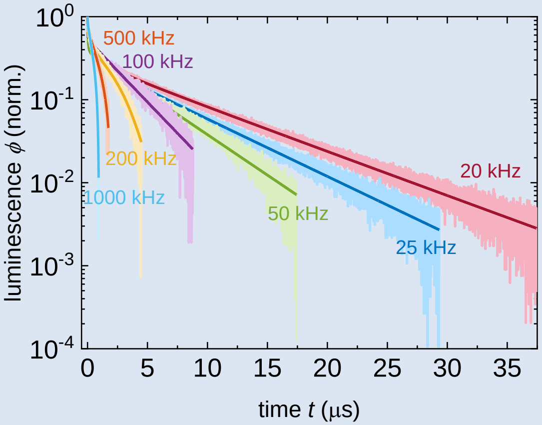
1) Charge separation vs. recombination

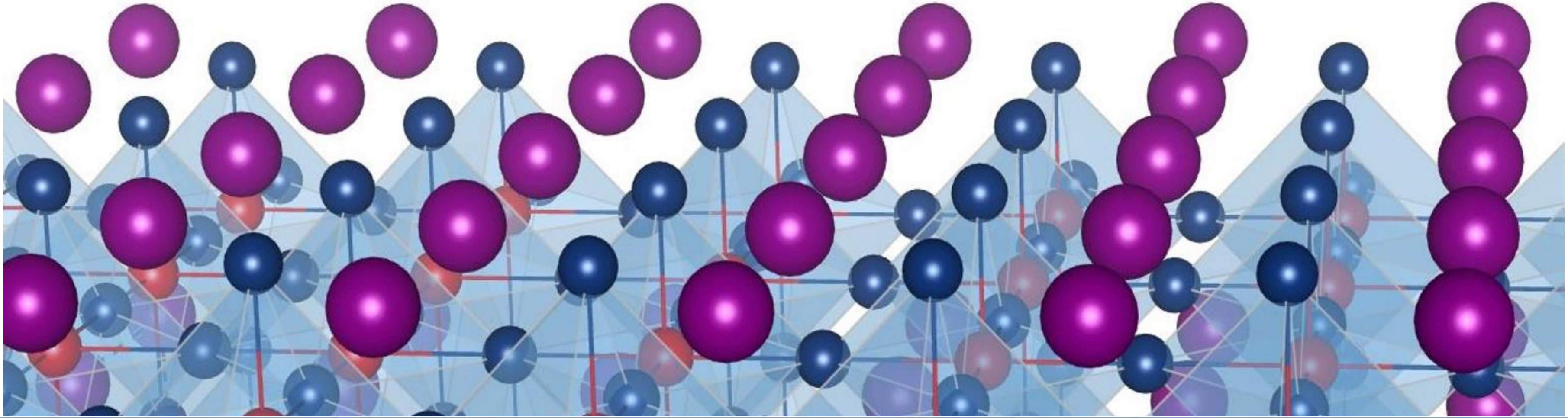


2) On the importance of shallow defects



3) On the importance of repetition rates





Part 0: Introduction

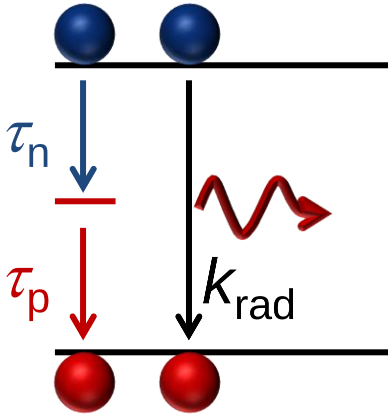
Transient Photoluminescence and Lifetimes

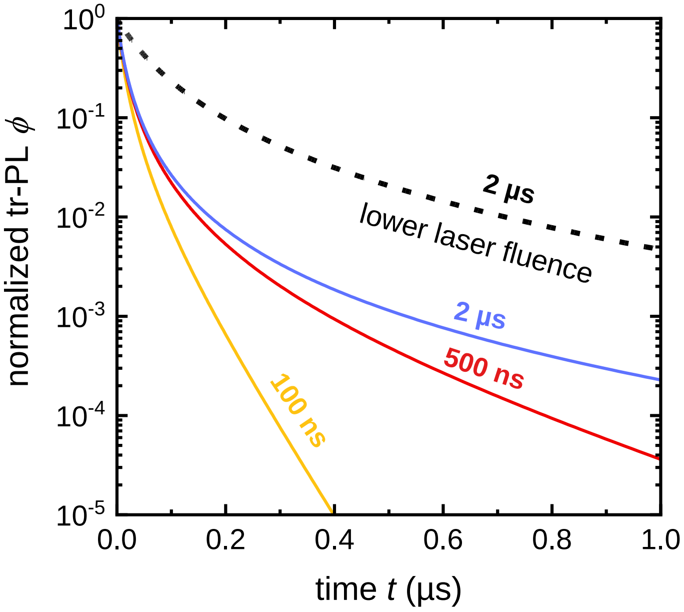
HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

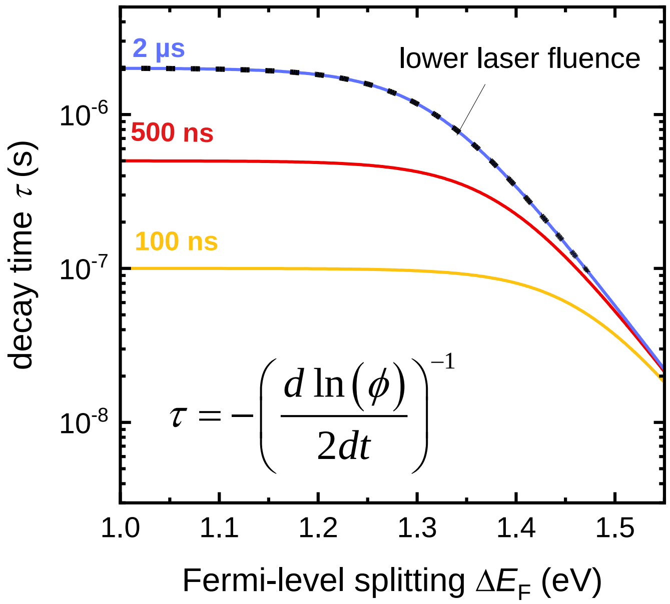
JÜLICH Forschungszentrum

Transient Photoluminescence

Layer on Glass – Bulk Recombination







$$\tau = -\left(\frac{d\ln(\phi)}{2dt}\right)^{-1}$$

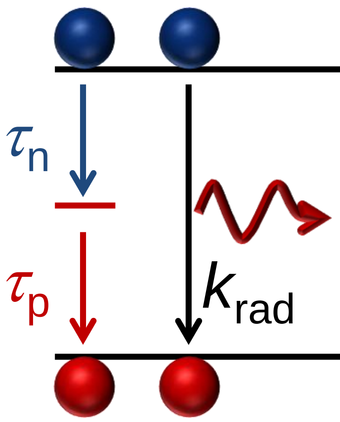
$$\frac{dn}{dt} = -k_{\mathrm{rad}} n^2 - \frac{n}{\tau_{\mathrm{p}} + \tau_{\mathrm{n}}}$$

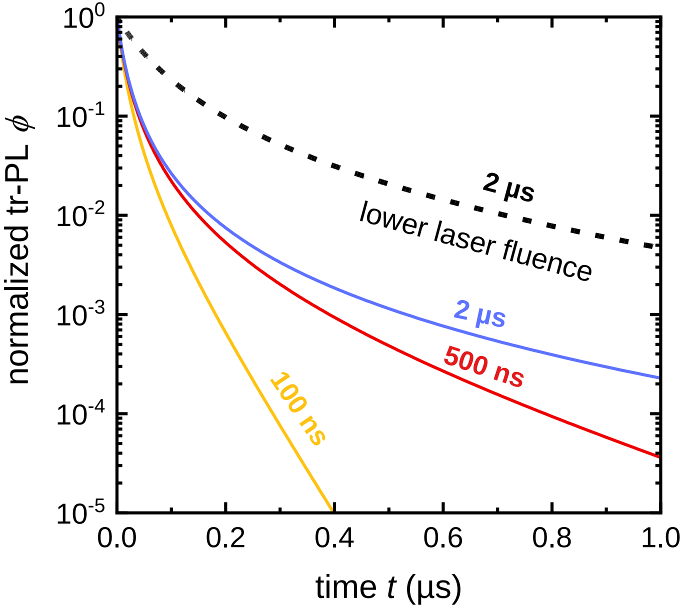
SRH + radiative recombination

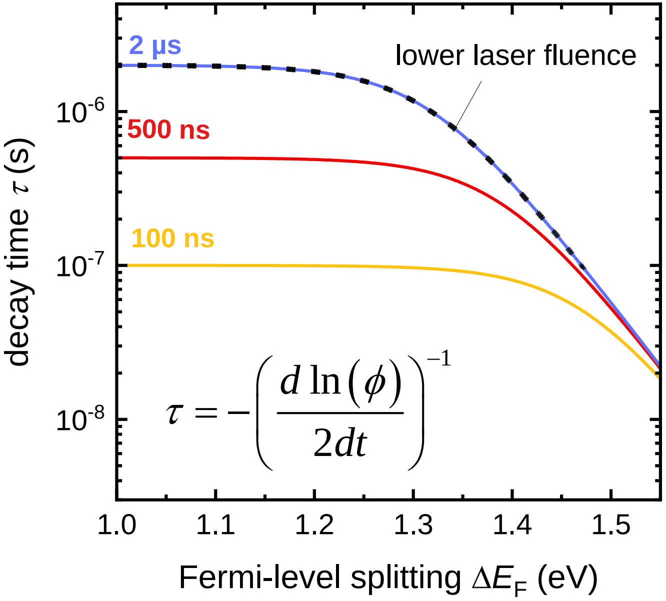
← time

Transient Photoluminescence

Layer on Glass – Bulk Recombination





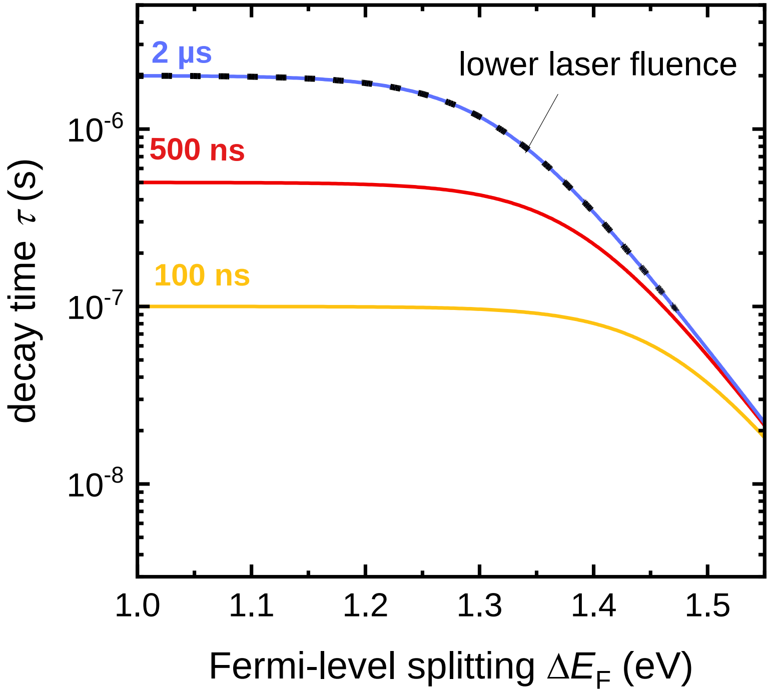


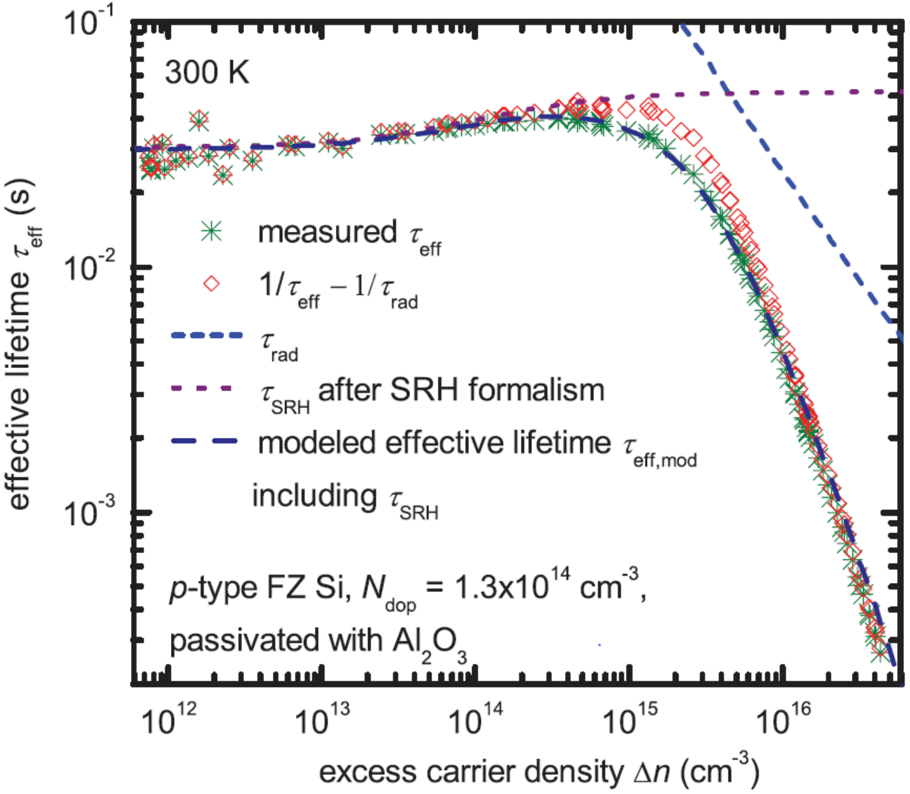
$$\tau_{diff} = -\frac{n}{dn/dt} = \frac{1}{k_{rad}n + \tau_p + \tau_n}$$

Decay Time

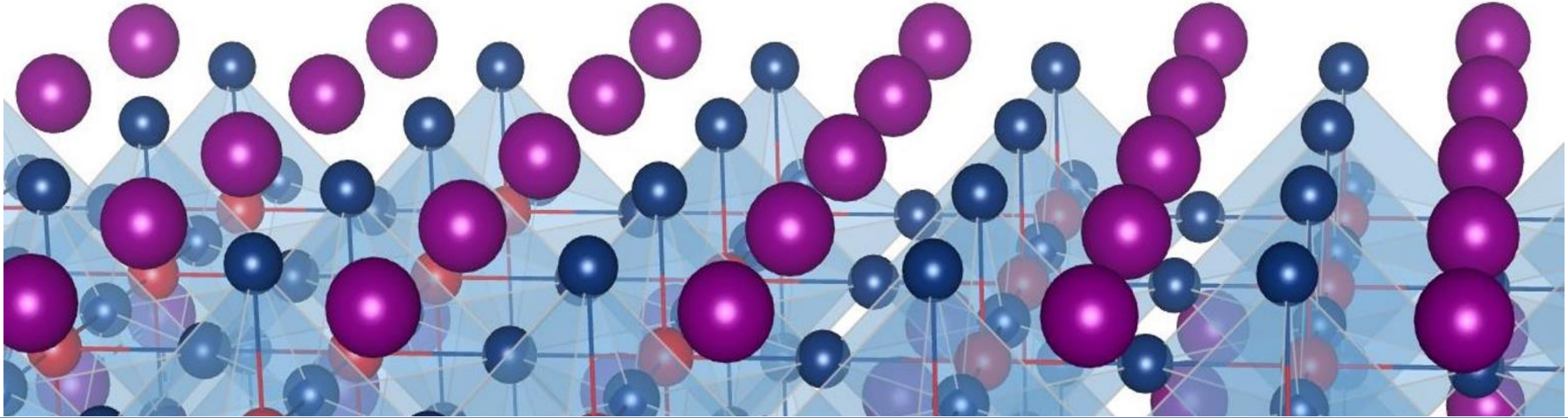
time

Differential decay times in passivated Si wafers





Richter et al. Phys. Rev. B **86**, 165202 (2012)



Part 1: Recap from HOPV 2022

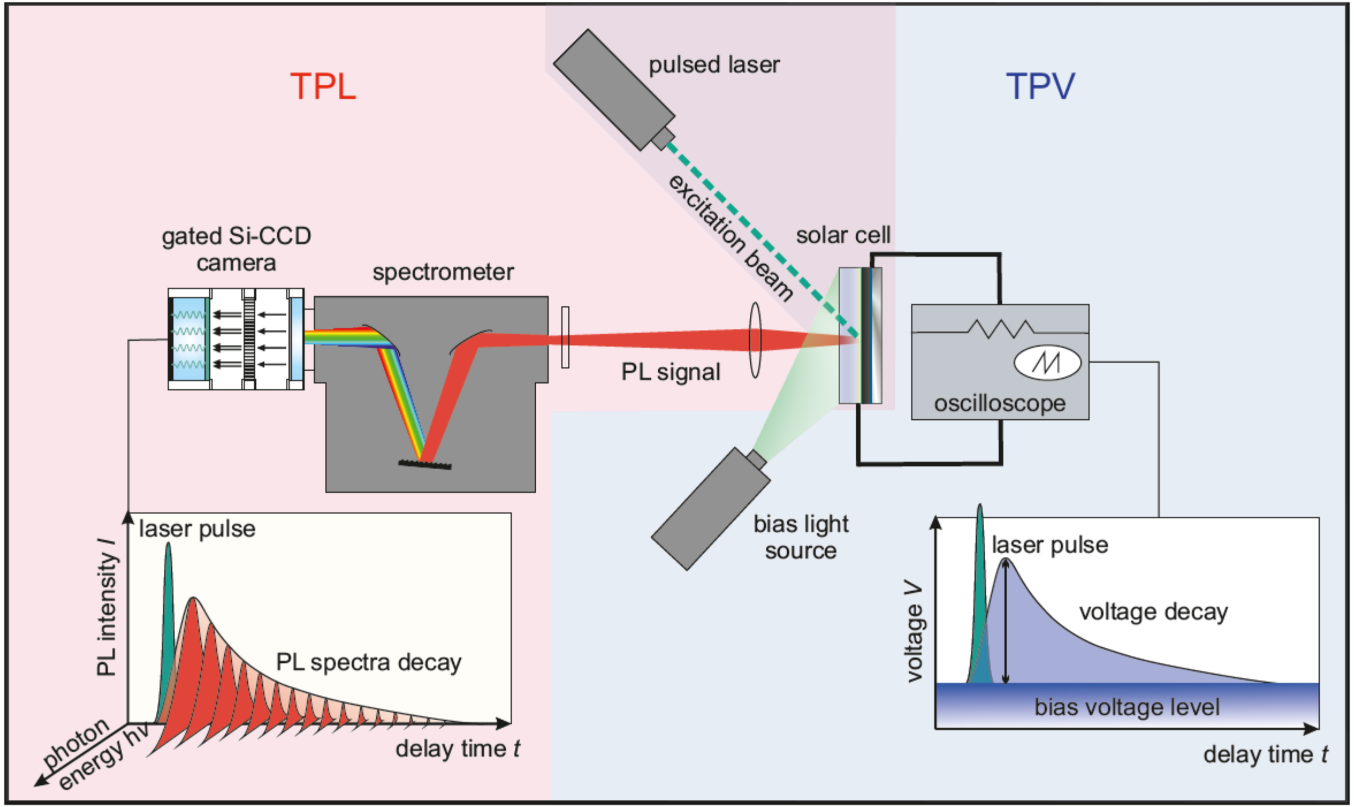
Transient Photovoltage vs. Photoluminescence

Transient Photoluminescence (TPL)

measures the luminescence decay

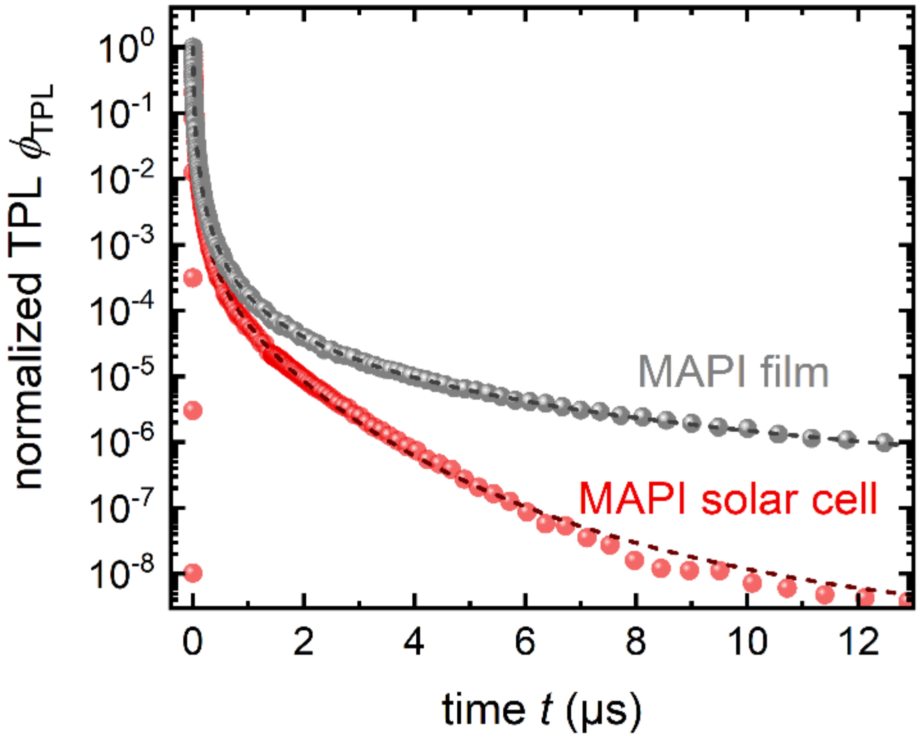
Transient Photovoltage (TPV)

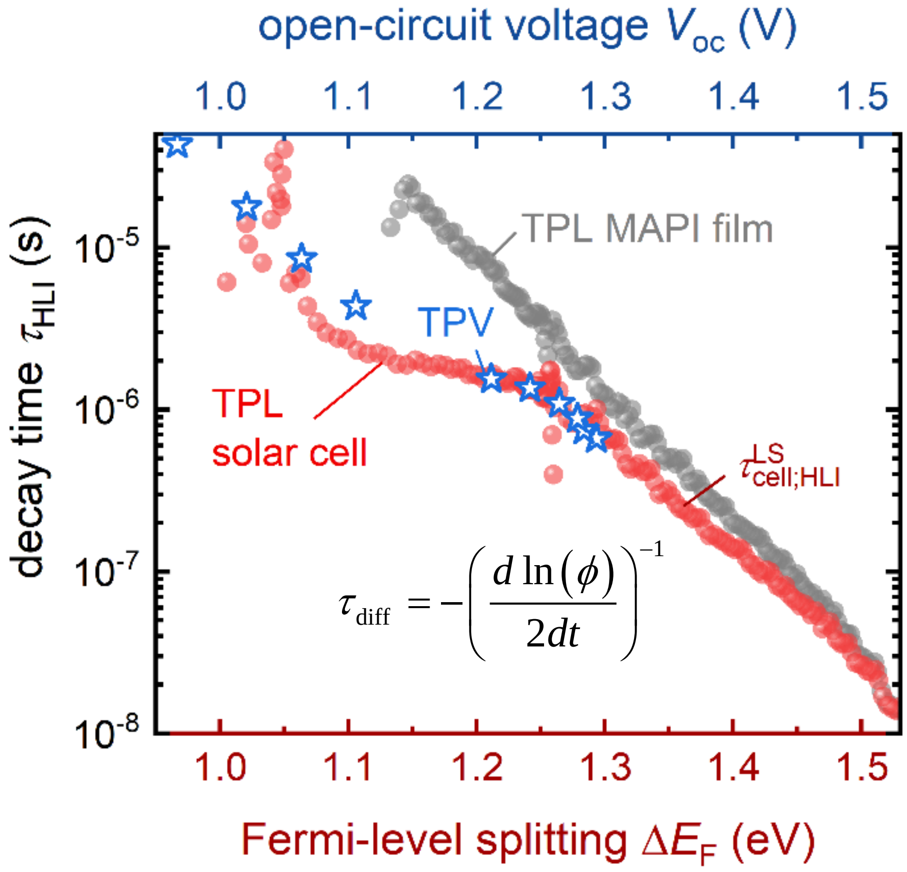
measures the decay of an external voltage



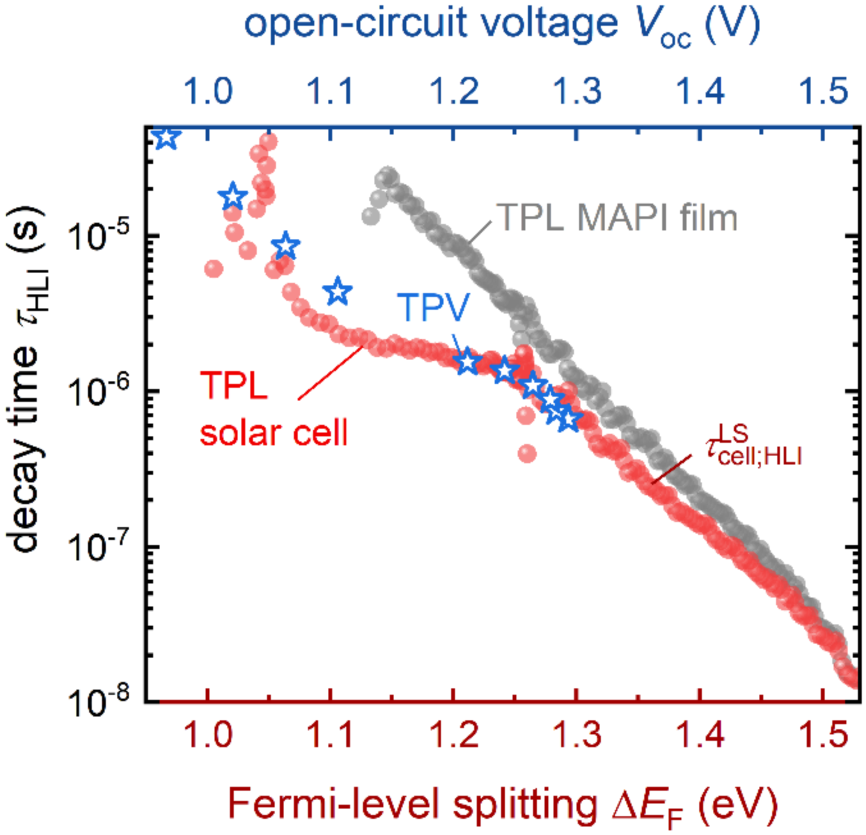
Transient Photoluminescence

Layer on Glass – Bulk Recombination





How to make sense out of it

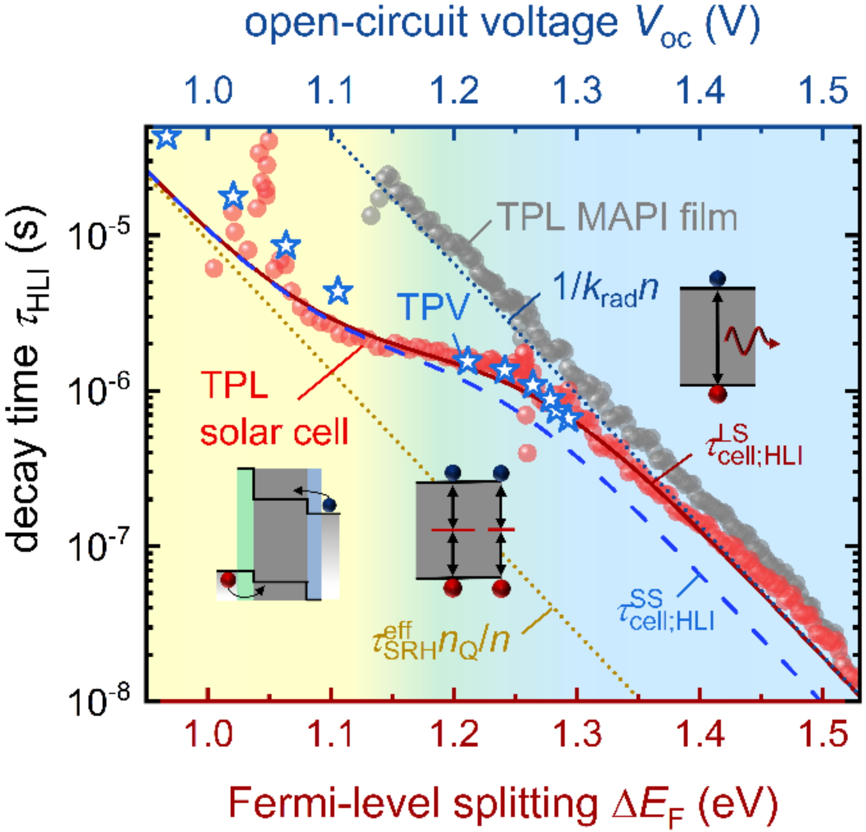


$$\frac{dn(t)}{dt} = -k_{rad} n(t)^2 - \frac{n(t)}{\tau_{SRH}^{bulk}} - \frac{C_{area}}{qd_{pero}} \frac{dV_{ext}(t)}{dt} + G$$

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

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

How to make sense out of it



Capacitive discharging of the electrodes

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

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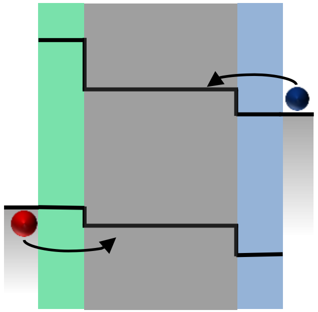
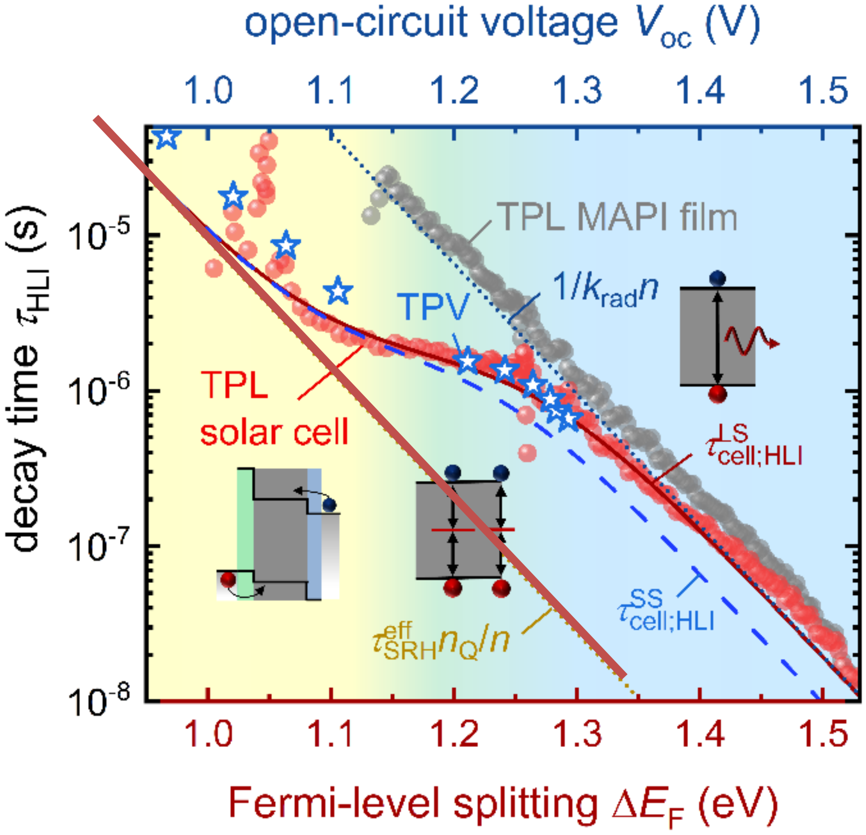


How to make sense out of it



Capacitive discharging of the electrodes

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

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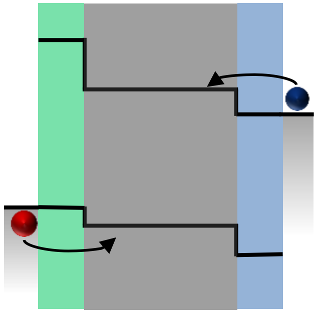
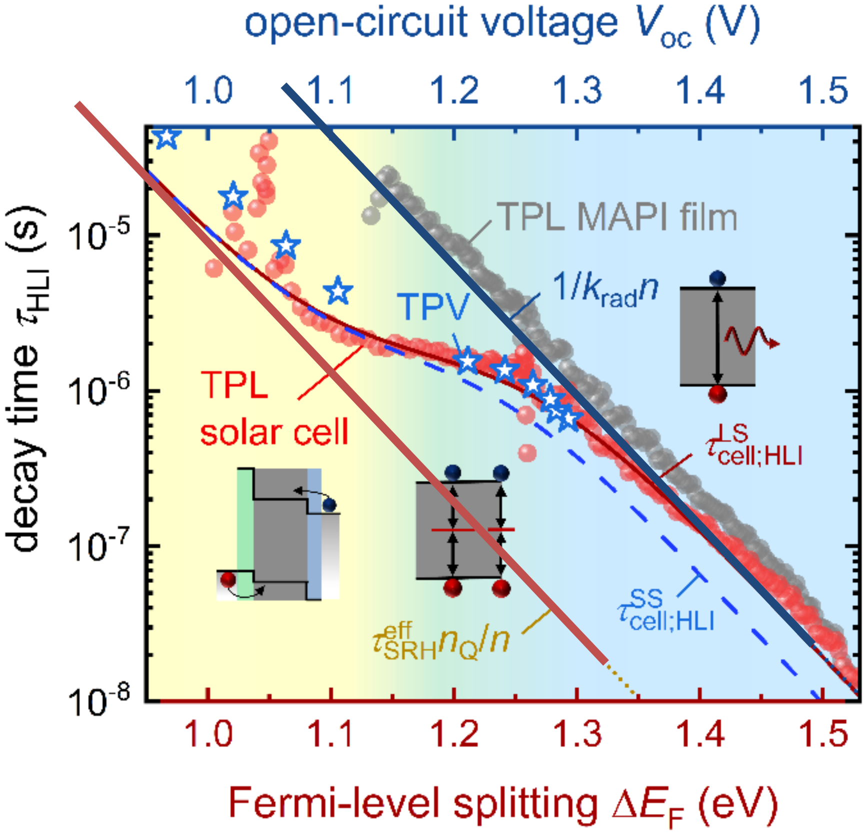
$$n_Q = 2C_{area}k_BT/\left(q^2d_{pero}\right)$$



Re-injection of carriers into the perovskite layer

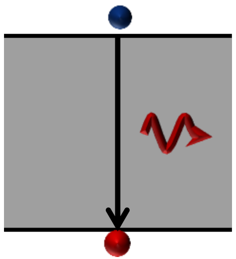
How to make sense out of it



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

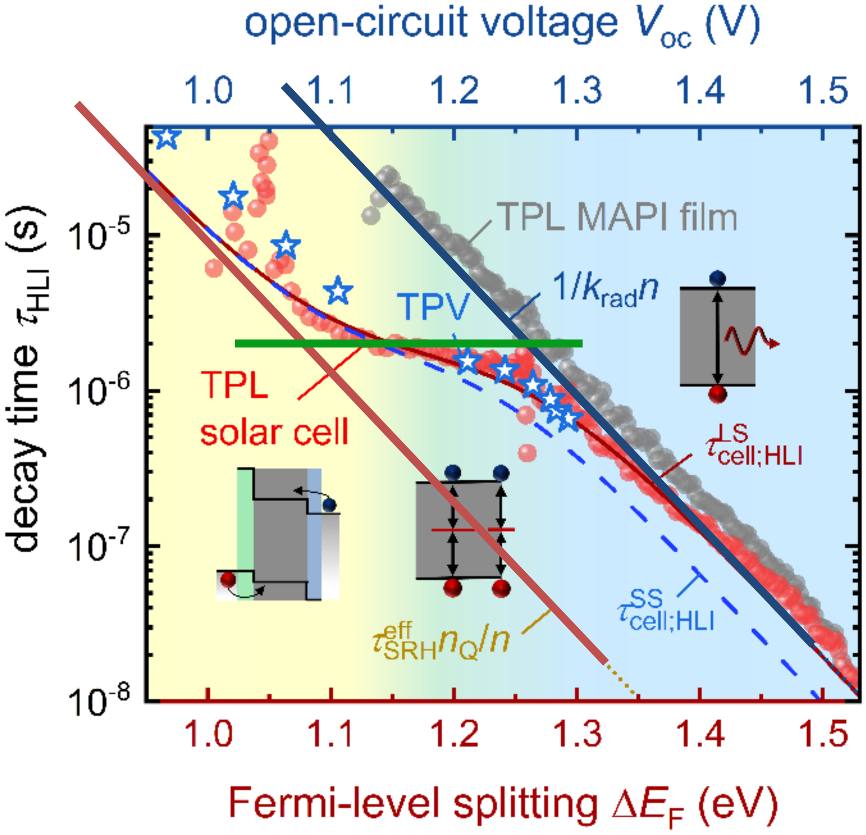
$$\tau^{LS}_{cell,\,HLI} = -\frac{n(t)}{dn(t)/dt} = \frac{n_Q/n(t)+1}{k_{rad} n(t) + 1/\tau^{eff}_{SRH}}$$

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



Radiative recombination

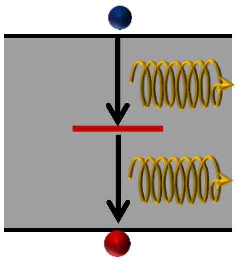
How to make sense out of it



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

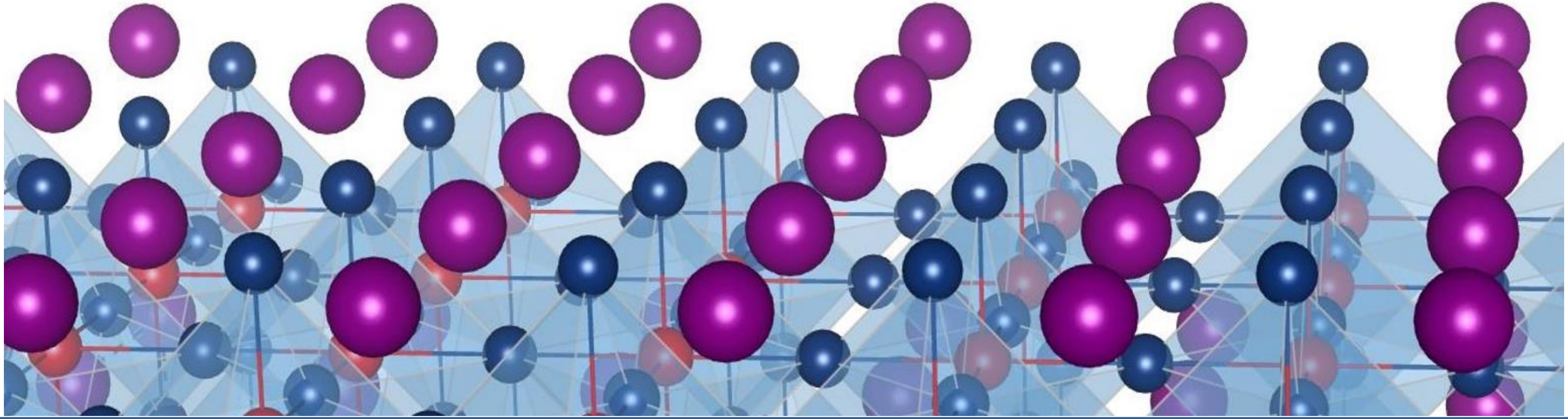
$$\tau^{LS}_{cell,\,HLI} = -\frac{n(t)}{dn(t)/dt} = \frac{n_Q/n(t)+1}{k_{rad}n(t)+1/\tau^{eff}_{SRH}}$$

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



Shockley-Read-Hall recombination

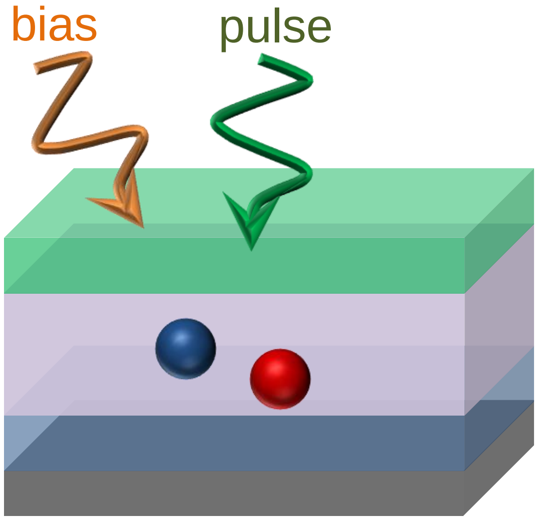
Krückemeier et al. Adv. Energy Mat. 2021, 11, 2102290

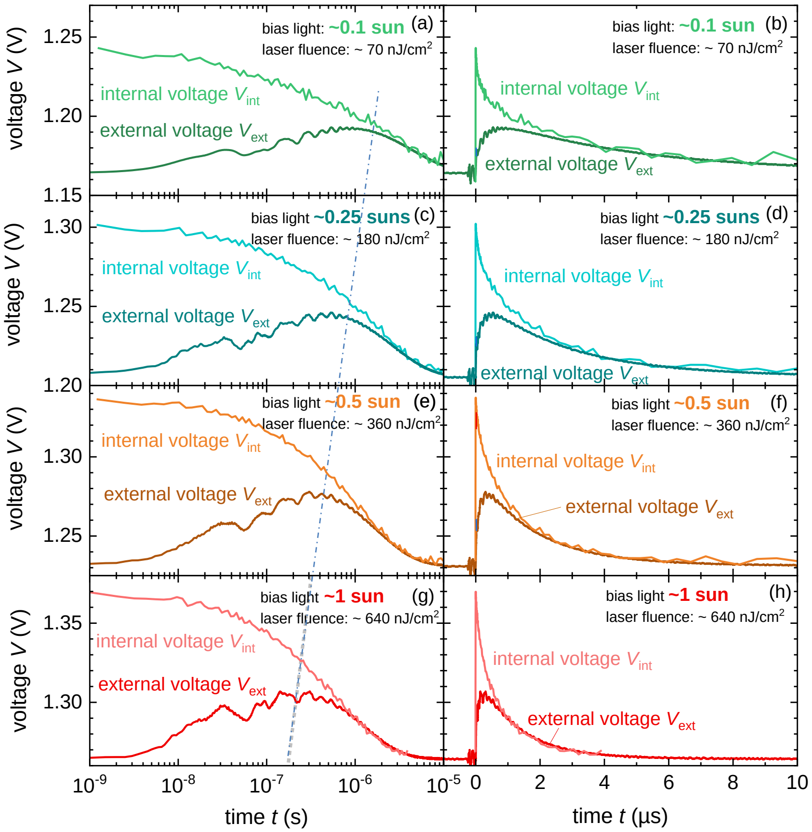


Part 2: Analysis of Small Signal Measurements

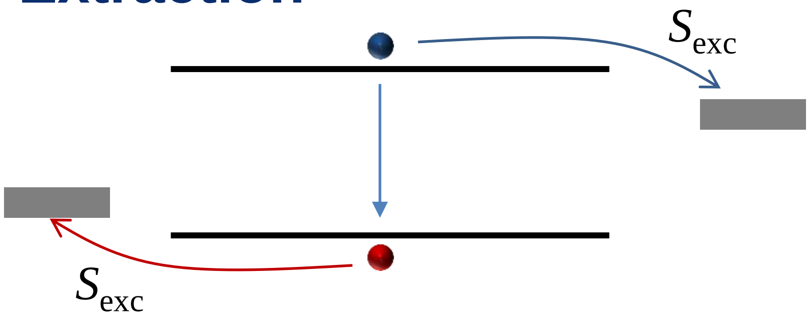
Recombination vs. Extraction

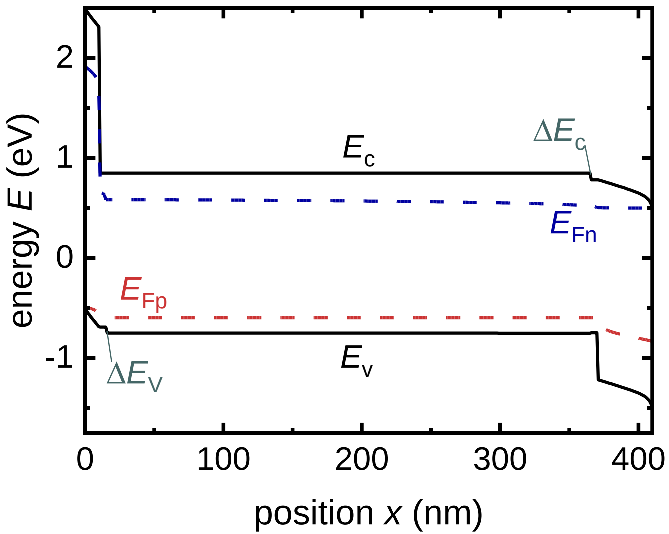
Experimental data – internal vs. external voltage





Transient Methods – Recombination and Extraction





$$\frac{dn}{dt} = -k_{rad} n^2 - \frac{n}{\tau_{SRH}^{eff}} - \frac{S_{exc}}{d}\left(n - n_i \exp\left(\frac{qV_{ext}}{2kT}\right)\right) + G$$

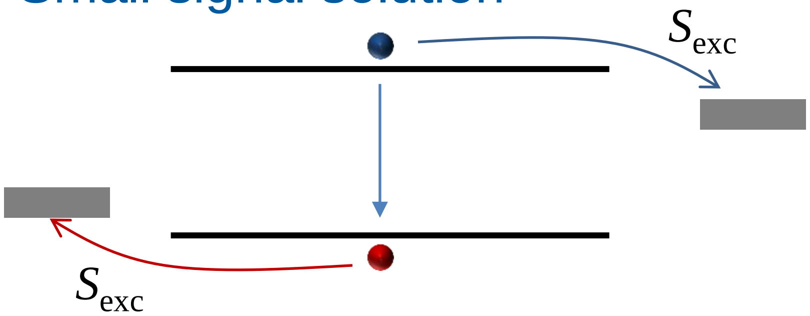
Recombination and extraction

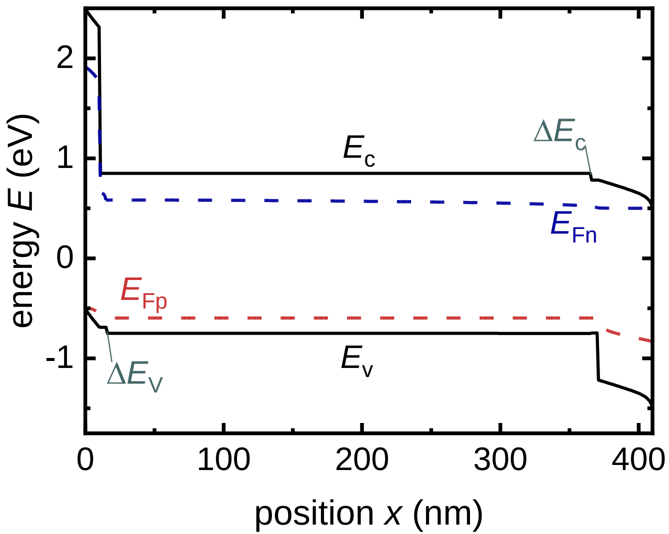
$$\frac{dV_{ext}}{dt} = \frac{qS_{exc}}{C_{area}}\left(n - n_i \exp\left(\frac{qV_{ext}}{2kT}\right)\right)$$

Electrode (dis)charging

Recombination and Extraction

Small signal solution





$$\frac{d}{dt}\begin{pmatrix}\delta V_{\mathrm{int}}\\ \delta V_{\mathrm{ext}}\end{pmatrix}=\begin{pmatrix}-\left(\frac{1}{\tau_{\mathrm{SRH}}^{\mathrm{eff}}}+2k_{\mathrm{rad}}n_{\mathrm{bias}}+\frac{S_{\mathrm{exc}}}{d}\right) & \frac{S_{\mathrm{exc}}}{d}\\ \frac{S_{\mathrm{exc}}n_{\mathrm{bias}}}{dn_{\mathrm{Q}}} & -\frac{S_{\mathrm{exc}}n_{\mathrm{bias}}}{dn_{\mathrm{Q}}}\end{pmatrix}\begin{pmatrix}\delta V_{\mathrm{int}}\\ \delta V_{\mathrm{ext}}\end{pmatrix}$$

$$\tau_{\mathrm{rise}}=\frac{2}{k_1+k_2+k_3+\sqrt{(k_1+k_2+k_3)^2-4k_1k_3}}$$

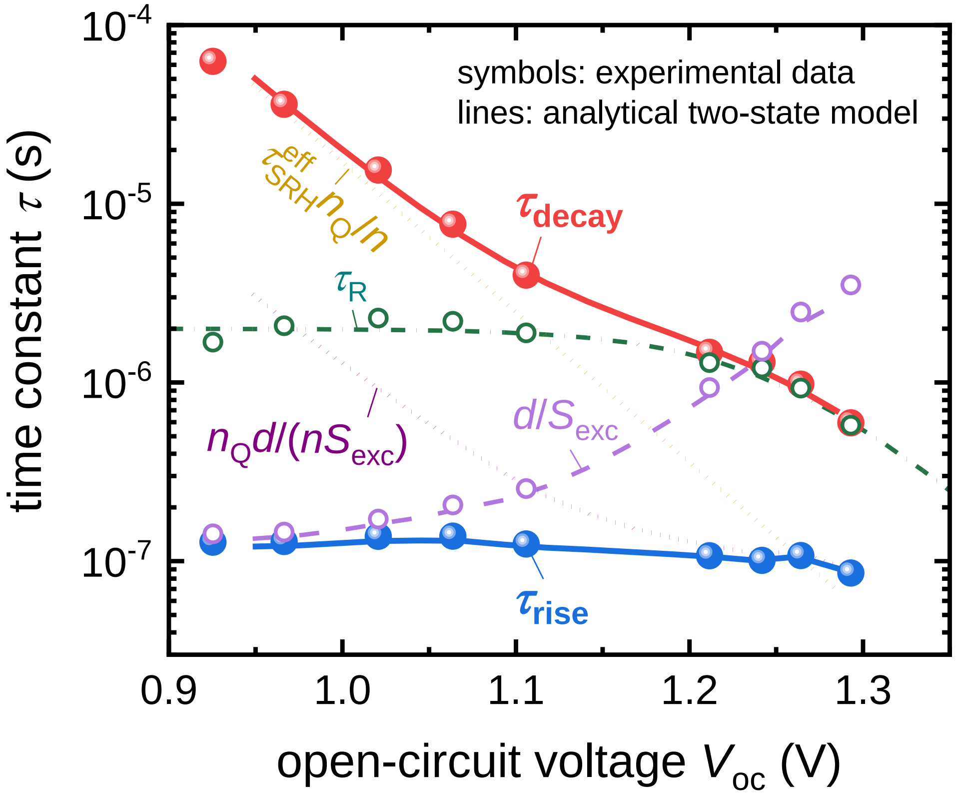
$$\tau_{\mathrm{decay}}=\frac{2}{k_1+k_2+k_3-\sqrt{(k_1+k_2+k_3)^2-4k_1k_3}}$$

$$k_1=\frac{1}{\tau_{\mathrm{SRH}}^{\mathrm{eff}}}+2k_{\mathrm{rad}}n_{\mathrm{bias}},\; k_2=\frac{S_{\mathrm{exc}}}{d},\; k_3=\frac{S_{\mathrm{exc}}n_{\mathrm{bias}}}{dn_{\mathrm{Q}}}$$

Inverse Eigenvalues of Matrix

Recombination and Extraction

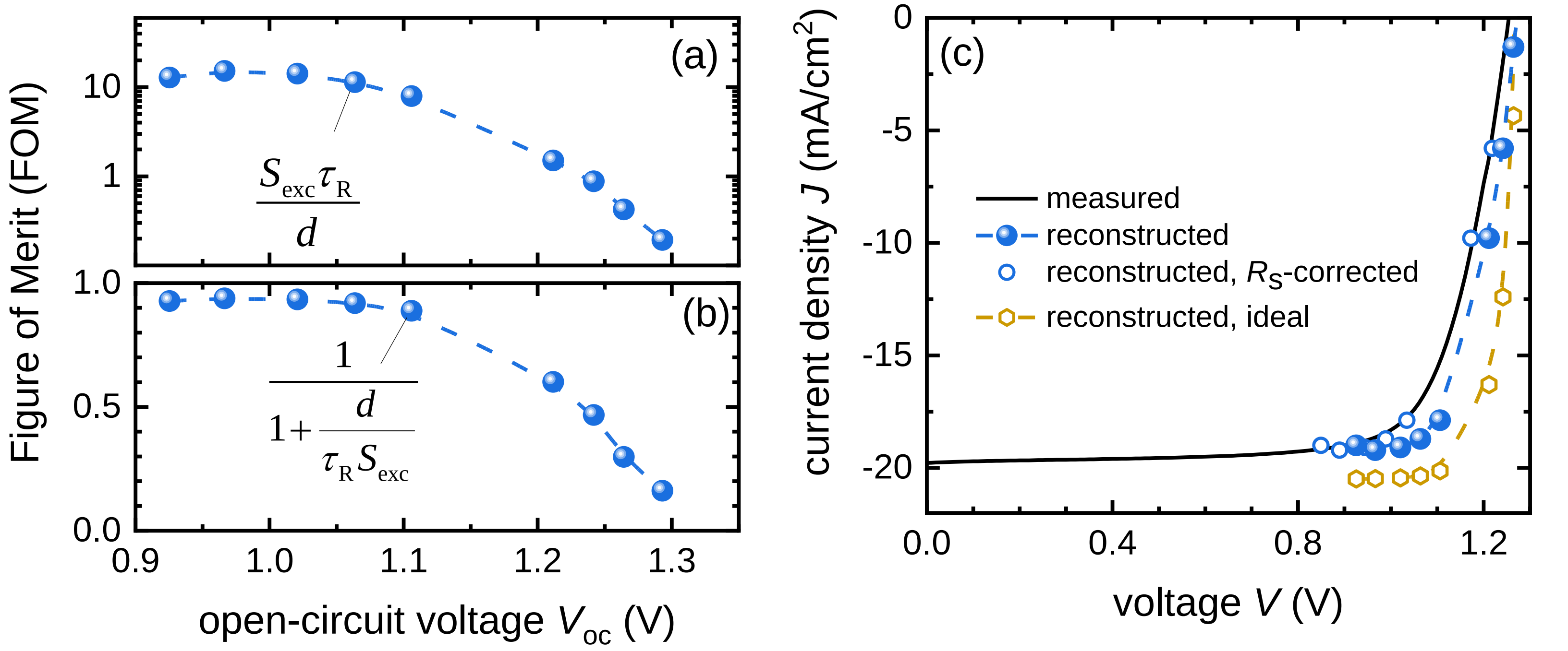
Comparison with Experiment



$$\tau_{\text{decay}} \approx \frac{dn_Q}{S_{\text{exc}} n_{\text{bias}}} + \frac{\tau_R n_Q}{n_{\text{bias}}} + \tau_R$$

$$\tau_{\text{rise}} \approx \left(\frac{1}{\tau_R} + \frac{S_{\text{exc}}}{d} + \frac{S_{\text{exc}} n_{\text{bias}}}{dn_Q} \right)^{-1}$$

Collection Efficiencies and Impact on *JV* curves

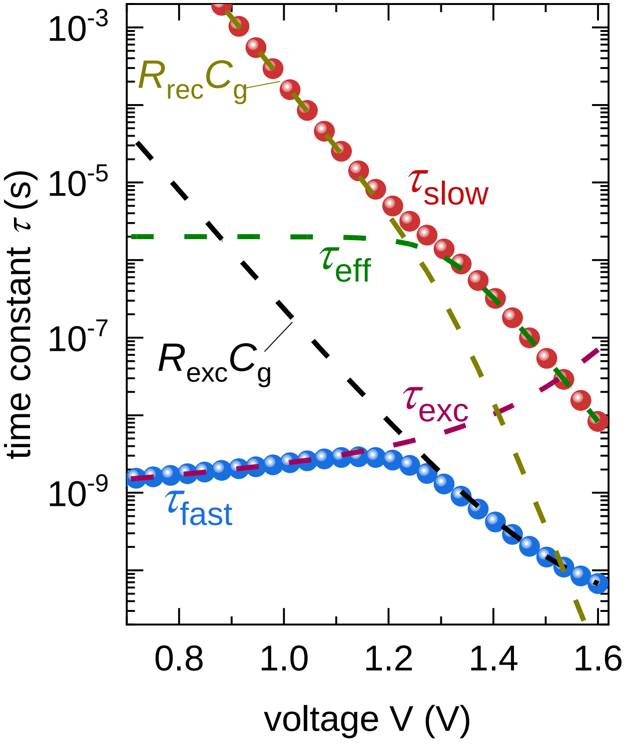


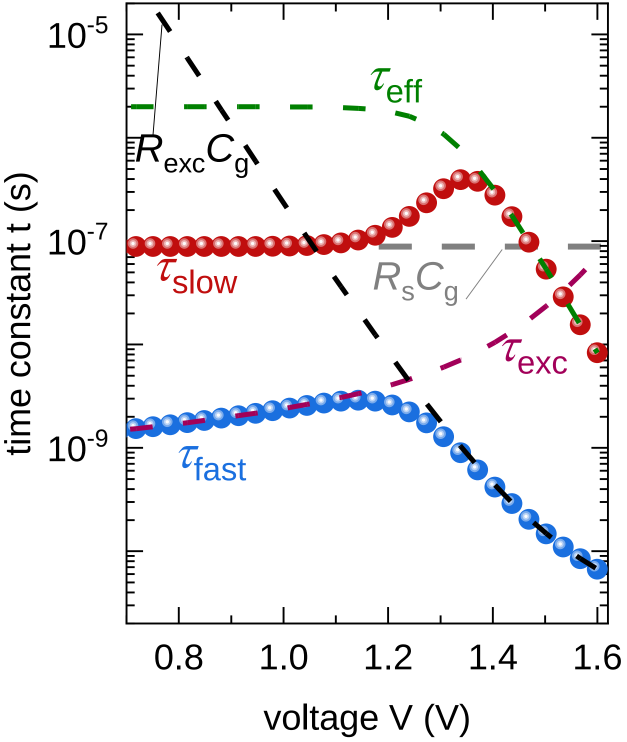
$$J = qd\left(R - G\right) = qd\left(\frac{1}{1 + d/\left(S_{exc}\tau_R\right)}\right)\left[\frac{n_0}{\tau_R}\exp\left(\frac{qV_{ext}}{2k_BT}\right) - G\right]$$

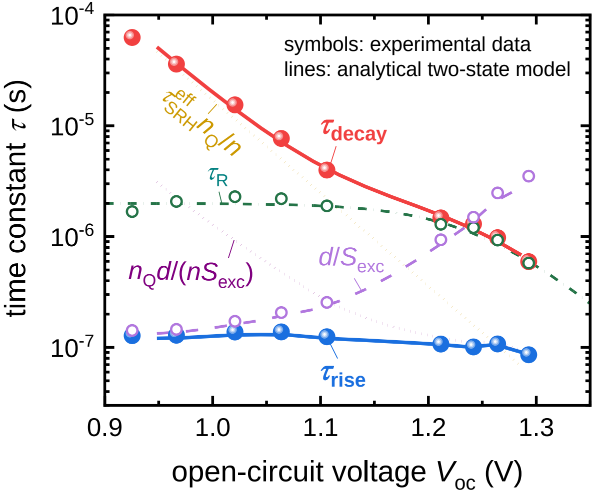
Krückemeier, L., et al. (2023),. Adv. Mater. 2300872. https://doi.org/10.1002/adma.202300872

Frequency-Domain Methods

simulated data (freq. domain)

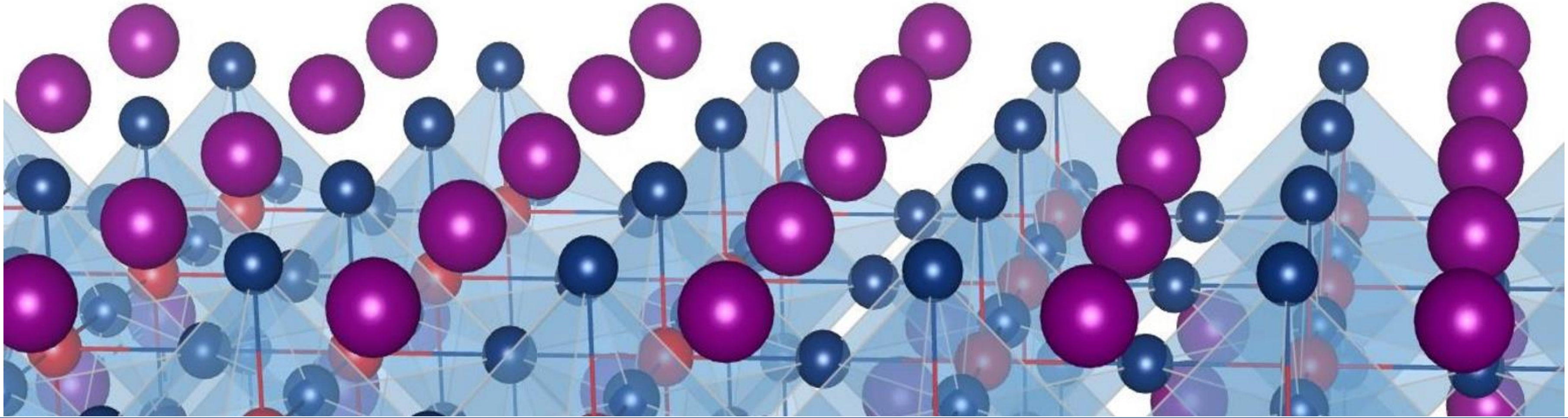






Experimental data (time domain)

Sandheep Ravishankar et al.
https://arxiv.org/abs/2303.09908 , https://www.researchsquare.com/article/rs-2978286/v1



Part 3: Shallow Defects

And how they change the situation

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

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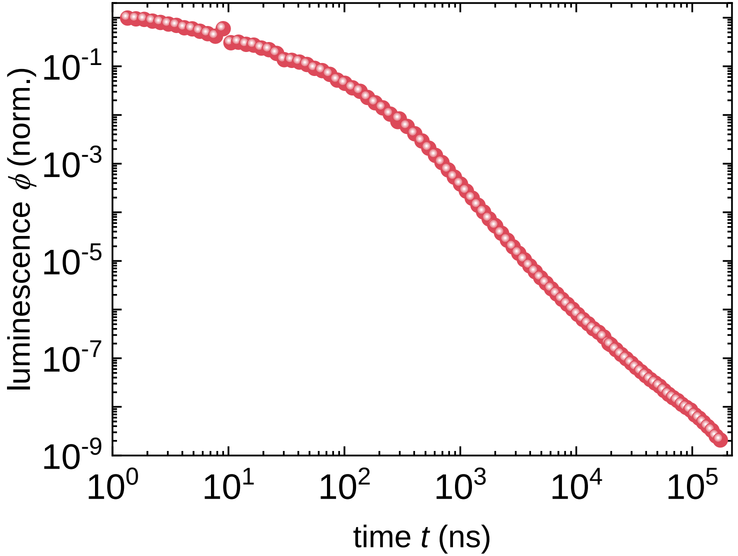
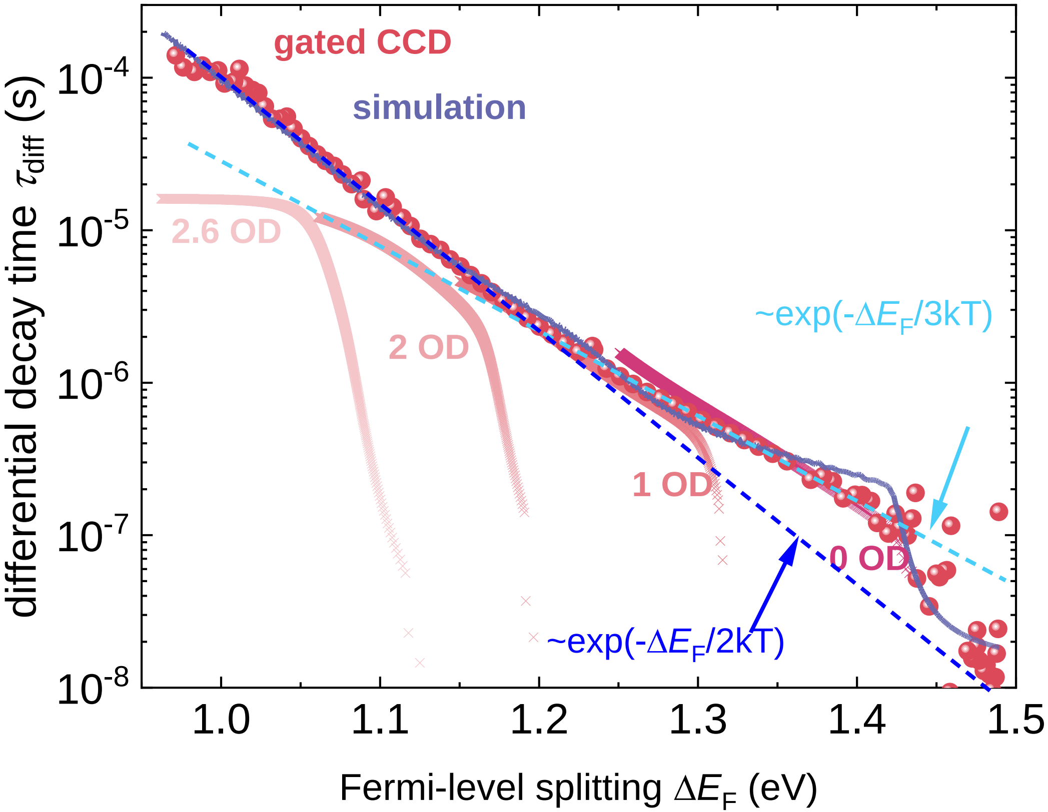
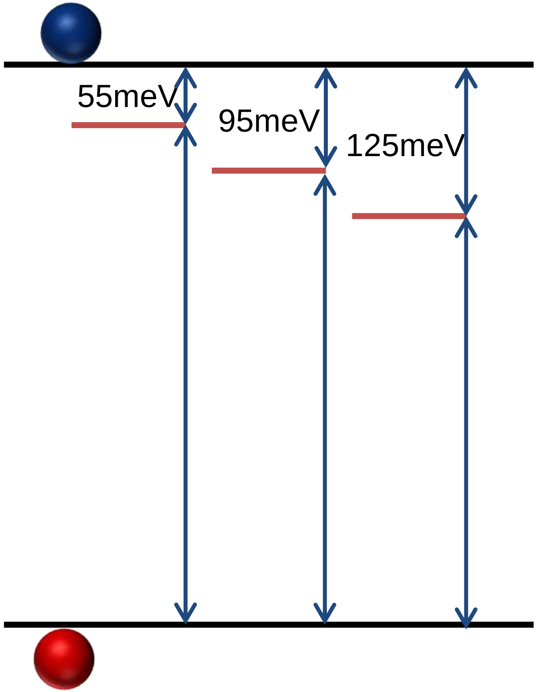
High dynamic range tr-PL

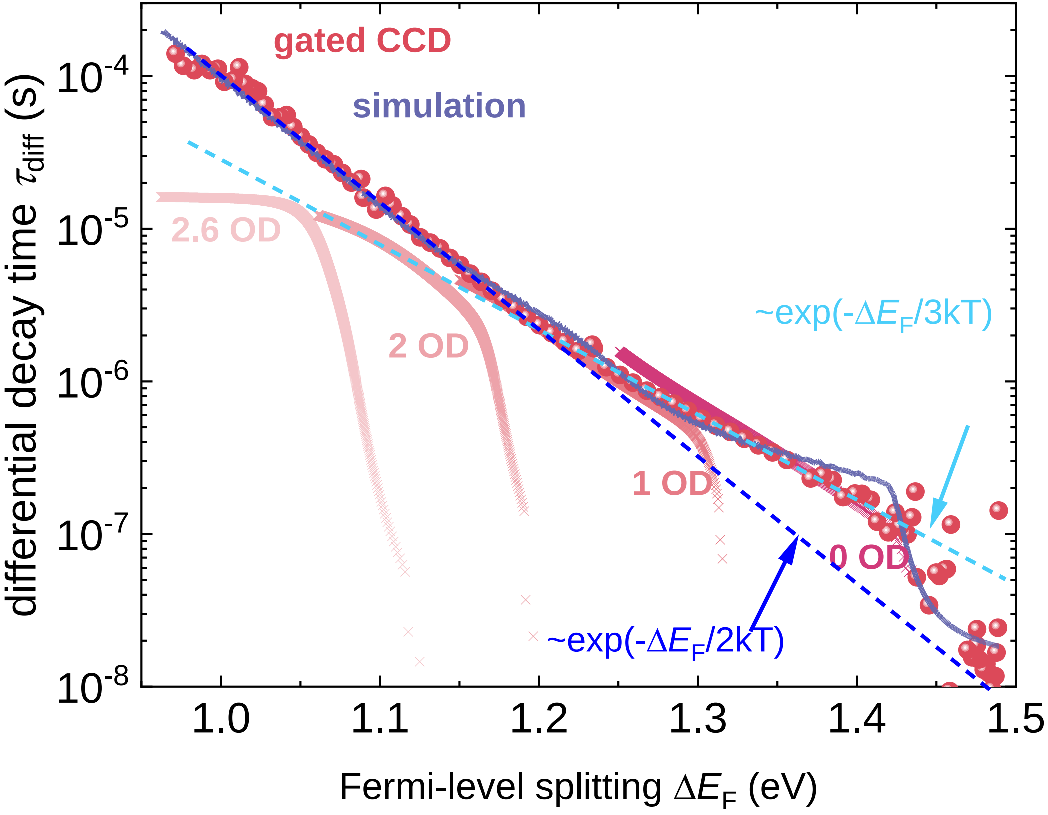




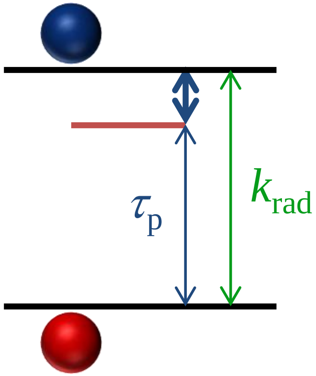
Defect levels assumed in the modelling



schematic not quite to scale

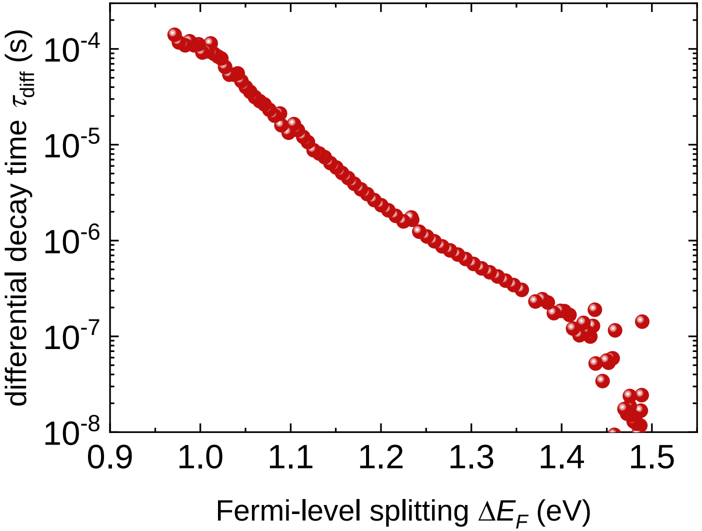


On the presence or absence of deep defects

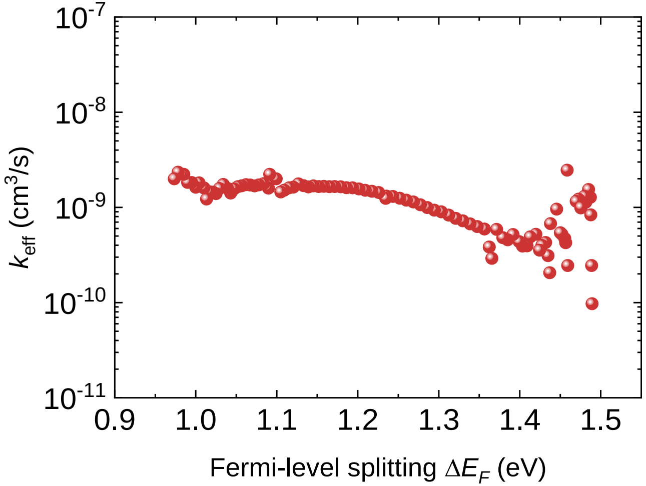


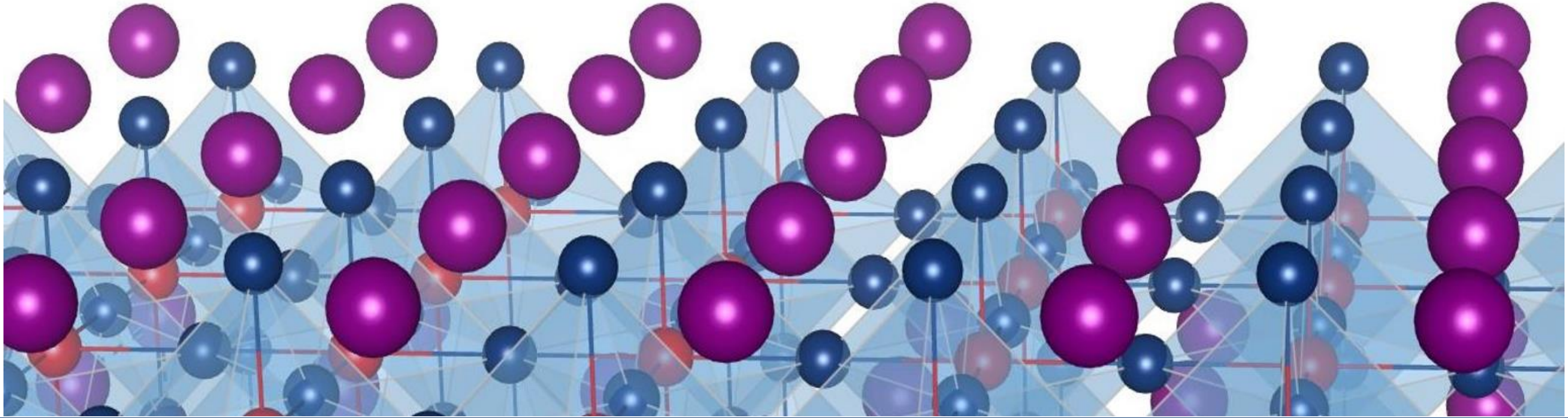
$$\tau_{diff} \approx \tau_p \sqrt{\frac{n_1 N_T}{np}} \frac{1}{1 + k_{rad}\tau_p n_1}$$

$$n_1 = N_C \exp\left(-\frac{E_C - E_T}{kT}\right)$$



$$k_{diff} \approx \frac{1 + k_{rad}\tau_p n_1}{\tau_p \sqrt{n_1 N_T}}$$

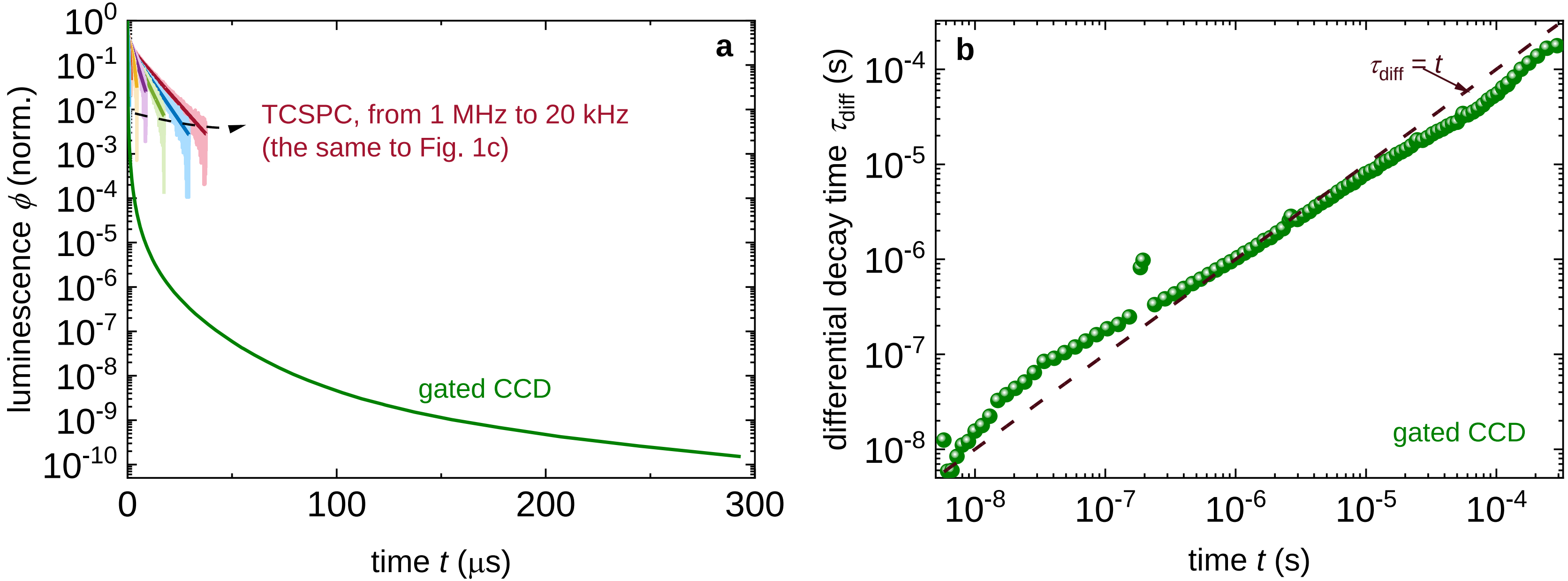




Part 4: Repetition Rates

And how they affect decay times

Why $\tau = t$ can be a decent approximation

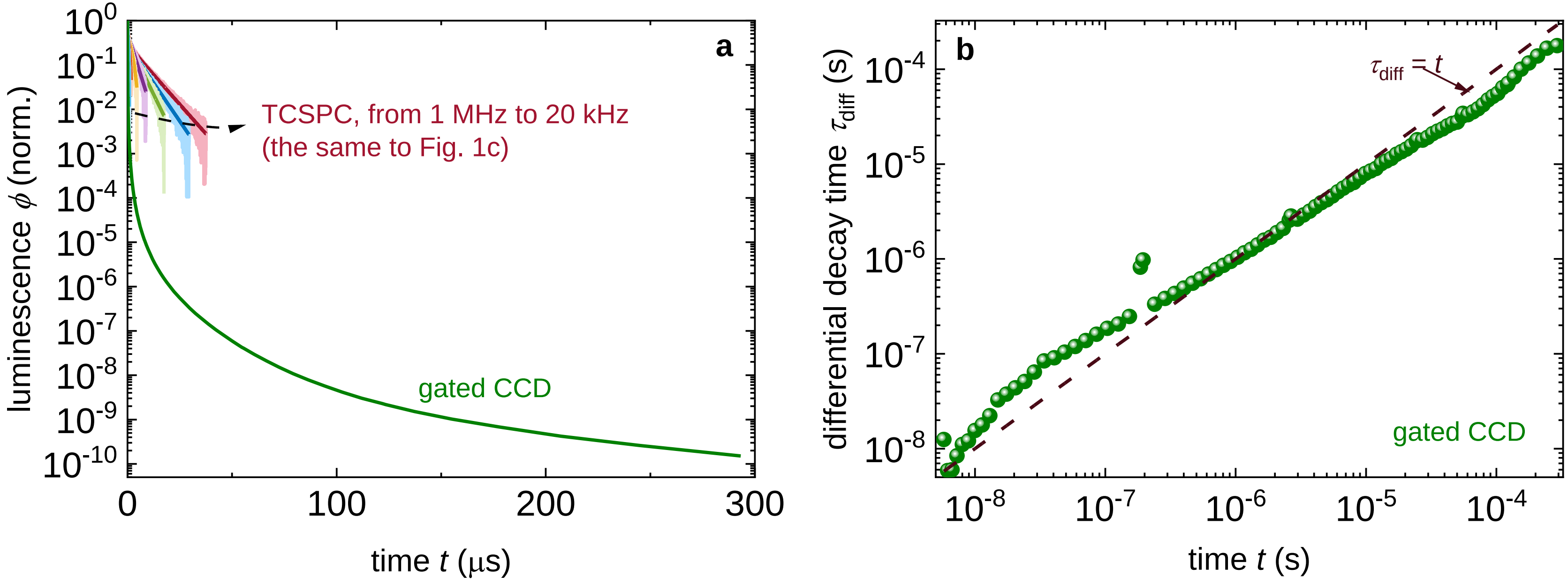


$$\frac{dn(t)}{dt} = -kn^2$$

$$\tau_{diff} = \left(kn(t)\right)^{-1}$$

$$n(t) = \frac{n(0)}{1 + n(0)kt} \approx 1/(kt)$$

Why $\tau = t$ can be a decent approximation



$$\frac{dn(t)}{dt} = -kn^2$$

$$\tau_{diff} = \left(kn(t)\right)^{-1}$$

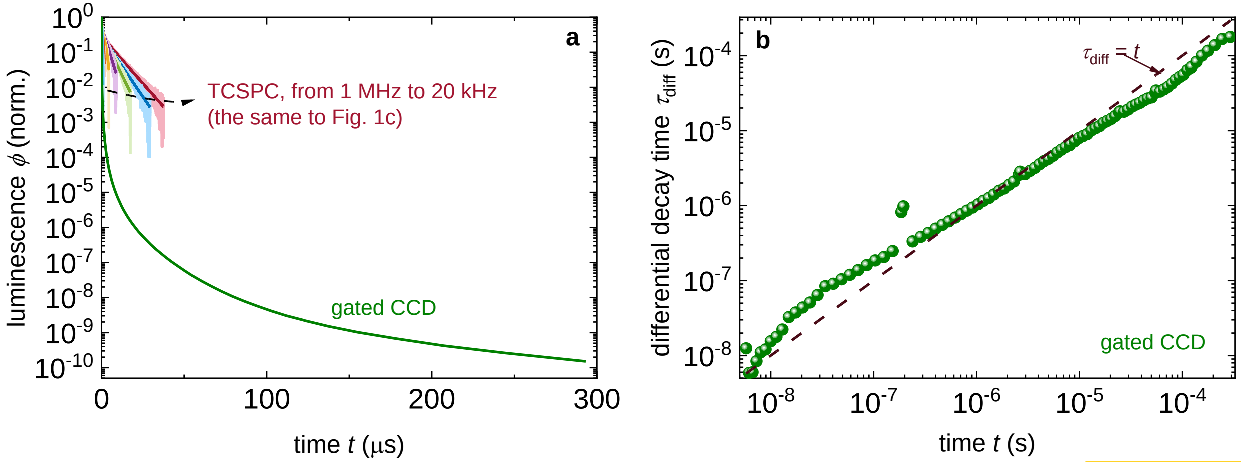
$$n(t) = \frac{n(0)}{1 + n(0)kt} \approx 1/(kt)$$

$$\tau_{diff} = t$$

Summary

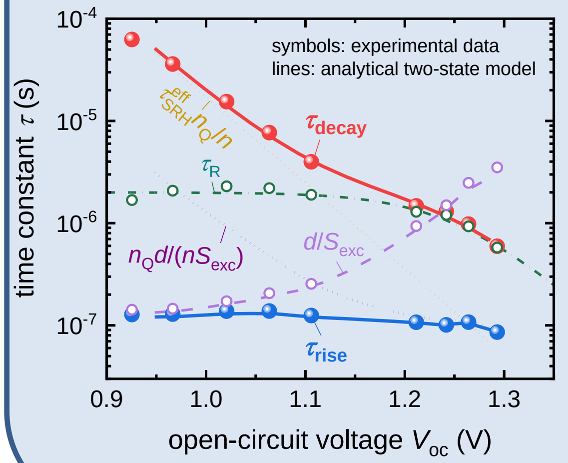
If a sample is intrinsic, the following holds:

- Every decay not dominated by a deep defect will lead to non-exponential decays.
- Those are often similar to radiative recombination (even if they are not)
- They will automatically lead to $\tau_{\mathrm{diff}} \approx t$ implying that decay times determined towards the end of a decay are ~ the inverse repetition rate.

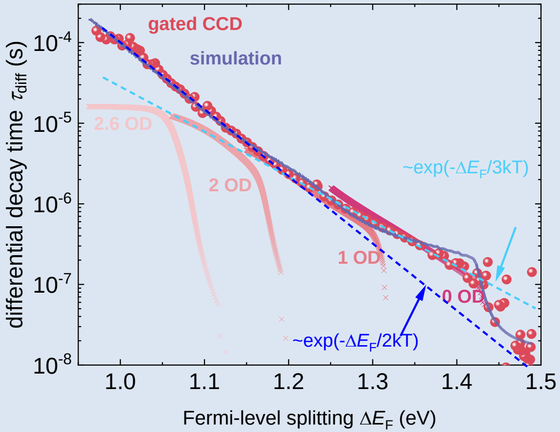


Outline

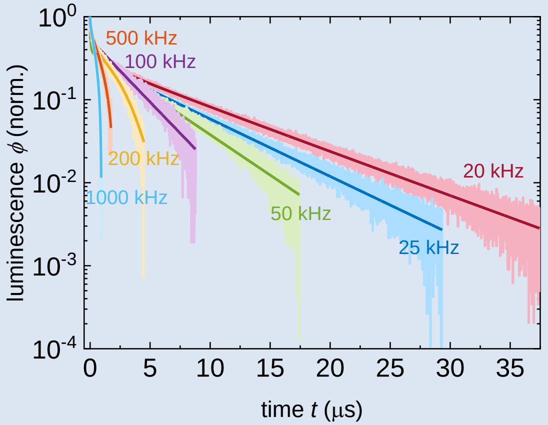
1) Rise and decay times → recombination and extraction times



2) Lifetime loses meaning. Effective k might be more useful.



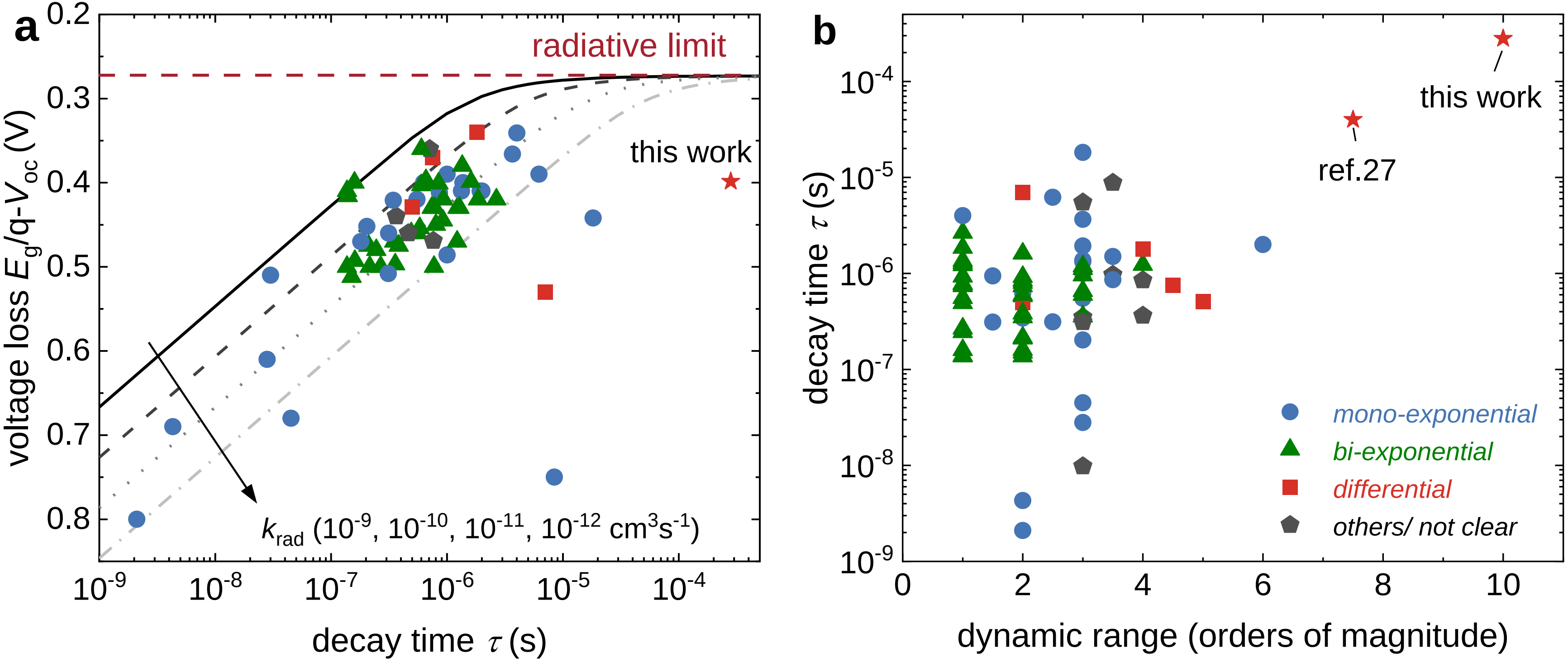
3) $\tau \sim 1/f_{rep}$ is a risk to consider.



Funding from
Helmholtz Association
DFG
OCPC Fellowships

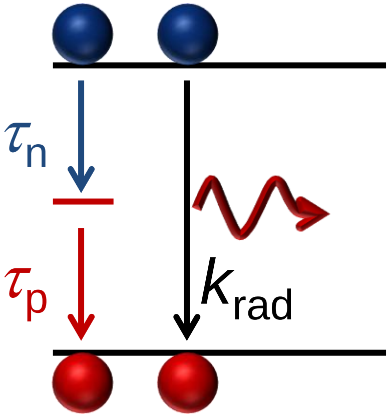
Thank you for your attention

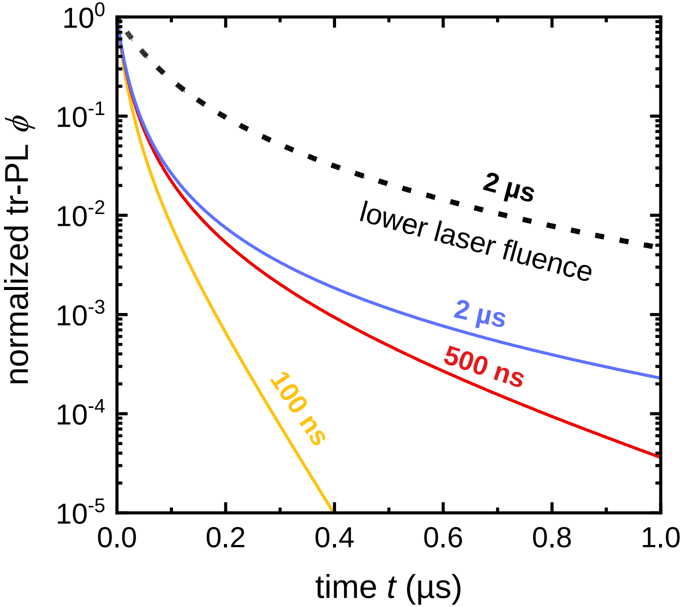
The importance of dynamic range

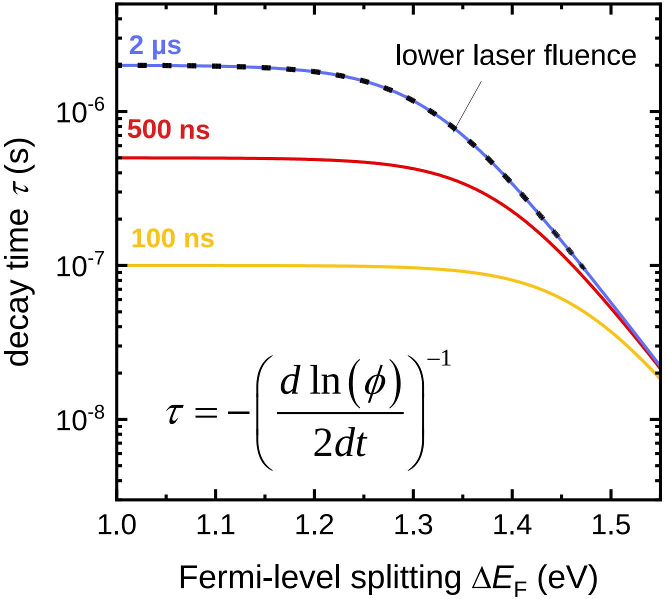


Transient Photoluminescence

Layer on Glass – Bulk Recombination







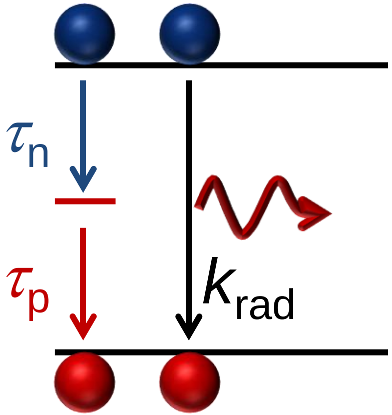
$$\frac{dn}{dt} = -k_{\text{rad}} n^2 - \frac{n}{\tau_{\text{p}} + \tau_{\text{n}}}$$

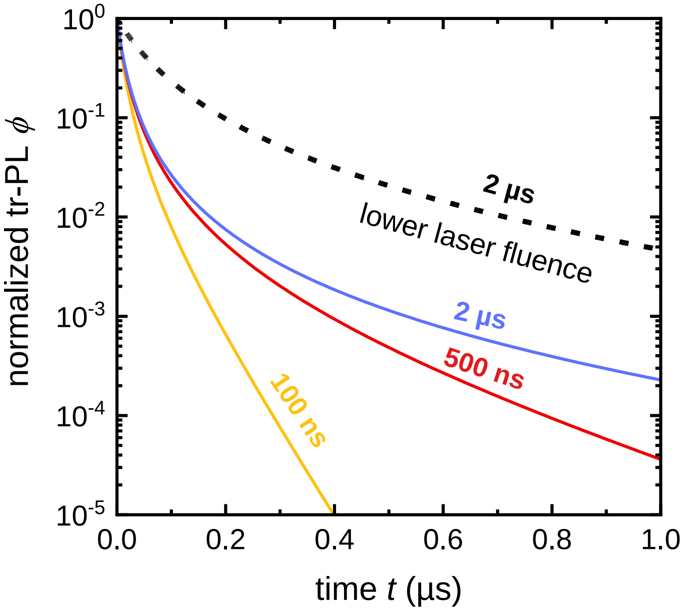
SRH + radiative recombination

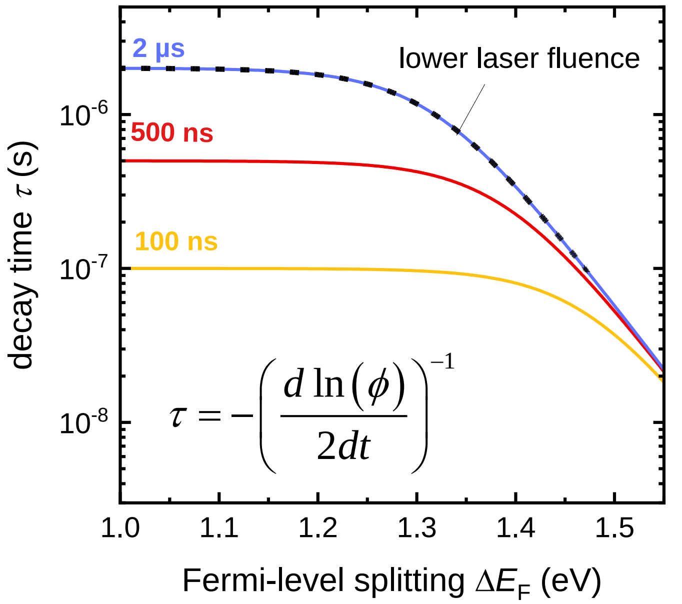
← time

Transient Photoluminescence

Layer on Glass – Bulk Recombination







$$\tau_{\text{diff}} = -\frac{n}{dn/dt} = \frac{1}{k_{\text{rad}} n + \tau_p + \tau_n}$$

Decay Time

time