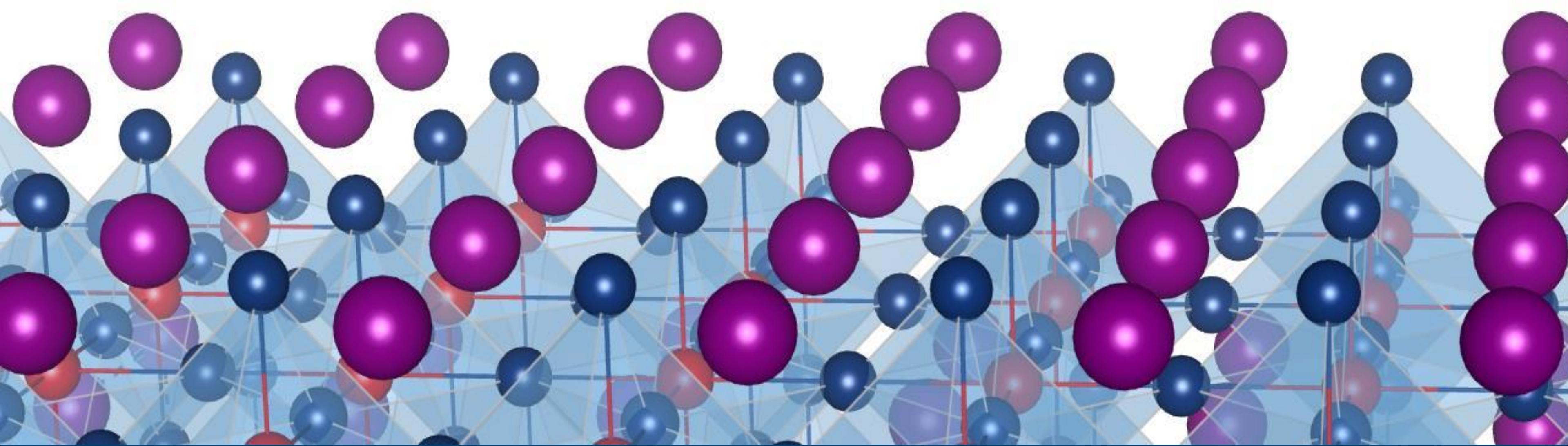


Shallow Defects and Long Charge-Carrier Lifetimes in Lead-halide Perovskites

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

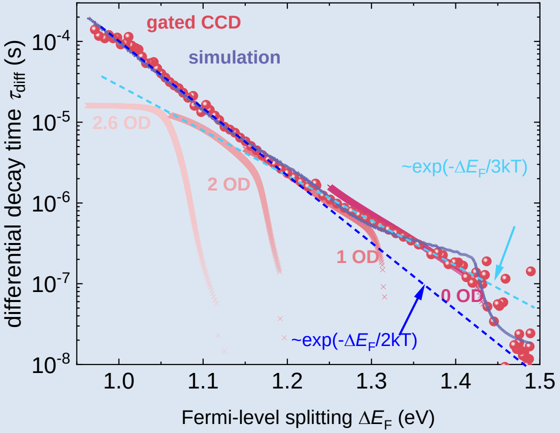
IEK-5 Photovoltaik, Forschungszentrum Jülich

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

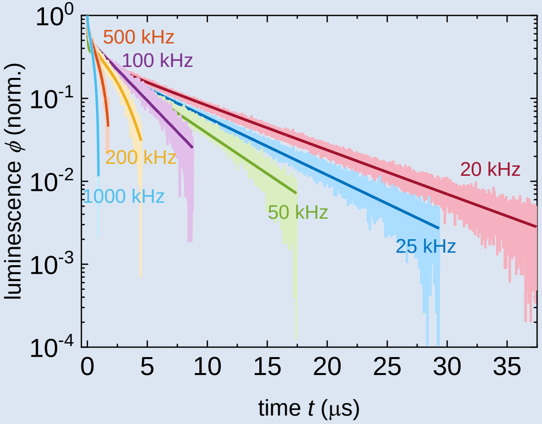
JÜLICH Forschungszentrum

Outline

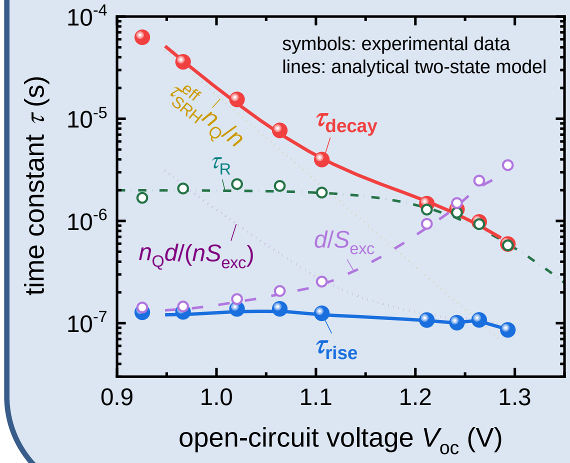
1) On the importance of shallow defects

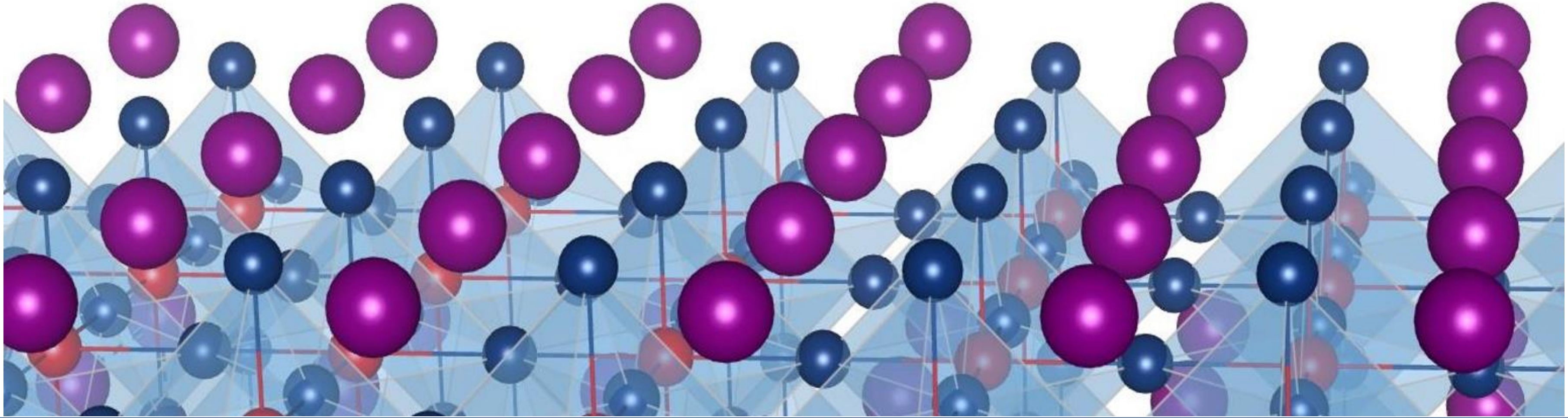


2) On the importance of repetition rates



3) Matrix models (for fans of linear algebra)





Part 0: Introduction

Transient Photoluminescence and Lifetimes

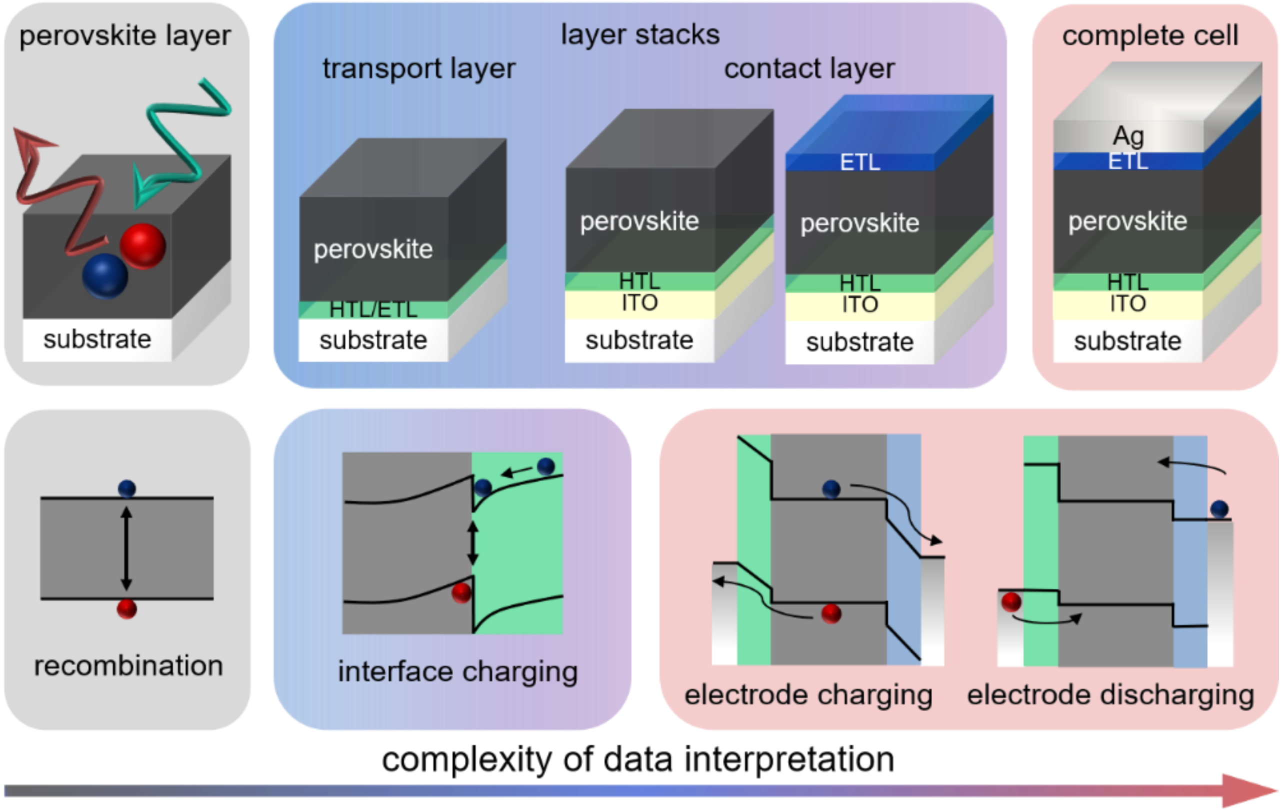
HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

JÜLICH Forschungszentrum

Transient Photoluminescence in Lead-Halide Perovskite Layer Stacks and Solar Cells

$$\phi_{PL} \propto np \approx n^2$$

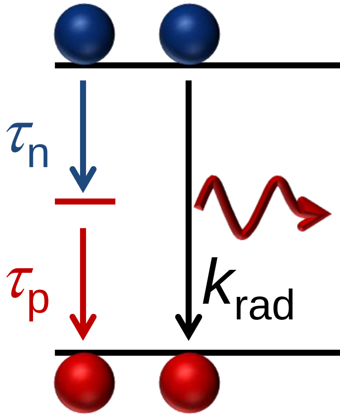
Our samples are intrinsic (i.e. have a very low dark carrier concentration)

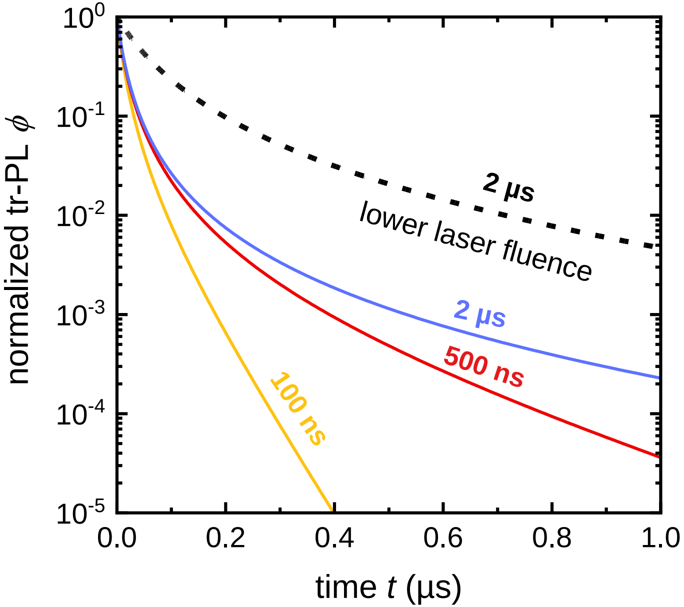


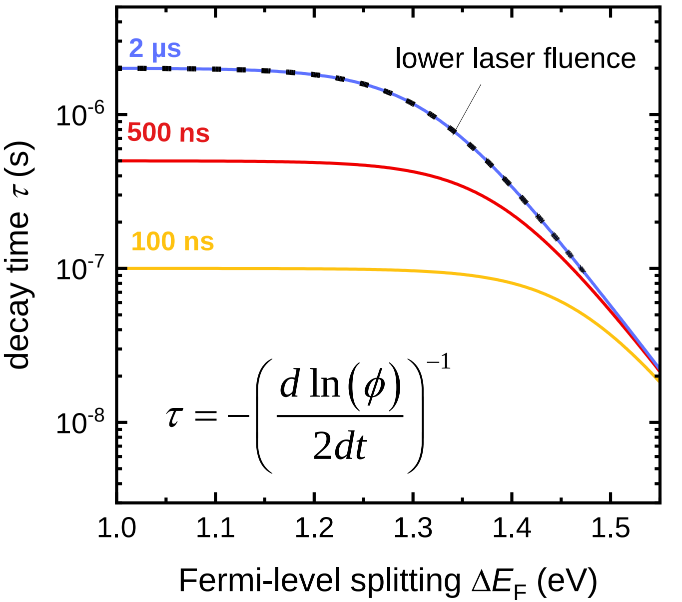
Krückemeier et al. Adv. Energy Mater. **11**, 2003489 (2021)

Transient Photoluminescence

Layer on Glass – Bulk Recombination







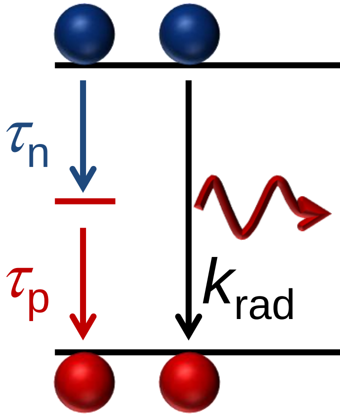
$$\frac{dn}{dt} = -k_{rad} n^2 - \frac{n}{\tau_p + \tau_n}$$

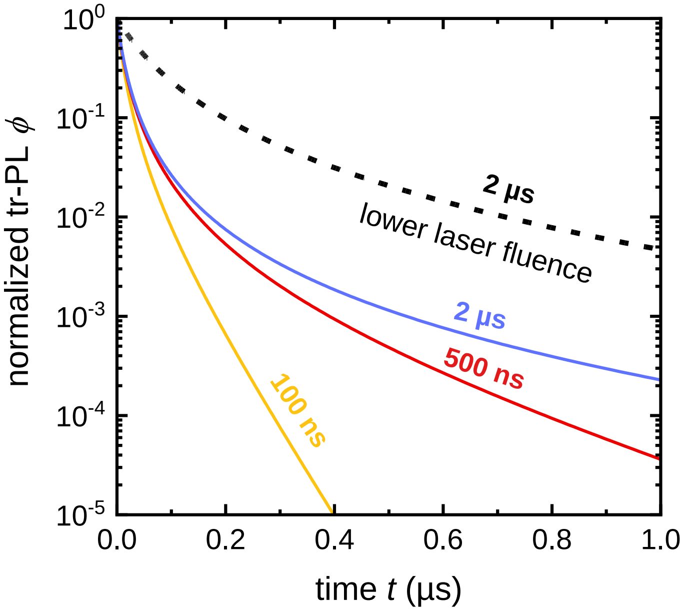
SRH + radiative recombination

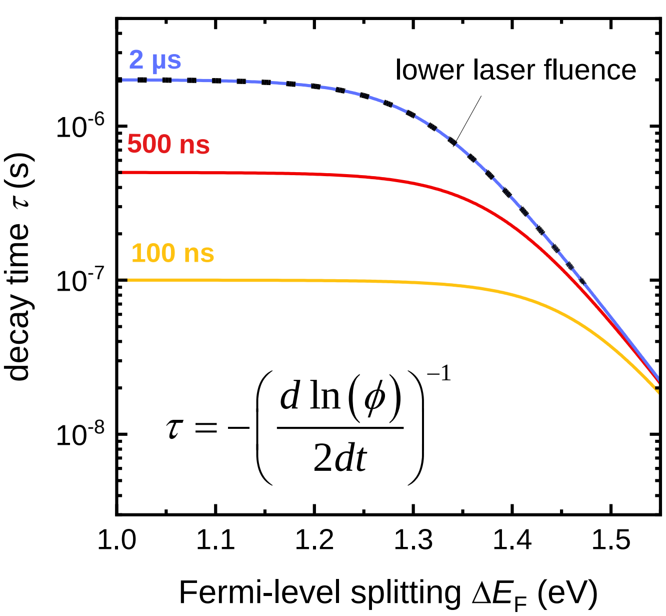
time

Transient Photoluminescence

Layer on Glass – Bulk Recombination



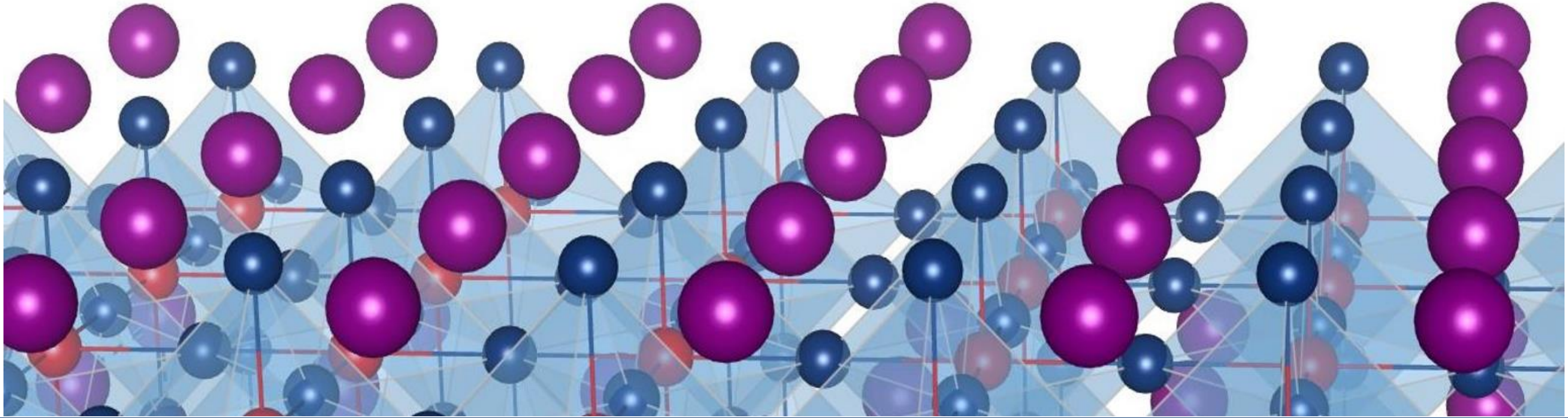




$$\tau_{\mathrm{diff}} = -\frac{n}{dn/dt} = \frac{1}{k_{\mathrm{rad}} n + \tau_{\mathrm{p}} + \tau_{\mathrm{n}}}$$

Decay Time

← time



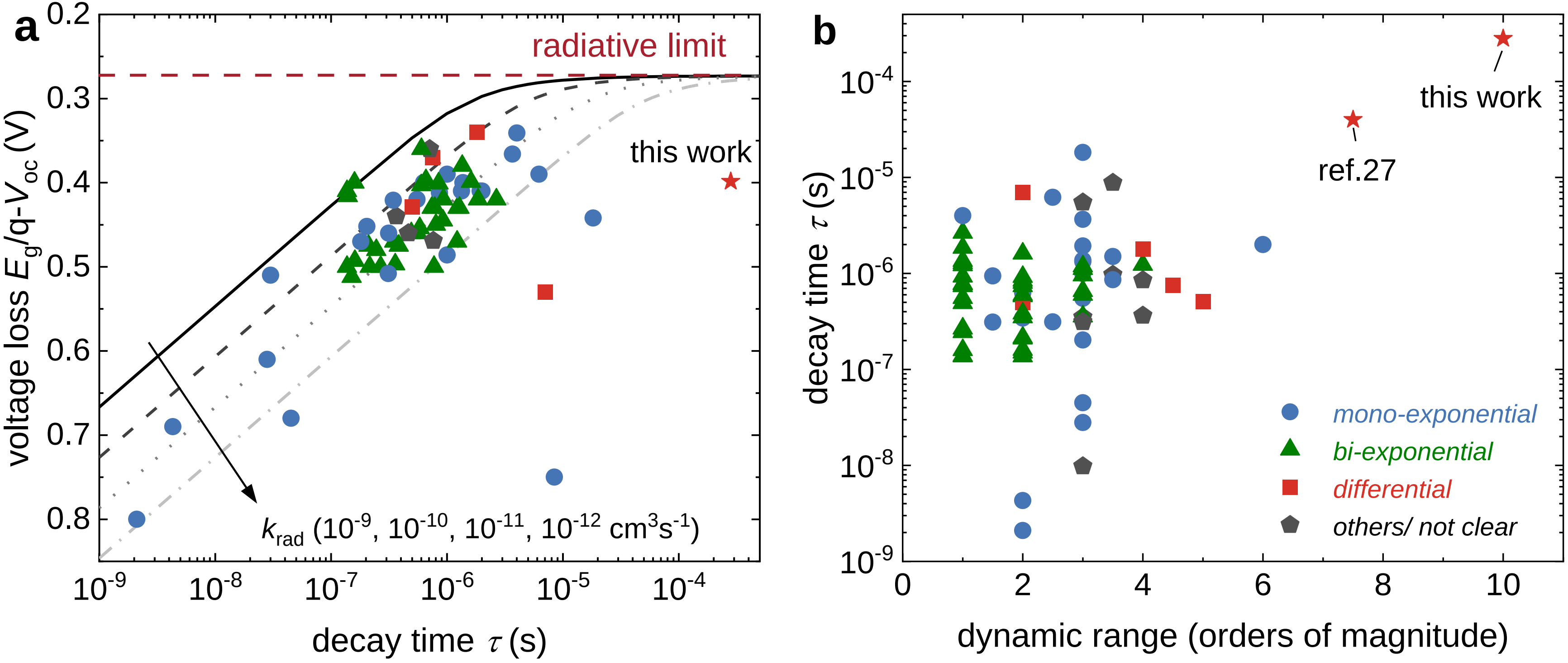
Part 1: Shallow Defects

And how they change the situation

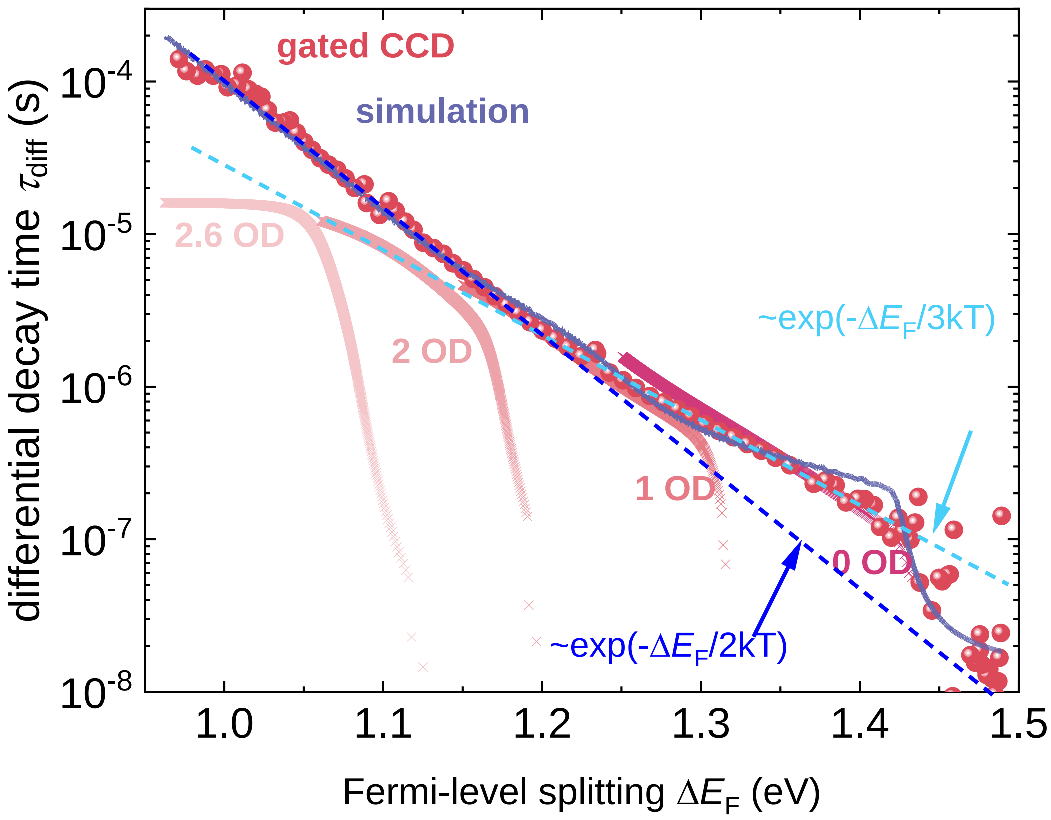
HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

JÜLICH Forschungszentrum

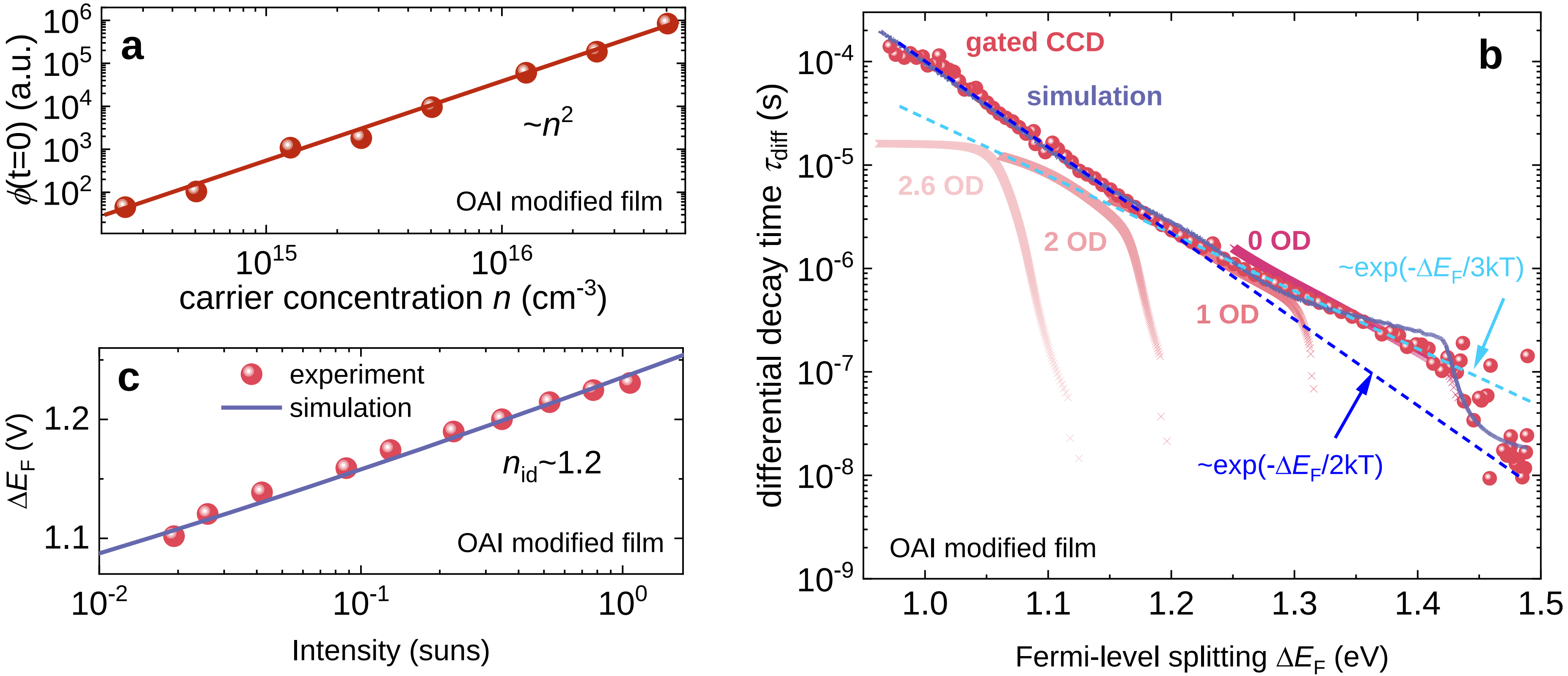
The importance of dynamic range



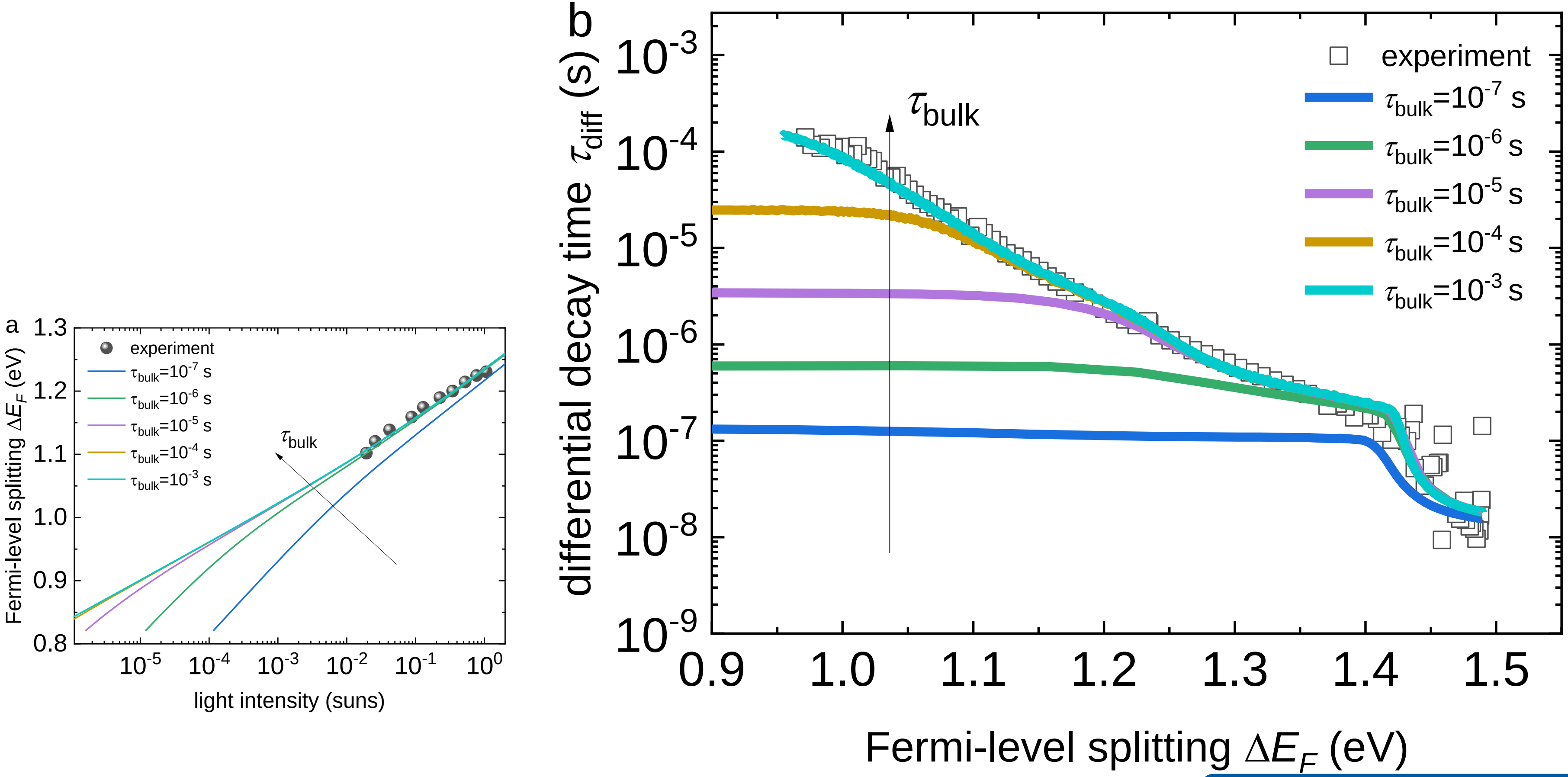
Steady state vs. tr-PL



Steady state vs. tr-PL



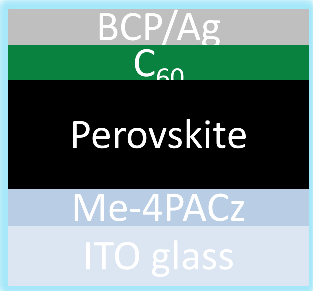
On the presence or absence of deep defects

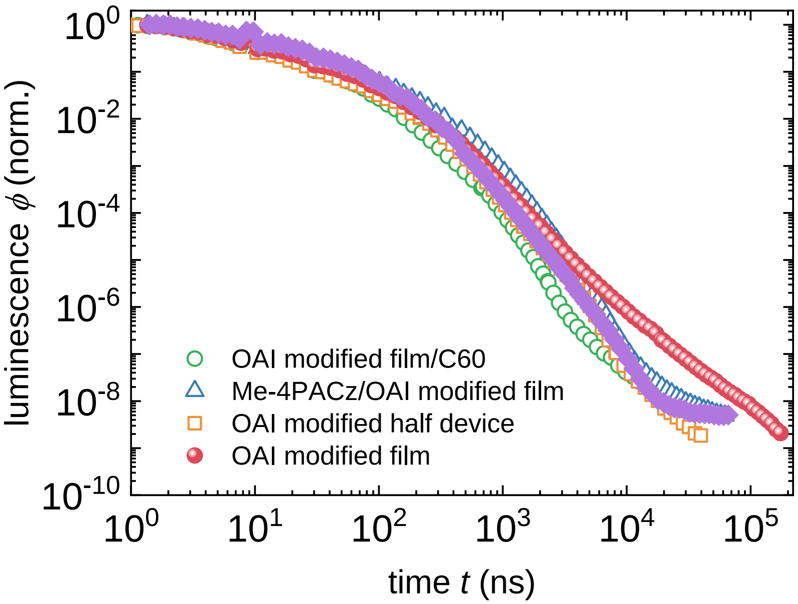


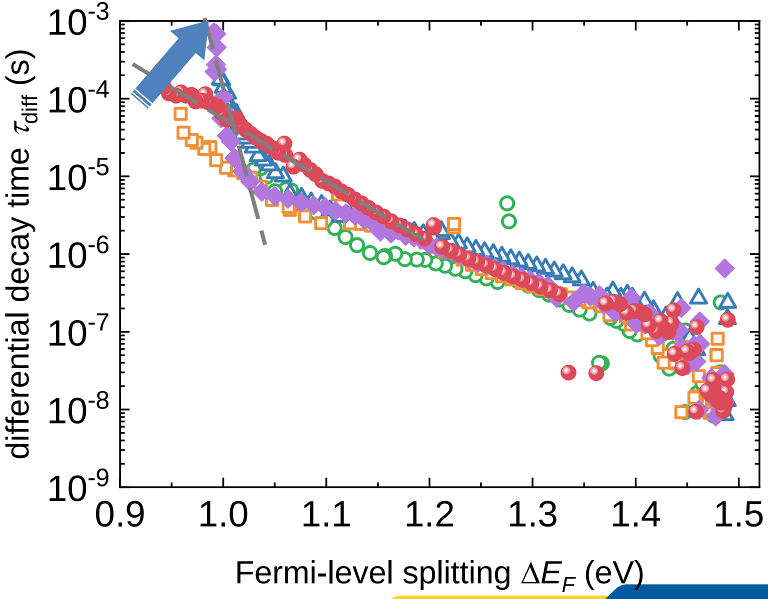
Pure film

stacks

full device



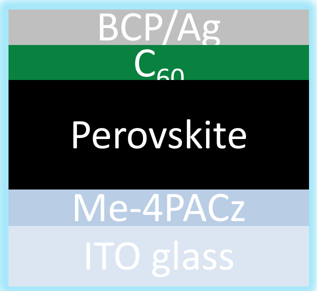


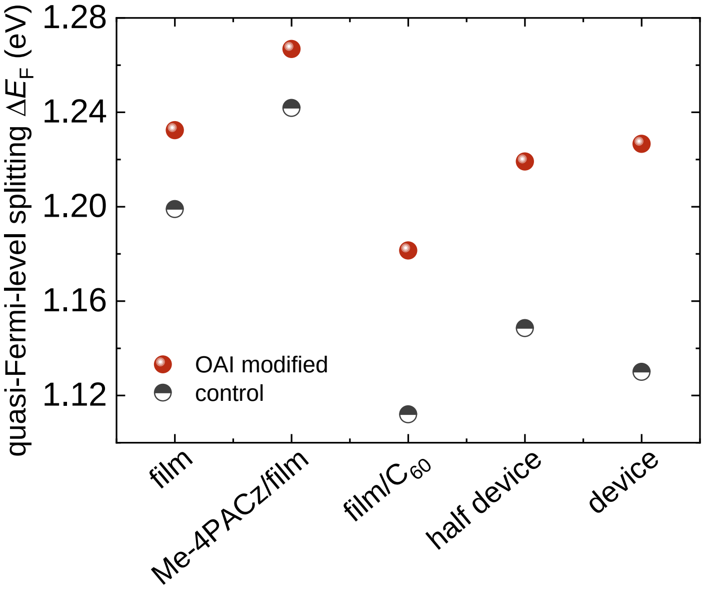


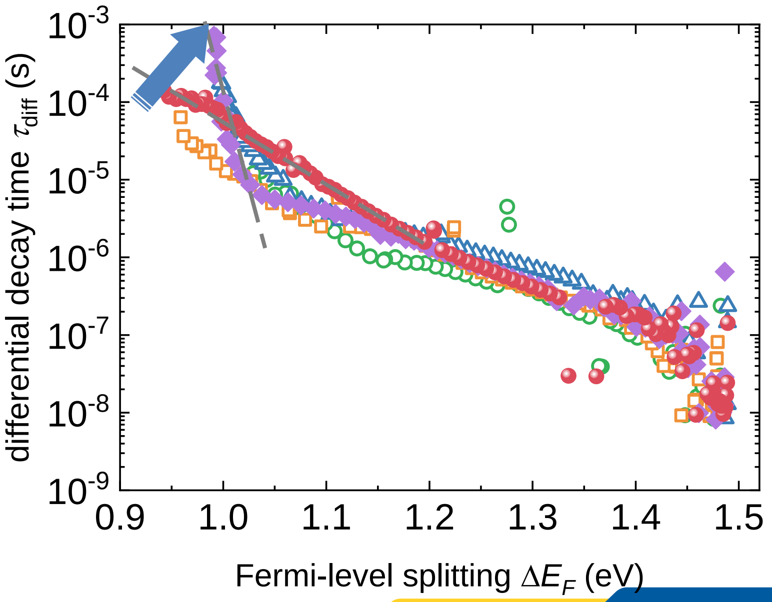
Pure film

stacks

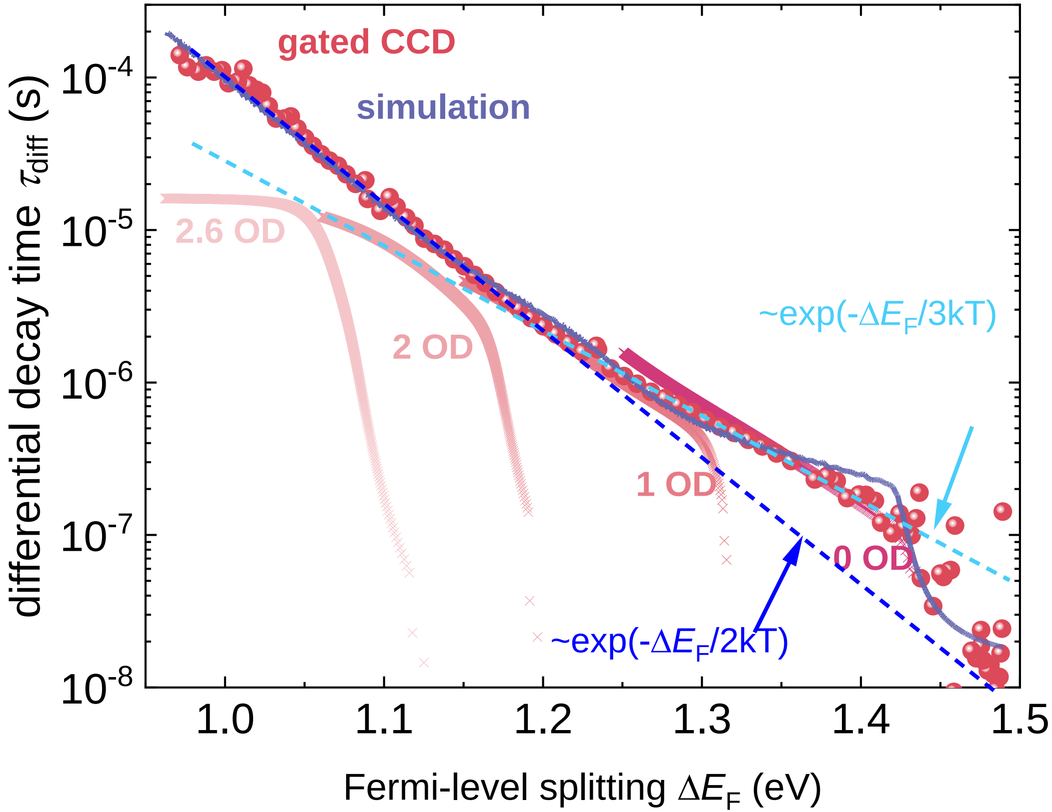
full device





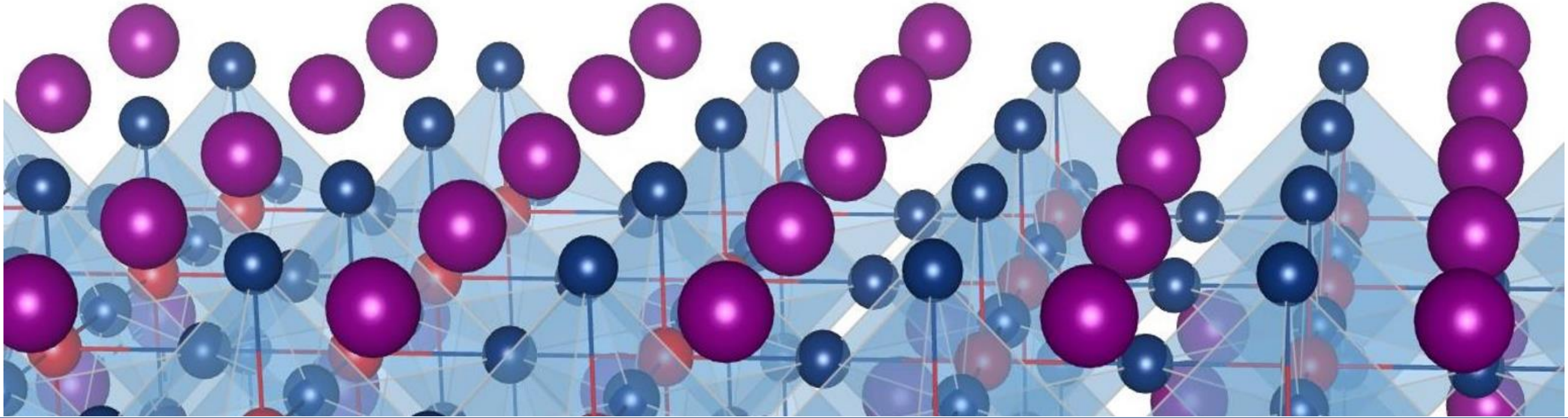


Summary



Shallow defects lead to non-integer n_{id} and continuously increasing decay times.
High defect density needed to fit the data.

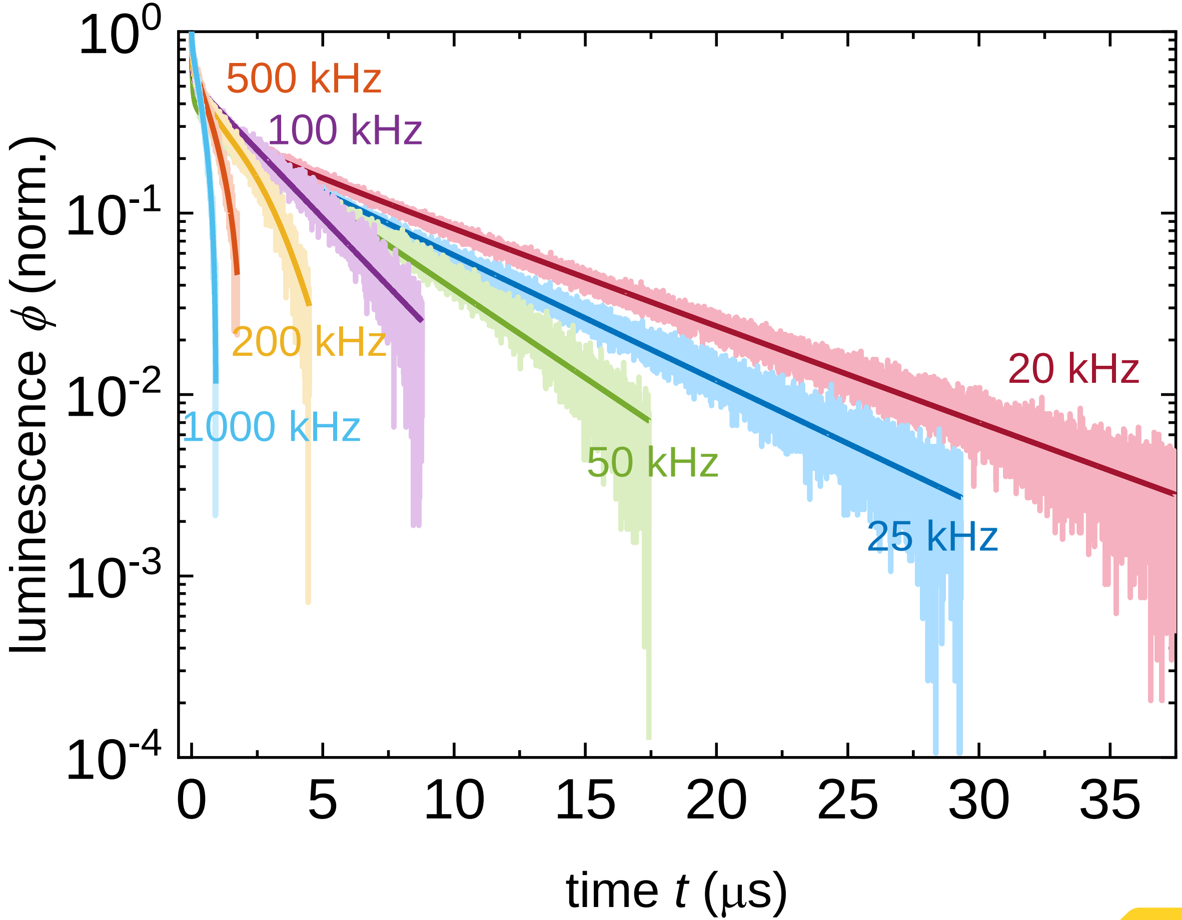
https://www.researchsquare.com/article/rs-2514593/latest.pdf



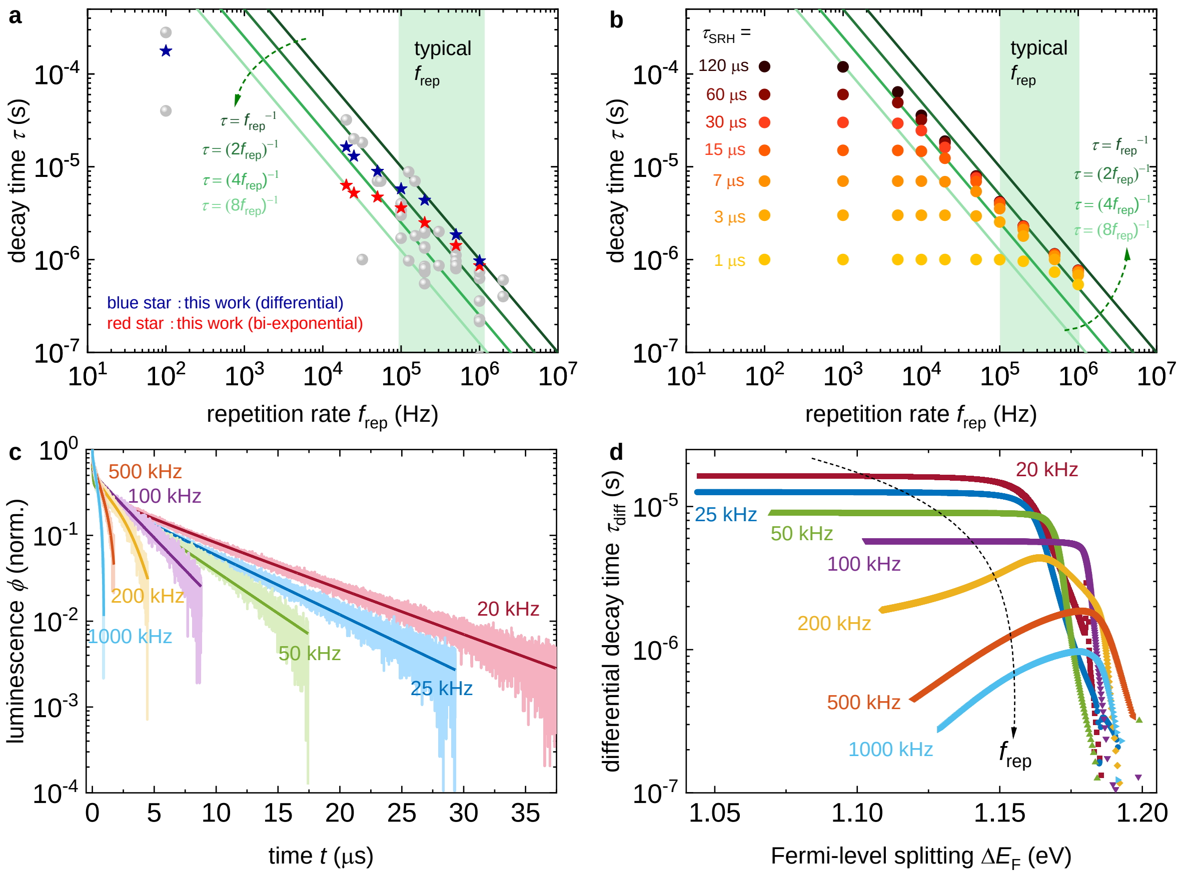
Part 2: Repetition Rates

And how they affect decay times

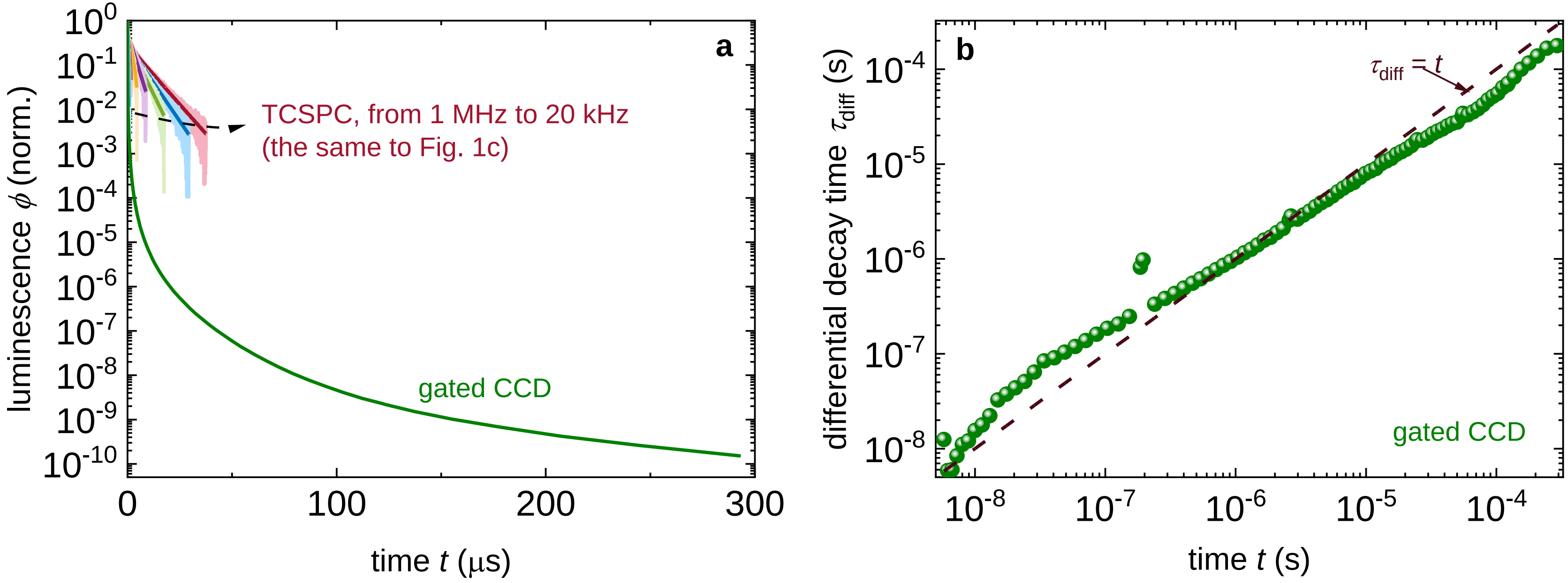
Decays vs. repetition rates



Decays vs. repetition rates



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

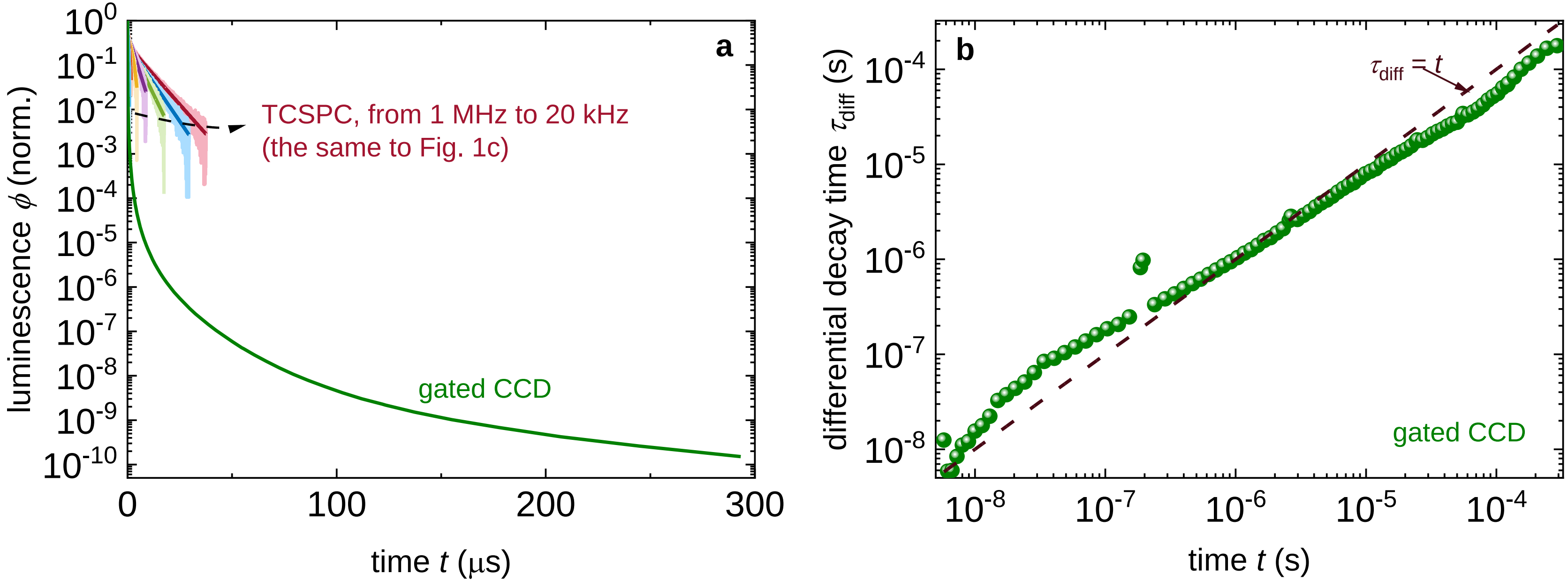


$$\frac{dn(t)}{dt} = -kn^2$$

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

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

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



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

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

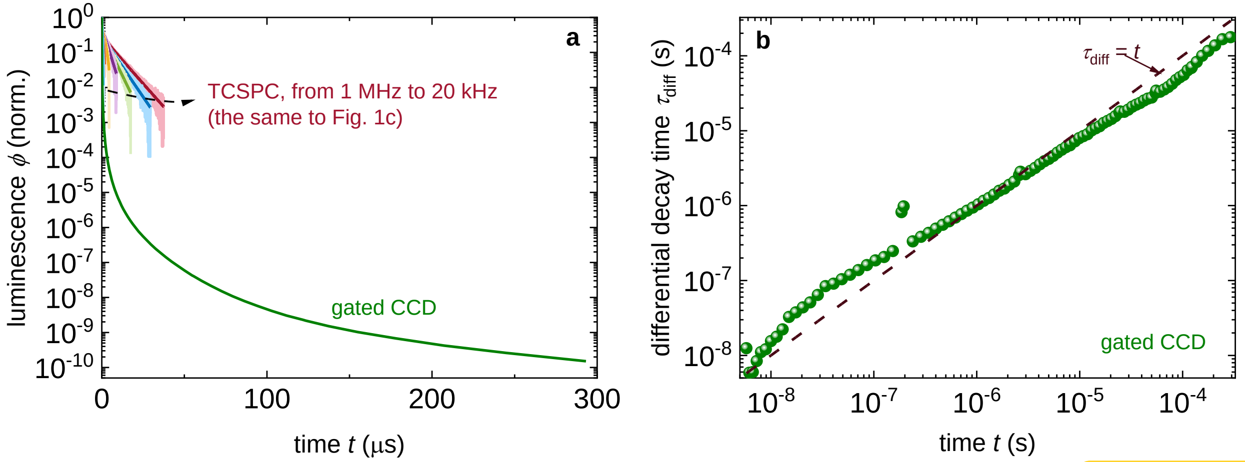
$$n(t) = \frac{n(0)}{1 + n(0)kt} \approx 1/(kt)$$

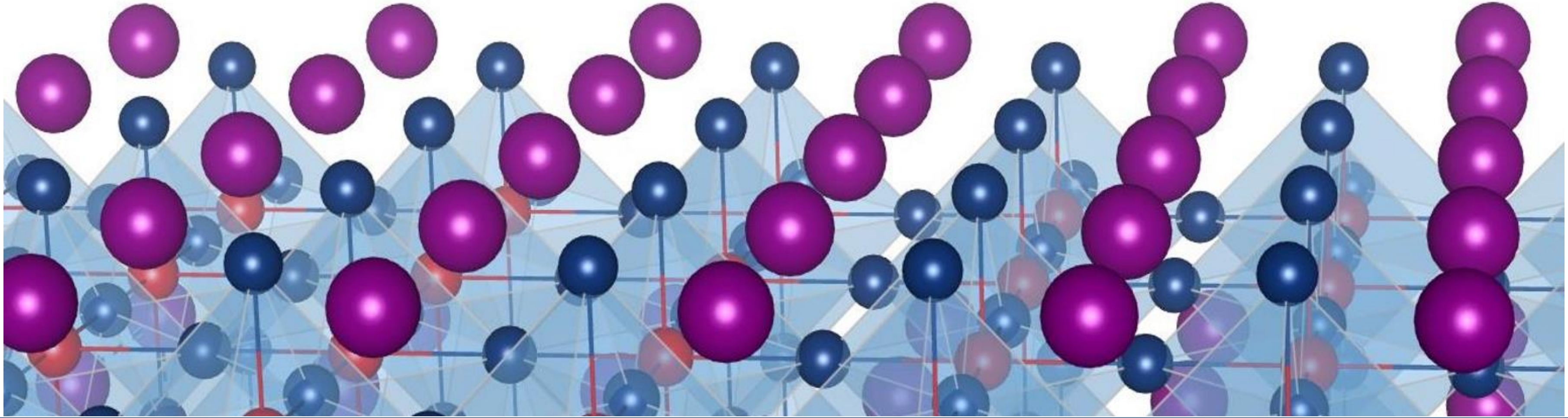
$$\tau_{diff} = t$$

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.





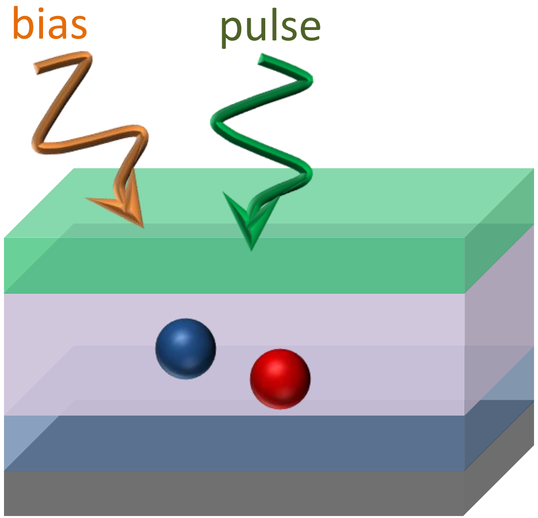
Part 3: Analysis of Small Signal Measurements

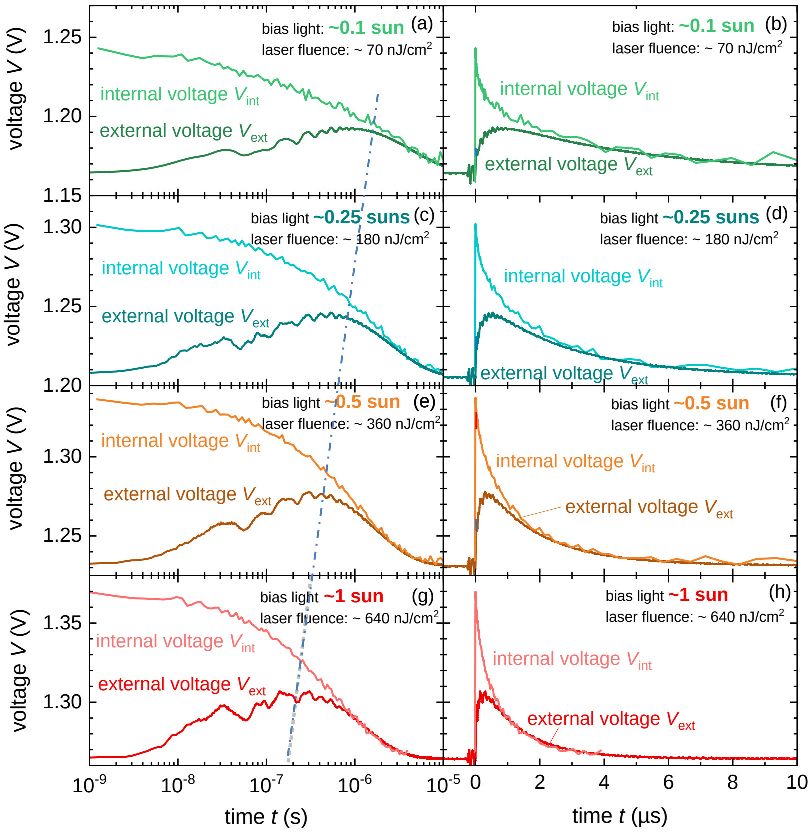
Eigenvalues of Matrices ☺

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

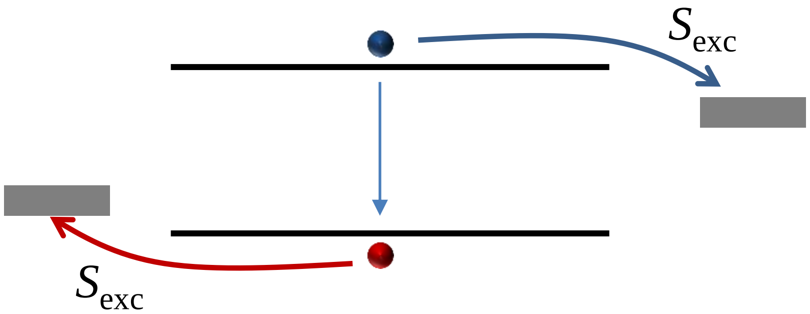
JÜLICH Forschungszentrum

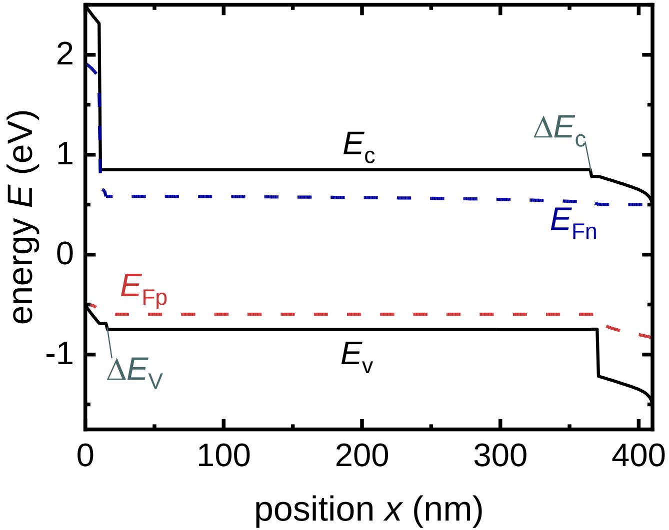
Experimental data – internal vs. external voltage





Transient Methods – Recombination and Extraction





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

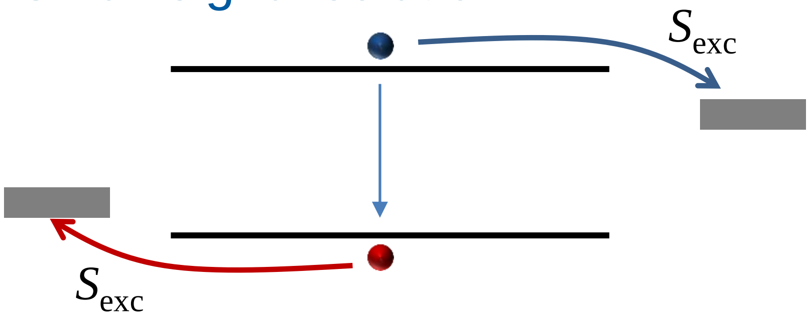
Recombination and extraction

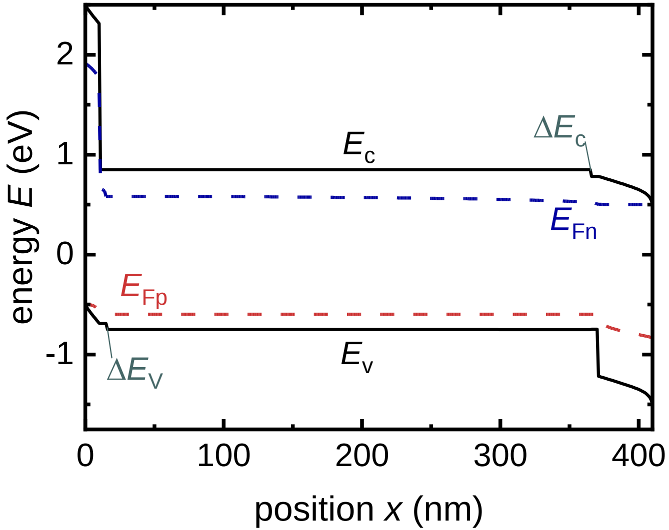
$$\frac{dV_{\text{ext}}}{dt} = \frac{qS_{\text{exc}}}{C_{\text{area}}}\left(n - n_{\text{i}} \exp\left(\frac{qV_{\text{ext}}}{2kT}\right)\right)$$

Electrode (dis)charging

Recombination and Extraction

Small signal solution





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

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

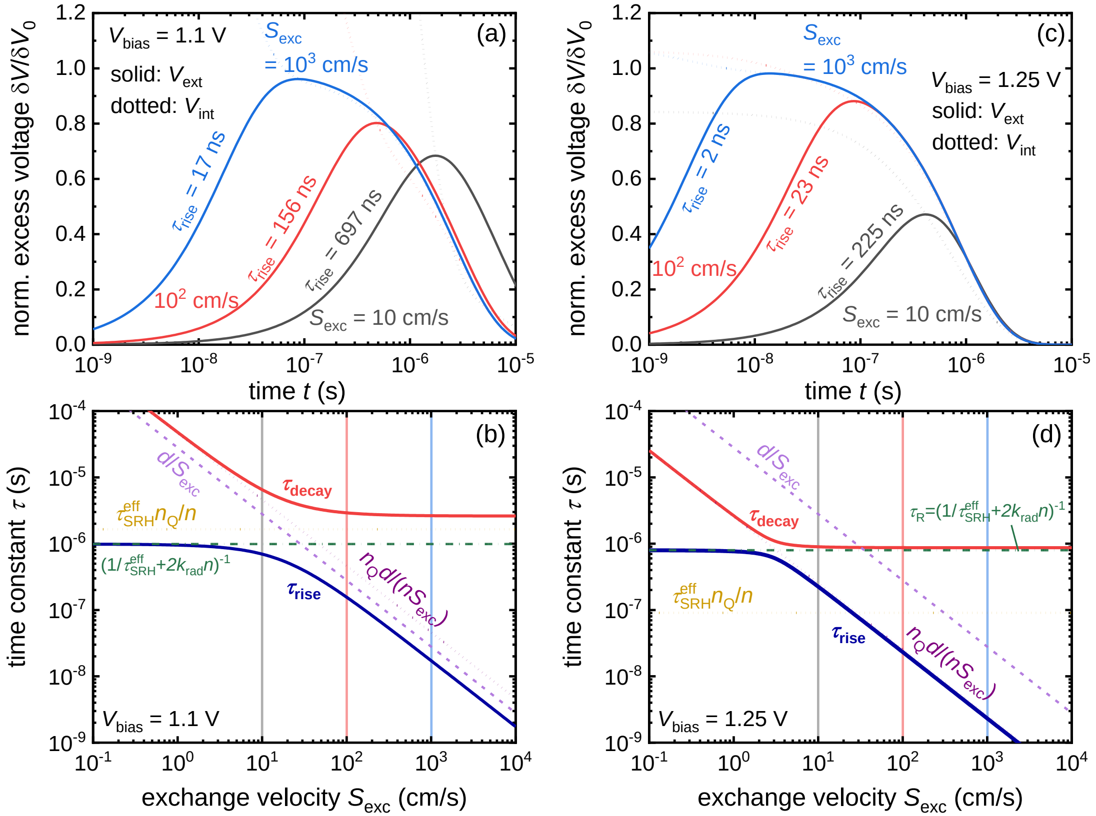
$$\tau_{\mathrm{decay}}=\frac{2}{k_1+k_2+k_3-\sqrt{\left(k_1+k_2+k_3\right)^2-4k_1k_3}}$$

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

Inverse Eigenvalues of Matrix

Recombination and Extraction

Variation of S_{exc}



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

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

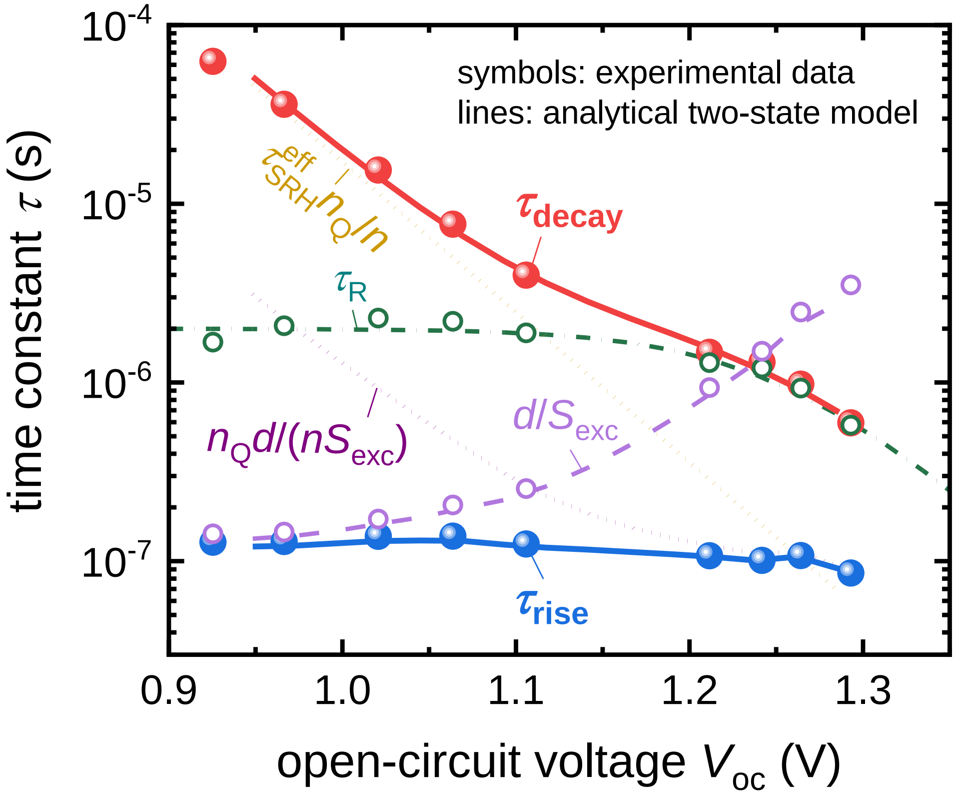
$$\tau_{decay}=\frac{2}{k_1+k_2+k_3-\sqrt{(k_1+k_2+k_3)^2-4k_1k_3}}$$

$$k_1=\frac{1}{\tau^{eff}_{SRH}}+2k_{rad}n_{bias},\ k_2=\frac{S_{exc}}{d},\ k_3=\frac{S_{exc}n_{bias}}{dn_Q}$$

Inverse Eigenvalues of Matrix

Recombination and Extraction

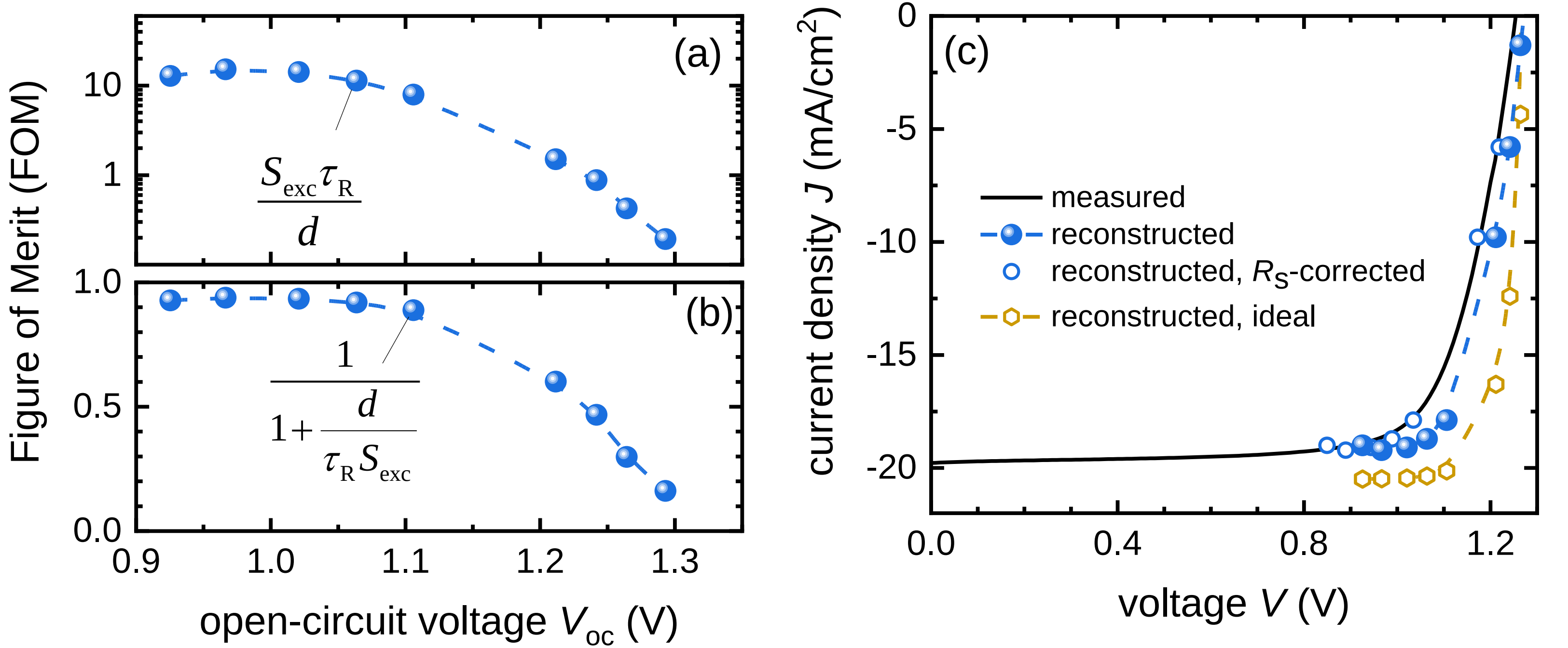
Comparison with Experiment



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

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

Collection Efficiencies and Impact on *JV* curves

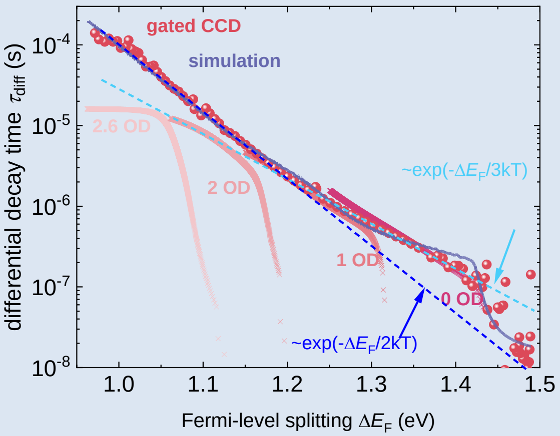


$$J = qd\left(R-G\right) = qd\left(\frac{1}{1+d/\left(S_{exc}\tau_R\right)}\right)\left[\frac{n_0}{\tau_R}\exp\left(\frac{qV_{ext}}{2k_BT}\right)-G\right]$$

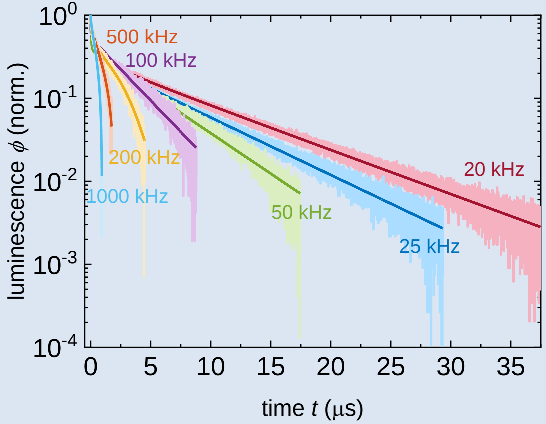
https://arxiv.org/abs/2302.03392

Summary

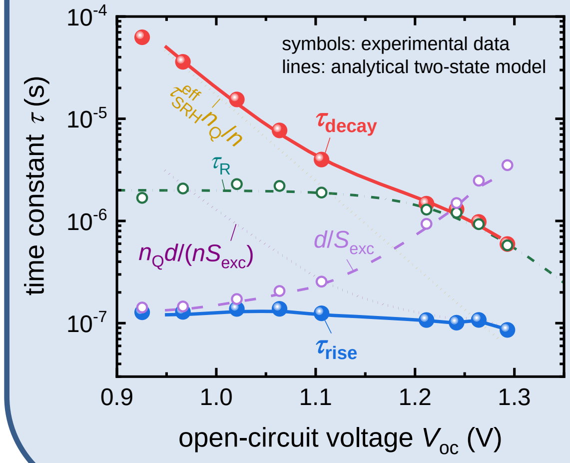
1) Decay time can continuously increase for shallow defect rec.



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



3) Small signal solvable via eigenvalues of matrix → information on extraction & recomb.



Funding from
Helmholtz Association
DFG
OCPC Fellowships

Thank you for your attention

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

JÜLICH Forschungszentrum