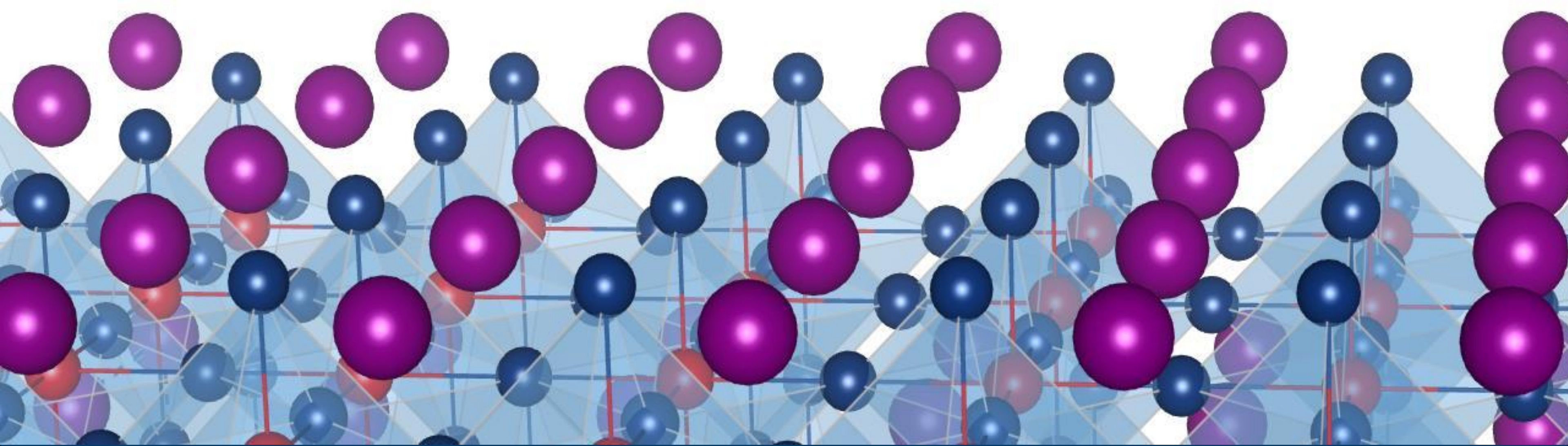

Shallow Defects and Long Charge-Carrier Lifetimes in Lead-Halide Perovskites

Thomas Kirchartz, Genghua Yan, Ye Yuan, Jürgen Hüpkes, Chris Dreessen, Uwe Rau

IEK-5 Photovoltaik, Forschungszentrum Jülich

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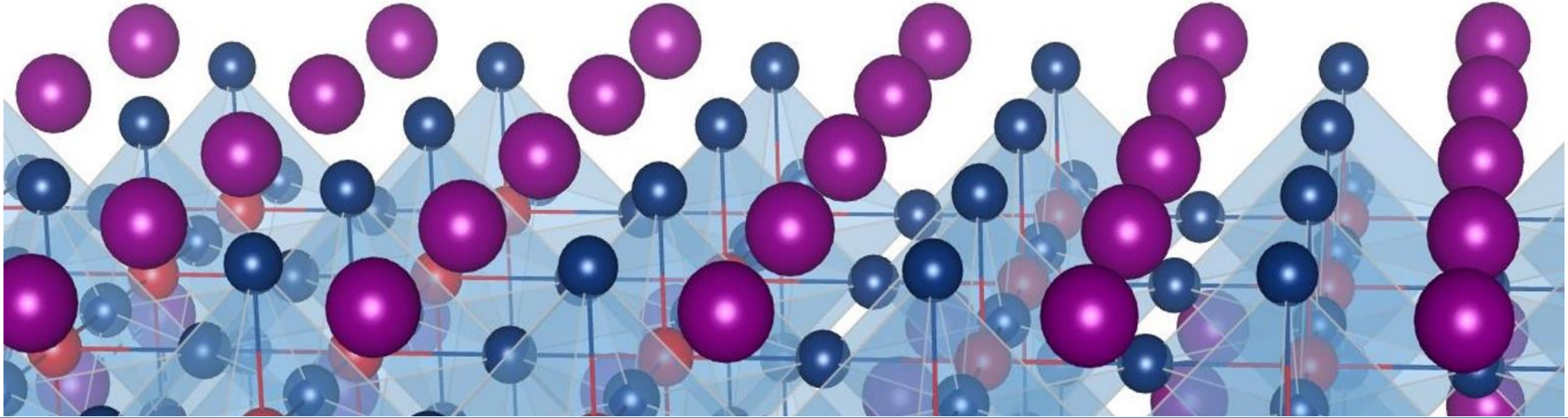
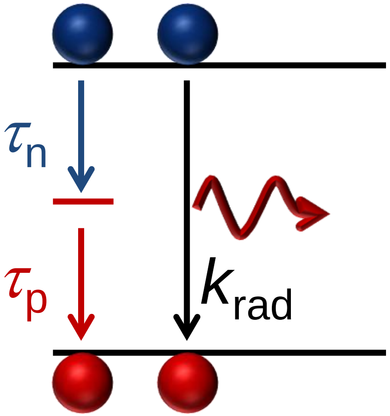


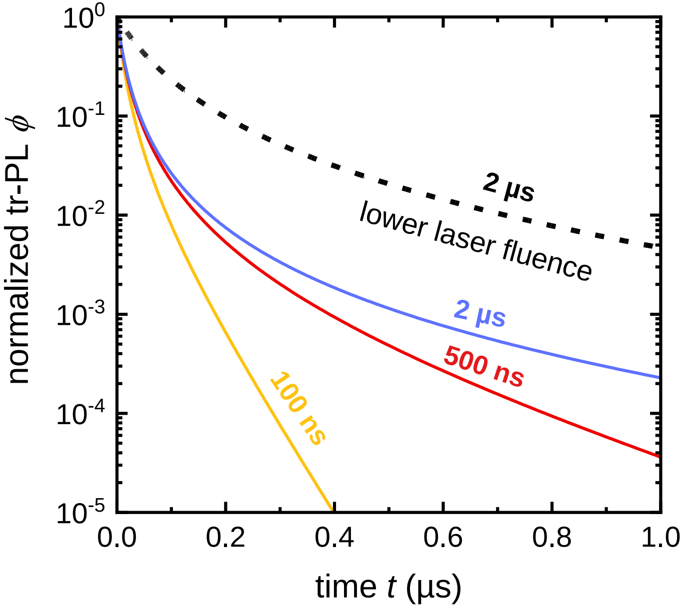
Part 0: Introduction

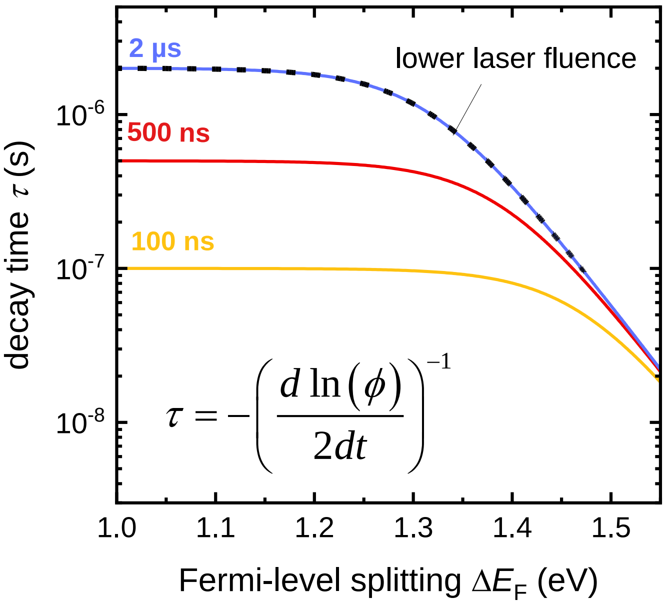
Transient Photoluminescence and Lifetimes

Transient Photoluminescence

Layer on Glass – Bulk Recombination







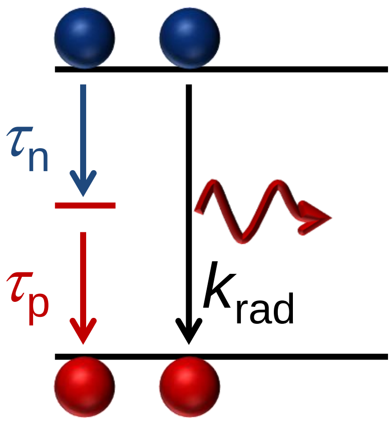
$$\frac{dn}{dt} = -k_{rad} n^2 - \frac{n}{\tau_p + \tau_n}$$

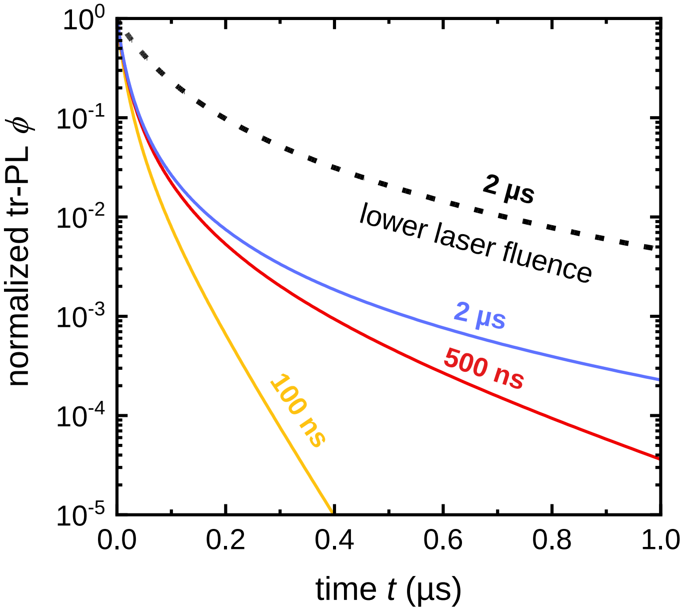
SRH + radiative recombination

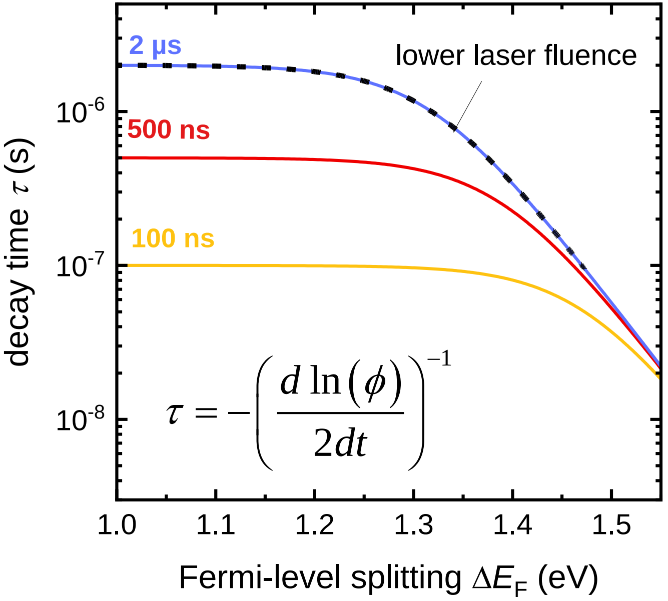
← time

Transient Photoluminescence

Layer on Glass – Bulk Recombination



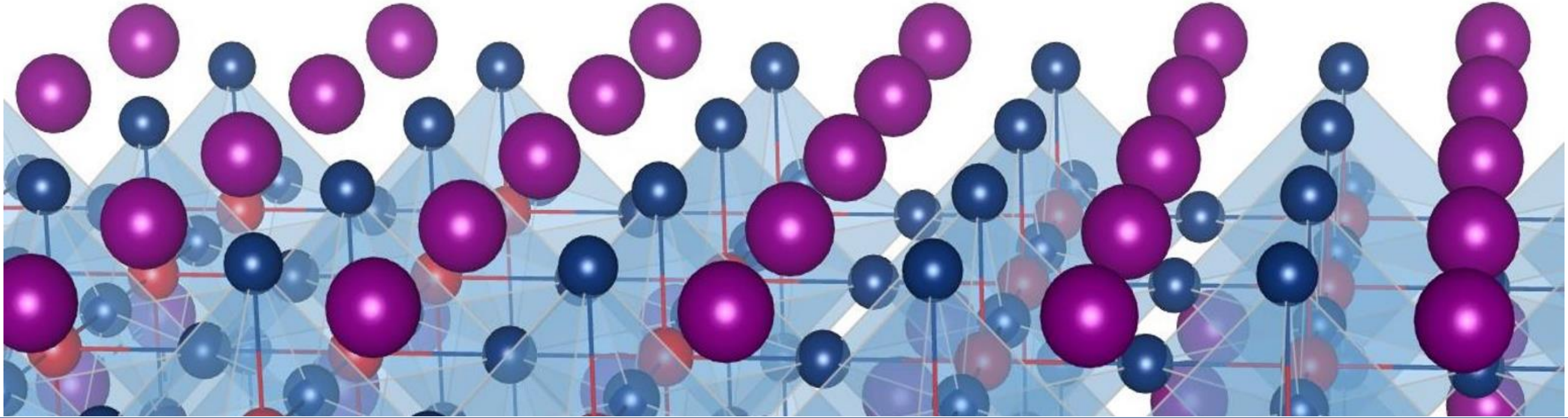




$$\tau_{diff} = -\frac{n}{dn/dt} = \frac{1}{k_{rad}n + 1/(\tau_p + \tau_n)}$$

Decay Time

← time



Part 1: Shallow Defects

and Power Law Decays

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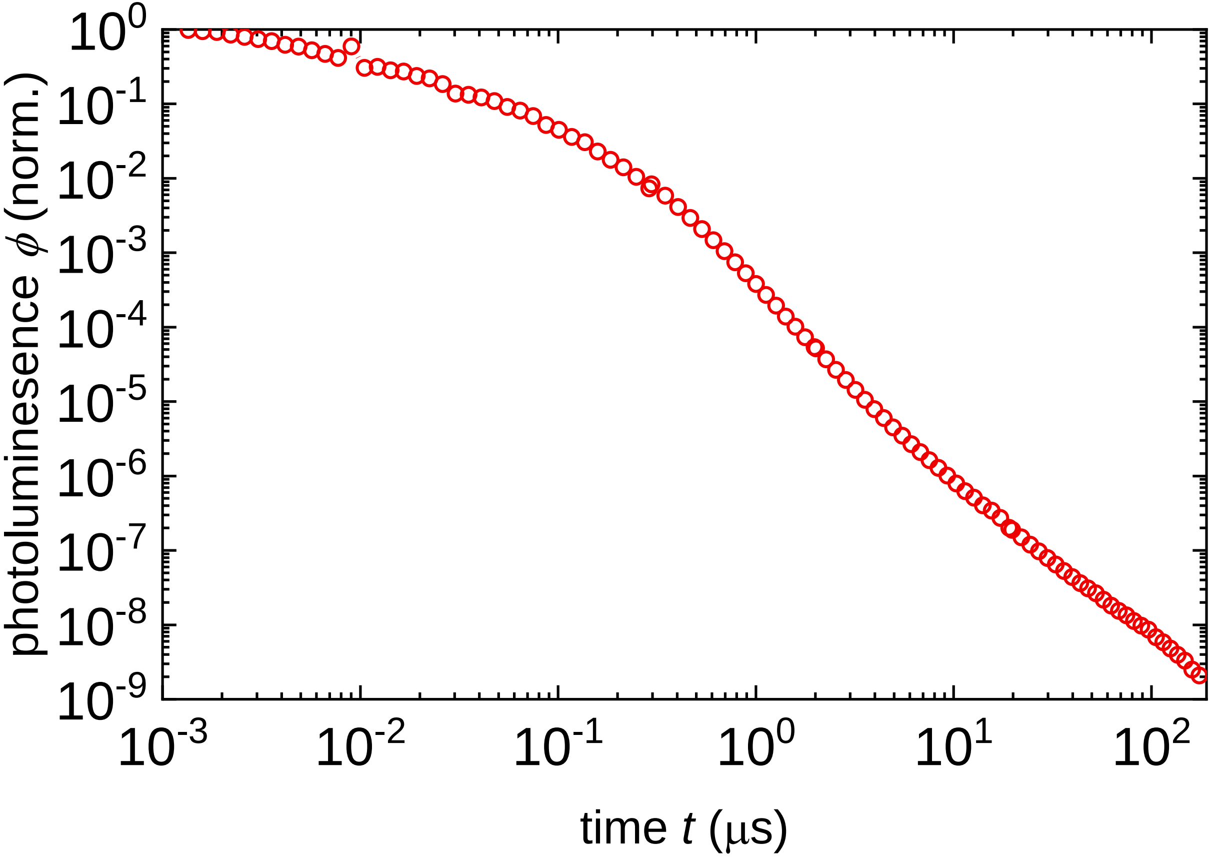
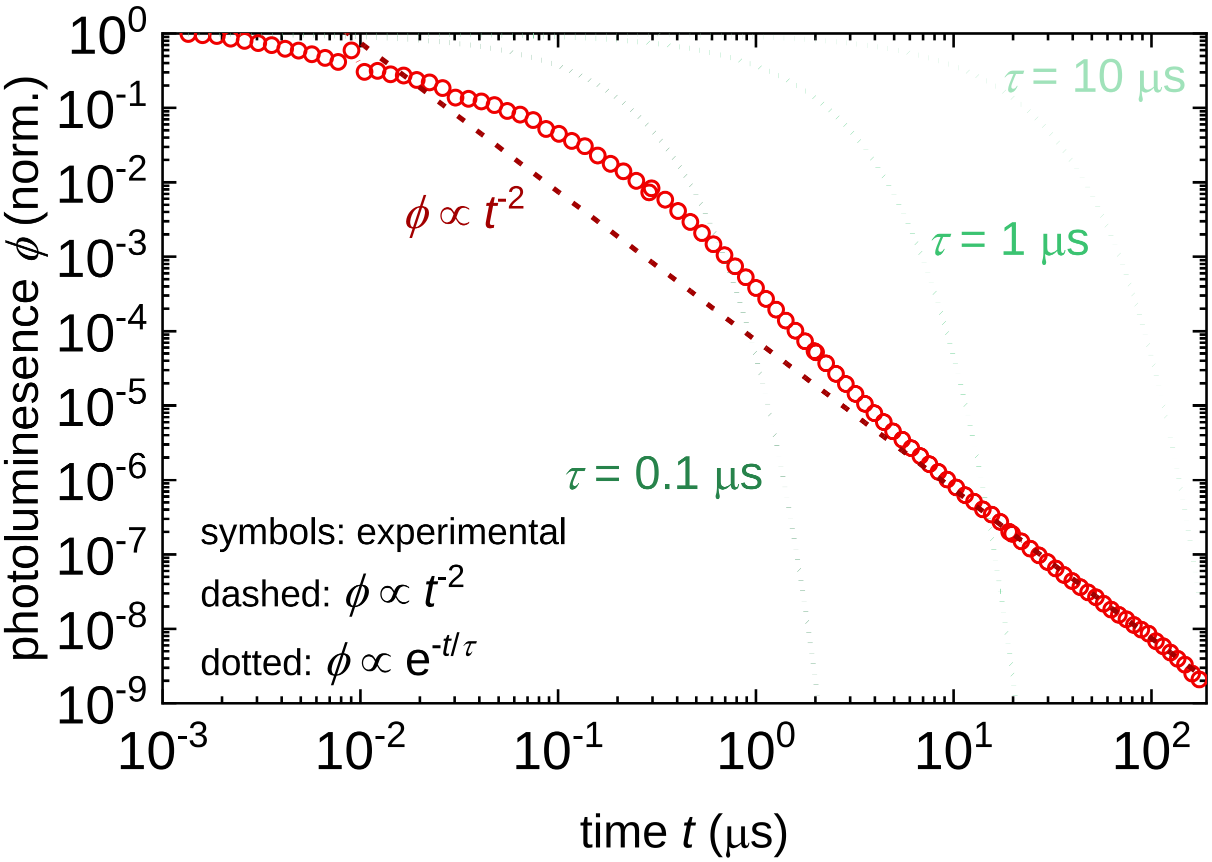
Power Law Decays vs. Exponential Decays



Power Law Decays vs. Exponential Decays



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

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

Power Law Decays vs. Exponential Decays

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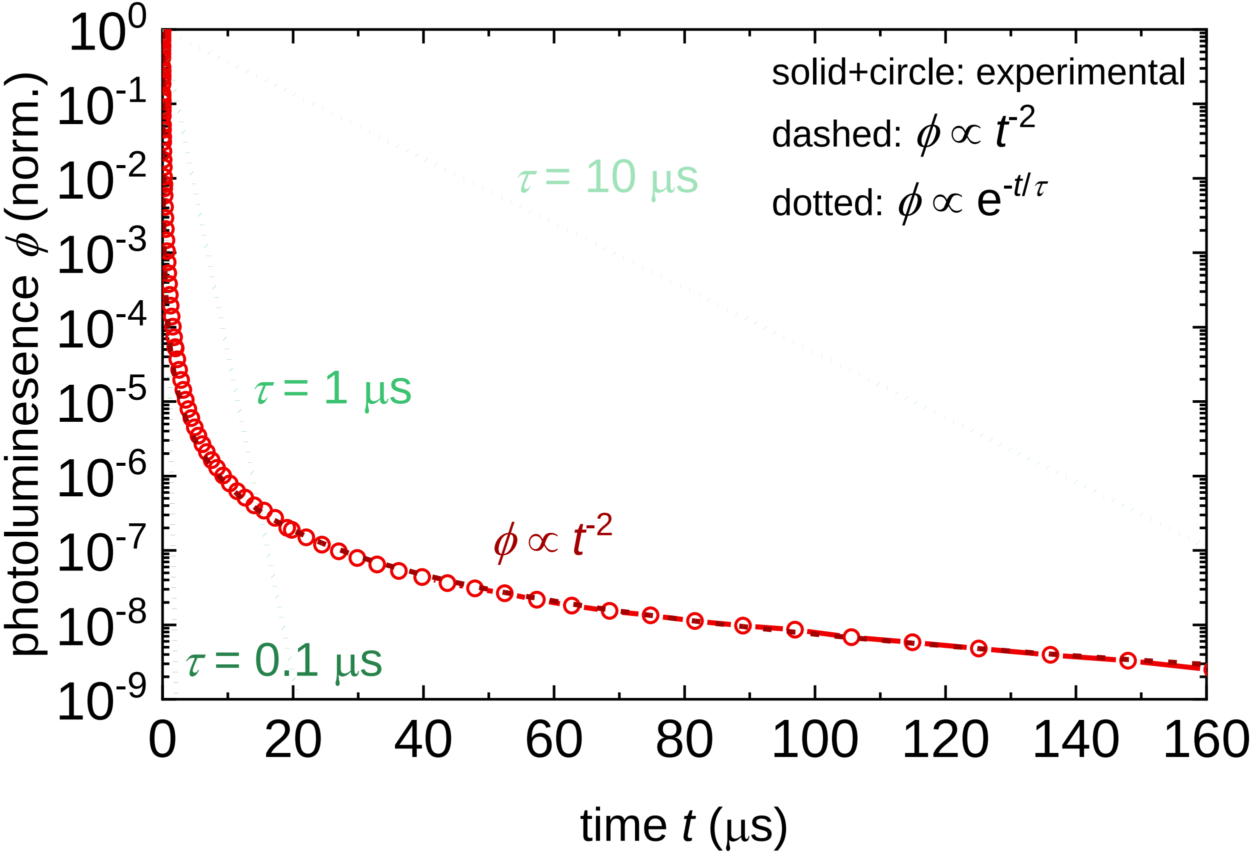
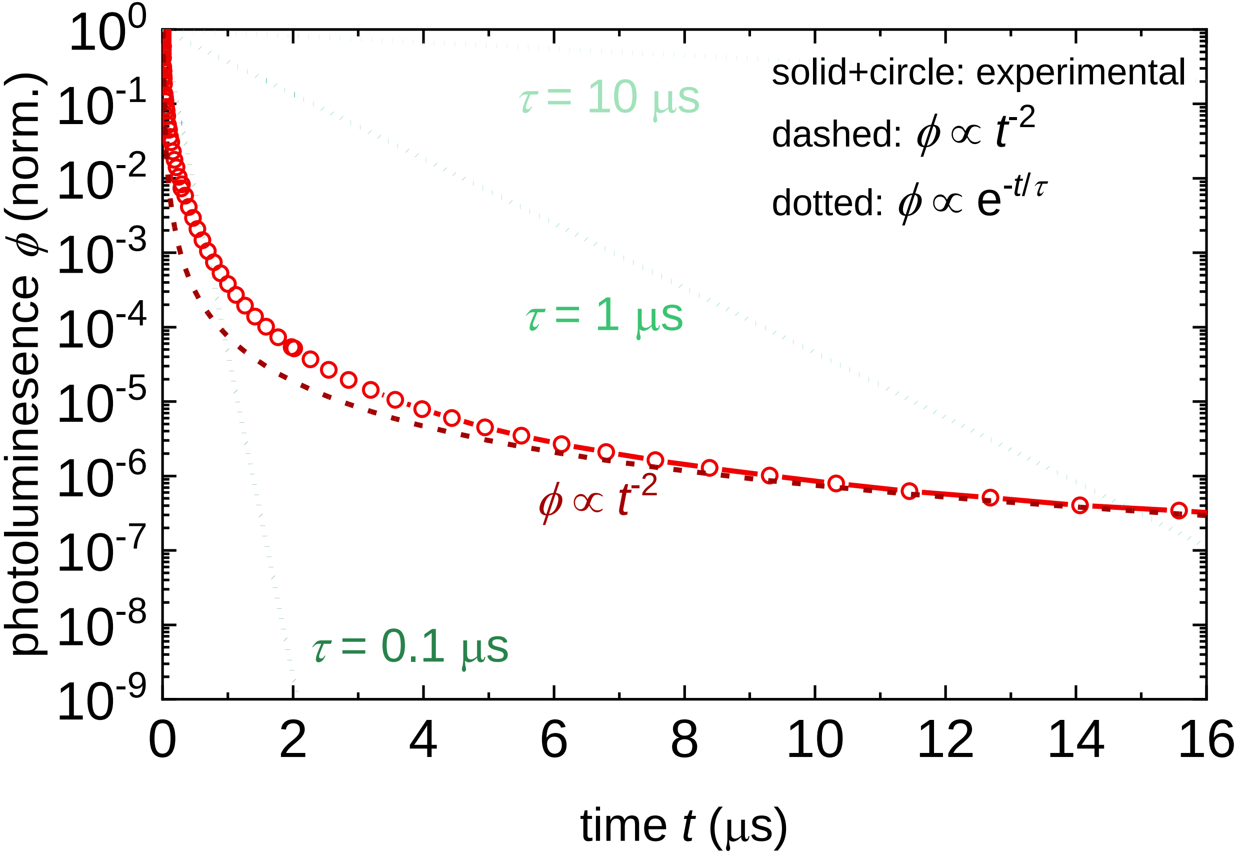


What would you use to fit the red line?

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

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

Power Law Decays vs. Exponential Decays



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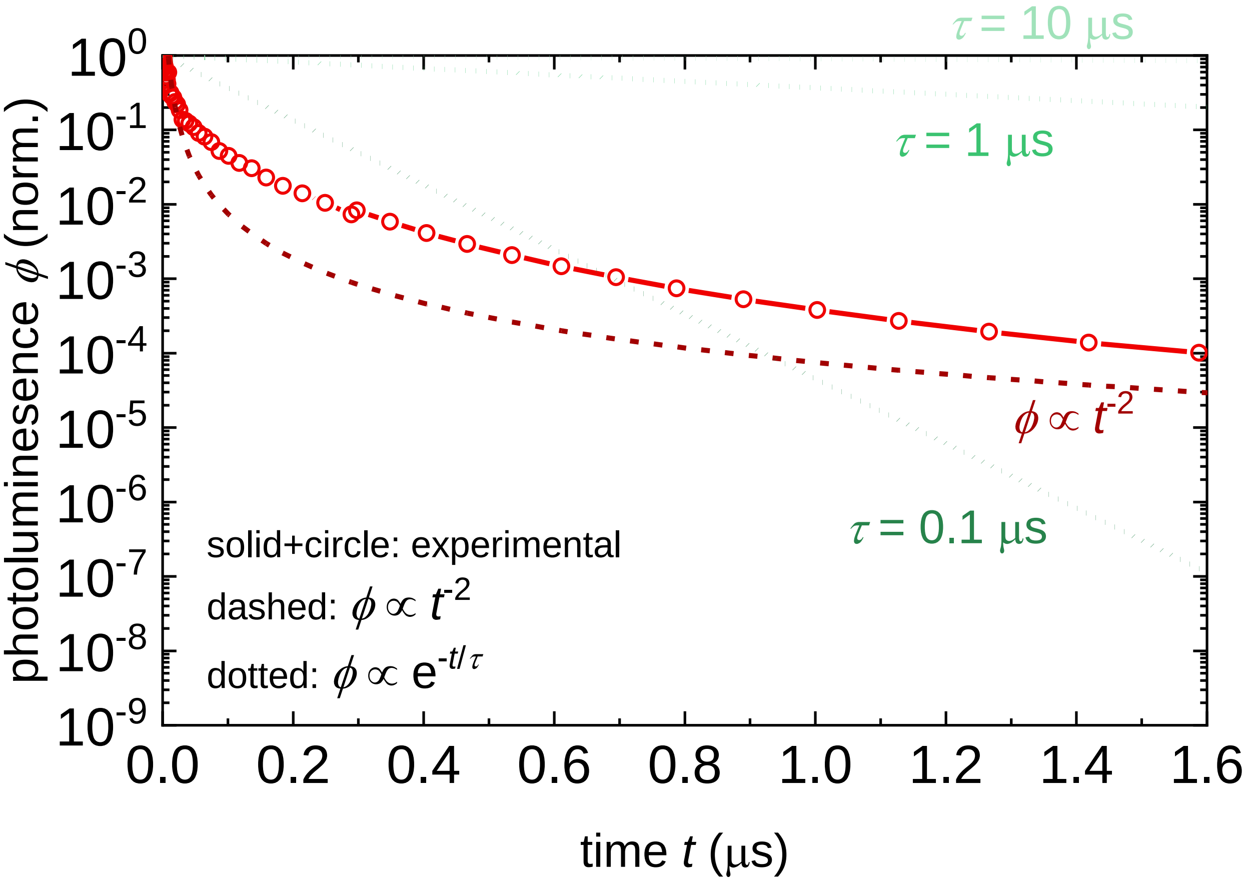
Power Law Decays vs. Exponential Decays

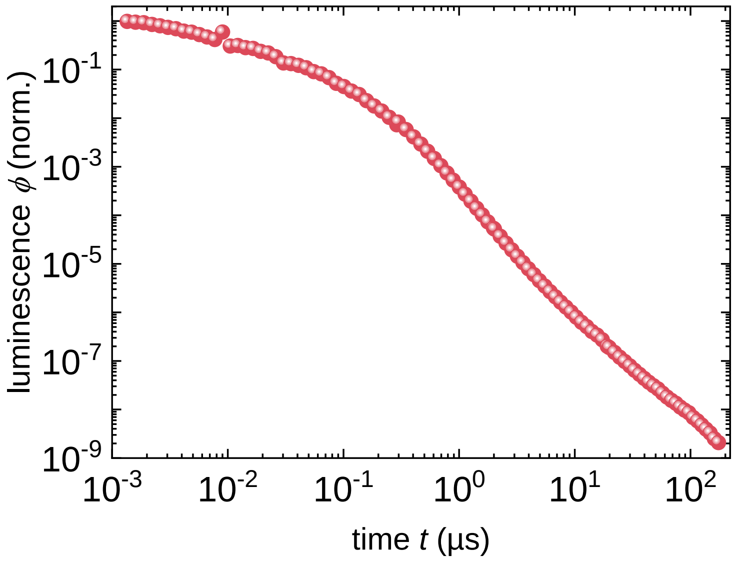


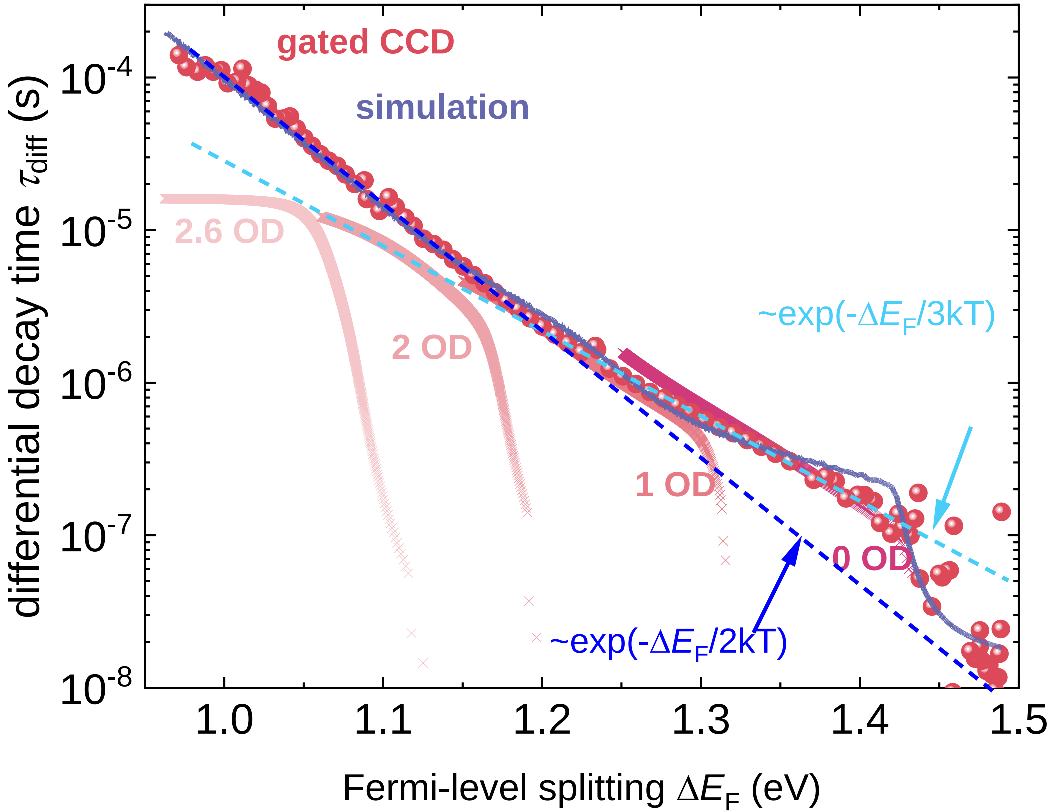
What would you use to fit the red line?

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

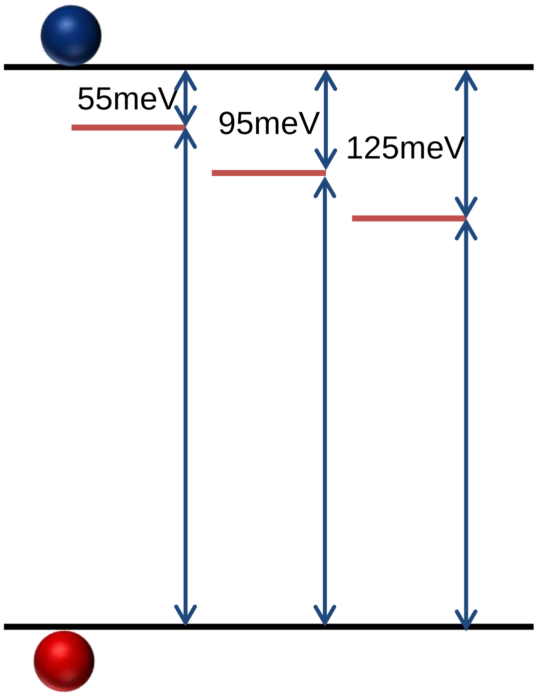
$$n(t) = \frac{n(0)}{1 + n(0)kt}$$

High dynamic range tr-PL

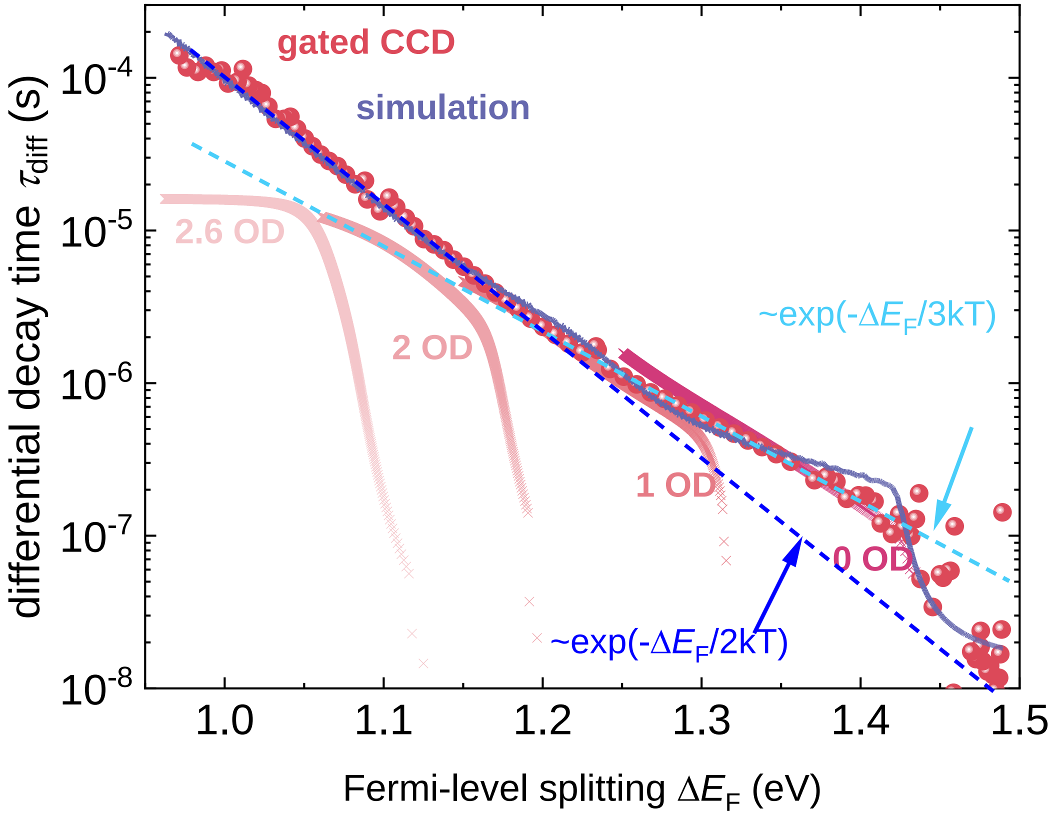




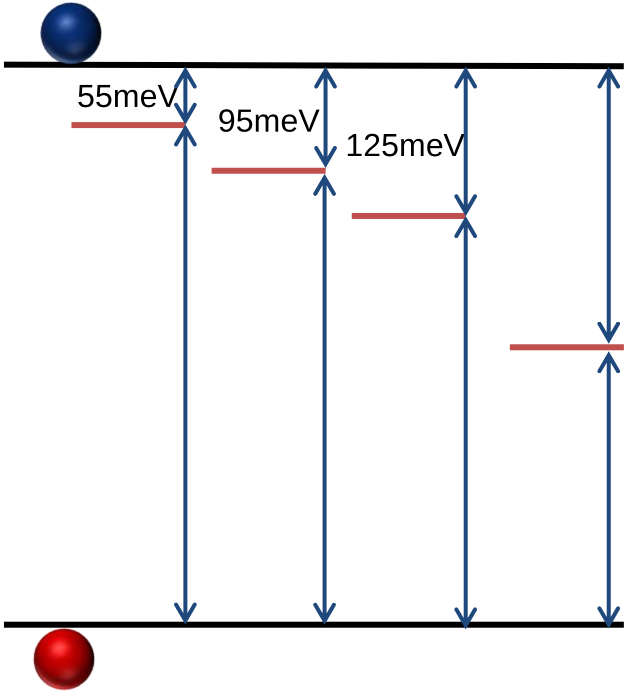
Defect levels assumed in the modelling

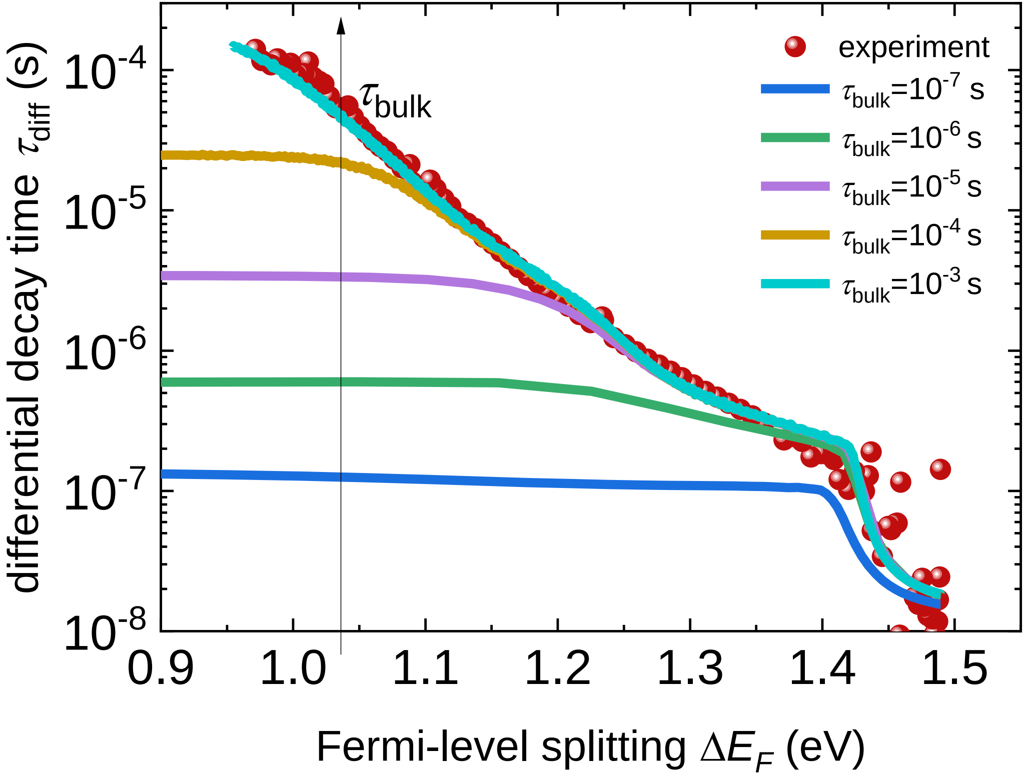


schematic not quite to scale

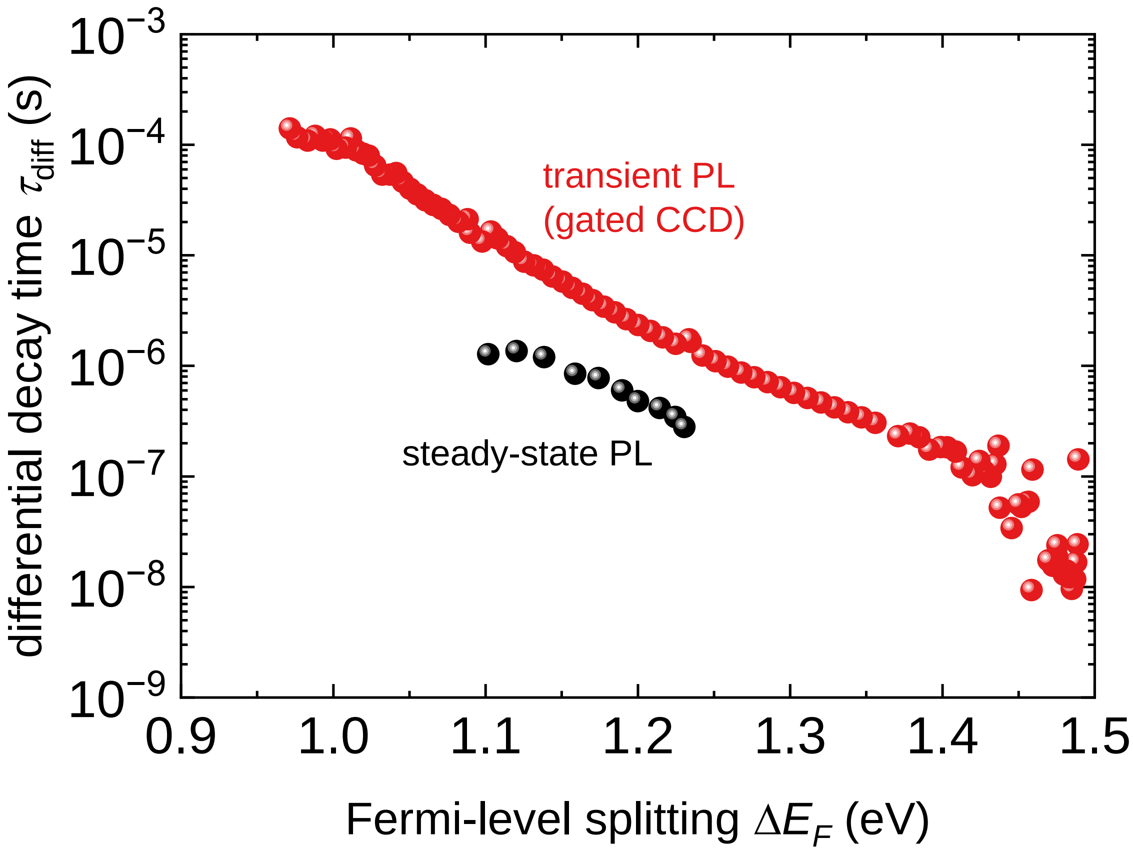


On the presence or absence of deep defects





Steady State vs. Transient Decay Time

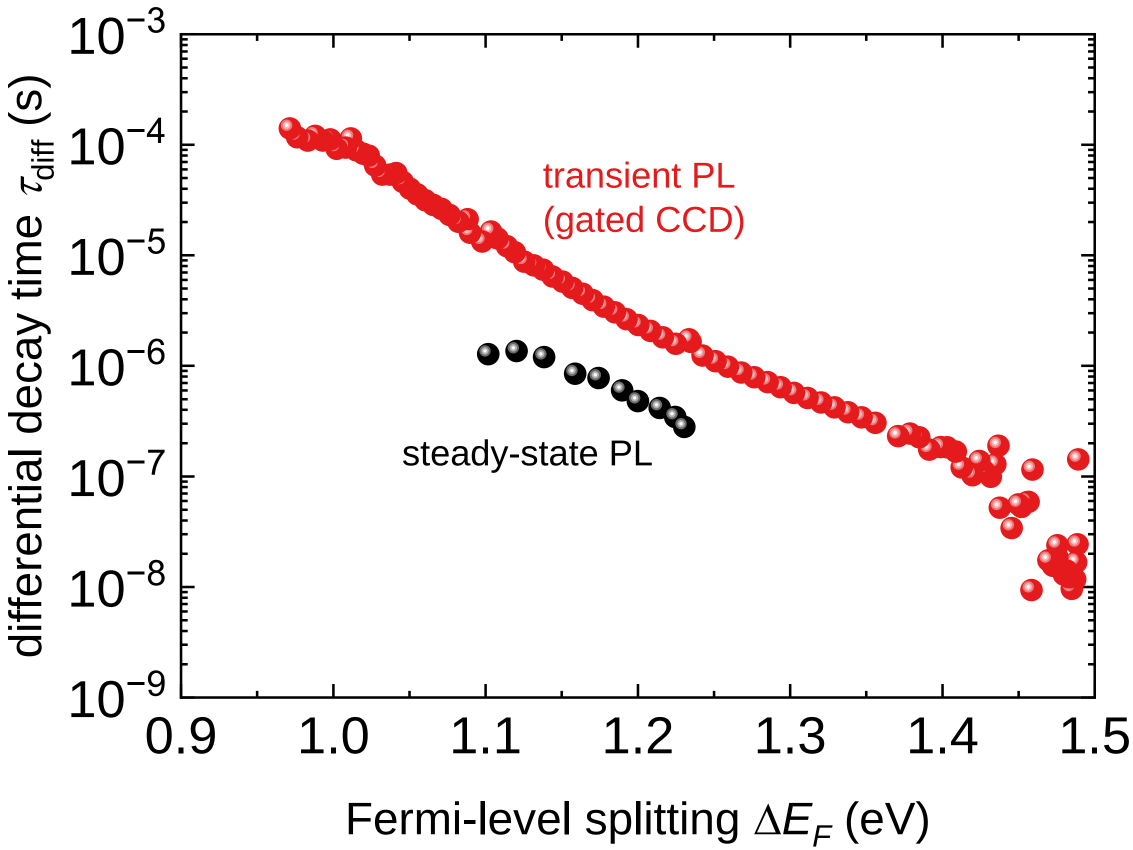


$$\tau_{\mathrm{diff}} \approx \tau_{\mathrm{p}} \frac{\sqrt{n_1 N_{\mathrm{T}}}}{n_{\mathrm{i}}} \frac{1}{1+k_{\mathrm{rad}}\tau_{\mathrm{p}} n_1} \exp\left(-\frac{\Delta E_{\mathrm{F}}}{2kT}\right)$$

$$R_{\mathrm{SRH}} = \frac{np - n_0 p_0}{(n+n_1)\tau_{\mathrm{p}} + (p+p_1)\tau_{\mathrm{n}}}$$

$$\approx \frac{np}{n_1 \tau_{\mathrm{p}}}$$

Steady State vs. Transient Decay Time



$$\tau_{\text{diff}} \approx \tau_{\text{p}} \frac{\sqrt{n_1 N_{\text{T}}}}{n_{\text{i}}} \frac{1}{1+k_{\text{rad}}\tau_{\text{p}} n_1} \exp\left(-\frac{\Delta E_{\text{F}}}{2kT}\right)$$

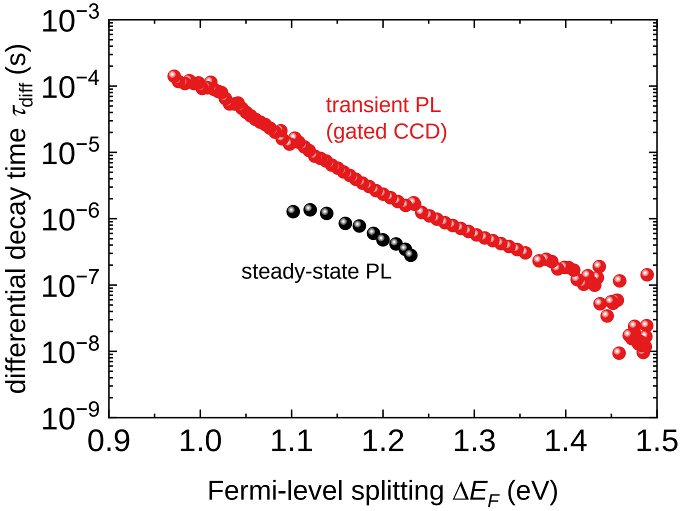
$$R_{\text{SRH}} = \frac{np - n_0 p_0}{(n+n_1)\tau_{\text{p}} + (p+p_1)\tau_{\text{n}}}$$

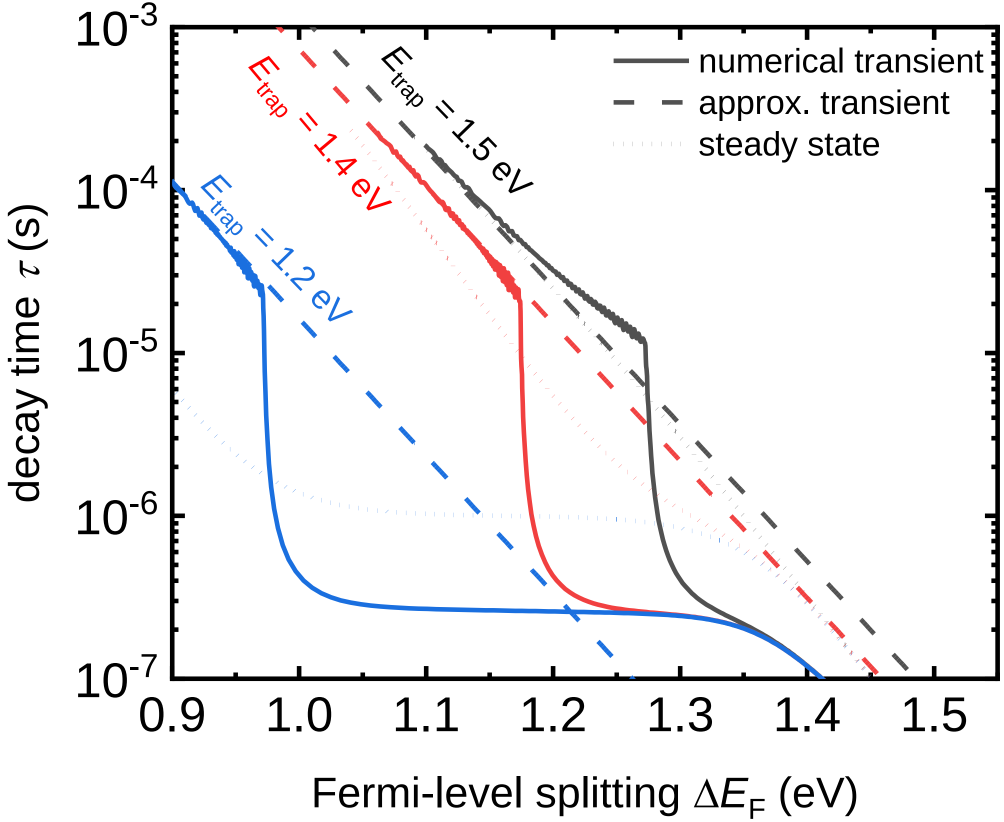
$$\approx \frac{np}{n_1 \tau_{\text{p}}}$$

$$\tau_{\text{eff}} = \tau_{\text{p}} \frac{n_1}{n_{\text{i}}} \frac{1}{1+k_{\text{rad}}\tau_{\text{p}} n_1} \exp\left(-\frac{\Delta E_{\text{F}}}{2kT}\right)$$

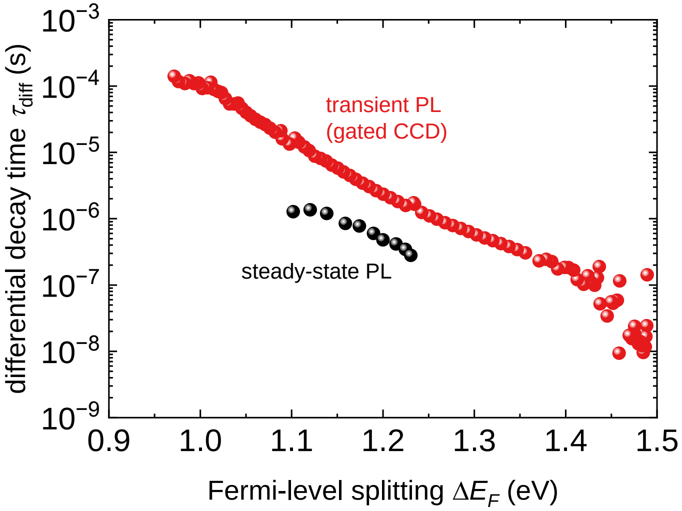
$$\frac{\tau_{\text{diff}}}{\tau_{\text{eff}}} = \sqrt{\frac{N_{\text{T}}}{n_1}}$$

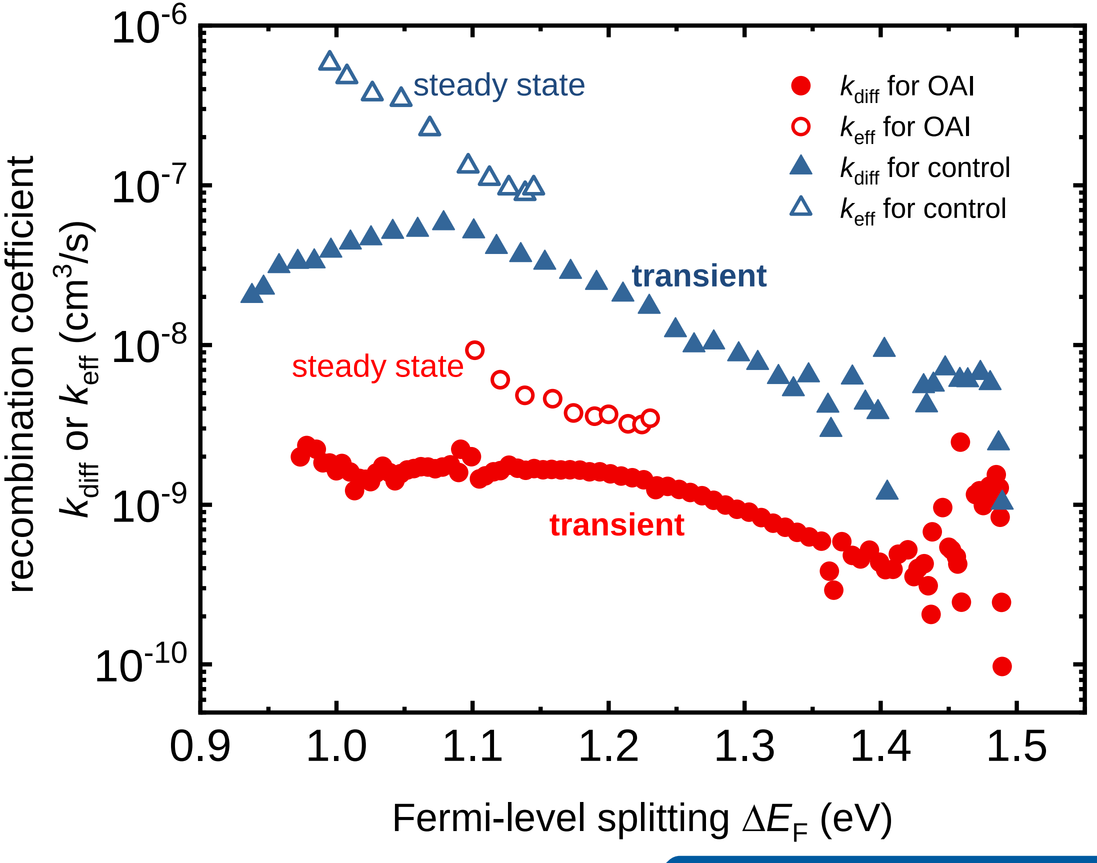
Simulations and Analytical Approximations





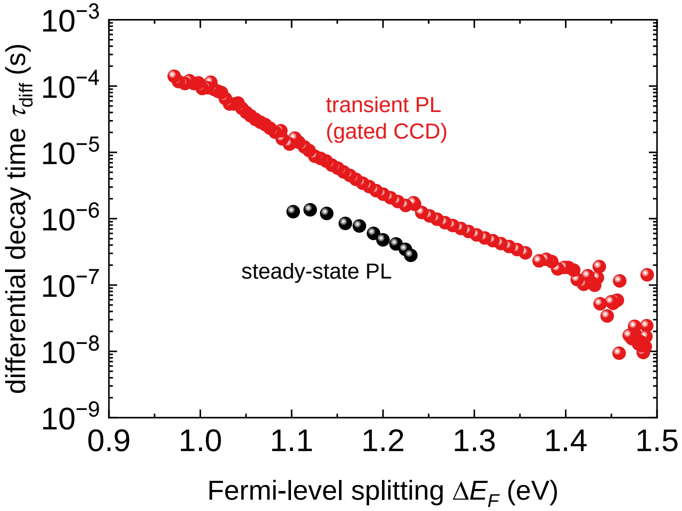
Steady State vs. Transient Decay Time





steady state	transient
$R = k_{eff}np$	$\frac{dn}{dt} = -knp$
$k_{eff} = k_{rad} + \frac{1}{((n+n_1)\tau_p + p\tau_n)}$	$k_{diff} \approx \frac{1+k_{rad}\tau_p n_1}{\tau_p\sqrt{n_1 N_T}}$

Steady State vs. Transient Decay Time



steady state

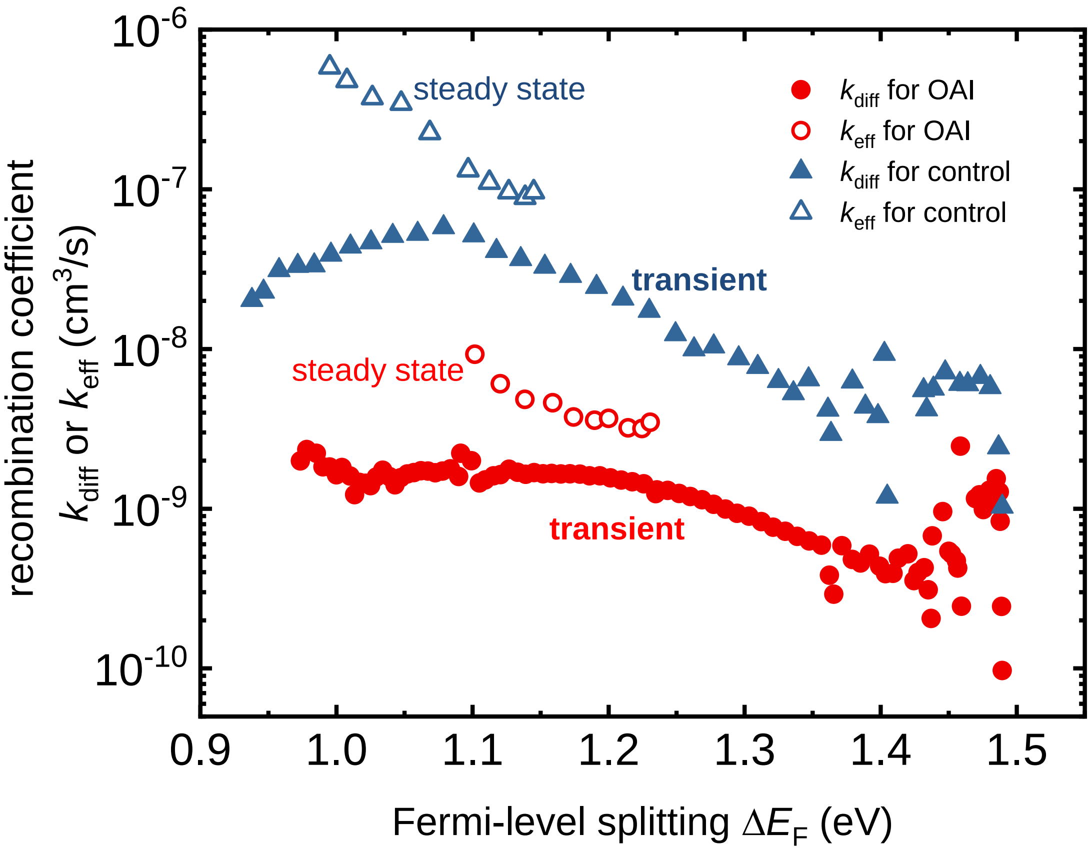
transient

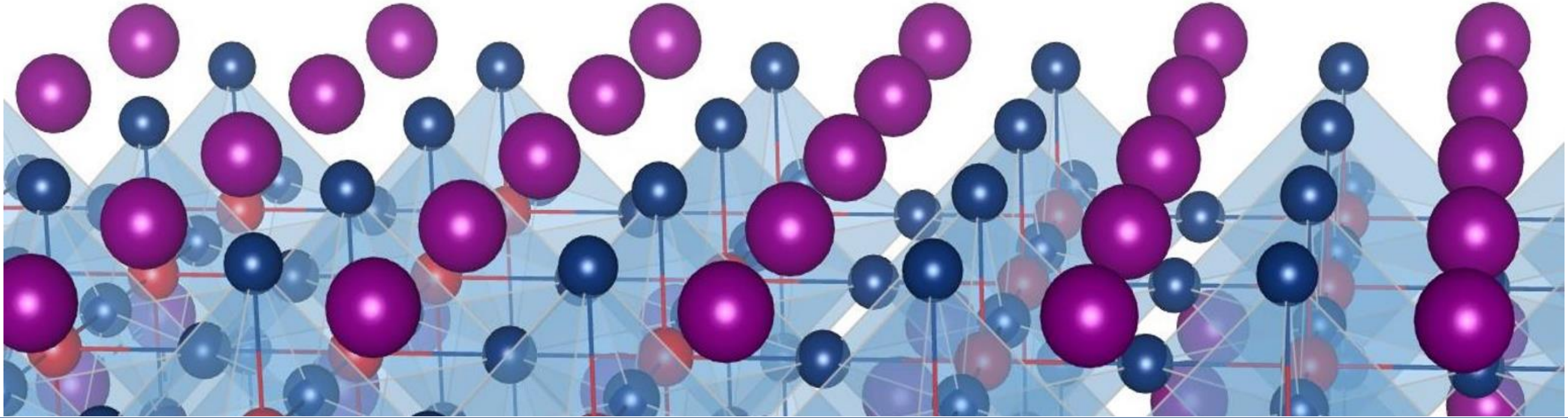
$$R = k_{eff} np$$

$$\frac{dn}{dt} = -knp$$

$$k_{eff} = \frac{1}{n_1 \tau_p}$$

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

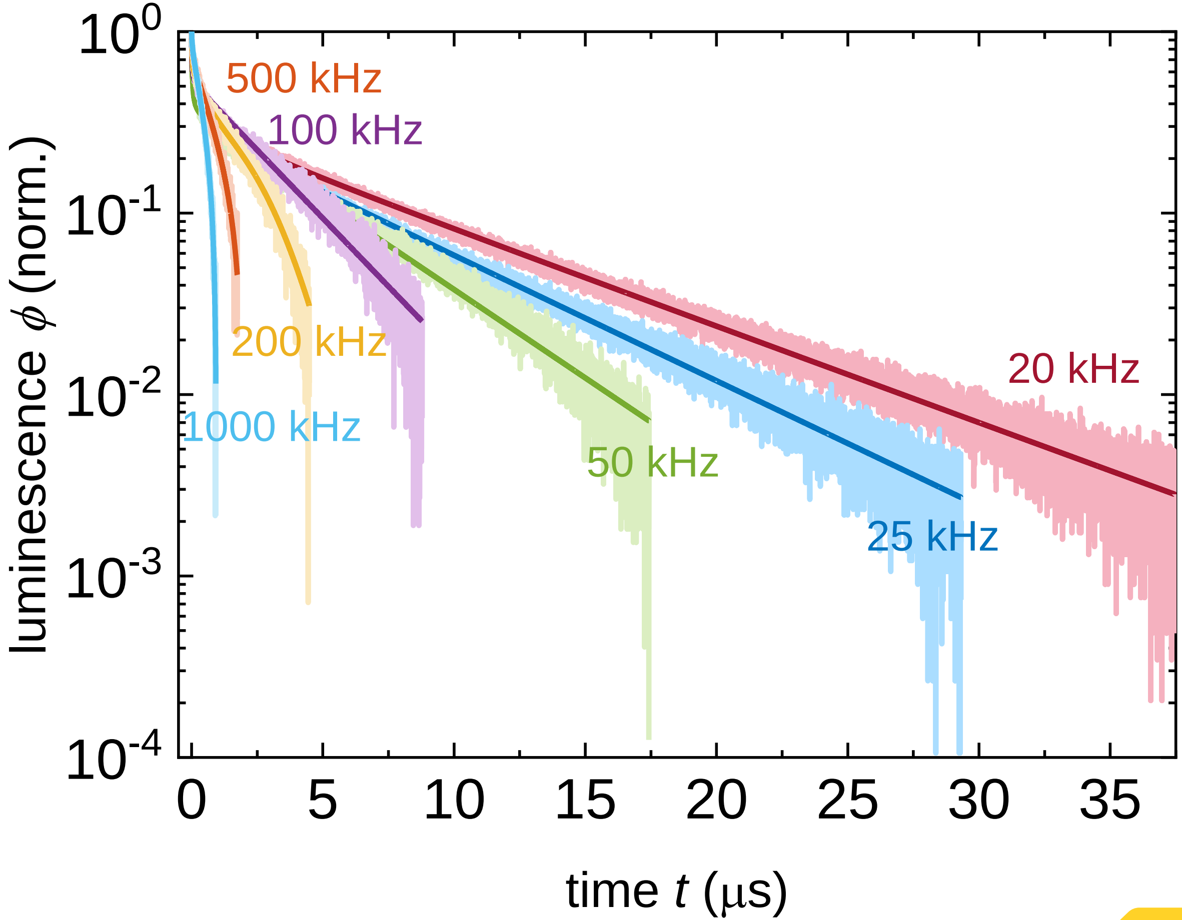




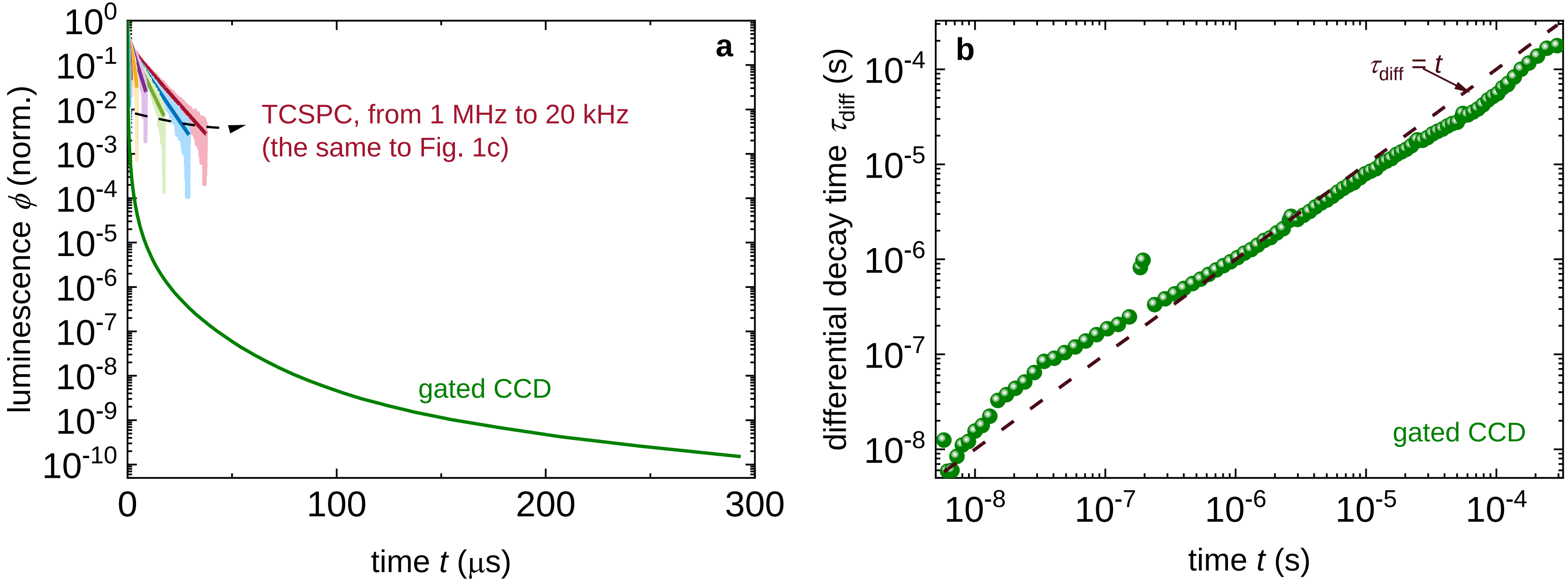
Part 2: Repetition Rates

And how they affect decay times

Decays vs. repetition rates



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

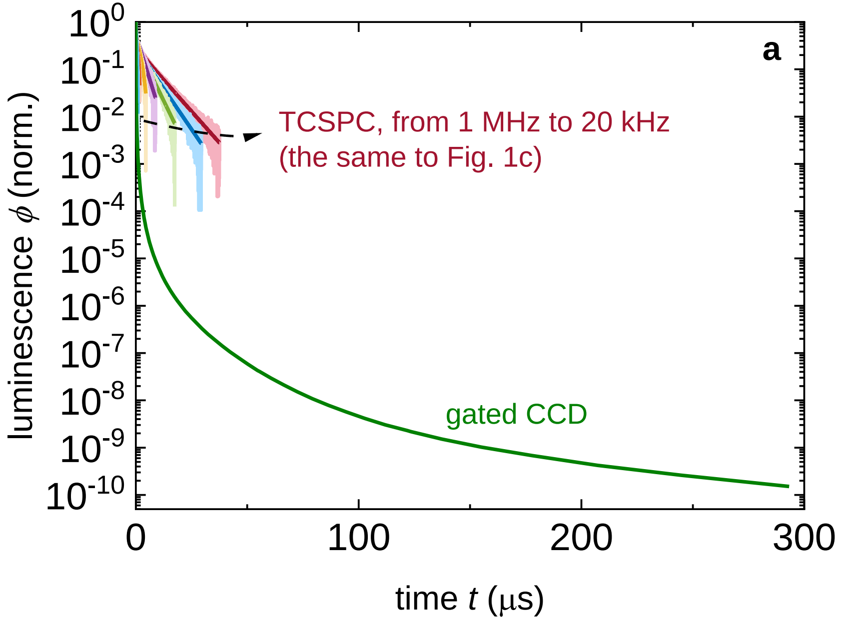


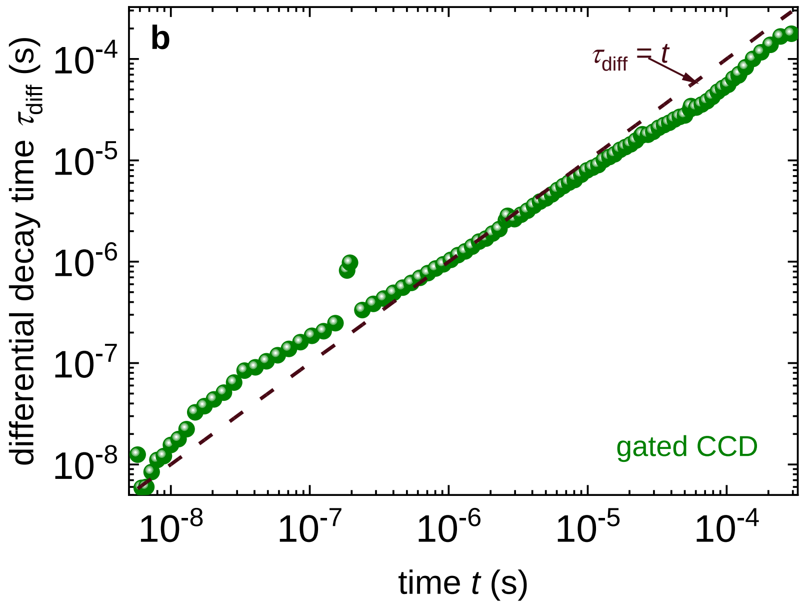
$$\frac{dn(t)}{dt} = -kn^2$$

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

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

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





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

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

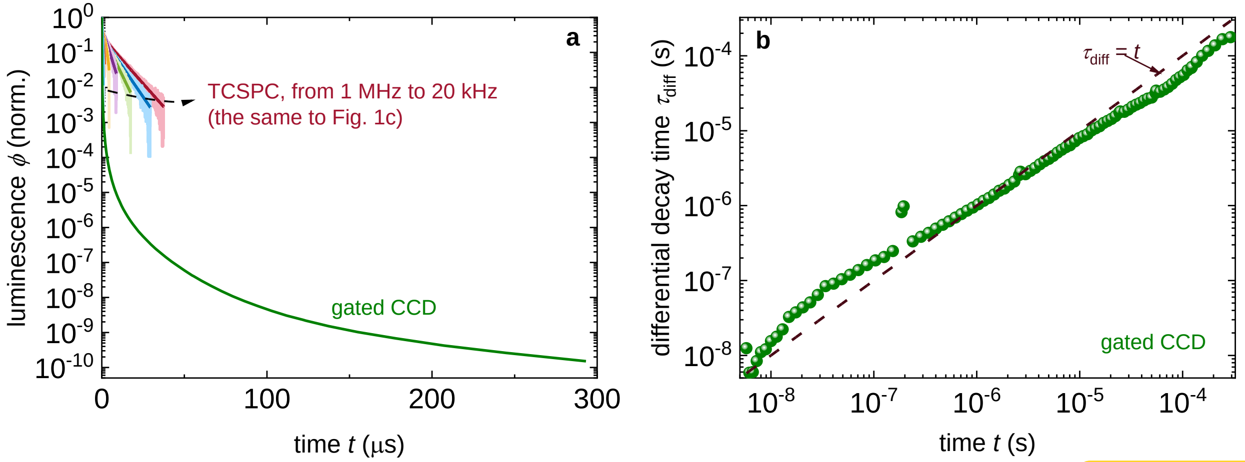
$$n(t) = \frac{n(0)}{1 + n(0)kt} \approx 1/(kt)$$

$$\tau_{\text{diff}} = t$$

Summary

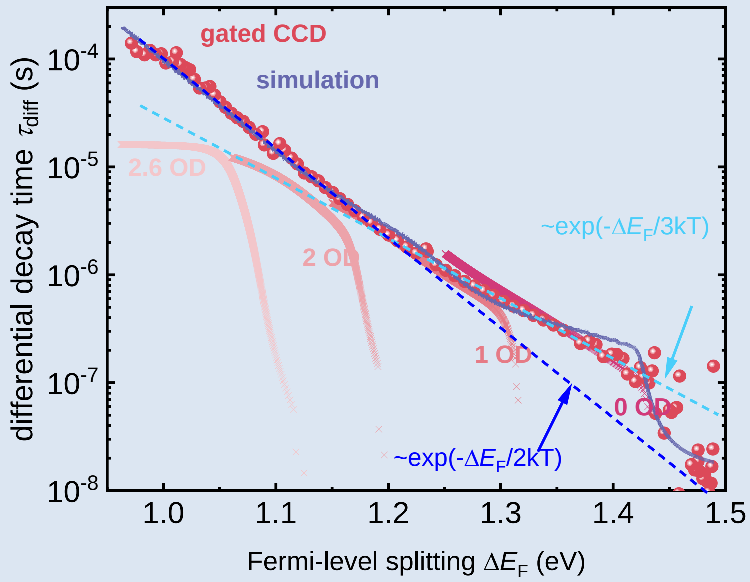
If a sample is intrinsic, the following holds:

- 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.

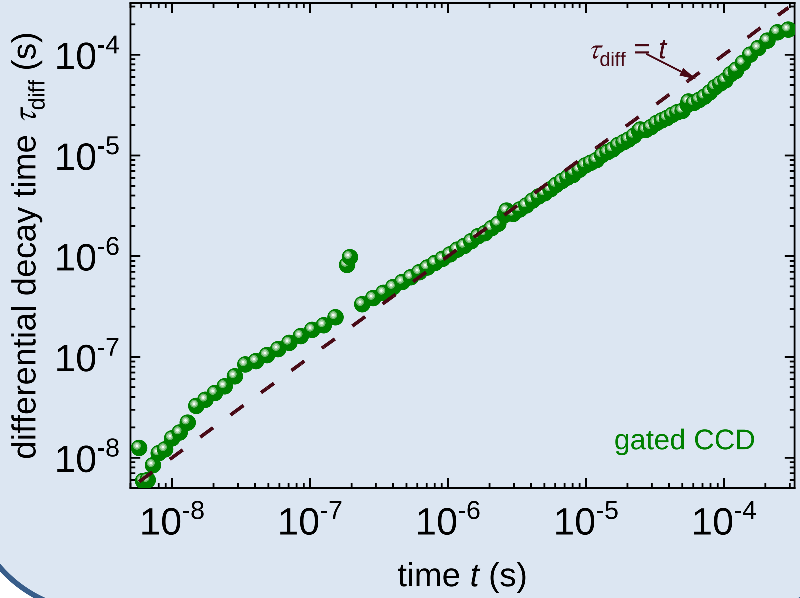


Summary

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



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



Funding from
Helmholtz Association
DFG
OCPC Fellowships

Thank you for your attention

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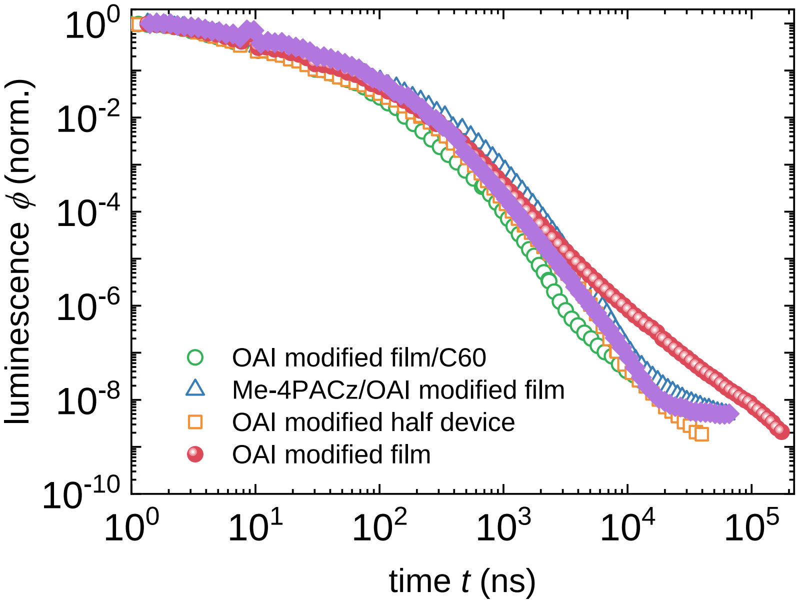
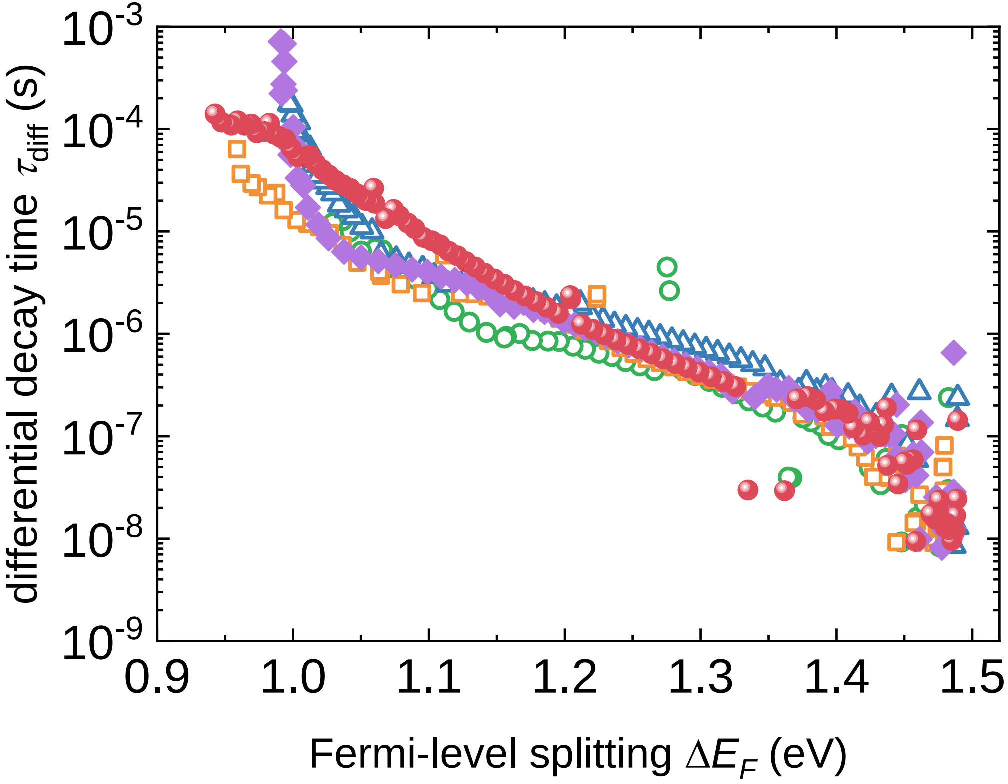
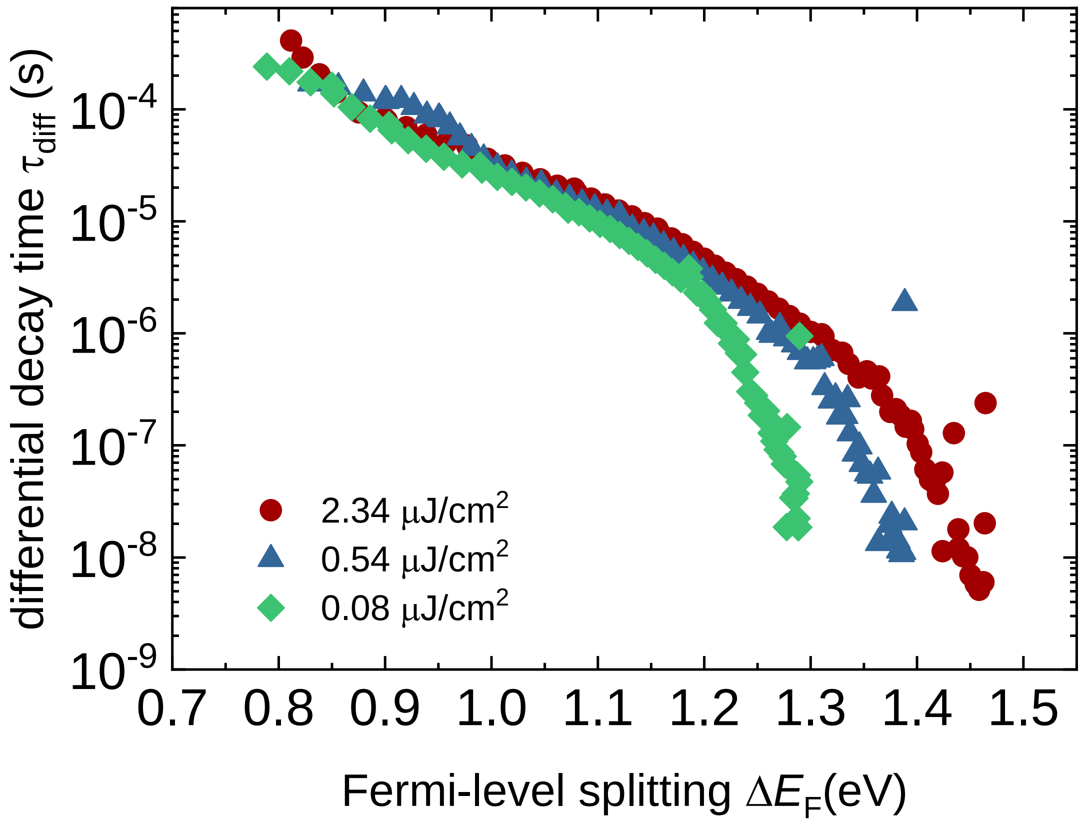
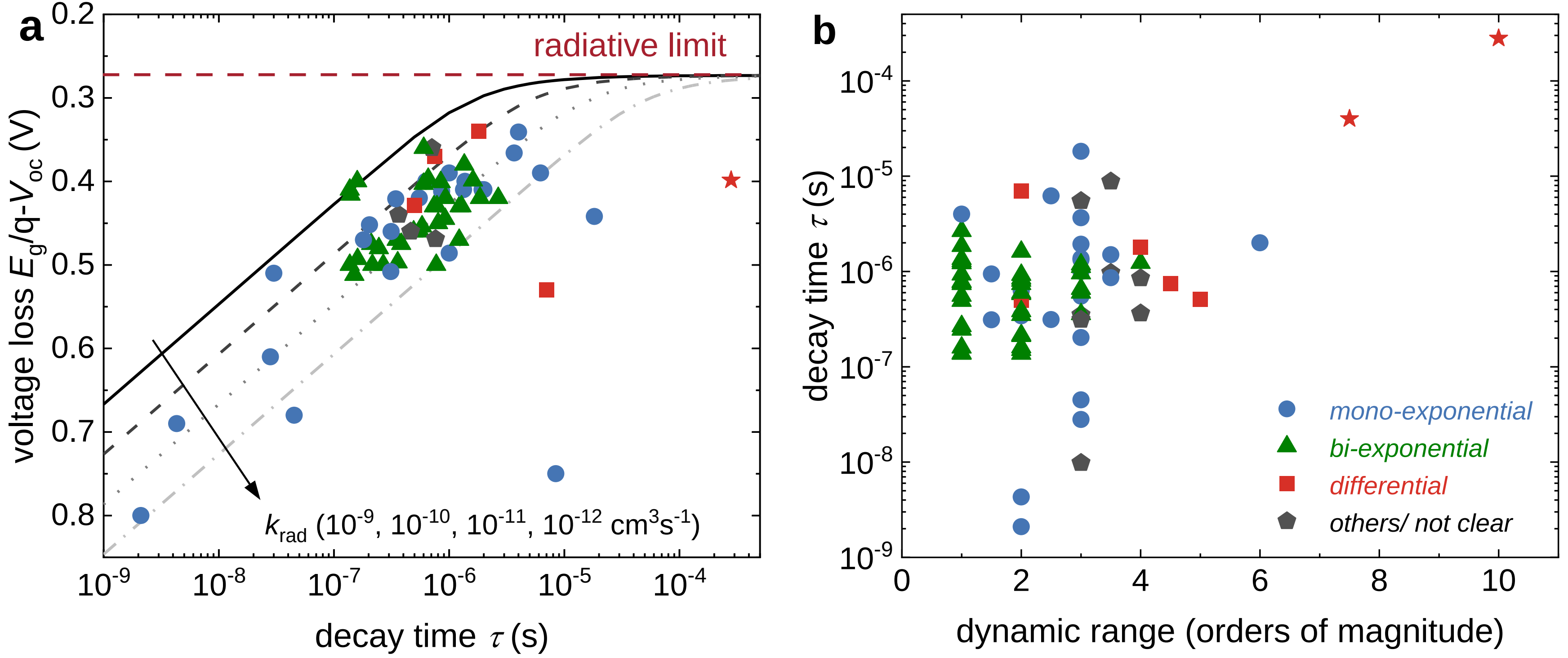

luminescence ϕ (norm.)
10^{0}
10^{-2}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
time t (ns)
OAI modified film/C60
Me-4PACz/OAI modified film
OAI modified half device
OAI modified film


differential decay time τ_{diff} (s)
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
0.9
1.0
1.1
1.2
1.3
1.4
1.5
Fermi-level splitting ΔE_F (eV)

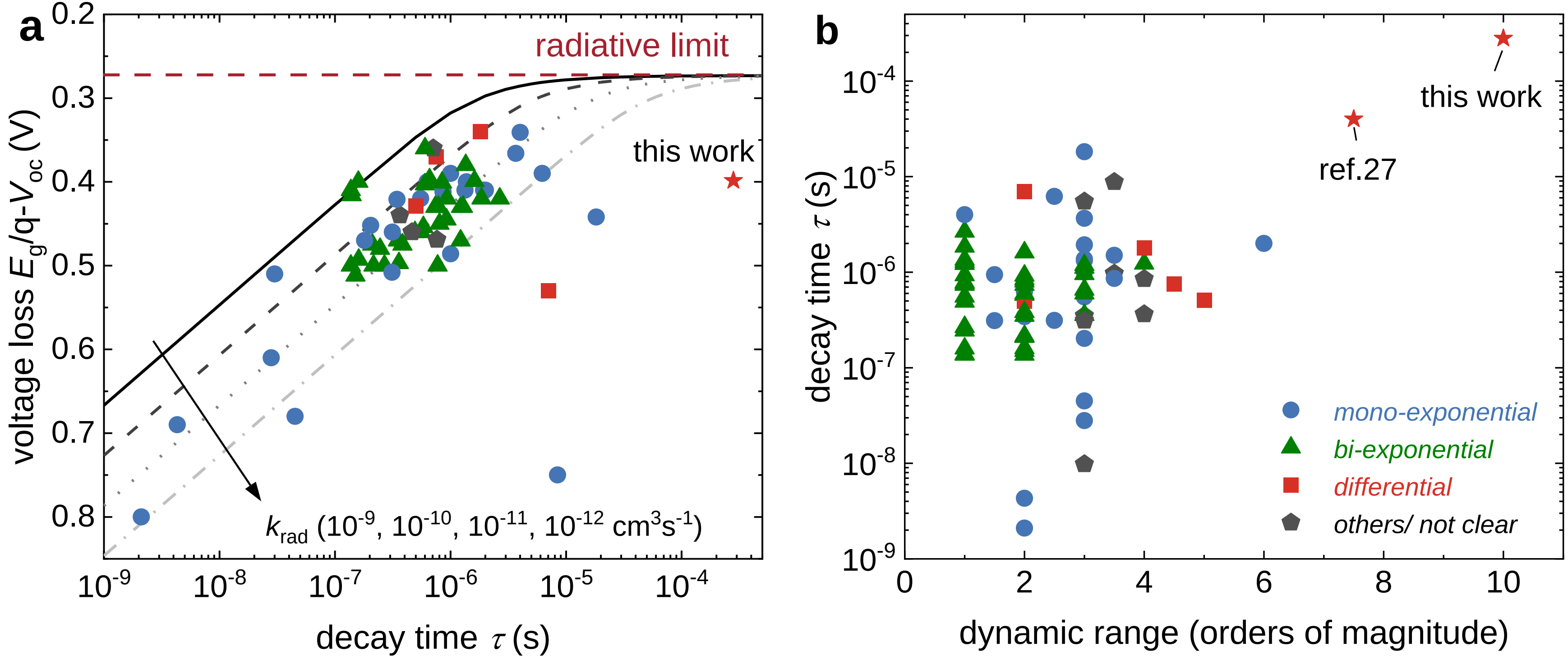
Fluence Dependence



The importance of dynamic range



The importance of dynamic range



Simulations and Analytical Approximations