

Supporting Information for:

Charge-Carrier Recombination in Halide Perovskites

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S.1 Derivation of simplified rate equation

Here we review some of the major assumptions made in simplifying the overall rate equation that describes the photoexcited carrier density as a function of time. In conventional semiconductors with low exciton binding energies and large dielectric constants, the carrier density primarily consists of free electrons and holes.¹ Electrons and holes undergo three main recombination mechanisms including first-order Shockley-Read-Hall (SRH) non-radiative recombination (first term in equation S1), second-order bimolecular recombination (second term in equation S1), and third-order, non-radiative Auger recombination (third and fourth terms in equation S1).²

$$-\frac{dn}{dt} = \frac{np - n_i^2}{n\tau_p + p\tau_n} + k_2(np - n_0p_0 - n_i^2) + k_{3,n}n(np - n_0p_0 - n_i^2) + k_{3,p}p(np - n_0p_0 - n_i^2) \quad (\text{S1}),$$

where n is total electron density, p is the total hole density, τ_p is the non-radiative hole lifetime, τ_n is the non-radiative electron lifetime, n_0 is the electron doping density, p_0 is the hole doping density, n_i is the intrinsic carrier density, $k_{3,n}$ is the non-radiative rate constant for an electron undergoing an Auger process, and $k_{3,p}$ is the non-radiative rate constant for a hole undergoing an Auger process.

Upon photoexcitation, commonly reported steady-state carrier densities are $\sim 10^{14}$ - 10^{16} cm^{-3} , which are significantly larger than the calculated intrinsic carrier densities ($\sim 10^5$ cm^{-3}) and doping densities.³ Therefore, equation S1 can further be simplified to equation S2:

$$-\frac{dn}{dt} = \frac{np}{n\tau_p + p\tau_n} + k_2(np) + k_{3,n}n(np) + k_{3,p}p(np) \quad (\text{S2})$$

Next, we assume that, upon photoexcitation, an equal number of electrons and holes are generated ($n=p$) and, furthermore, that the non-radiative lifetimes and Auger rate constants for electrons and holes are identical. Under these assumptions equation S2 further simplifies to:

$$-\frac{dn}{dt} = \frac{n^2}{2n\tau_n} + k_2n^2 + 2k_{3,n}n^3 \quad (\text{S3})$$

If we express the prefactor in front of the first term as a first order rate constant $k_1 = (2\tau_n)^{-1}$ and include the prefactor 2 in front of the last term into the third order rate constant, we arrive at the equation:

$$-\frac{dn}{dt} = k_1n + k_2n^2 + k_3n^3 \quad (\text{S4})$$

used in the main article and widely in the literature.

S.2 Estimate for trap densities allowed to achieve target non-radiative lifetimes

Section S.1 shows that k_1 in equation S4 is an approximation for the more complex description given in the first term of equation S1. Indeed, the non-radiative lifetimes (τ) of electrons (n) and holes (p) in equation S1 can be described by

$$\tau_n = \frac{1}{\Gamma_n N_T} \quad (\text{S5})$$

$$\tau_p = \frac{1}{\Gamma_p N_T} \quad (\text{S6}),$$

where $\Gamma_{n,p}$ is a kinetic factor that encompasses both the trap capture cross-section (cm^2) and thermal velocity of the carrier (cm s^{-1}) and N_T is the trap state density (cm^{-3}).

Within this description, a single trap captures both an electron and a hole, and therefore the effective non-radiative lifetime (τ_{eff}) can be calculated by inverting and summing the time it takes for an electron and a hole to be captured and subsequently recombine.

$$\frac{1}{\tau_p} + \frac{1}{\tau_n} = \Gamma_p N_T + \Gamma_n N_T \quad (\text{S7})$$

$$\frac{1}{\tau_{\text{eff}}} = (\Gamma_p + \Gamma_n) N_T \quad (\text{S8})$$

The trap state density which results in a predetermined non-radiative lifetime can be calculated by rearranging equation S8 to arrive at

$$N_T = \frac{1}{(\Gamma_p + \Gamma_n) \tau_{\text{eff}}} \quad (\text{S9})$$

In order to calculate the trap densities, we must have knowledge of the rate at which electrons and holes are captured (Γ_n and Γ_p). Importantly, both Γ_n and Γ_p must be evaluated separately for any defect that is not at the center of the gap as the capture cross-section is strongly dependent on the trap state energy relative to the carrier's respective bandedge. As these values are difficult to determine experimentally, we approximate them using a classic theoretical approach for multiphonon capture rates in semiconductors.^{4,5} This calculation involves first determining the Huang-Rhys factor (S_{HR}), which is related to the extent of electron-phonon coupling and atomic relaxation within the system upon photoexcitation.

$$S_{\text{HR}} = \frac{3}{2(\hbar\omega)^2} \left\{ \frac{q^2 (M_r/V_0) \hbar\omega^2}{M_r \omega q_D^2} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon} \right) \right\} \times I(-2, 2\mu, \frac{q_D a^* v}{2}) \quad (\text{S10})$$

Where q is the elementary charge, M_r is the reduced mass of the Pb-I atomic oscillator, V_0 is the volume of the perovskite unit cell, ω is the phonon frequency, ϵ_∞ is the high frequency dielectric constant and ϵ is the static dielectric constant, q_D is the radius of a sphere with the Brillouin-zone

volume, a^* is the effective Bohr radius, ν is a modifier for the radius of the wavefunction of the defect, and μ is an abbreviation for ν [$\mu = \nu$ (positive defects), $\mu = -\nu$ (negative defects), $\mu = 0$ (neutral defects)]. The function $I(a,b,c)$ is defined by⁴

$$I(a, b, c) = \frac{1}{(bc)^2} \int_0^1 \frac{y^a \sin^2(b \tan^{-1}(cy))}{[1+(cy)^2]^b} dy \quad (\text{S11})$$

Now, with knowledge of S_{HR} for a specific phonon frequency, the multiphonon transition rate ($\Gamma_{n,p}$) can be calculated using an equation previously derived by Markvart⁵

$$\Gamma_{n,p} (\text{cm}^3 \text{s}^{-1}) = \frac{V_T p^2 \omega \sqrt{2\pi}}{\sqrt{p\sqrt{1+x^2}}} e^{\left\{ p \left(\frac{\hbar\omega}{2kT} + \sqrt{1+x^2} - x \cosh\left(\frac{\hbar\omega}{2kT}\right) - \ln\left(\frac{1+\sqrt{1+x^2}}{x}\right) \right) \right\}} \quad (\text{S12}),$$

where V_T is the volume of the defect assumed to be a sphere with the radius given by $a^* \nu/2$, p is the number of phonons, \hbar is the reduced Planck constant, k is the Boltzmann constant, T is the temperature, and x is defined by the piecewise function:

$$x = \begin{cases} \frac{S_{\text{HR}}}{p \sinh\left(\frac{\hbar\omega}{2kT}\right)} & \text{for } S_{\text{HR}} < p \\ \frac{p}{S_{\text{HR}} \sinh\left(\frac{\hbar\omega}{2kT}\right)} & \text{for } S_{\text{HR}} > p \end{cases} \quad (\text{S13})$$

Using equation S12 and predefining target nonradiative lifetimes, we calculate the corresponding trap state densities according to equation S9.

Table S1. List of parameters and variables used to calculate the multiphonon capture rate using equations S9-S13.⁶

Parameter	Symbol or Equation	Value
Phonon energy	$E_{ph} = \hbar\omega$	16.5 meV (LO phonon)
Reduced Mass	$M_r = M_{Pb}M_I/(M_{Pb} + M_I)$	78.7 g/mol
Permittivity (frequency)	$\varepsilon(f)$	$\varepsilon = 33.5\varepsilon_0$; $\varepsilon_\infty = 5\varepsilon_0$
Lattice Constant	a_0	6.3 Å
Volume of Unit Cell	V_0	250.05 Å ³
Radius of Sphere with Brillouin Zone Volume	$q_D = (6\pi^2)^{1/3}/a_0$	6.2 nm ⁻¹
Effective Mass	m_{eff}	0.2 (assumed equal for electrons and holes)
Bohr Radius	$a_H = 4\pi\varepsilon_0\hbar/mq^2$	5.292x10 ⁻² nm
Effective Bohr Radius	$a = a_H\varepsilon/m_{eff}$	8.9 nm
Rydberg Energy	$R_H = q^2/(8\pi\varepsilon_0a_H)$	13.605 eV
Effective Rydberg Energy	$R^* = q^2/(8\pi\varepsilon a^*)$	2.4 meV
Defect Radius Modifier	$\nu = q(8\pi\varepsilon a^* \Delta E)^{-1/2}$	variable
Sommerfeld factor	$s_a = 4(\pi R^*/kT)^{1/2}$	2.2

S.3 Calculation of time-resolved photoluminescence with and without photon recycling

Here we use a set of coupled differential equations to describe the low-fluence kinetics of the photoexcited carrier and emitted photon (γ_λ) densities while taking into consideration the effects of photon recycling.

$$\frac{\partial n(t)}{\partial t} = G - k_1 n(t) - k_2 n(t)^2 + \frac{c}{n_r} \sum_\lambda \alpha_\lambda \gamma_\lambda \quad (\text{S14})$$

$$\frac{\partial \gamma_\lambda(t)}{\partial t} = -\frac{c}{n_s} \sum_\lambda \alpha_\lambda \gamma_\lambda(t) + (k_2 n(t)^2 P_{stay}) P_\lambda \quad (\text{S15}),$$

where G is the generation rate, c is the speed of light, n_r is the refractive index, α is the absorption coefficient, P_{stay} is the probability of an emitted photon being totally internally reflected and staying within the film, and P_λ is the probability of a photon being emitted at a wavelength of λ (determined from normalizing the integral of an experimentally measured perovskite photoluminescence spectrum).

Previously, P_{stay} has been defined elsewhere⁸ as

$$P_{stay} = 1 - P_{esc} = 1 - \frac{\int_0^\infty a(E) \phi_{BB}(T, E) dE}{\int_0^\infty 4\alpha(E) d n_r^2(E) \phi_{BB}(T, E) dE} \quad (\text{S16})$$

Where a is the material absorptivity, d is the film thickness, and Φ_{BB} is the black body spectrum:

$$\phi_{BB}(T, E) = \frac{2\pi E^2}{h^3 c^2} \frac{1}{e^{\left(\frac{E}{kT}\right)} - 1} \quad (\text{S17})$$

The photoluminescence decay traces, as shown in Figures 6a and b in the main article, are calculated using the solutions from equations S14 and S15 as inputs into equation S18:

$$PL(t) = (1 - P_{stay}) k_2 n(t)^2 \quad (\text{S18})$$

In order to evaluate the extent of photon recycling over different photoexcited carrier densities, we varied the initial conditions from $n_0 = 10^{14} \text{ cm}^{-3}$ to 10^{16} cm^{-3} , while initially fixing the nonradiative

monomolecular and radiative bimolecular rate constants at $k_1 = 1 \times 10^5 \text{ s}^{-1}$ and $k_2 = 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, respectively.⁷ Next, we continuously varied k_1 from 10^2 s^{-1} to 10^7 s^{-1} for fixed initial conditions to further explore the competition between radiative bimolecular recombination, which is a necessary process for photon recycling (c.f. equation S15), and nonradiative processes.

These simulations were compared against photoluminescence decay traces where photon recycling was neglected, which was achieved by setting $\alpha_\lambda = 0$.

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