# Direct measurement of radiative decay rates in metal halide perovskites

# **Supplementary Information**

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# S1: Light emitted from a thin film: the effect of vertical excitation inhomogeneity due to the finite light penetration depth





We specifically consider two hybrid perovskite thin films: a MAPB film with thickness d=80 nm, excited by photons with energy  $\hbar\omega_{\rm ex} = 2.9$ eV, emission occurs at the lower photon energy  $\hbar\omega_{\rm em} = 2.3$ eV; a MAPI film with thickness d=125 nm, excited at energy  $\hbar\omega_{\rm ex} = 2.0$ eV and with emission peaked at  $\hbar\omega_{\rm em} = 1.6$ eV. The following considerations are referred both to MAPB, considering left graphs Fig. S1 (a-d), and to MAPI, considering right graphs Fig. S1(e-h).

The absorptance (A), reflectance (R) and transmittance (T) spectra are shown in Fig. S1 (a,e). The absorption coefficient is then calculated as:

$$\alpha(\hbar\omega) = \frac{1}{d} \ln \frac{1 - R(\hbar\omega)}{T(\hbar\omega)}.$$
 (S1.1)

The film absorptance at depth z (z<d), namely the fraction of the exciting light absorbed by the film at penetration depth z, is:

$$AA_{ex}(z) = [1 - R(\hbar\omega_{ex})][1 - e^{-\alpha(\hbar\omega_{ex})z}].$$
 (S1.2)

The electron-hole pair density at z reads:

$$n(z) = \frac{dAA_{ex}(z)}{dz} \qquad (S1.3)$$

Fig. S1 (b,f) shows a sketch of the transversal section of the film with nuanced color: the darkest color at excited (front) surface stands for a higher carrier density with respect to that at the back surface. The vertical profile of the carrier density neglecting spatial diffusion (normalized to the value at the front surface  $n_{front}$ ) is shown as a red curve in Fig. S1 (c,g), a realistic approximation for pulsed excitation at t=0. The spatial profile of the spontaneous photon emission rate per unit of film volume,  $r_{int}(z)$ , proportional to  $n(z)^2$ , is shown with the blue curve in Fig. S1 (c,g). Despite the small thickness of the film, the light emission intensity at the front surface,  $r_{int}(0)$ , is three times higher than the one close to the back surface  $r_{int}(d)$ . The mean PL intensity, proportional to the square of the mean carrier concentration  $\bar{n} = \frac{AA_{ex}(d)}{d}$ , is the half of the value at the front surface  $r_{int}(0)$ . Yet, we can show that the light emitted from the front or back surfaces, assuming a constant carrier density  $\bar{n}$ , is virtually equal to that emitted considering the effective spatial carrier profile. To estimate the photon flux through the front or back film surfaces, we need to sum up the light emitted at any point of the film and the absorption process photons undergo before being transmitted externally, according to the rate equation:

$$\frac{dJ(z)}{dz} = \delta r_{int}(z) - \alpha(\hbar\omega_{em})J(z) \quad (S1.4)$$

where  $\delta r_{int}(z)$  is the spontaneous photon emission rate per unit volume within a small solid angle around the direction z. Fig. S1 (d,h) shows the solutions of this differential equation for photons propagating in the forward ( $J_f$ ) and backward ( $J_b$ ) directions, while  $J_{c,f}$  and  $J_{c,b}$  correspond to the approximated case obtained with constant carrier profile  $\bar{n}$ . The photon flux  $J_b$  and  $J_{c,b}$  at the front surface (highlighted with green circle) and  $J_f$  and  $J_{c,f}$  at the back surfaces (yellow circle) differ of just a few per cent, demonstrating that assuming a constant carrier density  $\bar{n}$  is quite a reasonable approximation both for MAPI and MAPB thin films.

# S2: Time resolution of PL measurements



*Figure S2:* Differential transmission measurement on MAPB thin film measured with femtosecond ultrafast transient absorption pump and probe technique, at different fluences in the same range of the TRPL measurements.

In order to exclude the presence of ultrafast features in the decay profile at t=0, that would be not detectable with the streak camera due to the time resolution (around 50ps), also differential transmission measurements were performed on the same samples, under the same pulsed optical excitation used to stimulate the photoluminescence. The DT/T signal was recorded with a differential transmission spectrometer (Helios from Ultrafast Systems), which measured individual probe and reference spectra with custom CMOS spectrometers, with a spectral resolution of 1nm and a time resolution up to 100fs, limited by the temporal length of the excitation pulses. In fig. S2 we report result for MAPB (without photohealing) as a representative case: the decay profiles of the bleaching signal are clearly showing that there is no evidence of any sharp feature at t=0, i.e., when carriers are injected into the material, analogously to what already observed in the same kind of materials.<sup>1,2</sup>

## S3: Evaluation of the internal and external light emission rates

The rate of light emitted perpendicularly to the front film surface per unit of film volume and solid angle is given by the Planck-Kirchhoff law, generalized by Würfel<sup>3</sup> to take into account the semiconductor electronic properties and optical excitations:

$$\delta r_{ext} = \frac{PL}{d} = e^{\frac{\mu}{kT}} \left[ \frac{1}{4\pi^3 \hbar^3 c_0^2 d} \int_0^\infty a \ (\hbar\omega)^2 e^{\frac{-\hbar\omega}{kT}} \right] = \frac{B_{ext}}{2\pi} n^2 \qquad (S3.1)$$

PL is the external radiance emitted perpendicularly to the film surface, d the film thickness, a the absorptance and  $\mu$  the chemical potential of electron-hole pairs. The right equation holds for a Lambertian emission. The factor of  $2\pi$  accounts for the Lambertian emission angle from the front and back surfaces, each contributing with a factor  $\pi$ . Neglecting multiple reflections and in the limit of thin films, one can approximate  $a \approx (1 - R)(\alpha d)$ , where R is the film reflectivity.

Light emission rate inside the semiconductor per unit of volume and solid angle reads:

$$\delta r_{int} = e^{\frac{\mu}{kT}} \left[ \frac{1}{4\pi^3 \hbar^3 c_0^2} \int_0^\infty \tilde{n}^2 \alpha (\hbar\omega)^2 e^{\frac{-\hbar\omega}{kT}} \right] = \frac{B_{int}}{4\pi} n^2 \quad (S3.2)$$

where  $\tilde{n}$  is the film index of refraction.

From which, one obtains:

$$B_{\text{int}} = \frac{4\pi\delta r_{\text{int}}}{n^2} = \frac{4\pi}{n^2} \frac{\int_0^\infty \tilde{n}^2 \alpha(\hbar\omega)(\hbar\omega)^2 e^{\frac{-\hbar\omega}{kT}}}{\frac{1}{d} \int_0^\infty a(\hbar\omega)(\hbar\omega)^2 e^{\frac{-\hbar\omega}{kT}}} \frac{PL}{d} \cong \frac{4\pi\tilde{n}^2}{(1-R)} \frac{PL}{dn^2} (S3.3)$$
$$\frac{B_{\text{int}}}{B_{\text{ext}}} = 2\frac{\delta r_{\text{int}}}{\delta r_{\text{ext}}} = \frac{d\int_0^\infty \tilde{n}(\hbar\omega)^2 \alpha(\hbar\omega)(\hbar\omega)^2 e^{\frac{-\hbar\omega}{kT}}}{\int_0^\infty a(\hbar\omega)(\hbar\omega)^2 e^{\frac{-\hbar\omega}{kT}}} \cong 2\frac{\tilde{n}(\hbar\omega_{PL})^2}{[1-R(\hbar\omega_{PL})]} (S3.4)$$

Where  $\hbar\omega_{PL}$  is the photon energy at the PL peak;  $\tilde{n}(\hbar\omega_{PL}) = 2.25$  and 2.41 for bromide and iodide perovskite films, respectively.<sup>4</sup> We get  $\frac{B_{int}}{B_{ext}} = 16.3$  (MAPB) and 15.9 (MAPI).

Our perovskite films are deposited on a glass substrate and overcoated with a PMMA layer. As shown in S5, *PL* is still provided by equation (S3.1), in which a and R are the absorptance and the reflectivity of the whole structure, respectively. Differences between back and front reflectivity are neglected.

# S4: Results of low-temperature measurements of Bext



**Figure S4**: Bext values obtained from absolute PL radiance measurements at low temperatures for the three different compounds, analogously to what reported in Fig.1 (b) in the main text. The B obtained from the fit are reported as red squares in Fig. 2 (d-f) and Table 1 in the main text.



# S5: Results of low-temperature measurements of $k_1$ , $k_2$ and $k_3$

**Figure S5:** Markovian plots with fits with rate equation as in Fig. 2(a-c) in the main text, at different low temperature values.  $k_1, k_2$  and  $k_3$  coefficients obtained from the global fits (black lines) with rate equation were reported as green, blue and black squares respectively in Fig. 2(d-f) in the main text.



# S6: PLQY measurements with the integrating sphere and Lambertian emission

**Figure S6** (a): Measurements of PLQY performed on MAPB sample with the integrating sphere setup (Fig. 3b in the main text) under the same pulsed excitation as in the absolute radiance measurements. Each black square in Fig. 3a in the main text is the result of one of the above reported PLQY measurements. (b) Representation of emission from a free-standing film over a solid angle  $d\Omega = 2\pi sin\theta_0 d\theta$  and (c) the Lambertian emission resulting from the integral of  $d\Omega$  over all the possible angles of emission from the front surface. (d) represents the case of a sample with capping, instead of free-standing one, where the portion of light emitted at solid angles with from a film with  $\theta > \theta_{cap}$  is totally internal reflected at the capping-air interface. The length of the blue arrows in the Lambertian emission pattern is proportional to the photon emission rate, which is higher at small  $\theta_{cap}$  and is not affected by the presence of the capping layer.

In Fig. S6(b),  $\theta_0$  represents the detection angle of the PL set-up.  $\theta_0$  being small, the effective Lambertian solid angle  $\Delta\Omega_L$  is almost equal to the detection solid angle  $\Delta\Omega_0$ :

$$\Delta\Omega_0 = 2\pi \int_0^{\theta_0} \sin\theta d\theta = 2\pi (1 - \cos\theta_0) \approx \pi \theta_0^2 \quad (S6.1)$$
$$\Delta\Omega_L = 2\pi \int_0^{\theta_0} \sin\theta \cos\theta d\theta = \pi \sin^2\theta_0 \approx \pi \theta_0^2 \quad (S6.2)$$

The whole Lambertian solid angle from the front surface of a free-standing film (represented by the green lobe in Fig. S6(c)) is equal to  $\pi$ . If we consider the emission from both the front and back surfaces,  $\Omega_L = 2 \pi$ .

In the presence of a capping dielectric layer (the glass substrate or the PMMA in our samples), a fraction of the light emitted from the surface will be totally internal reflected at the capping layer/air interface, as represented in Fig. S6(c) with the grey coloured portion of the Lambertian lobe. The total internal reflection condition at the capping layer/air interface reads:

$$\sin\theta_{\rm cap} = \frac{1}{n_{\rm cap}} \quad (S6.3)$$

Only light emitted at angles  $\theta < \theta_{cap}$  can exit from the surface of the capping layer (Fig. S6(d)), within a solid angle  $\Omega_{cap,L} = \pi \sin^2 \theta_{cap} = \pi / n_{cap}^2$  For the film architecture, perovskite/capping-layer/air, the expression of *PL*, after correction for the effective light speed in the dielectric layer, reads

$$PL \propto \Omega_{\text{cap,L}}/c^2 = \Omega_{\text{cap,L}} n_{\text{cap}}^2 / c_0^2 = \pi / c_0^2 \quad (S6.4)$$

which is the same expression of *PL* for a free-standing film without any capping layer (Fig. S6(c))., ensuring us that the radiance obtained from the absolute measurement is the same if we consider a free-standing film or one with capping.

For a fair comparison between the calibrated TRPL measurement and the one with the integrating sphere, we might consider that not all the light emitted by the perovskite layer into the capping-layer is transmitted externally through the capping-layer/air interface: in fact, this happens only to a fraction  $1/n_{cap}^2$ . The remaining fraction of light undergoes total internal reflection and is reflected back towards the film (see Fig. S6(d)). In the case of very thin films with high internal PLQY, remission processes can largely compensate for absorption. The back-reflected light can therefore propagate along the plane of the capping layer and come out from its edges. Since this in-plane guided light is not contributing to the Lambertian emission from the front and back surfaces, for a fair comparison with the results of absolute radiance measurements, it had to be excluded from the measurement in the integrating sphere: this was achieved by blackening the edge of the glass, resulting in a very good agreement between the two techniques. We also observed that, after blackening the edges, the PLQY measured inside the sphere diminished by a factor of  $\approx 2$ , confirming that the overall extraction efficiency from a film on glass can exceed the free-standing one by a factor between 1 and  $n_{cap}^2 \sim 2.25$ , as also represented with the yellow areas in Fig. 2(d-f) in the main text.

Considering that in the integrated-sphere measurement the collected PL comes from the whole excitation spot, not only from the central-homogenously excited region as in the TRPL measurement, the injected carrier density had to be rescaled by a correction factor of  $\sim$  2, estimated as the ratio between the peak power (at the centre of the spot) and the power averaged over the whole spot area.



#### S7: Experimental and theoretical absorption coefficient a and PL spectra for MAPI

**Figure S7:** Analogous of Fig. 4 in the main text, for MAPI film. Left side: theoretical absorption coefficient (continuous black curve) resulting from the contributions of exciton (pink) and valence-to conduction band transitions (light blue) according to Elliott equation (see also S8), compared with experimental absorption coefficient spectrum (green dots). Right side: experimental PL spectrum ( $PL_{exp}$ , continuous green curve) compared with the external  $r_{ext}$  (yellow dots) and internal  $r_{int}$  (red dots) luminescence estimated through the reciprocity relations from absorptance and absorption spectra, respectively, black line is the PL obtained from theoretical absorption coefficient through reciprocity relations.



#### S8: Fits to the absorption coefficient by using the Elliot's law for excitonic band-edge absoprtion

**Figure S8**: Absorption coefficient spectra for MAPI at 295K for our samples, compared with data reported in Ref. <sup>5</sup> for thin films of the same material at 295K (red) and 170K (blue): squares are experimental data, lines are best fits with Elliot function. Exciton binding energy as a function of temperature is reported in the inset, filled circles are experimental data from reference <sup>5</sup>, empty circle from the film measured in this work.

We modelled the absorption coefficient above the optical absorption edge in the framework of the Elliot's theory of Wannier excitons, <sup>6</sup> as done also in Reference <sup>7</sup> :

$$\alpha(\hbar\omega) = C \frac{\mu_{cv}^2}{\hbar\omega} \left[ \sum_n \frac{4\pi \sqrt{E_b^3}}{n^3} \delta(\hbar\omega - E_n^b) + \frac{2\pi \sqrt{E_b} \theta(\hbar\omega - E_g)}{1 - e^{-2\pi \sqrt{\frac{E_b}{\hbar\omega - E_g}}}} \right]$$
(S8.1)

where  $\mu_{cv}$  is the transition dipole moment;  $\hbar\omega$  the photon energy,  $E_b$  the exciton binding energy and C is a constant. The first term in equation (S8.1) describes transitions to exciton states with energy  $E_n^b = E_g - \frac{E_b}{n^2}$ . Transitions to continuum states with energies above the bandgap  $E_g$  are accounted for by the second term;  $\delta(x)$  and  $\theta(x)$  are the Dirac-delta and the unit step functions, respectively.

In order to avoid the introduction of nonlinear terms to account for non-parabolic dispersion of the conduction and valence bands, fits were restricted to 100 meV above the band-gap.<sup>8</sup> A gaussian line-broadening was assumed.

At room temperature, transition linewidths of MAPI are such that the excitonic peak is largely smeared out. To reduce the uncertainty in the evaluation of the exciton and band-gap energies, we performed a global fit to the MAPI absorption spectra in the tetragonal phase at different temperatures, down to T=170 K, as reported in Fig. S8. Absorption spectra vs temperature were taken from Reference <sup>5</sup>. We considered  $C\mu_{cv}^2$  in equation (S7.1) as temperature independent in the tetragonal phase and took it as a global fit parameter. The estimated values of  $E_b$  vs T were found to be weakly dependent on temperature, in agreement with recent ab-initio theoretical calculations, <sup>9</sup> and with optical f-sum rule.<sup>5</sup>

### S9: Evaluation of the radiative bimolecular recombination constant from the reciprocity law

The starting point for the evaluation of the radiative bimolecular recombination constant from the absorption/emission reciprocity is the equation:

$$B_{\rm int,rl} = \frac{\int_0^{\omega} r_{\rm sp,int} d(\hbar\omega)}{n_{\rm th}^2} \quad (S9.1)$$

The thermal population,  $n_{th}$ , should in principle accounts for both the majority population of electron-hole pairs  $(n_{eh})$  and excitons  $(n_x)$ . The equilibrium condition between these two species is provided by the Saha's law:

$$\frac{n_{eh}^2}{n_x} = \left(\frac{\mu_x k_B T}{2\pi\hbar^2}\right)^{\frac{3}{2}} e^{-\frac{E_B}{k_B T}} = n_{eq} \quad (S9.2)$$

where  $\mu_X$  is the effective reduced mass of excitons. We took  $\mu_X = 0.11 m_0$  and  $0.13 m_0$  for MAPI and MAPB,<sup>10</sup> respectively, leading to  $n_{eq} \sim 1 \div 2 \times 10^{16}$  cm<sup>-3</sup> for both perovskites. Chemical equilibrium implies that electron-hole pairs are the majority population up to  $n_0 < n_{eq}$ . As  $n_{th}$  is orders of magnitude lower than  $n_{eq}$ , we can safely approximate  $n_{th}$  by the free carrier population alone, which is given by the mass action law.  $n_{th}^2$  can thus be calculated as:

$$n_{th}^2 \cong 4(2\pi m_e kT/h^2)^{3/2} (2\pi m_h kT/h^2)^{3/2} e^{-E_g/kT}.$$
 (S9.3)

The electron and hole effective masses of MAPI were taken from reference  ${}^8 m_e = 0.22 m_0$  and  $m_h = 0.23 m_0$ . The hole effective mass  $m_h = 0.245 m_0$  of MAPB was instead taken from reference <sup>11</sup>. The electron effective mass was then estimated from the knowledge of  $\mu_X$ :  $m_e = 0.277 m_0$ .

As the expression of  $n_{th}$  does not account for line broadening of the carrier electronic levels,  $\int_0^{\infty} r_{\text{sp,int}} d(\hbar\omega)$  was also estimated at the same level of approximation from equation 5 in the main text and (S8.1) for the unbroadened absorption coefficient. It is worth noting that inclusion of line broadening in the calculation of the numerator and denominator of eq. S9.1 leads to the same results, within the experimental uncertainty. As a matter of fact, line broadening leads to an increased value of  $\int_0^{\infty} r_{\text{sp,int}} d(\hbar\omega)$ , which is however compensated by the higher value of  $n_{th}^2$  when this latter is numerically calculated by also including line broadening.

#### S10: Polaron model description

The interaction strength between charge carriers and the surrounding polar optical phonon cloud is typically quantified by the adimensional Fröhlich coupling constant<sup>12</sup>:

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \sqrt{\frac{m_{e,h}c^2}{2\hbar\omega_{L0}} \left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0}\right)}.$$
 (S10.1)

Here  $\varepsilon_0$  and  $\varepsilon_\infty$  are static and high-frequency dielectric constants, respectively, and  $\omega_{L0}$  the dominant longitudinal optical phonon frequency in the temperature range of interest; in fact, for polar semiconductors, diffusive transport at room T is typically dominated by carrier scattering with polar optical phonons. For  $\alpha << 1$  (*weak-coupling* regime), as in the case of covalent semiconductors, polarons do not form, and carriers move through the crystal as single particles with effective mass  $m_{e,h}$ ; for  $\alpha$ ~ 1 (*large-polaron* regime) carriers move while dragging a structural deformation extended for many lattice parameters around the carrier; from transport point of view, carriers can still be described as free particles, but with an enhanced (polaronic) effective mass. For strongly ionic materials,  $\alpha$  can be much larger than unity; in this limit the electronic ground-state follows adiabatically the lattice deformation, and carriers become self-trapped within a radius of just a few lattice parameters (*small-polaron* regime). Using values appropriate for MAPI at room T ( $\varepsilon_0 = 60$ ,<sup>13</sup>  $\varepsilon_\infty = 5$ ,<sup>14-17</sup>  $\hbar \omega_{L0} = 10$  meV,<sup>18,19</sup>  $m_{e,h} = 0.22 m_0$ ) we obtain  $\alpha = 3.02$ , which classifies MAPI as a material in the medium-large polaron regime. Our value is slightly larger than the  $\alpha = 2.40-2.60$ obtained by Frost,<sup>19</sup> mainly as a consequence of the use of calculated  $\varepsilon_0 = 24$ , which is much smaller than our adopted experimental  $\varepsilon_0$ . On the other hand, electron-phonon coupling calculations based on many-body perturbation theory obtain a much smaller  $\alpha = 1.4.^{20}$ 

The Fröhlich Hamiltonian<sup>12</sup> describes, from a quantum mechanical viewpoint, the interaction of carriers with polar optical phonons; while this Hamiltonian cannot be solved exactly, a very accurate approximation, valid at any coupling strength, was obtained by Feynman, based on the path integral formulation.<sup>21</sup> The Feynman model can be solved exactly by variational approach <sup>22–24</sup>, and accurate perturbative solutions can be found in both small- and strong-coupling limits, respectively. For the  $\alpha$  values of interest (0 <  $\alpha$  < 5), the polaron self-energy is well reproduced by the expression:<sup>25</sup>

$$\frac{\varepsilon_P}{\hbar\omega_{L0}} = -\alpha - 0.0159\alpha^2 \quad (S10.2)$$

and the corresponding polaron mass enhancement by:

$$\frac{m_P}{m_{e,h}} = 1 + \frac{\alpha}{6} + 0.0236\alpha^2 \quad (S10.3)$$

For MAPI we obtain  $\varepsilon_P = -32 \text{ meV}$ , and  $m_P = 0.34 \text{ m}_0$  (equal for electrons and holes, having assumed same electron and hole effective masses); these values, in good agreement with those reported in Ref. <sup>19</sup>, can be exploited to evaluate the changes in the

intrinsic carrier concentration due to the polaronic behaviour, and the corresponding  $n_{th}^2/n_{p^+p^-}^2$  ratio, as described in the main test; to the aim, we calculate the intrinsic carrier concentration as:

$$n = \int_{E_{CBB}}^{\infty} d\varepsilon \, D(\varepsilon) f(\varepsilon - \varepsilon_F) = \int_{-\infty}^{E_{VBT}} d\varepsilon \, D(\varepsilon) [1 - f(\varepsilon - \varepsilon_F)]$$
(S10.4)

where  $D(\varepsilon)$  is the 3D density of states in the effective-mass approximation, and  $f(\varepsilon - \varepsilon_F)$  the Fermi-Dirac distribution; the polaron enhancement is then simply evaluated by shifting the band extrema according to the polaron self-energies, and using the polaron mass in the density of states. From Equation S10.4 at room T we obtain  $n_{th} \sim 0.61 \times 10^5$  cm<sup>-3</sup>,  $n_p \sim 4.69 \times 10^5$  cm<sup>-3</sup>,  $n_{th}^2/n_{p^+p^-}^2 = 1.71 \times 10^{-2}$ .

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