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# B The relative quantum efficiency

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In absorption measurements, the intensity of light transmitted through a sample is given by

$$I_1 = I_0 \exp(-\alpha L), \quad (\text{B.1})$$

with  $I_0$  the incident intensity,  $L$  the sample thickness, and  $\alpha$  the absorption coefficient. (For this analysis, the reflection is neglected; in any case, wavelength-independent reflection will not influence the conclusion.) The fraction of photons that are absorbed from the beam, the absorbance signal  $S_{abs}$ , is thus:

$$S_{abs} = \frac{I_0 - I_1}{I_0} = 1 - \exp(-\alpha L), \quad (\text{B.2})$$

and ranges from 0 (full transmission) to 1 (full absorption). The number of photons absorbed per pulse is then equal to the number of photons incident on the sample (given by the product of the beam area  $A$ , the photon flux  $\phi$ , and the laser pulse length  $\Delta t$ ), and the fraction given above:

$$N_{abs} = \phi \Delta t A S_{abs}. \quad (\text{B.3})$$

(Measurements of absorption are performed at low intensity to avoid non-linear effects such as double-photon absorption). If PL occurs with an efficiency  $\eta$ , the number of photons emitted after each pulse is

$$N_{PL} = \eta N_{abs} = \eta \phi \Delta t A S_{abs}. \quad (\text{B.4})$$

The luminescence signal  $S_{PL}$  is proportional to the number of photons emitted:

$$S_{PL} = \chi N_{PL} = \chi \eta \phi \Delta t A S_{abs}, \quad (\text{B.5})$$

where the factor  $\chi$  is a function of the geometry of the setup, the efficiency of the photodetector, etc. We define the PL yield  $Y_{PL}$  as the derivative of the PL intensity vs. flux:

$$Y_{PL} \equiv \frac{dS_{PL}}{d\phi} = \chi \eta \Delta t A S_{abs}, \quad (\text{B.6})$$

## 94 B. The relative quantum efficiency

and the ratio of luminescence yield and the absorbance signal is given by

$$\frac{Y_{PL}}{S_{abs}} = \chi\eta\Delta tA. \quad (\text{B.7})$$

The above formula B.7 contains only constants, except for  $\eta$ , which can depend on the wavelength.

When changing to another setup,  $\chi$ ,  $\Delta t$ , and  $A$  can change. However, in order to be able to compare data from different setups, the measurements can be auto-calibrated on the saturation behavior. The saturation of photoluminescence intensity on increase of flux can be described as follows:

The number of emitters (Si NCs or  $\text{Er}^{3+}$ ) in the excited state that contribute to PL under illumination during the laser pulse,  $N^*$ , is governed by simple kinetics:

$$\frac{dN^*}{dt} = \sigma_{PL}\phi(N - N^*) - \frac{N^*}{\tau}, \quad (\text{B.8})$$

with  $t$  time,  $N$  the number of excitable units (for instance proportional to the number of NCs or  $\text{Er}^{3+}$  in the area under illumination),  $\tau$  the relaxation time, and  $\sigma_{PL}$  the PL excitation cross-section. When the laser pulse length  $\Delta t$  is short compared to  $\tau$ , as is the case in the current study, the second term, describing de-excitation, can be ignored. The solution, when allowing only for single PL excitation (one photon can produce only one excitation in the emitting center) is then given by:

$$N^* = N[1 - \exp(-\sigma_{PL}\phi\Delta t)]. \quad (\text{B.9})$$

By definition, the number of photons emitted is equal to  $N^*$ , when only radiative recombination is considered, and proportional to  $N^*$  when also non-radiative recombination is allowed. We assume here that maximum one exciton per nanocrystal can contribute to photon generation. It is well established that a strong Auger quenching takes place between excitons located within the same Si NC. Consequently, in case that multiple excitons per NC are generated during the laser pulse, only one of them will survive the non radiative recombination, and contribute a photon to the PL signal, either by emitting a photon (NC-related PL) or by transferring its energy to dopant (Er-related PL). This assumption is directly confirmed by the fact that the PL intensity saturation level is independent of the excitation wavelength—see Fig. 2.9 for the photon flux dependence of Er-related PL intensity. The time-integrated PL signal after excitation is then proportional to  $N^*$ , which thus saturates upon increase of photon flux  $\phi$ :

$$S_{PL} = \chi N_{PL} = \chi N^* = \chi N[1 - \exp(-\sigma_{PL}\phi\Delta t)]. \quad (\text{B.10})$$

The PL excitation cross-section  $\sigma_{PL}$  (and the product  $\chi N$ ) can be determined by fitting the measured PL intensity dependence on photon flux, also shown in Fig. 2.9. In particular, we note that at infinite flux and small flux the above equation gives, respectively:

$$S_{PL,max} = \chi N, \quad (\text{B.11})$$

$$Y_{PL} \equiv \left. \frac{dS_{PL}}{d\phi} \right|_{\phi \rightarrow 0} = \chi N \sigma_{PL} \delta t. \quad (\text{B.12})$$

Comparison of Eq. B.6 with the last equation tells us that  $N\sigma_{PL} = \eta S_{abs}$ . In other words, the quantum efficiency is linked to the experimentally measured parameters as:

$$\eta = \frac{N\sigma_{PL}}{S_{abs}}. \quad (\text{B.13})$$

Because knowledge of  $N$  cannot be obtained (only the product  $\chi N$  can be determined by fitting), only the relative quantum efficiency can be determined and is proportional to the ratio of the fitting parameter  $\sigma_{PL}$  and the measured absorbance signal  $S_{abs}$ .

Since the PL saturation level is independent of excitation wavelength, *i.e.*  $S_{PL,max}$  is independent of  $\lambda_{ex}$ , this implies that  $N$  is a constant not depending on  $\lambda_{ex}$ . Thus, plotting the ratio of PL cross-section and absorbance signal will directly give us information about the relative quantum efficiency  $\eta$ . This method has been used for preparation of Figures 2.16 and 2.17 in section 2.3.

