Microscopic investigation of the emission efficiency of nanostructures

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Quantum yield

PL QY offers a simple and robust way to assess the emission efficiency of light emitting materials, such as fluorescent proteins, dyes and semiconductor QDs, and is defined by the ratio of the numbers of emitted and absorbed photons. Common methods of QY measurement employ an integrating sphere (IS) technique that has been standardized and is used commercially and for research. In this chapter we test the validity of this method, both experimentally (Section 2.3) and theoretically (Section 2.4) and show that the QY methodology suffers from an artifact. This artifact results in an underestimation of the QY and depends on the absorption of the studied sample. The effect is present already under common experimental conditions and is therefore highly relevant for a number of published studies, which employ the QY methodology. To correct for the intrinsic absorption-dependence of the QY determination, in Section 2.5 we propose a dedicated calibration protocol, enabling the correct evaluation and interpretation of the QY of samples with varying absorption. These findings are applied to determine the QY of different types of Si-QDs.

2.1 Introduction

As generally for lighting applications, a crucial property for fluorescent materials is the emission efficiency, which can be quantified by the PL QY, defined as the ratio of emitted to absorbed photons:

\[ QY = \frac{N_{em}}{N_{abs}}. \]  

To measure this ratio, various techniques exist [66, 67], many of which rely on the comparison with a calibration standard of which the QY is known. Since this requires a QY standard which has similar absorption and emission as the sample of interest and of which the QY must be precisely known, finding a suitable calibration material is challenging, especially when the sample scatters and when emission is anisotropic or spectrally broad. A direct optical method, originally introduced by de Mello et al. [68] in 1997, avoids the problems associated with the comparative methods by implementing an
integrating sphere (IS) (Figure 2.1a). The IS, a reflectively scattering cavity, allows the
direct determination of the absolute number of emitted and absorbed photons. Originally
implemented as a three-step measurement [68], this method was later simplified into a
two-step measurement [69], and involves the comparison of the calibrated emission and
absorption spectra of the studied sample to a suitable blank.

The IS technique gained popularity in the research and development of new fluorescent
materials. Moreover, it has been employed to study the size-dependent [12, 37, 70],
excitation-energy-dependent [71–74] and concentration-dependent properties [71, 75] of
QD systems. However, the broad application of the IS methodology in literature raises
questions on the validity of the determined QY values. Several guidelines exist for QY
measurements [76, 77], discussing e.g. the effects of re-absorption [78] and excitation
geometry [79, 80]. In this work we study the validity of the IS methodology, over a broad
range of excitation wavelengths and for different sample concentrations. Specifically, we
focus on the effect of low sample absorption which is typically encountered for Si-QDs.
We show both theoretically and experimentally that the IS methodology suffers from
an experimental artifact that gives rise to underestimated QY values. We propose a
correction procedure and quantitative guidelines for more reliable QY determination.
Finally we apply these findings to quantify the emission efficiency of Si-QDs.

2.2 Integrating sphere methodology

In the implementation of the QY method described by Mangolini et al. [69], a sample (e.g.
a cuvette containing a solvent in which emitting nanoparticles are dispersed) is suspended
inside an IS (Figure 2.1a). The sample is excited from the entrance port, where a fraction
$F$ of the excitation beam impinges directly on the sample. The IS’ highly reflective
coating ensures that all the transmitted excitation and emission photons are captured
and distributed over the IS’ interior. After multiple reflections and scattering events
within the IS, the excitation and emission photons are ultimately detected, (re-)absorbed
in the sample or lost (e.g. absorbed by the coating). The detected spectrum is compared
to that of a blank reference sample (e.g. the cuvette with solvent) as shown in Figure 2.1b
for the QY calibration dye Rhodamine 6G (R6G). From the difference (Figure 2.1c) in
the detected photons intensities at the excitation ($\lambda_{exc}$) and emission wavelength ($\lambda_{em}$),
$I$ and $I^*$ respectively, the numbers of absorbed and emitted photons can be evaluated:

$$QY = \frac{N_{em}}{N_{abs}} = \frac{N^*_S - N^*_R}{N^*_R - N^*_S} = \frac{\int^{\lambda_{em}} I^*_S(\lambda) - I^*_R(\lambda) \, C(\lambda) \, d\lambda}{\int^{\lambda_{exc}} I^*_R(\lambda) - I^*_S(\lambda) \, C(\lambda) \, d\lambda},$$

(2.2)

where subscripts $S$ and $R$ refer to the sample and reference measurements and $N$ and
$N^*$ to the total number of photons at the excitation and emission wavelength, respectively.
The factor $C(\lambda)$ corrects for the spectral sensitivity of the detector and IS, for which an
additional calibration measurement is performed using an empty IS and a calibration
source with a known spectrum.
2.3 Experimental limitations of the IS methodology

To study the experimental range in which the IS method yields reliable QY estimates, we measure the QY of three very different materials (an organic dye and two types of inorganic QDs) in a wide range of excitation wavelengths and for various material concentrations commonly encountered in literature. For this we use a standard IS geometry (shown schematically in Figure 2.1a), with the excitation provided by a stabilized Xenon lamp coupled via a double-grating monochromator into a spectrally broad optical fiber. Light is detected using a second spectrally broad optical fiber coupled to a spectrometer equipped with a charge-coupled device (CCD) camera (for a detailed description, see QY setup 1 in the Materials & methods section). Moreover, additional measurements were carried out in an independent QY setup in a different laboratory (see QY setup 2 in the Materials & methods section).

**Rhodamine 6G**

First we study R6G in ethanol (for details, we refer to Section A.1), which is a well-known fluorescent dye that is commonly used as a calibration standard for comparative QY measurements and has a reported QY of about 95% [81]. We prepared several solutions of R6G in ethanol, with concentrations between ∼120 and 6 µM. Within this range, the shape of the absorption coefficient spectrum is unaltered (Figure 2.2a), indicating the absence of clustering effects or other material changes [82]. Moreover, the PL lifetime in the studied range is independent of excitation wavelength and concentration (Figure 2.2b), showing that the internal emission efficiency is constant. The PL spectra show a strong dependence on the concentration as a result of re-absorption effects (Figure 2.2c). This is commonly encountered for materials with overlapping emission and absorption spectra (see e.g. [78, 82]). We corrected our results for re-absorption using the procedure...
described in detail by Ahn et al. [78].

**Figure 2.2:** (a) Absorption coefficient of different concentrations of R6G in ethanol. The inset shows the absorption coefficient normalized to the value at 500 nm wavelength. The flattening of the absorption peak around 530 nm with higher concentration is due to absorption saturation effects, since transmission is close to zero [83]. (b) Time-resolved PL intensity excited at 485 nm for a 120 µM (red) and 6.4 µM (green) concentration of R6G in ethanol. Inset: PL lifetimes for different concentrations under 440 nm (black) and 485 nm (red) wavelength excitation. The lifetimes are obtained from a mono-exponential fit yielding ~3.8 ns. (c) Normalized PL spectrum of different concentrations of R6G in ethanol under 480 nm excitation. With increasing concentration the PL spectrum red-shifts as a result of re-absorption. The dashed line shows the PL spectrum of a 1.6 µM concentration sample, measured outside of an IS, for which re-absorption effects are negligible.

QYs obtained at various R6G concentrations excited between 300 and 520 nm are shown in Figure 2.3. For the highest concentration of 120 µM, we find a QY of ~83-89 % that is almost constant over the whole spectral range, which is expected due to the Kasha-Vavilov rule. We note that the absolute QY value is somewhat lower than that found in literature [81], which will be discussed in Section 2.5. Interestingly, as the concentration decreases and hence also the sample’s absorption, the determined QY drops significantly, at some points to as low as 38 %. The same drop in QY is observed when the concentration is fixed and the excitation wavelength is lowered below ~460 nm, for which the absorption coefficient of R6G decreases significantly. In contrast, no decrease is observed for higher absorption ranges, such as near the resonant absorption peak at 530 nm.

The effect of the sample absorption becomes even more apparent when plotting the QY in a different manner, against the single-pass absorption of the sample, showing that the QY decreases significantly at low absorption, independently whether the absorption is lowered via the sample concentration or via the excitation wavelength (Figure 2.3b). At around a critical absorption value ($A_{crit}$) of 10-15% there is an abrupt change in the behavior of the QY, where for absorption above $A_{crit}$ the QY is constant and close to the literature value, but decreases continuously with the absorption for $A < A_{crit}$. The same decrease is observed when we fix the concentration and excitation wavelength and decrease the single-pass absorption of the R6G solution by only changing the optical path length through the sample by using a thinner cuvette, as shown in Figure 2.4. This shows that the effect is

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1In this thesis the single-pass absorption is defined as the fraction of absorbed light upon a single passage through the sample, i.e. similar to the absorptivity or absorptance.
2.3. Experimental limitations of the IS methodology

not intrinsic to the studied material and seems to depend only on the sample’s absorption.

Figure 2.3: QY of R6G. (a) Determined QY values as a function of the excitation wavelength for different sample concentrations between 120 and 6 µM. Data are corrected for re-absorption effects using the procedure described in [78]. Dashed black lines serve as guides to the eye, the solid lines represents the single-pass absorption of the highest and lowest concentration sample (right axis). For comparison with literature, the QY values as determined by Faulkner et al. [79] for a 100 µM (the higher QY value) and 1 µM (the lower QY value) solution of R6G in ethanol are plotted in blue. (b) QY values from (a) plotted against the single-pass absorption to illustrate the dependence of QY on absorption. Red points represent QY values obtained for different concentrations under 380 nm excitation wavelength. Blue points are from Faulkner et al. [79], where the single-pass absorption has been estimated from the concentration assuming an optical path length of 10 mm. The vertical dashed line indicates the critical absorption, \( A_{\text{crit}} \), below which QY is underestimated.

To check if the effect is caused by our specific implementation of the IS method, we measure the QY also under indirect excitation conditions \((F = 0)\). Interestingly in this case, the QY approaches 95% at high sample absorption, as expected for R6G. However, similarly to under direct excitation conditions \((F = 1)\), the QY is underestimated for decreasing absorption (Figure 2.5a and b).

Figure 2.4: (a) QY versus excitation wavelength of R6G in ethanol (black: \( \sim 260 \) µM, gray: \( \sim 22 \) µM) for a 10 and 2 mm optical path length through the sample. For one and the same sample lower QY values are obtained when the path length is reduced. Solid line shows the single-pass absorption of the samples. (b) QY plotted against the single-pass absorption. A similar trend is observed as in Figure 2.3b.

We carefully confirmed this effect also in an independent experimental configuration. For this we use an IS with a different internal geometry, a laser-driven light source which
gives improved stability and a liquid nitrogen-cooled CCD camera to reduce the detection noise (for more details, see QY setup 2 in the Materials & methods section). Again, both under indirect (Figure 2.5c and d) and direct excitation (Figure 2.6) the QY is underestimated, although we note that the critical absorption \( A_{\text{crit}} \) below which this occurs varies slightly between the different setups (vertical dashed lines).

**Figure 2.5:** (a) QY versus excitation wavelength of R6G in ethanol \((\sim 14 \, \mu\text{M})\) with the sample under direct \((F = 1, \text{blue})\) and indirect \((F = 0, \text{red})\) illumination conditions. The solid line shows the single-pass absorption of the sample. (b) QY from (a) plotted against the single-pass absorption. (c) Comparison of the QY of R6G in ethanol under indirect excitation conditions measured in two independent experimental setups: The red symbols show the same data as in panels a and b (red), the green data show the QY measured in a different setup (QY setup 2). (d) QY from (c) plotted against the single-pass absorption. The vertical dashed lines in b and d indicate \( A_{\text{crit}} \).

**QD materials**

In addition to R6G, we demonstrate the effect also on dispersions of two types of semiconductor QDs - Si-QDs and CdSe QDs (for sample details see Appendix A.1) - in Figure 2.7. Both materials have very different optical properties from each other and from those of R6G, such as emission efficiency, single-pass absorption and emission spectra (Figure 2.7a). The most notable difference is the broad absorption spectrum, resulting from the band-like dispersion relation in semiconductors. Also, Si-QDs have a larger Stokes shift and a less abrupt absorption onset than CdSe QDs due to the indirect band-structure. Nevertheless, independently of the differences with R6G, the QY of both types of QDs decreases with longer excitation wavelengths (Figure 2.7b), when absorption drops below \( A_{\text{crit}} \). Again, the effect is more pronounced for lower concentrations.
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Figure 2.6: QY of a $\sim 60 \mu M$ (black) and $\sim 6 \mu M$ (gray) solution of R6G in ethanol under direct excitation plotted against the excitation wavelength (a) and single-pass absorption (b). The vertical dashed line indicates $A_{\text{crit}}$. The measurements (courtesy of J. Valenta, Charles University) are carried out in an independent experimental setup (QY setup 2).

One might argue that the process of emission and absorption is more complex for QDs than for organic dyes such as R6G, and that therefore the validity of the Kasha-Vavilov rule might be weaker or not hold at all [71, 84]. With that line of reasoning, the observation of explicit QY dependence on various parameters could be interpreted in terms of novel effects [12, 37, 70–73, 75]. Another alternative - more conservative - explanation of the dependence would be that the size-polydispersity of QD ensembles can lead to a broadening of the emission spectrum [8], which in turn could lead to excitation wavelength dependent QY via excitation of different subsets of the QD ensemble. Additionally, the concentration of QD dispersions is expected to affect QD interactions [71, 85], which strongly depend on the inter-particle distance. Nonetheless, when plotting the QY of the QDs versus their absorption (Figure 2.7c), the resemblance with the trend observed for R6G is striking in terms of the shape of the QY-dependence and the value of $A_{\text{crit}}$, suggesting that the excitation- and concentration-dependence is for the largest part described by the presented effect.

Figure 2.7: (a) Absorption coefficients and PL spectra (dashed lines) for three types of samples: R6G in ethanol (black), Si-QDs in toluene (red) and CdSe QDs in hexane (blue). (b) QY against the excitation wavelength of CdSe QDs and Si-QDs. The QY of Si-QDs below 360 nm is omitted because the solvent is non-transparent in this spectral region. (c) The QY of the CdSe and Si-QDs from (b) and of R6G (Figure 2.3) against the single-pass absorption. The dashed lines serve as guides to the eye, showing a similar trend of the QY independent of the studied material. The critical absorption is indicated by the vertical dashed line.
Conclusion

In summary, we have shown that we observe the same decrease of the QY when the single-pass absorption of the sample is lowered, either by lowering the sample’s concentration, excitation wavelength or by shortening the optical path and which shows independently of the experimental conditions, studied material and particular setup. Hence we conclude that it is an experimental artifact that manifests itself independently of the particular setup geometry or implementation of the IS methodology. The artifact generally occurs for materials with absorption in the range $A < A_{\text{crit}}$, where the QY value becomes critically underestimated as the absorption decreases. To the best of our knowledge, this artifact has not been noticed in the literature until now, despite the fact that, as we demonstrate here, it also occurs for well-known materials such as R6G in ethanol, which is commonly used as a calibration standard for QY measurements. For R6G, the artifact could have passed unnoticed due to the absence of broad studies in which the absorption is considerably varied through the excitation wavelength or concentration, such as reported here. Studies reporting on the QY of R6G typically probe only the excitation maximum situated around 530 nm wavelength [82, 86, 87], or show the QY only for a few concentrations [79], from which the artifact is not directly apparent. Hence, the absorption-dependence of the QY has not been identified as an artifact of the QY methodology and could have been misinterpreted in terms of physical effects. Nevertheless, when we add literature values obtained by Faulkner et al. [79] for two concentrations of R6G to our results in Figure 2.3, we find excellent agreement. This shows that while the artifact is not identified, it is present in other studies as well. Hence, even more for other materials that are not expected to fulfill the Kasha-Vavilov rule such as QD systems [12, 37, 70–73, 75], this effect has passed unnoticed. Therefore, it could have affected the conclusions drawn based on the excitation wavelength, concentration and QD-size dependence of the QY, all cases in which also the sample’s absorption is varied.

2.4 Theoretical model of the QY methodology limitations

2.4.1 Analytical model

For a detailed analysis of the artifact described in Section 2.3, we simulate the QY experiment in the IS setup using an analytical model (AM). For this we express the measured photons intensities $I$ in Equation 2.2, used to compute the QY, in terms of the probability that emission and excitation photons reach the detector port via multiple reflections within the IS.

To obtain an analytical expression, we generalize the IS and model it as a cavity with two small openings: an entrance port from which excitation light enters and an exit port equipped with a detector, as shown in Figure 2.8. The sample or reference is modeled as a spherical object in the center of the sphere with an absorption $A$, reflection $R$ and
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transmission \( T \), where \( A + R + T = 1 \). The interior of the IS is covered by a coating that is highly reflective over a broad spectral range \( R_w \) (usually > 97%) and acts as an ideal scatterer, i.e. the directionality of the light is lost after a single reflection from the walls. We model this by assigning a probability \( p \) that a photon impinges on an object inside the IS, by the relative area of the object to the area of the IS interior. For example the probability of hitting the wall \( (p_w) \), loss channel \( (p_l) \), detector \( (p_d) \) or sample \( (p_s) \), with \( 1 = p_l + p_d + p_s + p_w \). Since the ideally scattering walls ensure the spatially homogeneous distribution of the photons, we assumed for our generalized geometry that these probabilities do not depend on the exact location in the IS at which the photon scatters from the wall. However, the directionality of the light, which starts from a single point (i.e. excitation from the entrance port and emission from the sample) is not lost before it reflects of the ideally scattering coating. To account for this in our simulations, we separate the first round before the light reflects of the wall \( (n = 1) \) from the consequent ones \( (n \geq 2) \) (see Figure 2.8). We do this by assigning modified probabilities \( p_{0x} \) of hitting objects inside the IS, given by their visibility from the entrance port and sample. Again, \( 1 = p_{0l} + p_{0d} + p_{0s} + p_{0w} \) and \( 1 = p_0^* + p_0^* + p_0^* \). \( p_{0s} \) represents the fraction of the initial excitation light intensity, \( I_{\text{exc}}^0 \), that hits the sample directly, a parameter that is commonly varied in literature [68, 79, 80]. To separate this parameter from the other probabilities, we set \( p_{0s} = F \), where \( F = 1 \) for direct or \( F = 0 \) for indirect excitation conditions. Furthermore, in accordance with the standard IS methodology, direct detection of the excitation and emission photons is prevented by an inserted baffle, simulated by setting \( p_{0sd} = p_{sd} = p_{0d} = p_{0d}^* = 0 \) (dashed lines in Figure 2.8). For completeness, we finally assume that the measurement is in a regime in which the QY is independent of the excitation photon flux.

From the light paths illustrated in Figure 2.8 and their probabilities \( p_x \), we simulate the transmitted excitation intensities during the first \( (n = 1) \) up to the \( n \)-th reflection:

\[
I_1^{\text{exc}} = I_0^{\text{exc}}[p_{0w} + F(1 - A)p_{0sw}]R_w \\
I_2^{\text{exc}} = I_1^{\text{exc}}[p_w + p_s(1 - A)p_{sw}]R_w \\
I_3^{\text{exc}} = I_2^{\text{exc}}[p_w + p_s(1 - A)p_{sw}]R_w \\
\vdots \\
I_n^{\text{exc}} = I_{n-1}^{\text{exc}}[p_w + p_s(1 - A)p_{sw}]R_w = I_0^{\text{exc}}[p_{0w} + F(1 - A)p_{0sw}]R_w \\
\cdot \{[p_w + p_s(1 - A)p_{sw}]R_w\}^{n-2}.
\]

Here, \( p_{0sw} \) and \( p_{sw} \) indicate the probabilities of light passing through the sample and hitting the wall for the first and consecutive reflections, respectively. Similarly, we evaluate the absorbed intensity \( (I^{abs}) \) by the sample/reference and the intensity recorded
by the detector ($I^{det}$) at the exit of the IS by:

\[
I_{1}^{abs} = I_{0}^{exc} FA \\
I_{n}^{abs} = I_{n-1}^{exc} p_s A \\
I_{1}^{det} = I_{0}^{exc} [p_{0d} + F(1 - A)p_{0sd}] \\
I_{n}^{det} = I_{n-1}^{exc} [p_{d} + p_{s}(1 - A)p_{sd}].
\]

Figure 2.8: Schematics of the generalized IS setup used for our model. The IS cavity has a small entrance on the left side and an exit on the bottom side, where a detector is placed. The sample/reference is modeled as a spherical object suspended in the center. Lines represent the light paths between different objects inside the IS - wall (w), loss channel (l), detector (d) and sample (s). The parameters $p_{xy}$ represent the probabilities associated with each specific light path. Light paths shown in dashed lines are prevented by baffles. The light paths before the first reflection from the IS wall ($n = 1$) are considered separately to account for the inhomogeneity of the light field in that instance. This differs for excitation light (entering from outside) and emission (originating from the center). Emission (red lines) is assumed separately from the excitation (blue lines) due to different spectral ranges, where the reflectivity of the sphere and the sample’s absorption differ.

For the emitted light intensity ($I_{em}$) and its fraction recorded by the detector ($I^{det*}$), we consider a different reflectivity of the IS coating $R_w^*$ and an effective sample absorption $A^*$:

\[
I_{1}^{em} = I_{0}^{em} p_{0w} R_{w}^{*} \\
I_{n}^{em} = I_{n-1}^{em} R_{w}^{*}[p_{w} + p_{s}(1 - A^{*})p_{sw}]
\]
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\[
I_{\text{det}}^{\text{em}} = I_{\text{det}}^* = I_{\text{em}}^0 p_{0d} \\
I_{\text{det}}^{\text{em}} = I_{\text{em}}^0 [p_d + p_s (1 - A^*) p_{sw}].
\]

To account for re-absorption and subsequent re-emission, \( A^* \) is defined as \( A^* = A(\lambda_{em}) \cdot (1 - \eta) \). Here, \( \eta \) is the ‘real’ QY of the sample, i.e. the intrinsic QY unaffected by the measurement method, so that \( A^* \) gives the fraction of emission light that is absorbed by the sample, but not re-emitted. The initial emission intensity originating from the sample is given by \( I_{\text{em}}^0 = I_{\text{abs}}^{\text{tot}} c \eta \), where \( I_{\text{abs}}^{\text{tot}} \) is the total excitation intensity absorbed in the sample and \( c \) is the fraction of light absorbed by the emitters in the sample (i.e. \( c < 1 \) when the emitters are dispersed in an absorbing matrix or solvent). The total absorbed intensity by the sample during the measurement is calculated by summation of \( I_{\text{abs}}^{\text{tot}} \) over all reflection-steps. Using the geometric series, \( \sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \), we obtain:

\[
I_{\text{det}}^{\text{tot}} = \sum_{n=1}^{\infty} I_{\text{det}}^{\text{em}} = \sum_{n=1}^{\infty} \left[ I_{\text{exc}}^0 \left( p_{0d} + F (1 - A) p_{0sd} + R_w [p_{0w} + F (1 - A) p_{0sw}] \right) \frac{p_d + p_s (1 - A p_{sd})}{1 - R_w [p_w + p_s (1 - A) p_{sw}]} \right] (2.3)
\]

\[
I_{\text{tot}}^{\text{abs}} = \sum_{n=1}^{\infty} I_{\text{abs}}^{\text{em}} = \sum_{n=1}^{\infty} \left( I_{\text{exc}}^0 A \left( F + R_w [p_{0w} + F (1 - A) p_{0sw}] \right) \frac{p_s}{1 - R_w [p_w + p_s (1 - A) p_{sw}]} \right) (2.4)
\]

\[
I_{\text{tot}}^{\text{det}^*} = \sum_{n=1}^{\infty} I_{\text{det}^*}^{\text{em}} = \sum_{n=1}^{\infty} \left( I_{\text{exc}}^0 \left( p_{0d} + p_{0w} R_w^* \frac{p_d + p_s (1 - A^*) p_{sd}}{1 - R_w^* [p_w + p_s (1 - A^*) p_{sw}]} \right) \right) (2.5)
\]

To evaluate the spectral sensitivity correction factors \( C \) and \( C^* \) we assume an empty sphere \((A = 0)\) and compare the theoretical intensity, equal to the input intensity at the sphere entrance \( I_{\text{exc}}^0 \), with the detected intensity at the sphere exit. This is done separately for excitation and emission wavelengths, where in the latter case we replace \( R_w \) by \( R_w^* \):

\[
C = \frac{I_{\text{exc}}^0}{I_{\text{det}}^{\text{em}} (A = 0)} = \left[ p_{0d} + F p_{0sd} + R_w (p_{0w} + F p_{0sw}) \frac{p_d + p_s p_{sd}}{1 - R_w (p_w + p_s p_{sw})} \right]^{-1}. (2.6)
\]

For common IS conditions, such as a non-absorbing reference \((A_r = 0)\), no re-absorption \((A_S^* = 0)\) and inserted baffles \((p_{0d} = p_{0sd} = p_{0w} = p_d = p_{sd} = 0)\), the number of emitted \( N_{em} \)
and absorbed \( N_{\text{abs}} \) photons in Equation (2.2) can be expressed as:

\[
N_{\text{em}} = I_0^{\text{exc}} \left[ F + (p_{0w} + F(1 - A_S)p_{0sw})M p_s \right] A_S \eta \frac{p_{0w}M^* p_d}{(p_{0w} + F p_{0sw})M_{\text{cal}}^* p_d} \tag{2.7}
\]

\[
N_{\text{abs}} = I_0^{\text{exc}} \left[ 1 - (p_{0w} + F(1 - A_S)p_{0sw})M p_d \right] \tag{2.8}
\]

\( M \) and \( M^* \) are "sphere-multipliers", defined as \( M = R_w(1 - R_w[p_{0w} + p_s(1 - A)p_{0sw}])^{-1} \) and \( M^* = R_w^*(1 - R_w[p_{0w} + p_s(1 - A)p_{0sw}])^{-1} \) and describe how light is distributed over the IS interior and the objects inside it [77]. For the calibration measurements, \( M_{\text{cal}} = M(A = 0) \) and \( M_{\text{cal}}^* = M^*(A = 0) \). Assuming that loss channels are small, \( p_{0w} = 1 - F - p_{0l} \sim 1 - F \), Equations 2.7 and 2.8 reduce to the QY descriptions found elsewhere [68, 77, 79], which justifies the described approach. Our model enables one to express the measured QY in terms of the intrinsic QY of the studied material.

### 2.4.2 Ray-tracing simulations

In collaboration with the Computer Graphics Group from the Charles University\(^2\) we verify our AM using numerical ray-tracing simulations (RTS), described in Appendix A.2. In contrast to the AM, different photon paths are individually considered in the RTS approach, thus yielding solutions even for non-uniform photon distributions and IS geometries. Although the RTS approach is computationally more demanding, it enables us to model the setup more precisely.

We simulate the QY for an IS setup for a sample with a QY of \( \eta = 45\% \) and for a non-absorbing and non-emitting reference sample, i.e. \( N_{\text{Ref}}^* = 0 \). The results are shown in Figure 2.9a. Both models give QY estimates that are in excellent agreement with the input emission efficiency \( \eta = 45\% \), for single-pass absorption values between 1 and 100\%. Moreover, the QY estimate is independent of the reflectivity of the IS in the range between 0.9 and 1.0, which is properly accounted for through the spectral sensitivity correction.

The simulated number of absorbed \( (N_{\text{abs}}) \) and emitted \( (N_{\text{em}}) \) photons used to compute the QY, normalized to the total number of excitation photons \( (N_0^{\text{exc}} = \int I_0^{\text{exc}} dt) \), are shown in Figure 2.9b and c. The fraction of absorbed photons decreases roughly proportional to the single-pass absorption of the sample as shown in Figure 2.9b (solid lines). However, it is slightly increased with respect to the single-pass absorption, as a consequence of the multiple light passages through the sample, which shows especially when the reflectivity of the sphere is high (second term in Equation 2.7). The fraction of emitted photons (dashed lines) have a similar dependence on the single-pass absorption, but start at a lower value due to the QY used for these simulations \( (\eta = 45\%) \). Again, there is good agreement between the AM and RTS, from which we conclude that the generalizations made to derive the AM are well justified. Nevertheless, neither of the simulation approaches appears to exhibit an explicit bias in the QY for low absorption.

\(^2\)Courtesy of MSc. I. Kondapaneni, Dr. A. Wilkie and Dr. J. Krivanek (Charles University, Prague Czechia)
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values. This is further investigated in the following section.

![Figure 2.9](image)

**Figure 2.9:** (a) Simulated QY against the single-pass absorption, using the RTS approach (symbols) and the AM approach (solid line) for a sample with a QY, \( \eta = 45\% \). For the simulations, we used an IS with a diameter of 10 cm and set the diameter of the sample, input port and output to 1 cm, 4 mm and 1 mm respectively. Different values of the reflectivity of the IS are shown by colors for the RTS approach. For the AM approach these curves overlap perfectly and only a single value is plotted. (b,c) Simulated number of absorbed (b) and emitted (c) photons, normalized by the number of excitation photons \( N_{exc}^0 \), against the single-pass absorption. The solid black lines indicate a linear dependence. RTS courtesy of MSc. I. Kondapaneni and co-workers (Charles University, Prague, Czechia).

### 2.4.3 Bias resulting from experimental uncertainty

In our theoretical description so far the photon fluxes exiting the IS are described relative to the input photon flux \( I_{exc}^0 \) provided by the excitation source. In such a theoretical framework, the experimental uncertainties \( \alpha \) associated with the detected number of emitted and absorbed photons \( (N_{em}, N_{abs}) \) are usually assumed to contribute proportionally to the uncertainty in the determined QY [77, 88]:

\[
\alpha_{QY}^2 = \alpha_{N_{em}}^2 + \alpha_{N_{abs}}^2,
\]

where \( \alpha \) is the relative uncertainty of the variable. However, this approach might not reflect the uncertainty of a multi-variable function with a skewed, asymmetric distribution function, e.g. as a result of the distribution of the input variables [89].

To investigate the distribution function of the QY, we account for the measurement uncertainties associated with the number of detected excitation and emission photons in Equation 2.2. To do so, we describe those variables by a distribution function centered at the expected values predicted by our AM approach (Equations 2.3 and 2.5) as illustrated in Figure 2.10. The peak of the distribution indicates the most-likely sampled value of the variable (also known as the ‘mode’), whereas the standard deviation of the distribution \( \sigma \) indicates its fluctuations.

We study the error propagation in a our QY geometry described in Section 2.3, where we assume the reference sample to be non-absorbing and non-emitting \((A_R = 0 \text{ and } N_{Ref}^* = 0)\). We investigate two types of distributions to cover commonly encountered measurement uncertainties: a Poisson and normal distribution. The Poisson distribution is used to describe shot noise, which arises from the discrete nature of photons. This type of noise will show especially for low flux signals since the signal-to-noise ratio
increases with $\sqrt{N}$. For high $N$ the Poisson distribution can be well described by a normal distribution, which we use to model additional measurement uncertainties that arise e.g. from mechanical/electronic stability of the detection and excitation chains. The normal distribution thus describes a more general situation in which the relative uncertainty can be set independently of the flux.

![Figure 2.10: Normalized histograms of the detected number of emission ($N_{em}$) and excitation photons $N_S$ and $N_{Ref}$ for a sample absorption of 6%. The vertical dashed lines indicate the expected, noiseless quantities. A total number of $\sim 10^7$ excitation photons was used for the simulations.]

**Poisson distribution**

First, we study the effect of Poissonian distributed variables, given by $P(\mu, k) = \frac{\mu^k e^{-\mu}}{k!}$, where $\mu$ is the expected (mean) value and $P(\mu, k)$ the probability of measuring a value $k = 0, 1, 2, 3, \ldots$. We add this noise to the simulated numbers of detected photons (Equation 2.2) $N_S$, $N_S^*$ and $N_{Ref}$ by drawing semi-randomly from a Poisson distribution, $P(N_S, k)$, $P(N_S^*, k)$ and $P(N_{Ref}, k)$, as illustrated in Figure 2.10. We vary the relative uncertainty in the variables $\alpha = \sigma/\mu$, which goes with $\sim 1/\sqrt{N}$ for a Poisson distribution, via the single-pass absorption of the sample ($A_S$) and the total number of excitation photons ($N_{exc}^0$). The resulting QY distributions are shown in Figure 2.11 and 2.12a. For a relative uncertainty of 1% and for high sample absorption, the simulated QY distribution lies symmetrically around the expected QY value as shown in Figure 2.11 (dashed vertical line). The peak of the distribution, i.e. the value that will be most likely sampled in a single QY measurement, is in good agreement with the expected QY. Upon decreasing absorption, however, the distribution broadens and becomes asymmetric. The most-likely QY value shifts towards lower, underestimated values with respect to the expected mean QY value. For absorption of 1%, the most-likely QY is underestimated by more than a factor of 2, i.e. 200%. The absorption value for which a QY measurement yields underestimated values strongly depends on the relative uncertainty of the measurement, as shown in Figure 2.12a. For $\alpha = 0.1\%$, obtained under a high number of excitation photons ($N_{exc}^0 \sim 10^9$), the most-likely QY agrees very well with the expected QY, independently of the absorption of the sample. However, already for relative uncertainties of 0.5% ($N_{exc}^0 = 5 \cdot 10^7$), the QY estimate agrees with the expected QY only for absorption above $\sim 5\%$. For even higher uncertainties of 1% ($N_{exc}^0 \sim 10^7$), the absorption limit is as high as $\sim 15\%$. 

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2.4. Theoretical model of the QY methodology limitations

Figure 2.11: Simulated effect of shot noise on the QY: Normalized histograms of simulated QY values for different sample absorption. When absorption is high, the distribution of obtained QY values lies symmetrically around the noiseless QY value of 80% (dashed line). For decreasing absorption, the distribution shifts towards lower QY values and becomes asymmetric. A total number of $\sim 10^7$ excitation photons was used for the simulations.

To investigate if the noise affects mainly the estimated number of emitted or absorbed of photons, we break down the QY estimate and compute the fraction of emitted $N_{em}/N_{0}^{exc}$ and absorbed photons $N_{abs}/N_{0}^{exc}$, used to evaluate the most-likely QY value. The dependence of the fraction of emitted photons on the single-pass absorption is retained in the presence of measurement uncertainty and is in excellent agreement with the noiseless value (dashed colored lines in Figure 2.12b). In contrast, the fraction of absorbed photons is unaffected by the noise only when the single-pass absorption value is high with respect to the relative uncertainty (solid colored lines) and is overestimated compared to the noiseless estimate when the single-pass absorption is low. The overestimation in the absorption coincides with the underestimation of the QY. This suggests that the denominator in the QY definition, i.e. the number of absorbed photons, is critically affected by the measurement uncertainty and leads to the QY underestimation. Conversely, our findings show that the 'noisiness' of the nominator, i.e. the number of emitted photons, is not relevant.

Normal distribution

Next, we investigate normally distributed variables, given by $G(\mu, k, \sigma) = e^{-\frac{(k-\mu)^2}{2\sigma^2}}$. Here $\mu$ is the expected (mean) value and $\sigma$ the standard deviation as before. The results for a typical range of experimental uncertainties between 0.1 and 1% are shown in Figure 2.12c and d. Again, when the relative uncertainty is small ($\alpha \sim 0.1\%$) the simulated most-likely QY is in good agreement with the predicted value for a noiseless 'ideal' measurement. However, already for a relative uncertainty of $\alpha \sim 1\%$, the QY is underestimated (Figure 2.12c). Like in the case of the Poissonian distribution, this is accompanied by an overestimation of the number of absorbed photons (Figure 2.12d), whereas the number of emitted photons is determined correctly.

Analysis of both types of variable distributions shows that the QY estimation depends on the relative uncertainty of the measured photon intensities, but not on the specific type of noise (Figure 2.12). Indeed, for sufficiently high counts, a Poisson distribution can be well approximated by a normal distribution: $P(\mu, k) \sim G(\mu, k, \sqrt{\mu})$. Hence for a fixed
value of $\alpha$, any differences in our simulations between both distributions are expected to disappear. Only for $\mu \ll 50$, the Poisson distribution is clearly asymmetric, from which an additional bias could arise as was shown by Park et al. [89] for quantities defined by a ratio $X/Y$. However, in typical QY experiments the recorded counts $N_{\text{Ref}}$ and $N_S$ are usually very high ($10^5$ counts or more) and can otherwise easily be increased, either by extending the measurement time or by multiple runs of the same measurement. Therefore, the scenario where (Poissonian) shot noise dominates the signal is unlikely in practice.

Regarding the source of the bias, Figure 2.12 suggests that it arises purely from the relative uncertainty $\alpha = \sigma/\mu$ of the distribution, since the QY is underestimated especially when the fluctuations are high (i.e. comparable to the absorption of the sample, $\alpha \sim A_S$). The full dependence of the QY on the relative uncertainty is shown in Figure 2.13a for a sample with a single-pass absorption $A_S = 5\%$. When $\alpha$ is small compared to the absorption $\alpha/A_S < 10\%$, the QY is in good agreement with the unbiased result. However, for $\alpha/A_S$ larger than 10% (yellow area) the QY is increasingly underestimated. For $\alpha$ equal to the sample’s single-pass absorption, the QY is already underestimated to 50% of the unbiased value. A nearly identical curve is obtained for an arbitrary absorption value, even for absorption close to 100% (green curve). This shows that it is the ratio of the relative uncertainty and the sample absorption that plays a crucial role in the
underestimation of the QY and in the overestimation of the fraction of the number of absorbed photons \( N_{\text{abs}}/N_{\text{exc}}^0 \) (Figure 2.12b and d).

Figure 2.13: (a) Simulated most-likely QY against the relative measurement uncertainty, normalized to the sample’s single-pass absorption \( A_S = 5\% \), black line; \( A_S = 100\% \), green line). The measurement uncertainty is introduced by assuming a normal distribution of the variables. The arrows indicate the QY values corresponding to a relative uncertainty of \( \alpha = 0.1\% \) (red) and \( \alpha = 2\% \) (black). The shaded area indicates the FWHM and the horizontal black line indicates the noiseless QY value. For a relative noise level larger than 10\% of the single-pass absorption value, the QY is underestimated as indicated by the yellow area. (b) Simulated distribution of \( N_{\text{Ref}}, N_S \) and \( N_{\text{abs}} = N_{\text{Ref}} - N_S \) for a single-pass absorption of 5\% and a relative measurement uncertainties of 2\% (black) and \( \sim 0.1\% \) (red). The vertical dashed lines indicate the noiseless values.

Importantly, in the ideal case, in which noise is absent, the IS methodology itself does not yield biased results. Only when we account for measurement uncertainty in the simulated numbers of detected photons, predicted by Equations 2.3 and 2.5, the bias arises. This is illustrated in Figure 2.13b, where we show the simulated detected number of excitation photons \( N_{\text{Ref}} \) and \( N_S \) for a sample with single-pass absorption of \( \sim 5\% \). When the uncertainty in both variables is small (red curves), the number of absorbed photons \( N_{\text{abs}} = N_{\text{Ref}} - N_S \) can be precisely determined and the measurement yields a precise QY estimate (red arrow in Figure 2.13a). However, when the uncertainty in \( N_{\text{Ref}} \) and \( N_S \) approaches the difference between them, the distribution of \( N_{\text{abs}} \) broadens (black curves in Figure 2.13b) and the most-likely obtained QY value becomes underestimated (black arrow in Figure 2.13a). Hence, we conclude that the bias results purely from the relation from which the QY and, in particular the absorption part of the QY, is determined: \( QY \propto 1/(N_{\text{Ref}} - N_S) \). The bias is thus not specific to the QY methodology, but will show for any similarly defined quantity. This general impact of our findings will be discussed further in the next sections.

2.5 Comparison of model and experiment

We now combine our experimental and theoretical findings and use the AM and RTS approaches to simulate our specific experimental setup used to measure the QY of R6G in Section 2.3. First we compare the experimentally determined QY with the simulated values under ideal conditions, i.e. in the absence of experimental uncertainty (Figure 2.14a). The AM approach yields a flat QY dependence for single-pass absorption between 1 and 100\%, preserving the input value of the material’s QY of 95\% expected
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for R6G [81]. The RTS approach yields also a flat QY dependence, but with a slightly underestimated QY of \( \sim 87\% \). This predicted lower value for R6G is in good agreement with our experimentally determined values for absorption above 15\% (Figure 2.14a), showing the strength of the RTS approach for modelling of the IS set-up. From detailed analysis using RTS, it appears that the slight underestimation is related to the specific geometry of our IS setup, which contains home-built aluminum parts that serve as holders for the cuvette and the fibers. Indeed, when we replace the aluminum in our RTS by a Lambertian scatterer, we obtain a QY of 95\% (blue empty triangle in Figure 2.14a). Nonetheless, neither of the two simulations approaches shows a dependence of the QY on the sample’s absorption and, hence, the artifact cannot be explained by the standard IS theory.

We then separately analyze the measured fractions of emitted and absorbed photons which are used to evaluate the QY (Equation 2.2). Both fractions decrease roughly linearly proportional to the single-pass absorption of the sample, as shown in Figure 2.14b. This linear dependence holds over the full studied single-pass absorption range for the
emitted fraction (green symbols), whereas it deviates from the linear dependence for the absorbed fraction (black symbols), when the single-pass absorption drops below \( \sim 15\% \). This value coincides with the critical absorption \( A_{\text{crit}} \), below which we observe a decrease in the QY (dashed vertical line in Figure 2.14). Since the experimentally observed fraction of absorbed photons deviates from the simulated fraction (red line Figure 2.14b), whereas it is in good agreement for the emitted fraction (dashed red line), we conclude that the absorption is overestimated with respect to the IS theory, which gives rise to the underestimated QY values.

The dependence of the QY on the sample’s absorption is very similar to the behavior of the QY in the presence of experimental uncertainties, observed in our simulations (Section 2.4). Therefore, we compare the experimental QY values to the simulated results, where we take into account the effect of measurement uncertainties on the estimated QY value (Figure 2.14c and d)). For this we assume normally distributed variables, with a relative uncertainty of \( \alpha \sim 1\% \), a magnitude that is reasonable when compared to the typical uncertainties estimated for our setup (Figure 2.15a). The normal distribution of the measured variables is justified by the limited dependence of the measured QY on the detected number of photons (Figure 2.15b), showing that Poissonian distributed shot noise is not the dominant source of the experimental uncertainty.

**Figure 2.15:** (a) Estimated relative uncertainty \( \alpha = \sigma/\mu \) against the excitation wavelength for the two different experimental setups used in Section 2.3. The measurement uncertainty has been estimated from multiple measurements of the total number of detected excitation photons in the reference measurement (\( N_{\text{Ref}} \)) and from the fluctuations in the lamp intensity between different measurements (red squares). (b) Measured QY of R6G in ethanol (\( \sim 1.6 \) \( \mu \)M) against the detected number of excitation photons \( N_{\text{Ref}} \) under 440 nm wavelength excitation. \( N_{\text{Ref}} \) is changed by varying the acquisition time between 5 and 180 seconds. The measured QY is independent of \( N_{\text{Ref}} \), as indicated by the shaded guide area.

Unlike the simulations with noiseless quantities (red lines in Figure 2.14a and b), incorporation of the measurement uncertainty in our simulations gives good quantitative agreement with the observed experimental QY values (black curve in Figure 2.14c and d). This applies not only above the critical absorption \( A_{\text{crit}} \sim 15\% \) where the standard approach holds, but also below \( A_{\text{crit}} \) where the artifact is strongly present (Figure 2.14a and b). It also separately describes very well the overestimation of the fraction of absorbed photons (Figure 2.14d) as the cause of the QY underestimation and confirms the negligible influence of the fraction of emitted photons and its associated uncertainty.
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Furthermore, in the limit of disappearing uncertainties, the model converges to the ideal flat QY-dependence (Figure 2.14c, blue curve), where the assumption of proportionally increasing uncertainty in the QY estimate holds [77, 88]. We conclude that the non-linear propagation of error is indeed the source of the underestimated QY artifact.

Importantly, as shown in Section 2.4, the bias resulting from the experimental uncertainty is purely a consequence of the definition of the QY, i.e. $QY = \frac{N_S^*}{(N_{Ref} - N_S)}$. Hence, the presented experimental artifact is not limited to the IS implementation of the QY methodology, but applies to the QY methodology in general. We thus predict the artifact also for comparative and relative measurements, where the QY is obtained from separate measurement of the number of emitted and absorbed photons, the latter of which is determined by comparison of a sample with a blank reference (such as Equation 2.2). Our findings thus demonstrate the urgent need for a remedy.

2.6 Corrected QY methodology

For reliable QY determination first the critical absorption value $A_{crit}$ needs to be quantified for each specific QY setup. It is determined by the absorption of the sample and the uncertainty in the detected number of photons as shown in Figure 2.16, where we plot the general dependence of the QY on the fraction of absorbed photons $(N_{Ref} - N_S)/N_{exc}^0$ and relative measurement uncertainty $\alpha$. The critical absorption, below which the QY estimate becomes unreliable, is designated by the white dotted line in Figure 2.16. Based on the relative uncertainty associated with each specific experimental setup, the critical absorption can be easily estimated. As a rule of thumb $A_{crit}$ is roughly given by 10 times the value of the measurement uncertainty. As we have stressed before, the same dependence holds for any quantity in the general form $Z/(X - Y)$, when the uncertainty in $X$ and $Y$ becomes larger than $\sim 10\%$ of the value of $(X - Y)$ (Figure 2.16).

![Figure 2.16: QY (color bar) as a function of the absorption of the sample $(N_{Ref} - N_S)/N_{Ref}^0$ and relative uncertainty in the $N_{Ref}$ and $N_S$ estimates. The dashed white line indicates the threshold below which the QY is unreliable. This holds for any quantity given by the general relation $Z/(X - Y)$ where $(X - Y)/X^0$ is compared to the uncertainties associated with $X$ and $Y$.](image)
2.6. Corrected QY methodology

The critical absorption can also be determined experimentally, by measuring the QY of a reliable QY calibration standard, such as a high purity R6G dissolved in ethanol, in a wide range of absorptions reaching below and above \( A_{\text{crit}} \), such as shown in Figure 2.14a. Our results in Section 2.3 show that \( A_{\text{crit}} \) can be expected to be around 5-15% in a typical IS setup, so that the measured range should be for absorption between 1 and 30%. This absorption range can be accessed either by varying (i) the excitation wavelength, (ii) the standard’s concentration and/or (iii) the standard’s optical thickness, or even by a combination of the above since the artifact manifests itself independently of how the absorption is changed. Separately, one needs to ensure that the internal properties of the used standard remain unaffected within the measured range, by testing it for constant emission lifetime and absorption spectrum. The setup-characteristic critical absorption \( A_{\text{crit}} \) is given by the absorption for which the measured QY deviates from the expected constant value, such as shown in Figure 2.14a. In the next step, the QY of the sample of interest (\( QY_{S}^{\text{meas}} \)) is measured, from which a more reliable QY estimate (\( QY_{S}^{\text{cor}} \)) can be obtained in the range \( A < A_{\text{crit}} \), by comparison of the obtained QY dependence of the calibration standard \( QY_{\text{Cal}}(A) \), with the unbiased value \( QY_{\text{Cal}}(A > A_{\text{crit}}) \):

\[
QY_{S}^{\text{cor}}(A) = QY_{S}^{\text{meas}}(A) \frac{QY_{\text{Cal}}(A > A_{\text{crit}})}{QY_{\text{Cal}}(A)} \tag{2.9}
\]

We applied this correction procedure to the QY measurements presented previously in Figure 2.17. Indeed, the vast majority of the observed spectral and concentration dependence of the QY in Figure 2.7 can be explained by the described artifact. Our proposed procedure corrects for this, and therefore ensures reliable QY estimates in a much broader range of experimental conditions and sample variations. Alternatively, as follows from the statistical nature of this effect, the artifact might be resolved by taking a taking higher number of QY measurements, the average value of which will tend more towards the expected value of the unbiased QY.

![Figure 2.17: QY versus excitation wavelength, before (a) and after (b) correction for the absorption dependence of the QY methodology using Equation 2.9. Different symbols represent different sample concentrations (see Figure 2.3 and 2.7). After correction, the QY of the Si-QDs is constant at \( \sim 45\% \) and independent of the sample concentration. Part of the excitation and concentration dependence of the QY of the CdSe QDs persists after correction, potentially related to the ligands on the surface [74, 75, 90, 91]. The correction function was obtained by taking a moving average of the QY versus single-pass absorption dependence of R6G in Figure 2.14b. For reference, the corrected QY for the R6G is also shown.](image-url)
2.7 QY of Si-QDs

We apply the corrected QY methodology to different types of organically passivated Si-QDs, shown in Figure 2.18. For C:Si-QDs emitting below 600 nm wavelength the QY is limited to $\sim 20\%$, whereas for Si-QDs emitting in the near-IR the QY is much higher, between 45 and 65%. For intrinsic PL of Si-QDs, the increase of the QY with emission wavelength is commonly observed in literature (for an overview, see Dohnalova et al. [5]), which is typically argued to be the consequence of the increased number of surface defects with smaller Si-QDs [5, 12, 37, 38]. Our results are in good quantitative agreement with this trend (illustrated by the shaded area in Figure 2.18). In the next chapters, we will elaborate on the emission efficiency limit for the visible range emitting Si-QDs.

![Figure 2.18](image)

Figure 2.18: Corrected QY estimates against the peak emission wavelength of different types of organically passivated Si-QDs samples: Allylamine-terminated Si-QDs (am:Si-QDs)\(^3\), butyl (bu:Si-QDs) and methyl-passivated Si-QDs (me:Si-QDs)\(^4\), methyl undecanoate passivated Si-QDs (me-un:Si-QDs)\(^5\) and dodecane-passivated Si-QDs (do:Si-QDs)\(^6\). For more details on the samples we refer to Appendix A.1. The measured QY values are compared to literature values (gray symbols): Dohnalova et al. [2], Jurbergs et al. [10], Kusova et al. [11], Mastronardi et al. [12], Sangghaleh et al. [13] and Tu et al. [14]. The shaded area indicates the emission wavelength range for which high QYs are found.

2.8 Conclusion

In conclusion, we report on a critical artifact generally present in the QY methodology, leading to the underestimation of the QY value under common experimental conditions and which depends on the absorption of the studied material. This effect is critical.

\(^{3}\)Samples courtesy of Dr. N. Licciardello and Prof. Dr. L. De Cola (Karlsruhe Institute of Technology, Germany)

\(^{4}\)Samples purchased from Chemical Research Solutions (CRS, United States of America)

\(^{5}\)Samples in collaboration with Dr. I. Sychugov [13] (KTH-Royal Institute of Technology, Sweden). The samples were originally prepared by the Group of Prof. Dr. J.G.C. Veinot (University of Alberta, Canada)

\(^{6}\)Samples courtesy of MSc. S. Regli and Prof. Dr. J.G.C. Veinot, (University of Alberta, Canada)
not only for studies where QY is evaluated as an important material characterization, but also in studies where materials with different absorption are compared, or a single material is studied in a broad range of excitation wavelengths, concentrations or other parameters that are directly or indirectly linked to the material’s absorption. The effect manifests itself independently of the type of material and of the specific geometry of the experimental setup. By comparison with theoretical simulations, we show that the effect is due to a bias resulting from the experimental uncertainty in the detected photon intensities that are used to compute the QY. The critical absorption under which the artifact shows is roughly ten times the relative measurement uncertainty: e.g. for only 1% of experimental uncertainty materials with absorption below 10% are already affected. This leads even for calibration standards such as R6G to a strongly underestimated QY, when excited non-resonantly or studied at an insufficient concentration.

The artifact described here passed undetected for a long time, due to the common assumption that the error in the measured number of photons ($N$) propagates in a linear manner and that therefore low photon fluxes, obtained when measuring low-absorption or emission materials, merely result in a larger uncertainty in the obtained QY value [77, 88]. We show that is assumption is not justified and the QY, given by $QY = \frac{N_S}{N_{Ref} - N_S}$, is biased towards lower values when the uncertainty in the measured variables $N_{Ref}$ and $N_S$ exceeds 10% of the difference $(N_{Ref} - N_S)$ between them. Our findings apply to any methodology where a quantity with the general form $Z/(X - Y)$ is evaluated and hence we anticipate that, not only the absolute QY, but also relative and comparative QY methods suffer from this effect, as these methods rely on similar definitions [67].

The QY is frequently used also to characterize novel materials such as semiconductor QDs, to study the emission efficiency dependence, e.g., on size [12, 37] and density [70] of the QDs, excitation energy [71, 84] or to show ligand instability [75]. A critical assessment of these results and of the methodology is therefore needed, since the size, density and excitation energy are intimately linked to the magnitude of the absorption of the studied samples. To eliminate the artifact, we propose a dedicated calibration procedure that corrects for the intrinsic absorption-dependence of the QY determination. In this way it possible to establish robust and reliable QY measurements for materials developed for e.g. bio-imaging, bio-sensing or optoelectronic devices.

## 2.9 Materials & methods

### Samples

Rhodamine 6G (Sigma-Aldrich) was dissolved in UV-grade ethanol (Merck KGaA, Uvasol), from which different concentrations were prepared by dilution. The concentration was estimated by comparison of the measured absorption coefficients with the value specified by Birge [92]. For all optical measurements, ~1.5 mL of solution is contained in a UV spectroscopy-grade quartz cuvette (Hellma Analytics, 111-QS). CdSe/ZnSe/ZnS core/shell/shell QDs (CANdots Series A CSS) in hexane were purchased from the Center for Applied Nanotechnology (CAN) GmbH. High efficiency Si QDs were obtained
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from the group of Prof. Dr. J.G.C. Veinot (University of Alberta, Canada), prepared following the synthesis described in References [93, 94]. The concentration was estimated from the measured absorption coefficient and the absorption cross-sections reported in Reference [95].

QY setup 1

The sample is illuminated by a stabilized Xenon lamp (Hamamatsu, L2273) coupled to a double-grating monochromator (Solar, MSA130). The excitation beam is split using a spectrally broad bifurcated fiber (Ocean Optics, BIF600-UV-VIS), where one part is used to monitor the fluctuations of the excitation intensity using a power-meter (Ophir Photonics, PD300-UV) and the other part to excite the sample. A collimator lens is used to reduce the spot-size at the sample position to enable purely direct excitation of the sample ($F = 1$). The samples are suspended using an aluminum holder in the center of the IS (Newport, 70672) with a diameter of 10 cm. The use of such type of holder is verified using ray-tracing simulations (see Section A.2). Light is detected using a second spectrally broad optical fiber (Ocean Optics, QP1000-2-VIS-BX), coupled to a spectrometer (Solar, M266) equipped with a CCD (Hamamatsu, S7031-1108S). All measurements are corrected for the spectral response of the detection system determined by illuminating the IS via the excitation port with a tungsten halogen calibration lamp (Oriel, 63358) for the visible range and a deuterium lamp (Oriel, 63945) for the UV range (<400 nm). From the ratio between the theoretical ($I_{\text{th}}^{\text{cal}}$) and measured calibration spectrum, the correction function is determined: $C(\lambda) = I_{\text{th}}^{\text{cal}}(\lambda)/I_{\text{exp}}^{\text{cal}}(\lambda)$, where the measured calibration spectrum is corrected for the spectrometer’s stray-light contribution. For all measurements, ~1.5 mL of solution is contained in a UV spectroscopy-grade quartz cuvette (Hellma Analytics, 111-QS).

QY setup 2

Independent QY measurements, courtesy of Prof. Dr. J. Valenta (Charles University, Prague, Czechia) are carried out using an IS with a diameter of 10 cm and an inner surface covered by the Spectraflect coating. The excitation is provided by a laser-driven light source (LDLS, Energetiq, EQ-99X) coupled to the 15 cm monochromator (Acton SpectraPro SP-2150i). The monochromatized light (bandwidth of about 10 nm) is guided to the IS via a silica fiber bundle. The output signal from the IS is collected by another fused-silica fiber bundle placed in the direction perpendicular to the excitation axis and is shielded by baffles against the direct visibility of both the LED excitation source and the sample. The end of the fiber bundle (which has a stripe-like shape) is imaged to the input slit of an imaging spectrograph (30 cm focal length) and a liquid-nitrogen-cooled CCD camera is used for detection. The spectral sensitivity of the complete apparatus is calibrated over the broad UV-NIR spectral range (300-1100 nm) using two radiation standards (Newport Oriel): A 45 W tungsten halogen lamp (above 400 nm) and a deuterium lamp (below 400 nm). Again, special attention is paid to avoid stray-light effects in the spectrometer.
2.9. Materials & methods

Data analysis

QY is evaluated using Equation 2.2. Re-absorption effects were corrected for using the procedure described by Ahn et al. [78] by comparing the measured PL spectrum with that of low concentration sample for which re-absorption is negligible. Error estimates are obtained following procedures found e.g. in References [84, 88].

Time-resolved PL

Time-resolved PL was measured using an inverted confocal microscope (Olympus, FV1000) equipped with a TCSPC module (Picoquant, Picoharp). For excitation, we used a pulsed 440 or 485 nm wavelength laser diode (Picoquant, LDH-P-C-440B or LDH-P-C-485) operated at 20 MHz (~2.7µW or 0.4µW) focused to diffraction limited spot by a 60x water immersion objective (Olympus, UPLS Apo, NA = 1.2). Light is collected by the same objective lens, filtered through a 562 ± 20 nm band-pass filter and detected using an avalanche photon detector (MPD, PDM). For the measurements the R6G solutions were contained in a 96-well plate.

Single-pass absorption

Transmission of the sample ($T_S$) and reference ($T_{Ref}$) was measured using a dual-beam spectrophotometer (Perkin Elmer, Lambda 950), from which the sample’s single-pass absorption, i.e. the fraction of absorbed light upon a single passage through the sample, was evaluated: $A_S = 1 - T_S/T_{Ref}$. For this it is assumed that the reflection of the sample and reference is the same.