Response to "comment on 'Limits of emission quantum yield determination'" [AIP Advances 9, 039102 (2019)]

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In his comment[2] to our work,[1] Dr. Timmerman disputes our conclusion that QY measurements are biased for weakly absorbing samples due to a skewed QY values distribution. The author suggests that we incorrectly use the mode of the distribution to represent the measured QY values, instead of the mean or median of the distribution. He argues that the mean and median both lead to a bias in the experimentally determined QY values only for very low sample absorptance ($A < 3\ \sigma$), in which case the "*variability of the mean is already too high*" to consider such data at all. We appreciate the interest our work has sparked and will address the raised concerns.

First of all, we would like to clarify the terminology that is used throughout the comment of Dr. Timmerman. First, he mentions that *"It is the 'expectation value' (or 'mean') that is of relevance for statistical interpretation of experimental data"* and later adds that *"the variability of the mean value of the distribution is already > 50%"*. These statements are conflicting. In the first sentence we believe that Dr. Timmerman means the mean value of a probability distribution that is the first moment of the distribution (in probability terminology it is denoted as $E(X)=\int xdF$), which is a number with no variability. In the second sentence, we believe that Dr. Timmerman means 'sample mean', often called an 'arithmetic average' (in probability theory it is a random variable denoted as $\bar{X} = 1/n \sum X_i$), which in this case is also a random parameter that can have a distribution with defined mean and variance. The two parameters should not be mixed, as they have different meaning and properties.

Dr. Timmerman's main criticism is based on the assumption that: "*It is the 'expectation value' (or 'mean') that is of relevance for statistical interpretation of experimental data*". This is in general not true and lacks referencing. One clear example is a bimodal distribution whose mean (if defined) and median might fall into the gap between possible values, i.e. represent a value that could be sampled with very low or zero probability and therefore it cannot be relevant for statistical interpretation of the data. Indeed, the ratio distribution that we derive is bimodal when the absorptance is low and, moreover, does not have a defined first moment (mean), making the discussion about the 'mean' irrelevant to our work. The second reason is the skewness of the ratio distribution, for which the mean value is strongly influenced by extreme values and it is pulled in the direction of the outlying data values (see e.g., Pagano, M., Gauvreau, K. (2000): Principles of biostatistics. Pacific Grove, CA:Duxbury). Therefore, it is not relevant for statistical interpretation of the observed data. An illustrative, often used example is the average salary in some sectors.

For the same reason, the use of the median has little relevance for the QY distribution, because the ratio distribution is generally bimodal (especially for very low absorptances). For bimodal distributions the median is less suitable as a sample estimator as it can correspond to almost sure non-existing values. Moreover, estimating the median would require many measurements, something which is generally not done in QY experiments. QY measurements are typically done only very few times (often only once), insufficient to estimate the middle value (median). In fact, without knowledge of the exact distribution function, as demonstrated for this first time in our work, the need for using the median would not even be apparent. We therefore seriously doubt whether the mean or median of many measurements is used at all to characterize the QY of materials in literature, especially when this would mean considering 'unphysical' values, i.e. QY<0% or QY>100%.

We therefore anticipate that, following the principle of maximum likelihood, sparse QY measurements more likely yield the

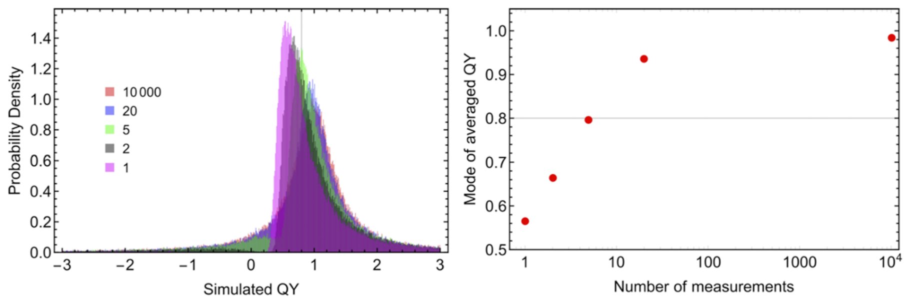

FIG. 1. Left: Simulation of the distribution of average QYs, obtained from the ratio distribution, assuming an absorptance of 2.5%. The distribution for larger numbers of averaging's (shown in the legend) converges to a normal-like distribution. For 5 averaging's (green), the peak of the average QYs coincides with the correct QY value, however diverges for higher and lower numbers of averaging. For N=10000, we obtain an overestimated QY of ~100%. This convergence value depends on absorptance. Right: Mode of the average QY distribution. The correct QY value is indicated by the gray line in both panels.

mode of the ratio distribution. While for symmetric distribution functions, this would be equal to the mean or median, we show in our work that the QY follows a skewed distribution (ratio distribution) for which this is not the case.

The second major argument of Dr. Timmerman is that *"There is a larger uncertainty for the mean value when going to smaller absorptance, but no preference for an under- or overestimation."* Considering that Dr. Timmerman here means by 'mean' a variability of the arithmetic average of the QYs, shown in his comment, this statement is true, but irrelevant to our work. This effect follows from the well-known Central Limit Theorem (CLT): The distributions of arithmetic averages converge under certain assumptions to a normal distribution, which will lead to no under- or overestimation. This is a logical consequence of the symmetricity of the limit normal distribution. However, CLT assumptions are violated in the case of the ratio distribution (i.e. non-existence of the mean). Also, this cannot be overcame by arbitrary truncation of the ratio (as Dr. Timmerman suggests and demonstrates by cutting the distribution's 25% lowest and highest values). Firstly, it is unphysical to truncate the distribution, and secondly, such a 'mean' depends on the truncation factor.

Furthermore, Dr. Timmerman suggests that averaging the QY over 'N' number of measurements is or could be used to estimate the QY value. Indeed, in Figure 1 of his comment, he shows that such an average has a distribution with a mode around the correct QY value for N=5. The choice of N=5, however, does not show the full picture as the averaged QY obtained from such procedure depends strongly on N, as shown in our Figure 1. In fact, only for N=5, the average QY yields good agreement with the correct QY value, but diverges for N>5 or N<5. Moreover it does not converge to the correct QY value for high N. E.g., for absorptance 2.5%, the average QY mode converges to ~100%, instead of the correct value of 80%, and for an absorptance of 1%, the same parameter converges to only 60% (Figure 2). This is a direct consequence of the fact that the main

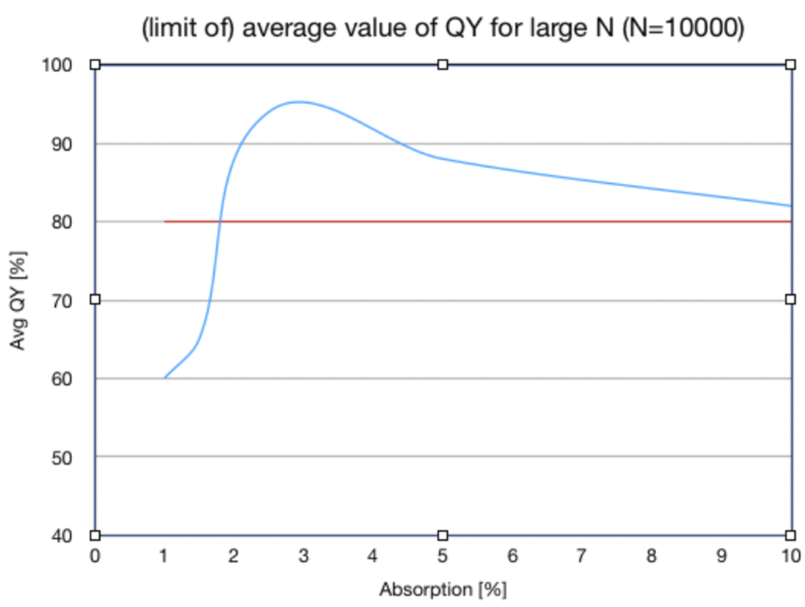

FIG. 2. Mode of the averaged QY simulated for various absorptances and very high numbers of averaging. However, we would like to note that this graph is only related to the response here and should not be confused for the QY distribution curve presented in our paper, as the measured QY is not described by this graph.

assumption of the CLT is violated, because the ratio distribution is skewed and heavy-tailed, rendering the suggested procedure as inappropriate and illustrates once again the importance of considering the probability distribution of the measured parameter.

Finally, we would like to point out that Dr. Timmerman rightfully suggests that the bias in QY measurements follows purely from the equation from which the QY is determined, i.e. $Z=X/(U-V)$, and not from the integrating sphere optics. We don't dispute this point, as it was in fact one of the major conclusions of our work, where we identify the equation itself as the source of the bias for QY measurements and similarly defined quantities.

Summarizing, we believe that the comment of Dr. Timmerman does not significantly affect the conclusions of our manuscript. The ratio distribution is clearly skewed and we anticipate that in sparse QY experiments the mode is most likely sampled, which can lead to underestimated QY values. Our findings are therefore important because they raise awareness over the skewed distribution of the QY and similarly defined quantities and point out the pitfalls that result from it. Moreover, the theoretical framework enables one to establish a working range in which the QY can be reliably determined, by comparison of the sample absorptance with the relevant experimental uncertainties (i.e. $A > 10\ \sigma$). This is preferred over an absorptance threshold (e.g. 10% as suggested by Dr. Timmerman) defined irrespective of experimental uncertainties, which might greatly differ between different experimental setups.

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