Case Study IV: Modeling Photoluminescence Decay

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Photoluminescence decay data taken under two different experimental conditions are examined with an exponential fitting model in order to extract the decay time constants. Issues of fitting data with systematic offset error and the influence of correlation are discussed.

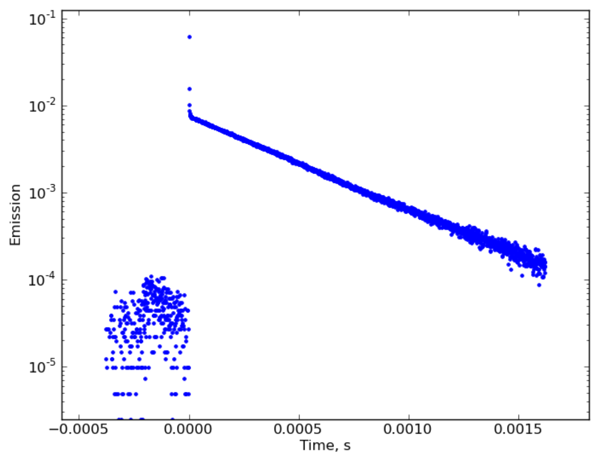

FIG. 1. Decay data with low noise (”data 1”), log scale.

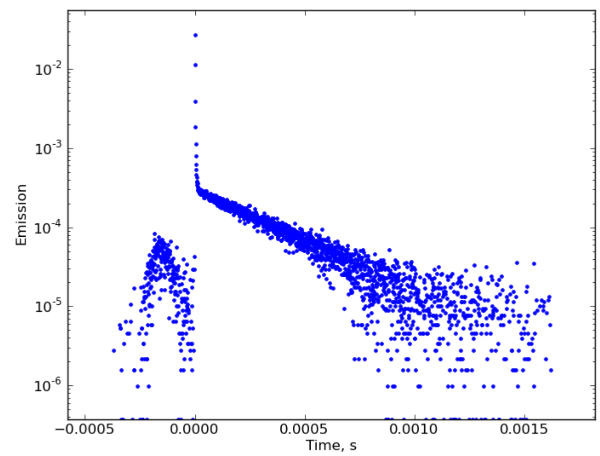

FIG. 2. Decay data with high noise (”data 2”), log scale.

This case study includes two data sets of photoluminescence decay with different signal to noise ratios. The decay is expected to have an exponential trend, suggesting the fitting function should be of the form:

$$I = I_o \exp\left(\frac{-t}{\tau}\right) \tag{1}$$

Where I is the emission intensity, I_o is the intensity at time zero, and τ is the decay time constant. If it is exponential it should appear as a straight line when plotted on a log scale, which is seen to be the case in Figs. 1 and 2. The initial scatter before time zero indicates background noise, and the few points just before the linear regime are a result of the delta function and can be disregarded.

The background is clearly not only very noisy compared to the data in both cases, but appears to have some features beyond a simple horizontal line with random noise. It also appears to be vertically offset from zero. There are different ways this could be handled. If the curve fitting algorithm allows for piecewise functions, a single function could be fit over the whole data range. Otherwise, the offset could be found first by fitting just the background region to a constant. This works reasonably well for the less noisy data, but for the other data the background fit gives a positive offset even though the

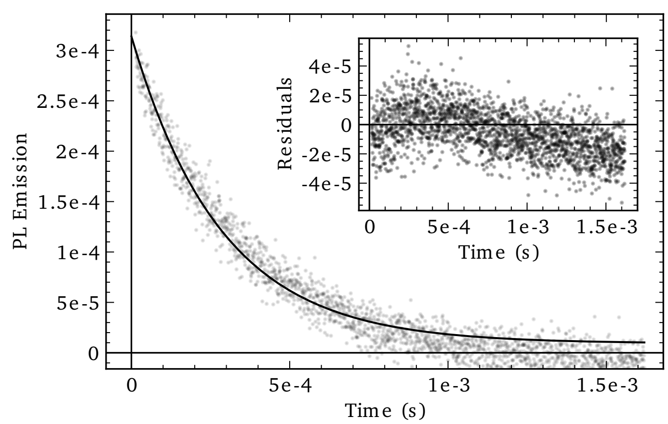

FIG. 3. Data 2, poor fit with background fit as offset.

data has many points that occur in the negative. Since the exponential function trends toward zero, the fit becomes poor in this region without a negative offset (Fig. 3).

This shows that the background data does not well represent the true offset, probably because its odd shape is some kind of artifact. A better fit could be obtained simply by including the offset as a fitting parameter b (Eq. 2) and fitting to the exponential region instead (Fig. 4). Applying the same method to the less noisy data

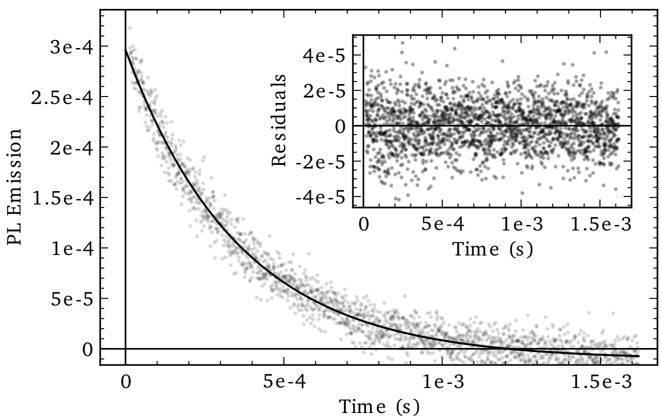

FIG. 4. Data 2 fit with parameter offset.

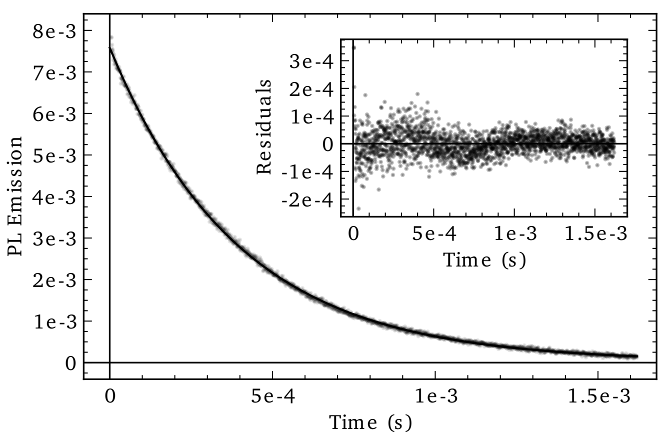

FIG. 5. Data 1 fit with background fit as offset.

yields Fig. 5.

$$I = I_o \exp\left(\frac{-t}{\tau}\right) + b \tag{2}$$

The time constants obtained from these fits are $\tau_1 = 396 \pm 1\mu s$ and $\tau_2 = 360 \pm 3\mu s$. From a physical standpoint, they both should probably give the same value if both measurements represent the same physical process. The results are reasonably close, but the difference is much larger than the standard deviation obtained from the covariance matrix, so the difference is outside the margin of error. The residuals from the Data 1 fit do seem to show some weak oscillations at shorter times, so it could be that the oscillation-like artifact seen in the background is also influencing the measurements.

Another possibility is correlation between τ and the other parameters, particularly the offset. The two fits give offset values of $b_1 = 2.55 \pm 0.23 \times 10^{-5}$ and $b_2 = -1.07 \pm 0.06 \times 10^{-5}$. Since the signal strength is different between the two data sets, there is no reason to expect them to have the same offset. However, if we consider the partial correlation matrices for data 1:

$$\begin{array}{cc} & \begin{array}{ccc} I_o & \tau & b \end{array} \\ \begin{array}{c} I_o \\ \tau \\ b \end{array} & \begin{pmatrix} 1 & -0.717 & -0.688 \\ & 1 & -0.911 \\ & & 1 \end{pmatrix} \end{array}$$

and data 2:

$$\begin{array}{cc} & \begin{array}{ccc} I_o & \tau & b \end{array} \\ \begin{array}{c} I_o \\ \tau \\ b \end{array} & \begin{pmatrix} 1 & -0.733 & -0.661 \\ & 1 & -0.890 \\ & & 1 \end{pmatrix} \end{array}$$

Both show large negative correlations of about -0.9 between τ and b. This suggests that a fairly good fit could still be obtained if τ and b were varied together.

Conclusion

Both data sets show exponential decay when offset by a small vertical shift. The time constants obtained are relatively close but differ by about 36 μs. Some artifacts as seen in the background data before time zero or correlation between the offset and τ could be influencing the fit, leading to this discrepancy.