Capabilities in Single Photon Counting With Reiterative Convolution; a Reply

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Summary We report experiments further defining the resolution in our single photon counting method, a method using reiterative convolution and directly measuring excited state lifetimes down to 100 ps; we clarify the irrelevance of 50 ps jitter cited in the literature as an objection to the method.

RECENTLY we reported[1] a method for measurement of exceedingly rapid excited singlet decay rates using the general method of single photon counting.[2] In principle, if one knows the intensity of the exciting lamp and of the sample's fluorescence emission as a function of time, one can determine the excited state concentration also as a function of time and thus the decay rate. However, the process of deconvolution has been noted[3] to be mathematically difficult. Our method circumvented these difficulties by simulating deconvolution, by a reiterative convolution in which a set of negative exponentials, with assumed rate constants, was taken together with the experimental lamp flash to calculate the theoretical emission as a function of time. The deviation of this theoretical emission from the experimental curve was used to formulate a second iteration with new, assumed rate constants. The method provided rapid convergence to an optimum fit.

However, a recent review article[4] questioned the ability of the method to obtain lifetimes as low as 100 ps on the basis that a jitter (*i.e.* instability) of up to 50 ps is often observed. We now reiterate the validity of our own studies, and also clarify that once the mathematical difficulties in deconvolution are overcome, the 50 ps jitter is not a factor limiting accuracy. Indeed, if instrumental jitter were significant in limiting accuracy, the *ca.* 1 ns transit time jitter of typical photomultipliers used in observ-

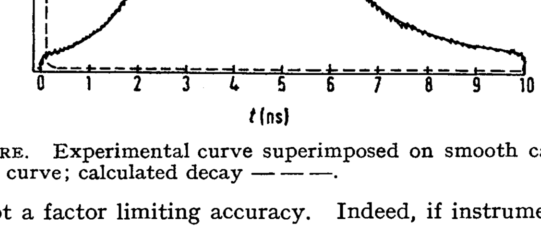

FIGURE. Experimental curve superimposed on smooth calculated curve; calculated decay — — —.

ing emission of the single photon from the sample would be more important than the lamp jitter.

The principle of deconvolution in such studies is given by equation (1). This matrix formulation thus gives

$$\begin{bmatrix} E_0 \\ E_1 \\ E_2 \\ \cdot \\ \cdot \end{bmatrix} = \begin{bmatrix} I_0 & 0 & 0 & \ldots \\ I_1 & I_0 & 0 & \ldots \\ I_2 & I_1 & I_0 & \ldots \\ \cdot & \cdot & \cdot & \\ \cdot & \cdot & \cdot & \end{bmatrix} \begin{bmatrix} D_0 \\ D_1 \\ D_2 \\ \cdot \\ \cdot \end{bmatrix} \cdot \begin{bmatrix} D_0 & 0 & 0 & \ldots \\ D_1 & D_0 & 0 & \ldots \\ D_2 & D_1 & D_0 & \ldots \\ \cdot & \cdot & \cdot & \\ \cdot & \cdot & \cdot & \end{bmatrix} \begin{bmatrix} I_0 \\ I_1 \\ I_2 \\ \cdot \\ \cdot \end{bmatrix} \qquad \text{(1a)}$$

$$\text{or } \bar{E} = \bar{\bar{I}}\bar{D} = \bar{\bar{D}}\bar{I} \qquad \text{(1b)}$$

emission intensity E at each delay from time zero as a sum of contributions. For example, $E_0 = I_0D_0$, $E_1 = I_0D_1 + I_1D_0$, and $E_2 = I_0D_2 + I_1D_1 + I_2D_0$. The I's are lamp intensities and the D's are values of the decay function at different delays from time zero. Since the $\bar{\bar{I}}$ matrix is near singular $\bar{\bar{I}}$ cannot be inverted directly to solve for D.

However, we need to recognize that the lamp intensity measured includes any electronic or optical jitter and thus the $\bar{\bar{I}}$ matrix gives only apparent intensities wherein $\bar{\bar{I}} = \bar{\bar{J}}\bar{\bar{I}}'$. Here $\bar{\bar{I}}'$ is the true intensity matrix and $\bar{\bar{J}}$ is a 'jitter matrix.' This $\bar{\bar{J}}$ matrix will include *all* jitter whether deriving from instrumental factors introduced before or after sample excitation.

Similarly, the observed fluorescence emission vector $\bar{E}$ gives only apparent intensities; that is, $\bar{E} = \bar{\bar{J}}\bar{E}'$. Again emission measured (*i.e.* $\bar{E}$) is modified from $\bar{E}'$ which would be observed in absence of jitter.

Since the jitter matrix $\bar{\bar{J}}$ occurs in both $\bar{E}$ and $\bar{\bar{I}}$, it is factored out in deconvolution and thus is not of concern as long as it is constant. Long term drift between measurement of $\bar{\bar{I}}$ and $\bar{E}$ is of concern.

As a test of drift of the $\bar{\bar{I}}$ matrix and $\bar{E}$ vector we have run a series of experiments, each consisting of two lamp flash measurements. To the extent that there is error, one of the two lamp flashes will appear broader as if a delay had been introduced. Thus deconvolution of one flash with the other will lead to an impossible result while the reverse will give a very fast but measureable decay time. This decay time is a measure of drift and our experimental error.

TABLE. Experimental drift and apparent decay times

	Estimated drift[a]/ps	Apparent decay time[b]/ps	A value[d]/%
	4	22·4	±2·2
	40[e]	19·3	±2·0
	26	16·9	±2·5
	23[e]	25·0	±2·0
	15	23·6	±2·2
	18	16·4	±1·4
	9	0[c]	—
	11	0[c]	—
	19	26·6	±2·3
Average	18·3	16·7	±2·1

[a] Estimated on the basis of centre of gravity shift between the flashes. [b] From iterative convolution of two lamp flashes. [c] Calculated decay converges to zero. [d] Defined as the ratio of the difference in areas between the experimental curve and the calculated curve to the area of experimental curve. [e] Runs 2 and 4 at 280 nm; other runs at 310 nm.

The Table summarizes the errors obtained both in this way and by comparing the centres of gravity of sets of flashes. The Figure gives a typical lamp flash along with the convoluted curve deriving from this and a second lamp flash. The deviation of the two curves is 1·9% of the total area under one curve. The average error in the Table for 9 sets of two-flash experiments is 18 ps. This error is smaller than the conservative error limit we published previously.

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