

INTERACTIVE MODELING OF SCINTILLATION PULSES BY VISUAL
OVERLAY OF COMPUTED PULSE SHAPES WITH THE RAW DATA*

by

J.M. Flournoy, S.S. Lutz, L.A. Franks, and C.B. Ashford
EG&G, Santa Barbara Operations
Goleta, California 93117

and

P.B. Lyons
University of California
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

INTRODUCTION

The modeling technique described in this paper was developed to aid in interpretation of the effects of various changes in scintillator formulations on the shape of scintillation pulses. For example, addition of quenchers to single-solute systems can quench either the solute or excited solvent, or both, and it is useful to understand these effects in tailoring a scintillator for optimum brightness or speed for a specific application. In multisolute scintillators, an understanding of the detailed energy transfer steps is also desirable.

Inspection of pulse rise and decay times often gives general information on these effects, but a more detailed interpretation is complicated by several factors. First of all, many scintillators are fast enough (1-2 ns FWHM) so that empirically determined pulse parameters, especially rise times, are significantly affected by the response time of the measuring system. In addition, decay times are difficult to determine until the signal has decayed considerably past the peak where noise can become a problem.

*This work was performed under the auspices of the U.S. Department of Energy under Contract No. DE-AC08-83NV10282. NOTE: By acceptance of this article, the publisher and/or recipient acknowledges the U.S. Government's right to retain a nonexclusive royalty-free license in and to any copyright covering this paper.

Reference to a company or product name does not imply approval or recommendation of the product by the U.S. Department of Energy to the exclusion of others that may be suitable.

NOTICE
PORTIONS OF THIS REPORT ARE ILLEGIBLE.

It has been reproduced from the best available copy to permit the broadest possible availability.

MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

EAB

It occurred to us that it might be possible to understand the effects of additives on the rise and decay constants that determine the true pulse shape if we synthesized theoretical pulse shapes, folded in the system response function, and overlaid the resulting curves on the raw data arrays. The results have been gratifying in that in most cases it has been possible to distinguish relatively unambiguously between quenching of the solvent and the solute when various heavy-atom quenchers were added to solutions of a series of substituted terphenyls.

EXPERIMENTAL

The scintillator solutions discussed here were excited with 50 ps (FWHM) pulses of 6-MeV electrons at 360 pulses per second from the DOE/EG&G linear accelerator (linac) at EG&G's Santa Barbara Operations facility. The raw data arrays are from a sampling oscilloscope which acquired signals from a fast micro-channel plate photomultiplier tube (PMT) arranged to collect fluorescent emissions from the samples with minimum interference from Cerenkov radiation. System response data were generated by detection of Cerenkov radiation from samples of fused quartz exposed to the same linac pulses and using the same data acquisition system. In all cases, the original data were collected in 1024 time channels of 5 to 20 ps per channel.

Computer processing routines were written for use with the graphics capability of Tektronix SPS BASIC as implemented on a Digital Equipment Corporation PDP-11/34A, with output to a Tektronix 4010 terminal. Hard copies of the data are by screen dump to a Tektronix 4631 thermal copy unit. This combination is particularly convenient for interactive modeling because of the ease of modifying the BASIC programs and changing parameter values from the terminal, and also because hard copies of each attempted fit can be obtained in a few seconds, which facilitates comparison between overlays with slight changes in the fitting parameters.

Most of the modeling was done with 256-point arrays in order to reduce processing time and to conform to the memory limitations of the computer. The 1024-point raw data arrays were usually sampled every fourth point, but sometimes it was more desirable to model a selected 256-point region of the data or every second point of a 512-point region.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

GENERATION OF THEORETICAL CURVES

The simplest form of a scintillation pulse in a two-component system involves a single exponential rise constant, k_s , describing the rate of transfer of energy from excited solvent molecules to the solute, and a single exponential decay constant, k_f , for the emission of light by the excited solute molecules. Quenching at either of these steps increases the rate of disappearance of the respective excited species (solvent or solute) in inverse proportion to the relative quantum yields, Q_s and Q_f for each step, as shown below. If we define k_{qs} and k_{qf} as rate constants for the quenching of the energy-transfer and fluorescence steps, respectively, then k_1 and k_2 describe the total rate of disappearance of excited solvent and solute, respectively. Thus, for the solvent step,

$$k_1 = k_s + k_{qs} \text{ and } Q_s = k_s/k_1 \quad (1)$$

and for the solute,

$$k_2 = k_f + k_{qf} \text{ and } Q_f = k_f/k_2 \quad (2)$$

It is important to note that Q_s and Q_f are defined relative to the unquenched system only and represent the fraction of the total rate which occurs by the useful paths described above by k_s and k_f .

Thus, for the two steps:



and



the concentrations, A and B, of excited solvent and solute molecules, respectively, are described as a function of time by:

$$dA/dt = - k_1 A \quad (5)$$

and

$$dB/dt = k_s A - k_2 B \quad (6)$$

The emission intensity is given by:

$$I(t) = k_f B(t), \quad (7)$$

and the explicit solution for B(t) is:

$$B(t) = A(0) \cdot Q_s \cdot R \cdot (E_1 - E_2) + B(0) \cdot E_2 \quad (8)$$

where

$$R = k_1 / (k_2 - k_1)$$

$$E_1 = \exp(-k_1 t)$$

$$E_2 = \exp(-k_2 t)$$

and

$$k_1 \neq k_2$$

In the case where $k_1 = k_2$, the solution of Eqs. (5) and (6) becomes

$$B(t) = [A(0) k_s t + B(0)] \exp(-k_2 t) \quad (9)$$

In our programs, this solution is used whenever k_1/k_2 is within ± 0.001 of unity.

It was originally anticipated that numerical methods, such as the Runge-Kutta, would be preferred, because they are inherently more efficient than the direct computation of exponentials. However, the Runge-Kutta method fails when very large values of the rate constants are introduced, as is often useful in isolating which of several energy-transfer steps is overall rate-determining. Furthermore, the computation of the pulse shapes is not the principal time-consuming step in the modeling programs.

Other sets of differential equations can be written to describe more complicated systems involving successions of energy transfer steps, chemical equilibria (e.g., dimerization or excimer formation), or emission of light by more than one species, for example. Some care must be taken that the relative quantum yields are taken into account properly, as they affect both the rates and the overall efficiency of the scintillator. Explicit solutions for these sets of differential equations can be derived, but as the equations become more complex, involving, for example, energy transfer through one or more intermediate wavelength shifters, the explicit solutions rapidly become quite cumbersome, and Runge-Kutta type solutions are more attractive. Following a method similar to a second-order Runge-Kutta, we write:

$$A(t + dt) = A(t) \cdot W_1 \text{ (excited solvent)} \tag{10}$$

$$B(t + dt) = B(t) \cdot W_2 + A(t) \cdot V_1 \text{ (excited solute)} \tag{11}$$

in which, for each time increment, dt,

$$W_1 = 1 - X_1 + 0.5 X_1^2 \text{ where } X_1 = k_1 dt \tag{12}$$

$$W_2 = 1 - X_2 + 0.5 X_2^2 \text{ where } X_2 = k_2 dt \tag{13}$$

and

$$V_1 = k_s \cdot dt \cdot [1 - (k_s + k_2) \cdot dt/2]. \tag{14}$$

The pulse integral (in either case) is given by the expression:

$$\text{Area} = [A(0) \cdot Q_s + B(0)] \cdot Q_f \quad (15)$$

There is also an interesting rate-constant redundancy in fitting pulse shapes only. If $k_2/k_1 = C$, exactly the same rise time, decay time, and FWHM are obtained as for $k_2/k_1 = 1/C$. However, the peak height and integral values differ by a factor of C^2 between the two cases.

CONVOLUTION WITH THE SYSTEM RESPONSE

Convolution with an actual Cerenkov-generated system-response (SR) array is the treatment of choice whenever possible. It is only necessary to adjust the amplitude of the SR array so that its integral is unity, in order that the pulse area will not be affected by the convolution. However, sometimes the appropriate SR data are not available for a set of runs, or perturbations are encountered which are not present in the SR data. In such cases we have had good success in approximating the system response by generating a synthetic Gaussian SR array of the appropriate FWHM and convolving it with the data.

OVERLAYING CURVES AND DATA

Three arbitrary graphing parameters are used to facilitate the visual overlay. Both the data and the modeled curve are normalized to unity at the maximum. However, since the highest single data point may be a noise "flyer," it is usually desirable to multiply the model array by a factor slightly less than unity in order to get a good fit through the visual center-of-gravity of the data near the peak. In addition, the model curve can be shifted vertically to match the zero baseline of the model with the real baseline value of the data. The model can also be shifted right and left in time; the resolution in this case is limited by the resolution of the 256-point arrays.

If one is interested in intensity comparisons as well as pulse shape changes, it is important that the peak and integral values of the modeled pulses be computed before the peak is normalized to unity.

The data are normally displayed as points and the modeled curves as solid lines to make the distinction easy.

The parameters which were used in the fitting process are printed out on the graph, along with computed pulse-shape parameters for the model curve, such as the 10-90% rise time, FWHM, etc., as desired.

One case in which the pulse was nearly as fast as the system response is shown in Figure 1. The system response, the theoretical curve, and the raw data are shown in Figure 1a, and the final convolved fit in Figure 1b. It is clear that the system response is far from a clean Gaussian shape, which could not have given nearly as good a fit to the data.

QUENCHING STUDIES

In studying the effect of quenching agents on a scintillation system, the first step is to achieve a satisfactory fit to a pulse from the system without added quenchers. In this case the relative quantum yields, Q_s and Q_f , are set equal to unity. The initial concentration of excited solvent molecules, $A(0)$, is also usually set equal to unity for the unquenched case. There remain then three adjustable parameters: k_s , k_f , and $B(0)$. The last of these represents a possibly non-zero initial concentration of excited solute molecules, as explained in the next paragraph. These three constants are adjusted to obtain a visual fit to the rise portion, decay portion, and width of the pulse.

One unexpected early result of the modeling work was the discovery that there was apparently some prompt excitation of the solute, i.e., that $B(0)$ was not necessarily equal to zero, as had been previously assumed. This came about when it was found that essentially perfect fits to the rise and decay portions of the pulse frequently yielded full-widths that were much too narrow. This could be resolved in many cases by introducing some $B(0) > 0$ and reducing the value of k_s , the energy-transfer step. The fast rise could thus be maintained and the FWHM increased at the same time. We believe the physical explanation for this non-zero $B(0)$ involves excitation of the solute by absorption of Cerenkov radiation, although some direct excitation of the solute by the electron beam is also a possibility.

Once a set of values for k_s , k_f , and $B(0)$ has been established for an unquenched scintillator of a given composition, it is usually possible to fit the quenched pulse shapes by changing only the quantum yields, Q_s and Q_f , provided that the original model is correct for the system under investigation. Figure 2 shows some of the results of a study of para-terphenyl in toluene,

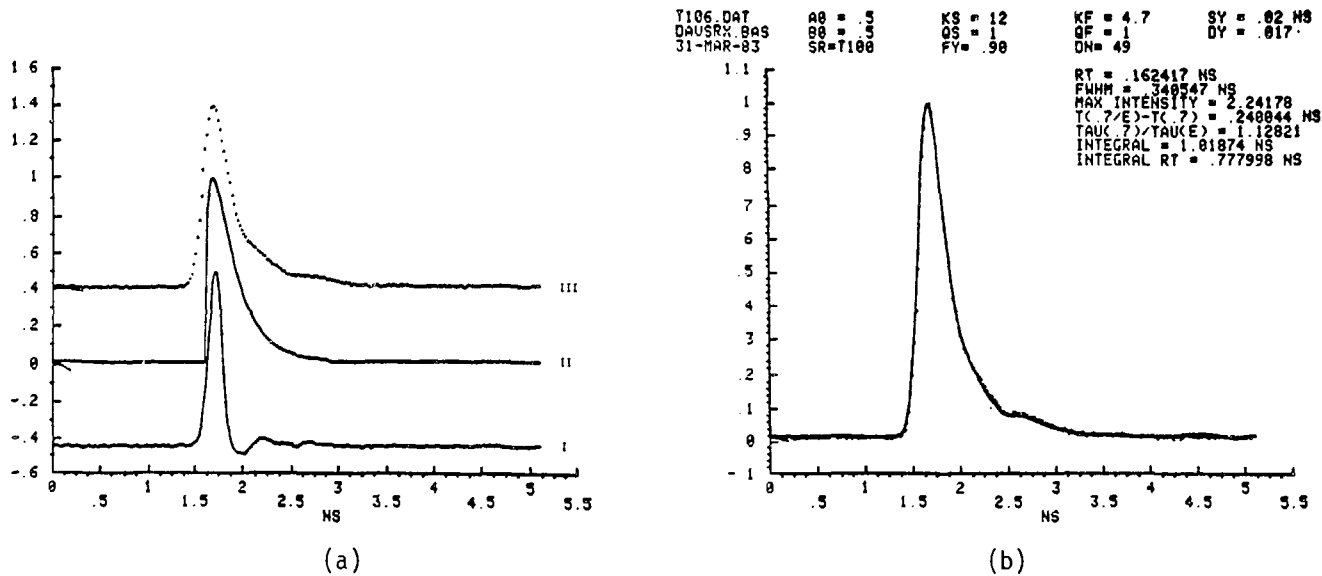
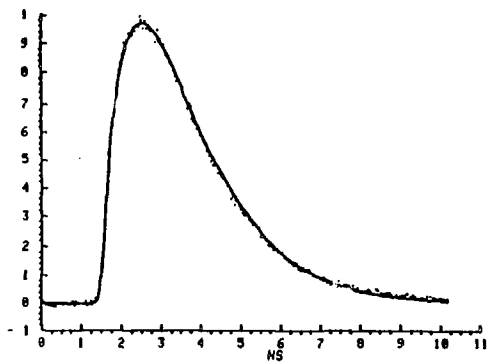


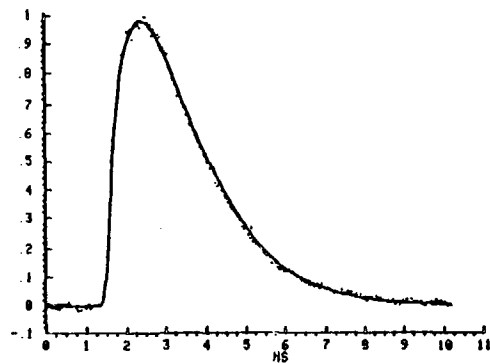
Figure 1. Convolution of a Cerenkov-generated light pulse (system response) with a computed curve for fluorescence from a 4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran (DCM) based scintillator at elevated temperature.

- (a) Bottom to top: (I) Cerenkov response, (II) computed pulse shape before convolution, and (III) normalized raw-data array.
- (b) Overlay of resulting curve (solid line) with raw data (points).

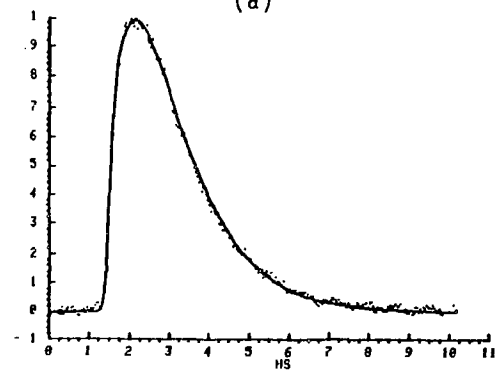
Legend information: SR is name of system response data file; SY is time increment of 256-point array in ns/channel; FY is vertical scaling factor; DN and DY are horizontal and vertical position-shifting parameters, respectively. Other variables are modeling parameters defined in the text.



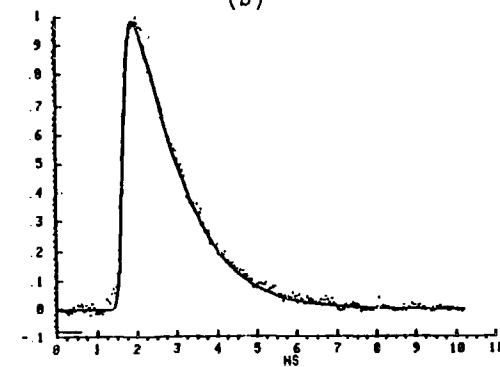
(a)



(b)



(c)



(d)

Figure 2. Quenching by bromobenzene of 0.015 M p-terphenyl in toluene: overlays of modeled curves (solid lines) with data (points). Plots (a) through (d) are for bromobenzene concentrations of 0, 0.015, 0.045, and 0.20 molar, respectively. Curve-fitting parameters and relative peak heights and areas are listed in Table 1.

quenched by bromobenzene. In this case the best fit was obtained by reducing Q_f and $A(0)$ and leaving Q_s unchanged. The reduction in $A(0)$ indicates that the bromobenzene reduced the initial yield of excited solvent molecules in a time short compared to the pulse rise time.

Table 1 lists the values of parameters used in modeling of Figure 2, along with calculated and observed relative peak heights and pulse integrals. Agreement is quite satisfactory.

Table 1. Para-terphenyl, 0.015 in toluene: quenching by bromobenzene; results of modeling in Figure 2 ($k_s = 1.0$, $k_f = 0.8$).

Quencher Molarity	A(0)	B(0)	Q_s	Q_f	Peak		Integral	
					Model	Expt	Model	Expt
0.0	1.0	0.2	1.0	1.0	1.00	1.00	1.00	1.00
0.015	0.8	0.2	1.0	0.85	0.78	0.80	0.71	0.73
0.045	0.75	0.2	1.0	0.67	0.66	0.70	0.53	0.56
0.20	0.45	0.2	1.0	0.40	0.40	0.35	0.22	0.21

Adjustment of the two or three parameters must give satisfactory values for five properties of the pulse — rise time, decay time, FWHM, maximum peak height, and area — in order to yield what we consider to be a satisfactory interpretation of the data. In some cases a set of quenching data have been adequately fit by changing only one of the Q 's.

SUMMARY

This interactive visual-overlay modeling technique has proven to be very useful in the analysis of scintillator response data. It has revealed cases in which the scintillation process is more complicated than might have been inferred from routine inspection of the ordinary pulse parameters. This method is especially valuable in providing basic information about energy transfer steps in a multicomponent scintillator, in order to tailor scintillator systems to specific applications.