COMPUTER-AIDED CHEMISTRY
IV: FAST FOURIER TRANSFORM ANALYSIS OF LUMINESCENCE
DECAY CURVES USING A DESK TOP MICROCOMPUTER

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Summary

An improved analytical procedure, which uses a fast Fourier transform (FFT) algorithm, has been developed to deconvolute luminescence decay curves. Using this procedure, the non-exponential fluorescence decay curves recorded from the excited singlet state of magnesium tetraphenylporphyrin in the presence of CBr_4 in frozen solution, in which both radiative transfer and electron transfer quench the excited state, have been examined. This procedure eliminates the common "overlap effect" that is inherent in previous uses of FFT methods when applied to the problem of deconvoluting decay curves, through a systematic reconstruction of the input data. The analysis may be performed either in the time domain or in the frequency domain. An interactive program, DECAYFIT, written in Fortran 77 was used to carry out the calculations on the IBM S9001 laboratory microcomputer. The program can be employed to deconvolute both model test data and real data, with a time for the analysis in the range of minutes.

1. Introduction

Luminescence decay data are used extensively in investigations of the photophysical properties of atomic and molecular systems [1]. The observed time-dependent emission from a sample excited by a pulse of energy input from a flash lamp results from the convolution of the excited state radiative decay function with the exciting lamp intensity function [2, 3]. The technique of time-correlated single-photon counting [1] is one of the most precise techniques available for providing numerical data that describe both the lamp function and the response function. The problem in the analysis, then, is to recover the decay function by deconvoluting

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the observed decay curves. The form of the decay function that best fits the observed luminescence decay gives a means of characterizing the photophysical system. The analysis of decay curves provides rate constant data for both radiative and non-radiative processes. Systems in which these latter routes are active can be difficult to solve, because the form of the decay law may be non-exponential.

In a number of papers, several methods of deconvoluting luminescence decay curves have been compared, including methods using the fast Fourier transform (FFT) algorithm [4 - 6]. The most popular methods of computer analysis are based on a variant of the technique of iterative convolution (IT), as, for example, the method that takes advantage of the recurrence formula of Grinvald and Steinberg [7]. Such an iterative convolution technique allows for simple one-, two- or three-exponential decay components in the decay law equation. The use of the FFT technique in the analysis of luminescence data has been characterized as giving less reliable results than other methods [4, 6]. The major problem in the application of the FFT algorithm arises from an "overlap effect" which is inherent in the convolution of two periodic functions. This effect tends to distort the synthetic curve and results in parameters which are incorrect. It is probable that such a solution could have arisen from the neglect of a proper treatment of the data before applying the FFT algorithm.

We describe in this paper details of a procedure which successfully uses the fast Fourier transform technique to deconvolute luminescence decay data. This new procedure overcomes the problem of the overlap effect by reconstructing the input data. The application program, DECAYFIT, was set up for use with a laboratory microcomputer and the deconvolution analysis is demonstrated for both model test data and for luminescence decay curves, obtained in single-photon counting experiments for magnesium tetraphenylporphyrin (MgTPP), where electron transfer severely affects the luminescence decay kinetics.

2. Experimental details

MgTPP was synthesized according to published procedures [8]. 2-Butyl chloride (BuCl) (BDH) was freshly distilled under nitrogen. CBr_4 (Kodak) was purified by recrystallization. The porphyrin was dissolved in BuCl to which CBr_4 was added. The sample solution was transferred to a quartz cylindrical tube (outside diameter, 8 mm) and quickly plunged into liquid nitrogen in order to obtain a glassy sample.

The low temperature fluorescence decay data were obtained with a Photochemical Research Associates Model 3000 nanosecond lifetime fluorometer, based on the technique of time-correlated single-photon counting [9]. A pulsed hydrogen arc lamp operated at about 30 kHz was used as the excitation source.

Model data sets were prepared by convoluting a simulated "long-tail lamp" function

$$e(t) = At^2 \exp(-Bt)$$

with a two-exponential decay function

$$h(t) = a_1 \exp\left(-\frac{t}{a_2}\right) + a_3 \exp\left(-\frac{t}{a_4}\right)$$

for various values of A, B and a_i. Random errors were added from a gaussian distribution.

3. Computational aspects

The observed response function f which describes the luminescence decay curve can be written in terms of the convolution integral of the lamp function e and the decay function h. For the discrete values of these functions the integral assumes the following form:

$$f(k) = \sum_{i=0}^{N-1} e(i)h\{(k-i)\} \tag{1}$$

and gives intensity values for $f(k)$ in each channel k of the period N [10]. Analytical procedures based on Fourier transforms provide a natural mathematical foundation for the solution of such complicated curves since the convolution in the Fourier space is the simple product

$$F(n) = E(n)H(n) \tag{2}$$

where $F(n)$, $E(n)$ and $H(n)$ are the Fourier transforms of $f(k)$, $e(k)$ and $h(k)$ respectively.

The aim in our analysis is to determine the decay function $h(k)$ when the lamp function $e(k)$ and the observed response function $f(k)$ are known, i.e. we have to deconvolute the response function $f(k)$. The analytic procedure described here is based on the application of the standard FFT algorithm [11]. The Fourier transforms can be defined, as usual, by

$$E(n) = \frac{1}{N} \sum_{k=0}^{N-1} e(k) \exp\left(-\frac{i2\pi nk}{N}\right) \qquad (n = 0, \ldots, N-1) \tag{3}$$

and analogously for $H(n)$. The calculation of the inverse discrete transform of $F(n)$ gives the convoluted response function $f(k)$:

$$f(k) = \sum_{n=0}^{N-1} F(n) \exp\left(\frac{i2\pi kn}{N}\right) \qquad (k = 0, \ldots, N-1) \tag{4}$$

However, in the use of the standard FFT algorithm for the convolution of two overlapping periodic functions, incorrect values of the response function $f(k)$ are obtained if the period is not properly chosen [10]. In order to eliminate such a result, which is known as the overlap effect, the input data should be restructured in the following manner. The period for the data should be chosen according to the relationship

$$N \geqslant 2K - 1 \tag{5}$$

where K represents the number of data points for the two functions to be convoluted. This condition requires the following modifications to the data before application of the Fourier transform:

$$e(k) = e(k) \qquad \text{for } k = 0 \text{ to } K - 1 \tag{6a}$$
but
$$e(k) = 0 \qquad \text{for } k = K \text{ to } 2K - 1 \tag{6b}$$
and
$$h(k) = h(k) \qquad \text{for } k = 0 \text{ to } K - 1 \tag{7a}$$
but
$$h(k) = 0 \qquad \text{for } k = K \text{ to } 2K - 1 \tag{7b}$$

This seemingly simple operation fills $K + 1$ to $2K$ channels with zeros, which gives a greater number of data points than the actual number K of experimental data. Convolution of these modified data sets, which includes the extra data points, results in the correct values of the calculated response function $f(k)$ in the whole 0 to $2K - 1$ region.

The next step is to carry out an iterative least-squares fitting calculation. There are two main routes to implement the least-squares fitting procedure for the determination of the decay function $h(k)$. The least-squares fit can be performed either in the time domain or in the frequency domain (Fourier space).

3.1. Fitting in the time domain using the FFT technique

In this procedure, the sum of squares of the errors between the observed, $f_o(k)$, and fitted, $f_e(k, a_i)$, response functions is minimized iteratively by changing the parameters a_i in the predicted function, $h_e(k, a_i)$, where $h_e(k, a_i)$ is usually a series of exponential decay functions but can also be a complicated function of non-exponential form. This may be written as the minimization of

$$\text{LSQ}(a_i) = \sum_{k = N_1}^{N_2} \omega\{f_e(k, a_i)\}\{f_o(k) - f_e(k, a_i)\}^2 \tag{8}$$

where the weighting factor $\omega\{f_e(k, a_i)\}$ is equal to $1/\sigma^2\{f_e(k, a_i)\}$. N_1 and N_2 denote the lower and upper bounds of the data (the channel number in the experimental set-up, typically between 1 and 256). In the single-photon-counting experiment, for which a Poisson distribution of errors is applicable, $\sigma^2\{f_e(k, a_i)\} = f_e(k, a_i)$.

It should be noted that the application of either the FFT or the conventional direct iterative convolution in minimizing eqn. (8) is expected to be rather time consuming, since the function $f_e(k, a_i)$ has to be calculated many times. This entails convoluting the excitation function with the new intensities generated by the predicted decay function $h(k, a_i)$ for each iteration. However, the use of a suitable FFT algorithm to compute the discrete convolution can be faster than the use of the direct iterative calculations. It can be shown that evaluation of N data points in the convolution by means of eqn. (1) requires a computation time proportional to N^2 multiplications. The computation time of the conventional radix-2 algorithm [10] is proportional to $N \log_2 N$, and thus the FFT will be faster when convolutions are required for data sets with large numbers of points.

3.2. Fitting in the Fourier space

A least-squares fitting procedure in the Fourier space has been proposed by Wild and coworkers [2, 12]. The fitting procedure is reduced to the minimization of

$$\text{LSQ}(a_i) = \sum_{n=0}^{\text{NC}} \omega_\text{R}(n)\{H_{e,\text{R}}(n, a_i) - H_{o,\text{R}}(n)\}^2$$

$$+ \sum_{n=0}^{\text{NC}} \omega_\text{I}(n)\{H_{e,\text{I}}(n, a_i) - H_{o,\text{I}}(n)\}^2 \tag{9}$$

where $H_{e,\text{R}}(n, a_i)$, $H_{e,\text{I}}(n, a_i)$ and $H_{o,\text{R}}(n)$, $H_{o,\text{I}}(n)$ are the real (R) and imaginary (I) parts of the Fourier transform coefficients of the observed (H_o) and fitted (H_e) decay functions respectively. The values of the Fourier coefficients for the observed decay function are calculated as

$$H(n) = \frac{F(n)}{E(n)} \tag{10}$$

The terms $\omega_\text{R}(n)$ and $\omega_\text{I}(n)$ in eqn. (9) are the weights of the Fourier coefficients that have been derived by Wild's group [12] to be

$$\omega_\text{R}(n) = \frac{1}{\sigma^2} H_\text{R}(n)$$

$$= u^2 \sigma^2 \{F_\text{R}(n)\} + 2uv \, \text{cov}\{F_\text{R}(n), F_\text{I}(n)\} + v^2 \sigma^2 \{F_\text{I}(n)\} \tag{11}$$

$$\omega_\text{I}(n) = \frac{1}{\sigma^2} H_\text{I}(n)$$

$$= u^2 \sigma^2 \{F_\text{I}(n)\} + 2uv \, \text{cov}\{F_\text{R}(n), F_\text{I}(n)\} + v^2 \sigma^2 \{F_\text{R}(n)\}$$

with

$$u = \frac{E_\text{R}(n)}{E_\text{R}(n)^2 + E_\text{I}(n)^2}$$

$$v = \frac{E_{\mathrm{I}}(n)}{E_{\mathrm{R}}(n)^2 + E_{\mathrm{I}}(n)^2}$$

and

$$2N\sigma^2\{F_{\mathrm{R}}(n)\} = F_{\mathrm{R}}(0) + F_{\mathrm{R}}(2n)$$

$$2N\sigma^2\{F_{\mathrm{I}}(n)\} = F_{\mathrm{R}}(0) - F_{\mathrm{R}}(2n)$$

$$2N\,\mathrm{cov}\{F_{\mathrm{R}}(n),\,F_{\mathrm{I}}(n)\} = F_{\mathrm{I}}(2n)$$

In eqns. (9) and (11), NC is the number of FT coefficients used in the calculations, and the subscripts R and I denote the real part and the imaginary part of the Fourier coefficients respectively. The number NC can be set to a low value since all the significant information resides in the first several (low frequency) Fourier coefficients. It is seen from eqn. (11) that the
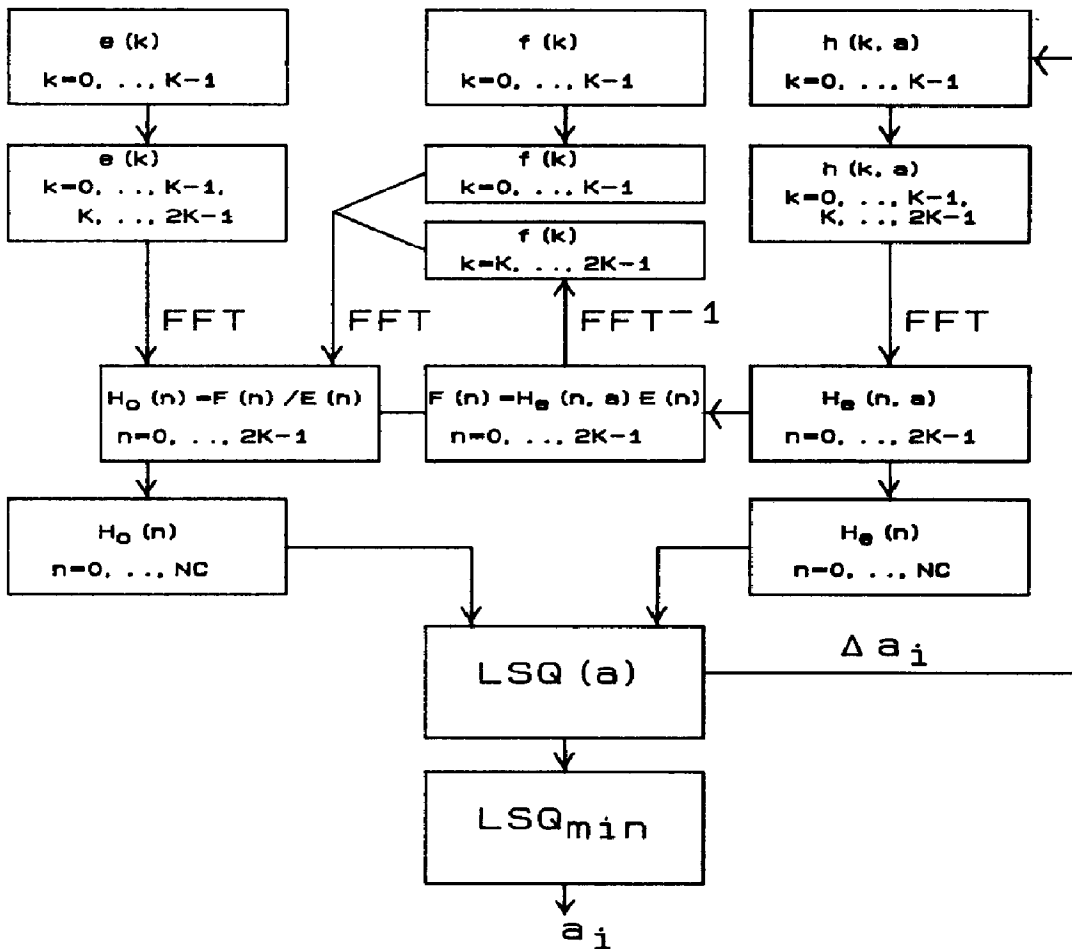

Fig. 1. Block diagram of the FFT deconvolution procedure in the Fourier space. FFT and FFT^{-1} denote forward and inverse fast Fourier transforms respectively.

weights of the Fourier coefficients are completely determined by the Fourier coefficients themselves. The Fourier transformation of response function $f(k)$, which is necessary for calculation of the Fourier coefficients $H(n)$ as in eqn. (10), is carried out according to the scheme shown in Fig. 1. Briefly, these values are calculated by the convolution of the lamp profile with data from the predicted decay function.

3.3. Details of the program

The program implementing both analytical routes, DECAYFIT, was written in Fortran 77 for the IBM S9001, a 16/32 bit laboratory micro-computer, which was interfaced with a Hewlett–Packard HP7550A plotter. The non-linear least-squares minimizing procedure developed by Marquardt [13, 14] was used. The conventional Sande–Tukey FFT algorithm [11] was employed. The execution of the FFT algorithm for 512 data points takes about 6 s on the IBM S9001 computer. The fit to real data usually requires only a small number of iterations (three or four) when good guesses of the initial values of parameters have been used, and the calculation is completed within minutes.

4. Analysis of test data

In our analysis, the differences between the experimental (observed or model) decay data and the fitted curve can be inspected using a number of statistical quantities.

As a numerical test, the reduced chi-square statistics, χ_ν^2, can be calculated as

$$\chi_\nu^2 = (K - p)^{-1} \sum_{i=1}^{K} R_i^2 \tag{12}$$

where the R_i are the "weighted" residuals defined by

$$R_i = \frac{f_o(i) - f_e(i, a_j)}{\sigma\{f_e(i, a_j)\}}$$

where $\sigma\{f_e(i, a_j)\} = \{f_e(i, a_j)\}^{1/2}$ as in eqn. (8), and p is the number of parameters (a_j). The randomness of the residuals R_i can also be inspected by plotting the residuals on the screen.

Figures 2 and 3 show the deconvolution analysis results for the noise-less and noisy model decay curves respectively, which were obtained by convolution of the lamp function with a two-exponential decay function. A highly accurate recovery of the input parameters for the decay function is seen for the noiseless decay curve, with the residual values of the order of the round-off error of the computer (Fig. 2). The fit to the noisy profile (Fig. 3), which included added gaussian-type noise, gives a random distribution of the residuals, with $\chi_\nu^2 \approx 1$, as expected for this type of distribution of errors.
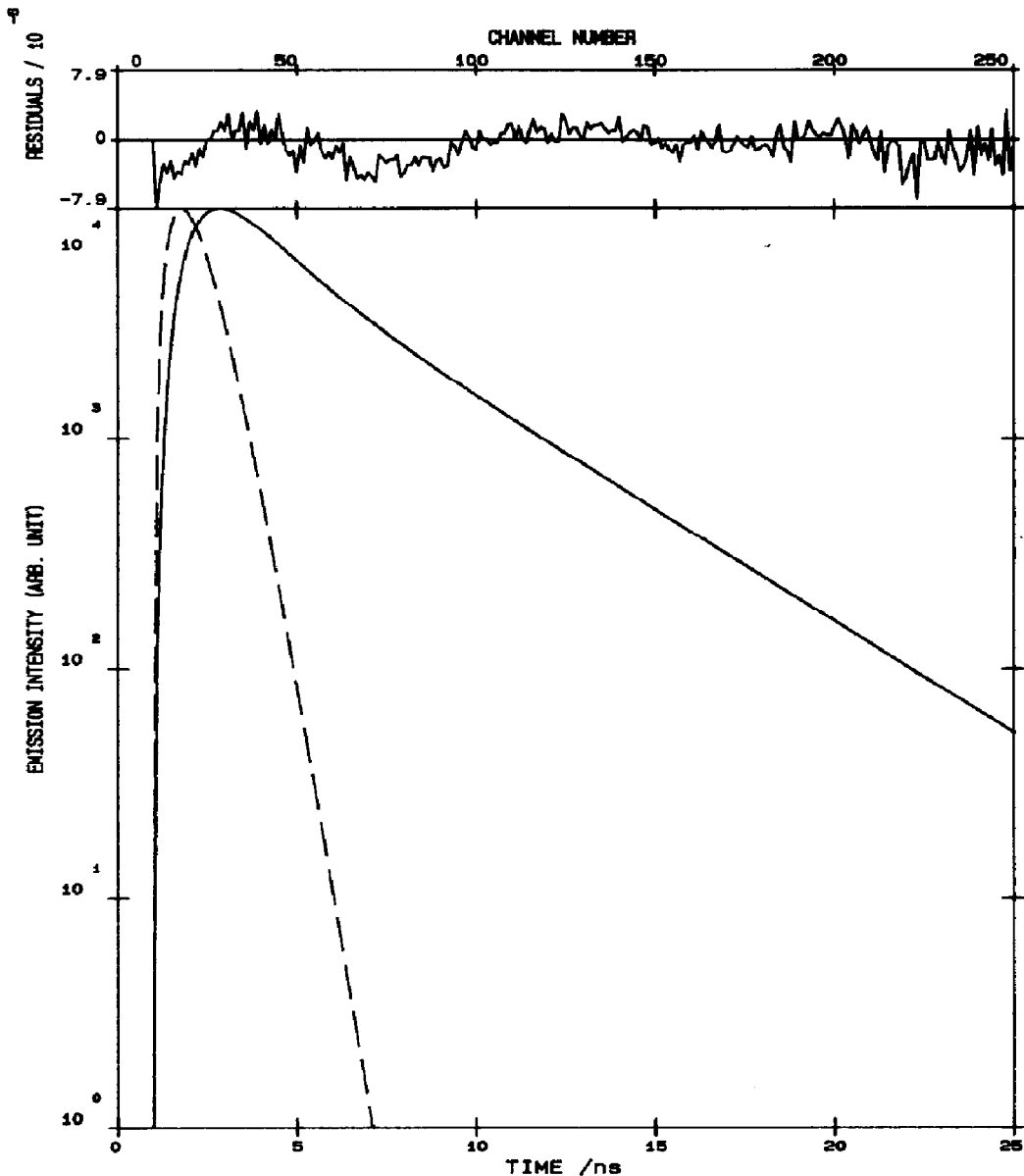
Fig. 2. Deconvolution of the normalized simulated response function (noiseless). The response function was obtained by a convolution of a double-exponential decay function ($a_1 = 0.5$, $\tau_1 = 1.0$ ns, $a_2 = 0.5$ and $\tau_2 = 10.0$ ns) with the lamp intensity function ($e(t) = 295562t^2 \exp(-2.5t)$) (fitting in the Fourier space).

Table 1 shows the results of the deconvolution of several sets of model data for both noiseless and noisy decay curves. The performance characteristics of two FFT deconvolution approaches as indicated by the values of either the root-mean-square error (RMS) or χ_ν^2 are similar, with the fitting in the time domain being slightly more accurate. These characteristics
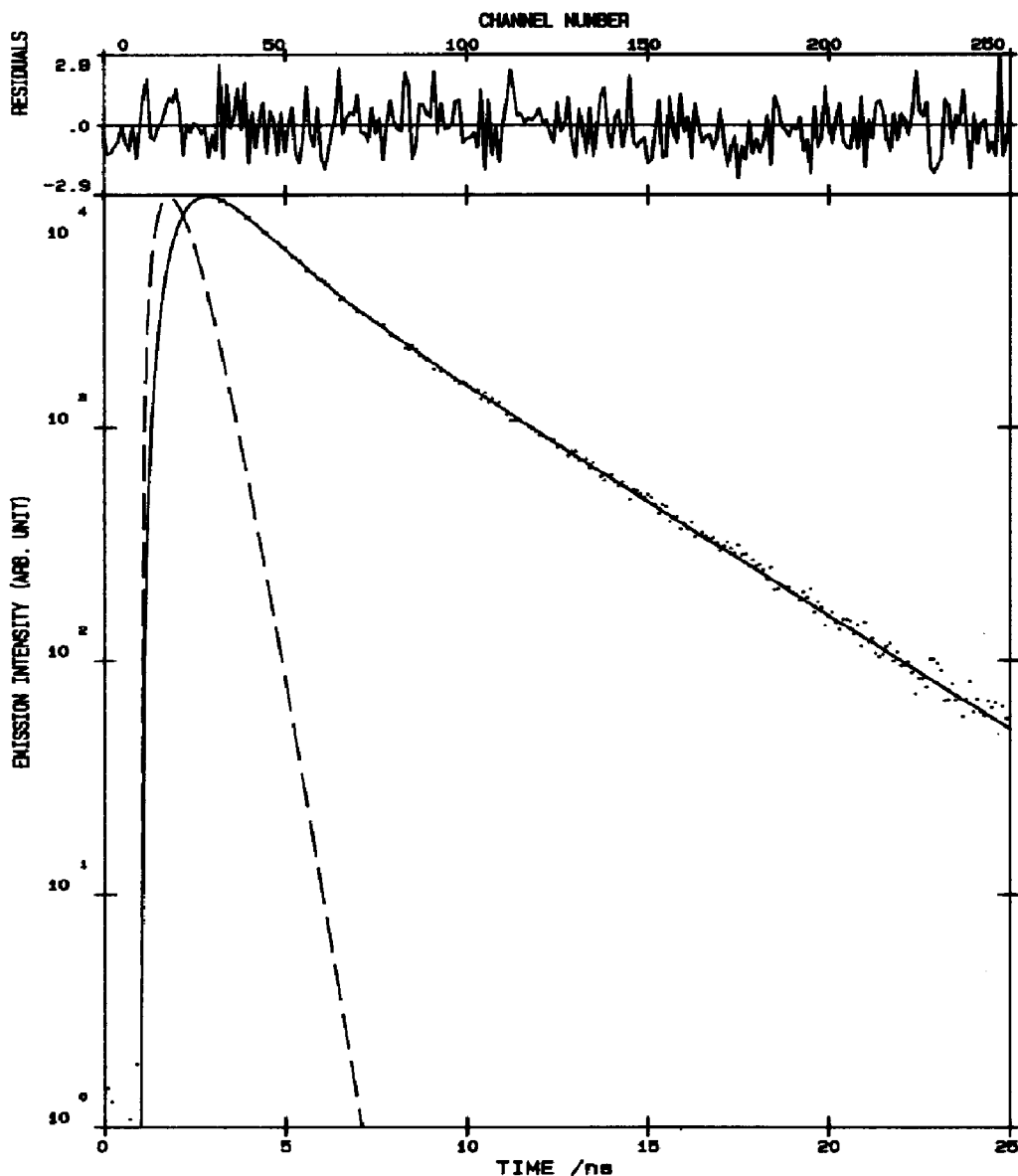
Fig. 3. Deconvolution of the normalized simulated response function with added noise of the gaussian type. The response function was obtained by a convolution of a double-exponential decay function ($a_1 = 0.5$, $\tau_1 = 1.0$ ns, $a_2 = 0.5$ and $\tau_2 = 10.0$ ns) with the lamp intensity function ($e(t) = 295562t^2 \exp(-2.5t)$) (fitting in the Fourier space).

are comparable with those obtained by the iterative convolution method [6].

Figure 4 shows the weighted residuals R_i obtained in the deconvolution analysis of the same decay profile, either noiseless (plots (a), (b), (c) and (d)) or with noise added (plots (e), (f), (g) and (h)), under various

TABLE 1

Performance characteristics of typical runs of the FFT and iterative procedures for 256 data point deconvolution programs

Method of convolution (noise level)	FFT fitting in the time space		FFT fitting in the Fourier space		Iterative convolution[b]	
	RMS[a]	χ_ν^2	RMS[a]	χ_ν^2	RMS[a]	χ_ν^2
Iterative (no noise)	8.46×10^{-4}	—	2.58×10^{-3}	—	7.37×10^{-4}	—
FFT (no noise)	3.81×10^{-4}	—	2.42×10^{-3}	—		
Iterative (10000)	5.50×10^1	0.9242	5.88×10^1	0.9959	5.59×10^1	0.9798
FFT (10000)	5.82×10^1	1.0292	5.51×10^1	0.9903		
Iterative (3000)	3.24×10^1	0.9857	3.10×10^1	0.9655	3.11×10^1	0.9648
FFT (3000)	3.07×10^1	0.9538	3.25×10^1	0.9830		

The test decay profile was obtained by convolution of the decay function

$$f(t) = a_1 \exp(-t/\tau_1) + (1 - a_1) \exp(-t/\tau_2)$$

with $a_1 = 0.5$, $\tau_1 = 10$ ns and $\tau_2 = 100$ ns, with a long-tail lamp function $e(t) = at^2 \exp(-bt)$, and with $a = 2955.62$ ns^{-2} and $b = 0.25$ ns^{-1}. The convoluted response function was normalized to a 10 000 maximum for the noiseless data. The noisy data were obtained by adding random gaussian noise to the response function profile which had been normalized to the maximum indicated level. The gaussian noise was calculated for the normalized function.

$$^a\text{RMS} = \left[\frac{\sum_{i=1}^{N} \{f_o(i) - f_e(i)\}^2}{N} \right]^{1/2}$$

[b] Using a published iterative deconvolution program [6] based on a recurrence formula of Grinvald and Steinberg [7].

conditions. A comparison of the residuals indicates that the correct deconvolution results are only obtained when the rules of the scheme in Fig. 1 are closely followed, as in plots (a) and (e) of Fig. 4.

Thus it is shown here that serious systematic error is introduced into $H'(n) = H_R'(n) + iH_I'(n)$, where $H'(n) = F'(n)/E'(n)$, when $F'(n)$ and $E'(n)$ are calculated by a straightforward FFT of the raw data obtained directly from the decay profile and the lamp profile respectively (Figs. 4(d) and 4(h)). The same error problem is inherent in the calculation using the FFT technique whatever instrumental method is used. For example, the instrumental method used by Wild et al. [2], where the multiperiodic superposition of the lamp and decay profiles was obtained, will suffer to the
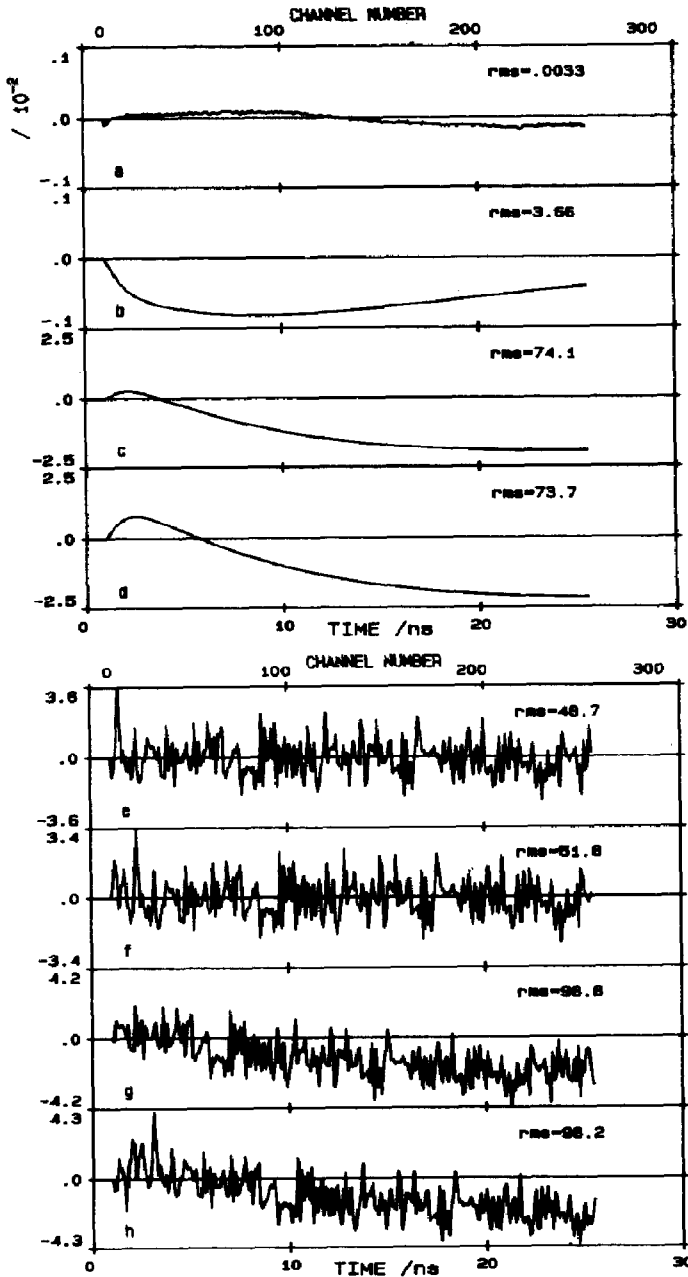
Fig. 4. Weighted residuals R_i obtained in the deconvolution calculations for either noise-less (plots (a), (b), (c) and (d)) or noisy (plots (e), (f), (g) and (h)) profiles. The decay profile was obtained by a convolution of the lamp profile ($e(t) = 295562t^2 \exp(-2.5t)$) with the exponential decay function ($h(t) = \exp(-t/\tau)$), with $\tau = 5.0$ ns in (a), (b), (e) and (f) and $\tau = 10.0$ ns in (c), (d), (g) and (h). Deconvolution procedure in (a) and (e) follows the scheme in Fig. 1 with a 512 point FFT. The procedure in (b), (c), (f) and (g) assumes zero values for the decay profile in the extended region (257 - 512 channels). The procedure in (d) and (h) is based on the 256 point FFT of the raw data. The parameters recovered are $\tau = 5.000\,00$ ns in (a) and $\tau = 5.003\,72$ with $\chi_\nu^2 = 1.020\,35$ in (e).

same extent as the technique of single-photon counting, where the data are collected in one period [15]. The truncation of the Fourier coefficient at frequency NC in the evaluation of eqn. (9) is equivalent to a confinement to a low frequency window (0 - NC). However, a low value of NC decreases the time of computing. As can be seen from Table 2, the precision of fitting is not affected over a wide range of values for NC, and values of NC as low as 10 - 30 can be applied.

TABLE 2

Test of the FFT fitting in the Fourier space: effect of the number NC of Fourier coefficients on the root-mean-square error RMS

NC	Noiseless data		Noisy data		
	LSQ	RMS	LSQ	RMS	$\chi_\nu{}^2$
	4.923×10^{-10}	2.244×10^{-3}	9.852×10^{-3}	4.563×10^1	1.0434
10	—	—	3.901×10^{-2}	4.505×10^1	1.0022
20	—	—	4.126×10^{-1}	4.522×10^1	0.9870
30	1.292×10^{-9}	2.265×10^{-3}	7.255×10^{-1}	3.908×10^1	0.9246
50	4.296×10^{-9}	2.105×10^{-3}	1.288×10^1	4.253×10^1	0.9687
100	2.055×10^{-7}	2.244×10^{-3}	1.446×10^3	4.455×10^1	1.0466
150	5.686×10^{-6}	1.995×10^{-3}	2.083×10^4	4.971×10^1	1.3527
200	6.898×10^{-5}	2.244×10^{-3}	2.437×10^5	6.529×10^1	1.9735
256	9.988×10^{-3}	5.233×10^{-3}	2.119×10^6	1.123×10^2	5.1971

Model data were prepared as in Table 1. The decay function had $a = 1.0$ and $\tau = 30$ ns. Gaussian noise was calculated for a maximum counting level of 10 000. Other conditions were as in Table 1.

5. Analysis of decay curves that involve non-exponential decay functions

In most cases of luminescence decay, an exponential model that relates the decay to a simple radiative process is appropriate, i.e. the decay function is simply related to the lifetime of the excited state by the equation $h(t) = \exp(-t/\tau)$ [1]. In some cases, however, especially when high precision is used in the analysis, it is found that there is significant non-exponentiality in the luminescence decay curve. There are a number of physical reasons to account for such behaviour [16 - 18]. In order to deconvolute this type of non-exponential decay curve, a decay law comprising a sum of exponentials is frequently used [1]. A third situation arises in other processes, for example time-dependent diffusion-controlled fluorescence quenching in solution [16] and donor–acceptor distance-dependent energy transfer in the solid state [17, 18], where the observed, non-exponential decay curves cannot be described by even a sum of a series of exponentials. Such is the case when electron transfer reactions compete for natural decay processes [19]. Our studies on the luminescence of porphyrins in rigid matrices containing an electron acceptor have shown [20, 21] that

non-exponential luminescence decay arises as the result of the distance dependence of the electron transfer rate.

Figure 5 shows the fluorescence decay profile recorded for MgTPP in a glassy BuCl solution containing 1 vol.% pyridine in the presence of 0.4 mol dm^{-3} CBr$_4$ at 77 K. Decay profiles fitted on the basis of exponential functions were found to deviate significantly from the observed response
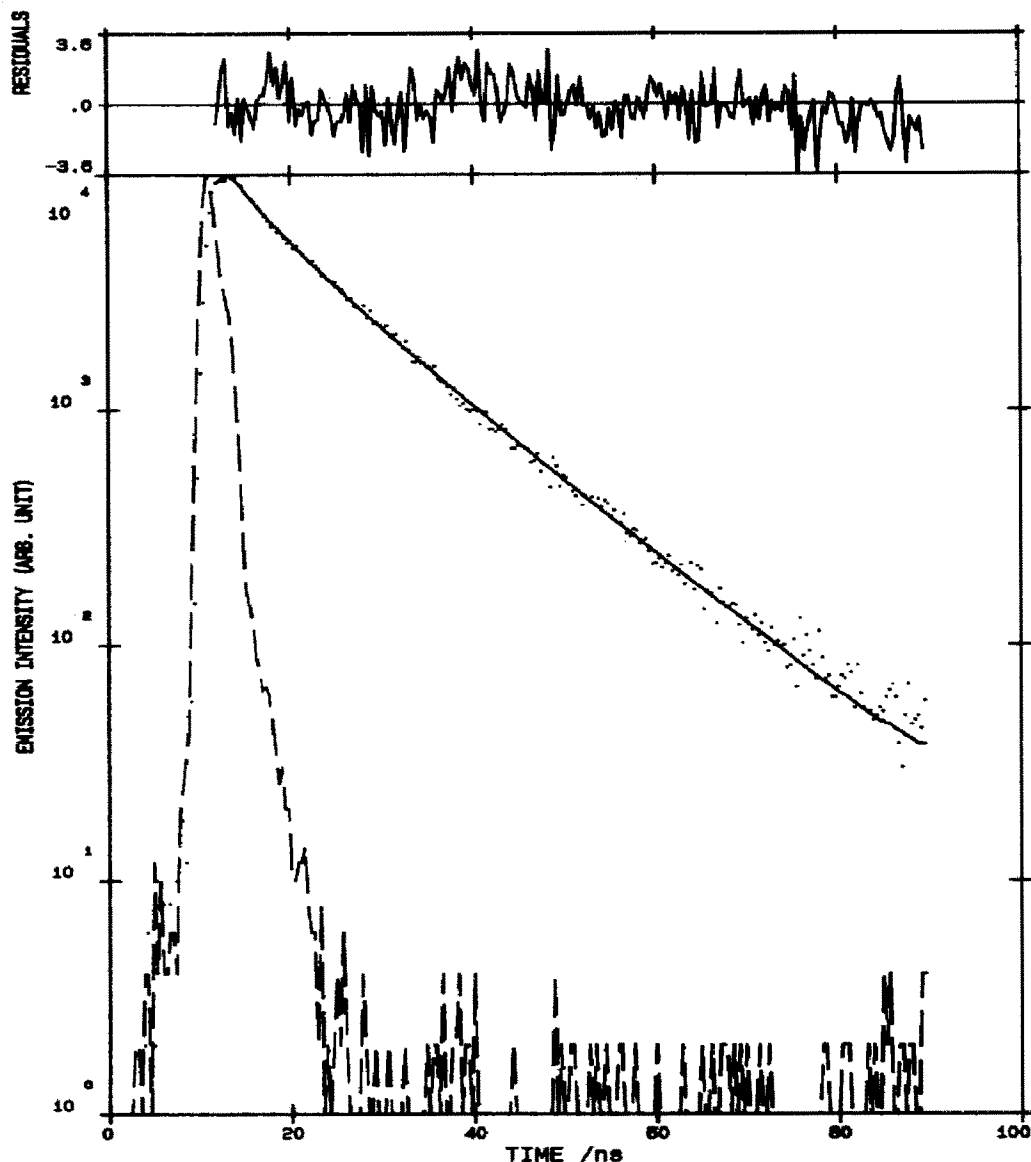

Fig. 5. Deconvolution of the fluorescence decay of MgTPP in glassy BuCl containing 1 vol.% pyridine in the presence of 0.4 mol dm^{-3} CBr$_4$ at 77 K using the decay function as in eqn. (14). The values of the fitted parameters obtained are $a = 0.81$ Å and $\nu = 1.2 \times 10^{13}$ s^{-1}. The lifetime, $\tau_0 = 15.5$ ns, of MgTPP fluorescence without CBr$_4$ was found in a separate experiment.

curve. We attribute this deviation to an electron transfer from the excited singlet state of the porphyrin to the CBr_4 acceptor molecule [20, 21] according to the reaction

$$MgTPP^* + CBr_4 \longrightarrow MgTPP^+ \cdot + CBr_4^- \cdot \tag{13}$$

The addition of an electron transfer pathway for quenching the excited state in a system in which electron donors and acceptors are randomly distributed in an inert matrix changes the time dependence of the emission intensity $h(t)$ to [18, 19]

$$h(t) = A \exp\left[-\left\{\frac{t}{\tau_0} + \frac{4}{3} \pi a^3 Cg(t)\right\}\right] \tag{14}$$

In eqn. (14), A is a constant, τ_0 is the fluorescence lifetime in the absence of the acceptor, C is the acceptor concentration and a is defined by the dependence of the electron transfer rate constant $k(R)$ on distance R as $k(R) = \nu \exp(-R/a)$ (here ν is the electron transfer rate constant for donor–acceptor pairs in contact). The function $g(t)$ in eqn. (14) is well approximated for $\nu t > 10$ by [18]

$$g(t) = (\ln \nu t)^3 + 1.732(\ln \nu t)^2 + 5.934(\ln \nu t) + 5.445 \tag{15}$$

We have found the FFT method described in this paper to be very useful in analysis of such complicated decay functions. The values of a and ν were obtained by fitting this theoretical decay law equation to the experimental data. The magnitudes of the parameters of eqn. (14), as obtained from the fit in Fig. 5 ($a = 0.81$ Å, $\nu = 1.2 \times 10^{13}$ s^{-1}) are reasonable when the effects of the distance dependence of the electron transfer rate are considered theoretically. For example, the value of a is close to the average value of 0.83 Å determined by Miller *et al.* [22] for the reaction of radical anions of aromatic hydrocarbons with organic molecules. Measurements of fluorescence quenching by others have yielded $a = 0.7$ Å [23] and $a = 0.57$ Å [24], for two different electron donors, the ruthenium phenanthroline complex and indole respectively.

6. Conclusions

New procedures employing FFT in the deconvolution of luminescence decay curves have been described. These procedures avoid the common error which can arise from the overlap effect in convolution of two overlapping periodic functions with the use of the discrete Fourier transform. A Fortran program DECAYFIT written for the IBM S9001 microcomputer allows for fitting, in a matter of minutes, of an arbitrarily chosen decay function to model or real luminescence decay data. The analysis may be performed in either the time domain or the frequency domain. The fitting in the time domain is slightly more accurate, but it is a slower procedure.

The Fourier transform method presented here is as accurate as the iterative convolution method and does not suffer its limitation to only one type of decay law equation.

Two general notes on the application of FFT to deconvolution seem to be appropriate. Firstly, the efficiency of the convolution calculation can be increased by application of the FFT procedures which allow for the transform of $2N$ samples by an N-sample transform [10]. Secondly, the improvements in the accuracy of the calculation of the discrete Fourier coefficients, as those reported recently [25], have a negligible effect on the results.

Acknowledgments

References

1 W. R. Ware, in A. A. Lamola (ed.), *Creation and Detection of the Excited State*, Vol. 1, Dekker, New York, 1971.
2 U. P. Wild, A. R. Holzwarth and H. P. Good, *Rev. Sci. Instrum.*, *48* (1977) 1621.
3 W. R. Ware, L. J. Doemeny and T. L. Nemzek, *J. Phys. Chem.*, *77* (1973) 2038.
4 A. E. McKinnon, A. G. Szabo and D. R. Miller, *J. Phys. Chem.*, *81* (1977) 1564.
5 D. V. O'Connor, W. R. Ware and J. C. Andre, *J. Phys. Chem.*, *83* (1979) 1333.
6 D. V. O'Connor and D. Phillips, *Time-correlated Single Photon Counting*, Academic Press, London, 1984, pp. 158 - 210.
7 A. Grinvald and I. Z. Steinberg, *Anal. Biochem.*, *59* (1974) 583.
8 J. H. Fuhrhop, in K. M. Smith (ed.), *Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam, 1975, pp. 757 - 869.
9 E. Gudgin, R. Lopez-Delgado and W. R. Ware, *Can. J. Chem.*, *59* (1981) 1037.
10 E. O. Brigham (ed.), *The Fast Fourier Transform*, Prentice—Hall, Englewood Cliffs, NY, 1974.
11 P. Bloomfield, *Fourier Analysis of Time Series: An Introduction*, Wiley, New York, 1976, pp. 61 - 76.
12 H. P. Good, A. J. Kallir and U. P. Wild, *J. Phys. Chem.*, *88* (1984) 5435.
13 D. W. Marquardt, *J. Soc. Indian Appl. Math.*, *11* (1963) 431.
14 P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, Mc-Graw-Hill, New York, 1969, p. 235.
15 J. C. Andre, L. M. Vincent, D. O'Connor and W. R. Ware, *J. Phys. Chem.*, *83* (1979) 2285.
16 F. Heisel and A. Miehe, *J. Chem. Phys.*, *77* (1982) 2558.
17 T. M. Searle, *Philos. Mag. B*, *46* (1982) 163.
18 M. Inokuti and F. Hirayama, *J. Chem. Phys.*, *43* (1965) 1978.
19 R. P. Domingue and M. D. Fayer, *J. Chem. Phys.*, *83* (1985) 2242.

20 Z. Gasyna, W. R. Browett and M. J. Stillman, *Inorg. Chem.*, *24* (1985) 2440.
21 Z. Gasyna, W. R. Browett and M. J. Stillman, *ACS Symp. Ser.*, *321* (1986) 298.
22 J. R. Miller, J. V. Beitz and R. K. Huddleston, *J. Am. Chem. Soc.*, *106* (1984) 5057.
23 S. Strauch, G. McLendon, M. McGuire and T. Guarr, *J. Phys. Chem.*, *87* (1983) 3579.
24 A. Namiki, N. Nakashima and K. Yoshihara, *J. Chem. Phys.*, *71* (1979) 925.
25 M. Proeyen and L. Hellemans, *Rev. Sci. Instrum.*, *56* (1985) 2325.