Journal of Photochemistry, *27* (1984) 171 - 178

APPLICATION OF THE λ INVARIANCE TEST ON NON-EXPONENTIAL DECAYS

SATOSHI HIRAYAMA

Faculty of Textile Science, Kyoto Technical University, Matsugasaki, Sakyo-ku, Kyoto 606 (Japan)

(Received January 3, 1984; in revised form April 18, 1984)

Summary

Isenberg's λ invariance test is applied to the non-linear least-squares (LS) method developed for the deconvolution of non-exponential decays to investigate its ability to determine the number of exponentials required for the deconvolution. The test verifies the conclusion reached using the LS method, namely that the quenched fluorescence of 9,10-dicyanoanthracene in poly(methyl methacrylate) decays with three exponentials.

1. Introduction

Fluorescence decays, when analysed precisely, are often found to be non-exponential for various reasons. For instance, time-dependent diffusion-controlled fluorescence quenching in solution [1], donor–acceptor distance-dependent energy transfer in solid states [2] and fluorophores which undergo solvent relaxation or relax to intermediate states [3] obviously lead to non-exponential decays. In the gas phase a large number of compounds exhibit non-exponential decay especially when they are excited to the higher energy states in the isolated molecule limit [4]. The biologically important compound tryptophan also presents an interesting example of multiexponential decay [5, 6].

Although the recent improvement in the lifetime measurements on the subnanosecond and picosecond time scale has enabled us to have confidence in the observed non-exponential behaviour [7, 8], there is still some debate as to the number of exponentials into which the non-exponential decay can be deconvoluted [6, 9, 10]. Non-exponential decays would provide more detailed information on the fate of excited states than single-exponential decays do because non-exponential decay is characterized by more parameters than is single-exponential decay. To characterize non-exponential decay, it is essential to establish a method of determining the number of exponentials that the observed non-exponential decay comprises.

0047-2670/84/$3.00

Recently, Isenberg has proposed the λ invariance test [11] as a method of resolving this problem. He applied it to the moment displacement (MD) method developed by himself [12] and showed it to be useful in selecting the appropriate number of exponentials required for the deconvolution.

However, as has been discussed by several researchers [13, 14], in many respects the non-linear least-squares (LS) method appears to be superior to the MD method. Therefore, it is worth applying Isenberg's λ invariance method to the LS method to establish whether or not it is of use as a test or a check on the calculation results attained by the LS method.

As an example in which the fluorescence exhibits non-exponential decay, the quenched fluorescence of 9,10-dicyanoanthracene (DCA) in poly(methyl methacrylate) (PMMA), containing a small amount of triethylamine (TEA) (about 5 vol.%) as a quencher, was chosen, since the fluorescence quenched in the solid phase is generally expected to decay non-exponentially [2, 15]. To measure the fluorescence lifetimes, the conventional time-correlated single-photon counting technique was employed, the details of which will be published elsewhere [3].

2. Results and discussion

2.1. Non-exponential decays observed on fluorescence quenching of 9,10-dicyanoanthracene in poly(methyl methacrylate)

Although the fluorescence of DCA in PMMA exhibits single-exponential decay with a lifetime of 11.27 ns, the fluorescence quenched by TEA in a PMMA matrix no longer follows single-exponential decay. The observed non-exponential decay curves are shown in Figs. 1 and 2, where the best-fit decay curves convoluted with two (Fig. 1) and three (Fig. 2) exponentials are indicated by full lines. The non-random residual distribution displayed in Fig. 1 definitely indicates that the decay curve cannot satisfactorily be convoluted with two exponentials and that instead it requires at least one more exponential. (When a decay curve deconvoluted with two exponentials gives a W-shaped residual distribution as is exemplified in Fig. 1, it can be said from our experience that one more exponential with a lifetime shorter than the other two is required to achieve a better fit.) In fact, the addition of one more exponential reduces χ^2 further (from 2.205 to 0.947) and leads to a random residual distribution as is shown in Fig. 2.

Analysis with four exponentials did not result in any significant improvement in χ^2 (from 0.947 to 0.938). In addition, the shortest lifetime (fourth component) was calculated to be 0.27 ns which was of the same magnitude as its standard deviation (0.25 ns). Thus, it seems to be most appropriate to conclude that the fluorescence of DCA quenched by TEA in PMMA decays with three exponentials at least within the limit of the time resolution of our present apparatus (channel width, 0.0858 ns).

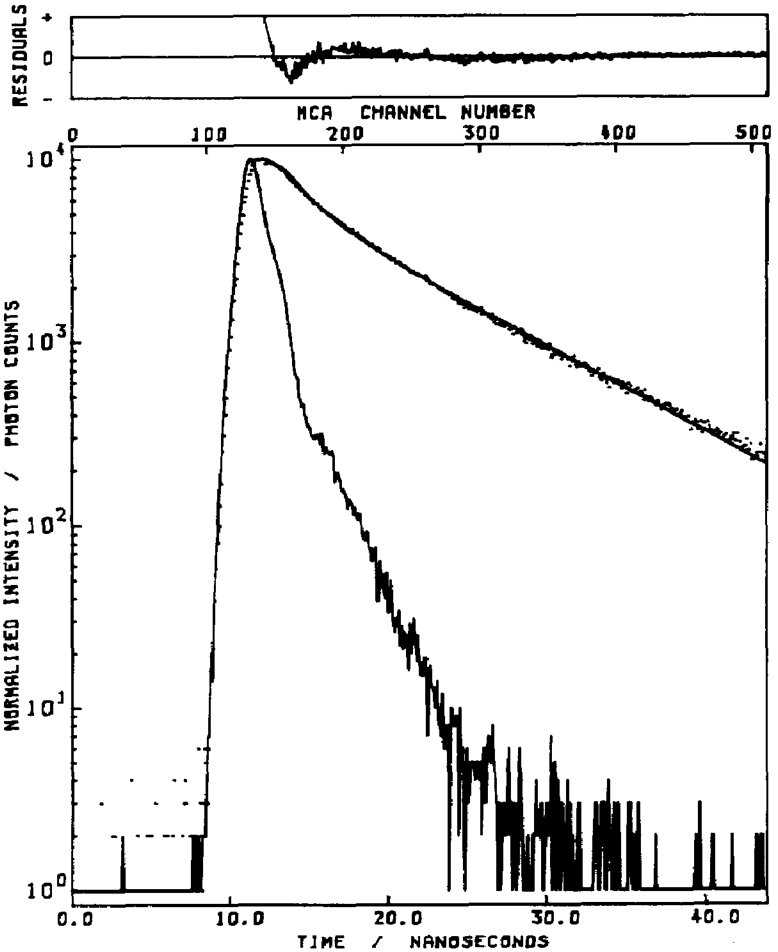

Fig. 1. Non-exponential decay of the quenched fluorescence of DCA in PMMA containing TEA (about 5 vol.%) as a quencher. The full line through the points represents the best-fit decay curve convoluted with two exponentials. The residuals, which are normalized to the maximum, are not the reduced residuals.

2.2. λ invariance test

At present there is no conclusive way of knowing how many exponentials the decay comprises, although the residual distribution, autocorrelation, Durbin and Watson parameter [7] and some other manipulations [16] help to confirm the results of analysis. Therefore, it is worth examining whether or not Isenberg's λ invariance test is effective in verifying the deconvolution based on the LS as well as on the MD method. To our knowledge, such an attempt has not yet been carried out.

When it is assumed that the true fluorescence decay can be expressed by a sum of exponentials, the time evolution $F(t)$ of the fluorescence can be convoluted by the response function $L(t)$ of the lamp as follows:

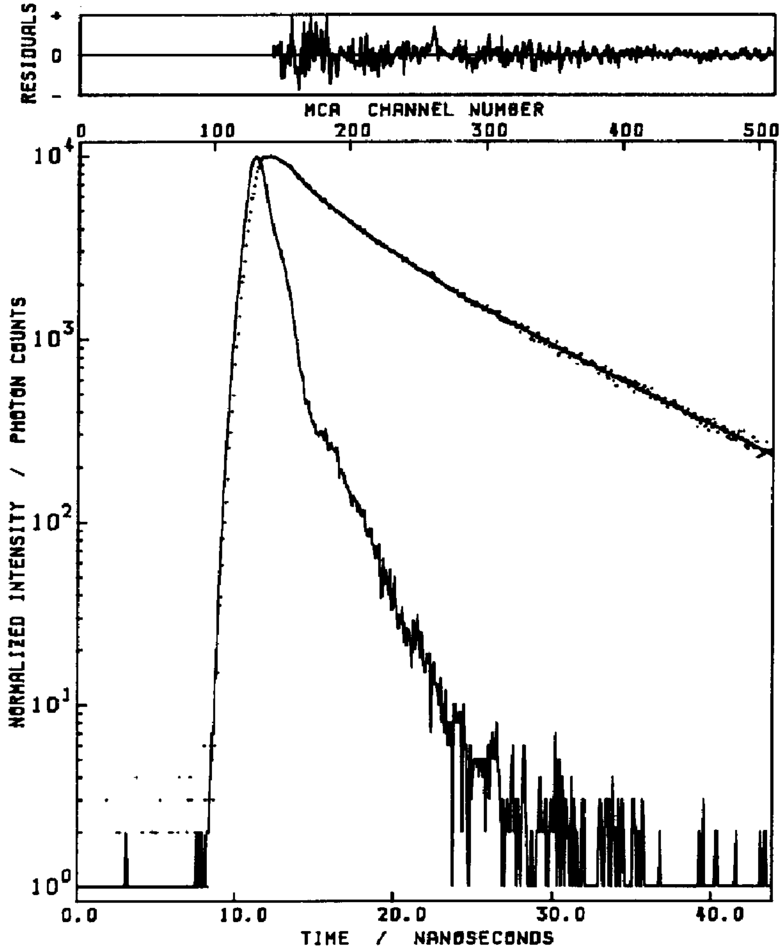

Fig. 2. Non-exponential decay of the quenched fluorescence of DCA in PMMA containing TEA (about 5 vol.%) as a quencher. The full line through the points represents the best-fit decay curve convoluted with three exponentials. The lifetimes obtained are 10.16 ± 0.11 ns, 3.16 ± 0.16 ns and 0.60 ± 0.06 ns with pre-exponential factors of 0.0221 ± 0.0006, 0.0270 ± 0.0011 and 0.0608 ± 0.0047 respectively. The residuals, which are normalized to the maximum, are not the reduced residuals.

$$F(t) = \int_0^t L(t') \sum_{i=1}^{n} A_i \exp\left(-\frac{t-t'}{\tau_i}\right) \mathrm{d}t' \quad (1)$$

On multiplying both sides of eqn. (1) by $\exp(-\lambda t)$, eqn. (1) reduces to

$$F(t)\exp(-\lambda t) = \int_0^t L(t')\exp(-\lambda t') \sum_{i=1}^{n} A_i \exp\left\{-\left(\frac{1}{\tau_i} + \lambda\right)(t-t')\right\} \mathrm{d}t' \quad (2)$$

When $F(t)\exp(-\lambda t)$ and $L(t')\exp(-\lambda t')$ are rewritten as $F'(t)$ and $L'(t')$ and are redefined as the modified decay and modified lamp profile respectively

$$F'(t) = \int_0^t L'(t') \sum_{i=1}^{n} A_i \exp\left\{-\left(\frac{1}{\tau_i} + \lambda\right)(t - t')\right\} dt' \tag{3}$$

is obtained.

The implications of eqn. (3) are that when the modified decay curve $F'(t)$ is deconvoluted by the modified lamp profile $L'(t')$ the lifetimes obtained are $\tau_i/(1 + \lambda\tau_i)$ and that the pre-exponential factors A_i should be invariant within a certain error when λ is varied.

Figures 3 and 4 illustrate the result of the deconvolution of the modified decay curve when λ is taken to be equal to $0.15 \times 10^9\ s^{-1}$. Again,

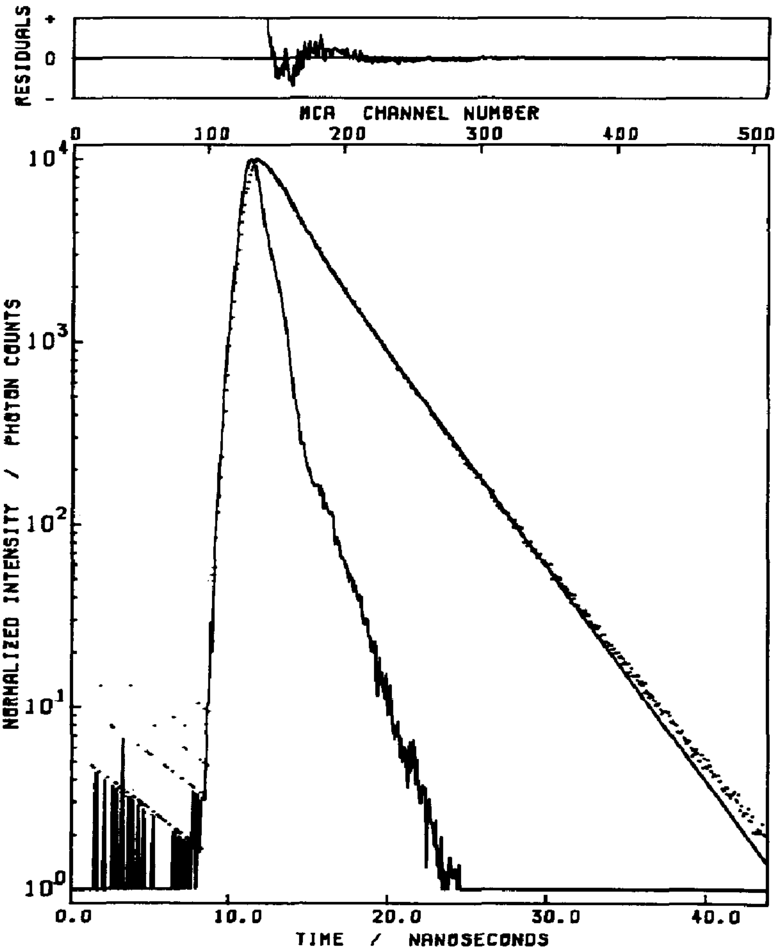

Fig. 3. Convolution with two exponentials of the modified decay curve. The decay curve given in Fig. 1 is modified according to eqn. (2) with $\lambda = 0.15 \times 10^9\ s^{-1}$. It is seen that the dual-exponential analysis does not give randomly distributed residuals. Compared with Fig. 1 the residuals given here exhibit a rapid decay to very small values. This is because they are multiplied by $\exp(-\lambda t)$.

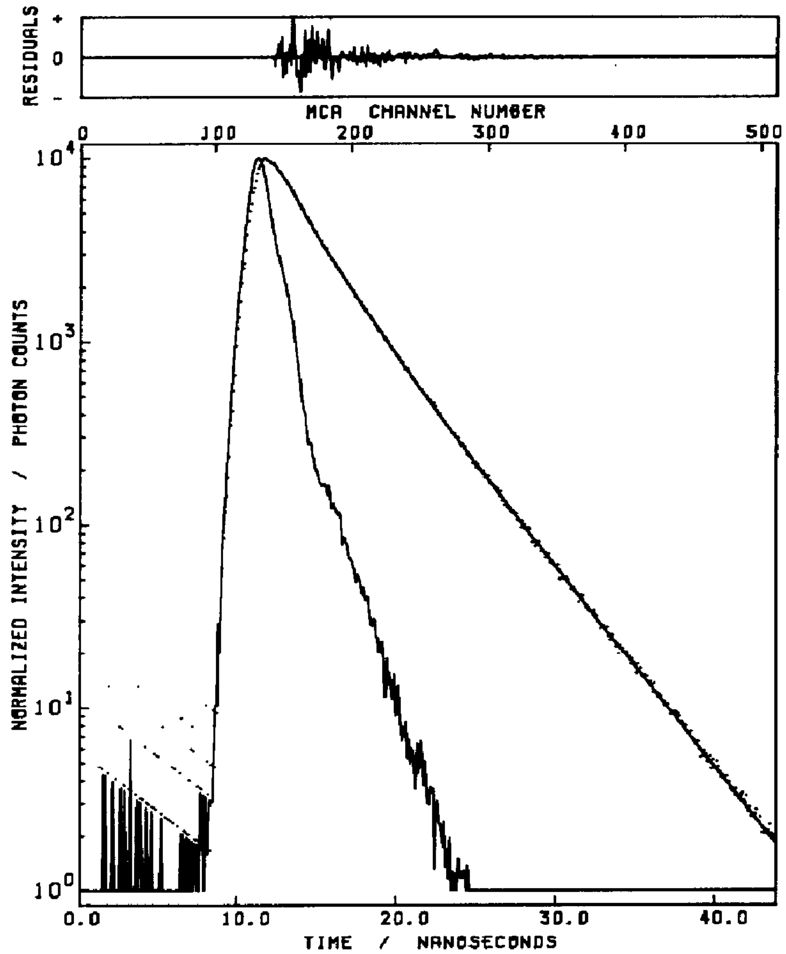

Fig. 4. Convolution with three exponentials of the modified decay curve. The decay curve given in Fig. 2 is modified according to eqn. (2) with $\lambda = 0.15 \times 10^9$ s^{-1}. The modified lifetimes of the three exponentials are 3.98 ± 0.06 ns, 1.97 ± 0.17 ns and 0.472 ± 0.09 ns with pre-exponential factors of 0.0249 ± 0.0020, 0.0295 ± 0.0020 and 0.0790 ± 0.0121 respectively. Compared with Fig. 2 the residuals given here exhibit a rapid decay to very small values. This is because they are multiplied by $\exp(-\lambda t)$.

for the two-exponential analysis, the residual distribution is notably non-random. By contrast, as is seen in Fig. 4, the three-exponential analysis gives a satisfactory random residual distribution with modified lifetimes of 3.98 ± 0.06 ns, 1.97 ± 0.17 ns and 0.43 ± 0.09 ns, from which the τ_i values are calculated to be 9.86 ns, 2.82 ns and 0.46 ns respectively. These values are slightly lower but almost the same as those obtained from the original unmodified decay curve.

Similar calculations were carried out by taking λ values of 0.05×10^9, 0.10×10^9 and 0.20×10^9 s^{-1}, and the results obtained are shown in Fig. 5, from which it is seen that neither single- nor dual-exponential analysis yields invariant lifetimes but that the lifetimes of the three exponentials are reasonably constant for all values of λ. In addition, the pre-

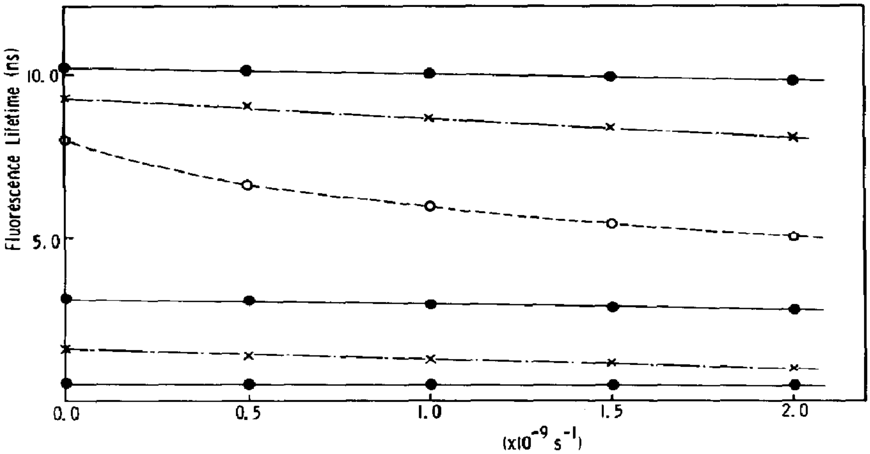

Fig. 5. λ invariance test on single-exponential (--○--), dual-exponential (— · —×— · —) and triple-exponential (—●—) analyses. It is seen that the lifetimes of the triple exponentials are almost invariant with λ, verifying the conclusion that the present decay is satisfactorily deconvoluted with the three exponentials. Rather poor results were obtained when the test was applied on the four-exponential analysis.

exponential factors of the three exponentials are only modestly affected by variations in λ, being compatible with the prediction of eqn. (3).

When this test was applied to the four-exponential analysis of the decay presented here, we obtained poor results. The variations in the lifetime and in the pre-exponential factor are much greater than those of the three-exponential analysis. This is presumably because the test is highly dependent on a large uncertainty in the shortest lifetime (fourth component).

Thus it can now be said that the λ invariance test verifies the conclusion reached by the LS method that the present decay curve is most satisfactorily deconvoluted with three exponentials. Therefore, before observed decays are specified as dual, triple or quadruple exponential, it is recommended that the number of exponentials is confirmed by applying the λ invariance test, which is very easily introduced since, once the observed decay curves and lamp profiles have been modified according to eqn. (2), the modified decay can be deconvoluted in exactly the same manner as are the original decays.

The non-exponential decay presented here is not specific to TEA, but is generally recognized for other quenchers such as triphenylphosphine and 1,3-cyclohexadiene.

Finally, the following two points are worth noting.

(i) The present method only predicts the most appropriate number of exponentials required to fit an observed fluorescence decay curve; it does not rationalize the physical model deduced from multiexponential decay. For the model to be accepted, other indications must be available. Thus, it is necessary to examine the effect of temperature on the decay feature and/or the dependence of the decay components and lifetimes on the observation wavelength.

(ii) Decay functions other than a sum of exponentials should also be used in an attempt to deconvolute non-exponential decays and the goodness of the fit must be compared with that of multiexponential analysis, because in some cases the physical significance of the multiexponential decay may well be obscured even if a satisfactory fit is achieved. From our preliminary results, it appears that the function $A \exp(-at - bt^{1/2})$ gives a poorer fit to the present decay curve than a sum of three exponentials.

Further study is now in progress in our laboratory.

Acknowledgments

The author is grateful to Mr. Y. Shimono and Mr. K. Kawamoto for carrying out the lifetime calculations. This work is partly supported by Grants-in-aid 54670006 and 56540260 for Scientific Research from the Ministry of Education of Japan.

References

1 F. Heisel and A. Miehe, *J. Chem. Phys., 77* (1982) 2558.
2 T. M. Searle, *Philos. Mag. B, 46* (1982) 163.
3 S. Hirayama and Y. Shimono, *J. Chem. Soc., Faraday Trans. I*, in the press.
4 A. E. W. Knight, B. K. Selinger and I. G. Ross, *Aust. J. Chem., 26* (1973) 1159.
5 A. G. Szabo and D. M. Rayner, *J. Am. Chem. Soc., 102* (1980) 554.
6 H. Leismann, H.-D. Scharf, W. Strassburger and A. Wollmer, *J. Photochem., 21* (1983) 275.
7 R. A. Lampert, L. A. Chester, D. Phillips, D. V. O'Connor, A. J. Roberts and S. R. Meech, *Anal. Chem., 55* (1983) 68.
8 D. P. Millar, R. J. Robbins and A. H. Zewail, *J. Chem. Phys., 75* (1981) 3649.
9 L. J. C. Love and L. A. Shaver, *Anal. Chem., 52* (1980) 154.
10 A. H. Kalanter, *Comput. Phys. Commun., 28* (1983) 315.
11 I. Isenberg and E. W. Small, *J. Chem. Phys., 77* (1982) 2799.
12 I. Isenberg, *J. Chem. Phys., 59* (1973) 5696.
13 A. E. Mckinnon, A. G. Szabo and D. R. Miller, *J. Phys. Chem., 81* (1977) 1564.
14 D. V. O'Connor, W. R. Ware and J. C. Andre, *J. Phys. Chem., 83* (1979) 1333.
15 M. Inokuti and F. Hirayama, *J. Chem. Phys., 43* (1965) 1978.
16 A. H. Kalanter, *J. Lumin., 27* (1982) 13.