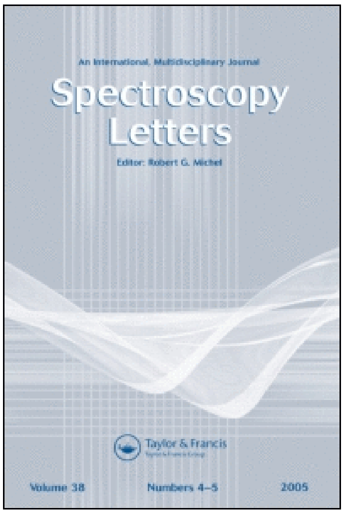

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Cagigal, N. P. , Prieto, J. , Cagigal, M. P. and Prieto, P.(1994) 'Sine Transform of the Autocorrelation Function Applied to Single-Photon-Decay Spectroscopy.', Spectroscopy Letters, 27: 5, 639 — 648
To link to this Article: DOI: 10.1080/00387019408000858
URL: http://dx.doi.org/10.1080/00387019408000858

SPECTROSCOPY LETTERS, 27(5), 639-648 (1994)

SINE TRANSFORM OF THE AUTOCORRELATION FUNCTION APPLIED TO SINGLE-PHOTON-DECAY SPECTROSCOPY.

Key Words: Life-time determination, Single-photon-decay spectroscopy

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ABSTRACT

In this paper we present the sine transform of the Autocorrelation Function of the time interval probability density, TIPD. It not only improves the Signal-to-Noise Ratio (SNR) obtained from a direct measurement of TIPD but even that obtained from the sine transform of TIPD.

Expressions for variances and SNR are given. This technique is compared to the sine transform of TIPD when analyzing a Single-Photon-Decay Spectroscopy signal for low fluorescence intensity.

INTRODUCTION

The usual method for obtaining information in a Single-Photon-Decay Spectroscopy (SPDS) experiment is to estimate the time interval probability density (TIPD), that is the probability of the first photon to be detected at time t after the end of the excitation pulse, $P_f(t)$. The signal information is obtained from fitting between theoretical and experimental values of $P_f(t)$.

In many cases the fluorescence intensity is very low, which makes it necessary to repeat the experiment a large number of times in order to obtain a reasonable statistical accuracy. To overcome this problem, techniques have been developed to obtain a good enough Signal-to-Noise Ratio working with small number of samples.

The positive effects of several kinds of transforms of $P_f(t)$ on the error that appears in the parameter determination has been analyzed. The Laplace[(1)], Fourier[(2)], and Sine[(3)] transforms have been used. All of these allow us a more precise parameter determination. Another kind of processing used to produce a better SNR is evaluation of the autocorrelation function of $P_f(t)$[(4)].

In this paper we combine both techniques in order to reduce the error in the parameter determination. The sine transform of the autocorrelation function of $P_f(t)$ is evaluated. The method followed to determine the decay constant is the same used when the sine transform of $P_f(t)$ is measured. However, in our case, the average over the cross products of $P_f(t)$ produces an important increase of the SNR. This technique can also be applied when the fluorescence signal contains more than one exponential.

Finally, it is interesting to note that the sine transform of the autocorrelation function of $P_f(t)$ can be obtained in two different ways. The first involves evaluating the autocorrelation function of $P_f(t)$, as was done in a previous paper[(4)], and then to performing the sine transform while the other directly evaluates the sine transform of the autocorrelation function[5]. We will use the latter way since it is faster and produces a better SNR.

Since the sine transform of $P_f(t)$ presents a much better SNR than the direct measurement of $P_f(t)$[3], we will compare the two sine transform methods.

THEORY

We will analyze a fluorescence signal composed of a single exponential over a constant background:

$$I(t) = I_0 \exp(-\alpha t) + I_F \tag{1}$$

where α is the decay constant.

The TIPD for a light signal I(t) is given by[6]:

$$P_f(t) = I(t) \exp\left(-\int_0^t I(t')\, dt'\right) \tag{2}$$

For very low intensities, the exponential in Eq.(2) can be approached by 1 and the expression of $P_f(t)$ becomes:

$$P_f(t) = I(t) = I_0 \exp(-\alpha t) + I_F \tag{3}$$

The autocorrelation function of $P_f(t)$ is defined by:

$$G^{(2)}(\tau) = \left\langle P_f(t)\, P_f(t+\tau) \right\rangle \tag{4}$$

where the angle brackets denote an average over the time t.

By substituting Eq.(3) in Eq.(4) we obtain:

$$G^{(2)}(\tau) = I_0' \exp(-\alpha t) + I_F' \tag{5}$$

where:

$$I_0' = I_0 I_F \alpha^{-1} (1 - \exp(-\alpha P)) + \tfrac{1}{2} I_0^2 \alpha^{-1} (1 - \exp(-2\alpha P))$$

$$I_F' = I_F^2 P + I_0 I_F \alpha^{-1} (1 - \exp(-\alpha P)) \tag{6}$$

and P is the largest detectable value of the time interval. In practice the experiment must be repeated a large number of times and P is the interval between excitation pulses.

It can be seen that the autocorrelation function shown in Eq.(5) is an exponential function with the same decay constant. However, an estimate of the autocorrelation is obtained by averaging a series of cross products of $P_f(t)$ and hence it presents a better SNR.

The sine transform of $P_f(t)$ is given by:

$$T_sP(f) = \int_0^{+\infty} \sin(2\pi f t)\, P_f(t)\, dt = 2\pi f\, I_0\, D_\alpha(f) \tag{7}$$

where f denotes the Fourier frequency and $D_\alpha(f) = \left[\alpha^2 + (2\pi f)^2\right]^{-1}$.

Equivalent equation is obtained for the sine transform of the $G^{(2)}(\tau)$:

$$T_sG(f) = \int_0^{+\infty} \sin(2\pi f \tau)\, G^{(2)}(\tau)\, d\tau = 2\pi f\, I_0'\, D_\alpha(f) \tag{8}$$

It is important to note that although $G^{(2)}(\tau)$ is a symmetrical function, only the positive values of τ are taken in order to obtain an expression similar to Eq.(7). If both the positive and negative values of τ were taken, the sine transform will be equal to 0 for all the frequencies and no information will be obtained from it.

The cosine transform of $P_f(t)$ is:

$$T_cP(f) = \alpha\, I_0\, D_\alpha(f) \tag{9}$$

The corresponding cosine transform of $G^{(2)}(\tau)$ ($T_cG(f)$) can be obtained by replacing I_0 by the expression of I_0' shown in Eq.(6).

$$T_cG(f) = \alpha I_0' D_\alpha(f) \quad (10)$$

Figure 1 shows the curve obtained for $T_sP(f)$ from Eq.(7). The shape of $T_sG(f)$ is the same since $T_sP(f)$ and $T_sG(f)$ only differ by a constant factor. It can be seen that a clear maximum appears for the frequency $2\pi f = \alpha$. We will use this fact for a precise determination of α.

The experimental estimator of $T_sP(f)$ is given by:

$$\hat{T}_sP(f) = (1 / N_c) \sum_{j=1}^{Nc} \sin(2\pi f t_j) \quad (11)$$

where N_c is number of times the excitation pulse is repeated.

The estimator of $T_sG(f)$ [5]:

$$\hat{T}_sG(f) = \left(1 / N_c'\right) \sum_{j=1}^{Nc} \sum_{k>j}^{Nc} \sin(2\pi f \tau_{jk}) \quad (12)$$

were $\tau_{jk} = |t_k - t_j|$ are the positive values of the delay. Since in this case two time-intervals are used in each term of the sum, the number N_c' is given by: $N_c' = N_c(N_c-1)/2$.

Another estimator of $T_sG(f)$ could be obtained by estimating first $P_f(t)$, correlating it as indicated by Eq.(5) and then performing the sine transform. However, this requires far more post processing time and gives a poorer SNR.

It is easy to obtain the expression of the variance of the sine transform:

$$\mathrm{Var}(T_sP(f)) = \frac{1}{2 N_c}\left(\frac{I_0}{\alpha} - T_cP(2f) - 2(T_sP(f))^2\right) \quad (13)$$

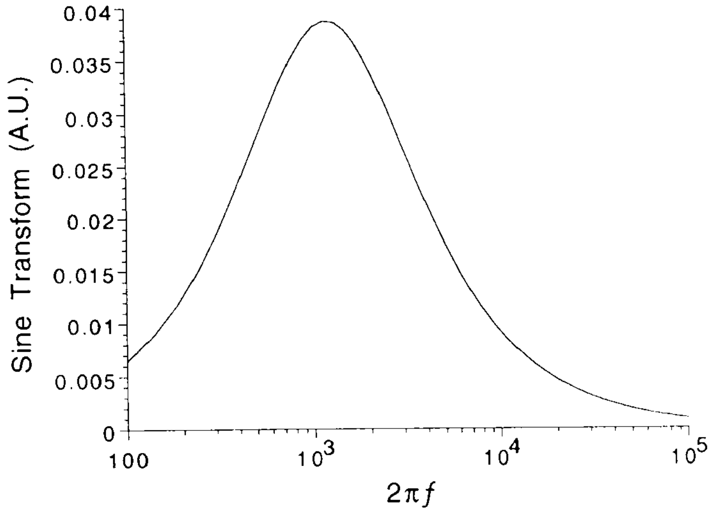

Fig. 1.- Theoretical values of the sine transform of $P_f(t)$ once normalized. The curve coincides with the normalized sine transform of the autocorrelation function of $P_f(t)$.

where T_sP and T_cP are given by Eq.(7) and (9).

The corresponding variance for $T_sG(f)$ is:

$$\mathrm{Var}(\,T_sG(f)\,) = \frac{1}{2\,N_c^{'}}\left(\frac{I_0^{'}}{\alpha} - T_cG(2f) - 2\,(\,T_sG(f)\,)^2\right) \tag{14}$$

where T_sG and T_cG are obtained from Eq.(8) and Eq.(10).

The SNR for $T_sP(f)$ is:

$$\mathrm{SNR_P}\,(f) = \frac{(N_c\, I_0)^{1/2}\, D_\alpha(f)}{\left[\,2\,\alpha^{-1}\, D_\alpha(2f) - I_0\,(D_\alpha(f))^2\,\right]^{1/2}} \tag{15}$$

The corresponding SNR for $T_sG(f)$ is:

$$SNR_G(f) = \frac{\left(N_c' I_0'\right)^{1/2} D_\alpha(f)}{\left[2\,\alpha^{-1} D_\alpha(2f) - I_0' (D_\alpha(f))^2\right]^{1/2}} \quad (16)$$

NUMERICAL EXAMPLE

As a numerical example we have introduced in Eqs. (15) and (16) typical SPDS values. In order to compare the theoretical results obtained here with those obtained in previous experiments[3,4], the values used in wereN$_c$=10^3 samples, I_0=95 counts/s, I_F=5 counts/s and α=1200 μs^{-1}.

Figure 2 shows that $SNR_G(f)$ is about 15 times greater than $SNR_P(f)$ and in the region used for α determination the difference is even greater. This means that a much smaller number of samples is needed to obtain the same SNR if the estimator $T_sG(f)$ is used instead $T_sP(f)$.

It is also interesting to compare the error in determining the parameter α from the two methods. The error in percent is defined as:

$$e_\alpha = 100 \cdot (\mathrm{Var}\ \alpha)^{1/2} / \alpha \quad (17)$$

The value of Var α will be evaluated from:

$$\mathrm{Var}_P\ \alpha = \left(\frac{\partial T_s P(f)}{\partial \alpha}\right)^{-2} \mathrm{Var}(\, T_s P(f)\,) \quad (18)$$

$$\mathrm{Var}_G\ \alpha = \left(\frac{\partial T_s G(f)}{\partial \alpha}\right)^{-2} \mathrm{Var}(\, T_s G(f)\,) \quad (19)$$

where derivatives can be calculated from Eqs.(8) and (10) and the variances of the sine transform from Eqs.(13) and (14).

Figure 3 shows the error in percent obtained from the two methods for the same experimental conditions: N_c=10^3 samples, I_0=95 counts/s, I_F=5 counts/s and α=1200 μs^{-1}.

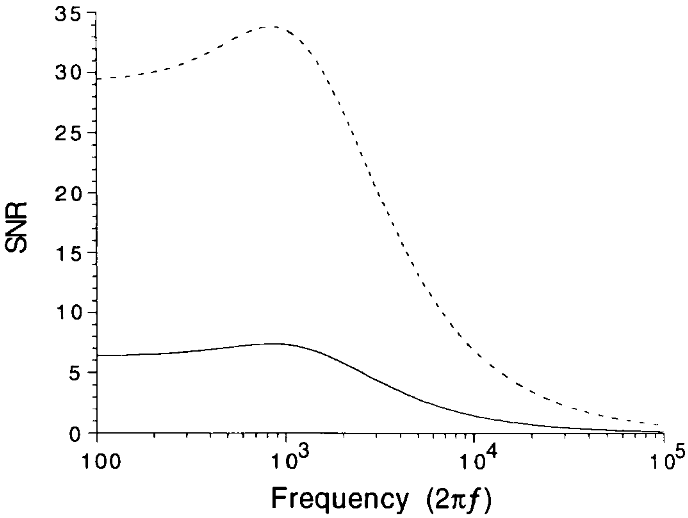

Fig. 2.- SNR obtained for the sine transform of $P_f(t)$ (solid line) and for the sine transform of the autocorrelation of $P_f(t)$ (dashed line) as a function of the frequency $(2\pi f)$. A factor of about 15 appears between the two methods.

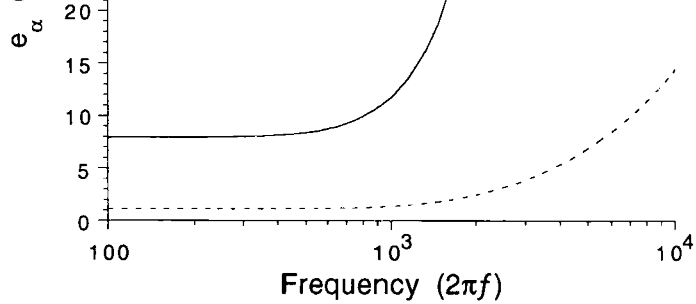

Fig. 3.- Theoretical values of e_α obtained for the sine transform of $P_f(t)$ (solid line) and for the sine transform of the autocorrelation function of $P_f(t)$ (dashed line) as a function of the frequency $(2\pi f)$.

It can be seen that although the SNR of the sine transform of the autocorrelation function is about 15 times greater than that obtained from the sine transform of $P_f(t)$, the value of e_α is only about 6 times smaller when using the sine transform of the autocorrelation function. Nevertheless, the increase in the accuracy of the parameter determination is still very important.

CONCLUSIONS

We conclude that in an SPDS experiment in which the intensity is very low the error in e_α can be reduced if direct estimation of the sine transform of the autocorrelation function of the TIPD is used. This allows us to reduce the number of samples we have to measure to obtain a good SNR.

This technique improves the results from the classical measurement of $P_f(t)$, and even those obtained from more sophisticated techniques such as the sine transform of $P_f(t)$.

ACKNOWLEDGEMENT

P. Prieto is grateful to the "Vicerrectorado de Investigacion" of the University of Cantabria for his Research Grant.

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Date Received: December 14, 1993
Date Accepted: March 8, 1994