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THE ACCURACY OF DIFFUSION-CONSTANT MEASUREMENTS BY DIGITAL AUTOCORRELATION OF PHOTON-COUNTING FLUCTUATIONS

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Résumé. — On discute la précision d'une mesure de la largeur de raie spectrale par la méthode de corrélation digitale « à simple seuil » (*) des fluctuations du taux de comptage de photons, pour un flux lumineux donné et un temps de mesure fixé. Cette précision est limitée par les effets statistiques dus à la nature aléatoire du champ lumineux et du processus photovoltaïque ; en conséquence, toutes choses égales par ailleurs, le résultat sera d'autant plus précis que l'expérience aura duré un temps plus long. On présente des résultats théoriques et expérimentaux concernant les précisions que l'on peut espérer, en fonction du temps d'échantillonnage, de la surface du détecteur et du seuil.

Abstract. — We discuss the accuracy of a measurement of a spectral linewidth using the method of digital correlation of single-clipped photon counting fluctuations with a given light flux and a given duration of experiment. Statistical effects due to the random nature of the light field and the photovoltaic process limit this accuracy, so that the longer the duration of the experiment the more accurate the result, if all other factors are equal. Theoretical and experimental results are presented which show the accuracies obtainable as functions of the sample time, detector area and clipping level.

We have investigated, over the past two years, light-scattering spectra from a number of biological molecules from various laboratories, by correlation of clipped photon-counting fluctuations [1]. A list of these is given in an appendix. In many cases we have found satisfactory values for diffusion coefficients under various conditions, while in other cases work is still proceeding. We have also studied Rayleigh scattering from organic liquids and, following Yeh and Keeler [2], have examined some metal-sulphate solutions by the same methods. The techniques have proved to be very powerful, enabling low light fluxes to be studied with high precision. A commercial version of our equipment is now being manufactured under licence to the National Research and Development Corporation.

In order to support this activity and to give guidance to potential users of the method we have undertaken an extensive study, by both analytical and computational methods, of the statistical variations to be expected in such measurements of spectral linewidth.

The results of the analytical work may be found in detail in a paper by Jakeman et al. [3]. We should like here to summarize these and to present the results of some more recent computations performed by Dr. A. Hughes, together with new experimental confirmation of them by Dr. C. J. Oliver, both of this laboratory. Special cases of the problem have been studied by Benedek [4], Haus [5], Cummins and Swinney [6], Pusey [7], and Degiorgio and Lastovka [8]. The relation of these calculations to ours is discussed by Jakeman et al. [9].

We first briefly introduce the ideas behind the method. The light scattered from randomly moving particles has the statistical properties of a Gaussian-distributed complex vector which were studied in detail in connection with radar problems in the early 1940's. Statistical theorems of great practical value were developed connecting the zero crossings of Gaussian radiation fields and their spectra [10]. It was shown, for instance, that the temporal autocorrelation function of a two-level (one-bit) signal (clipped or hard-limited signal) was simply related to that of a Gaussian signal with the same zero crossings and, further, that little statistical information was lost in passing from one to the other. We have extended [1] these results to the case of optical signal processing where the initial signal consists of a stochastic train of impulses resulting from photodetections. The analogue of clipping the electric field at its zero value is the assignment of an integer clipping level \( k \) (associated with a fixed sampling time \( T \)) such that the signal has one or other of two levels (1 or 0) according as the number of photons detected in a sample time exceeds \( k \) or not. In practice we prefer to correlate such a clipped signal not with itself, as in the radar case, but with the original signal (single clipping) since multiplications by ones or zeroes are easy to perform electronically on any number.

(*) « Single clipped ».
It turns out that the relations between single-clipped correlation functions and unclipped or true autocorrelation functions are even simpler than the original radar formulae. In fact, if a signal is clipped at its mean level these functions are theoretically identical. Work which had the same motivation, that of reducing the electronic complexity of a true fast parallel correlator, was pursued independently by Chen at Harvard and MIT and by Pusey at IBM. Our clipping solution is slightly different from their techniques. Lastovka at MIT was also an early worker in this area and Cummins at John Hopkins used a commercial analogue correlator for this application in 1967 [11]. For most molecules, however, as Cummins discovered, the information recovery rate of commercial electronic correlators is little better, if at all, than that of the wave-analysers first used by himself [12] and by Benedek’s group at MIT [13] for macromolecular studies; this is particularly true for smaller molecules.

It is usually desirable to work with low concentrations of biological molecules due to the concentration dependence of the diffusion coefficients, if not sometimes the scarcity of the material. For this reason we have used a clipping level of zero for many practical cases.

The linewidth accuracy can be found analytically in this case. This is done by first calculating the statistics of the correlation coefficient estimators and then by calculating an optimised, weighted, least-squares two-parameter fit of the assumed exponential form of the correlation function. The parameters are the decay time and the value at the origin, the value at infinity is given by normalisation channels in the correlator.

For higher clipping levels the analytical work becomes exceedingly cumbersome and we have resorted to computer simulation.

The number of correlation coefficients computed is also an important parameter, determining the bulk of the cost of high-speed real-time equipment. We have made calculations for 20, 100, and an infinite number of channels.

The ratio of the sample time to the coherence time or inverse linewidth of the intensity fluctuation spectrum must be decided; for a fixed number of channels there will be an optimum value for this ratio. If too small the count rates will be low and the points will sample the function in a highly correlated fashion, if too large the points will give uncorrelated samples but in the region of low correlation coefficient. In practice, depending on the number of channels and count rates, the optimum occurs when a total delay of two or three coherence times is covered.

The area of the detector is another experimental variable. As this increases so the correlation coefficients decrease [14], [15], but the light flux increases. In fact these effects compensate asymptotically [16] so that little is gained, even with the lowest light fluxes, where photon statistics dominate, by using more than one coherence area. With high values of light flux the area of the detector can be reduced to well below a coherence area to diminish the averaging effects of the signal statistics without losing accuracy from photon statistics. The break-even point will vary with number of channels and clipping level but a value of 10 photodetections per coherence time is, in practice, effectively an infinite light flux as far as photon statistics affect the accuracy of the linewidth estimate.

We refrain from giving lengthy formulae in this publication but show useful practical results in three figures. In figure 1 the effect of changing the sample time/coherence time ratio is shown for fixed values of the number of channels (twenty), detector area (0.01 coherence area), experiment duration (10⁴ coherence times) and for single clipping at zero. In addition to points already mentioned the loss of accuracy as the count rate gets too high for the zero clipping level can be seen. The ordinate scales as the square root of the number of coherence times in the experiment duration. The points are experimental values obtained by programming the correlator to complete 25 experiments for each set of parameters chosen. The RMS deviations were then extracted by two-parameter computed curve fitting.
In figure 2 is shown the effect of increasing the detector area, again with single clipping at zero and with sample time/coherence time ratio set at 0.1, which is near optimum for this number of channels unless count rates are too high. The behaviour of the points follows reasonably closely that which would be predicted from figure 1 taking into account only the change of count rate. The effects of clipping dominate the effects of signal statistics at the large area end of the curves.

In figure 3 is shown the effect of clipping levels. We should say that we have now verified our original theoretical formulae [16] for the effects of clipping on the correlation functions. The errors have a minimum value which is very flat at clipping levels between one half and two times the mean counting rate. Increasing the light flux will always improve the accuracy to some extent if the appropriate clipping level is chosen but the improvement quickly saturates, depending on the number of channels, as the number of counts per coherence time goes beyond about 10.

**Appendix**: list of biological molecules studied at RRE to date

Lysozyme  
BSA  
Tamm-Horsfall glycoprotein  
Histone 2 A 1  
α-crystalline  
Haemocyanins  
Helix pomatia α  
Helix pomatia β  
Archachatina marginata  
Pila leopoldvillensis  
Murex trunculus  
Sheep colonic mucosa glycoprotein  
Adenovirus  
Myxovirus (influenza)  
Thyretin  
RNA polymerase  
γ-globulin  
Aldelase  
Catalase

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Prof. R. Lontie, Biochemistry Laboratory, Catholic University of Louvain, Belgium.  
Dr. E. Wood, Dept of Physiology, Royal University of Malta.  
Dr. Kent, Dept of Biochemistry, University of Oxford.  
Prof. Belyavin, University College Hospital, London.  
Dr. B. Nicholson, Dept of Biochemistry, University of Reading.
Aspartate amino transferase (enzyme)
T3 bacteriophage
Turnip yellow mosaic virus
Fibrinogen
Keyhole limpet (haemocyanin)
Haemoglobin
Algae (alive and dead)

Dr. P. Bayley, National Institute for Medical Research, Mill Hill London.
Dr. P. Sprag, Dept of Chemistry, University of Birmingham.
Dr. D. Pepper, Blood Transfusion Unit, Royal Infirmary, Edinboro.
Dr. G. Beaver (through).
Dr. W. Gratzer, Kings College, London.
Prof. Guttfreund, Dept of Biochemistry University of Bristol.
Prof. Thonemann, from Marine Biology Dept, University of Swansea.

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