

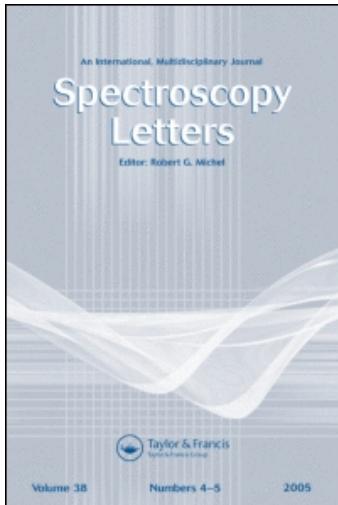
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Publisher *Taylor & Francis*

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Spectroscopy Letters

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597299>

Error Improvement in the Analysis of Macromolecules by Photon Statistics

F. Moreno^a; M. P. Cagigal^a; M. A. Rebollo^a

^a Departamento de Optica y Estructura de la Materia. Facultad de Ciencias, Universidad de Santander, Spain

To cite this Article Moreno, F. , Cagigal, M. P. and Rebollo, M. A.(1984) 'Error Improvement in the Analysis of Macromolecules by Photon Statistics', *Spectroscopy Letters*, 17: 6, 345 — 351

To link to this Article: DOI: 10.1080/00387018408062692

URL: <http://dx.doi.org/10.1080/00387018408062692>

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ERROR IMPROVEMENT IN THE ANALYSIS OF MACROMOLECULES
BY PHOTON STATISTICS

F. Moreno, M.P. Cagigal and M.A. Rebollo.

Departamento de Optica y Estructura de la Materia.
Facultad de Ciencias. Universidad de Santander.
Spain.

ABSTRACT

In this paper we study the improvement which is obtained in the analysis of macromolecules in solution by measuring the spatial coherence constant in a previous experiment. Results are discussed for a binary mixture of spherical particles in solution.

I.- INTRODUCTION.

During the last twenty years photon statistics has proved to be a useful technique for the analysis of light scattered by macromolecules in solution¹⁻². The mean sizes, standard deviation of sizes, relative concentrations of the different macromolecules in solu-

tion, etc., have been obtained. Usually, this information has been obtained by measuring the normalized intensity correlation function, $g^{(2)}(\tau)$, or the normalized second-order factorial moment, $n^{(2)}(\tau)$. These quantities depend on the spatial coherence properties of the analyzed light beam. Therefore, when fitting the experimental values of $g^{(2)}(\tau)$ or $n^{(2)}(\tau)$ to the theoretical ones, the spatial coherence appears as an unknown parameter that can be obtained from the fitting. If we reduce the number of parameters to be found by fitting, the errors involved in determining these parameters will be reduced. Therefore, the results can be improved if the spatial coherence parameter is already known.

In this paper we study, as an example, the improvement in the analysis of a binary mixture of spherical particles in solution when the spatial coherence parameter is known from a previous experiment and $n^{(2)}(\tau)$ is measured.

II.- THEORY.

Let us consider an experiment where macromolecules in solution scatter laser light. If the number of macromolecules in the scattering volume is large, the scattered light is Gaussian. Moreover, since the scattered light is quasimonochromatic, it will exhibit the property of cross-spectral purity². Therefore, the normalized intensity correlation function can be expressed²⁻³ as

$$g^{(2)}(\tau) = 1 + f(A) |g^{(1)}(\tau)|^2 \quad (1)$$

where

$$f(A) = \frac{1}{A^2} \int_A d\vec{r}_1 \int_A d\vec{r}_2 |g^{(1)}(\vec{r}_1, \vec{r}_2)|^2 \quad (2)$$

A being the area of the detector and $g^{(1)}(\vec{r}_1, \vec{r}_2)$ being the first-order degree of spatial coherence. The function $f(A)$ does not de-

pend on the spectral properties of the analyzed light.

In the case of scattered Gaussian light from macromolecules, these macromolecules operate as an incoherent source of uniform in tensity. If a circular diaphragm of radius R_1 is placed on the source and another circular diaphragm of radius R_2 is placed on the detector, it is found ²⁻³ that

$$f(A) = \sum_{s=0}^{\infty} \frac{[(2s+2)!]^2}{[(s+2)!]^2 [(s+1)!]^4} \left(-\frac{\pi R_1 R_2}{\lambda z} \right)^{2s} \quad (3)$$

where λ is the wavelength and z the distance between the source and the detector. It is clear that $f(A)$ depends on the positions and radii of the two diaphragms but it does not depend on the spectrum of the analyzed light. I.e. if diaphragms remain unchanged and the solution of macromolecules is replaced by another that produces a different spectrum the value of $f(A)$ does not change.

To calculate $n^{(2)}(\tau)$ we can use the relation²

$$\frac{\partial^2}{\partial \tau^2} \left\{ \tau^2 n^{(2)}(\tau) \right\} = 2 g^{(2)}(\tau) \quad (4)$$

from which we can derive

$$n^{(2)}(\tau) = 1 + [2f(A)/\tau^2] \int_0^{\tau} d\tau' \int_0^{\tau'} d\tau' \left| g^{(1)}(\tau') \right|^2. \quad (5)$$

Since in a real experiment, the diaphragm is not actually on the source but some distance from it (the same being true for the detector and its diaphragm) Eq. (3) cannot be used and $f(A)$ must be determined from the experiment. In order to do this we can use ca librated spheres in solution. In this case² we have

$$\left| g^{(1)}(\tau) \right|^2 = \exp(-2\Gamma\tau) \quad (6)$$

where

$$\Gamma = \frac{16 \pi n^2 \sin^2(\theta/2)}{6 \eta \lambda^2 r} k_B t \quad (7)$$

In Eq. (7) Γ is the spectral width of the Lorentzian profile of the light scattered by the spheres, n is the refractive index of the solvent, θ the scattering angle, k_B the Boltzman constant, t the temperature of the solution expressed in Kelvins, η the solution viscosity, λ the wavelength of the exciting light, and r the radius of the spherical particles. Using Eqs. (5) and (6) we obtain

$$n^{(2)}(T) = 1 + f(A) \left[\frac{1}{\Gamma_T} - \frac{1}{2(\Gamma_T)^2} + \frac{\exp(-2\Gamma_T)}{2(\Gamma_T)^2} \right]. \quad (8)$$

If the quantities n , θ , t , η , λ , r and T are known, the value of $f(A)$ can be obtained with a very small error by fitting experimental and theoretical values of $n^{(2)}(T)$. If the macromolecules in solution are changed but the experimental installation remains unchanged, the value of $f(A)$ can be used for subsequent experiments.

III.- APPLICATION TO A BINARY MIXTURE OF SPHERICAL PARTICLES.

Let us consider a binary mixture of spherical particles with diameters d_1 , d_2 and concentrations c_1 , c_2 . It can be shown⁴ that $n^{(2)}(T)$ is a function of d_1 , d_2 , the concentration ratio $c_{21} = c_2/c_1$ and the spatial coherence constant. The concentration ratio c_{21} depends on the intensity ratio

$$\alpha = I_2 / I_1 \quad (9)$$

I_2 being the intensity scattered by the spheres of diameter d_2 and I_1 the intensity scattered by the spheres of diameter d_1 . All the above-mentioned parameters (d_1 , d_2 and c_{21}) can be obtained by fit

ting the experimental values of $n^{(2)}(T)$ to the theoretical ones. Instead of measuring $n^{(2)}(T)$ we simulated values of this quantity by using a fast computer simulation method⁵. By using this method one can simulate the value of $n^{(2)}(T)$ which corresponds to an experimental determination of this quantity from N samples of the number n of photoelectrons counted in a time interval T . The simulations were made for a value of d_1 (1200 Å), five values of d_2 (750 Å, 600 Å, 450 Å, 300 Å and 150 Å) and nine values of α (10, 5.2, 3, 1.7, 1, 0.6, 0.3, 0.17 and 0.1). In all 45 cases θ was 90° and we simulated a light beam whose intensity was 10 photopulses per coherence time τ_c . For each case $n^{(2)}(T_i)$ ($i = 1, 2, \dots, 45$) was simulated in such a way that

$$T_1 = 0.1 \tau_c, \quad T_{45} = 2 \tau_c$$

$$n^{(2)}(T_i) - n^{(2)}(T_{i+1}) \approx \frac{1}{44} \left[n^{(2)}(T_1) - n^{(2)}(T_{45}) \right]. \quad (10)$$

For each T_i the value of $n^{(2)}(T_i)$ simulated was equivalent to the experimental one obtained from N_i samples of n in such a way that $N_i \cdot T_i = \text{constant}$ for all values of i ($i=1, 2, \dots, 45$). The total measurement time $t_m = \sum_{i=1}^{45} N_i T_i$ was $t_m = 10^8 \tau_c$. The values of the parameters d_1 , d_2 , c_{21} were obtained by fitting the simulated values of $n^{(2)}(T_i)$ ($i=1, 2, \dots, 45$) to the theoretical ones. By repeating this operation ten times, the relative errors in $d_1(e_{d1})$, $d_2(e_{d2})$ and $c_{21}(e_{c21})$ can be evaluated by means standard deviation of the different values of d_1 , d_2 and c_{21} .

For each case, the values of $n^{(2)}(T_i)$ ($i=1, 2, \dots, 45$) were first fitted to the theory to obtain c_{21} (d_1 , d_2 were assumed to be known). By repeating this operation ten times the error in c_{21} was evaluated. This was done by assuming the spatial coherence constant to be known in order to obtain $e_{c21}^{k.c.}$ and separately by considering it unknown to obtain $e_{c21}^{u.c.}$. The values of $e_{c21}^{k.c.}/e_{c21}^{u.c.}$ corresponding to the 45 cases were average. Moreover, the average

of $e_{c_{21}}^{k.c.}$ was divided by the average of $e_{c_{21}}^{u.c.}$. After that, the same operations were performed when fitting to obtain c_{21} and d_2 (d_1 was assumed to be known) and when fitting to obtain c_{21} , d_1 , d_2 . The results are listed in table 1.

It can be observed that the values of $f_{c_{21}}$, f_{d_2} and f_{d_1} are close to 0.5. Therefore, the errors are reduced by half if the spatial coherence constant is measured in a previous experiment. Since in general $g_x \approx f_x$, the error reduction for large values of e_x is approximately equal to the error reduction for small values of e_x .

TABLE 1

$e_x^{k.c.}$ = relative error in the parameter x obtained when the spatial coherence parameter is known; $e_x^{u.c.}$ = relative error in the parameter x obtained when the spatial coherence parameter is unknown; $f_x = \langle e_x^{k.c.} / e_x^{u.c.} \rangle$ and $g_x = \langle e_x^{k.c.} \rangle / \langle e_x^{u.c.} \rangle$. The value of $f(A)$ was 0.5.

| PARAMETERS DETERMINED FROM THE FITTING | | | |
|--|----------|---------------|--------------------|
| | c_{21} | c_{21}, d_2 | c_{21}, d_2, d_1 |
| $f_{c_{21}}$ | 0.455 | 0.505 | 0.455 |
| $g_{c_{21}}$ | 0.460 | 0.476 | 0.317 |
| f_{d_2} | | 0.461 | 0.465 |
| g_{d_2} | | 0.494 | 0.488 |
| f_{d_1} | | | 0.588 |
| g_{d_1} | | | 0.429 |

This is true except for two cases. When fitting c_{21} , d_2 and d_1 it can be observed that $g_{c_{21}}/f_{c_{21}}$ and g_{d_1}/f_{d_1} are significantly smaller than unity. Therefore, for large values of $e_{c_{21}}$ or e_{d_1} , the errors are reduced more than for small ones.

From the preceding study it is clear that the results obtained in the analysis of macromolecules in solution, by photon statistics, can be improved if the spatial coherence constant is known from a previous experiment where this constant is the only unknown parameter. The error reduction can be considerable, especially if the errors are large.

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Received 4-10-84

Accepted 5-16-84