

## Generalized Pareto distribution function for Au colloidal systems.

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### Abstract

The Raman signal can be enhanced by the SERS (Surface-Enhanced Raman Scattering) technique that uses metallic nanoparticle (NP) colloids to intensify the electric field of incident light. In this work we explore from a theoretical point of view, through simulation, the behavior of the distribution of the intensification factor (F) on the surface of Au spherical NPs formed by different aggregates (dimers and trimers) and mixtures thereof, which can be described by the Pareto distribution function.

### Key words:

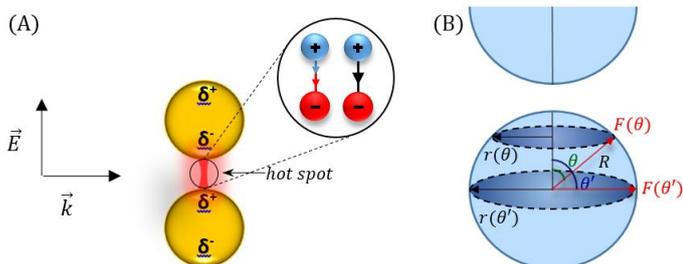
Raman Spectroscopy, SERS, Plasmon.

### Introduction

Raman spectroscopy is a vibrational technique that allows access to vibrational and electronic information of the molecule under analysis. One of the obstacles encountered in the use of the technique is the low signal produced by Raman scattering, which limits its analytical application, for example. There are some ways to increase the signal from this type of spectroscopy and SERS is one of them. The intensification of the signal attributed to the electromagnetic mechanism arises from the resonant excitation of modes of collective oscillation of the electrons of the NP surface. Such modes of collective excitation are called surface plasmon and depend on the properties of the metallic substrate used<sup>1</sup>. We can estimate the SERS intensification by an intensification factor (F), which relates the local electric field intensity,  $E_{local}$ , to the electric field of the incident radiation,  $E_0$ , as follows:

$$F = \left( \frac{E_{local}}{E_0} \right)^4$$

The F factor can reach several orders of magnitude, (for example  $10^{10}$ ), mainly in interstices between two particles with distances of the order of 1nm. These regions are called hot spots (HS)<sup>2</sup> and can be seen in image 1A.

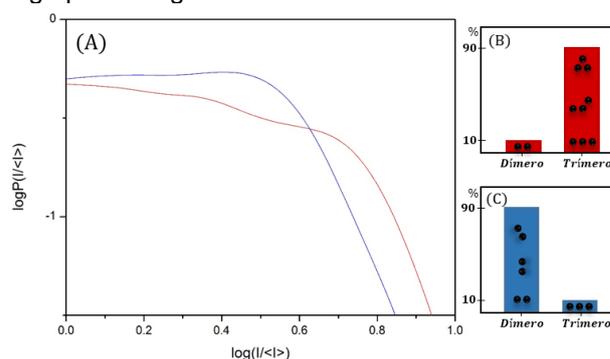


**Image 1.** Dimer's hot spot (A) and dependence of F on  $\theta$  (B).

The dependence of F ( $\theta$ ), seen in image 1B, reveals that the probability of adsorption of molecule in a region of the surface ( $\theta$ ) with high values of F factor is small. Determining such a distribution in different systems involving Au spherical NPs can indicate which geometric system is most efficient for SERS applications, which corresponds to the most fundamental point of discussion in this work.

### Results and Discussion

The simulations were performed through the Mie theory and the F factor determination was done through an event histogram of F for a set of  $10^6$  randomly drawn points on the surface of the NPs. The results showed that dimers present better sensitivity to the SERS technique than trimers. As a consequence, in a mixture of dimers and trimers, image 2, it is perceived that the probability of finding high field intensities is higher in colloids with a large percentage of dimers than trimers.



**Image 2.** Simulation (in  $\lambda = 633\text{nm}$ ) of the probability of finding high field intensities (A) using a mixture of NPs with 10% (B) and 90% (C) of dimers.

### Conclusions

It was concluded that in dimers higher field intensification factors were obtained ( $\log F = 11.2$ ) than in trimers ( $\log F = 10.7$ ). In addition, the Pareto distribution results showed that a molecule is more likely to feel large F's in colony-containing dimers than trimers. As a consequence, in a mixture of these aggregates the colloid with the highest proportion of dimers will have the highest probability of high intensification of the field.

### Acknowledgement

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<sup>1</sup> Ru, E. C. L.; Etchegoin, P. G. *Principles of Surface-Enhanced Raman Spectroscopy And Related Plasmonic Effects*; Elsevier: Amsterdam, 2008.

<sup>2</sup> Le Ru, E. C.; Etchegoin, P. G.; Meyer, M. *Journal of Chemical Physics* **2006**, *125*.