

Electric field and solvent model for Electrochemical SERS: excited-state and enhancement tuning

Francisco García-González^{*,a} Daniel Aranda,^{a,b} Francisco J. Ávila Ferrer,^a Juan C. Otero^a

a) Departamento de Química Física, Universidad de Málaga, Blvr. Louis Pasteur 31, E29071, Málaga, Spain.

b) Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, c/Catedrático José Beltrán, 2, 46980 Paterna, Spain.

**frgarcia@uma.es*

Being SERS a promising technique due to it potentially combining the well-known characterization prowess of Raman with the high sensitivity arising from nanoparticle-associated enhancement,¹ understanding the mechanisms due to which SERS differs from Normal Raman is key to accomplish effective applications of this technique. Following the consensus about the theoretical background that establishes the enhancement mechanisms in SERS,² and focusing on electrode potential as a variable in Electrochemical (EC) SERS, for our work we have studied Pyridine (Py) SERS spectra modelling an EC-SERS nanostructured surface through an Ag₆ cluster in different orientations, with an electric field parallel to the Ag₆-Py axis reproducing electrode potential, as depicted in Figure 1. The objective of such model is to simulate Pyridine SERS spectra and rationalizing these results based on well-established properties, accounting for symmetry considerations, coupling terms and the influence of the solvent on the system to carry out a straightforward understanding of SERS enhancement mechanisms. Our results are able to effectively reproduce the main relative intensities of Pyridine SERS spectra, shedding light on the influence of the aforementioned properties on the calculated lineshapes and intensities.

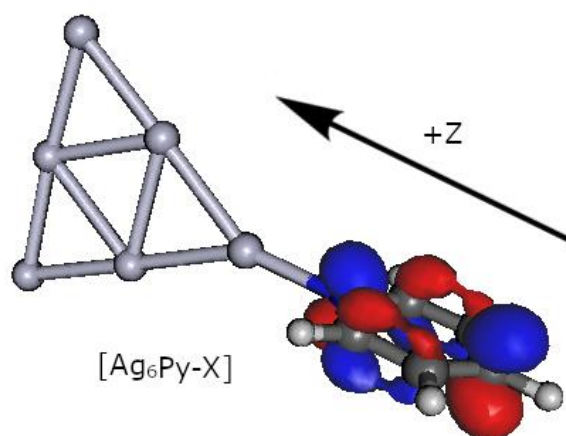


Figure 1. Ag₆Py model, being Z+ the electric field vector parallel to the Pyridine-Cluster axis.

References

1. Langer, J. et al. Present and future of surface-enhanced Raman scattering. *ACS Nano* 2019, 14, 28–117.
2. Morton, S. M.; Silverstein, D. W.; Jensen, L. Theoretical studies of plasmonics using electronic structure methods. *Chem. Rev.* 2011, 111, 3962–3994.