

Electric field and charged cluster dual model for Potential Dependent Surface-Enhanced Raman Spectroscopy

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

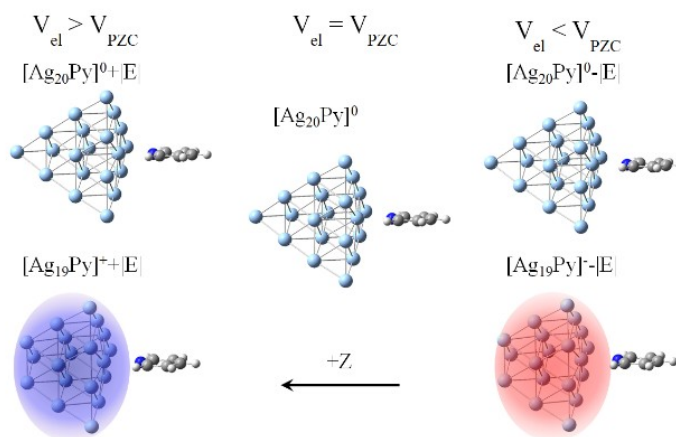
^a Universidad de Málaga, Andalucía Tech, Departamento de Química Física, Facultad de Ciencias, Málaga, E29071, Spain

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

*frgarcia@uma.es

The computation of electrochemical systems is very challenging because of the many variables involved.¹ Among them, the effect of the electrode potential is particularly complex to be introduced in atomistic models. In this work, we propose a model where the surface excess of charge has been modelled with the tetrahedral-like clusters [Ag₁₉]⁺, [Ag₂₀]⁰ and [Ag₁₉]⁻. We then modulate the effect of other surface charges implicitly as an external electric field and correlated a calculated magnitude like the electric charge on the adsorbate with the electrode potential, a purely experimental one.

This model is tested with the potential-dependent Surface-Enhanced Raman Scattering (SERS) of pyridine. Namely, we investigated the changes in the Raman shifts and relative intensities due to the potential, and evaluated the different contributions (electromagnetic, charge-transfer) to the SERS spectra. Our preliminary results nicely reproduce the experimental trends and reveal that enhancement factors up to 107 are achieved when the charge-transfer state interact with the bright local excitations of the metal cluster.



References

- [1] Roldan, A. (2018). Frontiers in first principles modelling of electrochemical simulations. Current Opinion in Electrochemistry, 10, 1-6.