# Modelling Potential Dependent Surface-Enhanced Raman Scattering: electric field and charged cluster dual model.

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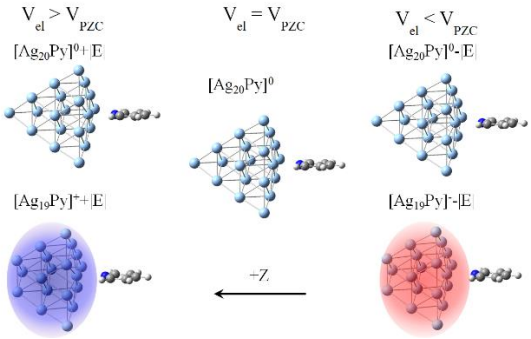
The computation of electrochemical systems is very challenging because of the many variables involved.[1] Among them, the effect of the electrode potential is particularly complex to be introduced in atomistic models. In this work, we propose a model where the surface excess of charge has been modelled with the tetrahedral-like clusters $[Ag_{19}]^+$, $[Ag_{20}]^0$ and $[Ag_{19}]^-$. 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 $10^7$ 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.