

**Abstract of Contribution 290****ID: 290 / WeP - O - 008: 4****Contribution****Oral Presentation***Topics:* Surface enhanced Raman spectroscopy, Theoretical developments and calculations*Keywords:* charge-transfer, SERS, TD-DFT, nanostructures**Charge transfer in the nanoscale and SERS: understanding the huge efficiency of the electrode potential in tuning CT states****Silvia Centeno, Cristina Ruano, Jessica Roman-Perez, Isabel López-Tocón, Juan Soto, Juan C. Otero**Universidad de Málaga, Spain; [sccenteno@uma.es](mailto:sccenteno@uma.es)

This work deals with the unexplained efficiency of the electrode potential ( $E_V$ ) in tuning the energy of Charge Transfer ( $E_{CT}$ ) electronic states of hybrid systems formed by molecules and metal nanostructures. Huge energy gain ( $G$ ) up to 5 eV/V observed in electrochemical SERS experiences are in conflict with classical picture of metal-adsorbate CT mechanisms where  $G=1$ . Supported on electronic structure calculations of metal-molecule systems  $[M_n-A]^q$  we are able to demonstrate that this “anomalous” gain is due to two different contributions. The first one ( $S$ ) is related to the sensitivity of the CT electronic states of each particular metal-molecule complex on the effective charge excess of the metal  $q_{eff}=q/n$  ( $E_{CT} = S q_{eff} + E^0$ ). The energies of the CT;  $M^-A^+$  states are very dependent, and almost linearly, on  $q_{eff}=q/n$ . The second contribution is originated by the enhanced electric capacitance of metallic nanoclusters and is discussed in another communication.