

# IL1 Modeling the effect of the electrode potential in SERS by electronic structure calculations

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Surface Enhanced Raman Spectroscopy (SERS), due to the ability of greatly intensify the weak Raman signal of molecules adsorbed to metal surfaces, has proven to be a very useful tool to investigate changes in the electronic structure of metal-molecule surface complex.[1] A deep knowledge of the electronic structure of these metal-molecule hybrid systems is key in electrochemistry, catalysis,[2] plasmonics, molecular electronics,[3] and in the development of selective and ultra-sensitive analytical sensors. The origin of this huge enhancement in SERS is due to two contributions: the electromagnetic (EM), related to surface plasmons, and the chemical mechanism, due to resonant charge transfer (CT) process between the adsorbate and the metal (CT-SERS)[4,5] and/or important changes in the electronic structure of the metal-molecule hybrid system.[1] Moreover, electrochemical SERS has proven to be a useful tool to identify resonant CT process and to investigate the effect of the electrode potential in the electronic structure of the surface complex.[4-8] Unfortunately, the SERS implies very complex phenomena where the molecule and the metal nanoparticle are involved. This fact makes challenging to build realistic theoretical models that take into account both the metal and the molecule at quantum level. We propose a methodology, based on Density Functional Theory and ab initio electronic calculations, to simulate the effect of the electrode potential on the absorption, on the charge transfer states energies, and on the electronic excitations in metal-molecule hybrid systems from a microscopic point of view, with special emphasis on their impact on the CT-SERS mechanism. This methodology consists on the prediction of Raman intensities from ab initio calculations of the geometries or the energy gradients at the excited states Franck-Condon point, bringing the possibility to predict the intensities in CT-SERS as well as in resonance Raman without the need to know the excited state geometries, not always feasible to compute. The microscopic model adopted to mimic the effect of the interphase electric potential consist in a molecule adsorbed to a linear silver cluster  $[Ag_n\text{-Adsorbate}]^q$ , where  $n$  is the number of silver atoms, and the total charge of the system ( $q$ ) is zero for  $n=2$  and  $q=\pm 1$  for  $n=1, 3$  and  $7$ . The combination of the charge and the metal size permits to tune the energy of the CT electronic states though the microscopic parameter  $q_{eff}=q/n$ , the microscopic analogue of the surface excess of charge.[4-8]  $q_{eff}$  can be correlated with the applied potential in electrode SERS experiments, opening the possibility to plot the CT states energies vs  $q_{eff}$ , to predict the conditions for CT processes and to reproduce the effect of the electrode potential in the SERS-CT intensities and, as a consequence, in the selection rules.

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