

Surface-enhanced photoinduced charge transfer processes in metal-molecule nanoclusters

S.P. Centeno, C. Ruano, J. Román-Pérez, I. López-Tocón, J. Soto, J.C. Otero

Department of Physical Chemistry, University of Málaga, Campus Teatinos S/N, E-29071 Málaga, Spain, scenteno@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 gains (G) of up to 5 eV/V observed in electrochemical SERS experiences have been tentatively explained by a local increase of the electric potential at specific adsorption sites.[1] This gain, which is in conflict with the classical picture of the metal-adsorbate CT mechanism ($G=1$), can be quite relevant since it means that a relatively small change in the applied voltage can produce a large shift in the CT states, and consequently, it can greatly modify the resonant conditions in a SERS experiment. [2] Supported on electronic structure calculations of metal-molecule nanoclusters, we are able to elucidate that this “anomalous” gain is mainly due to two different contributions, firstly, the sensitivity of the CT electronic states of each particular metal-molecule system on the effective charge excess of the metal, and, secondly, to an enhanced electric capacitance of the metallic nanocluster with respect to the macroscopic values. We associate this last contribution with the so-called “edge effect” that causes inhomogeneities in the density charge at local sites of the metallic surface which could correspond to the very popular “hot spots” between the SERS community.

[1] L. Cui, D-Y Wu, A. Wang, B. Ren, Z-Q Tian, *J. Phys. Chem. C*, **2010**, *114*, 16588-16595.

[2] A. Otto, *Surface Science*, **1984**, *138*, 319-338