

The influence of electrode potential on SERS through the electronic structure of nanostructured metal-cyanide interfaces

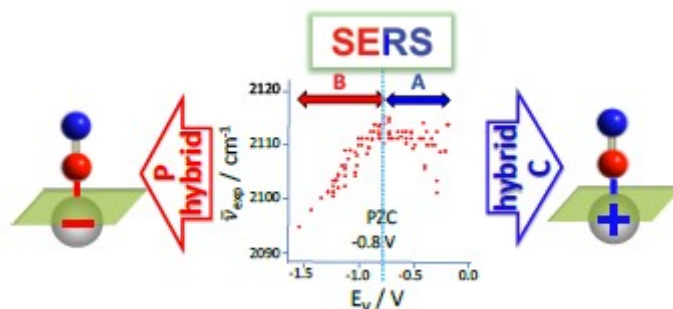
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Abstract

Experimental and theoretical calculations confirm the existence of two different electronic structures of a surface complex formed by a particular molecule bonded to charged metal electrodes, clusters, or nanoparticles. Each electronic structure of the metal-molecule hybrid system is selected by sign of the surface excess of charge of the metal at potentials more negative or positive than its potential of zero charge (PZC).

Surface-enhanced Raman scattering (SERS) of cyanine adsorbed on a silver electrode shows two regions, which are selected by the voltage and characterized by the differentiated response of the vibrational wavenumbers of the $\nu(\text{CN})$ stretching band. The combination between the experimental SERS and theoretical DFT calculations has allowed for relating the two regions to chemisorbed (C-hybrid, region A) and physisorbed (P-hybrid, region B) surface complexes, where cyanide is bonded through the carbon on top of a single silver atom of the surface. The electrode potential selects one or another type of electronic structure of the system, which are of different nature having a differentiated response to the applied voltage. Electric potentials tune smoothly the wavenumbers, bond energies, and injected charges of the P-hybrid at more negative potentials than PZC, but the very strong C-hybrid prevents significant changes of these properties at positive excesses of charge. The existence of the dual electronic structure of metal-molecule interfaces might require reinterpreting experiments that are usually discussed by resorting to, for instance, the reorientation of the adsorbate, the formation of complexes with different stoichiometries, the existence of nonequivalent local sites on the surface, or to instrumental artifacts. Moreover, this dual behaviour also determines the properties and responses of technological devices where metal-molecule interfaces are involved.



Key Words: Electrochemical SERS, Electronic structure, DFT calculations.

References

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