

## About the Unexpected Structure and Properties of Molecules Bonded to Metal Nanoclusters

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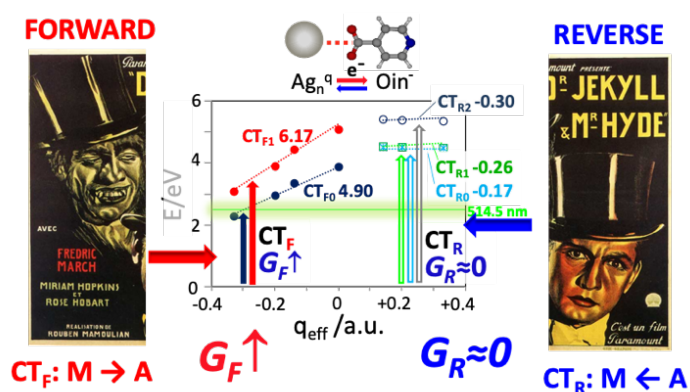
### ABSTRACT

SERS (Surface-Enhanced Raman Scattering) is a very powerful technique to gain insight into the nature of metal-molecule hybrids on a molecular level. We show the results of combining SERS and theoretical calculations (1) to analyze the subtle electronic structure of metal-molecule (M-A) interfaces, especially to study the dependence of their structure and properties on applied electric potentials or fields. An example of this is the huge efficiency of the potential ( $E_V$ ) in tuning the energies ( $E$ ) of metal-molecule charge transfer (CT) states. An equivalence between both quantities is expected on the basis of classical electrochemistry ( $G=E/E_V=1$  eV/V) but observed energy gains up to  $G=4$  or  $5$  eV/V can be explained by combining the dependence of the CT energies ( $E$ ) on the excess of charge of the metal ( $q_{\text{eff}}$ ) (see Graphical Abstract) and the capacitive enhancement located at metallic nanostructures (2).

Moreover, theoretical calculations predict a dual electronic structure of the M-A surface complex in the case of charged molecules bonded to charged metals. These two types of surface states of the same hybrid system are of a very different nature and are selected by the sign of the metal charge ( $q_{\text{eff}}$ ). It is predicted that a single M-A complex can be very strongly bonded (chemisorbed) or form weak and very polarizable complexes (physisorbed) depending on the charges of both the ionic species and the surface excess of the metal which is modulated by the applied potential. These two types of complexes determine the properties of the overall system in the ground electronic state, like the behavior of the wavenumbers of the CN stretching band adsorbed on metals (3-4), as well as in excited states, like the forward and reverse metal-molecule CT states of the isonicotinate anion bonded to positive (chemisorbed,  $G\sim 0$  eV/V) or negative (physisorbed, high  $G$ ) silver clusters (5), respectively (see Graphical Abstract).

The dual electronic structure of M-A suggests a differentiated mechanism for oxidation and reduction of molecules in interfaces that could play a key role in electrochemistry, adsorption or heterogeneous catalysis, providing a supported analysis of unexplained results.

### GRAPHICAL ABSTRACT



**Figure Caption:** DFT calculated energies ( $E$ ) of forward (F) and reverse (R) metal-molecule charge transfer (CT:M-A) states of isonicotinate anion bonded to  $\text{Ag}_n$  silver nanoclusters with different excess of charge ( $q_{\text{eff}}$ ).

## ACKNOWLEDGEMENT

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## REFERENCE

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## BIOGRAPHY

My career has been developed in the Universities of Extremadura, Granada and Malaga (Spain) where I became full professor. My research is mainly of basic character in the fields of spectroscopy and molecular structure, having carry out pre- and postdoctoral stays at the Universities of Coimbra and Florence. I am coauthor of ca. 170 articles (JCR h-index=33) mainly focused to the study of SERS, where we have made relevant contributions on the origin of the phenomenon, that is, on the mechanisms involved in the enormous enhancement of the Raman signal of molecules close to nanometric metal aggregates.

This issue has been controversial since the discovery of SERS and has limited its development for fifty years due to the complexity of the phenomenon where interfaces with systems of different sizes (nano/macrosopic metals and single molecules) are involved as well as other key experimental factors such as the surface excess of charge of the metal, electric fields and photon excitation.

My interest is to develop a methodology for analyzing SERS able to predict the effect of different mechanisms on a particular spectrum. We have proposed theoretical tools to simulate the effect of the electrical potential of the interface, i.e., of the metal excess of charge, in SERS. Faced with simplistic views based on Coulomb interactions, our results indicate that the metal charge is a key factor in the electronic structure of the surface complex, tuning the energy of metal-molecule charge transfer (CT) states in an unexpected way as well as of the states located inside the metal or in the adsorbate itself.

These results can also be useful in physics (molecular electronics, nanoplasmonics, photovoltaics, etc.), materials (molecular materials, optoelectronics, LED devices, etc.) or in other specialties of chemistry, such as adsorption, heterogeneous catalysis or electrochemistry with or without photonic excitation. In all these fields, the complex and very little-known electronic structure of charged metal-molecule hybrids controls their structure and properties, so that the SERS can become a very powerful technique to gain insight into charged hybrid systems with molecular detail.