

NANOSTRUCTURED METALLIC SUBSTRATES FOR MICRO-SERS BIOLOGICAL APPLICATIONS

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The combination of SERS spectroscopy and electrochemistry techniques allows us to record *in situ* Raman spectra of an adsorbed molecule on a metallic electrode. Therefore we are able to get both structural and conformational information of our molecules. In general SERS spectra are susceptible to potential changes in the metal-electrolyte interface, both the overall and the relative SERS intensities. Consequently there exists an important difference between electrode and colloid SERS experiences: in the first case, we can easily modify the interface electric potential of the interface with a potentiostat instrument but in the second case, the potential is not homogeneous into the colloid bulk and it could be changed with the aging of the system.

SERS has been widely used to analyze proteins, peptides, and amino acids adsorbed on silver substrates. The vibrational study of amino acids adsorbed on metal surfaces is quite complex, given that the species giving rise to the SERS spectra may be the anion, the cation, or even the zwitterion. Moreover, the interaction with the metal may take place through only one or both functional groups or even through an additional functional group present in the side chain. In general Generally speaking, the selective enhancement of some SERS bands is explained on the basis of the electromagnetic mechanism (EM) in connection with the surface orientation of the adsorbate. Nevertheless, the different enhancements shown by modes of the same symmetry cannot be easily explained on the basis of the EM mechanism, and could be attributed to the contribution of the charge transfer mechanism (CT) [1].

The SERS-CT enhancement mechanism is a process analogous to a Raman Resonance one, but in SERS experiments the incoming photon produces the resonant transfer of an electron from the metal (M) to the adsorbate (A) or vice versa. The so formed transient radical anion will be more stable if the molecule contains aromatic rings as in our samples [2]. The current work analyzes the experimental Raman and SERS spectra of two α -aminoacids, phenylglycine and phenylalanine, on both Ag colloid and electrode substrates on the basis of the EM and CT mechanism. It has been confirmed that all the studied systems support two negative charges in the excited state. This is a new result because in the case of pyridine or similar neutral adsorbates the monoanionic specie is involved in the SERS-CT process. In every SERS spectra of the studied molecules the CT features have been detected at more positive electrode potential than in the case of pyridine. This means that the charge transfer in these α -aminoacids is more favoured than in pyridine.

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References:

- [1] J.F. Arenas, M.S. Woolley, I. Lopez-Tocon, J.C. Otero, J.I. Marcos, *J. Chem. Phys.* 112 (2000) 7669, and references therein.
- [2] J.L. Castro, M.R. López-Ramírez, I. López-Tocón, J.C. Otero, *J. Colloid Interf. Sci.* 263 (2), (2003) 357-363.

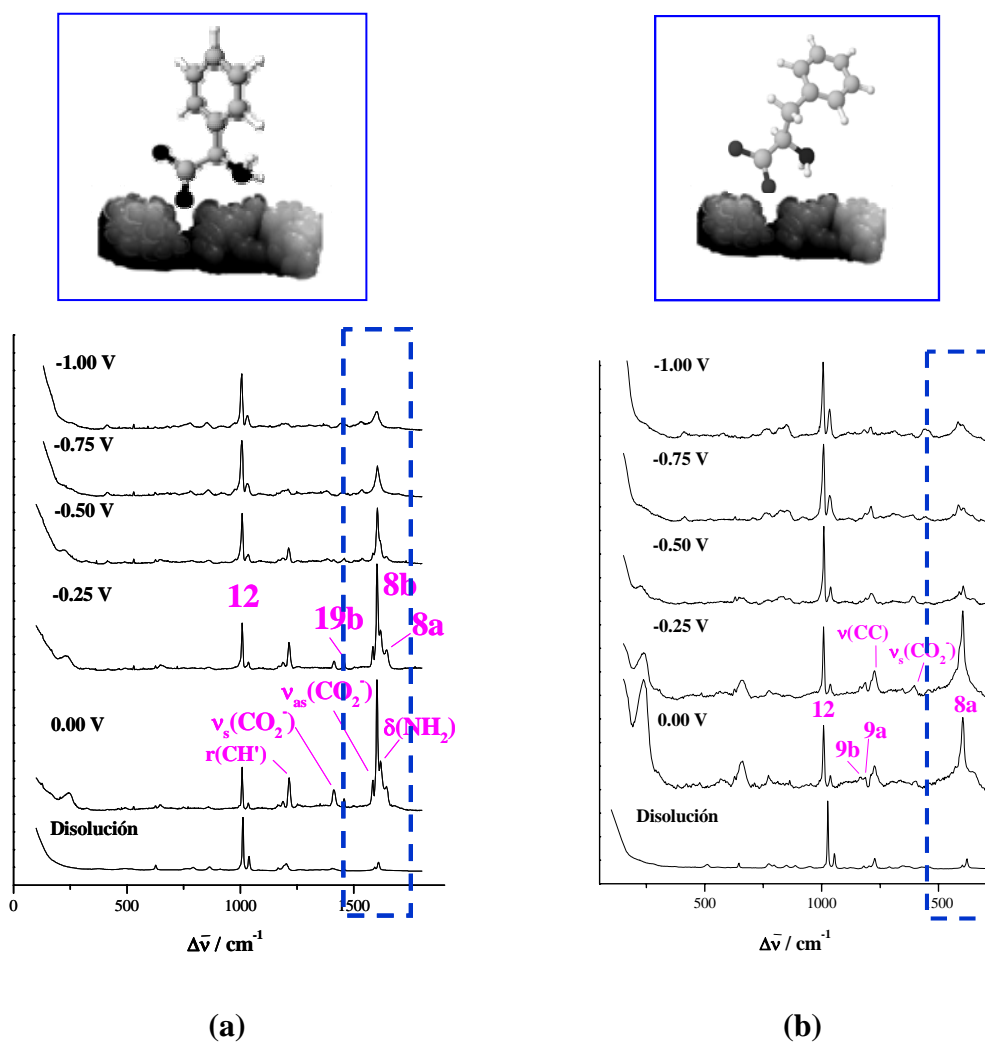


Figure 1. Raman spectra of an aqueous solution and SERS of: a) Sodium phenylglycinate and b) Sodium phenylalaninate recorded on silver electrode at different electrode potential.