## Effect of different excitation wavelength on SERS spectra of pyridine

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The analysis of electrochemical SERS experiences of aromatic acids like benzoic1 and isonicotinic2 acid and heterocyclic aromatic molecules such as, pyridine, pyrazine, pyrimidine3, etc. has allowed us to shed light on the nature of SERS phenomena and, above all, to recognize and identify the contribution of the charge transfer (CT) mechanism on a SERS record. In few words, the CT mechanism is similar to a resonance Raman process in which a certain charge transfers from the Fermi level of the metal (M) to vacant orbitals of the adsorbate (A), resulting a charge redistribution between the ground electronic state of the superficial M-A complex and other excited states (M-A + h → M+-A-). In any resonance process, the resonance condition is fulfilled when the photon of the excitation wavelength matches with the energy of the electronic transition. In a SERS-CT process there is another more variable to take into account in achiving the resonance conditions and that is the electrode potential, because of the CT electronic state of the M-A complex can be tune by the electric potential of the interphase4, which is macroscopically controlated by a potenciostat in the electrochemical experiences.

SERS spectra of pyridine has been already recorded on a silver electrode in a potential range from 0.0 to -1.40 V with a saline solution, pyridine / KCl (0.1M / 0.1M), by using the 514.5 nm exciting line5. Under these experimental conditions, the maximum intensity of the enhanced 8a and 9a bands is reached at -0.75 V and -1.20 V, respectively, being the 9a band what dominates the spectrum at negative electrode potential. We intend now to record pyridine SERS spectra under the same experimental conditions but varying only the excitation wavelength, 488 nm and 785 nm, in order to check how it affects to the relative intensities and to vibrational wavenumbers of the bands. The analysis of the relative intensities of the bands vs the electrode potential at different excitation wavelength allows to detect the resonance condition. From the analysis of SERS spectra, it can be concluded that no significant wavenumbers shifts have been detected, while the relative intensities of the bands and the electrode potential to which the maximum intensity is reached are slightly different at 785 nm, as expected for an incident radiation at low energy.

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